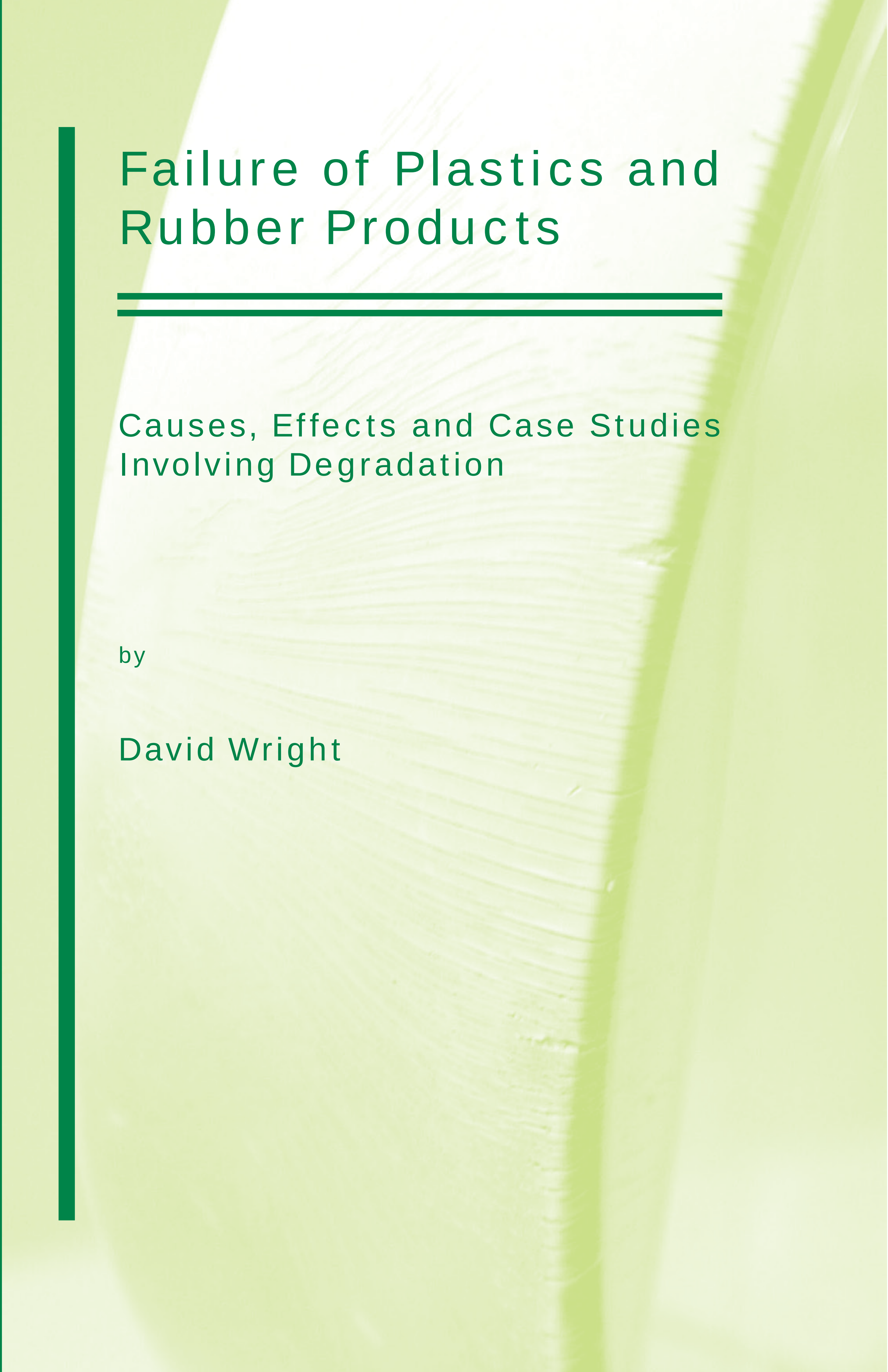

Failure of Plastics and Rubber Products

Causes, Effects and Case Studies Involving Degradation

by

David Wright

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rapra
TECHNOLOGY

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Preface and Acknowledgments

In 1998 Rapra were awarded support from the UK Department of Trade & Industry through the "Degradation of Materials in Aggressive Environments" programme to disseminate information aimed at raising awareness of the causes and consequences of polymer product failures arising from environmental degradation. This book is one of the outputs, together with training courses/workshops, and a series of phenomenological reviews. All rely on the proposition that awareness of representative historical failures will reduce their future incidence, and that the economic benefits to industry justify the support.

As formally required by the contract, an advisory committee was selected to ensure that the content and style of presentation were suitable for the intended "audience" (designers, engineers, and product specifiers). I am indebted to the following individual members of the committee for their support and advice over the past two years:

Maan Kanona – Johnston Pipes Ltd – Composites
Frank Norton – BNFL – Nuclear radiation applications
Peter Lewis – Open University – Forensic Engineering
Graham Le Poidevin – EA Technology – Electrical applications
Ian Robinson – ICI – Thermoplastics

As anticipated at the start of the project, the majority (59) of case studies chosen for inclusion in this book were extracted from Rapra files. The remainder (11) came from two external sources. David Watkins of Associated Octel provided the background details for cases 5.6.1 and 7.6.5. Graham Le Poidevin of EA Technology generously provided the texts and illustrations for cases 2.8.1, 3.6.2, 3.6.3, 3.6.6, 5.6.7, 5.6.9, 7.6.1, 7.6.2, and 7.6.3. My thanks to David and a particular thank you to Graham.

I hope the contents and format of this book achieve and justify its respective purpose and support. Others may then consider adopting or adapting the format to address the remaining causes of real polymer product failure (creep, stress relaxation, fatigue, impact, wear and abrasion, and the influence of design errors and processing faults). There is no shortage of interesting and instructive case studies, and there is no reason why we should not learn from the mistakes and misfortunes of others.

David Wright

January 2001

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Failure Analysis – A Personal Perspective

1.1 Introduction

Rapra Technology Ltd has provided technical and information services to the rubber and plastics industries and their customers for 80 years. During that time it has dealt with the problems and opportunities of a very diverse clientele. In response to demand, its technical activities have increasingly concentrated upon problem solving and in particular upon failure analysis. This trend was resisted by those who regarded the activity as second rate compared with 'research at the cutting edge'. In this overview I argue the case for promoting the status of failure analysis as a strategic, constructive, and less covert, activity.

There is a good reason why demand for the activity is on the increase. It is safe to assume that as technological disciplines mature there is a relative shift in emphasis away from basic research (new knowledge generation) to best practice (exploiting and sharing current knowledge). At any given time this trend should apply to most disciplines (current exceptions include IT, genetic engineering, and pharmaceuticals). Small companies tend to be most aware of the law of diminishing returns and follow the trend with the minimum of phase lag. Large companies can afford to support corporate research laboratories for many years before the axe falls. The massive cutback in basic research funding by the plastics supply sector over the past 10 years may be interpreted as a natural if somewhat delayed response to the maturing process. The same changes occurred somewhat earlier in the (more mature) rubber sector. Many of the technical staff released from the 'cutting edge' are now to be found in 'technical service' or 'customer liaison' roles promoting best practice, troubleshooting, fault-finding, and analysing the cause of failures.

The 'owners' of products that have failed are, for obvious reasons, generally reluctant to publicise the fact. Diagnosticians are generally restrained from doing so by confidentiality and 'conditions of employment' agreements. For these reasons the activity is predominantly covert and the potential benefits such as learning from the mistakes and misfortunes of others, and identifying priorities for research and critical issues in product development are far from being fully exploited.

1.2 Identification of strategic weaknesses

During my 30 years at Rapra I enjoyed the stimulation of a regular supply of failures. Each one was interesting and many contained surprises. By the end of this phase of my career I had accumulated a portfolio of ~ 5,000 case studies and a particular perspective of material, institutional, and supply chain weaknesses. The last of these are mainly concerned with the quality of 'public domain' information that is available within the supply chain and the quality of its communication. At one end of the supply chain, material suppliers' trade literature tends to eulogise specific materials. At the other end original equipment manufacturers (OEMs) tend to publicise successes. For example in the early 1970s a manufacturer of domestic products decided to invest in the development of a plastic electric kettle. Just prior to this, Noryl (a blend of mainly polyphenylene oxide (PPO) and polystyrene (PS)) had been launched into the market with a characteristic blend of energy and confidence. As a result of testing, the material supplier correctly claimed that Noryl had excellent resistance to hot water hydrolysis, low moisture absorption and a heat distortion temperature in excess of 100 °C. The material was marketed as the choice for hot water applications. The OEM took this as the answer to its requirements and invested heavily in design, tooling, and manufacture.

A search of the literature for this period reveals many press releases from the OEM. All promised success. However, the product did not materialise and no reasons were released for the failure. A search of the literature some years later, reveals one paragraph in one item from a million or so that comprised the store of public domain information. It makes reference to the likelihood that the Noryl kettle suffered from two weaknesses. Firstly it was susceptible to environmental stress cracking (ESC) in contact with fluids (e.g. vegetable oils) that are common in the kitchen. Secondly its fatigue resistance was not sufficient to accommodate the stresses generated by repeated thermal cycling (ambient to 100 °C). For the next reference to the subject we must wait a further 10 years for an OEM in another country to announce the anticipated success of a novel Noryl kettle. Evidently and not surprisingly the unfortunate 'pioneer' had overlooked the prior critical reference. Also the material supplier had evidently failed to recollect the historical problem and therefore failed to advise the customer appropriately.

This is one example of many that demonstrates a serious lack of **awareness** of critical issues. 'Awareness' is not simply about the collection of information. It is primarily a hierarchy of rules that prioritise actions and enquiry. By way of an analogy; if we wish our children to survive on our roads we give them a few rules, one of which is that before crossing they must 'listen, look right, look left, look right again, and if clear cross over'. We do not present them with massive collections of data giving the braking distances of all known vehicles in wet and dry conditions in the hope that they may acquire the means of survival by inference.

From my perspective the most critical issues are those concerned with ‘slow degradation/deterioration’ processes, because:

1. A principle objective of the designer of products is the avoidance of premature failure.

2. The premature failure of a whole population of a product is the most damaging prospect for a manufacturer.

3. ‘Slow degradation/deterioration’ processes (mechanical, physical, and chemical) are the most common cause of endemic failure within a product population.

These may be regarded as fundamental rules of engagement for both material suppliers and OEMs. For the OEM the rules stimulate enquiries such as ‘what are the priority factors/sensitive issues that may lead to endemic premature failure of this particular product?’ For the material supplier, the rules should stimulate priority actions to characterise the ‘slow degradation processes’ that in practice are likely to cause problems. In fact the Noryl supplier gave priority to publishing the degradation characteristics which were most favourable to the material (thermo-oxidation and hydrolysis) and therefore least likely to lead to problems.

Material suppliers may claim that they cannot test under all conditions, as this would be very expensive and take many years to complete. However, this is not a credible defence in this case, for at the time the supplier would have been aware of two further rules:

4. Glassy amorphous thermoplastics, without exception, offer poor resistance to dynamic fatigue.

5. Glassy amorphous thermoplastics, without exception, offer poor ESC resistance to a wide range of (mainly) organic fluids in the presence of processed-in or applied stress.

Noryl is a glassy amorphous thermoplastic. Therefore in the absence of data it would have been safe to assume that the rules applied and to warn potential customers of the risks. This was not done and is it rarely done either clearly or voluntarily by other suppliers. They are able to operate by their own rules because their customers lack awareness and fail to ask or insist upon answers to critical questions. It is true that material users have access to vast amounts of information, but much of this is confusing, highly conditional, contradictory, and indigestible. They are busy people who do not have the time to infer rules or extract pearls of wisdom from a very large pile of red herrings.

However, this is not a one-sided problem for even when presented with the pearls of wisdom, repeated reminders of their value are required to maintain interest in them. This has been found to be the case for even quite simple rules, such as those concerned with the avoidance of sharp corners. Another example is as follows. A company was engaged by the military to assemble land mines. These were encased in high density polyethylene mouldings. The mines were stored in vast quantities for the war, which hopefully would never come. Within a year of storage the casings started to split. I was engaged to diagnose the cause of the failures. This was not difficult, because silicone grease was detected on the fracture surfaces, and this is known to be a modest stress cracking agent for polyethylene. The company was using the grease as a lubricant to assist assembly. An alternative lubricant was recommended and the problem was solved. However, about 10 years later the same company asked me to diagnose the cause of exactly the same problem. All their technical staff had been replaced and my original report was lost in one of the many filing cabinets that propagate so well in such an environment. They had reverted to using silicone grease. This is an example of poor knowledge management or, to be more precise, a failure to recognise that knowledge is a valuable strategic asset that deserves security, care, and attention.

From my experience the major barrier to the systematic management of technical knowledge is the attitude of technical specialists. They have a strong tendency to regard their own knowledge as a personal weapon. They will use the weapon but they will not willingly share its secrets for two reasons. Firstly it is common to claim that individual knowledge cannot be systematically captured, stored, and made accessible (it has a mystical quality). Secondly, although this is rarely stated, in the land of the blind 'the one eyed man is king'. Therefore knowledge management systems aimed at reducing product faults and failures must be imposed from above.

1.3 Identification of human and material weaknesses

The 5,000 failures referred to above were all plastics products that had been sent to me for inspection/analysis. In terms of material type, product type, industrial sector, and service environment, the sample is considered reasonably representative of the whole. However inspection and analysis can be expensive and this creates some bias in terms of failure mode. Failures due to abuse or accidents (impact, fire, etc.) are underrepresented for these are often obvious and rarely invite heavy commercial or economic consequences. The sample numerically overrepresents failure modes that threaten the whole population of a product and which may invite the need for recall and the possibility of litigation. However this bias is beneficial if the sample is to be used to reveal the commercial significance of the various material and human causes of failure.

Figure 1.1 gives a breakdown of the material/phenomenological causes of failure within the sample. It should be stated that the singular designation of a material cause is open

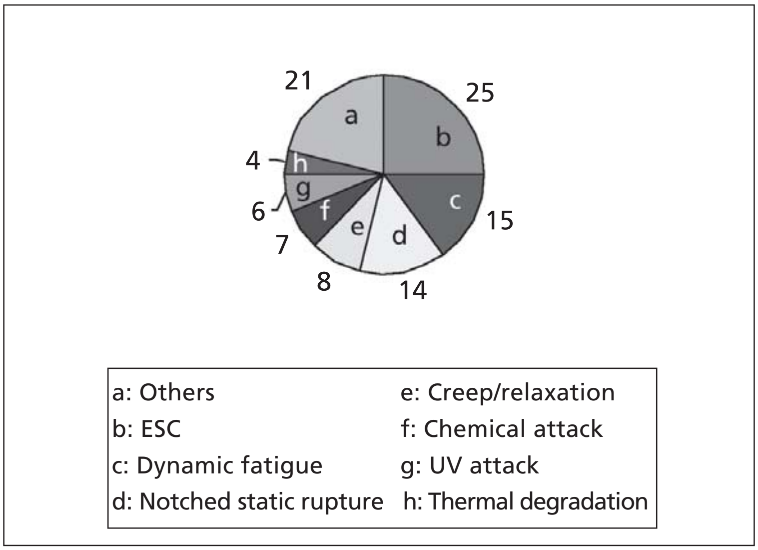


Figure 1.1 Material/phenomenological causes of failure (percentages)

to (favourable) interpretation in many cases. If a part has failed by impact there may be strong commercial pressure to designate this as the basic cause, but there is little point in this designation unless either the material is intrinsically fragile or the product has been subjected to impact abuse. On further inspection, if the impact failure is due to product rather than intrinsic material brittleness, then further inspection is required to identify the cause of product brittleness. If this reveals hydrolytic degradation due to processing without adequate drying then the fundamental material weakness is hydrolytic instability, this being a subclass of chemical attack.

With few exceptions we cannot blame an inanimate material or hold it responsible for our failures. The fundamental material cause is generally the result of human error or weakness. This again is open to interpretation and applying a single designation can be difficult. However, for the example above, the human cause of failure is clearly ‘poor processing’. Obviously if embrittlement was due to hydrolytic degradation during service then the human cause would be either material misselection, abuse, or poor specification depending upon historical circumstances. If for example a ‘hot water’ condition was specified or could be reasonably inferred from the application, then the human cause would be material misselection. Figure 1.2 gives the breakdown of the human causes of plastics product failure within the sample.

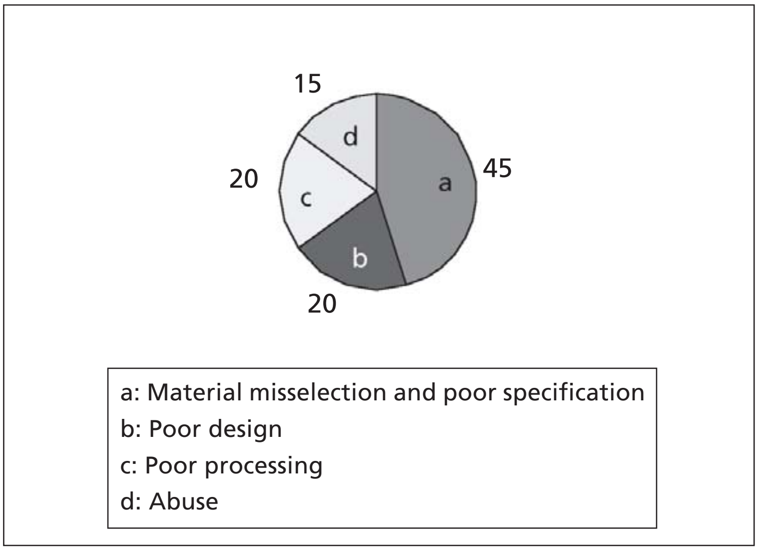


Figure 1.2 Human causes of plastics product failure (percentages)

Inspection reveals that the vast majority of the product failures involve embrittlement and/or brittle fracture, resulting from slow degradation or deterioration processes. With reference to Figure 1.1, ESC, dynamic fatigue, notched static rupture, thermal degradation, UV degradation, and a high proportion of failures due to chemical attack fall into this category, even when the material involved is claimed to offer high (initial) ductility. All ‘tough’ plastics exhibit ductility over a limited range of service or test conditions. For a given time under stress, the range of the ‘ductility peak’ is bounded by a critical low temperature and high temperature. For a given temperature as indicated in Figure 1.3, it is bounded by a short-term and a long term transition. The low temperature/short-term transition is well understood and characterised for this determines integrity under conditions of impact. The ductility peak is narrowed under these conditions by decreasing time under stress (increasing impact velocity), decreasing temperature, the presence of stress concentrations and material degradation. The higher temperature/longer term transition is not so well understood or characterised yet it is this transition that most commonly determines the durability of real products (see for example Figures 1.4 and 1.7). Durability is reduced by intermittent stressing (cyclic fatigue), increase in temperature, stress concentrations and material degradation induced by UV (ultraviolet), ionising radiation, oxidation, and hydrolysis. Structurally, the material is in only in a safe condition when it operates between the two transitions, and therefore within the ‘ductility peak’.

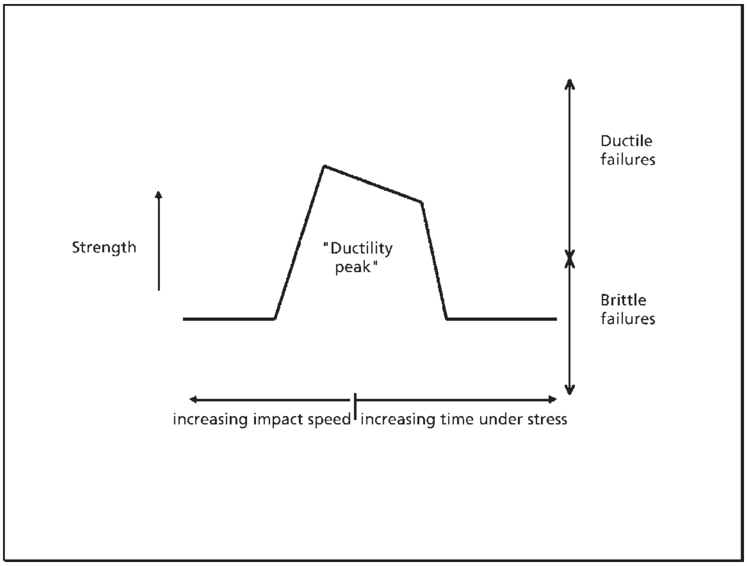


Figure 1.3 The generalised effect of stressing time on strength and ductility

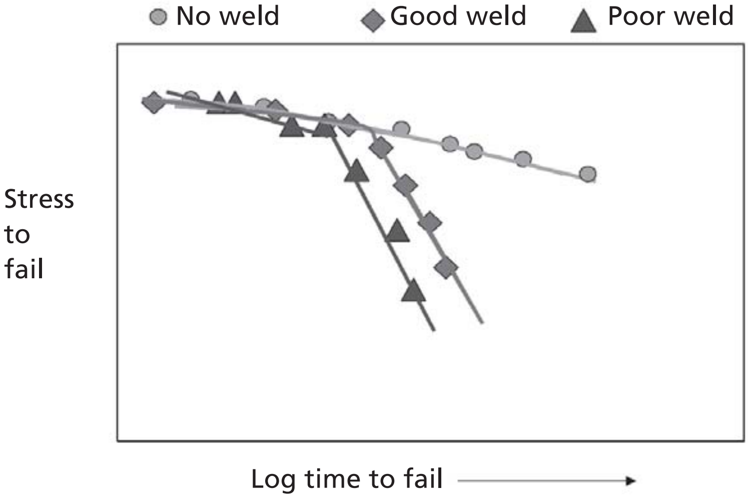


Figure 1.4 Notches associated with welds accelerate the long term ductile to brittle transition, but this would not be revealed in very short term (high stress) tests

These observations lead to another rule:

6. It is prudent for the designer to assume that when a plastic product fails in service it will do so by brittle fracture. Therefore any product test that fails to induce brittle failure is unlikely to replicate service performance or provide a sound basis for the prediction of product durability.

In many cases this rule is broken by choosing to test at high stresses for short periods of time. For example, when welds are tested under these conditions they tend to fail by yielding at high stress, because the stress concentrations associated with the weld do not have sufficient time to develop into cracks, or they are deactivated by crack tip blunting. As a result it is commonly claimed that a particular welding process is as strong or even stronger than the parent material. However as shown in Figure 1.4, the real differences made by welding and indeed by welding quality will only be apparent under conditions that lead to weld fracture, which are generally those that apply in real service.

Environmental stress cracking (ESC) is the most common failure mechanism, whereby mainly organic fluids accelerate crack initiation and growth under conditions of applied or processed-in stress. Glassy amorphous thermoplastics are most susceptible and the most common fluids that cause the problem are lubricants (oils and greases), adhesives, corrosion inhibitors, surfactants, cleaning agents, solvents, paints, and aerosol propellants.

ESC is the result of a physical interaction involving highly localised plasticisation via stress enhanced fluid absorption at points of weakness. It does not involve chemical change or degradation.

The phenomenon has been the subject of research for more than 50 years, but interestingly, much of this work was directed towards the problem of ESC in polyethylene (a semicrystalline thermoplastic). Awareness of the more significant problem of ESC of amorphous plastics has been deflected and slow to develop. The historical emphasis has a rational explanation. The molecular architecture, and in particular the density, length, and degree of entanglement of intercrystalline (tie) molecules, has a very profound influence on environmental stress cracking resistance. For polyethylenes, 'cutting edge' research to optimise the architecture has been intensive and extremely beneficial. In the case of glassy amorphous thermoplastics (e.g. polycarbonate, polystyrene, polymethyl methacrylate, polysulphone) there are no tie molecules, and therefore the options to improve ESC resistance are restricted. As problems with solutions are publicised more frequently than problems without solutions, it should not be surprising if the degree of awareness does not correlate with the real risks.

The phenomenon briefly attracted public attention following the introduction of a new motorcycle crash helmet. This was injection moulded from polycarbonate (a glassy amorphous thermoplastic) selected for its very high impact resistance. The new product was tested and found to provide excellent protection. However a few years later it was realised that rider fatalities due to head injuries had not declined to the expected degree. The problem was traced to the habit of adorning helmets with solvent-based paints and adhesive labels. These substances, in combination with high residual processed-in stress, resulted in environmental stress cracking. The cracks which were hidden from view by the paint or the labels, dramatically reduced impact strength.

The human cause of this failure would be abuse because the helmet manufacturer could not be expected to anticipate the habit of adornment. However to emphasise the difficulty of designating a single cause, the solution to the problem was to reduce the level of residual stress in the moulding. If the problem returned the human cause would be poor processing.

Dynamic fatigue is the second most common cause of failure within the sample and, as with ESC, brittle fracture ultimately results. Interestingly there appears to be a strong correlation between the two failure mechanisms, in that materials tend to have either good (semicrystalline thermoplastics) or poor (amorphous thermoplastics) resistance to both. Both involve the physical steps of craze initiation and slow crack growth without significant chemical modification. Resistance to both is improved by selecting grades with higher molecular weight or, more specifically in the case of semicrystallines, by increasing the chain length of intercrystalline tie molecules.

The high incidence of dynamic (cyclic) fatigue failure requires explanation. In a large majority of cases the designer failed to realise that the product was exposed to the risk of such failure. Fatigue resistance was not specified as a required property for the purposes of material selection, and appropriate design calculations were not carried out. The lack of awareness is most apparent in products subjected to very low frequency fatigue. Most designers and engineers do not realise that a product which is periodically stressed at the rate of a few times a day may accumulate enough cycles over a service life of a few years to cause fatigue failure, with the more susceptible plastics.

Figure 1.5 is an example of a low frequency dynamic fatigue failure. It is a polycarbonate air line filter bowl that failed catastrophically after 10 years of service involving 0.6 MPa on/off pressure cycles at a rate of a few per day. Figure 1.6 is a close up photograph of the failure initiation site. The 'tree growth ring' striations are symptomatic of incremental craze growth under cyclic loading. At the completion of this phase the craze has grown to a critical length (about 20 mm) and then suffered fast brittle fracture during the last pressure cycle.

When the product was designed and polycarbonate selected, a two inch thick manual was freely provided by the material supplier that covered even the most esoteric of subjects in the finest of detail. However only one sentence was dedicated to the issue of fatigue

Figure 1.5 Failed polycarbonate filter bowl

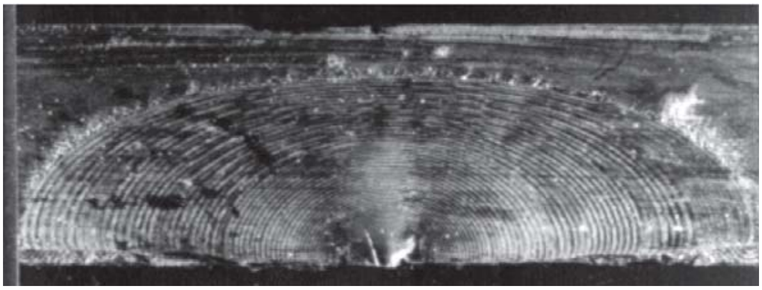


Figure 1.6 Dynamic fatigue failure initiation site on failed polycarbonate filter bowl

and this warned the reader that there was evidence to suggest that the fatigue properties were not very good. A cynic may interpret the motives for this subliminal advice in many ways but not as an effective means of promoting awareness of critical issues. It reminds one of the road safety analogy mentioned earlier.

The low frequency fatigue characteristic of polycarbonate is shown in Figure 1.7. It reveals a dramatic transition from high strength ductile failure to low strength brittle failure at about 20,000 cycles. Such a presentation is sufficient to attract the attention of the busy designer. However, suppliers often choose to present the data over the restricted range of 10^4 to 10^7 cycles (boxed in Figure 1.7) which at a glance indicates such an unremarkable decline in strength that its significance may be overlooked.

Notched static rupture is another common source of brittle failure. As a general phenomenon this has been the subject of a long and relatively successful awareness campaign. The fact that designers and engineers sometimes forget the rule that 'sharp corners should be avoided', highlights just how difficult it is to maintain awareness or to make awareness universal.

Within the sample, failures of this type were mainly due to processed-in stress concentrations, such as internal weld lines in injection mouldings or spider lines in extrusions, rather than sharp corners. As with external welds, (see Figure 1.4) the stress concentrating feature may not reveal its detrimental potential under short-term testing conditions. Thus simple quality control tests on products often indicate consistently high strength and toughness, whilst a proportion of the same product population will fail prematurely in service by brittle fracture. When faced with this situation the product vendor may be tempted to accuse the user of abuse, whilst the response of the latter may be to accuse the former of poor quality control. In many cases neither is correct.

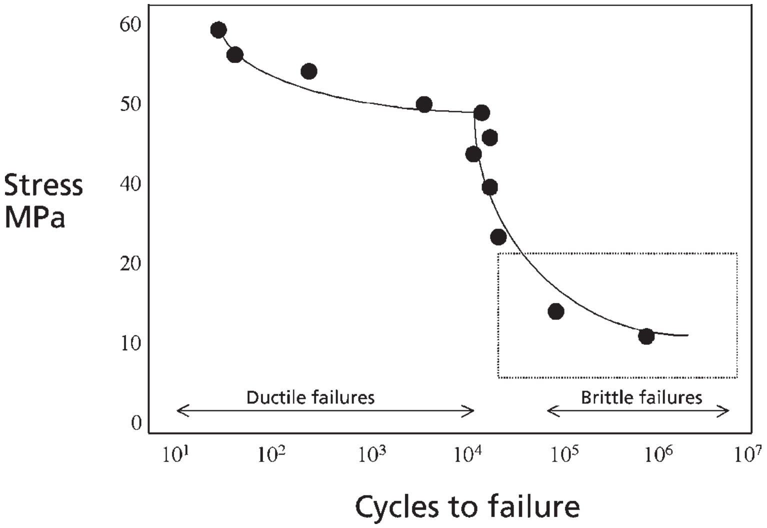


Figure 1.7 Dynamic fatigue of polycarbonate at 0.5 Hz

By way of an example, injection moulded polypropylene seat shells used in sports arenas suffered a 10% failure rate within 2 years of service. The shells that failed did so consistently by linear splitting along a central axis. This is indicative of slow crack growth under modest stress rather than abuse. The moulder had failed to notice that the split initiation point coincided with a processed-in weld located at the mid point of the shell edge, and that this coincided exactly with the point of maximum flexural stress in service. The phenomenological features of the service failures could therefore be rationally explained, but the moulder and the user were unconvinced because this did not explain why, with a common stress concentrating feature, there was such a large variation in the durability of the product population.

The confusion here is that human beings think in terms of linear time, whilst most damage processes accumulate at a rate that is proportional to the logarithm of time. All other factors being the same, the crack growth rate is proportional to about the fourth power of the applied stress. Therefore the time to brittle failure is very sensitive to slight variations in applied stress or slight variations in the stress-concentrating power of the weld or notch. Nearly identical products under nearly identical service conditions will exhibit a range of durability that is rarely less than a factor of 5. Thus if a small proportion of a product population fails by brittle fracture within two years then it is often prudent to accept the possibility that the whole population will fail in the same manner within 10 years.

The solution to the problem was quite simple and very effective. The processed-in weld was eliminated by the addition of a strategically placed flow leader in the mould cavity. The lesson is also simple. Statistical analysis is only a tool and may be counterproductive if it is applied without knowledge of materials or detailed inspection.

It is of interest to note that the 8 year old problem has recently resurfaced. In an article entitled Mystery of the Cracked Stadium Seats [1] it is reported that in Japan a significant proportion of high density polyethylene (HDPE) stadium seats developed centre line cracks soon after installation. The hypothesis for the cause was high residual stresses. However the unpublicised history of the similar product with a similar failure mode would suggest that the hypothesis is probably incorrect. The example clearly reinforces the cardinal purpose of this perspective, which is to promote the benefits of learning from the mistakes of others.

Chemical attack most frequently leads to embrittlement and/or brittle failure due to chain scission. It includes hydrolysis, acidolysis, and halogenation. Although failures due to oxidation in air (usually at elevated temperatures) should formally fall into this category, it is more conventional to treat this separately under the heading of thermal degradation (or thermo-oxidative degradation).

Material suppliers are generally to be complimented on the quantity of information that they provide. Chemical compatibility tests involve immersing the material in the chemical for a standard period (usually two weeks) at ambient and elevated temperatures. Weight change and changes in tensile strength and strain at break are assessed, and on this basis various descriptions are awarded, ranging from resistant to not recommended.

There are three major limitations in these data sets that lead to a significant proportion of failures due to chemical incompatibility. The tests concentrate on bulk fluids (beer, ketchup, milk, kerosene, etc.) and pure chemicals (propanol, acetone, etc.). This is fine for food and chemical processors, but many applications involve mixtures and these are generally not covered. Secondly the detrimental effect of trace amounts of (usually) metallic ions which catalytically promote degradation is virtually ignored. Thirdly, because the tests involve stress free immersion they do not specifically identify susceptibility to ESC or stress corrosion cracking (SCC).

ESC and SCC are distinctly different phenomena, yet the distinction is often ignored even in modern textbooks. It is true that both involve crack initiation and growth under the simultaneous influence of fluid contact and stress, but as highlighted earlier, ESC proceeds without irreversible material modification or degradation. SCC involves chemical attack, whereby the rate of attack is significantly increased by stress.

Figure 1.8 illustrates a typical SCC failure. It shows an injection moulded acetal part exposed to cider, which contained trace amounts (~1%) of acetic acid. The plant and

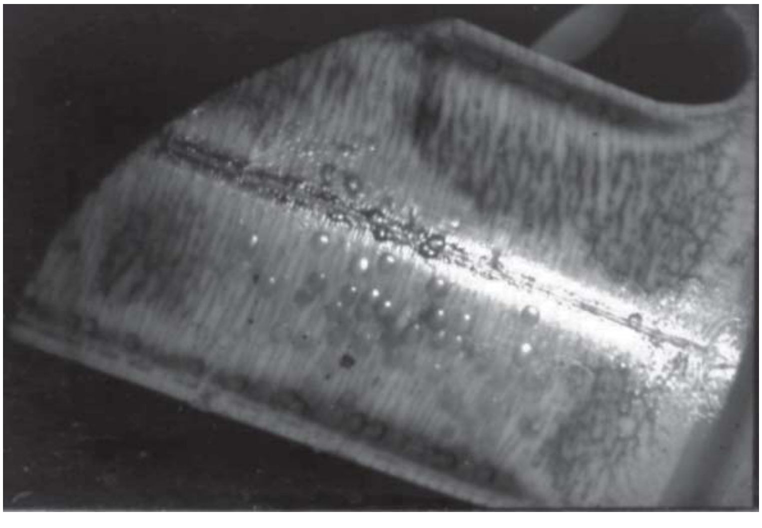


Figure 1.8 Embrittlement of an injection moulded acetal part, due to surface stress corrosion cracking of acetal in cider

therefore the part were subjected to periodic steam sterilisation, and it was during these high temperature excursions that absorbed acetic acid attacked the part. The microcracking pattern reflects the residual stress/molecular orientation distribution within the moulding. Discolouration and degradation maximise at the microcrack surfaces.

Hydrolysis is the most common form of chemical attack within the sample of failures. A significant proportion of these arise from degradation during the processing of inadequately predried material, particularly polycarbonates and thermoplastic polyesters.

Thermal degradation failures also commonly arise from processing as well as exposure to service conditions. As with cooking, the same amount of material change can arise from short periods of time at high temperatures (e.g. during melt processing), long periods of time at modest temperatures (e.g. during service) or other equally effective combinations of time and temperature. Readily accessible data and guidance on this important phenomenon are rather sparse. One end of the ‘cooking’ spectrum is covered loosely by the ‘maximum continuous use temperature’ or more precisely the ‘UL temperature index’ (Underwriters Laboratories) which is the temperature that will give rise to a 50% reduction in short-term mechanical properties following an exposure period of 100,000 hours (11.4 years). At the other end of the spectrum the critical time temperature combination is covered by the allowable ‘residence time’, this being the time (usually in minutes) that the material can be held at its melt processing temperature without excessive degradation.

Prior to failure by thermal degradation, most products have experienced a complex thermal history perhaps including predrying, melt processing, melt reprocessing (use of regrind), thermal welding, and a range of temperatures in service. Even without further complication, predicting product durability by summation requires a high degree of insight and effort.

Additional complications include the type and concentration of antioxidant additives, the presence of mechanical stress, and the surface area to volume ratio of the product. Thin film or fine powder will degrade more rapidly than the same material in bulk form, because of enhanced access to atmospheric oxygen. An example that demonstrates the potentially deleterious consequences of these additional factors concerns the use of polyethylene film as a damp-proof membrane in buildings. The grade was tested using 3 mm thick specimens and although the maximum continuous use temperature was only 50 °C, implying only modest antioxidant protection, this was regarded as adequate for the relatively cool climate of Scandinavia. The film was used extensively but within a few years the membranes started to fail due to thermo-oxidative degradation and cracking at areas of high stress (e.g. at folds). The effect of the stress factor is the most significant. The effect of simultaneous stress on 3 mm thick specimens is to reduce the durability at the claimed maximum continuous use temperature (50 °C) from an expected 100,000 hours to ~ 1000 hours. In effect the maximum use temperature is reduced to ~ 30 °C. The thin film nature of the product is estimated to have reduced the maximum continuous use temperature by a further 10 °C.

Failures due to **UV degradation** are usually the easiest to identify and for this reason the phenomenon is probably underrepresented within the sample. Discolouration on surfaces that are directly exposed to sunlight or artificial light sources usually precedes embrittlement and therefore in most cases the complaint is one of aesthetics and the cause is visibly obvious. This is reinforced by the fact that many of the commodity products that are intended for long term exposure, such as guttering, sidings, and window frames, only need to be tough during assembly and installation.

A high proportion of the failures in the sample involve cases where the service conditions did not include exposure and therefore stabilisation was not specified, but the unprotected material was then exposed to intense light levels for a period prior to service (e.g. the storage of stock).

Creep and relaxation failures within the sample range from delayed buckling to the decline in mechanical jointing forces. For the vast majority of commercially available plastics, creep data are unavailable or are not sufficiently comprehensive to allow the designer to predict the modulus of a chosen material after long periods of time under sustained stress. Although the high cost of long term testing is fundamentally responsible for this state of affairs, other well intentioned influences have made matters worse. Test standards developed in the late 1960s (e.g. BS 4618) were constructed by experts who gave all consideration to precision and repeatability and none at all to the affordability of the methods. In particular, emphasis was given to the need to characterise creep over a range of stress levels to accommodate nonlinearities. Once this has been done at ambient temperatures few material suppliers are willing to repeat the exercise at 10 or 20 °C intervals up to the maximum service temperature. As a result, the user is presented with precise information about a minor nonlinear viscoelastic effect and very little information about the very much more important influence of elevated temperatures. I am acutely aware of this because 28 years ago I set up a large plastics creep facility, and although it was used for research and many phenomenological investigations, it was never gainfully employed to comprehensively characterise a commercial material.

Other failure modes include impact, wear, water treeing, electrical breakdown, radiation, plasticisation, deplasticisation, and permeability.

The human causes of failure fall into fewer categories and are dominated by **material misselection**. This includes the choice of the wrong generic material, grade, or compound, due to either poor specification of material requirements or poor understanding of material properties and characteristics. In particular by comparing Figures 1.1 and 1.2 it is apparent that inadequate attention is given the issue of durability at the specification and selection stages.

We know that in many cases material selection is effectively carried out by the material supplier. This is not reliable for the selection of generic plastics because the materials portfolio of even the largest supplier is only a fraction of the total. Material suppliers should be used to confirm a generic selection and to select the best grade. We also know that selection is often driven by the advice and recommendations of moulders. However it should be pointed out that the priority interests of the moulder rarely include durability. Their professional and commercial interests centre upon issues for which they are responsible. These are dominated by dimensional and or aesthetic requirements. These requirements are also commonly perceived as priorities by the product specifier. It is a fact that glassy amorphous thermoplastics (acrylonitrile-butadiene styrene, styrene-acrylonitrile, polycarbonate, polymethyl methacrylate, polystyrene, etc.) satisfy these perceived priority requirements better than semicrystallines. Mould shrinkage is less, and more consistent, and hence dimensional tolerances are more easily achieved and maintained. Related shrinkage problems such as warping and sinking are more easily avoided. Colouring qualities and surface finish (e.g. gloss) are also superior. These facts, together with rules 4 and 5, help to explain the high incidence of ESC and fatigue failures and material misselection.

In recent years an increasing proportion of failures due to **poor design** can be traced to an overreliance on computerised stress analysis. The ability to predict stresses to fifteen significant figures is of little value if the allowable or safe design stress is erroneously optimistic by a factor of two or three. Errors of this magnitude are not uncommon. In one case 40% glass fibre Nylon 66 was used to mould cantilever supports for a heavy duty store shelving system. A comprehensive stress analysis was carried out at considerable cost. The allowable stress was taken to be one-third of the short-term ultimate flexural strength as published in the supplier's data sheets. Three years later one of the supports failed, the shelf unit collapsed, and via a dramatic domino effect the total storage facility collapsed. For critical structures it would be rare to recommend a safe stress of greater than one-fifth of the ultimate, but in this case there was an added reason to be even more conservative. The cantilever was gated at mid-span and onto the surface that would be subjected to tensile stress. Obviously at this point the glass fibres are orientated at right angles to the principal stress, and not surprisingly this was the failure site.

It was felt that in this case and many other similar cases the design had not been considered holistically, and that the use of powerful computerised stress analysis had actually deflected attention away from critical issues.

Poor processing includes:

- Poor mixing/compounding,
- Hydrolytic degradation,
- Thermal degradation,
- Voiding,
- Weak weld lines,

and also problems associated with various post-processing activities such as welding, machining, and bonding. In fact the most expensive failure in the sample involved the bonding of a glass reinforced plastic (GRP) product. Several hundred kilometres of filament wound GRP pipe for pumped sewage had been installed up to 10 metres deep in Arabian sand. Pipe diameters ranged up to 2 metres. Prior to installation each 6 metre pipe length had been pressure tested. However when the pipework system was pressure tested the water loss rate was very high.

I ventured to inspect the system and discovered that about 10% of the pipe lengths were perforated adjacent to bell and spigot joints. These perforations were clustered and up to 2 cm in diameter and were deemed to be sufficient to account for the leakage.

A leaking joint was removed and sectioned. The bond between the bell and the pipe had delaminated creating a leakage path. The perforation clusters were located at the end of the path. An adhesive tape was found between the bell/pipe interface (as shown in Figure 1.9 and schematically in Figure 1.10).

Discussions with the pipe supplier revealed that the adhesive tape had been applied to solve a minor fabrication problem. To fabricate the bell, the pipe end was butted against a male bell mould and overwrapped with resin and glass. Gaps between the two mating parts caused resin leakage and the tape was applied to avoid this inconvenience. The bond between the tape and the resin was so poor that the cleavage stresses generated by gasket compression could be sufficient to debond the embedded tape to a depth of about 20 mm. During pressure testing of the installation this 20 mm deep ‘precrack’ grew rapidly, creating a leak path via delamination.

So, what about the perforations? When a leakage path between the pipe and bell housing had developed, a water jet of considerable force was temporarily absorbed by the sand backfill. As shown in Figure 1.11 erosion of a backfill cavity eventually leads to deflection of the water jet (via a stone) which now is laden with sand. A high pressure sand slurry

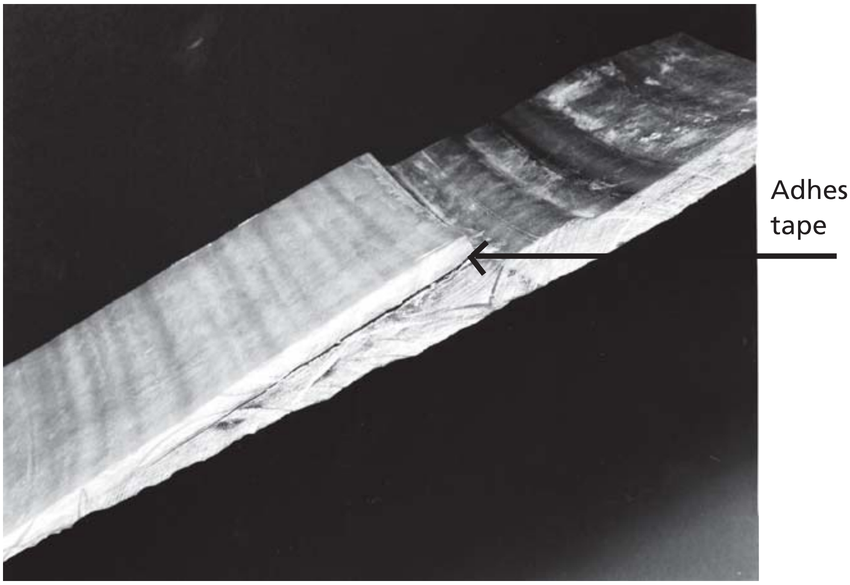


Figure 1.9 Section of a leaking joint (adhesive tape is arrowed)

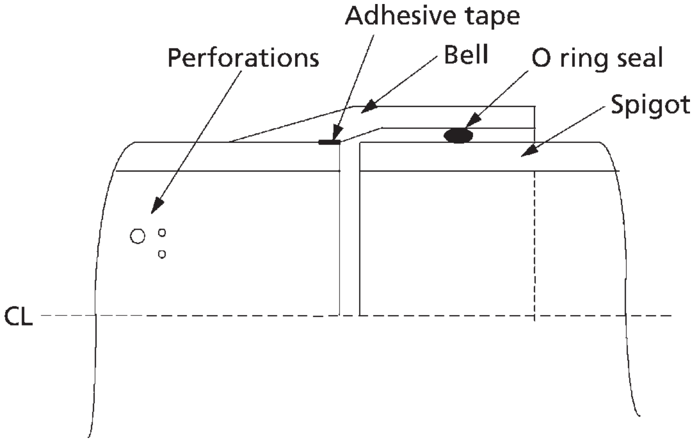


Figure 1.10 Schematic section of a leaking joint

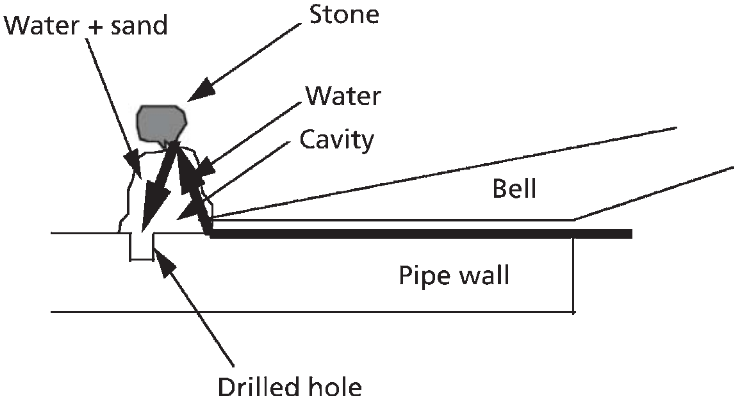


Figure 1.11 The cause of the perforations

is an effective means of drilling holes in GRP. Obviously the result of the first drilled hole is an even more powerful water jet. Holes rapidly multiply.

1.4 Identification of product testing weaknesses

It might be reasonable to expect that product testing prior to product launch would be an effective means of identifying material and human weaknesses, and therefore of avoiding the massive consequential losses of a globally distributed and defective part. We do not know how effective the safety net is, but we know that it sometimes fails, and in many cases why it fails. For example the initial cleavage stresses in the bell and spigot joints discussed above, maximise when the gasket compression maximises. This will occur where dimensional variations coincide i.e.:

- maximum external diameter of spigot,
- minimum internal diameter of bell,
- coincidence of major axis (spigot) and minor axis (bell) ovality.

During the pressure testing of individual 6 metre pipe lengths, the maximum cleavage stress due to the mating of joints was about one-half of that which could apply in service. This arises because in testing the spigot end was mated with a precisely machined metal bell and the bell end to a metal spigot. Thus the quality control test was not severe enough to replicate the highest stresses that could be imposed in service.

It is extremely important that destructive tests induce the same mode of failure as anticipated in service; otherwise the test is not valid either for quality assessment or durability prediction purposes. In particular, the large sample of product failures discussed above would lead us to anticipate that the mode of failure of a component is most likely to involve embrittlement and or fracture in the longer term, and therefore an accelerated destructive test that results in ductile/yield failure is unlikely to be valid. This problem most frequently arises because the test duration is too short to induce the longer term ductile/brittle transition (as shown in Figure 1.1).

An outstanding example of invalid testing of this type can be revealed by a search of academic papers relating to the dynamic fatigue of thermoplastics over the period 1965 – 1985. Test frequencies were often as high as 30 Hz, and this combined with high stress amplitudes ensured that failures were predominantly induced by hysteresis heating and thermal softening. The fact that such failures would never be experienced in service without a gross error on the part of the designer was ignored. Furthermore, the authors of the work proceeded to develop elegant theories to predict the temperature rise in different materials of various shapes at these ludicrously high levels of mechanical power input. The effort and public funds applied to this work generated large amounts of data very quickly (which was convenient for the researchers) but added little of value to our understanding of even the mechanisms involved in the fatigue failure of real products under sensible service conditions.

The polypropylene seat shell discussed earlier contained a defect that effectively narrowed the ductility peak. Any long term static or dynamic fatigue test or any short-term impact test would have resulted in brittle fracture of the whole population. However at an intermediate test duration that coincides with the peak, all or (in this case) most of the production may appear to be tough and ductile. A fundamental design error then appears to be a sporadic quality problem. Defects do not reduce yield strength, but as previously illustrated in Figure 1.4 they do accelerate the onset of low strength brittle failure.

In the late 1960s and mainly in the USA, high tension distribution cable insulated with polyethylene rapidly replaced traditional systems. The insulation was designed (on the basis of accelerated laboratory testing results) to survive for a minimum of 40 years. Some years later failures started to be reported and the frequency of failures accelerated dramatically. Failure diagnosis revealed the cause to be degradation in response to electrical fields in the presence of moisture. This phenomenon, now known as ‘water treeing’ was totally unexpected, based on the intuitive reasoning that polyethylene is known to be extremely hydrophobic. Therefore long term and accelerated product testing had been performed in a dry environment. Eventually, but only after considerable costs had been incurred by the utilities, the problem was identified, replicated under laboratory test conditions, and water tree resistant grades successfully developed.

Another example on a less dramatic scale concerned the degradation and cracking of polyvinylidene fluoride (PVDF) pipe transporting dry chlorine gas. Testing together with published chemical resistance data indicated compatibility. Diagnosis revealed that degradation was due to attack by aggressive chlorine radicals (atomic chlorine) resulting from the reaction of (molecular) chlorine gas with ultraviolet radiation. The PVDF pipe was translucent and when exposed to sunlight or intense artificial light, attack was initiated.

These cases and many others demonstrate that failures are most commonly due to the synergistic action of two or more service related factors in addition to time and temperature (e.g. chlorine + UV, electric field + water, ozone + stress, gamma radiation + oxygen, solvent + stress). They demonstrate that even large powerful companies dealing with high volume products (e.g. pipe and cable), cannot reliably predict the most critical combinations for product testing, and nor can they afford to test under all conditions.

1.5 Priorities for future consideration

If we wish to reduce the future incidence of failures we must accept and act upon the fact that these are due to human error, misunderstanding, and ignorance. We must also accept that the time and effort that engineers and designers can afford is limited and therefore knowledge transfer needs to be more efficient.

I observed many years ago that plastics (and rubber) training courses for engineers and designers seemed to devote much time to the chemistry of polymers, structure/property relationships, viscoelasticity, rheology, and all other elements that form the academic basis of a full time polymer technology course. I could not accept that this was an efficient means of knowledge transfer. Rapra therefore introduced two courses (one on rubber and one on plastics) dedicated to meeting the priority needs of designers. Material selection, product design, and processing are covered, with the emphasis on specific material weaknesses and fault/failure avoidance. Real examples of each type of fault/failure are employed to stimulate awareness and interest. As with any face-to-face interaction, very particular interests can be accommodated by questions. These courses have proved to be very popular but they can only benefit a very small fraction of the manufacturing community.

This leads us to consider the means of large scale knowledge dissemination. The difficulty here has been that the priority interests of manufacturers differ, and to cover all these interests in sufficient depth would require a massive library of information, data, and rules. The difficulty however has been eased by the rapid development of IT products for the low cost storage of information and very efficient interactive access to stored text, data, and procedures. One compact disc can store the equivalent amount of text and line diagrams to a 30 metre high pile of A4 paper. Every word can be searched and accessed within seconds. We calculated that, provided we were selective, one disc each for rubbers and plastics could carry sufficient information to cover most of the critical issues that may be faced by a medium to large manufacturer at the end of the supply chain.

About seven years ago we set about the task of developing these 'knowledge base systems' (KBS). The discs would comprise a large body of selected 'public domain' information provided by Rapra, together with a shell for the storage of private in-house information. Emphasis was given to material weaknesses, degradation phenomena, processing faults, material selection, product design and all the other issues and procedures that are identified as critical via failure analysis. Interactive procedures for minimising the risk of failure have been constructed. Procedures for failure analysis are planned.

Given time these systems will contain and secure all the 'pearls of wisdom' from the public domain. A search on 'kettle' or 'kettle NEAR Noryl' or 'kettle AND Noryl' will warn the user. The facility to add value by securing in-house pearls of wisdom is also extremely important for minimising the risk of repeating historical failures. Centralised 'knowledge management' systems of the type described here would slowly but surely become a major corporate asset. 'Lubricant NEAR mine' would be sufficient to avoid the repetition of the problem described earlier. 'Silicone NEAR polyethylene' would have been sufficient to avoid the problem in the first place.

Eventually the critical issues that apply to all mature technologies will be captured and shared freely on the Internet. However, unless there is a radical change of direction in the development of this apparently all-powerful vehicle, the benefits may be far more modest than expected. More pearls of wisdom in a larger pile of red herrings is not the best route to awareness. A high degree of editorial discipline would be required to ensure that information is presented hierarchically, with priority given to rules and fundamental truths. Perhaps the national institutions and federations that represent these technological businesses should consider how they might apply themselves to this task.

In 1998 Rapra were awarded a contract from the DTI (Department of Trade and Industry), as part of their 'Degradation of Materials in Aggressive Environments' programme, to compile and publish this compendium of polymer product failures. Most awards from this source have been to develop best practice procedures and test methods as a means of avoiding failure, and it is refreshing that at the highest strategic level, knowledge of the past mistakes and misfortunes of others is now regarded as a powerful awareness tool. If this continues to be the case then:

i) Analysts should accept that the knowledge they have acquired is of considerable value but only if it is effectively disseminated.

ii) Dissemination should reduce the incidence of failures and stimulate those at the end of the supply chain to ask searching questions about critical technical issues.

iii) Searching questions from customers (market pull) will eventually convince suppliers to be more open and less ambiguous about the weaknesses and limitations of their materials.

References

1. Injection Moulding, 2000, **8**, 3, p.123.

2 Thermo-oxidation

2.1 Introduction

It is safe to assume that all polymers will degrade when in contact with a potentially oxidising medium (and therefore with air) and that the rate of degradation will increase with increasing temperature. For simple hydrocarbon polymers (R_1H) the initiation step generally involves the reaction of adventitious hydrocarbon free radicals $R_1^\bullet$ with oxygen to form peroxide radicals $R_1O_2^\bullet$.

$R_1^\bullet + O_2 \rightarrow R_1O_2^\bullet$ (reaction (a))

All materials and products will, via their polymerisation and processing history, have developed a concentration of peroxide radicals. The propagation of further oxidation then depends on slower reactions and in particular the abstraction of hydrogen from adjacent polymer molecules by the peroxide:

$R_1O_2^\bullet + R_2H \rightarrow R_1OOH + R_2^\bullet$ (reaction (b))

to produce another free radical $R_2^\bullet$ (which immediately reacts with oxygen to replenish the peroxide concentration) and an unstable hydroperoxide which via decomposition or other reactions generate a further two reactive species.

$R_1OOH \rightarrow R_1O^\bullet + OH^\bullet$ (reaction (c))

The conversion of peroxides to hydroperoxides is the rate determining step for the chain reaction.

The rate and extent of degradation may be monitored by:

- Quantitative analysis of reaction by-products such as carbonyls,
- Changes in molecular weight distribution,
- Consumption of oxygen,

- Detection and quantification of reaction exotherms,
- Changes in mechanical properties.

These will all reveal that degradation proceeds in two stages as shown in Figure 2.1. The induction time (which reduces with increasing temperature) may be regarded as the safe lifetime of the material under the test conditions. At the end of the induction period there is a rapid increase in reaction products, reaction exotherm, oxygen consumption, and (usually) a rapid decrease in molecular weight and ductility (strain at break, impact strength etc.).

In addition to temperature, the induction time and therefore the durability depend upon:

- The physical and chemical structure of the polymer,
- The efficacy of the stabilising additives,
- The presence of metal catalysts,
- The presence of stress,

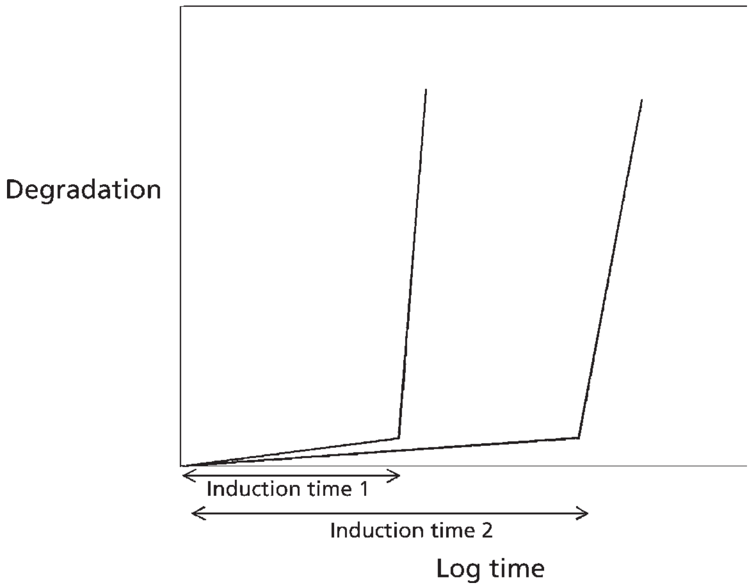


Figure 2.1 Thermo-oxidative degradation develops rapidly after an induction period. High temperature (1) lower (2)

- The power of the oxidising medium.

This chapter will concentrate mainly upon long-term degradation in service. However it needs to be emphasised that in-service durability is dependant upon the degradation accumulated during processing. It is inevitable that during hot melt processing (e.g. injection moulding, extrusion etc.) thermoplastics will degrade to some extent. Thermo-oxidation and hydrolysis (see Section 5.5) are the most common modes of process-related degradation, leading generally to chain scission, a reduction in molecular weight, a reduction in melt viscosity, and products with reduced resistance to fracture. Chain scission due high shearing forces also contributes.

In injection moulding the most frequent cause of thermo-oxidation is excessive residence time in the barrel. For uninterrupted production, the residence time:

$$= \frac{\text{Barrel capacity} \times \text{cycle time}}{\text{mould cavity volume}}$$

The use of machines of excessive capacity is therefore to be avoided. Also for obvious reasons, where process interruptions cannot be avoided, overcooked melt should be purged prior to process resumption.

In extrusion the ‘hang-up’ of hot melt is the main culprit. This is caused by stagnation at ‘dead spots’ (mainly in the die head region). In extreme cases a small fraction of the product is so severely degraded that ‘black spots’ are visible.

In the case of polyethylene, and in particular linear low density polyethylene (LLDPE), the main effect of hang-up is the formation of gels resulting from thermo-oxidative induced crosslinking. In extruded film these will be visible as elongated (in the direction of extrusion) features called ‘fish-eyes’ which seriously impair the structural properties of the film and its appearance.

A screen pack can usually be relied upon to entrap the largest gels. However, the gels are deformable, and at modest to high die head pressures larger than expected gels will squeeze through the pack. Remedial action includes:

- Avoid recycled material (predegraded and perhaps pregelled),

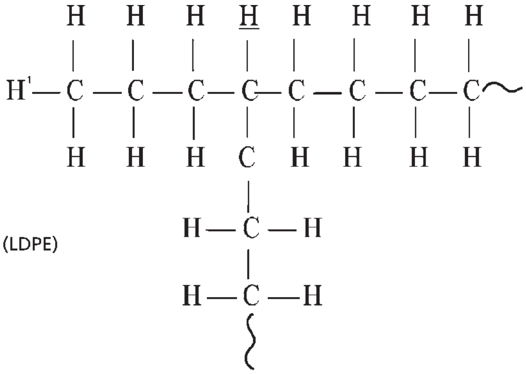
- Reduce LLDPE content in blends with low density polyethylene (LDPE),

- Avoid or remove hang-ups and dead spots in the die head,

- Increase level of antioxidant protection.

2.2 The influence of polymer chemistry

The resistance conferred by the generic chemical structure of the polymer is generally associated with its resistance to hydrogen abstraction. This is the rate determining propagation reaction (b) above. For saturated aliphatic hydrocarbon polymers, tertiary hydrogen atoms CH offer the least resistance to abstraction, followed by secondary (CH_2), followed by primary (CH_3). Hydrogen abstraction resistance is in the proportion 1:6:17 (tertiary:secondary:primary). For polyethylene, main chain hydrogens are secondary but at chain branches they tend to be tertiary.



Branched Polyethylene (LDPE)

Primary hydrogen H^1
Secondary H
Tertiary H

For this reason alone, highly branched PE (LDPE) offers less resistance to thermo-oxidation than the more linear high density polyethylene (HDPE). Additionally LDPE is more permeable to oxygen than HDPE and this enhances the difference. Non-branched LLDPE offers intermediate resistance.

The resistance of unsaturated (C = C) aliphatic polymers is poor because of the ease of abstraction of allylic hydrogen.

Polymers with a high aromatic hydrocarbon content offer the best resistance (e.g. polyether ether ketone (PEEK) > polycarbonate > polystyrene > polyethylene). However the intrinsic resistance of polymers arising from their chemistry cannot be compared because in practice this is rarely assessed. Invariably tests are carried out on compounds containing stabilising additives.

The resistance of commercial polymer grades to thermo-oxidation is most commonly indicated by its UL temperature index (Underwriters Laboratories). If this is (say) 100 °C then it implies that the material is reasonably safe to use in air for up to 100,000 hours (11.4 years) at this temperature. It may also be referred to as the 'maximum continuous use temperature' (MCUT). For any given polymer type the UL index or MCUT will cover a range of values depending on the quality of antidegradation protection. Tables 2.1 and 2.2 list the 'generic minimum' values for plastics and rubbers that can be relied upon for commercial grades with minimum protection (i.e. that generally required to stabilise the material under processing conditions). Although the generally unspecified type and concentration of additives mask the detailed influence of polymer chemistry, a rough order of merit is still apparent.

These temperature limits are inferred from monitoring the decline in such properties as impact strength and strain at break as a result of oven ageing (cooking) at higher temperatures. The time taken to reduce the properties by 50% is interpolated for a series of temperatures. The temperature that will reduce the properties by 50% after 100,000 hours is then inferred by extrapolation. The selection of test conditions may be assisted by assuming that the relationship between time and temperature to equivalent damage is approximated by the Arrhenius relationship:

$$\text{Reaction rate} = Ae^{-E/RT}$$

Where A is a constant, E is the activation energy of the reaction, R is the universal gas constant (8.3 J/mol/K) and T is the absolute temperature. If E is independent of temperature then integration of the reaction rate equation reveals a linear relationship between the logarithm of the time to accumulate a given amount of reaction induced damage and the reciprocal of the absolute temperature:

$$\ln(\text{critical time}) = \frac{A}{T} + E$$

Where the criterion is chosen to suit the experimental method (e.g. a 50% reduction in elongation at break, or a given volume of oxygen consumption, or the initiation of an oxidation exotherm etc.) activation energies typically range from 50 to 150 kJ/mol/K. For the most common activation energy of ~ 100 kJ/mol/K, a 10 °C increase in temperature increases the rate of reaction/degradation by a factor of between 2 and 3.

For most applications, the intended lifetime differs from 100,000 hours and/or the service temperature varies. The methodology for accommodating any specified thermal history can be revealed by example. Will a material with an MCUT of 100 °C be adequate under the following conditions?

i) 50 years at a continuous temperature of 80 °C.

ii) 5 years at a continuous temperature of 110 °C.

iii) 1 year at 100 °C + 0.1 years at 140 °C.

Table 2.1 Generic maximum continuous use temperatures for plastics

Materials	MCUT (°C)	Material	MCUT (°C)
ABS (medium impact)	70	Ethyl. Propyl. Copolymer	60
ABS/PSul alloy	125	EVA (25% VA)	50
ABS/PVC alloy	60	FEP	150
Acetal (homopolymer; 30%gfr)	85	Furane	150
Acetal (copolymer; 30%gfr)	100	HDPE	55
Acetal (copolymer)	90	HIPS	50
Acetal (homopolymer)	85	Ionomer	50
Acetal (homopolym; PTFE lub.)	90	LDPE	50
Acrylic (general purpose)	50	MF (cellulose filled)	100
Alkyd (mineral filled)	130	OL TPE	85
ASA	60	PA (RIM)	70
Bisphenol polyester laminate (glass fill)	140	PA (transparent)	90
CA	60	PA 11	70
CAB	60	PA 12	70
CEE TPE	85	PA 4/6	100
Chlorinated PVC	90	PA 6	80
CP	60	PA 6/10	70
CPE	60	PA 6/12	70
CTFE	150	PA 6/6	80
DAIP (mineral filled)	180	PA 6/6-6	80
DAP (mineral filled)	160	PA 6/9	80
ECTFE	130	PA/ABS alloy	70
EEA TPE	65	PAI	210
Epoxy resin (gp)	130	PBT	120
Epoxy resin (high heat)	170	PC	115
ETFE	160	PC/PBT Alloy	115

Table 2.1 Continued

Materials	**MCUT (°C)**	**Material**	**MCUT (°C)**
PE Foam	50	PPO	80
PEEK	250	PPO/PA Alloy	80
PEI	170	PPS (40% gfr)	200
PES	180	PPVC (<100% elongation at break)	50
PET (amorphous)	60	PS	50
PET (crystalline)	115	PTFE	180
PET (mineral filled)	140	PU (hard cast elast)	80
PET 35% gfr; supertough)	140	PU (soft microcell elast)	70
PF (foam)	120	PU (structural foam)	80
PF (gfr; high impact)	160	PU TPE 70A	70
PF (mica & glass fib fill; electr)	180	PVC (crosslinked)	95
PF (mica fill; electrical)	170	PVC (structural foam)	50
PF (mineral fill; high heat)	185	PVDF	150
PF (nat fibr fill; gen purpose)	150	PVF	150
PF (wood fill; gen purpose)	150	SAN	55
PF laminate (cotton fab)	105	SBS TPE 35A	50
PF laminate (glass fabric)	150	SEBS TPE 45A	85
PF laminate (paper)	90	Silicone	240
PFA	170	SMA (copolymer)	75
Polyarylamide (30%gfr)	125	SMA (terpolymer)	75
Polyarylate	130	Styrene-butadiene (K resin)	55
Polybutylene	90	TPX	75
Polyester DMC	130	UF (cellulose filled)	75
Polyimide	260	UHMWPE	55
Polysulphone	150	UPVC	50
PP (copolymer)	90	Vinyl ester	140
PP (homopolymer)	100	XLPE	90

Table 2.2 Generic maximum continuous use temperatures for rubbers

Material	Designation	MCUT (°C)
Bromobutyl	BIIR	120
Butadiene		60
Butyl	IIR	100
Butyl (resin cured)	IIR	130
Chlorinated PE	CPE	120
Chlorobutyl	CIIR	120
Chloroprene	CR	90
Chlorosulphonyl	CSM	120
Ebonite		80
Epichlorohydrin	CO	130
EPDM (sulphur cured)	EPDM	120
EPDM (resin cured)	EPDM	150
Ethylene vinyl acetate	EVM	110
Ethyl acrylate	ACM	150
Fluoroelastomer	FPM	210
Fluorosilicone	FVMQ	200
Isoprene	IR	60
Natural rubber	NR	60
Nitrile (< 20% ACN)	NBR	110
Nitrile (> 20% ACN)	NBR	120
Nitrile/PVC polyblend	PNBR	90
Nitrile (carboxylated)	XNBR	110
Nitrile (hydrogenated)	HNBR	150
Perfluoroelastomer	FFKM	260
Styrene-butadiene	SBR	70
Urethane (ester)	AU	75
Urethane (ether)	EU	75

For most polymers a 10 °C rise in temperature will increase the rate of degradation by a factor of between 2 and 3. For the 80 °C application, and in the absence of specific additional information, we must conservatively assume the lower factor (i.e. 2). At 20 °C below the UL index, the rate of reaction will be decreased by a factor of 4 so we should expect a durability of 4 x 11.4 = ~ 45 years. For the 110 °C application we must conservatively assume the higher factor (i.e. 3). At 10 °C above the UL index, the rate of reaction will be increased by a factor of 3 so we should expect a durability of 11.4/3 = < 4 years. For the third application, 0.1 years at 40 °C above the UL index is equivalent to 3^4 x 0.1 = 8.1 years at 100 °C. The intended exposure is therefore equivalent to 9.1 years at 100 °C. Therefore it would be safe to assume that the material is not adequate for i) and ii) but it is adequate for iii).

2.3 The efficacy of stabilising additives

Commercial polymer compounds invariably include heat stabilising additives. The major classes of stabilisers are described below.

'Primary antioxidants' or 'chain breaking antioxidants' These in the main act as labile hydrogen donors (AH). They compete favourably with the polymeric hydrogen abstraction reaction (b) above:

$$RO_2^{\bullet} + AH \rightarrow ROOH + A^{\bullet}$$

Where $A^{\bullet}$ is more stable than $R^{\bullet}$.

Hindered phenolic compounds and secondary aromatic amines dominate this class. Figure 2.2 is an example of a low molecular weight phenolic. Hydrogen is donated from the OH group. In addition the additive will act as a free radical scavenger or trap via:

$$A^{\bullet} + RO_2^{\bullet} \rightarrow AOOR$$

This 'mopping up' process is favoured over reaction (b) above when the mobility of the additive (AH) is greater than the mobility of the polymer (RH). Amines act as hydrogen donors via the relatively low bond energy of H-N groups.

Although amines as a group are technically more powerful antioxidants than phenolics they suffer from other limitations. A major disadvantage of amines is their greater tendency to discolour as a result of stabilising reactions. Common by-products are diimines which are powerful chromophores. For this reason amine-based antioxidants are rarely used for stabilising plastics but are used for rubbers (which are normally black). Also many amines are weak carcinogens.

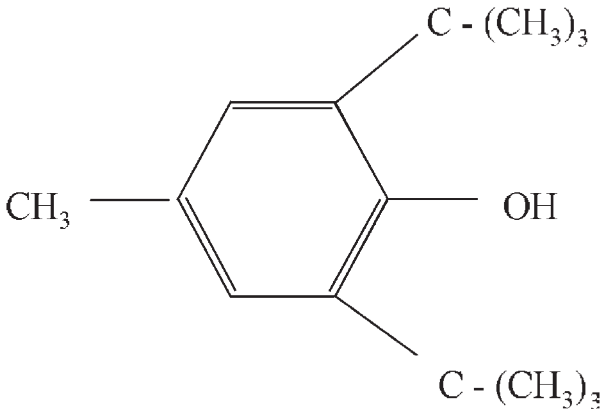


Figure 2.2 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene or BHT)

Phenolic antioxidants are also responsible for a variety of discolouration problems. 'Gas fading' is due to the oxidation of phenolic antioxidants by ambient gases such as nitrogen oxide and sulphur dioxide. The use of gas heaters during processing or subsequent storage should be avoided, otherwise phenolic content should be reduced, to be replaced by high activity phosphites. Another problem involves the reaction between resin catalysts and phenolics. Modern catalysts can be very acidic and these may react with the antioxidant by-products to produce quinone chromophores. It has been reported [1] that butylated hydroxytoluene (the least expensive phenolic antioxidant) is the most common culprit, and for critical applications should be avoided in favour of higher molecular weight, more hindered, phenolics.

The portfolio of primary antioxidants is too large to list here. As a general rule the lower molecular weight types are preferred to protect the polymer during processing, and the higher molecular weight types for long-term protection during service.

'Secondary antioxidants' or 'preventative antioxidants' These in the main act as hydroperoxide decomposers (A) in competition with reaction (c):

$ROOH + A \rightarrow ROH + AO$

where the oxidised stabiliser and the alcohol ROH are stable. Additives in this class include phosphorus-containing compounds such as phosphites and sulphur-containing compounds such as thioesters. Phosphites such as tris-nonylphenyl phosphite tend to be selected for protection during processing and have the advantage of FDA approval. A major disadvantage in many applications is their poor hydrolytic stability. Aliphatic phosphites are less resistant to hydrolysis than aromatic phosphites. Thioesters are more useful for protecting the polymer in service but impart an unpleasant odour/taste and achieving FDA approval is extremely difficult. Another disadvantage of thioesters is that they degrade the protection offered by hindered amine light stabilisers (HALS).

Antiozonants and waxes

Ozone (O_3) cracking will limit the durability of unsaturated rubber products that are subjected to surface tensile stresses. The ozone cleaves ethylenic double bonds.

Physical protection is provided by the addition of waxes that migrate to the surface of the product and thereby act as a barrier to ozone ingress. High molecular weight paraffinic waxes (microcrystalline waxes) form a more cohesive protective layer than low molecular weight waxes but the latter provide protection more rapidly after processing. A mixture of waxes is therefore beneficial.

In dynamic applications (e.g. cyclic loading and sliding) the protective layer tends to flake off and chemical protection via antiozonants is necessary. Antiozonants are dominated by phenylenediamine-based additives. These react preferentially with ozone and, as with the waxes, migration of the additive to external surfaces is essential.

Antiozonants are susceptible to leaching. The pH of the contacting water has a significant influence on the durability of stabilised products. Under test conditions [2] that simulate acid rain in the USA (pH down to 4.2) the increased rate of leaching with increasing acidity was quantified for a range of antiozonants of different molecular weight and basicity. The best combination was a mixture of *N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine (6PPD), with a molecular weight of 268, and 2,4,6-tris-(*N*-1,4-dimethylpentyl-*p*-phenylenediamino)-1,3,5-triazine (TAPDT), with a molecular weight of 693.

Antiozonants do not stabilise against thermo-oxidation via molecular oxygen and antioxidants do not stabilise against ozone attack.

Acid scavengers/acceptors

For some polymers, acids are the principal by-product of degradation (see PVC below), and for many others (e.g. acetals) small amounts of acid promote other forms of degradation (e.g. hydrolysis). Scavengers are designed to mop up and deactivate such acids.

Metal deactivators

See Section 2.4 Metal catalysis.

For applications such as cable and wire insulation, or other applications involving heat and contact with copper, it is now common practice to use compounds containing metal deactivating additives. These are mainly chelating agents that capture metallic ions to form stable compounds. Chelating agents for polyethylene, crosslinked polyethylene, and polypropylene in contact with copper have been reviewed [3].

It follows that in general, stabilisation involves a combination of additives. There is an obvious functional synergism between secondary and primary antioxidants, because the former attempt to prevent the initiation of degradation reactions and the latter are designed to prevent propagation. In addition it is common practice to employ different antioxidants for protection during processing and in service, where the latter are less mobile than the former. Optimisation of stabilisation packages for specific materials and applications is a massive endeavour for the material supply and compounding sectors.

Although maximum synergy is the positive objective it is the unexpected antagonism between additives that cause most problems and some premature failures. An example is the complex influence of carbon black.

The surface of carbon black particles contains phenolic groups and it is generally regarded as a weak antioxidant as well as a powerful UV stabiliser. Oxygen activated carbon black is more powerful. Sulphur activated grades are even better. In combination with certain conventional sulphur-based antioxidants (e.g. thio-bis-naphthol) the result is definitely synergistic. However it was shown many years ago that in combination with most hindered amine and some phenolic antioxidants, carbon reduced rather than enhanced the degree of protection [4]. Specifically the degradation induction time at 140 °C for polyethylene was as follows:

- 450 hours when protected with 0.1% *N*,*N*′-diphenyl-*p*-phenylenediamine alone,
- 100 hours when protected with 0.1% *N*,*N*′-diphenyl-*p*-phenylenediamine + 3% carbon black,
- 20 hours when protected with 3% carbon black alone.

The degradation induction time (or oxidative induction time (OIT)) is normally associated with the complete loss of effective stabilisation via a combination of:

- Chemical reactions,
- Leaching or exudation,

- Additive precipitation.

At the high temperatures of melt processing or OIT testing, depletion is dominated by chemical reactions. It has been established that for phenolic stabilised polyolefins, the rate of chemical consumption of antioxidant (AO) and therefore the rate of increase in peroxide radical concentration, is inversely proportional to the square root of the residual antioxidant concentration [5]. It would therefore be reasonable to suppose that the OIT, which may also be called the time to embrittle (t), would have the form:

$$t \propto [AO]^{0.5}$$

where [AO] is the initial antioxidant concentration. This was reported to be the case over a range of antioxidant concentrations and for a number of different antioxidant types [6]. For convenience the features of interest are shown diagramatically in Figure 2.3. Notably:

i) Durability is sensitive to antioxidant type as well as concentration. For example, a 0.4% concentration of Irganox 1010 (described as type AO-1) in PP gave a lifetime of 175 days at 135 °C compared with only 60 days for type Irganox 1076 (AO-2). A 0.2% concentration of Irganox 1330 (AO-3) in HDPE gave a lifetime of 500 days at 120 °C compared with only 200 days for type AO-2.

ii) There is a departure from the square root law at low antioxidant concentrations (~ 0.1%). The 'departure concentration' was observed to increase with increasing molecular mass of the antioxidant. This was explained as follows. Oxidation reactions are confined to the amorphous regions of the polymer. The probability that a discrete amorphous region will not be stabilised increases as the stabiliser content reduces and the molecular weight of the stabiliser increases.

However at the lower temperatures and longer times of in-service degradation, additive mobility and solubility are important and in most cases act as the rate determining factors. One model [7] proposed that the induction period for thermo-oxidation with antioxidant protection was dominated by the ratio:

$$\frac{S^2}{D}$$

Where S is the solubility of the additive in the polymer and D is its diffusion coefficient.

Additive precipitation has been reported to reduce effective primary antioxidant levels by 80% [8]. The material was a medium density polyethylene (MDPE) pipe grade compound containing 0.3% phenyl sulphide stabiliser. After cooling from the melt the

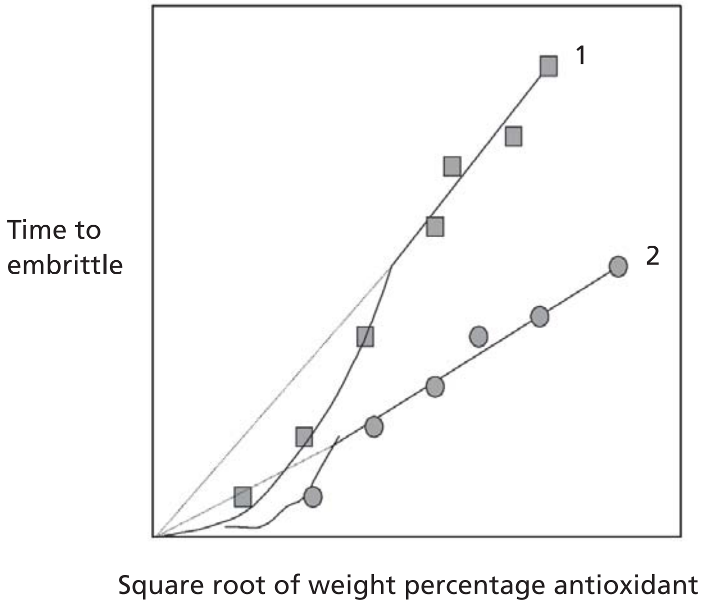


Figure 2.3 Relationships between durability and initial antioxidant content. 1 is a higher molecular weight AO than 2

stabiliser was well dispersed, even though the equilibrium solubility at ambient temperatures would only have been ~ 0.03%. The low mobility of the additive at ambient temperatures maintained a supersaturated solution. However after 1000 hours at ~ 100 °C, the time and mobility were sufficient to initiate and grow antioxidant crystals from solution leaving an equilibrium solution of ~ 0.06%. Antioxidant crystals do not act as stabilisers and may even act as catalysts for degradation. After this phase, antioxidant loss is dominated by leaching or evaporation from the surface of the material.

Loss via chemical reaction in polybutylene and polyethylene pipe is reported to be negligible [9]. When tested at elevated temperatures with water on the inside and air on the outside, stabilised pipe degraded and failed from the bore surface. However for unstabilised pipe it was the external surface that degraded. This confirms that depletion in contact with water is dominated by leaching and that air is a more powerful oxidising medium than water. Obviously the stabilisation package used would provide excellent protection against degradation during high temperature processing (the predominant consideration for common polymeric components), and would appear to provide good protection under short-term, high temperature testing (e.g. OIT), but the package did not appear to be optimised for long-term resistance to less severe temperatures.

It also follows that predicted durability values based upon the extrapolation of short-term (inexpensive) tests are generally suspect. For example the OIT for pipe grade polybutylene was monitored [10] over a wide temperature range (220 °C to 140 °C) and therefore a wide range of test durations (OIT = 3 hours to 5000 hours). The gradient of the $\log_{10}$ (OIT) versus $\log_{10}$ (reciprocal absolute temperature) plot reduced from 212 kJ/mol at the highest temperature to 108 kJ/mol at the lowest temperature. If lifetime extrapolation relied only upon the highest temperature tests then this would have predicted a lifetime of many thousands of years at 90 °C. Linear extrapolation of the gradient at 140 °C to 90 °C would predict a lifetime of about 50 years. However if the decline in activation energy is assumed to continue between 140 °C and 90 °C then the predicted OIT at 90 °C would be only ~ 5 years. It has been suggested that some of the problems of test acceleration may be overcome by testing at high oxygen pressures rather than excessive temperatures [11].

2.4 Metal catalysis

The presence of certain metals or metal ions (M^+, M^{++}, etc.) promotes thermo-oxidative degradation by their catalytic action. The interaction is complex but is assumed to be dominated by promotion of the decomposition of hydroperoxides.

$$ROOH + M^+ \rightarrow M^{++} + RO^\bullet + OH^-$$

or

$$ROOH + M^{++} \rightarrow M^+ + ROO^\bullet + H^+$$

The main sources of metal ions in polymer products are pigments, catalyst residues from the polymerisation stage, contamination during processing, and direct contact with metal substrates or salt solutions in service. Polyolefins (polyethylene, polypropylene and polybutylene) are particularly susceptible. Transition metal catalyst residues are unavoidable and therefore the most common source of problems. These residues, dispersed at a concentration of only a few ppm, act as the sites for initial degradation and explain the appearance of discoloured spots on the surface of products prior to more homogeneous degradation.

The most common pigment is titanium dioxide and this is known as a weak promoter of thermo-oxidation [12]. The effect of different grades of the pigment incorporated in LDPE film at 0.5% concentration was assessed by monitoring the build up of hydroperoxides and carbonyls during oven ageing. An unpigmented control offered the best resistance. Compounds containing uncoated anatase grades offered the worst resistance with an implied reduction in durability of about 50%. Coated rutile grades were relatively more stable. However in a later paper [13] and applying similar techniques to polypropylene film the effects were quite different. For unstabilised grades the coated rutile reduced implied durability by a factor of ~ 30, whilst uncoated anatase produced no deleterious effects. With antioxidant stabilised grades durability was in the order unpigmented > rutile > anatase. However with mixtures of antioxidant and hindered amine light stabilisers, unpigmented = rutile = anatase. This emphasises the complexity of interactions and the difficulty of optimising the stability of real compounds.

Table 2.3 lists the oxygen induction time for polypropylene powder/metal stearate mixtures. Under these test conditions, the copper anion, which is the metal ion most likely to be encountered in service, reduces OIT, and by implication, durability, by a factor of about 10.

The severity of catalysis depends on the valency of the metal ion. The higher the valency the greater the catalytic activity (for example cupric oxide is 15 times more reactive than cuprous oxide). However the activity is most affected by the nature of the bond between the metal and its ligand or anion. Simple salts with mainly ionic bonds are the most damaging. More complex organometallic compounds with a high degree of covalent

Table 2.3 The effect of various metal stearates (0.5% by weight) on the OIT of polypropylene as measured at 125 °C [3]

Metal stearate	Oxygen induction time in min
Cobalt	5
Chromium	8
Manganese	8
Copper	10
Iron	12
Vanadium	15
Nickel	18
Titanium	28
Zinc	40
Cadmium	50
None	125

bonding are the least damaging and may in fact retard rather than accelerate thermo-oxidation (for example copper oximide reduces the rate of degradation by a factor of 2). The severity also depends upon the concentration of metal ions. It has been shown [14] that polyethylene containing low concentrations of copper stearate suffers reduced resistance to degradation, but at higher concentrations the copper acts as a weak stabiliser. The transition from promotion to inhibition occurs at a concentration of ~ 1000 ppm Cu. It has been proposed that at higher concentrations of Cu the following stabilising reaction predominates:

$$RO_2^{\bullet} + Cu^{+} \rightarrow RO_2^{-} + Cu^{++}$$

It is emphasised that metal catalysis is complex and this leads to considerable confusion and misinterpretation. For example it is possible that accelerated tests (e.g. using high metal ion concentrations) will tend to mask or even reverse the reactions that will occur in service.

Another associated problem with residual metal catalysts is that they may ‘poison’ the stabilising additives by generating Brönsted acids or Lewis acids. Primary antioxidants such as amines are protonated by acid reaction and can no longer act as free radical scavengers. Secondary antioxidants such as phosphites are hydrolysed by the acids. Primary phenolic antioxidants combine with metal chlorides to form metal phenolates, which have no stabilising potential and furthermore are highly coloured. The addition of acid scavengers (e.g. calcium stearate) will minimise these problems.

An interesting example of copper catalysed failure of polypropylene occurred in a German hospital [15]. The combined cold and warm water system was originally installed using copper pipe but some failures occurred ‘shortly after commissioning’ because of ‘microbiologically influenced corrosion’ (MIC). The precise mechanism was not identified but it led to serious pitting and the release of large quantities of copper into the potable water. Periodic flushing with citric acid retarded the process. About 50% of the system was reinstalled using polypropylene pipe. 71 failures occurred in the polypropylene pipe between 4 and 5 years after installation within the warm part of the system, but none within the cold part. High rates of thermo-oxidative degradation at the relatively modest temperature of 55 °C were put down to copper catalysis. It was then noted that raising the water temperature to 55 °C eliminated MIC from the copper. The optimum system would therefore be copper for warm water (avoiding MIC) and PP for cold water (avoiding thermo-oxidation).

Cases 2.8.1, 2.8.2 and 2.8.7 show the effect of copper anions on the durability of polyethylene film, rubber expansion joints, and rubber hot water bottles, respectively.

2.5 The influence of stress

It is important to emphasise that that the vast majority of published data on thermo-oxidative degradation (including those in Tables 2.1 and 2.2) have been collected by ‘cooking’ the material in an unstressed state. It is generally observed that when the material is cooked whilst under the simultaneous application of stress, the rate of degradation increases and MCUT decreases. The subject has been reviewed [16]. Tensile stresses are not sufficient to break bonds and thereby increase radical concentration, but can be expected (by bond stretching) to reduce the activation energy (E) of the rate process. Tensile stresses can also be expected to increase oxygen diffusion rates via volume dilation.

The creep rupture characteristics of polymers under constant stress and elevated temperatures typically reveal two transitions as shown in Figure 2.4. Failures up to the first transition (type I) are determined solely by the viscoelastic characteristics of the material (the dependence of yield strength on time and temperature). Type I failures exhibit no degradation and are independent of the oxidising medium or the efficacy of stabilising additives. Failures in the longer term and after the second transition (type III) are virtually independent of stress. The time to failure is virtually equal to the degradation induction time in the absence of stress. Type II failures involve a combination of stress and degradation effects.

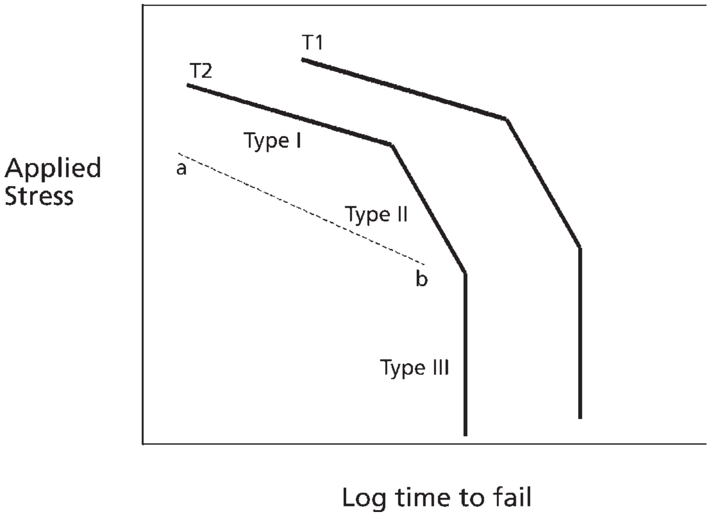


Figure 2.4 Elevated creep rupture characteristics. Type 1 failures are ductile and are insensitive to degradation, Type II failures are due to stress corrosion cracking, Type III are due to degradation embrittlement and are insensitive to stress. Temperature T2>T1

Line ab in Figure 2.4 may be regarded as the time to initiate crazes or microcracks. Under conditions that lead to type I failure, bulk yielding occurs prior to the attainment of critical crack length. However at lower stresses, a critical crack length has time to develop prior to yielding and type II brittle fracture is the mode of failure. This occurs in air more rapidly than in a vacuum. Oriented PP fibres at 130 °C fail after 100,000 s in vacuum and 10,000 s in air at a stress of 30 MPa [17]. It must be assumed that the very high surface to volume ratio of crazed material promotes rapid oxygen absorption within the craze fibrils, leading to accelerated and highly localised thermo-oxidative degradation, premature fibril rupture, increased crack growth rates, and reduced creep rupture time. In this respect type II failures may be classified as a form of stress corrosion cracking (SCC).

As shown in Figure 2.5 for HDPE, the log of transition time to type II failure reduces linearly with increasing temperature. At ambient temperatures and under stress, localised thermo-oxidation threatens product durability after only ~100,000 hours (11 years). This is significant for many polyethylene products (pipe, cable, geotextiles) with a typical design life expectancy of 50 years. The premature failure of a polyethylene film used as a damp-proofing membrane for buildings was observed to initiate at film folds where

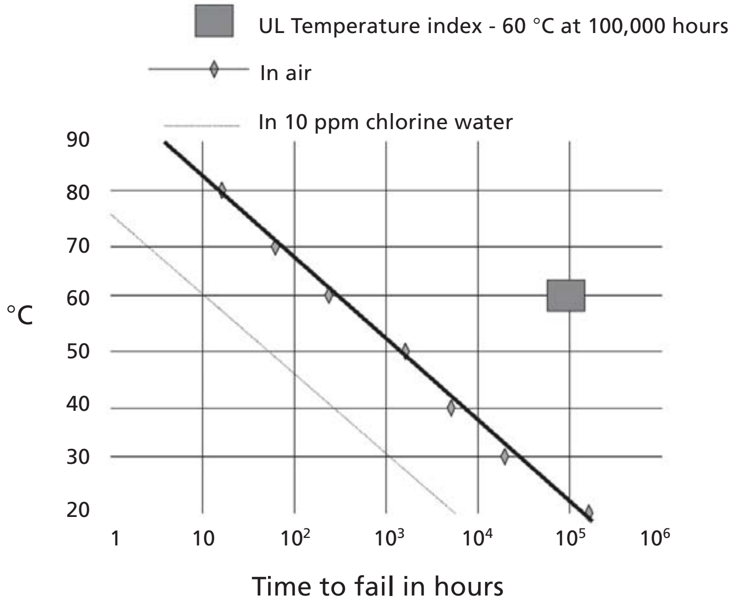


Figure 2.5 The ductile to brittle transition time (type I to type II failure) for HDPE as a function of temperature

stresses are maximum. The product specifier had assumed that a material with a UL temperature/MCUT of 60 °C would not embrittle within 50 years at ambient temperature.

Figure 2.5 also reveals that oxidising media that are more powerful than air (e.g. chlorinated water) will further accelerate the transition from ductile to brittle failure. This is discussed in the following section.

2.6 The oxidising medium

The molecular oxygen (O_2) in air or dissolved in water has a modest oxidation potential compared with oxygen in some other states. Ozone (O_3) and atomic or singlet oxygen are for example more aggressive. Singlet oxygen is probably the more common cause of premature oxidative degradation in plastics whilst ozone is the major culprit with rubbers (see Case 2.8.6).

Rubbers with very poor ozone resistance are those with unsaturated (C=C) bonds in the main chain. These include butadiene and isoprene rubbers such as NR, IR, BR, SBR, and NBR. Those with modest but usually inadequate resistance include IIR, CR, HNBR, and CO. Rubbers with good intrinsic resistance are those with saturated main chain bonds including ACM, CSM, EPDM, FKM, CPE, and silicone.

Blends of resistant and non resistant polymers have been used to satisfy standard accelerated ozone tests but where possible this should be avoided. IBM [18] discovered ozone cracking in flexible computer cooling hose after 9 months in service. The hose was a blend of PVC/NBR and it was known that a ratio of at least 20/80 should have been specified. However analysis revealed a ratio of only 14/86. To avoid repetition of such failures IBM changed their specification. The product test was made more severe (100 mPa partial pressure ozone, 25% strain, 50 °C, for 168 hours) and to minimise gross compounding errors, blends were disallowed in favour of intrinsically resistant rubbers of EPDM, CPE or chlorosulphonated PE.

The poor corrosion resistance of copper pipe in hot chlorinated water and its installation costs invited the plastics industry to consider domestic heating and hot water applications as an important market. Three major candidates were identified:

i) Crosslinked polyethylene (XLPE or PE-X).

ii) Chlorinated PVC (CPVC).

iii) Polybutylene (PB).

By the 1980s PB had become the frontrunner in the USA. In the southern States PB pipes were installed in a significant proportion of new homes. By the early 1990s failures of PB pipe and the associated acetal fittings were being publicly reported and several local class actions against the supply chain had been initiated. In 1995 DuPont, a supplier of acetal homopolymer for some of the fittings, announced a $120 million settlement to cover future remedial costs. In the same year Shell Chemicals (supplier of the PB material) and Hoechst Celanese (supplier of acetal copolymer for the pipe fittings) agreed to a $850 million resolution of a national class action. This settlement, which is believed to be the largest of its kind for a polymeric product, would be used to fund the cost of replacing leaking plumbing systems for both current and future complainants.

At one stage it was regarded as a possibility that degradation of the acetal fittings might trigger degradation of the PB pipe via (acidic) reaction products, but this turned out to be unlikely. Therefore it is reasonably safe to separate the two issues and concentrate our attention here on the failure of the main part of the system, the PB pipe. There were several types of avoidable failure including those associated with poor installation such as local bending and twisting. However it was apparent that the durability of the systems was fundamentally limited by thermo-oxidative degradation.

The bore of a PB pipe after failure is shown in Figure 2.6. Through the wall thickness there is a progressive discolouration (yellowing), loss of antioxidant, and reduction in molecular weight. The embrittled inner surface microcracks under the influence of tensile stresses generated by hydrostatic pressure, pipe bending and jointing. Hot chlorinated water comes into contact with highly stressed crack tips which then leads to localised degradation, crack growth and eventually through-thickness splitting. This may be safely described as an example of stress corrosion cracking (SCC). Thermo-oxidative chain scission is the dominant degradation mechanism. Chlorine (added to domestic water

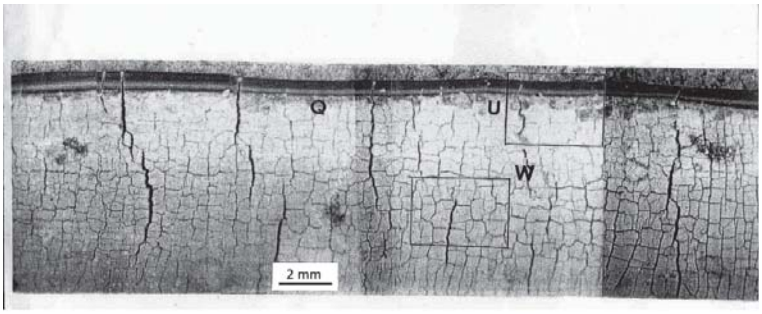
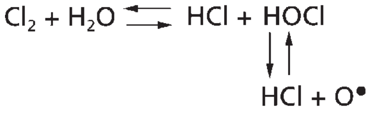


Figure 2.6 The bore of a failed PB hot water pipe

supplies as a disinfectant at typically ~ 1 ppm) accelerates this mechanism by providing a source of highly reactive nascent (atomic) oxygen via a secondary dissociation reaction:



$$\begin{array}{l} \mathrm{Cl_2 + H_2O \rightleftharpoons HCl + HOCl} \\ \qquad\qquad\qquad\qquad\quad \downarrow\uparrow \\ \qquad\qquad\qquad\qquad \mathrm{HCl + O^{\bullet}} \end{array}$$

The potential power of this oxidising medium is partially determined by the concentration of chlorine in the water. The actual power is determined by the stability of the hypochlorous acid (HOCl).

The supplier had calculated that even under conditions of continuous use, the material would comfortably last 50 years. However an evaluation of in service durability [19] revealed a most probable life expectancy of about 15 years. This was based upon an inspection of 1,150 pipes between 8 and 22 years old. 64% of these were visibly degraded and 42% contained penetrating cracks.

The difference between a predicted life of > 50 years and a most probable life of 15 years is the crucial factor that deserves particular attention. In early tests the effects of chlorination were ignored. Pipe was pressure tested at elevated temperatures using the medium of static water. At the recommended maximum pressure stress the times to rupture were as shown in Table 2.4.

Assuming a constant activation energy this would predict by extrapolation a failure time of 316 years at a continuous temperature of 60 °C. When the supplier later carried out the tests in circulating water containing 1 ppm chlorine the results were as shown in Table 2.5.

Table 2.4 Times to failure at elevated temperature in static water

Temperature (°C)	Failure time (hours)
115	8000
105	20000
95	53000

Table 2.5 Times to failure at elevated temperature in circulating water containing chlorine

Temperature (°C)	Failure time (hours)
115	2500
105	5500
95	12000

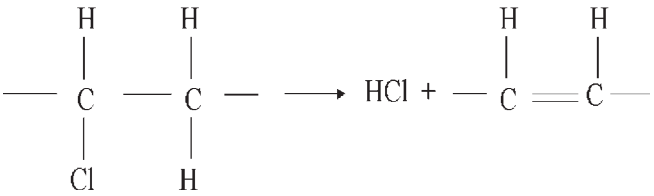
Assuming a constant activation energy this would predict by extrapolation a failure time of 29 years at a continuous temperature of 60 °C. The lifetime was reduced by ~50% for each x3 increase in chlorine concentration. Bearing in mind the significant nonlinearity of the Arrhenius relationship for PB referred to earlier [10], the lifetime is likely to be further reduced.

With static water the leaching out of antioxidants is initially high, but when the water reaches equilibrium saturation, loss by leaching is negligible. Bearing in mind the subsequent finding [9] that the OIT of PB is determined by the physical losses (e.g. precipitation, leaching, evaporation) rather than chemical losses, it is apparent that testing in circulating water would have significantly reduced predicted durability.

It would be generous to suggest that the initial test method was chosen because the supplier assumed that durability would be limited by creep rupture rather than material degradation. It would be less generous to suggest that the supplier chose to take the risk of adopting a test method that did not replicate the real severity of the intended service condition, on the grounds that it was less expensive. Even after countless days of cross examination the errors that gave rise to the litigation cannot be clearly stated. This is perhaps surprising to those of you who regard the legal process as a dedicated search for truth carried out by giant intellects. It is less surprising to those who have direct experience of similar proceedings.

2.7 Oxidation and stabilisation of polyvinyl chloride

The principle reaction of PVC in response to heat is dehydrochlorination.



$$-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}- \longrightarrow HCl + -\overset{H}{C}=\overset{H}{C}-$$

Hydrochloric acid then catalyses further dehydrochlorination. The unsaturated product of the reaction is a polyene which is sensitive to thermo-oxidation and photo-oxidation and may act as a strong chromophore.

The evolution of HCl due to thermal degradation is an important issue in hot melt processing. The acid will attack moulds and machinery and it is normal practice to employ special steels to minimise the problem. Process machinery that has been used with PVC needs to be scrupulously cleaned prior to use with certain other plastics otherwise residual HCl may (as with acetal) initiate an explosive reaction. HCl evolved from the burning of PVC is a major reason why the material is under pressure from environmental pressure groups. The corrosion and damage to communications equipment, caused by the combustion of PVC insulated cables in warships during the Falklands conflict, stimulated the search for alternative halogen-free materials.

Dehydrochlorination is accelerated in the presence of oxygen, but conventional chain breaking antioxidants do not significantly retard the process. Secondary (hydroperoxide decomposer) antioxidants such as tris-nonylphenyl phosphite and naphthyl disulphide are beneficial. However, the heat stabilisation of PVC relies mainly on additives that are effective acid (HCl) scavengers.

Lead-based compounds are the most powerful stabilisers for PVC. These include lead carbonate (the cheapest), tribasic lead sulphate, dibasic lead phosphite, and dibasic lead phthalate (the most expensive). Increasing concern (and in some cases restrictive regulation) about the toxic effect of lead threaten its traditional dominance, although it is estimated that in the UK it still accounts for over 50% of the PVC stabiliser market. Synergistic combinations of cadmium/barium compounds (e.g. phenates) also proved to be powerful but restrictions on the use of cadmium have likewise impaired their future use. The current optimum for safe stabilisation centres upon organo-tin compounds or synergistic combinations of Ca/Zn or Ba/Zn compounds plus secondary antioxidants.

2.8 Case studies

2.8.1 Low density polyethylene insulation covers

History

Glass fibre or mineral wool jackets of the segmented type are commonly used as cheap and removable insulation for domestic water storage cylinders. The insulation is covered by a thin red polymeric film, which is typically a plasticised PVC or a low density polyethylene.

After periods of time varying from a few months to ten years, PVC and LDPE types of material were found to have disintegrated at the areas of contact with the hottest parts of the cylinders. Brown to black discolouration was observed in both failed PVC and LDPE, but was more pronounced in the latter. Some customers thought that ‘burning’ of the plastic coverings had occurred and that this might lead to a fire. In fact, these failures were never catastrophic in terms of system operation, but the customer concern and the aesthetically unacceptable end result dictated that the problem be diagnosed and a remedy found.

Cracking failure of thin wall LDPE insulation on copper conductors has been experienced in the USA, where telecommunications wiring is brought into pedestals which are exposed to solar radiation. The two problems of LDPE failures are related.

Inspection and analysis

On inspection of the insulation covers from the hot water cylinders it was found that severe discolouration and cracking had occurred towards the top of the water tank, where temperatures are generally at their highest. Near the bottom there were some slight colour changes, but there was no obvious embrittlement. It was noticeable also that the discolouration and disintegration (multiple cracks) were also associated with areas where the natural wrinkles in the materials had been smoothed out. This can be assumed to be the result of the high temperature and the good contact brought about by the modest pressure of the ties.

Infrared spectra between 1500 and 2000 cm^{-1}, shown in Figure 2.7 were obtained for the polyethylene from the outside of the insulation jackets (a) and fragments close to the cracks (c). The large concentration of carbonyl (C=O) in (c) is indicative of gross oxidation.

Separate ageing experiments were carried out, whereby polyethylene from the outside of the insulation jacket was sandwiched under a fixed load, between glass-fibre insulation and either an aluminium or a copper substrate. The contact at 80 °C was carried out for 550 hours until the degree of oxidation of the sample contacted with copper was identical to (c) in Figure 2.7 and the sample was brittle. After the same time the oxidation observed in the sample contacted with aluminium was much less, and similar to that indicated by curve (b) in Figure 2.7. It can be deduced from this that copper is a catalyst of the oxidation process - if the aluminium is assumed to have no effect.

Similar ageing experiments were carried out with PVC samples. Copper and aluminium substrates were used. A comparison was also made between ageing in an air oven set at 80 °C and on a hot plate set at 80 °C. The latter simulates real life usage. In both instances the sandwich arrangement was adopted (Figure 2.8). In the first case the temperature was constant in the whole of the sandwich. In the second the temperature declined from 80 °C at the hot plate surface to a few degrees above ambient over the upper surface of the insulation.

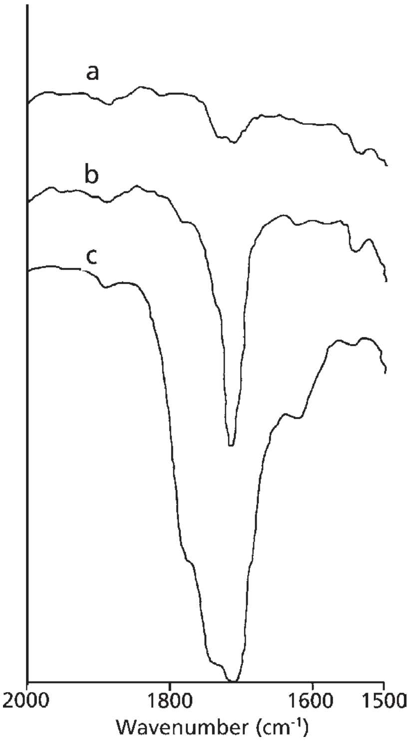


Figure 2.7 IR Spectra of polyethylene samples: (a) outside, (b) inside away from cracks, (c) inside adjacent to cracks

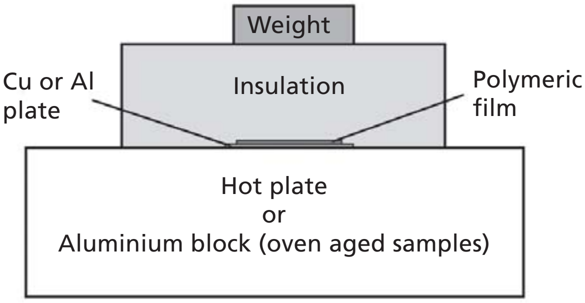


Figure 2.8 Sandwich structure for comparison of oven and hot plate ageing

It was found that embrittlement occurred after about a year in the case of PVC film aged on the hot plate, whilst the PVC aged in the hot air oven was still flexible after this time. There was no difference between time to brittleness on copper and aluminium substrates. Measurement of weight indicated that when plasticised PVC film is aged on the hot plate, embrittlement is partly due to loss of plasticiser. The other factors are almost certainly oxidation and dehydrochlorination of the PVC. The driving force for plasticiser loss is the temperature gradient and the consequent drop in vapour pressure from the surface of the PVC to the interior of the insulation. However, fibreglass insulation contains some lubricating oil. It appears that when there is no temperature gradient across the insulation (as in the air oven case) plasticiser loss is low because the vapour pressure of plasticiser and oil are rather similar.

The life of the PVC coverings is of the order of one year at 80 °C, as opposed to 550 hours for the particular LDPE covering examined.

Failure diagnosis

Copper catalysed oxidative failure is the principal cause of polyethylene failure.

Embrittlement by plasticiser loss and oxidation are implicated in the cracking of PVC coverings.

Lessons and consequences

1. Thin PVC film (containing phthalate and chlorinated paraffin plasticisers) and LDPE films are prone to degradation and embrittlement when in prolonged contact with hot water cylinders, and their use should only be contemplated in such situations if customers can accept what are effectively ‘cosmetic’ changes rather than catastrophic failures.

2. Plasticised PVC film should be used in preference to LDPE because of its longer life expectancy. Another argument in favour of PVC is that, increasingly, fire retardant grades are being specified and it is much easier to achieve good retardancy with PVC compounds.

3. Examination of the literature on the related problem of copper catalysed oxidative embrittlement of LDPE insulated copper wires indicates that substantial improvements can be achieved by judicious selection of antioxidant and the addition of a copper deactivator, but that even this is unlikely to yield a life much beyond that achieved for thin film PVC.

4. Experiments on PVC containing a polymeric plasticiser and with high heat stability showed that a much longer life could be achieved than for LDPE or 'conventional' PVC. Other materials, e.g. thermoplastic polyurethane film, with similar drape characteristics to PVC, were also shown to have long lives (no embrittlement after 1 year at 80 °C or 1000 hours at 135 °C). These alternatives, however, are more expensive than the commodity PVC and LDPE materials.

2.8.2 Rubber expansion joints

History

The axial expansion and contraction of pipe systems is commonly accommodated by rubber expansion joints in the form of convoluted bellows.

The case reviewed here concerns a central heating system for a hospital in Crete. The system was constructed with metal pipe of 100 mm inside diameter and was designed to operate at pressures of up to 0.6 MPa and water temperatures up to 85 °C.

60 fabric reinforced expansion joints were required of the general form shown in Figure 2.9.

Figure 2.9 Bellows cross section (unused)

Within 2 years of installation, 20 joints had failed by complete rupture or leaking. These were first noticed soon after the heating system was switched on at the end of the summer.

Inspection and analysis

The rubber was identified using Fourier transform infrared (FTIR) spectroscopy as a blend of natural rubber and polychloroprene.

The rubber at the bore of the failed bellows was friable to such an extent that parts had been eroded by the action of pumped water. The inside surfaces were coated in a yellow deposit as shown in Figure 2.10. On analysis this was found to comprise a mixture of silicon, zinc, and copper oxides. The local water supply was found to contain high levels of these oxides.

Failure diagnosis

A blend of natural rubber and polychloroprene should be able to provide long service in water at 85 °C without unacceptable thermo-oxidation or hydrolysis.

It is known that for many rubbers and plastics (e.g. polyolefins and nylons), certain metal ions accelerate thermo-oxidation by catalysing the reaction. At 85 °C it is estimated

Figure 2.10 Cross section of a failed bellows

that the high level of ionic copper would reduce durability of the rubber blend by a factor of about 10.

The leaking was evident on restarting the system because under this condition, thermal expansion of the piping was at a minimum and bellows expansion was at a maximum (crack opening).

Lessons and consequences

1. The durability of rubber (and plastics) components at elevated temperatures is seriously impaired by contact with transition metals in solution.
2. Metal ions may be naturally present (as in this case) or they may arise from other sources. A common source is chemical attack of metallic components (e.g. zinc and brass) by the contained/immersion fluid. Thus for example, chlorine water will attack a brass coupling, generate copper chloride in solution, and the ionic copper will catalyse thermo-oxidation of the polymer.
3. The bellows had been purchased through an intermediary and selected by them simply on the basis of cost and resistance to water at 85 °C. For rubber components with a critical structural function, direct contact between the supplier and the end customer is strongly recommended.
4. The bellows were replaced using a compound with superior resistance to catalysed thermo-oxidative degradation.

2.8.3 Vehicle tyres

History

A large number of vehicles are stored by Government Agencies (e.g. The Home Office in the UK). They are reserved for use in the event of national emergencies and include fire engines (known affectionately as ‘Green Goddesses’), and ambulances.

Green Goddess fire engines were employed extensively during a strike by civilian fire fighters in the late 1970s. The vehicles were manned by the military. A high incidence of tyre failures was reported leading in some cases to serious accidents. It was suspected that these might be due to either degradation of the tyres in storage or the indelicate driving skills of the military.

The Home Office required answers to the following questions:

i) Are the tyres currently safe for the projected use, i.e. one or two thousand miles of emergency use?

ii) If the tyres are safe, will they remain so for a further 10 years?

Inspection and analysis

The tyres were visually inspected for surface cracking. The extent of cracking was classified as severe, moderate, mild, or none. Those with 'severe' cracking would be readily classed as illegal and could be dismissed from future consideration. Tyres which were in visibly good condition (supplied mainly from Goodyear) were also excluded from further consideration. Figure 2.11 illustrates typical 'moderate' cracking.

Tyres were dissected and the component parts analysed. The cord reinforcement was an early form of viscose rayon and the tread was a natural rubber containing ~ 50% carbon black. The hardness of the tread was measured at 70 Shore A. The tensile strength and elongation at break of the cord were both respectable, being 250 N and 22.5%, respectively.

Tyres with moderate cracking were subjected to simulated service at 40 mph for up to 3,000 miles on a test drum. Figure 2.12 illustrates tread cracking on completion of the

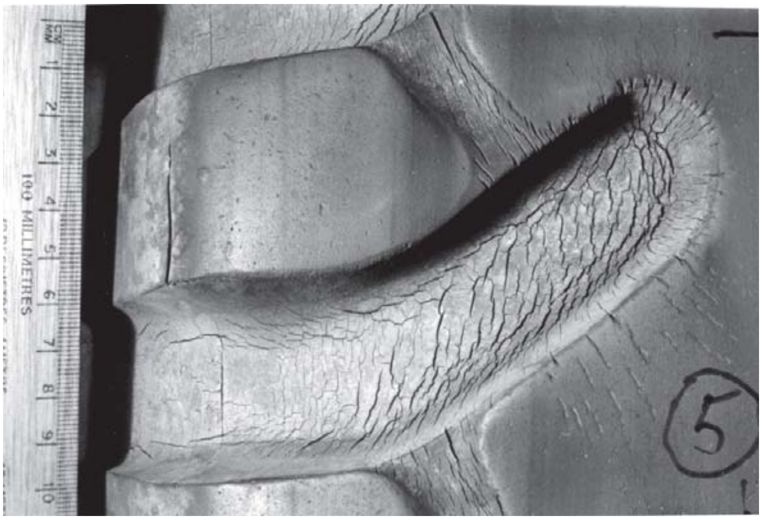


Figure 2.11 The surface of a moderately cracked vehicle tyre prior to testing

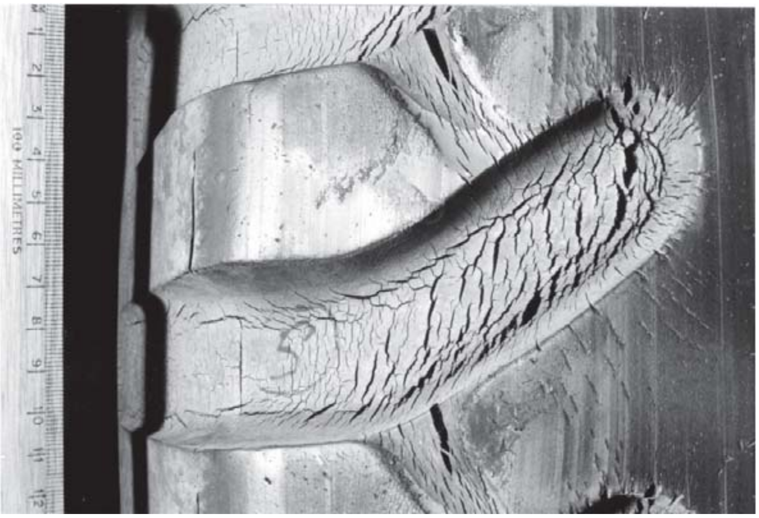


Figure 2.12 Surface as shown in Figure 2.11 after additional 3000 miles travel

tests. A visual comparison of Figures 2.11 and 2.12 reveals a significant increase in crack opening displacement, and this is indicative of crack growth through the tread thickness.

The peel strength between the rayon cord and the tyre carcass, and the tensile properties of the rayon cord, were monitored prior to, during, and after the tyre tests. The averages of the results were as follows:

Table 2.6 Properties of rayon tyre cords

Sample history	Peel strength to BS 903 A12 (N)	Cord strength (N)	Elongation at break (%)
0 miles	255	250	22.5
1,060 miles	207	265	5.3
3,000 miles	177	265	5.0

Failure diagnosis

The retention of rubber hardness during long-term storage suggests minimal thermo-oxidation of the bulk of the rubber. The cracking is due to ozone. The growth of ozone initiated cracks during 3000 miles of drum testing is modest and not in itself sufficient to render the tyres unsafe for future emergency use.

The cord peel strength and elongation at break are both surprisingly good after > 20 years of storage and not dissimilar to the values expected of a new tyre. However the declines in these values after simulated service on the drum testing machine are significant. The reduction in peel strength after 3000 miles is similar to that expected from a new tyre after 30,000 miles. The reduction in the elongation at break of the rayon cord is of critical concern. Such a reduction would impair the tyre's ability to sustain impact loads.

Viscose rayon has poor resistance to thermo-oxidation and hydrolysis. However, provided it is encased in rubber, access to atmospheric oxygen and moisture is severely restricted. Cords from untested tyres were removed and exposed to ambient air for 6 months and then tested for elongation at break. Exposure to air over this period reduced the elongation at break from an average of 22.5% to 11%. This reduction is far greater than would be expected from virgin cord.

It is apparent that although the long-term storage of the tyres has had little direct effect on the properties of the reinforcing cord it has sensitised the cord to future degradation. This may be due to the accumulation of free radicals, which only on exposure to oxygen or moisture then lead to rapid degradation. Evidently the surface cracks in the as-stored tyres do not provide sufficient access to atmospheric degradants. Under running conditions, crack growth and/or the increase in temperature, will provide sufficient access to sustain a degradation chain reaction.

Lessons and consequences

1. Testing for durability without a comprehensive simulation of service conditions can lead to gross errors. In this case the effect of storage on material properties is minor but the effect of storage on future in-service durability is massive.

2. Long-term storage of the tyres has sensitised the tyre reinforcement to future degradation in service. As a result the tyres will have poor resistance to impact.

3. In emergencies and where vehicles are driven by enthusiastic amateurs, a high incidence of kerb side impacts are to be expected.

4. Consequently, tyres with any visible cracking were deemed to be unsafe.

2.8.4 Flexible hose (example 1)

History

Flexible hose is used in a wide range of sizes to convey liquids under pressure. The usual construction is essentially a composite of rubber layers reinforced with steel wire in various configurations. The configuration and complexity of the reinforcement depends on the size of hose and the operating pressure. The rubber compound is selected according to the liquid to be carried and the environmental conditions.

One particular design of hose was used to convey water which in one application involved pressures of 0.7–0.8 MPa and temperatures in the range of 20–80 °C. Failure occurred by rupture of a hose, raising concern that this was not an isolated problem and the other hoses in service could be at risk. The failed hose is shown in Figure 2.13.

Figure 2.13 The failed hose

Inspection and analysis

The hose was relatively small bore and had a simple construction. By sectioning the hose into two halves by means of a band saw it was found that there was a single extruded tube with no inner reinforcement. The rubber tube was covered with a wire braided layer with a single spiral reinforcement on the outside. After removal of the spiral reinforcement the braiding was exposed and it could be seen that the braiding was 'shiny' over much of the length, but there were signs of corrosion near one end fitting. The leakage point through the braiding could be readily seen.

Examination of the inside surface of the hose revealed a split in the rubber beneath the failure point, which was clearly the direct cause of leakage. Another feature found was a depression in the inner surface, which in all probability was caused by contamination in the rubber compound.

The most important observation was that the rubber compound had become embrittled. Bending the cut hose quickly caused cracks to appear on the inner surface and these readily propagated. These cracks are shown in Figure 2.14.

A small portion of rubber was cut from the tube, and after sheeting on a hand mill extracted with methanol. A portion of the extracted sample was pyrolysed and an infrared spectrum recorded. This analysis showed that the polymer base was a blend of nitrile and styrene-butadiene rubbers, in a ratio of between 80/20 and 60/40.

Figure 2.14 Cracking/splitting of the bore caused by bending

Failure diagnosis

The leakage was clearly due to a split in the rubber tube. The embrittlement of the rubber is a very strong indication that it had been degraded through heat ageing. The ageing results in loss of elongation at break. Splitting of the hose then becomes likely where the inner surface is under tension, such as at a bend, because the strain exceeds the very much reduced ultimate elongation of the rubber. If, as suspected, contamination was present then this would further decrease the strength of the hose.

Nitrile rubber is regarded as having a maximum continuous service temperature of the order of 100–120 °C. However, blending the nitrile with SBR will lower the maximum service temperature, the magnitude of the drop depending on the SBR content. For the blend identified the maximum allowable service temperature would probably be in the 70–80 °C range.

The conclusion was that the rubber compound used could not withstand long-term service at the maximum temperature of 80 °C and suffered considerable degradation through heat ageing. The consequence of ageing was reduced tensile properties and splitting of the hose.

Lessons and consequences

1. For long-term use a rubber with an adequate continuous service temperature for the conditions expected must be chosen. The material here would have probably been satisfactory at a slightly lower temperature.

2. The problem suffered would not become apparent until after a considerable time of service and has implications for all other hoses of the same construction in similar applications.

2.8.5 Flexible connectors

History

An industrial heating system using 80 mm diameter steel pipe connected by rubber expansion bellows failed after 18 months in service. The system carried water at 120 °C at pressures of 0.5 MPa. Fortunately the burst did not cause any injuries, but it did destroy adjacent electrical control units. The product had a long successful record in similar applications and under similar service conditions.

Inspection and analysis

An external view of the failure is shown in Figure 2.15.

The rubber was confirmed by analysis to be sulphur cured EPDM containing carbon black, naphthenic process oil and inorganic fillers. The process oil content in an unused bellows was found to be 22%, compared with 11% and 9% in rubber removed from the inner and outer layers of the failed bellows. The respective sulphur contents were 2.5%, 5.8%, and 6.1%. The respective elongations at break were 600%, 450%, and 90%.

Failure diagnosis

The loss of process oil by evaporation is not unexpected at these high operating temperatures. This would contribute to the loss of elongation at break, but clearly it is not a major contribution. The inner and outer layers of the failed bellows have similar oil content but it is only the outer layer that has suffered a severe deterioration in structural properties. This is consistent with thermo-oxidative degradation. Although the outer layer is cooler than the inner layer, it degrades more rapidly because of contact with air.

Figure 2.15 General view of the failure site

The maximum continuous use temperature recommended for sulphur cured EPDM (see Table 2.2) is 120 °C. However this applies to a properly formulated and processed compound. In this case the sulphur content in the failed component is excessive. Excess sulphur acts as a 'pro-oxidant' to accelerate degradation.

Failure is due to an error in compounding which compromised the product's resistance to thermal degradation.

Lessons and consequences

1. Thermal degradation can be accelerated by external catalysts as discussed in Case 2.8.2, or by internal pro-oxidants such as free sulphur.
2. When products are expected to operate at or near to known material limits this needs to be recognised and reflected in the rigour of quality control and assurance procedures.
3. The product manufacturer agreed liability for the consequential losses of the failure.

2.8.6 Lift pump diaphragms

History

A diesel engine manufacturer used fuel lift pump diaphragms from two suppliers. The product from one would typically split after 50,000 miles, whilst the other functioned without any reported failures for more than 100,000 miles. The engine manufacturer needed to maintain a dual supply of the component and therefore was obliged to investigate the cause of the problem.

Inspection and analysis

Two failed diaphragms were inspected. The fabric reinforced rubber in both had split and torn. In addition and as shown in Figure 2.16, the surfaces of the diaphragms exposed to air were extensively microcracked. The cracks were aligned circumferentially and therefore normal to the direction of the applied principal tensile strain. Surfaces exposed to the fuel were undamaged.

Products from both sources were analysed to establish their composition. Both were nitrile/PVC blends with similar ratios (80/20). The main differences in composition were

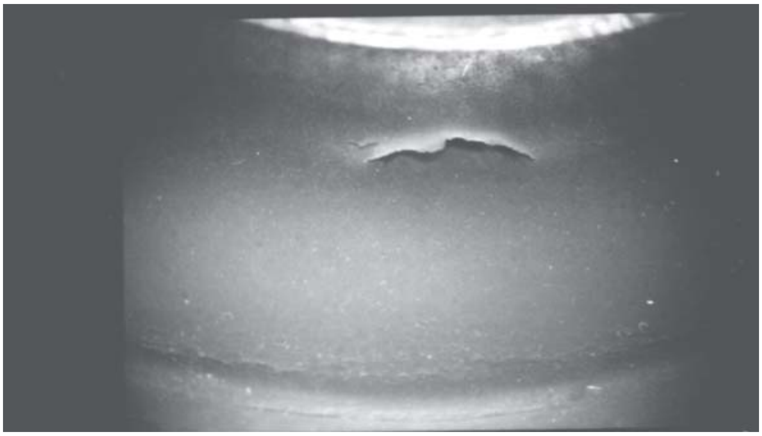


Figure 2.16 Microcracking on the air side surface of a fuel pump diaphragm

the concentration and type of plasticiser. The inferior product was plasticised with di-(butoxyethoxyethyl) formal to a level of 12%. The superior product contained alkyl sulphonic ester of phenol to a level of 7%. As a direct result of the different degree of plasticisation, the superior product was significantly stiffer.

Failure diagnosis

Failure is due to ozone cracking via atmospheric ozone. An inspection of superior diaphragms after 100,000 miles of service also revealed air side cracking.

In service the diaphragm is cyclically deformed by the action of a spring with a fixed force amplitude. Therefore the more flexible (inferior) diaphragm will be exposed to higher principal tensile strains and hence the penalty of reduced durability.

Lessons and consequences

1. It is apparent from the absence of antiozonants in both formulations, that neither supplier had considered that ozone attack would be a limiting factor. For added protection both suppliers were advised of the need to improve the ozone resistance of their product.

2. Ozone attack is triggered and promoted by tensile strain rather than tensile stress.

3. The supplier of the inferior product was instructed to increase the hardness (and hence modulus) of their rubber formulation.

4. The addition of an antiozonant, plus a reduction in the level of plasticisation, solved the problem and satisfied the durability requirements.

2.8.7 Hot water bottle

History

Over the years an appreciable number of cases have been reported of hot water bottles failing in service. In one instance a bottle failed catastrophically after about 3 months use, resulting in hot water coming into contact with the user. The failure is shown in Figure 2.17.

It was understood that the bottle had been used according to instructions, being filled with hot rather than boiling water.

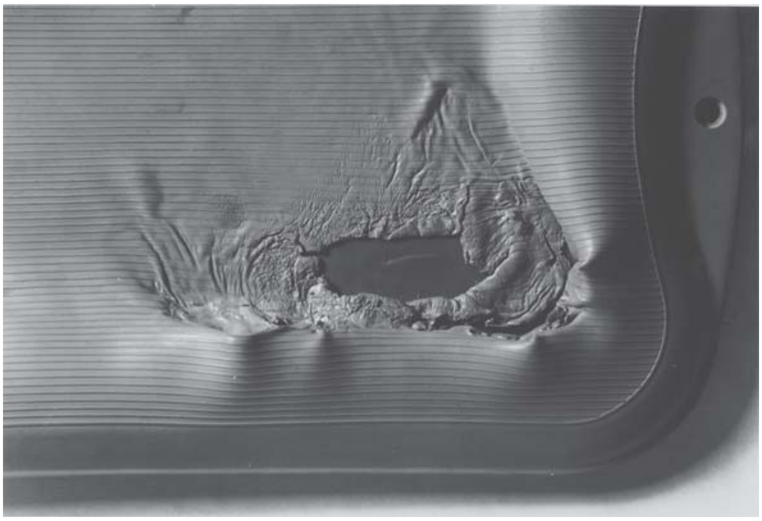


Figure 2.17 Close-up of the failure illustrating extensive viscous flow

Inspection and analysis

The bottle had been moulded with one side externally smooth and the other externally ribbed. It was the smooth side that had split. The bottle was cut open and the inside surfaces examined. As can be seen from Figure 2.18, the whole of the split side was visibly degraded, whilst the opposite side was in good condition.

Samples were taken from the undamaged area and tensile stress strain properties measured in accordance with BS 903 Part A2. The undamaged rubber was found to comply with the requirements of BS 1970, the specification for rubber hot water bottles.

Samples were taken from the damaged side and energy dispersive x-ray analysis (EDAX) carried out to determine metal content on both the inner and outer surfaces. The results showed that there was copper and nickel present in the inner degraded surface but not in the outer surface.

Failure diagnosis

There have been cases where the sort of damage visible on the outside had been caused by the bottle being stored against a hot water pipe, but it was clear in this case that the

Figure 2.18 The inner surface of the failed side reveals degradation

whole of one side was badly degraded on the inside. The undamaged side of the bottle conformed with BS 1970 in respect of strength and elongation, so it had been manufactured from a satisfactory compound.

It is well known that copper causes a catalytic action in natural rubber (which is used for hot water bottles) in the presence of oxygen, resulting in rapid degradation (depolymerisation) at elevated temperatures. There is a rough correlation between the frequency of premature failure and the concentration of copper in the water supply. As copper was detected on the inside degraded area but not on the outside it could be concluded that the failure was caused by copper accelerated ageing.

It was, however, curious that only one side of the bottle had degraded and that the degradation was particularly severe in a short space of time. Two factors emerged about the details of how the bottle was used. The owner filled it from the hot water cylinder, which was made of copper, so there was likely to be a high copper content in the water. She was also a person of habit and always placed the bottle in the bed with the smooth side uppermost. Hence, for much of the time the degraded side was in contact with a pocket of hot air, which is an ideal circumstance for rapid oxidation.

Lessons and consequences

1. The frequency of hot water bottle failures combined with the risks of serious injury would suggest that the testing and quality standards for this product are not sufficiently rigorous or demanding. For example BS 1970 demands a level of property retention after immersion in water, but the quality of the water is not defined. Therefore the durability of the product in contact with hot water containing higher than normal levels of copper has been ignored or overlooked.

2. This case clearly demonstrates the general rule that air is a more powerful medium for thermo-oxidation than water at the same temperature. BS 1970 includes an air ageing test. However this case reveals clearly that the most aggressive ageing condition is first exposure to hot water (absorption of copper ions) followed by exposure to hot air.

3. For similar reasons, the thermo-oxidative degradation in a wide range of fluid storage products is most severe at the fluid/air interface (i.e. the splash zone).

2.8.8 Flexible hose (example 2)

History

Failures were being experienced in hoses used to convey hot water, although the exact nature of failure and the frequency were not reported. Two samples of hose were supplied complete with end fittings. One had been used with cold water and one with hot water, with the hot water hose having been cycled to temperatures up to 85 °C. Both hoses had been in service for about 4 years.

Inspection and analysis

The hoses appeared very similar and had roughly the same length and weight. There were no obvious signs of leakage having occurred. The outer braid was removed when no damage or holes could be seen. The hoses were cut in half axially which showed that the construction was a simple plain tube inside the outer protective wire braid.

The inside of the hot water hose was heavily coated with a reddish brown deposit and the cold water hose with a whitish deposit. When the deposits were cleaned away no signs of splitting or pinholing were found in the body of the hoses away from the end fittings.

Under the crimped end fittings of the hot water hose it was apparent that the thickness of the tube was considerably reduced where the rubber had taken a high degree of set. Also, small circumferential splits were found at both ends of the tube below the end fittings. The cold water hose did not exhibit the same degree of set and no splits were present.

The hardnesses of the hose bodies were measured and found to be 96 IHRD for the hot water hose and 82 IHRD for the cold water hose.

Samples cut from the hoses were analysed by FTIR after methanol extraction, and after extraction followed by pyrolysis. Thermogravimetric analysis (TGA) was carried out on samples from the bulk and from below end fittings.

The analyses indicated that both hoses were based on a styrene-butadiene (SBR) copolymer and that the hot water hose compound contained a slightly higher level of inorganics than the cold water hose. It could also be deduced that the hardening of the hot water hose was not due to extraction of a liquid component (process oil) from the rubber compound.

Failure diagnosis

It was clear that the hot water hose had taken a high degree of compression set under the end fittings and had hardened considerably. These are both symptoms of crosslinking via oxidative degradation. The service history of the hose was estimated as 2.5 years at 20 °C and 1.5 years at 85 °C. If we assume an acceleration factor of 3 per 10 °C, then 1.5 years at 85 °C would be equivalent to 4.5 x 1.5 = 6.75 years at 70 °C. SBR has an MCUT of 70 °C. A critical level of degradation might be anticipated after about 100,000 hours (11.4 years) at this temperature, or after about 7 years of service life with a hot (85 °C) to cold (20 °C) ratio of 1.5:2.5. These considerations revealed that SBR should not have been selected for this application. In addition, they reveal that the actual service life (4 years) is less than that predicted by simple time temperature equivalence (7 years).

It is of interest that the hose under the crimped end fittings suffers the most rapid degradation. In this region the reduced access to water and airborne oxygen, and the overall compressive stress might be expected to reduce the rate of degradation. However crimping will always induce high (axial) tensile stress, and the development of circumferential surface splitting would suggest that in this case the induced tensile stresses at the end fittings exceed the pressure stresses applied to the hose in general.

The hoses examined did not show signs of having failed in service but the set and splits under the end fittings of the hot water hose indicated that failure was fairly imminent. The cause of the deterioration was heat ageing and probably leakage past the end fitting due to set would occur first.

Lessons and consequences

1. The maximum continuous use temperature of a polymer is assessed by ageing under zero stress. For stressed applications it would be prudent to de-rate claimed MCUT values by 20 °C.

2. SBR is unsuitable for this application. The error in selection could not be pinned down but it is suspected that the user made the common mistake of employing a time average service temperature to estimate the effective continuous ageing temperature.

3. The loss of sealing pressure due to the development of excessive compression set often precedes other symptoms of thermal degradation.

2.8.9 Polypropylene laminated steel sheet

History

Metal cans used principally for the containment of beer and soft drinks were dominated by aluminium. Although more expensive than steel, the material had the advantage of adequate intrinsic resistance to corrosion. The steel industry eventually gained a significant market share by introducing a range of products protected by polymeric films and lacquers. Films included polypropylene and polyethylene teraphthalate. The details of the technology used for laminating the film to the thin gauge steel are generally not revealed in the public domain literature. A polypropylene/steel laminate produced under licence at many sites was successful. However the laminate produced by the same technology at one site was unsuccessful in that the transparent film ‘stress whitened’ when the laminate was shaped into a can form.

Inspection and analysis

A sample of the inferior laminate was bent so as to apply tension to the polypropylene film. The stress whitening complaint was replicated by this means. Examination with the aid of low power microscopy revealed dense microcracking as illustrated in Figure 2.19. Samples of superior laminates from other sources did not microcrack under equivalent flexural deformation.

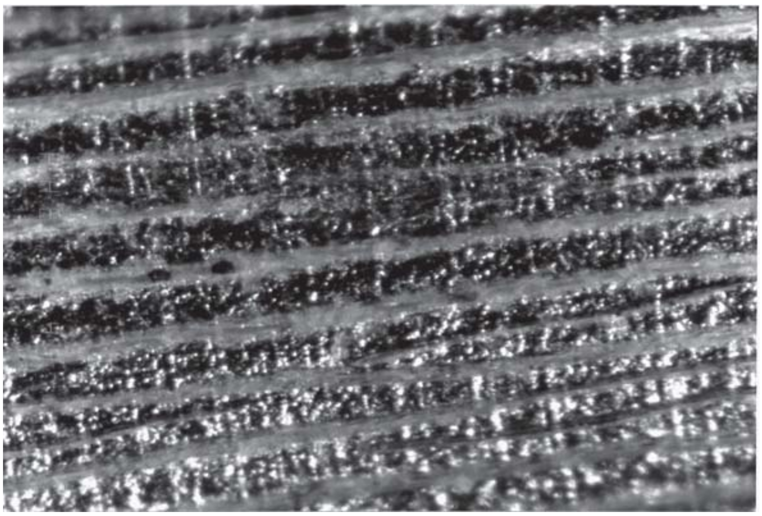


Figure 2.19 Dense microcracking of a laminated polypropylene film under flexural deformation

Microscopic examination of the microcracks through the (40 micron) film thickness revealed greater crack opening displacement at the surface in contact with the steel. This would suggest that the cracks initiated at the internal surface, where in fact flexural stresses are at a minimum.

The molecular weight of films prior to and after lamination was assessed by dissolution of the polypropylene in boiling 1,2-dichlorobenzene, followed by gel permeation chromatography. The results are listed in Table 2.7.

Failure diagnosis

The film on the inferior laminate has been severely degraded during the process of lamination to the steel. There can be little doubt that this is due to thermo-oxidation and it is probable that the severity of degradation is maximum at the film surface in contact with the steel. This could be confirmed by assessing the carbonyl ratio through the film thickness via infrared spectroscopy.

The lamination process in all plants was ostensibly the same and involved press rolling the film onto steel sheet preheated to 250 °C. In the absence of more detailed processing details three potential causes of excessive degradation were suggested:

1. Although the films from all sources are similar in terms of molecular weight, the residual and effective antioxidant protection may vary significantly, depending upon initial concentration and consumption during the film extrusion stage. The oxidative induction time (OIT) test on film supplies would constitute the most cost effective means of monitoring film quality in this respect.

Table 2.7 The weight average molecular weight of PP film prior to and after lamination

Sample	**M_w**
'Good' film	242,000
'Superior' laminate	238,000
'Suspect' film	241,000
'Inferior' laminate	21,500

2. 250 °C is the recommended upper temperature limit for the hot melt processing of PP. It is unlikely that the residence time at this temperature during lamination exceeds that involved in extrusion or injection moulding. However if the temperature of lamination was (say) 20 °C above the specified nominal temperature this might be sufficient to account for the degradation.

3. The steel sheet may accelerate oxidative degradation via the presence of alloyed metal catalysts or surface contamination. An example of the latter would be residual pickling acids.

Lessons and consequences

1. The thermal history applied during the lamination process approaches the limit that can be sustained by polypropylene. Modest variations in material quality or process variables may be sufficient to render the polymer fragile via thermo-oxidative degradation.

2. It was eventually established that the film prior to lamination had virtually zero oxidative induction time at 250 °C.

3. The new process had been developed with little or no awareness of the risks of degradation. Hence the relevant material qualities were not specified or assessed, and process variables (the residence time and the maximum temperature) were not adequately controlled.

2.8.10 Acrylic bulkhead light covers

History

A manufacturer of bulkhead lights decided to change from their traditional glass to plastic covers. The lights being mainly installed outdoors to illuminate passages and porches were susceptible to impact damage, and plastic covers would allow the product to be promoted as 'vandal-proof'. However, improved aesthetic appeal derived from the design freedom offered by injection moulded plastic, was the main incentive for change.

The technical development personnel were not knowledgeable about plastics but managed via discussions with various material suppliers to recommend a material. They chose polycarbonate mainly because it would best satisfy the vandal-proof claim. The marketing staff chose polymethyl methacrylate (PMMA) because of its superior aesthetics. An unequal struggle resulted in the selection of high impact PMMA (an acrylic toughened by acrylate rubber). Two years after the new product was launched complaints were received with increasing frequency.

Inspection

The light covers suffered from discolouration, reduction in transparency, and embrittlement. The discolouration as indicated in Figure 2.20 was not uniformly distributed. It maximised in areas of the cover that were closest to both the tungsten filament light source and (rising) hot air. This would suggest degradation via thermo-oxidation and/or photo-oxidation.

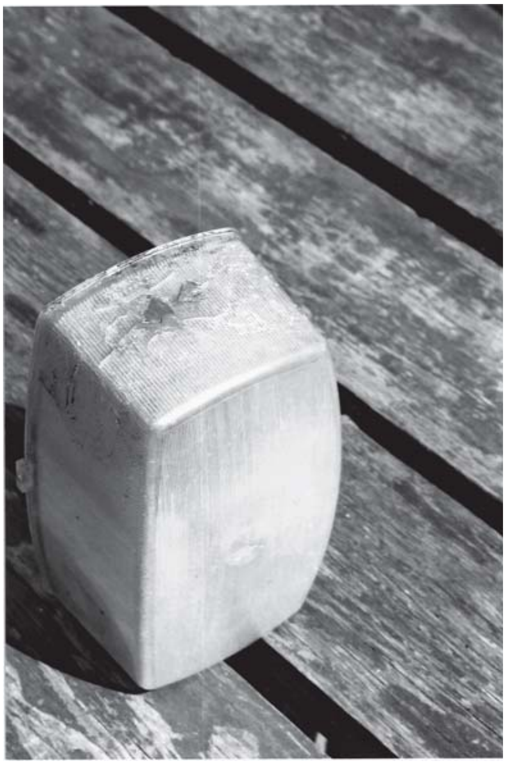


Figure 2.20 A cracked and discoloured bulkhead light cover

Failure diagnosis

The radiation from tungsten light bulbs is characteristically low in UV and high in infrared intensity. Acrylate-modified PMMA has excellent resistance to photo-oxidation but modest resistance to thermo-oxidation. Therefore excessive heat is the main suspect.

A thermocouple was embedded into the inside upper surface of a cover and the near surface temperature was measured with the resealed unit exposed to a light source at the maximum recommended power rating. The surface temperature equilibriated at 55 °C above ambient. During its operation in a temperate climate the actual temperature would range from about 55 to about 75 °C. This compares with a 100,000 hour maximum continuous use temperature for an acrylic of only 50 °C (see Table 2.2).

The pattern of discolouration was replicated by continuous exposure to the light source for 3 months at an ambient temperature of 25 °C (an inner surface temperature of 80 °C). This was deemed to be reasonably equivalent to two years of normal use.

The discolouration, loss of transparency, and embrittlement were primarily due to thermo-oxidation. Secondary or subsequent additional degradation due to photo-oxidation would contribute to the chain reaction by way of UV induced reactions with the by-products of thermo-oxidation.

Lessons and consequences

1. Polycarbonate should have been selected. It offers a maximum continuous use temperature in excess of 100 °C. The light source should not have been positioned near to the upper surface of the cover.
2. All products that involve exposure in service to heat or light should be tested for durability prior to product launch.
3. Marketing may be the modern route to success but it should not be allowed precedence over product fundamentals.

References

1. L. Manolis Sherman, Plastics Technology, 1996, 42, 7, p.42.
2. P. K. Greene, S. W. Hong, J. K. Galloway and E. S. Landry, 152nd ACS Rubber Division Meeting, October 1997, Paper 110, p.36.

3. Z. Osawa, Polymer Degradation and Stability, 1988, 20, 3/4, p.203.

4. W. L. Hawkins, Journal of Applied Polymer Science, 1959, 1, 1, p.37.

5. F. Gugumus, Angewandte Makromolekulare Chemie, 1985, 137, p.189.

6. F. Gugumus, Polymer Degradation and Stability, 1998, 60, p.119.

7. J. Y. Moisan and R. Lever, European Polymer Journal, 1982, 18, 5, p.407.

8. J. Viebke, M. Hedenqvist and U. W. Gedde, Polymer Engineering and Science, 1996, 36, 24, p.2896.

9. U. W. Gedde, J. Viebke, H. Leijstrom and M. Ifwarson, Polymer Engineering and Science, 1993, 34, 24, p.1773.

10. E. Kramer and J. Kopplemann, Polymer Engineering and Science, 1987, 27, 13, p.947.

11. R. W. Thomas, C. R. Ancelet and J. E. Brzuskiewicz, Proceedings of Antec 93, Volume II, New Orleans, LA, 1993, p.2005.

12. N. S. Allen, H. Khatami and F. Thomson, European Polymer Journal, 1992, 28, 7, p.817.

13. N. S. Allen, M. Edge, T. Corrales and F. Catalina, Polymer Degradation and Stability, 1998, 61, 1, p.139.

14. S. Sack, S. Schaer, E. Stegar and H. Wanger, Polymer Degradation and Stability, 1984, 7, 4, p.193.

15. D. Wagner, H. Siedlarek, M. Kropp and W. R. Fischer, Plastics Pipes IX, IOM, 1995, p.497.

16. B. Terselius, U. W. Gedde and J. F. Jansson in Failure of Plastics, Eds., W. Brostow and R. D. Corneliussen, Carl Hanser, Munich, 1986, p.273.

17. J. R. White and N. Y. Rapoport, Trends in Polymer Science, 1994, 2, 6, p.197.

18. R. M. Gallagher, Proceedings of the 142nd ACS Rubber Division Meeting, Nashville, TN, November 1992, Paper 40, p.7.

19. Z. W. Zhou, A. Chudnovsky, X. Niu and S. S. Stivala, Proceedings of Antec 96, Volume III, Indianapolis, 1996, p.3265.

3 Photo-oxidation

3.1 Introduction

The exposure of polymer surfaces to a combination of sun or artificial light, plus oxygen or other oxidising media induces degradation via photo-oxidation. The mechanism and the consequences are similar to those of thermo-oxidation (Chapter 2) and the response to ionising radiation in the presence of oxygen (Chapter 4). The consequences include:

i) Embrittlement (surface microcracking, reduced impact strength, reduced strain at break).

ii) Discolouration due to degradation of the polymer and pigment reactions (see Case 3.6.3).

iii) Loss of gloss or transparency.

iv) Changes in molecular weight (usually a decrease).

v) Accumulation of oxidation reaction products (peroxides, hydroperoxides, carbonyls, vinyl unsaturation, etc.).

These consequences are the result of surface or near surface degradation. For some compounds which naturally absorb ultraviolet (UV) radiation or are rendered opaque to UV by additives, the depth of surface degradation is controlled by the depth of UV penetration. For others that are virtually transparent to UV radiation, the depth is controlled by the diffusion of atmospheric oxygen. A characteristic of UV transparent materials, as illustrated in Figure 3.1, is that sufficient UV will penetrate the material thickness to induce degradation at 'unexposed' or 'hidden' surfaces. This can lead to misdiagnosis and confusion. Where products are subjected to combined UV exposure and flexural stress, with 'hidden' surfaces under tension and the external surfaces under compression, fracture will tend to be initiated at the hidden surface. Preferential failure of the less degraded inner surface may even occur under pure tension [1].

The embrittlement resulting from photo-oxidation depends primarily upon the depth and severity of surface degradation. However, the relationship is not straightforward. The strength and strain at break of polymers do not always decline monotonically with

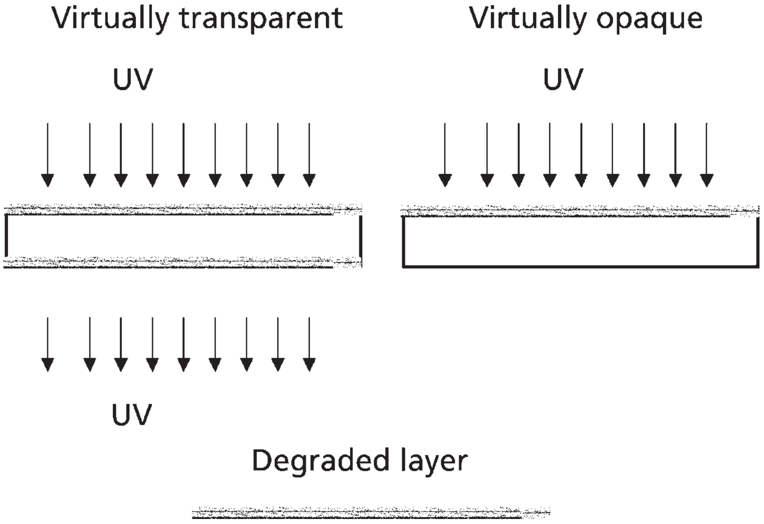


Figure 3.1 Surface degradation of transparent and opaque materials

increasing exposure to UV. For example it has been reported [2] that nucleated polypropylene (PP) exhibits a 60% strength loss after 6 weeks of UV exposure (UV-A 340, see Section 3.2), whilst after 20 weeks the loss is only 30%. A tentative explanation given for this apparently anomalous behaviour is as follows. Failure is dominated by a process known as 'sympathetic fracture'. This is observed to occur, for example, when tough materials are coated with brittle lacquers. Under increasing stress the brittle layer will fracture at modest strains. If the bond between the lacquer and the substrate is good, there is a probability that the crack will propagate 'sympathetically' through the tough material. This probability increases as the energy release rate and strain rate at the crack tip increases. There is evidence to suggest that highly degraded surface layers become partially detached from the undegraded substrate thus subduing sympathetic fracture. Also a highly degraded surface layer will crack at such low strains that the energy release rate may be insufficient to continue the propagation.

The durability of a polymer product in applications that involve exposure to light depends upon:

- The severity of exposure,
- The polymer type,
- The quality of the stabilisation package.

3.2 The severity of exposure

The quantised energy of a photon of light is inversely proportional to its wavelength. The energy is sufficient to rupture the weaker covalent bonds in polymers at wavelengths of less than 400 nm and the strongest bonds at 300 nm. Only ~ 6% of solar energy is associated with radiation of wavelength less than 400 nm.

The spectral energy distribution of terrestrial sunlight within the UV region is shown in Figure 3.2. The distribution, and in particular the 'cutoff' wavelength, are affected by several factors, the most important of which is the path length of radiation through the earth's atmosphere. The cutoff wavelength, or shortest UV wavelength transmitted, is expressed in Table 3.1 in terms of the azimuth angle of the sun. Oxygen is an efficient absorber of radiation at wavelengths below ~ 200 nm. The resultant atomic oxygen reacts to form ozone and this gas has a peak absorbance at 255 nm, tailing off to zero at about 320 nm. In temperate climates, the increase in intensity at 320 nm between winter and summer is a factor of ~ 8. At high altitudes the UV intensity is further increased and the cutoff wavelength is decreased. Behind window glass the cutoff wavelength is increased to ~ 320 nm.

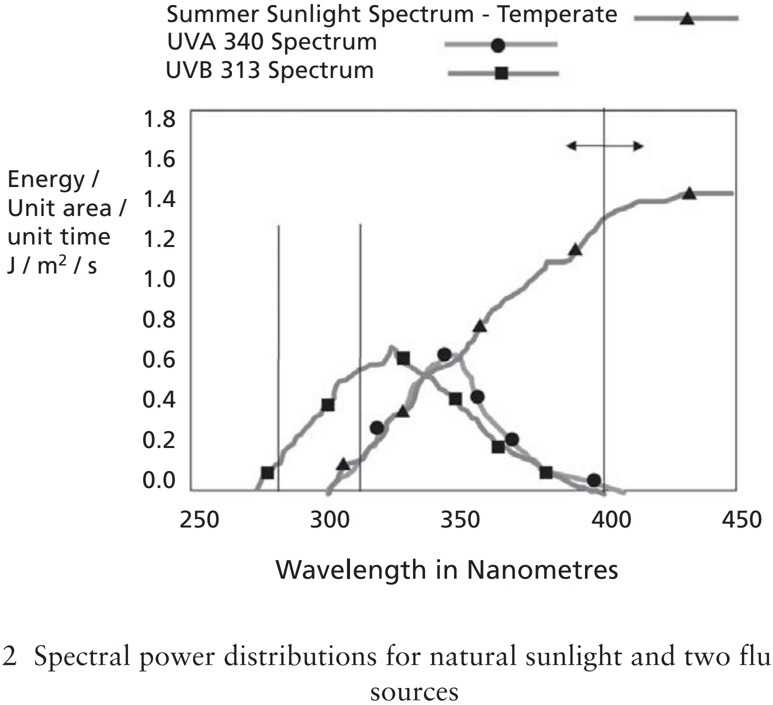


Figure 3.2 Spectral power distributions for natural sunlight and two fluorescent light sources

Table 3.1 Terrestrial short wavelength cutoff limit as a function of the sun's azimuth angle

Sun-horizon angle (degrees)	Shortest UV wavelength transmitted (nm)
<15	315
15 – 20	310
20 – 40	303
40 – 60	300
>60	295

The severity of a location is primarily defined by its mean annual solar energy dose per square metre expressed as MJ/m^2. This ranges from ~ 4000 MJ/m^2 in temperate climates to ~ 10,000 MJ/m^2 in dry equatorial regions. In terms of the most damaging radiation (300 – 400 nm) the annual dose ranges from 240 to 600 MJ/m^2. Other factors to be considered are temperature and humidity/rainfall.

Where products are exposed to direct sunlight, the surface temperature will depend upon:

- the ambient temperature,
- the light intensity,
- the angle of incidence,
- the colour,
- heat transfer (wall thickness, air circulation etc.).

The surface temperatures listed in the Table 3.2 are indicative of the influence of colour and ambient temperature.

For all polymers, an increase in surface temperature will increase the rate of photo-oxidation. One reason for this is that the increase in temperature increases the rate of oxygen diffusion into the surface. Another reason is that thermo-oxidation creates oxidation products such as hydroperoxides and carbonyls that absorb UV and break down to initiate chain reactions. In service, thermo-oxidation and photo-oxidation are difficult to separate and the consequences of heat together with light can be surprising.

Table 3.2 Surface temperatures of coloured plastics products all exposed to sunlight under the same conditions

Colour	Ambient = 26 °C	Ambient = 34 °C
White	33	46
Yellow	38	52
Red	40	55
Blue	41	56
Green	43	59
Grey	47	63
Brown	49	65
Black	50	67

The degradation of high density polyethylene (HDPE) was monitored [3] at monthly intervals at two different sites. The equatorial site had a reasonably constant mean monthly air temperature of 23 °C whilst this value ranged from 3 to 27 °C at the temperate site. Contrary to what might have been expected, it was found that there was no correlation between the monthly dose of solar radiation and the monthly increase in degradation. The rate of degradation did however correlate well with increasing air temperature.

In laboratory tests it is possible to differentiate between thermo- and photo-oxidation and thereby assess their synergy in combination. This is demonstrated in a study of heat resistant transparent plastics, with particular emphasis on polycarbonate, which is outlined in Section 3.5.

Significant variations in the rate of photo-oxidative degradation are known to occur due to the influence of moisture on UV exposed surfaces. With two notable exceptions, moisture accelerates degradation. The exceptions are acetal and polyvinyl chloride (PVC) where, in both cases, the active chain reaction intermediates (formaldehyde/formic acid and HCl, respectively) are partly removed or leached by surface water. Otherwise there are two reasons for acceleration. Firstly rainwater and particularly dew are demineralised, and consequently act as powerful leaching media for antioxidants and other protective additives. Secondly there is evidence that condensed water vapour is a more aggressive oxidising medium than air. Moisture is also an essential ingredient in the phenomenon of ‘chalking’ in titanium dioxide pigmented materials. UV and moisture together hydrolyse the pigment surfaces and this catalyses the breakdown of oxygenated water to $OH^\bullet$ and $OOH^\bullet$ radicals. These degrade the polymer matrix and the unbound pigment is exposed as a ‘chalky’ surface residue.

A consequence of all these factors is that the relationship between durability under accelerated test conditions and real service conditions is far from simple. Enclosed carbon arc and sunshine carbon arc light sources are early examples of the problem. The former provided little or no energy below 330 nm and a great deal at two spectral peaks (355 nm and 380 nm). This would not accelerate UV attack on most plastics. The latter had a cutoff at ~ 270 nm and was therefore overly aggressive in terms of its spectrum. The xenon arc offers the best overall match with sunshine from wavelengths above ~ 310 nm right through the visible spectrum. However, in the most critical region, i.e. below 310 nm down to its cutoff (~ 280 nm) it does not match the sunshine spectrum and in this respect is overly aggressive. The use of appropriate filters reduces the discrepancy. Filters are also used to attenuate the IR end of the spectrum.

Fluorescent tubes are now the most common light sources for artificial weathering:

i) The UV-B 313, which as shown in Figure 3.2, has a cutoff at ~ 270 nm. It constitutes a very aggressive test.

ii) The UV-A 340, which offers the best match with the spectrum of summer sunshine within the critical range 295 – 370 nm. Also because it is a cold source (little in the IR spectrum range) a high power density can be applied without excessive surface heating of the material. (It may actually be necessary to separately heat the material surface to match the temperatures reached in service.)

iii) The UV-A 351 offers the best match with the spectrum of summer sunshine as transmitted through window glass.

The most common accelerated outdoor test method involves the use of mirrors that focus the sun's energy onto the material. EMMA (equatorial mount with mirrors for acceleration) employs 10 highly polished mirrors. Due to relatively low reflectance of UV radiation the arrangement typically increases the intensity of damaging radiation by a factor of ~ 5. EMMAQUA is similar but with the addition of a water spray of 8 minutes in every hour. Cooling of the surface with air blowers is essential.

All these tests have value. At the crudest level they can be used to rapidly assess the relative efficacy of stabilising additives. However for service durability purposes outdoor natural weathering tests at sites that correspond to those anticipated for the product are recommended. The most comprehensive source of natural test data is the PDL Handbook [4].

3.3 The influence of polymer chemistry

Although UV radiation is energetic enough to rupture all polymer bonds, to do so the radiation must be absorbed. The absorbance characteristics of some plastics are illustrated in Figure 3.3.

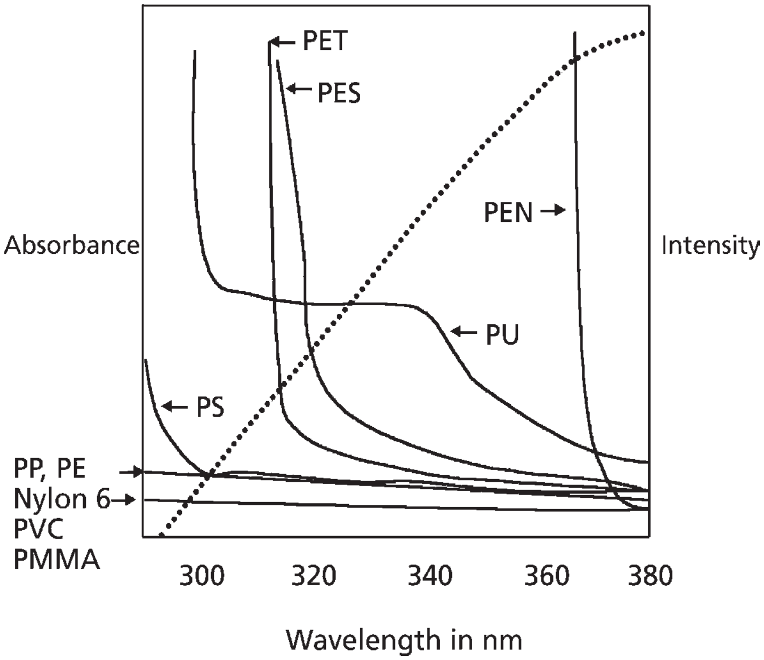


Figure 3.3 UV absorbance of various plastics compared with the intensity of natural sunlight (•••••)

Many pure polymers are virtually transparent to UV radiation. In addition to those indicated in Figure 3.3, these include several fluoropolymers and most other aliphatic polymers. Initial interaction between UV and these materials takes place at impurities and imperfections including chain ends, residual unsaturation, catalyst residues, and most importantly by absorption at preoxidised sites such as hydroperoxides and carbonyl groups (for example arising from hot melt processing). These imperfections and impurities trigger oxidatative degradation, and the products of degradation propagate the process.

As with thermo-oxidation certain metal ions catalyse photo-oxidation. There is a direct correlation between the concentration of residual titanium catalyst in polypropylene (PP) and photostability. However the correlation is not found in HDPE [5]. Here the polymerisation route, and in particular the resulting level of unsaturation, determine both photo- and thermo-oxidation resistance, rather than catalyst residues.

A necessary but not sufficient requirement for excellent UV resistance is low UV absorbance. This is only satisfied by fully saturated aliphatic polymers. The best materials in this respect are polytetrafluoroethylene (PTFE) and polymethyl methacrylate (PMMA) but some of the least resistant materials such as PP, polyethylene (PE), and polymethylpentene (TPX) are also from this group. Polymer technologists seeking a simple explanation for these gross differences are likely to be disappointed. The outstanding resistance of PMMA is put down to its purity (optimised to exploit and maintain its outstanding optical clarity). In other words PMMA lacks the photosensitive chromophores that initiate photo-oxidation in aliphatic polymers. A different explanation is required for PTFE (and other fluorinated aliphatic polymers). Here such chromophores are present and it is the resistance to propagation rather than initiation that accounts for its superiority. As a general rule, materials with good photo-oxidative resistance must also have good thermo-oxidative resistance unless and exceptionally (as with PMMA) initiation can be suppressed. The polyolefins such as PP, PE, and TPX (without stabilisation) have poor thermo-oxidation resistance. As previously mentioned, once initiated by UV it is difficult to discriminate between thermo- and photo-propagation. Some reports [3] indicate that temperature rather than UV intensity dominates the propagation stage.

Unsaturated polymers have higher levels of UV absorbance and therefore interact directly with the radiation regardless of polymer purity and imperfection. Unsaturated elastomers such as polybutadiene have very poor resistance to photo-oxidation and this explains the very poor UV resistance of acrylonitrile-butadiene-styrene (ABS).

Aromatic polymers also interact directly with UV radiation but here the correlation is not clear cut because aromatic content generally improves thermo-oxidation resistance. Polyurethanes based upon aromatic diisocyanates are more resistant to UV than those based on aliphatic precursors. Polyether ether ketone (PEEK) has high aromatic content, outstanding resistance to thermo-oxidation and good resistance to photo-oxidation. Polysulphone has high aromatic content and good resistance to thermo-oxidation, and poor resistance to photo-oxidation. As with intrinsically nonabsorbing polymers there is a strong connection between thermal and UV resistance.

3.4 Stabilisation

Additives that provide a degree of protection against photo-oxidation fall into four major classes: antioxidants, UV absorbers and light screens, quenchers, and radical scavengers or traps.

Antioxidants

The primary and secondary antioxidants (AO) used to stabilise polymers against thermo-oxidation during processing and in service also provide modest protection against photo-oxidation. The degree of protection is rarely quantified because compounds made into test specimens necessarily contain antioxidants. However two sources are given here.

Firstly Figure 3.4 [6] shows the build up of carbonyl oxidation products in a polypropylene copolymer film with UV exposure time. In one test run the film is well protected by primary and secondary antioxidants and in the other most of the protection has been removed by acetone extraction. The antioxidants more than double the induction period but subsequently provide no benefit. As might perhaps be expected, all other factors being equal, the induction period is inversely proportional to the intensity of exposure. However the rate of degradation following the induction period is proportional to the square root of the light intensity. This is just one of the many factors that complicate the interpretation of accelerated UV test results.

The second source demonstrating the improved UV durability arising from antioxidants is revealed in Table 3.3 [7]. This also reveals that far from being synergistically beneficial, the combination of antioxidants and hindered amine light stabilisers (HALS) can be significantly antagonistic.

UV absorbers and light screens

By definition UV absorbers are ideally characterised by high absorption in the range 290 – 400 nm and low absorption within the visible range of the spectrum (> 400 nm). Thus

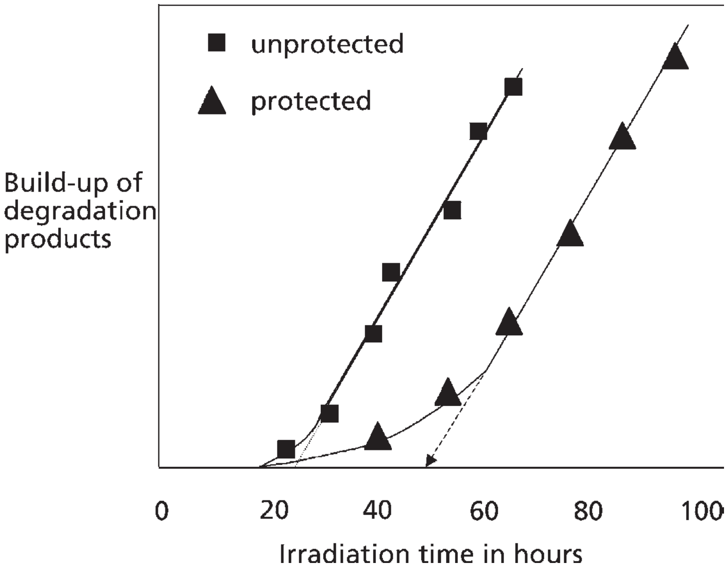


Figure 3.4 Build up of photo-degradation in polypropylene with and without antioxidant protection

Table 3.3 UV embrittlement times (in hours) for various PP film compounds

	Pigment (1.0%)			
Additive (0.1%)	**None**	**Cadmium yellow**	**Green chromium oxide**	**Blue copper phthalocyanine**
None	80	95	135	210
AO (Irganox 1010)	410	500	520	630
HALS (Tinuvin 770)	2750	5620	5000	5750
HALS + AO	2120	3500	3700	6750

damaging radiation is attenuated without coloration. Additives that absorb UV and visible light are defined as light screens. Carbon black is therefore a light screen even though it is a very powerful absorber of UV radiation. Pigments and dyes that selectively absorb visible light may also absorb UV. The white pigment titanium dioxide is a particularly effective UV absorber.

Carbon black is by far the most cost effective additive for imparting UV resistance. At concentrations of > 2% it is only necessary that the black is finely dispersed (particle size ~ 20 microns) and well distributed to provide excellent protection against the most severe of climatic conditions. Premature UV failures are generally due to poor distributive mixing of carbon black masterbatch as exemplified in Case 3.6.1. However there is another associated mode of premature failure that cannot be ignored. As previously mentioned, the surface temperature of irradiated black products (see Table 3.2) is raised significantly, and protecting against UV will promote thermal degradation. Consequently, thermally sensitive materials such as PVC intended for long-term outdoor applications are preferably grey rather than black. The black is mixed with a white pigment.

Pigments other than carbon black and titanium dioxide generally provide modest protection by their screening action. Inspection of the times to embrittlement that have been summarised in Table 3.3 reveal that pigments are generally weak UV stabilisers.

The green and yellow pigments are inorganic particulates and in common with talc and calcium carbonate (see for example Case 3.6.10) it has been suggested that the surfaces of the particles are sites for adsorption of the AO and the HALS. In close proximity the degradation of one of the additives promotes either the degradation or the deactivation of the other. The role of particle surfaces is also apparent from results reported on the effects of titanium dioxide pigmentation [8]. Of the two crystalline forms that are commercially available, the anatase form was found to be detrimental. The rutile form was beneficial in combination with a phenolic antioxidant but, as with the other pigments in Table 3.3, it was detrimental in combination with AO plus HALS. Coated rutile TiO_2 offered the better performance presumably because of reduced surface adsorption.

It is generally agreed that absorbers operate by converting UV energy into low frequency bond vibration and hence heat. Carbonyl groups are good absorbers and for example it is the intramolecular hydrogen/carbonyl bonds in hydroxybenzophenones (see Figure 3.5) and salicylates that resonate.

The selection of an absorber for a given material and application, as with the selection of optimum antioxidants, includes consideration of many factors. These include cost, toxicity, volatility, leachability, thermal and photostability, and the absorption spectrum of the additive. The absorption spectra of some of the more popular absorbers can be compared in Figure 3.6.

The benzotriazole group offers the broadest and most intense absorption and is frequently chosen to stabilise polystyrene (PS), high impact polystyrene (HIPS), ABS, polybutylene terephthalate (PBT), and polyethylene terephthalate (PET). The benzophenones are less efficient and more prone to yellowing during processing but they are cheaper than the benzotriazoles. Antagonistic reactions involving these absorbers are rare but it is worth noting that there is an incompatibility between cadmium sulphide pigments and benzotriazoles [9] and benzophenones [10].

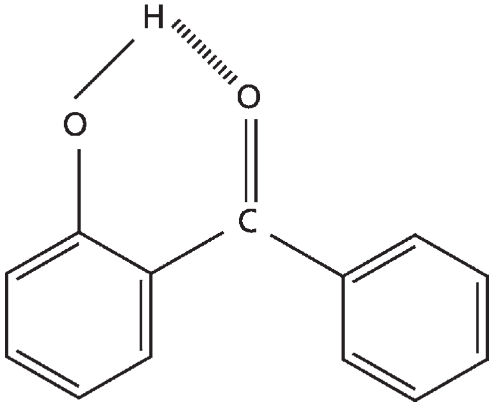
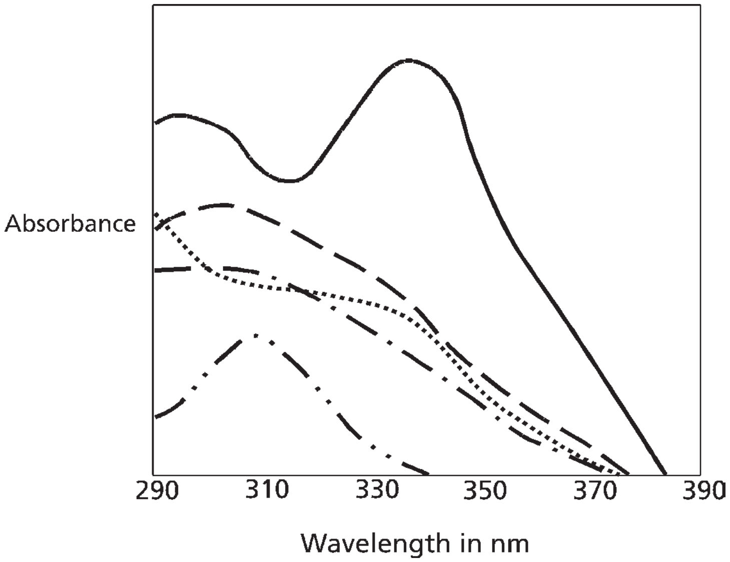


Figure 3.5 The active elements of hydroxybenzophenone absorbers



Absorber	
Hydroxymethylphenylbenzotriazole	———————
Ethylcyanodiphenylacrylate	— — — — — —
Hydroxyoctyloxybenzophenone	▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪ ▪
Oxanalide	— ▪ — ▪
Phenyl salicylate	— ▪ ▪ —

Figure 3.6 Comparative absorbance spectra of UV absorbers

Finally, both glass and carbon fibre reinforcements generally protect polymers, by acting as UV absorbers and by reducing the fragility of the degraded surface layer. As exemplified in Table 3.4 the benefits in terms of structural properties can be very significant. However it is generally the case that the deterioration of aesthetic qualities (e.g. gloss and lustre) is accelerated by fibrous reinforcement.

Quenchers

Quenchers are additives that impede the initial stage of photodegradation. Absorption of UV by the polymer chromophores induces electronic excitement. The excitement energy is mobile and without intervention it will transfer along the chain until the weakest bond is ruptured. Quenchers impede this process by deactivating the excited state, absorbing the energy, and then dissipating the energy as heat.

Table 3.4 The resistance of 'engineering plastics' to natural weathering in Japan [11]

	Months of exposure to reduce strain at break by 50%
PPO (polyphenylene oxide) - unstabilised	11.5
PPO - with stabilising absorber	13.1
PPS (polyphenylene sulphide)	108
PPS - with glass fibre	93.8
Nylon 6	17.2
Nylon 6 - with glass fibre	332
PEI (polyetherimide)	1.8
PEI - with carbon fibre	84.1

The most commonly used quenchers are organonickel compounds such as nickel dithiocarbamates and 2,2´-thiobis(4-octylphenolato)-*N*-butylamine nickel. The main advantage of quenchers over absorbers and radical scavengers is the fact that they are nonmigratory due to their high molecular weight. This advantage is particularly beneficial in thin cross-sectioned products such as polypropylene films and fibres. The main disadvantage is that they impart colour.

Radical scavengers or traps

Hindered amine light stabilisers (HALS) are now the dominant means of stabilising nonblack polymeric products exposed to UV radiation. They have overtaken absorbers because in most applications they offer superior cost effectiveness. Absorbers are less expensive but to provide equivalent durability, 3 to 4% of the additive is required compared with less than 0.5% of HALS.

It is often claimed that HALS can match the performance of carbon black (but not in cost terms). However such claims are generally based upon short-term accelerated tests. Under the longer term conditions expected in real service the claims cannot be justified. Under natural weather exposure in Jedda [1] the performance of carbon black and HALS protected polypropylene was compared over a period of 8 years. Results are shown in Figure 3.7.

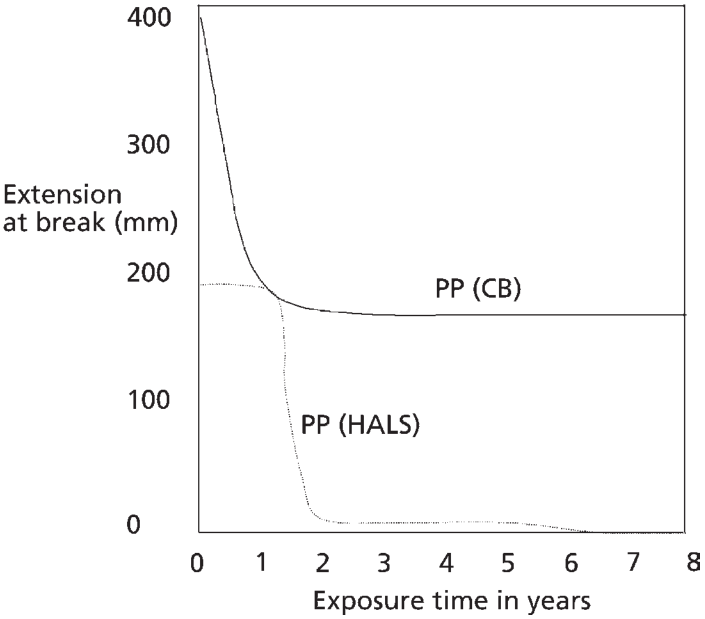


Figure 3.7 A comparison of carbon black and HALS stabilised PP under natural weathering conditions in Jedda

Evidently:

i) The addition of HALS reduces the extension at break of PP.

ii) HALS provides excellent UV protection in PP for up to one year but after this 'induction period' the efficacy declines rapidly such that after 2 years of exposure the material is fragile.

iii) After a rapid initial decline the useful structural properties of carbon black filled PP are retained for > 8 years of further exposure.

The initial decline in PP(CB) properties would be due to incomplete absorption of UV by the carbon black at the exposed surface. The induction period of about one year for the PP(HALS) may be assumed to be the time taken to exhaust or deplete the HALS by chemical reaction, or physical loss (evaporation or leaching). Thus the induction period for the initiation of significant photo-oxidation is generally dominated by the physical properties of the stabilising additive. This has also been shown to be true for thermo-oxidation. The time T to induce a critical level of degradation under accelerated UV exposure was recorded [12] for polypropylene and polyethylene stabilised with HALS 1, 2, or 3 (e.g. Tinuvin 770, Tinuvin 622 or Chimasorb 944, respectively) at two concentrations. An empirical model gave an excellent fit to the experimental data:

$$\ln T = \exp(A + B \ln (S^2/D))$$

where A and B are material constants, S is the solubility of the additive in the polymer and D its diffusion coefficient. The factor A is the degradation time of the unstabilised polymer. The durability of a HALS stabilised polymer is dominated by the solubility (S) and the diffusion (D) of the additive in the polymer. High solubility demands that the partial solubility parameters of the additive and the polymer are similar. Thus the class of stabiliser HALS 4 is virtually non polar and for this reason alone they are reported [13] to be optimum for non polar polyolefins. Low diffusion is promoted by high molecular mass of the additive. High molecular weight oligomeric Chimasorb 944 has been shown [14] to be the best light stabiliser for low density polyethylene (LDPE). Future significant improvements, as with antioxidants, are likely to arise from further development of polymer bound (and therefore virtually immobile) stabilisers.

A more complex model based upon radiative heat loss [15], and the physical parameters S and D also proved to be effective, as can be appreciated from Table 3.5. This model has the advantage of accommodating the influence of material thickness.

Table 3.5 The agreement between experimental data [12] and model predictions [15]

Polymer	Stabiliser	Stabiliser concentration (%)	Sample thickness (mm)	Measured critical degradation time (hours)	Predicted critical degradation time (hours)
LDPE	HALS 1	0.1	0.15	3080	2990
LDPE	HALS 1	0.15	0.2	4200	4440
LDPE	HALS 1	0.25	0.15	4210	4180
LDPE	HALS 2	0.15	0.2	2350	2380
LDPE	HALS 2	0.15	0.065	1230	1040
LDPE	HALS 2	0.15	0.045	840	850
PP	HALS 2	0.15	0.1	900	900
PP	HALS 2	0.15	0.06	840	850

One method of monitoring the progress of photo-oxidation is to measure the rate of atmospheric oxygen consumption during UV exposure. It has been found that the photo-oxidative embrittlement of HALS stabilised PP requires twice the oxygen consumption of unstabilised PP [16]. It was suggested [17] that in the case of the stabilised material the oxygen was mainly consumed via the production of water, which supports the theory that HALS stabilisers act as charge transfer complex quenchers. However the current level of knowledge concerning stabiliser reactions is poor. The high basicity of the earlier generation HALS has been identified as the cause of several secondary antagonistic reactions that result in pink or yellow discolouration, or gas fading [18]. Lower basicity HALS are now available which are less prone to these problems but they are also less reactive. The penalty is higher stabiliser concentrations and therefore higher costs.

An example of a secondary antagonistic reaction involving HALS stabilised ethylene-vinyl acetate follows below.

3.5 Material and application examples

Ethylene-vinyl acetate (EVA)

Peroxide crosslinked, HALS stabilised EVA has been a popular choice of material for the encapsulation of photovoltaic cells. However there have been reports of severe encapsulant discolouration, which obviously impairs the efficiency of the cells in converting solar energy to electrical energy. It was initially proposed [19] that the discolouration was due to the photo-oxidative degradation of the vinyl acetate groups leading to light-absorbing conjugated double bonds and acetic acid. More recently [20] it was demonstrated that the cause of the discolouration is not degradation of the polymer but rather it is due to the interaction between residual peroxide and the stabilising additives. By a process of elimination, photolysis of Cyasorb UV 531 in the presence of peroxide was determined to be the main cause of the discolouration described above.

Ethylene-propylene-diene (EPDM)

The solar heating of water for swimming pools used to be dominated by copper and then polypropylene panel heat exchangers. In the late 1970s EPDM/carbon black sheets known as solar mats were introduced and rapidly gained more than 50% of the market. However after a service life of less than 7 years a problem known as ‘black pool’ [21] was widely reported, this being caused by the leaching out of carbon black from the EPDM compound.

This example highlights the fact that screens such as carbon black do not retard surface degradation but rather they restrict the depth of the degraded layer. If, as in this application, the surface layer is exposed for extended periods of time to flowing water, then the thin degraded layer will be removed, releasing carbon black and exposing the fresh surface to further degradation and erosion.

It is evident that the solar mat manufacturers did not anticipate this problem or detect it via product testing. In this case it is unlikely that an effective test method could have been devised without some specific awareness of a potential problem. An accelerated test method would need to increase both UV intensity and water flow rates.

EPDM sheeting is used extensively as a roofing membrane. In one reported failure case [22] areas of the membrane were observed to have discoloured (with brown staining) and within these areas the EPDM had degraded. The problem was traced to the diffusion of asphaltic adhesive through the membrane. The adhesive was rapidly photo-oxidised, hence the staining. Aromatic fractions sensitised the EPDM to photo-oxidation.

High temperature transparent light fittings

Polycarbonate is the preferred alternative to glass for vandal-proof glazing of high power light sources. The material offers the best resistance at modest cost to UV and high temperatures in combination.

The discolouration of polycarbonate has been compared under both the single and combined influence of heat and light [23]. After 4 days the increase in yellowness (ΔY1) of a light stabilised PC was reported to be:

100 °C without UV	< 0.5
35 °C with UV	3
100 °C with UV	7

The detrimental synergy of heat and light is significant but less so than with some potential competitors such as transparent nylon where ΔY1 was:

35 °C with UV	6
100 °C with UV	16

Other materials including polysulphone, polyarylsulphone, polyarylate, and polyetherimide were also assessed. However although heat resistant, the initial optical qualities of these materials (particularly their inherent yellowness) renders them unsuitable for clear lens applications.

Polymethyl methacrylate (PMMA) versus acrylate-styrene-acrylonitrile (ASA)

Examples of external automotive trim include grilles, mirror shells, and decorative strip. Colour is usually black and finish can be glossy or matt. Materials chosen for these applications include impact modified PMMA (HI-PMMA), ASA, polycarbonate (PC)/ ASA blends, and PC/PBT blends. A major requirement of these materials in these applications is that they reasonably maintain their jet black colour and, if appropriate, their gloss after several years exposure to natural sunlight. Changes in colour will tend to be black to grey accompanied by loss in gloss.

Unmodified PMMA would be expected to offer the best UV resistance, but the material does not have the good impact performance of ASA. Impact modified PMMA (with acrylate rubber) is a good compromise and therefore a comparison of HI-PMMA versus ASA is of interest in the selection of the optimum material for retaining aesthetic qualities in outdoor applications. PC/PBT and PC/ASA blends would not compete in the same league.

Colour change ΔE for the materials moulded with a high gloss surface can be compared in Figure 3.8. The UV exposure is via a xenon arc with an irradiance of 0.55 W/m^2, at a wavelength of 340 nm. Gloss retention was also measured over the same range of exposure conditions at two reflectance angles (60 degrees and 20 degrees) and the results can be compared in Figure 3.9. It is evident from this work [24] that HI-PMMA outperforms ASA.

The differences between the materials may be masked or accentuated by the measurement geometry, and the fact that changes in gloss and changes in colour are not completely separable. This can be appreciated from Figure 3.9, which shows that, when viewed at an angle of 20 degrees from the normal to the surface, the differences in gloss retention between the materials is accentuated. It will also be appreciated by comparing Figure 3.8 with Figure 3.10 that changes in colour are accentuated by discounting changes in gloss.

Acrylonitrile-butadiene-styrene (ABS)

UV degradation has been deemed to be responsible for several large scale recalls in the United States. These include Ford Tracer bumpers, Chevrolet Corvette arm rests, and more recently a widespread problem with seat belt components.

In 1995, newspapers reported that 8 million vehicles in the US were on the verge of a mandatory recall due to malfunctions of seat belt locking and release mechanisms made by the Takata Corporation. The problem had been responsible for 900 complaints and 90 injuries. The vehicles involved were manufactured mainly by Honda and Nissan during the period 1986 to 1991 but also included other makes. The cost of a recall on this

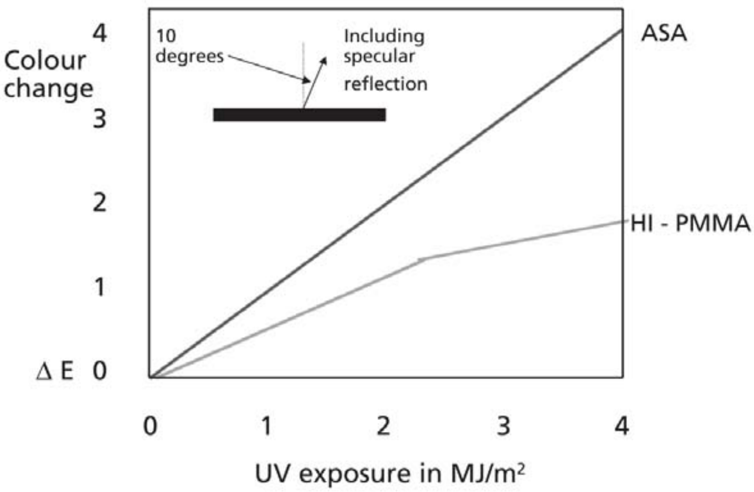


Figure 3.8 Colour change including changes in specular reflectance/gloss

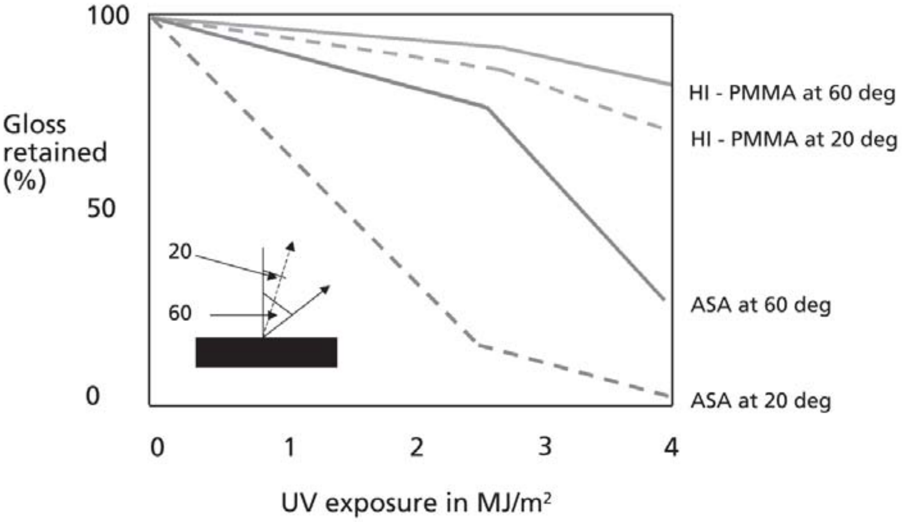


Figure 3.9 Gloss reduction at two angles of reflectance

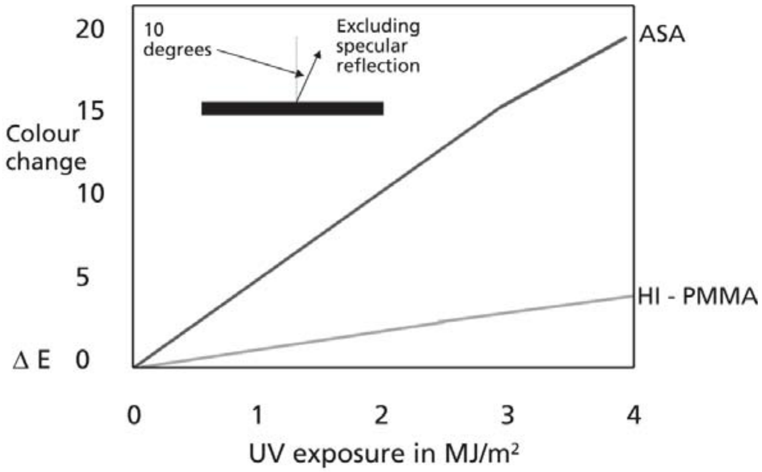


Figure 3.10 Colour change excluding changes in specular reflectance/gloss

massive scale would have exceeded one billion US dollars. This was avoided however by peremptory action involving a less expensive but still costly voluntary recall.

The ABS release button exhibited signs of degradation including discolouration and surface crazing. In some cases small fragments of the button had become lodged in the mechanism, rendering some seat belts impossible to release and others impossible to lock.

An inspection carried out jointly by the Universities of Tulsa and Illinois [25] concluded that the principle cause of embrittlement and fragmentation was UV degradation (photo-oxidation). ABS is known to offer relatively poor resistance to UV, even when well stabilised. This is mainly due to the butadiene phase which, being unsaturated, is very susceptible to photo-oxidation. Together with the observed discolouration and surface crazing this was regarded as sufficient evidence for the conclusion.

The Takata Corporation phased out the use of ABS for these components in 1990. From 1991 onwards, acetal copolymer was the favoured material.

Although the conclusion is probably a correct one, and the replacement of ABS in this application is certainly correct, there are some doubts that are worth raising. The first one is that any ABS part will discolour and surface craze after several years of exposure to sunlight. However this has not precluded its widespread use in vehicle interiors or elswhere. The second doubt arises from the fact that other seat belt manufacturers have used ABS for the same application without any serious problems. This doubt might be eliminated by proof that the Takata component employed an ABS compound that was substandard in terms of UV stabilisation. However no such comparison was reported. The third doubt is raised by the location of fragmentation. We should expect this to coincide with the area of the button exposed to UV, but if this was the case the fragments would not readily find their way into the mechanism. In fact photographs of typical failures reveal that fragmentation occurs at the point of maximum stress generated by repeated manual engagement and release, where UV exposure is slight.

The possibility that cyclic fatigue had a causative role in these failures appears to have been virtually ignored. ABS has very poor cyclic fatigue resistance, and even in the absence of environmental degradation the material will exhibit a change in failure mode from ductile yielding to brittle fracture after ~ 10,000 stressing cycles. If this had a significant role then the detailed design of the component rather than the degree of UV stabilisation would be the critical issue. Also the intensity of use (distance travelled, frequency of use, etc.) would correlate better with failure incidence than accumulated UV dose (age of vehicle, climate, etc.). Unfortunately no statistical correlations of this nature were reported.

The fact that acetal copolymer was chosen to avoid the problem would suggest that Takata did not share the conclusions of the independent investigators. If UV degradation was accepted as the primary cause then for several reasons the manufacturers would presumably have preferred to select an alternative with higher UV resistance but otherwise similar to ABS. In particular they would have been keen to use another glassy amorphous thermoplastic with similar mould shrinkage to ABS, as otherwise the injection moulds would have to be scrapped and replaced. Impact modified PMMA and ASA both have excellent inherent UV resistance and match ABS in terms of mould shrinkage, yet neither was chosen, perhaps because they both suffer from poor fatigue resistance and therefore also poor resistance to repeated impact. The choice of acetal copolymer with its expensive consequences and relatively modest UV resistance, but excellent fatigue resistance, suggests that the latter quality was the dominant concern.

It is impossible without an exhaustive enquiry to prove which of the two candidate degradation mechanisms was primarily responsible for the failures. However it is safe to assume that had the material selection exercise been carried out via the application of priority rules (see Chapter 1), then ABS would have been rejected for both these weaknesses. The inference that the rules were not applied by the component manufacturer is interesting, bearing in mind the intellectual investment that could and should have been afforded during the development of a fail-safe product of such commercial importance. It is even more interesting that ‘independent experts’, with the benefit of hindsight, fail to apply the rules retrospectively to ensure that all potential causes are given the attention they deserve.

Polyethylene (PE)

Polyethylene film is used extensively as a mulch in commercial horticulture. The film helps retain soil moisture and suppresses weed growth. Carbon black stabilised film had been formulated and tested to provide acceptable durability. However in the late 1980s there were reports of premature degradation of mulch film during the winter growing season in Florida. Pesticide sprays were suspected as being the source of accelerated degradation. This was checked by field trials [26] using the following pesticides in varying concentrations:

- Cupric hydroxide,
- Magnesium ethylenebisdithiocarbamate (Mg-EBDC),
- Crop oil,
- Cupric hydroxide + crop oil,
- Cupric hydroxide + Mg-EBDC.

with water as the control. Retention of strain at break was periodically monitored over the 34 week growing season. The order of merit and the percentage retention of strain at break are listed in Table 3.6. It had been expected that cupric hydroxide would have the most serious effect (via metal catalysis) but in solution this is apparently very similar to

Table 3.6 Retention of strain at break for polyethylene film after 34 weeks exposure in Florida

Crop spray	% retention of strain at break
Crop oil high dose	0
Crop oil moderate dose	0
Cupric hydroxide both doses	10
Water	10
Cupric hydroxide + crop oil	15
Cupric hydroxide + Mg-EBDC	40
Mg-EBDC moderate dose	70
Mg-EBDC high dose	75

the effect of the control (water). The deleterious effect of crop oil is rather surprising. The oil is an aliphatic and will therefore be absorbed by the film. The interaction is probably physical and due to a softening/swelling effect. The beneficial film orientation will be reduced by softening and oxygen permeability will be increased. The beneficial effect of Mg-EBDC arises from the fact that this complex is an antioxidant for polyethylene.

Polystyrene (PS)

Styrenics such as styrene-acrylonitrile (SAN), PS, HIPS, and ABS are used extensively for the moulding of business machine and computer hardware housings. Discolouration due to fluorescent or sunlight exposure after the point of sale is tolerated by most customers. Discolouration prior to the point of sale is not tolerated. Modem housings made from high impact polystyrene (HIPS) were rejected by customers for this reason. Two mistakes had been made. Firstly, and for sophisticated marketing purposes, the housings were stored and displayed in transparent packaging. Secondly the brominated flame retardant employed in the HIPS compound had been selected without any consideration of its effect on UV resistance.

The UV degradation resistance of polymers is generally (but not always) impaired by the addition of flame retardants. The degree of impairment is very dependent upon the specific chemistry of the additive. In one study [27] the influence of nine brominated flame retardants was monitored in polystyrene. The greatest degree of impairment was found with TBA (tetrabromobisphenol A). However two of the additives were found to be neutral or beneficial, these being ETBP (1,2-bis(tetrabromophthalimido) ethane) and TBNPP (tris(tribromoneopentyl)phosphate). All the flame retardants are more powerful absorbers of UV in the 280 – 350 nm range than polystyrene. It was suggested that the UV stability of the retarders is the determining factor. If (rarely) this is superior to polystyrene then the additive can act as a weak screen, but generally being inferior, the photodegradation products of the additive initiate degradation of the polystyrene.

Polyvinyl chloride (PVC)

When optimally compounded, PVC offers good resistance to photo-oxidation, and this is proved by the fact that window frames will retain their appearance and structural integrity after 20 years exposure in a temperate climate. Such compounds rely heavily upon the screening effects of dense (white) pigments and rubber impact modifiers. Typically, modern PVC window profile compounds comprise:

78% PVC with a molecular weight of the order of 80,000
5% $CaCO_3$
4% TiO_2
8% butyl acrylate rubber
5% stabilisers (Pb, or Pb/Ba/Cd, or Ca/Zn, or Sn mercaptide)

TiO_2 is a powerful UV absorber but it also catalyses photodegradation of the polymer. Consequentially the additive increases the rate of degradation but restricts this to a thin surface layer. As the impact resistance of PVC windows and other building products (guttering, sidings, etc.) is mainly required for handling and installation, the reduction in toughness during service is not of prime interest. The supply chain concentrates on measuring and optimising resistance to discolouration. It is worth noting however that discolouration does not develop linearly with time and severity of exposure, but fluctuates with time in response to several mechanisms:

i) Yellowing due to unsaturated polyenes (first surface degradation products).

ii) Bleaching/whitening due to oxidation of polyenes.

iii) Regeneration via erosion of surface layer.

Therefore it is possible for a vendor to select conditions and times that make an inferior product appear to be superior. As compounds are generally similar, the quality differences between window frames is dominated by their processing history. Excessive melt temperatures and/or shear stresses are mainly responsible for products of inferior UV resistance, due to the catalytic action of thermo-oxidation by-products.

In other applications where exposure to sunlight is not anticipated and UV stabilised/screened compounds are not used, problems can often occur. For example [28], corrugated PVC drainage pipe (intended for burial) was stored above ground in Egypt for a year. As a result the mean drop height for impact fracture decreased from 1.8 m to 0.35 m. In another example crosslinked PVC wire insulation in telecommunication loop installations suffered radial cracking after only three years in service [29]. The insulation was exposed in service to low level illumination from fluorescent lighting. This had not been considered as severe enough to warrant attention at the specification and testing stages, and therefore the PVC compound contained no added UV protection. It transpired that electron beam irradiation used to crosslink the material had sensitised the PVC to UV degradation, via photolytic decomposition of peroxides formed by the oxidation of radiation induced free radicals. An unusual aspect of this failure was UV embrittlement without discolouration. It was suggested that conventional dehydrohalogenation did not operate at low levels of UV exposure.

3.6 Case studies

3.6.1 Polyethylene irrigation pipe

History

Medium density polyethylene (MDPE) pressure pipe has been used to irrigate golf courses in the UK. Typically about 95% of the pipework is buried in shallow trenches. The above-ground remainder is usually adjacent to sprinkler heads, rocky ground, or water hazards. Carbon black compounds are traditionally specified for this application to provide the necessary resistance to UV degradation, and such systems had an excellent record of good service.

At one site installed two years previously and still under warranty for workmanship and materials, ten burst failures occurred approximately simultaneously, immediately following first use for ~ 8 months. All failures were in above-ground pipe, and all failures were brittle in the form of linear axial splits.

The contractor was ordered to repair the leaks but refused to do so on the grounds that the warranty did not cover ‘vandalism or abuse’. It was claimed that the pipe had been cut with a sharp implement at locations (above ground) which allowed for easy access. The golf club (which happened to have a chartered engineer on its greens committee) did not accept this claim or the suggestion that its membership included a knife-wielding saboteur.

Inspection and analysis

On inspection it was established that the axial splits all coincided with one of the four ‘spider lines’. Spiders are essential support elements within a pipe extrusion die which interrupt the flow, causing it to separate and rejoin. This creates a feature that is usually just visible to the naked eye as a linear surface depression. Spider lines, as illustrated in Figure 3.11, are similar to ‘knit lines’ in injection mouldings. Both act as stress concentrators. This finding alone was sufficient to disprove vandalism.

At this stage it would be normal practice to assess the strength of the spider lines. A (low cost) short-term burst strength test however is not satisfactory. For MDPE and other highly ductile materials, high stress causes the sharp feature to blunt by local yielding. The deleterious reduction in strength is only fully apparent under modest stress static (or

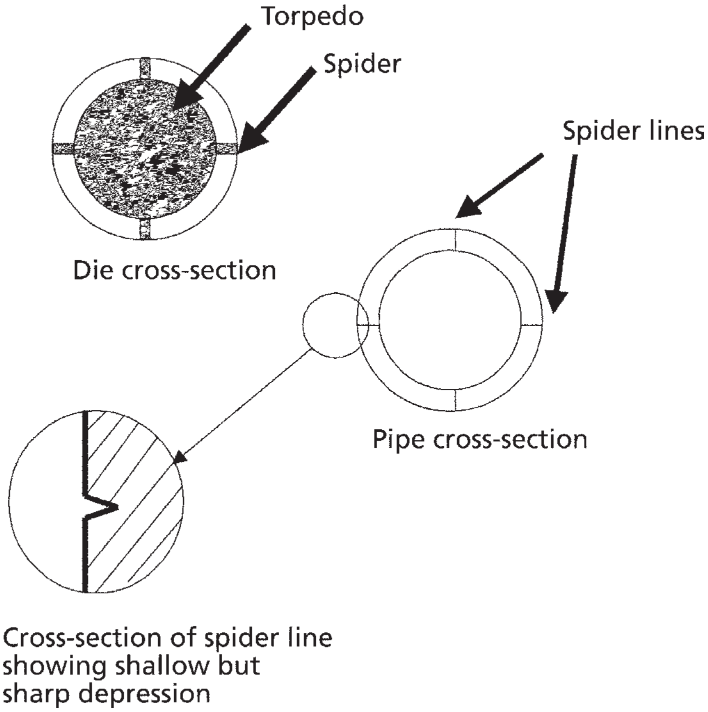


Figure 3.11 Spider lines in an extruded pipe

cyclic) fatigue. However, the fact that failures only occurred above ground would suggest that the intrinsic strength of the features is not the culprit. UV degradation was suspected, but if this was the underlying cause why should this lead to spider line failure?

The pipe was cross-sectioned into ultra thin slices by microtoming. A photograph of one section is shown in Figure 3.12. The four equally spaced spider lines are now visible together with swirls of transparency and opacity. These are regions of low and high carbon black concentration, respectively. They signify poor distributive mixing of the carbon masterbatch by the extruder. It is also apparent that all external surfaces have little or no carbon content and that this deficiency is most severe at the spider lines. Unprotected polyethylene offers very poor resistance to UV degradation.

Failure diagnosis

Localised UV degradation in the vicinity of a stress concentration.

Figure 3.12 A microtomed cross-section reveals poor carbon black distribution

Lessons and consequences

1. It is common for suppliers to blame failures on abuse, particularly if abuse is the only cause for which they are not responsible.

2. UV stabilisation by carbon black is very effective but only if it is well dispersed and distributed.

3. Avoid processing carbon black masterbatch unless the extruder screw includes a mixing element of proven efficency. Otherwise use precompounded material.

4. The golf club had the above-ground pipework replaced by well compounded pipe at the expense of the contractor. It has since, to the author's knowledge, performed without mishap for at least 15 years.

3.6.2 Polyvinyl chloride power line insulation

History

In the UK, overhead conductors are often covered by PVC at locations where it is necessary to give protection to telecommunications lines crossing underneath them, for conductor protection in corrosive atmospheres, and where it is necessary to protect the public in case of brief accidental contact with the power lines. The requirements for the PVC insulation of low voltage power lines (Type 8, black PVC) and high voltage lines (Type 16, green PVC) are laid out in British Standard BS 6485: 1999.

The black PVC is very resistant to weathering (no doubt because the small amount of carbon black pigment added is a very effective UV screening agent), but performance of the green PVC has been found to be very variable.

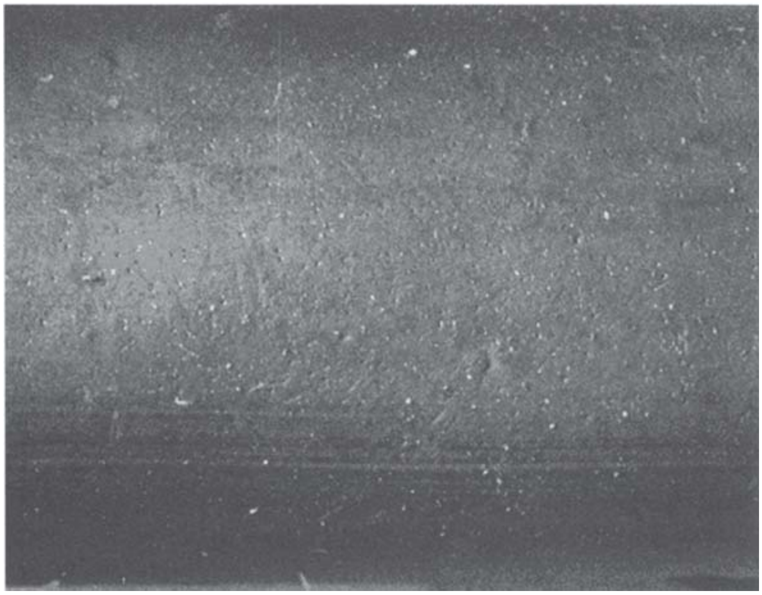
Severe weathering of some formulations of green PVC has been observed after extended exposure. Mechanical failure has sometimes occurred, with bulk cracking having been initiated at the badly weathered surface.

Inspection and analysis

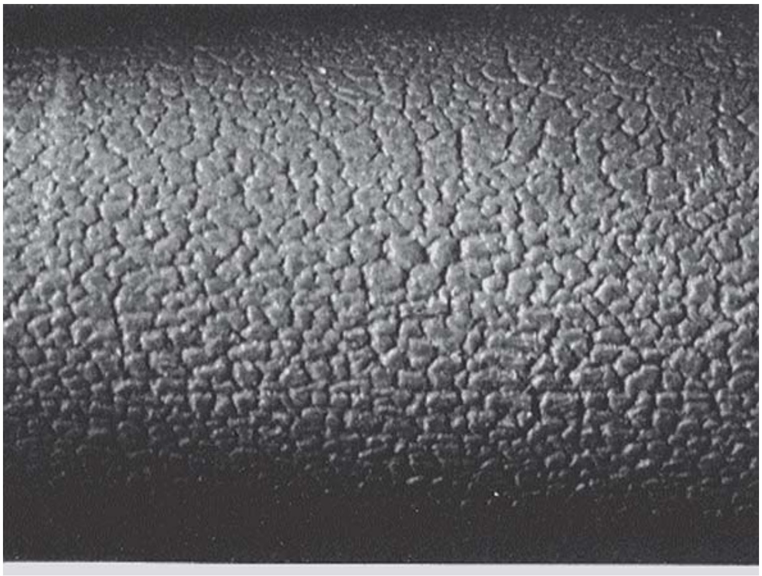
After 15 – 20 years outdoors the manifestation of weathering can, as illustrated in Figure 3.13, range from mild surface roughening (a), through to a moderate degree of 'mud cracking' (b), and eventually to very severe surface damage (c). On their own these phenomena, which are restricted to less than 1 mm of an overall thickness of 5 mm of insulation, are of academic interest. However, it transpires that a badly weathered surface can permit heavy ice accretion in severe winter conditions. When this occurs the mechanical loading on the PVC stranded conductor can be sufficient to induce fatigue failure of both covering and conductor.

The typical transverse fatigue cracks of the PVC can been seen in Figure 3.14. Fatigue failure of the underlying conductor is associated with pitting corrosion, a process which often takes place before the failure of the PVC. (Water and pollutants can enter the stranded conductor at high points of the line and work their way along.)

Analysis of many different green PVC formulations has confirmed that the relationship between resistance to weathering and composition is complex. Some of the more important factors are listed in Table 3.7.



(a) Mild surface degradation



(b) Moderate surface degradation

Figure 3.13 Type 16 green PVC insulation after 15 – 20 years of outdoor service

(c) Severe surface degradation

Figure 3.13 (continued) Type 16 green PVC insulation after 15 – 20 years of outdoor service

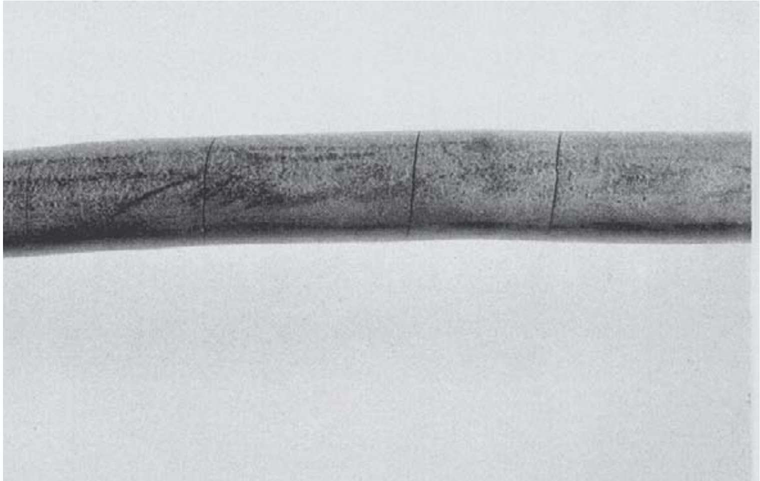


Figure 3.14 Fatigue cracks in PVC insulation due to the accretion of ice on weathered surfaces

Table 3.7 Notes on the influence of compounding ingredients on the properties of green PVC formulations

Additive	Examples	Effect
Stabiliser	Dibasic lead phosphite	Very effective against weathering.
	Basic lead carbonate	Does not directly protect against weathering, but compounds containing it tend to be highly heat stable, which has some small positive benefit.
Lubricant	Calcium or lead stearate	Positive because they improve heat stability.
	Paraffin wax	Reduced weathering resistance compared to stearates, possibly associated with lower heat stability of compounds (unlike stearates it is not a co-stabiliser), also because it blooms to the surface, and on weathering forms a very brittle layer which seems readily to permit initiation of bulk cracking.
Pigment	Pigment green B	Very poor light stability. The decomposition products of this pigment appear to be potent weathering agents.
	Phthalocyanine green	Very weather-fast.
	Rutile titanium dioxide	An excellent absorber of UV light, and confers improved weathering resistance when comparison is made of PVCs with or without TiO_2 but otherwise similar in composition.
UV absorber	Benzophenones	UV absorbers of this type increase resistance to surface weathering.
Antioxidant	Organic phosphites	Improved weathering resistance (see also dibasic lead phosphite heat stabiliser)
Plasticiser	Di-alkyl phthalates Diaryl phosphates Chlorinated paraffin	No clear-cut effect on weathering can be discerned, but many compositions contain 2 or even 3 different plasticisers and the alkyl and aryl constituents are variable, so a proper comparison is difficult.
Filler	Chalk Talc Kaolin	No clear-cut effect on weathering. Most fillers are only mild opacifiers and so do not act as strong UV blocking agents.

Failure diagnosis

Mud cracking occurs as follows. Cyclical variation of temperature imposes a type of stress fatigue on the material. This physically induced stress fatigue is caused by the non-uniform dimensional changes that result from thermal and moisture content gradients between the surface and the bulk of the polymer, and from inhomogeneities and defects inherent in the material. With weathering, the polymer at the exposed surface undergoes gradual photo-oxidation which reduces its strength. When the fatigue limit at a micro-site becomes lower than the physically induced stresses, the resin undergoes fracture, producing microcracks.

Wide cracks are characteristic of the mud cracks. In part, at least, this is probably because of the presence of plasticisers. The plasticisers can be removed from an exposed surface by mechanisms involving some or all of oxidation to more volatile fragments, evaporation, hydrolysis and leaching by water. Loss of plasticiser from the polymer close to the surface will impose higher skin stresses than those simply caused by the aforementioned cyclical moisture and thermal gradients. Consequently the ‘islands’ between cracks will be pulled far apart by shrinkage.

Weathered PVC presents pits and cracks where water can accumulate. This water will freeze when temperatures are low enough. Having readily keyed on to the weathered surface, this first layer, combined with the right weather conditions, forms the template for further ice accretion. When the ice layer builds sufficiently, failure of the covered conductor will occur because of the sheer weight of ice, aeolian (i.e. wind induced) vibration and incipient corrosion fatigue of the underlying conductor.

Lessons and consequences

1. Non-black PVC compounds for overhead lines need to be carefully formulated to give adequate weathering resistance. This is important to prevent ice accretion and failure.

2. If possible formulations should be based upon known good natural weathering performance. However, accelerated artificial weathering can weed out the worst materials.

3. Experience has shown that the best long-term weathering resistance has been obtained with green PVC compounds containing rutile TiO_2 as an opacifier and phthalocyanine green as a pigment, but that it is important to have the whole formulation package correctly specified.

3.6.3 Colour instability of pigmented polymers

History

Red is the warning colour for the polymeric sheathing of medium/high voltage power cables (11 kV and higher), whilst black is used for low voltage. For safety reasons it is important that such colour distinctions be retained during service life, so that no confusion occurs concerning the assets of the various utilities, e.g. black and red (power cables), yellow (gas pipes) and blue (water pipes and telecommunication wiring).

In fact several spectacular colour changes have been observed in certain pigmented PVC and LDPE compounds, both in overhead and underground situations:

1. a particular green PVC compound used for PVC covering of 6.6–11 kV overhead lines (as specified by BS 6485 for such) was found to have changed to a bright blue;
2. red PVC sheaths of buried 11 kV cables changed to black (the colour associated with *low* voltage cables).
3. when a section of 11 kV cable was removed the PVC sheath appeared to be yellow instead of red;
4. the yellow background of an LDPE warning tape for buried cable had turned black, making it impossible to distinguish the (black) lettering.

Inspection and analysis

1. **PVC: green → blue (overhead).** After a service life of about 20 years, the outer surface was bright blue. An x-ray fluorescence analysis revealed the presence of lead, barium, sulphur and cadmium. Infra-red spectroscopy of the separated filler suggested the presence of basic lead carbonate (stabiliser) and $BaSO_4$ (which is a component of a yellow cadmium lithopone pigment, i.e. $CdS.BaSO_4$).
2. **PVC: red → black (underground).** The blackening is initially close to the surface, but the ‘front’ between red and black gradually moves inwards with time. High concentrations of lead-based stabilisers were indicated by x-ray fluorescence analysis. Unexpectedly high levels of sulphur were also detected, especially in the black outer layer.
3. **PVC: red → yellow (overhead and underground).** As in Cases 1 and 2 the colour change was concentrated close to the surface. Another factor was that only when the cable sheath was saturated with water (as it is underground) was the yellow colour pronounced. When it dried out the surface appeared as an orange-red. No lead was

found in the PVC, indicating that it had been formulated without lead stabilisers. Cadmium and barium, however, were detected in addition to calcium (chalk filler).

4. **LDPE film: yellow → black (underground)**. The yellow LDPE film had turned black. An X-ray fluorescence analysis of the aged film revealed the presence of lead, chromium and sulphur.

Failure diagnoses

1. **PVC: green → blue (overhead).** The root cause of the problem was the poor weatherfastness of the cadmium lithopone pigment (which probably slowly oxidised to a white basic cadmium sulphate). The 'green' pigment was a composite of phthalocyanine blue + yellow cadmium sulphide. The phthalocyanine blue, however, has excellent stability to weathering and remains unaltered after years of outdoor exposure.
2. **PVC: red → black (underground).** In certain clay soils sulphate reducing bacteria are present. These bacteria thrive in anaerobic conditions and especially when the cable operates warm (but not very hot). The sulphides produced, including hydrogen sulphide, attack white lead salts (usually basic lead sulphates or carbonates) to form black lead sulphide.
3. **PVC: red → yellow (overhead and underground).** The root cause is somewhat similar to that implicated in Case 2 above, in that anaerobic, sulphate reducing bacteria are involved in the colour reaction. In the present case the resulting sulphides convert the colourless cadmium salt (from the cadmium/barium stabiliser package) to yellow cadmium sulphide. However, an additional step is involved. Before laying, the cable had been exposed to sunlight for several weeks or months on the drum. It was observed that this had the effect of fading the surface layer of the particular PVC compound involved in the colour change, i.e. the red pigment was not light or weather-fast. When put into service the now colourless surface layer of the sheath turns yellow in the soil. However, the strong yellow is only apparent when there is a high water content, which has an opacifying effect, preventing the underlying red pigment from dominating the perceived coloration.
4. **LDPE film: yellow → black (underground)**. This is a further example of the action of sulphate reducing bacteria. However, in this case the sulphides generated attacked the yellow lead chromate pigment to produce black lead sulphide.

Lessons and consequences

1. Care must be exercised in the selection of pigment and stabiliser packages for a polymeric component to ensure that colour can be retained against all environmental agents that will be encountered by that item.

2. Where colour retention is important, lead stabilisers or pigments should be avoided when the polymer is buried in soil. Organic yellows such as benzidine yellow are unaffected by sulphides.

3. Cadmium/barium stabilisers - sometimes used as replacements for lead stabilisers in PVC sheathing - may be subject to yellowing by sulphide attack in the soil. Whilst this may be acceptable with strong colorations, with lighter shades or faded colours, it could result in unacceptable colour shifts. If outdoor exposure is likely to precede burial, then pigments in the Cd/Ba stabilised package should be weather-fast.

3.6.4 Low density polyethylene tube

History

Pneumatic logic control devices are often preferred to their electronic equivalent for reliability in applications involving mechanical shock or vibration. Signals and activation connections within and between devices employ plastic tubing that transmits changes in air pressure. Maximum pressures are typically ~ 0.1 MPa. Black Nylon is the conventional material of construction.

A maintenance engineer in a factory using these devices to control safety locks on steel presses observed that one tube with a particularly tight bend radius was partially buckled and kinked. Having no black tube in stock, the engineer used his initiative and replaced the part with a longer length of translucent tubing of similar inner and outer diameter. The bend radius was increased to ~ 1 m.

The control device ceased functioning about six months later under circumstances that invited enquiry by the Health and Safety Executive.

Inspection and analysis

The failed tube is shown in Figure 3.15. It exhibits some discolouration, extensive circumferential microcracking, and two totally brittle fractures.

The material was analysed by FTIR and differential scanning calorimetry (DSC) and found to be low density polyethylene (LDPE).

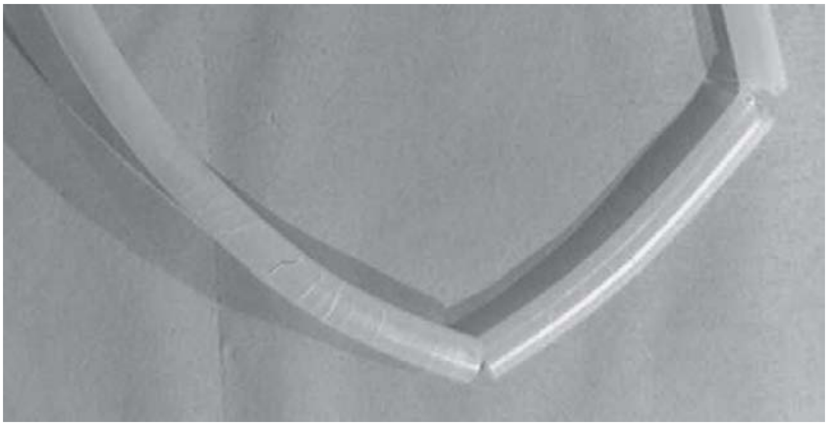


Figure 3.15 The failed LDPE tube

The molecular weight of the material taken from several locations on the tube was assessed using gel permeation chromatography (GPC). The weight average molecular weight (M_w) ranged from site to site from 30,000 to 125,000.

Failure diagnosis

The failed tube had been located behind a south facing window. This together with the discolouration, embrittlement, and reduction in molecular weight indicates degradation by photo-oxidation. The highest molecular weight (125,000) applied to material removed from the tube ends. Here the material was hidden from sunlight by mechanical couplings. The lowest molecular weight (30,000) applied to material removed from the external south facing surface of the tube. The north facing and bore surfaces comprised material of molecular weight 65,000 and 32,000, respectively.

Material removed from the tube ends was analysed for the presence of hindered amine light stabilisers. These were absent or, if present, were at concentrations of less than 0.01%.

Lessons and consequences

1. Unstabilised, unpigmented LDPE offers very poor resistance to photo-oxidation even where sunlight is filtered through window glass. The useful life of a few weeks to a few months is all that can be expected of a mechanically stressed product. A well stabilised HALS or carbon black containing compound would withstand the same service conditions for many years.

2. People (including maintenance engineers) should realise two facts behind the term 'black plastic'. Firstly 'plastic' like metal is a generic term. Secondly 'black' has more significance than colour.

3. Unpigmented natural LDPE is highly transparent to radiation within the UV spectrum. This explains the almost insignificant difference between the internal and external surfaces (M_w 32,000 cf. 30,000). The superior resistance of the north facing outer surface (M_w = 65,000) is due partly to attenuation of UV intensity, but mainly to the fact that in this region the bend in the tube induced compressive stresses.

3.6.5 Acrylonitrile-butadiene-styrene pipework

History

ABS piping systems are favoured over PVC in installations that are exposed to the possibility of heavy impact. They are commonly chosen for the distribution of air and water services in factories.

In this case 250 mm diameter ABS pipe was used to remove process cooling water and to provide space heating to cooler parts of the premises. Inlet temperatures were 60 °C and outlet temperatures were typically 30 °C. Inlet pressure was reported to be 0.3 MPa.

After eight years of continuous service, a burst occurred near the thermally lagged inlet end of the system. Only one pipe end fragment of the failed section was available for inspection.

Inspection and analysis

The external surface of the fragment was partly discoloured but the bore surface was not. An axial feature of about 30 mm in length was observed within the discoloured area at the pipe end. Figure 3.16 reveals its depth through the pipe wall.

Inspection of intact pipe adjacent to the failed section revealed no discolouration or microcracking.

Failure diagnosis

An initial diagnosis by a structural engineer concluded that as the adjacent pipework was in good condition and had been subjected to exactly the same service conditions as the failed section, the failed section must have been substandard. The axial feature was

Figure 3.16 A deep crack in the pipe end fragment

correctly identified with the extrusion spider line. The pipe supplier was therefore exposed to the liability. Discolouration was put down to thermo-oxidation. UV degradation was not considered on the grounds that the pipe, being heavily lagged, could not have been exposed to UV.

As a result of our inspection we were convinced that UV degradation was the primary cause. If the discolouration had been due to thermo-oxidation then the bore surface would also have been discoloured.

As part of an arbitration procedure, a meeting was held at the factory. Whilst all parties were viewing the failure site it was observed that the section that had failed had at some time been re-routed. This was evident from paintwork and redundant bracket holes on and in the supporting wall. It transpired that the pipework had been modified two years prior to the failure. It was observed that the section that failed was longer than any section that could have been removed and reused. In response to the obvious question "where did the section that failed actually come from?", the party was taken to an outside compound.

It was admitted that the section that failed had been exposed to sunlight for six years.

The stored ABS pipe in the compound had discoloured but to a less severe extent than that observed with the failed section. It was subsequently proved that exposure of the stored pipe for 6 weeks at 90 °C (equivalent to 2 years at 60 °C) was sufficient to replicate the visual condition of the failed section.

Lessons and consequences

1. When objective inspection and analysis contradict circumstantial evidence, suspect the latter.
2. Even UV stabilised ABS compounds will degrade significantly after a few years of direct exposure to sunlight.
3. UV degraded material will be severely impaired with regard to its subsequent resistance to thermo-oxidation.
4. The pipe supplier had, in its documentation, warned the customer against protracted outside storage of their product. However it was agreed that this could have been more emphatic. Apologies were exchanged and relationships returned to normal.

3.6.6 Crosslinked polyethylene (XLPE) pole terminated waveconal cable

History

Waveconal cables are often terminated up overhead line poles. The method of termination may leave the core insulation exposed to natural sunlight.

Where this has been done in certain cases the insulation was found to have failed. In one case a red insulation had faded almost completely to a natural colour and had cracked. Some bending stress may have been applied to the cable during installation, and may have persisted during use, but this was not thought to have been excessive.

Inspection and analysis

XLPE insulation from the cable leading to the termination, but unexposed to sunlight, was intact and apparently as new. The infrared spectrum of this insulation is shown in Figure 3.17. The presence of C-O-Si bonds is indicated by the highly characteristic absorption (trough) at 1100 cm^{-1}. This informs us that the insulation had been silane crosslinked. An x-ray fluorescence analysis revealed the presence of silicon and tin, the former arising from the silane crosslinkages and the latter from an organotin catalyst. The lack of absorptions (troughs) at 1720 cm^{-1} (carbonyl, C=O) or at 3400 cm^{-1} (hydroxyl, OH) in Figure 3.17 shows that no oxidation had occurred.

A very different picture emerges for the insulation exposed to the sunlight. As the infrared spectrum of Figure 3.18 indicates, there are large absorptions at both 1720 cm^{-1} and 3400 cm^{-1}. The degree of oxidation of the XLPE was quite substantial.

Failure diagnosis

The oxidation observed could have been caused by thermo-oxidative or by photo-oxidative degradation but the following observations support the latter:

1. the core insulation exposed to the sunlight had cracked; yet that near to it, but not exposed, was intact and flexible.

2. insulation exposed to the sunlight was bleached. This commonly occurs when polymers containing non-light-fast colorants are exposed to UV light. It is worth pointing out that had the insulation been black the problem would almost certainly not arisen, because very small concentrations of carbon black are effective in giving most polymers (and certainly XLPE) long-term protection against the ravages of weathering.

Lessons and consequences

1. Coloured or natural XLPE insulation should not be exposed to UV light. The XLPE insulation is never intended for such use and is not protected against it. The main

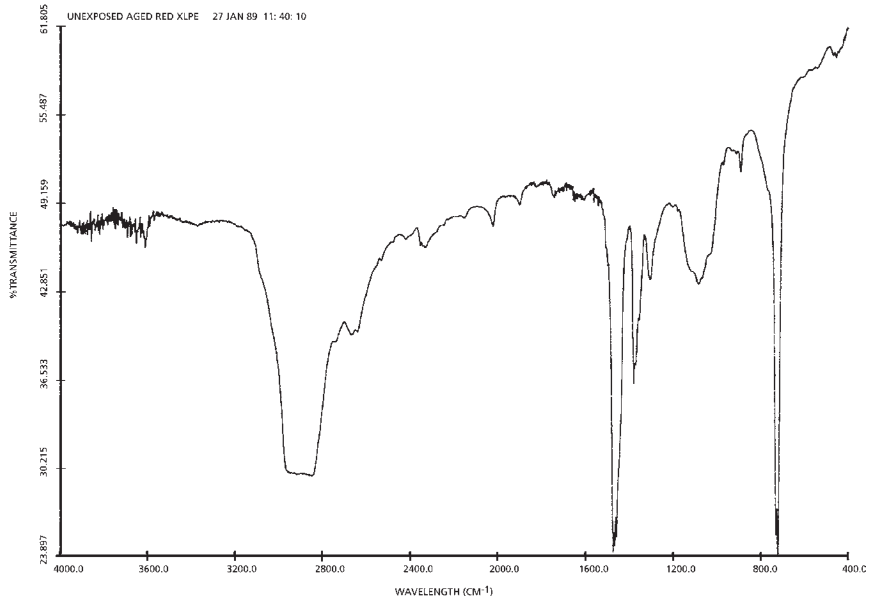


Figure 3.17 Infrared spectrum of covered XLPE

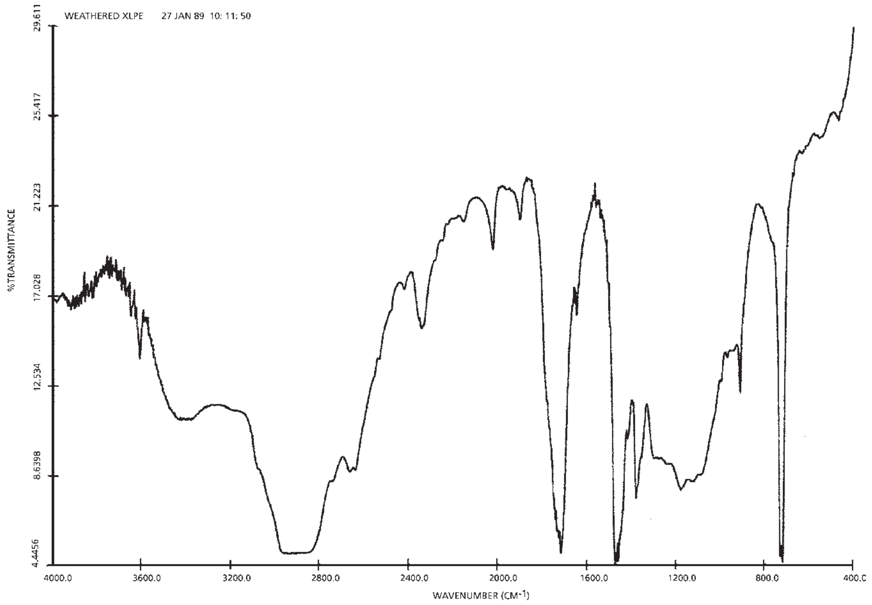


Figure 3.18 Infrared spectrum of exposed XLPE

exception to this rule is where the XLPE contains carbon black. This should be sufficient to prevent deterioration by weathering over the long-term. Of course, most polyethylene oversheaths contain carbon black (at less than 3% by weight), in part to confer weathering resistance. However, some high voltage cables have red sheaths, which may be susceptible to deterioration.

2. Users should be aware that weathering is a potential threat to the integrity of components used outdoors in the electricity network. Suppliers should be consulted where there are doubts about the stability of these materials.

3. The distribution company that carried out the practice of exposing the insulation to the elements had to go through an expensive programme of replacement. This is a very good example of how basic knowledge of materials could have prevented a serious problem from arising.

3.6.7 High impact polystyrene jug handle

History

A consumer affairs magazine received a complaint about the risks of injury due to the fragility of a kitchen jug handle. The handle had broken in use whilst (fortunately) the jug only contained cold milk. The magazine invited readers who had purchased such jugs to inspect the item and confirm or deny the problem. Only one response was received. This complained of fine cracks but the handle was still intact. The magazine decided to fund a modest forensic examination.

Inspection and analysis

The handle is shown in Figure 3.19. The pattern of striations emanates from the gate location. The surface has been etched and this rather than ‘fine cracks’ is the cause of the striations.

The handle was analysed using Fourier transform infrared (FTIR) spectroscopy and confirmed to be moulded from high impact polystyrene.

Failure diagnosis

The owner of the jug claimed that the pattern was not apparent at the time of purchase and that it had become noticeable after about 3 years of use.

Figure 3.19 A surface degradation pattern resulting from UV stabiliser depletion

The similarity between the etched striation pattern and splay marks suggests that the problem is due to volatiles in the melt. Excessive water due to inadequate drying, volatile additives, and contaminants are the suspects.

Etching implies local degradation. This suggests that the etched lines coincide with either a high concentration of volatile degradant or a low concentration of volatile stabiliser. The presence of a degradant in the melt would normally be expected to result in homogeneous degradation. Therefore local stabiliser depletion was the principal suspect.

A new jug was acquired and exposed to an energy density of 600 MJ/m^2 via a UV-A 351 lamp; this being deemed to be equivalent to 3 years exposure to sunlight in a south facing kitchen. Close inspection revealed faint markings emanating from the gate. Sand blasting replicated the etched pattern. It would be reasonable to propose that in service sunlight locally degrades the material along lines of UV stabiliser depletion that emanate from the gate and that these are locally eroded by scouring/cleaning/repeated manual contact.

Lessons and consequences

1. UV stabilisers need to be carefully selected to ensure low volatility at the maximum anticipated processing temperature.

2. Splay marks due to volatiles are often invisible in highly opaque pigmented mouldings. White pigmentation is the most efficient means of hiding splay marks.

3. Trial mouldings using unpigmented material are recommended to ensure that problems are detected at an early stage.

3.6.8 Artificial ski slope filaments

History

White PVC filament matting used in artificial ski slopes suffered from unacceptable levels of discolouration (yellowing) and embrittlement. In one case replacement was necessary after only 6 months in service. In others the product performed satisfactorily for several years before remedial action was required.

The product supplier suspected that variations in the PVC formulation were responsible for the inconsistent performance. It was anticipated that chemical analysis would prove this and provide insights for optimising the formulation to achieve a reliable service life of at least 5 years.

In terms of parts by weight the specified formulation was:

PVC resin	100
Tin stabiliser	2
Internal lubricant	1
External lubricant	0.2
Acrylic modifier	0.5
UV stabiliser*	0.2
Rutile TiO_2	2

* Tinuvin 328

Inspection and analysis

1. Raman spectra from unused and used (discoloured) filaments were compared. The spectrum for the unused filaments was crisply defined with no absorption in the 1450 – 1600 cm^{-1} range. The spectrum for the discoloured filaments was not well defined due to background fluorescence. However high levels of absorption in the 1450 – 1600 cm^{-1} range were evident, indicating the presence of conjugated double bonds (polyenes) and confirmation of degradation via photo-oxidation.

2. Pigment extracted by dissolution (in hot tetrahydrofuran) of filaments with very poor and modest service performance were compared by X ray diffraction analysis. Both revealed a crystalline structure compatible with the (superior) rutile form of titanium dioxide.

3. The presence of the UV stabiliser in good and bad samples was confirmed by UV spectroscopy but the levels could not be quantified.

Thirty differently formulated and processed filaments were produced and exposed to radiation via UV-B fluorescent tubes. A comparison of changes in yellowness index revealed the benefits of:

i) Doubling the TiO_2 concentration from 2 to 4%.

ii) Doubling the UV stabiliser concentration from 0.2 to 0.4%.

iii) Optimising the heat stabiliser type.

iv) Optimising the UV stabiliser type.

v) Decreasing the residence time during hot melt processing.

vi) Precompounded TiO_2 versus masterbatch TiO_2.

Of these vi) was the most significant. Both methods of incorporation were known to have been used in the past but this could not be traced. The cause of inferior performance of the masterbatched product could not be identified. The benefits of doubling the TiO_2 concentration suggests that poor dispersion of this highly UV absorbing pigment is the culprit.

Points v) and iii) in combination confirm the sensitivity of PVC photo-oxidation to prior levels of thermo-oxidation.

Failure diagnosis

The variability in UV resistance of the filaments is due to processing rather than poor formulation control. Poor dispersive mixing of pigment masterbatch is probably the major culprit followed by thermal degradation during hot melt processing.

The formulation is not optimum. Higher levels of UV stabiliser than those recommended by the additive supplier are required to provide long-term protection even to well processed filaments.

Lessons and consequences

1. Variable resistance to UV degradation without the benefit of traceability is a difficult and expensive problem to resolve.
2. For PVC, processing history rather than formulation is most often the source of poor and inconsistent UV resistance.
3. Formulations are rarely optimum. The effort required to optimise formulations can usually only be afforded by vendors of high volume products.
4. In this case the processing conditions and formulation were improved and the target lifetime of 5 years was achieved but at a cost that would never have been justifiable without the imperative of failure.

3.6.9 Polyvinyl chloride shrouds

History

Outdoor mains electrical connections require protection against rainwater ingress. Conventionally this is achieved by tight fitting of elastomeric shrouds. The shrouds cannot be replaced without disconnection and for this reason there is a tendency to ignore the first visible signs of degradation and to delay replacement.

In this case a 30 year old installation at a cold store failed. By the time the problem was detected, and the fault traced and repaired, the contents of the store had perished. The store owners submitted a substantial claim to their insurers. This was promptly settled but reinsurance would depend upon an independent evaluation of the condition of the installation.

Inspection and analysis

At the time of the inspection the cold store that had failed had been rewired and the original wiring disposed of. The owners were suspiciously vague about the failure location. Detailed inspection of the brickwork however revealed burn marks behind a new external junction box. This was sufficient to remind the owners of the exact failure location.

The burn marks contained orange coloured debris. This was collected and via FTIR analysis was found to be dioctyl phthalate (DOP) plasticised PVC.

Old junction boxes with orange coloured shrouds were found in other parts of the site. Analysis revealed that these were also DOP plasticised PVC. They were predominantly located on internal walls and as shown in Figure 3.20 were in good condition. However those located on external walls were severely degraded. The example shown in Figure 3.21 is on a west facing wall and clearly offers no protection against rainwater ingress.

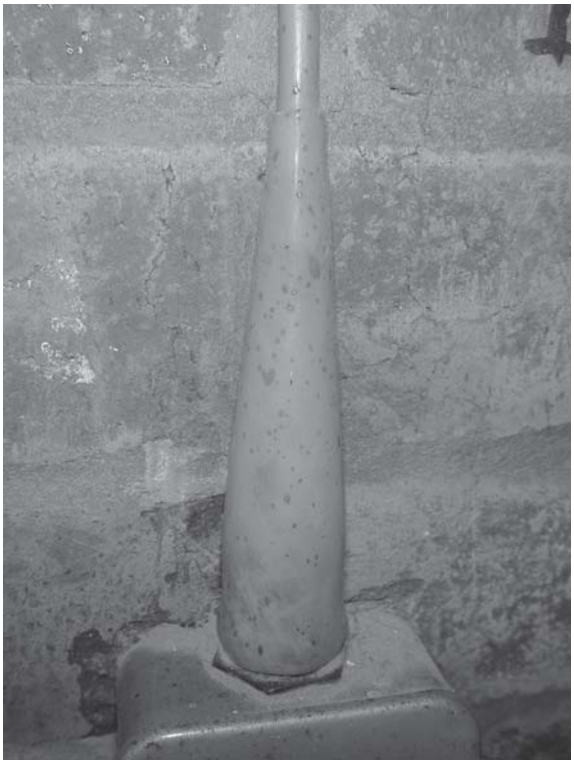


Figure 3.20 A PVC shroud after 30 years service without direct exposure to sunlight

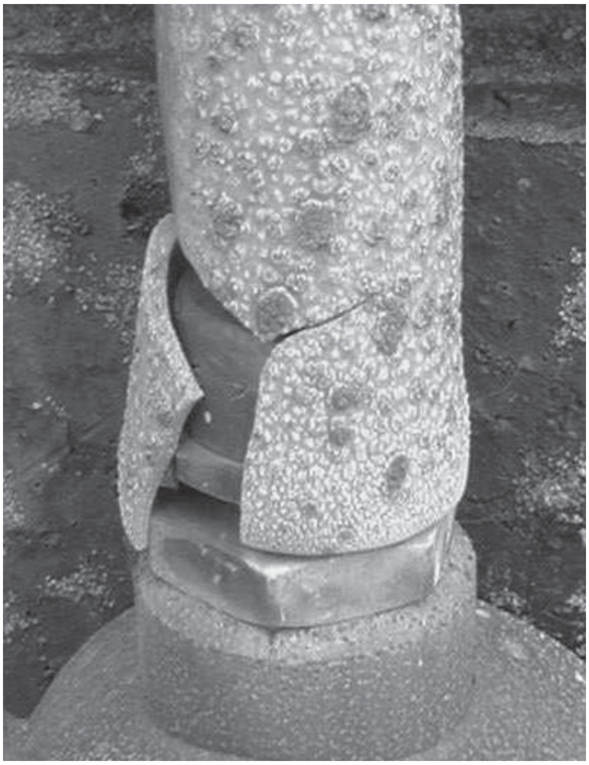


Figure 3.21 A PVC shroud after 30 years service involving direct exposure to sunlight

Failure diagnosis

It was agreed that the failure was caused by photo-oxidative degradation of an orange pigmented PVC shroud after 30 years of natural weathering.

Lessons and consequences

1. The owners admitted that poor maintenance was responsible for the failure because the poor condition of externally sited shrouds would have been clearly evident many years before the failure.

2. The condition of the shrouds after 30 years exposure to a temperate climate would suggest that they were not intended for external use.

3. Carbon black filled EPDM or polyolefin thermoplastic elastomers would be the modern choice for the application.

3.6.10 Polypropylene starter units

History

Fluorescent lighting starter units encased in mineral filled polypropylene developed 'chalky' surfaces within a few months of use. As the mineral was calcium carbonate the manufacturer thought that this was a manifestation of excess filler that had somehow migrated to the surface. As appearance of the initially white casings was otherwise unimpaired the problem was ignored.

A starter unit with approximately two years of service collapsed under finger pressure when being unplugged by an electrician. Fortunately the unit had been switched off on this occasion.

Inspection and analysis

The 'chalky' surface of the failed unit was removed by abrasion. The abraded particles were dissolved in boiling solvent (1,2-dichlorobenzene) and filtered. The filtrate was confirmed to be calcium carbonate.

The solvent/polypropylene solution was submitted to gel permeation chromatography. The weight average molecular weight of the polymer was assessed to be 35,000, compared with 340,000 for material removed from a newly manufactured unit.

Failure diagnosis

Starter units, being adjacent to fluorescent tubes, are exposed to high levels of ultraviolet radiation. Surface degradation due to photo-oxidation is to be expected resulting in the disintegration of the polypropylene down to a fine (white) powder – hence the 'chalky' surface. Stabilisers and fillers will not prevent this effect, but if selected correctly the bulk of the material will be protected and whole body embrittlement should by this means be delayed sufficiently.

The moulding compound was specified as being UV stabilised with 0.15% of the HALS poly-(*N*-b-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperdinyl) succinate and mineral filled with 15% calcium carbonate. This is far from optimum. Firstly it is known [30] that calcium carbonate adsorbs light stabiliser and severely reduces their photostabilising efficiency. Secondly calcium carbonate is ineffective as a UV absorber.

Lessons and consequences

1. Mineral fillers such as calcium carbonate and talc will reduce the efficiency of many stabilising additives, including antioxidants. To compensate for this, additive levels should be increased.

2. Without an effective UV absorber or light screen, HALS stabilised polypropylene will not protect against whole body embrittlement in the longer term (see Figure 3.7).

3. The compound had been approved on the evidence of accelerated (short-term) tests and the change in surface appearance. This approach is not satisfactory in this case because the critical issue is the slow decline in structural properties.

4. The manufacturer upgraded the compound by increasing the HALS concentration to 0.25% and by adding 1.5% coated rutile titanium dioxide pigment (as a UV absorber). Chalking still occurs but there have been no further structural failures.

3.6.11 Polyvinyl chloride running rails

History

Running rails alongside horse racing tracks are constructed from plastic tubing, mostly PVC. The overall strength and stiffness of the rails are mainly determined by dimensions, spacing, and fixing of the rails and in these respects the product (from various manufacturers) has been satisfactory. However, concern was expressed when some failures occurred due to impacts and the broken tubes exhibited sharp jagged fractures. Brittle fractures could result in very serious injuries to horses or jockeys.

The quality of rails from candidate suppliers had been screened by a single impact test (at one impact velocity and one temperature) without ageing. This ‘go/no go’ test could not discriminate between products that would be reliably safe in the longer term under the most severe impact conditions and those which would be prone to fracture under these conditions.

Inspection and analysis

A more comprehensive mechanical testing programme was undertaken using both new and old (used) rails. Impact tests were carried out by several different methods covering a range of impact velocities and temperatures.

As expected for a given rail geometry and impact velocity there was a temperature below which the product failed in a brittle manner. This critical temperature T_b increased with increasing:

- Service life (as illustrated in Figure 3.22),
- Impact velocity,
- Profile stiffness.

The brittle failure of a product with high geometrical stiffness (multi-ribbed) is illustrated in Figure 3.23.

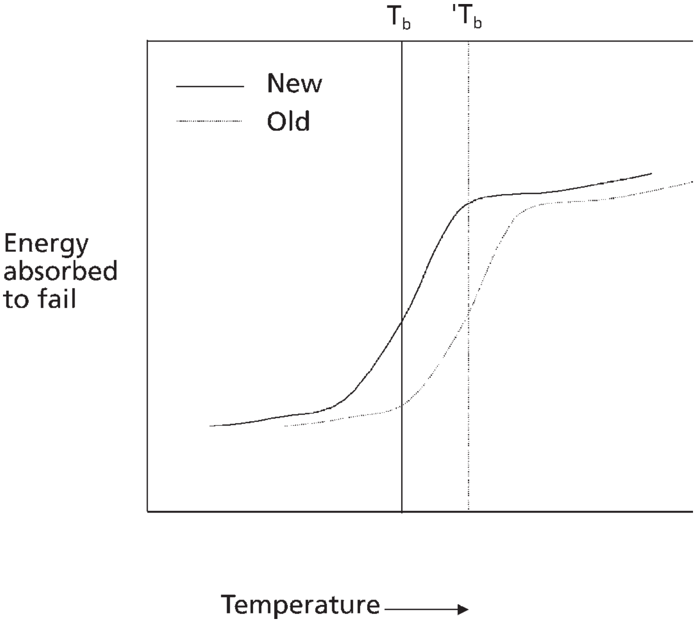


Figure 3.22 Graph showing the relationship between T_b and service life

Failure diagnosis

In service, degradation due to UV radiation will progressively raise the critical temperature, or lower the critical velocity, at which fracture of the rails is no longer ductile.

The screening test had not been satisfactory for two reasons. Firstly the impact velocity that could occur in service had been underestimated. At the highest expected velocity and the lowest expected temperature some of the products (particularly those with multiple ribbing) were brittle even when new. (Ribs introduce stress concentrations.) All products would eventually degrade with service life to the point when they would be prone to brittle fracture.

Lessons and consequences

1. Impact strength is dominated by a ductile/brittle transition. If this transition is not located by comprehensive testing then the sensitivity of a product to changes in materials or processing quality or changes due to degradation may not be detected.

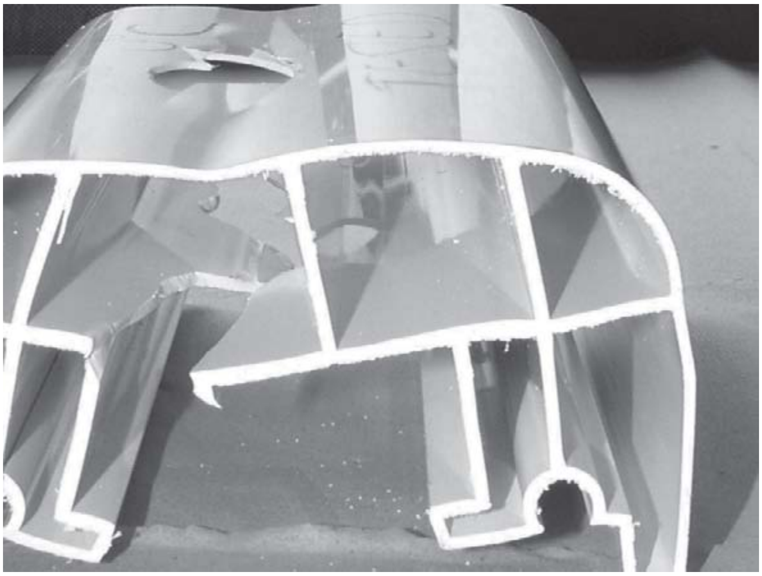


Figure 3.23 The cross-section of a failed running rail

2. The well known fact that PVC has been used successfully in outdoor applications (window frames, guttering, etc.) should not be taken as proof that the material is highly resistant to photo-oxidation. Building products (unlike running rails) are rarely exposed to high velocity impact, and it is this that explains their durability.

References

1. M. M. Qayyum and J. R. White, Polymer Degradation and Stability, 1993, 41, 2, p 163.
2. M. S. Rabello and J. R. White, Journal of Applied Polymer Science, 1997, 64, 13, p.2505.
3. R. Satoto, W. S. Subowo, R. Yusiasih, Y. Takane, Y. Watanabe and T. Hatakeyama, Polymer Degradation and Stability, 1997, 56, 3, p.275.
4. The Effect of UV Light and Weather, PDL, Morris NY, 1994.
5. A. J. Chirinos-Padron, P. H. Hernandez, E. Chavez, N. S. Allen, C. Vasiliou and M. DePoortere, European Polymer Journal, 1987, 23, 12, p.35.
6. J. L. Philippart, C. Sinturel and J. L. Gardette, Polymer Degradation and Stability, 1997, 58, 3, p.261.
7. N. S. Allen and A. Parkinson, Polymer Degradation and Stability, 1983, 5, 3, May, p.189.
8. N. S. Allen, J. L. Gardette and J. Lemaire, Dyes and Pigments, 1982, 3, p.295.
9. M. Mlinac, J. Rolich and M. Bravar, Journal of Polymer Science, Polymer Symposia, 1976, 57, p.161.
10. S. Bigger and O. Delatycki, Journal of Materials Science, 1989, 24, 6, p.1946.
11. I. Narisawa and T. Kuriyama, Angewandte Makromolekulare Chemie, 216, March 1994, p.87.
12. J. Malik, D. Q. Tuan and E. Spirk, Polymer Degradation and Stability, 1995, 47, 1, p.1.
13. J. Malik, A. Hrivik and D. Alexyova, Polymer Degradation and Stability, 1992, 35, 1, p.125.

14. F. Gugumus, Oxidation Inhibition of Organic Materials, Vol. 2, CRC Press Inc., Boca Raton, FL, 1990.

15. P. D. Calvert and N. C. Billingham, Journal of Applied Polymer Science, 1979, 24, p.357.

16. J. Rose and F. R. Mayo, Macromolecules, 1982, 15, p.948.

17. P. Gijsman, J. Hennekens and D. Tummers, Angewandte Makromolekulare Chemie, 216, March 1994, p.37.

18. L. Manolis-Sherman, Plastics Technology 1996, **42**, 7, p.42.

19. F. J. Pern and A. W. Czanderna, Solar Energy Materials and Solar Cells, 25, 1992, p.3.

20. M. Ezrin, G. Lavigne, P. Klemchuk, W. Holley, S. Agro, J. Galica, L. Thomas and R. Yorgensen, SPE Antec Vol. III, May 1995, p.3957.

21. B. Meyer, Rubber and Plastics News, 27, 8, 17 March 1997, p.40.

22. R. M. Paroli, O. Dutt and C. Lavallee, Rubber and Plastics News, 21, 12, 23 December 1991, p.15.

23. J. J. Laski and M. H. Chipalkatti, SPE Antec, Vol. III, May 1995, p.3260.

24. D. R. Hone, Color Quantification: Adding Value With Instruments, SPE CAD RETEC Proceedings, September 15 1997, Paper 4.

25. J. M. Henshaw, V. Wood and A. C. Hall, Engineering Failure Analysis, 1999, 6, p.13.

26. G. Hochmuth, W. Stall and R. Hopper, Plasticulture, 1993/1994, 100, p.36.

27. A. Torikai, T. Kobatake, F. Okisaki and H. Shuyama, Polymer Degradation and Stability, 1995, 50, 3, p.261.

28. A. M. Eleiche, Plastic Pipes V, PRI, 8 – 10 Sept. 1982, p.221.

29. P. C. Warren, Plastics in Telecommunications VI, PRI, London, September 16 – 18, 1992, p. 29/1.

30. X. Hu, H. Xu and Z. Zhang, Polymer Degradation and Stability, 1994, 43, 2, p.225.

4 Degradation Due to Ionising Radiation

4.1 Introduction

Reported failures due to the exposure of plastics and rubbers to ionising radiation are relatively rare. The nuclear energy industry has succeeded by, where possible, avoiding the use of polymers where a high radiation dose would be accumulated, or otherwise by employing conservative schemes of preventative maintenance based upon the results of extensive materials and product testing.

The vast majority of failures that do occur are due to the process of radiation sterilisation (gamma or electron beam) which has now replaced ethylene oxide (EtO) gas (diluted with a gaseous carrier), as the preferred method of sterilisation prior to product distribution. Disposable medical products dominate this category. US Food and Drug Administration (FDA) guidelines limit the concentration of EtO to 25 ppm for blood contacting parts and otherwise < 250 ppm, on evidence that the gas is mutagenic. The gas is initially absorbed into the surface of the product to (typically) a concentration of several thousand ppm. In the presence of chlorine or chlorides, the EtO is converted to the even more toxic ethylene chlorohydrin. The time to degas down to the required limits has been the principal concern and the major reason for the increased use of radiation sterilisation.

4.2 Degradation mechanisms

Ionising radiation includes gamma rays, x-rays, electron beams, protons, neutrons, alpha particles, and other nuclear fragments. They are defined as having sufficient quantised energy to create ion pairs either directly, as with charged particles (electrons, protons, alpha particles), or indirectly, as with uncharged quanta (high energy photons (gamma and x-rays) and neutrons). In polymers, ions result directly or indirectly from the respective stripping or excitation of orbital electrons. They are unstable and lead to the rupture of covalent bonds. The competing termination and propagation reactions of these highly unstable molecular fragments (free radicals, $R^\bullet$) determine the nature and extent of degradation.

Two major competing degradation routes are chain scission which leads to a reduction in molecular weight, and crosslinking which increases molecular weight. As a reduction in molecular weight usually promotes the more severe impairment of mechanical properties, materials that are prone to chain scission such as polypropylene and polytetrafluoroethylene are generally classed as less resistant to ionising radiation than (say) polyethylene or polystyrene which favour crosslinking.

As polyethylene is chemically the least complex it will be used to demonstrate the general features of the initiation, propagation and termination reactions.

Initiation

As shown in Figure 4.1, initial ionisation routes fall into two classes. Scission of the C-H bond to generate secondary radicals requires 19 electron volts (eV) of energy. Scission of the backbone C-C bond to generate primary radicals requires 135 eV.

The most common industrial source of gamma rays is cobalt 60 which generates photons of either 1.17 or 1.33 MeV. The high energy photons collide with bound electrons and via a process known as Compton scattering, up to ~ 80% (but more typically 50%) of the energy is transferred to a recoil or secondary electron. The most energetic secondary

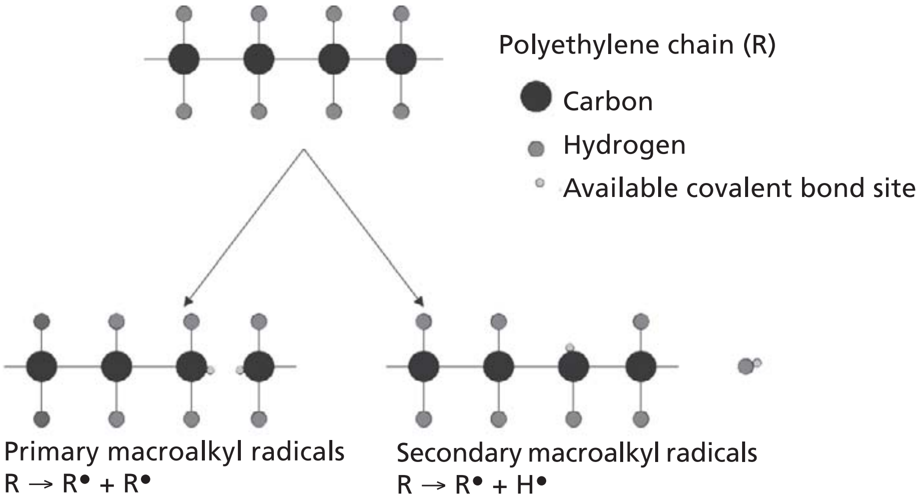


Figure 4.1 Initiation stage in polyethylene on exposure to ionising radiation

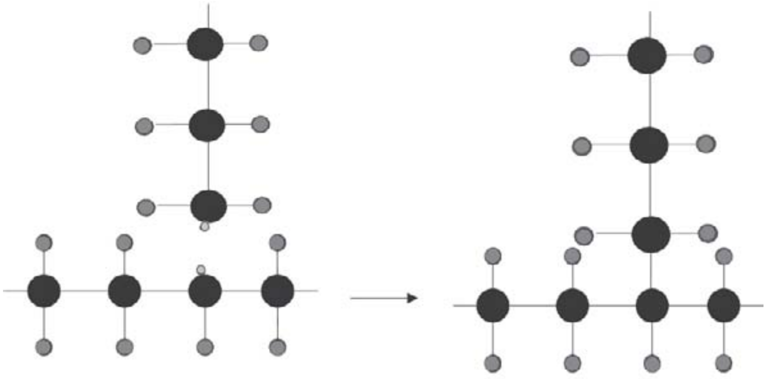
electrons (~ 1 MeV) are each capable of then generating up to 40,000 ion pairs. These are generated equally in the crystalline and amorphous regions and the population of radical products will be approximately proportional to the absorbed radiation energy.

The initial response of polyethylene on exposure to ionising radiation is to reduce in molecular weight via the rupture of main chain C-C bonds and the creation of primary macroalkyl radicals.

Propagation and termination in the absence of oxygen

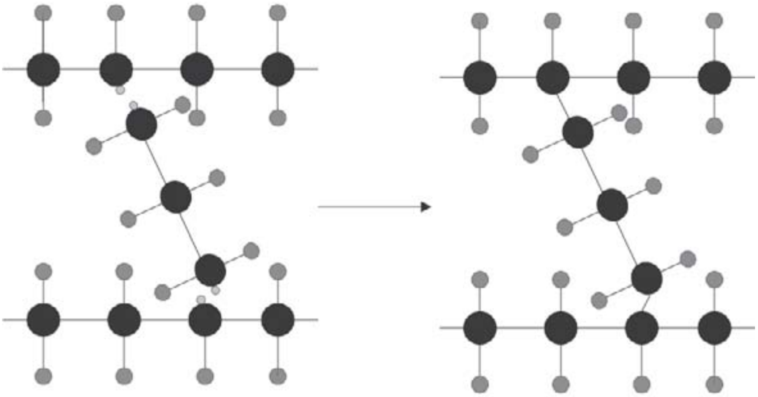
In principal all the reactions that produce free radicals are reversible. Due to the low mobility of primary macroalkyl radicals a significant proportion will recombine (intermolecular). Other slower and less probable termination (intramolecular) processes include branching as shown in Figure 4.2, and crosslinking as shown in Figure 4.3.

Hydrogen ions (protons) are very mobile and will rapidly diffuse away from the parent secondary macroalkyl radical. Protons will, by extraction of bound hydrogen, cause a combination of termination and propagation reactions. For example Figure 4.4 shows the termination of a primary and the propagation of a secondary alkyl radical, Figure 4.5 shows the termination of a secondary radical by the creation of an unsaturated C=C bond, and Figure 4.6 shows termination by crosslinking.



$$R^\bullet + R^\bullet \rightarrow R$$

Figure 4.2 Termination of two alkyl radicals by chain branching



$R^{\bullet} + R^{\bullet} + R^{\bullet\bullet} \rightarrow R$

Figure 4.3 Crosslinking between two secondary and one primary alkyl radicals

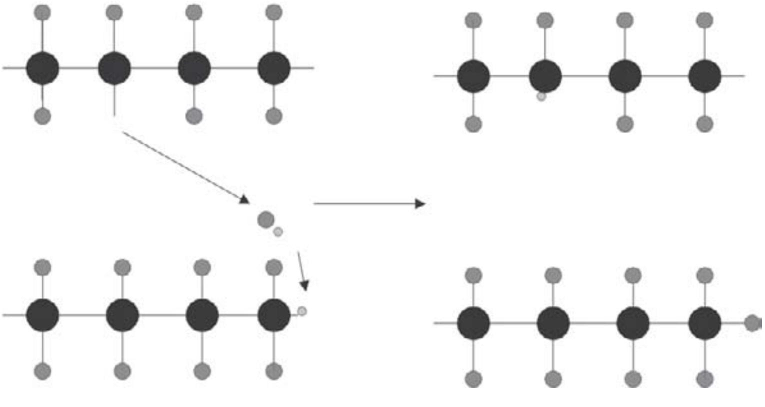


Figure 4.4 Termination of a primary alkyl radical and propagation of a secondary radical by intermolecular hydrogen extraction

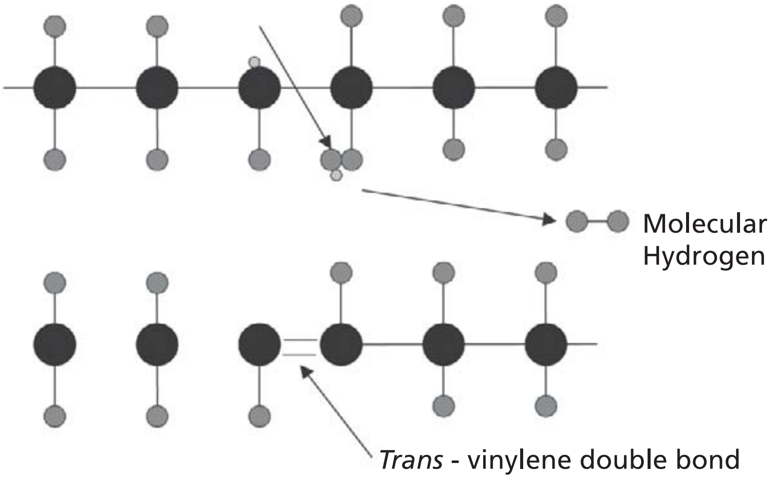


Figure 4.5 Termination of a secondary alkyl radical by adjacent intramolecular hydrogen extraction

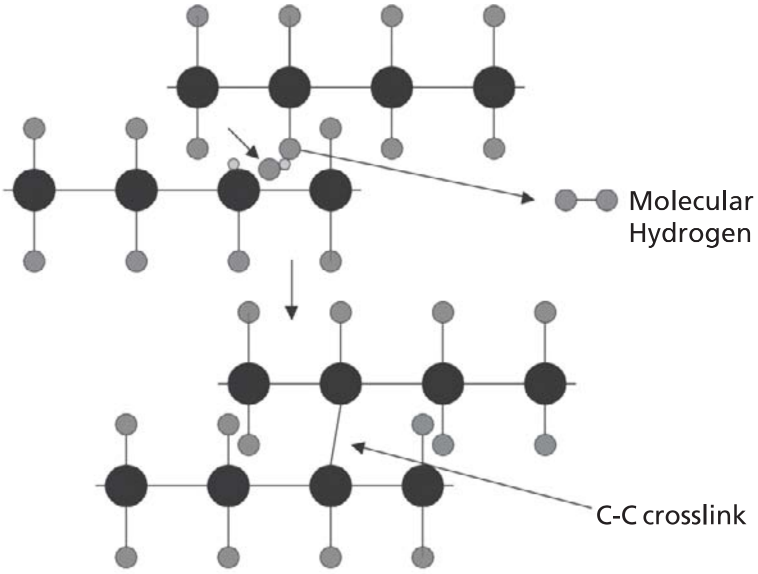


Figure 4.6 Termination of a secondary alkyl radical by intermolecular hydrogen extraction

Propagation and termination in the presence of oxygen

In the presence of absorbed oxygen (the common case) a wide range of other propagation and termination reactions will take place. Absorbed oxygen (which is relatively mobile) reacts with free radicals to produce unstable products as shown in Figure 4.7 such as peroxy radicals ($RO_2^\bullet$), intermediate products such as hydroperoxides ($RO_2^\bullet + H^\bullet$ to ROOH) and stable products such as carbonyls (R=O). The last includes ketones, alcohols, esters, and organic acids. These propagation and termination processes tend to occur in the intercrystalline (amorphous) regions of the material which are more open to oxygen permeation and absorption.

The hydroperoxides decay slowly ($ROOH \rightarrow RO^\bullet + OH^\bullet$), and by this chain reaction, oxidation will propagate with time. The absorbed free oxygen is consumed by these various reactions and subsequently the rate of chemical degradation is often limited by the rate of free oxygen replenishment via permeation.

4.3 Radiation resistance of polymers

Tables 4.1, 4.2, and 4.3 list the threshold dose for significant damage for a reasonably comprehensive range of thermoplastics, thermosets, and rubbers, respectively. The data

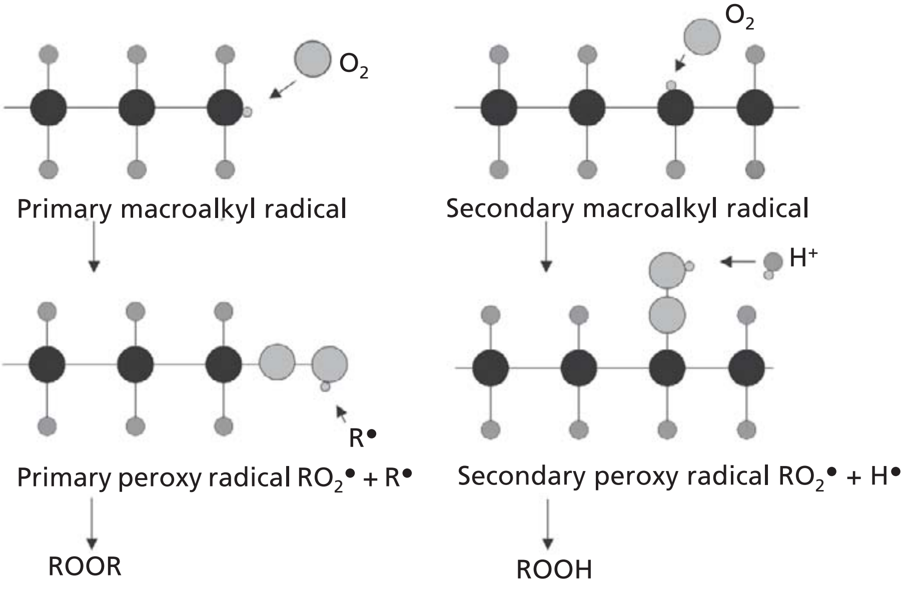
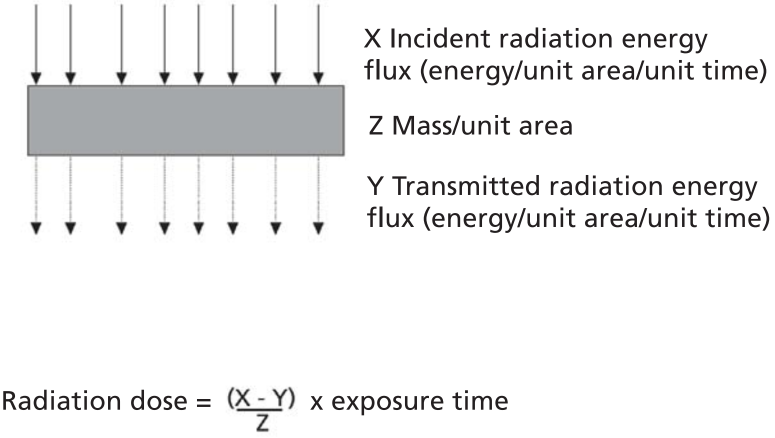


Figure 4.7 Oxidation of free radicals

have been compiled [1] from four sources. It should be noted that the ‘critical dose’ is that required to generate detectable damage. The following points should be taken into account.

i) One Gray (Gy) = 1 J/kg and therefore 1 kGy = 1 kJ/kg. It is a measure of the radiation energy absorbed per unit mass of the material. Another unit commonly used is the Mrad (one million rads), which equates to 10 kJ/kg. Therefore 1 Mrad = 10 kGy.



ii) The radiation dose for critical damage increases with increasing dose rate. This effect ranges from negligible to gross depending upon the material. For example [2], for one rubber at ambient temperatures a ten fold increase in dose rate increased the dose to equivalent damage (DED) by a factor of 5. For another rubber (probably silicone) at ambient temperature, the same increase in dose rate increased DED by only a few percent. For unplasticised polyvinyl chloride (UPVC), DED increased by a factor of 3 under these conditions. In a nuclear energy plant a polyethylene cable had completely embrittled after only 12 years at a dose rate of 0.25 Gy/hour (i.e. a dose of 30 kGy). Testing at 10 kGy/hour had indicated 50% strain at break retention up to 500 kGy. This and other dose rate effects arise from the fact that oxygen is essential for the generation of such degradation products as peroxides and carbonyls. Initially there is sufficient oxygen dissolved in the material to initiate the degradation process. In the case of polyethylene the dissolved oxygen is consumed by the free radicals produced by a dose of 5 kGy, i.e. within half an hour of testing at a dose rate of 10 kGy/hour. For the remaining 49.5 hours of the test, the rate of degradation is limited by the rate of oxygen permeability into the bulk of the material. In service at a dose rate of 0.25 Gy/hour the rate of oxygen consumption would never exceed the rate of replenishment via permeation. It is probable that materials with the lowest oxygen permeability (e.g. polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), and Nylon) will exhibit the highest dependence on dose rate, whilst polytetrafluoroethylene (PTFE), polymethylpentene (TPX), low density polyethylene (LDPE), polybutadiene, and natural and silicone rubbers with high permeability will show the least dependence.

iii) It follows that as most test data (including those given here) have been generated using high dose rates and short exposure times, they cannot be used safely for predicting the service life of products exposed to much lower dose rates. It also follows that the rate of degradation will tend to maximise at or near the surfaces of the material (with access to atmospheric oxygen). It also follows that degradation will probably continue after exposure to radiation. Under the accelerated test conditions for the polyethylene (PE) cable a proportion of the free radicals generated by 495 kGy of radiation will be available to react with permeated oxygen after completion of radiation exposure. Strain at break or other mechanical properties will decline by 'post radiation' degradation.

iv) DED decreases with increasing temperature. This is only partly due to thermal degradation, and in most cases it can be taken to be the result of increased oxygen permeability with temperature. However it can also be the result of other synergistic mechanisms. It was reported by Westinghouse [3] that "until recently, service life estimates (for elastomeric seals in a nuclear reactor environment) were based upon single stress tests". For an application requiring a lifetime of 40 years at 50 °C and a radiation dose rate of 0.012 kGy/hour (life dose of < 5 kGy) a fluoroelastomer (Viton B) was chosen. The seal would be immersed in silicon oil thus reducing the rate of thermal/oxidative degradation or radiation induced oxidation. 'Single stress' tests involving radiation alone and in the absence of oxygen indicated negligible damage after a dose of 1000 kGy. Single stress tests involving temperature alone indicated, by extrapolation, a lifetime of 40 years at 145 °C. On this evidence, and particularly in the absence of oxygen, it would have been normal practice to assume that under the combined conditions of thermal and radiation exposure, the seal would satisfy the durability specification. Fortunately this assumption was not made and tests to predict durability under the combined influence of temperature and radiation were carried out. These indicated that thermal degradation was significantly accelerated by concurrent exposure to radiation. It was calculated that at 0.012 kGy/hour and 50 °C the seal might fail after a service life of only 21 years (life dose of only ~ 2 kGy). The timing and implications of this work would suggest that premature seal failure in the nuclear industry was a risk for many years.

v) DED decreases when radiation exposure and applied stress are concurrent. Figure 4.8 shows the overall effect on the creep rupture characteristics of polysulphone (Udel 1700) [4]. Qualitatively, radiation induces an acceleration of the long term ductile to brittle transition to shorter times. The reduction in creep rupture strength and the

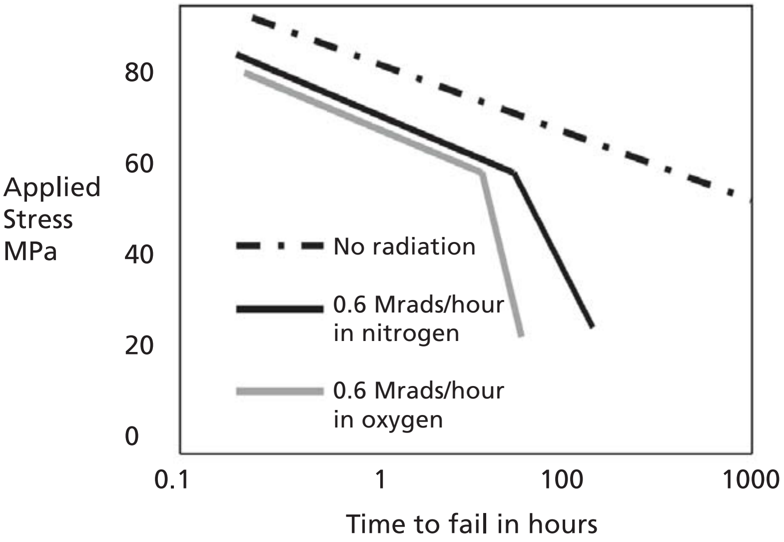


Figure 4.8 Creep rupture characteristics of polysulphone

change in the mode of failure are also observed with heat plus stress, UV plus stress, stress corrosion cracking and environmental stress cracking.

The ambient temperature long term design strength of polysulphone is ~ 20 MPa. At this stress and an exposure rate of 0.6 Mrads/hour we can expect brittle failure after ~100 hours and therefore after a radiation dose of only 60 Mrads (600 kGy). Radiation exposure in air but in the absence of stress indicated a 50% reduction in strength after 200 Mrads (2000 kGy).

These results are extremely significant for designers in the nuclear power or reprocessing industries who contemplate the use of plastics in load-bearing structures.

vi) DED decreases with decreasing material thickness. Thin films, coatings, fibres, and powders will degrade more rapidly than bulk materials. Again this is due to the increased rate of oxygen replenishment.

vii) DED increases with increasing antioxidant protection. For gamma sterilisation where doses of ~ 25 to 35 kGy are typically applied, important marginal materials such as polypropylene would not be suitable unless heavily protected. 'Radiation stabilised' grades are now available which can be safely sterilised by gamma radiation. These grades are thought to contain special combinations of antioxidants (alkylated phenols, thiodipropionates, and phosphites) together with mobilising additives such as polyethylene waxes and oils.

viii) At dose rates that are below the threshold for significant structural damage other undesirable effects are observed including loss of gloss, increased haze, colour change, and odour.

ix) Colour change usually involves yellowing. These changes generally reverse (fade) with time after radiation exposure. The rate of fading increases with storage temperature and when exposed to light/UV (photobleaching). Notable exceptions include thermoplastic polyurethane (in which the colour change is permanent) and UPVC which continues to discolour on storage after radiation exposure.

x) Seals and gaskets are critical components and rubbers in general offer comparatively poor resistance to ionising radiation. Some early seal leakage failures stimulated investigations into the effect of radiation dose on the rate of stress relaxation, and in particular on the increase in the accumulation of compression set, as this determines the sealing pressure across a compressed seal or gasket. Radiation induced crosslinking may only increase material modulus by a modest degree, but if this occurs whilst the material is mechanically deformed then there will be a significant loss of 'elastic memory'. Model relationships between radiation dose, dose rate, stress, temperature and relaxation have been developed [5] and reviewed [2]. For elastomeric gaiters and other stretched components the main cause for concern would be the decline in tensile elongation to failure and in particular the effect of ozone. In air, ionising radiation generates ozone and ozone cracking (see Section 2.6) is likely to be the factor that limits durability in components under tensile stress.

4.4 Performance of specific materials

Polystyrene (PS)

Polystyrene is a partly aromatic polymer and in bulk form reacts to ionising radiation by crosslinking. After exposure to 700 kGy of electron beam radiation the tensile strength reduced from 43 to 41 MPa and the strain at break from 6% to 5% [6]. However as the material is intrinsically brittle these very modest declines in structural properties should not be taken *a priori* as proof of high radiation resistance. It was observed that after exposure to doses above 300 kGy, tensile failure occurred without visible surface crazing. This would imply that the molecular weight of the material (initially 350,000) had reduced to below ~ 35,000 (the minimum for chain entanglement). Material starved of oxygen

Table 4.1 Critical gamma radiation dose for thermoplastics in air at ambient temperatures

Material	Critical dose (kGy)
Polyimides	1000
PET	1000
PPO, PPE, (e.g. Noryl)	700
PSul	700
PES	700
PS	600
UPVC	300
Nylons	300
PVDC	250
Polycarbonate	250
ABS	200
Polyacrylonitrile	100
PVA	100
PE and XLPE	100
Ionomer	100
PVDF, ECTFE, ETFE	100
Cellulose acetate	100
EVA	100
PMMA	60
CTFE	60
Cellulose nitrate	40
FEP	40
Polypropylene	10
Acetal	10
PTFE	4

Table 4.2 Critical gamma radiation dose for thermosets in air at ambient temperatures

Material	Critical dose (kGy)
Polyester (glass filled)	10,000
PU	10,000
Silicone (mineral or glass filled)	10,000
Epoxy (novalac)	7,000
Epoxy (diglycidyl ether of bisphenol A)	2,000
Silicone (unfilled)	1,000
Polyester (mineral filled)	700
MF	40
UF	15
Phenolic	15
Polyester (unfilled)	3

Table 4.3 Critical gamma radiation dose for elastomers

Material	Critical dose (kGy)
EP, EPDM	400
PU (MbOCA crosslinked)	300
Butadiene styrene (Buna S)	300
Nitrile	100
Chlorosulphonated PE (Hypalon)	100
Butadiene	100
Polysulphide	90
Butyl	40
Polyacrylate	40
Chloroprene (Neoprene)	40
Silicone	40
Hexafluoropropylene-vinylidene fluoride (Viton)	8

(e.g. in the bulk) will crosslink whilst material with access to sufficient oxygen (e.g. at free surfaces) will suffer chain scission and therefore a reduction in molecular weight. PS in fine powder form when irradiated suffers oxidative degradation and chain scission.

The same source compared the resistance of polystyrene with a tough polystyrene blend (containing 3% polybutadiene (PB)). As shown in Figure 4.9 the strain at break of the tough blend reduces from 20% to ~ 6.5% with exposure to only 100 kGy. After exposure to doses above 300 kGy, tensile failure occurred without visible surface crazing and the strain at break of the blend was the same as that of pure polystyrene.

On this evidence alone it would be considered reasonable to describe the radiation resistance of the blend as poor and that of the pure polystyrene as very good. However it seems unreasonable to blame this gross effect on the presence of small amounts of rubber (~3%) that is known to exhibit radiation crosslinking. A more reasonable explanation is that the surfaces of both materials are degraded to a similar extent forming a brittle layer. When this cracks, the bulk cracks by 'sympathetic fracture' whether the bulk is undegraded PS or the very much tougher PS/PB. This would imply that the (apparently) good resistance of polystyrene is at least partly due to its intrinsic lack of ductility, and the fact that resistance is often monitored by assessing the reduction in ductility.

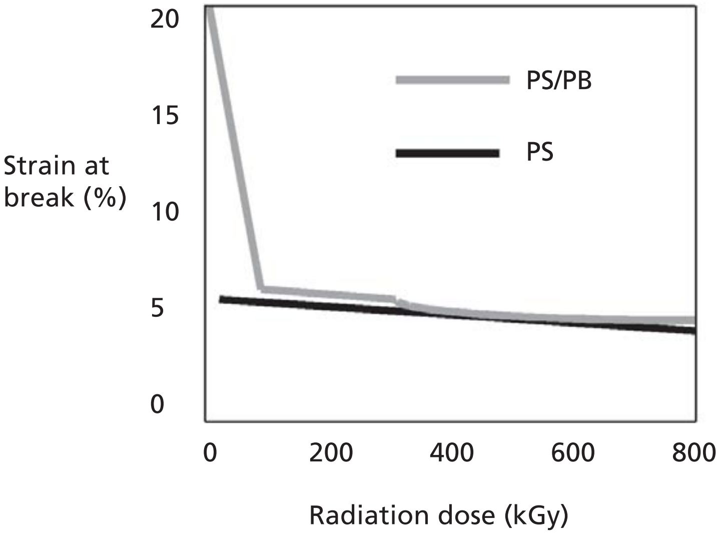


Figure 4.9 Comparison of polystyrene (PS) and high impact polystyrene (PS/PB)

Polycarbonate (PC)

Discolouration and the associated reduction in transparency are the most common problems. Standard polycarbonate will discolour (yellowing) at dose levels required for sterilisation. After 33 kGy of gamma radiation the change in yellowness index (ΔY1) has been reported to be 32 units [7]. This fades to 16 units after 30 days of storage in the dark. The addition of 0.8% of dicyclohexyl phthalate reduces this to 18 and 6 units, respectively. Fading is more rapid if the product is exposed to light (photobleaching) or heat.

The yellowing has been traced to isolated phenoxy radicals or other conjugated chromophores. Fading has been linked to reaction of these species with permeated oxygen [8].

Polyvinyl chloride (PVC)

As with polycarbonate, discolouration during exposure to low doses is the major problem. After 25 kGy of gamma radiation the change in yellowness index (ΔY1) has been reported to be 177 units for a standard grade of UPVC [9]. Furthermore, as the chain of reactions that leads to discolouration starts with autocatalytic dehydrochorination, the yellowness and loss of transparency increases after irradiation has ceased. After 68 days of storage ΔY1 = 226 units and light transmission = 7% (down from 69% prior to radiation). However radiation stabilised compounds are claimed to be effective. After the same exposure and storage conditions ΔY1 = 12 units and light transmission = 70%.

Plasticised PVC is significantly more resistant to radiation induced discolouration than UPVC [10]. The more expensive plasticisers with high aliphatic/aromatic ratios offer the best retention of optical properties. Traditional non-toxic mixed metal stabilisers (Ca/Zn) promote discolouration.

Polymethyl methacrylate (PMMA)

Much of the interest in the response of PMMA to electron beam radiation arises from its use by the microelectronics industry as a positive photoresist. The material has modest resistance and responds solely by chain scission. Interestingly, the presence of oxygen reduces the rate of scission (oxygen acts as a free radical scavenger).

The reduction in number average molecular weight with gamma radiation dose [11] is indicated in Table 4.4.

Unfortunately the source does not reveal whether irradiation was carried out in the presence of oxygen. If in air (probable) the data would imply significant reduction in

Table 4.4 Reduction in the number average molecular weight of PMMA with increasing gamma dose

Dose (kGy)	Molecular weight
0	1,900,000
50	140,000
100	57,000
150	43,000
200	32,000

molecular weight under sterilisation doses. The critical dose of 60 kGy quoted for PMMA in Table 4.1 and this reduction in molecular weight data would seem to be in reasonable agreement.

Polytetrafluoroethylene (PTFE)

PTFE is the least resistant of all generic polymers. Exposure in air to only 40 kGy of gamma radiation reduces strain at break by a factor of 100 [12].

PTFE suffers from chain scission and this is accelerated by access to oxygen (generating peroxy radicals). However oxygen permeability is high and therefore dose rate effects are small.

Radiation degradation of high molecular weight PTFE powders is used to facilitate blending with inks, lubricants, coatings, rubbers and plastics.

Polyvinylidene fluoride (PVDF)

Chain scission is the predominant effect and this is reported to induce a significant increase in the degree of crystallinity [13]. The reduction in molecular weight of the amorphous phase increases molecular mobility and ease of crystal nucleation and growth. Both effects combine to cause a severe impairment of toughness. As shown in Figure 4.10, the data are not inconsistent with the critical dose of 100 kGy as listed in Table 4.1.

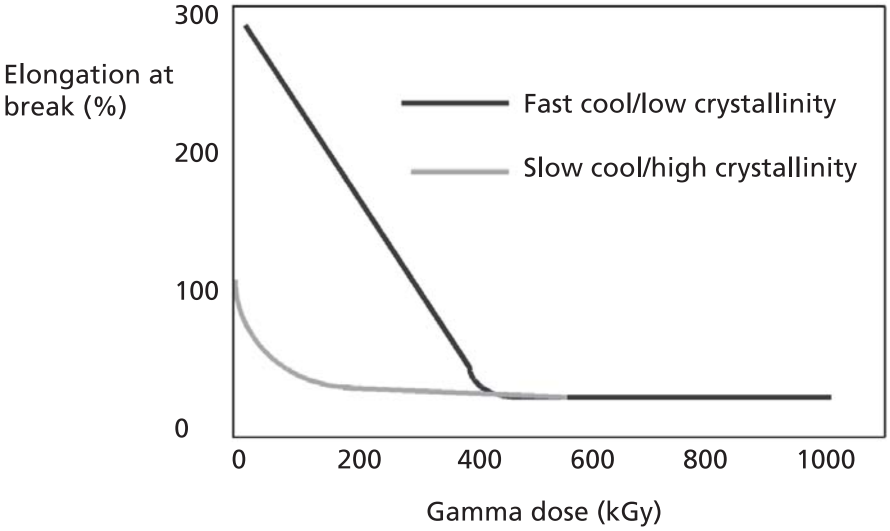


Figure 4.10 Reduction in elongation at break of PVDF with gamma dose

Polyethylene (PE)

Radiation crosslinking of polyethylene is a standard process for improving many of the material properties and in particular the resistance to creep and creep rupture at elevated temperatures. Typically the material is modified in this manner by exposing the PE to a 'saturation dose' of gamma radiation in the absence of air/oxygen. This dose ranges from 100 to 300 kGy depending upon material grade and formulation. Up to the saturation dose, the crosslink density as measured by gel content (by xylene extraction) increases linearly with dose. Above this level the gel content is independent of dose suggesting dynamic equilibrium between chain extension and chain scission. The saturation dose is increased by the action of antioxidants that stabilise macroalkyl radicals. It follows that antioxidants are (partly) consumed as a result [14]. The saturation dose is decreased by the addition of 'radiation sensitisers', which include trifunctional monomers such as trimethylolpropane trimethacrylate and triallylcyanurate.

It is generally accepted that for the more usual case of radiation exposure whilst in contact with air, crosslinking is depressed and chain scission is enhanced. As polyethylene is a popular material for disposable medical devices, considerable effort has been applied to assessing its response to radiation sterilisation. In experiments up to 75 kGy [15] and

200 kGy [16] it has been reported that most mechanical properties improve with radiation exposure. Slight discolouration due to phenolic-based antioxidants and particularly in combination with hindered amine light stabilisers was one detrimental observation. The other was a modest reduction in slow speed tear strength. Therefore the critical dose of 100 kGy listed for PE in Table 4.1 would seem to be pessimistic. However some caution is required because of the complex competition between oxygen starved crosslinking and oxygen rich chain scission. For a bulky component the result may be a thin surface layer of degraded material with low resistance to crack initiation, but the main material mass not being degraded, and indeed possibly being enhanced by crosslinking. Radiation resistance as measured by changes in properties will vary depending upon the test methods employed. Tests that investigate bulk properties such as heat distortion temperature and failure by yielding will be insensitive to surface degradation and will therefore imply high radiation resistance. Tensile tests will be less sensitive to surface degradation than flexural tests. This is well known (and sometimes exploited) by material suppliers. An extreme example of favourable exploitation is a notched impact test where the notch is machined in, and therefore the brittle layer removed, after radiation exposure.

In the failure analysis of integral hinged medical products made from injection moulded high density polyethylene (HDPE) [17] the contribution of radiation sterilisation (35 kGy) was investigated. It was established that gamma sterilisation had reduced the oxygen induction time from 22 minutes to 5 minutes. Thus a large fraction of the antioxidant had been consumed whilst scavenging for radiation-induced free radicals. However under conventional circumstances the remaining fraction of stabiliser should have been sufficient to prevent in-service embrittlement. Microscopic examination revealed that at the centre line of the hinge cross-section, a string of microvoids had been created during moulding due to air entrapment and inadequate packing. These would act as stress concentrators but again, on their own would not be sufficient to induce brittle fracture. It was inferred that the thin walled microcellular structure had suffered complete antioxidant depletion due to very localised radiation induced degradation. The coincidence of embrittled material and stress concentration was deemed to be responsible for the failures.

Ultra high molecular weight polyethylene (UHMWPE)

Gamma radiation sterilised UHMWPE is used extensively by the orthopaedic community for artificial hip and knee components. In some designs contact stresses approach the yield stress (~20 MPa) of the material. Wear and fatigue fracture are two of the most common causes of premature failure.

The changes in short term mechanical properties of UHMWPE following exposure to 30 kGy of gamma radiation are listed in Table 4.5.

Table 4.5 Effects of gamma radiation sterilisation (30 kGy) on UHMWPE (GUR 415 from Hoechst)

Property	Unsterilised	Gamma sterilised
Hardness (Shore D)	66	67
Compressive modulus	538 MPa	677 MPa
Yield strength	20 MPa	24 MPa
Ultimate tensile strength	40 MPa	43 MPa
Elongation at break	353%	315%
Impact strength	107 kJ/m^2	86 kJ/m^2

These apparently modest changes indicate a reduction in molecular chain mobility. However the effect on long-term properties and hence durability can be far more significant [18]. Figure 4.11 reveals that under reverse bending fatigue there is little effect of radiation exposure up to 2 million cycles but above this limit the penalty of sterilisation becomes significant. At 10 million cycles the fatigue strength is reduced from 31 MPa (unsterilised) to 18 MPa (sterilised).

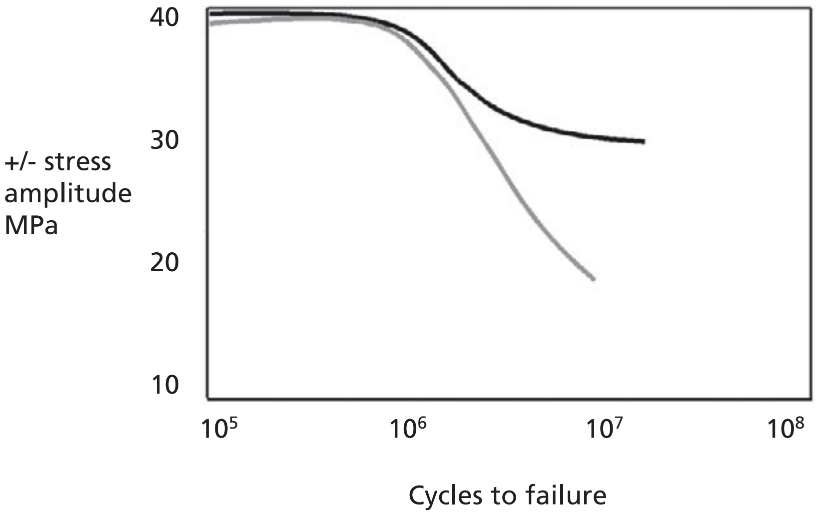


Figure 4.11 The effect of gamma sterilisation on the dynamic fatigue resistance of UHMWPE

In both states the transitions from ductile to brittle failure coincide at ~ 10^6 cycles. In the brittle mode, the time to fail is dominated by the crack growth rate. It may be inferred that the major effect of gamma sterilisation is to reduce the threshold stress intensity range (ΔK) for slow crack growth.

It has been reported in an analysis of 122 artificial knee joint failures [19] that the maximum shear stress in these components was located approximately 1 mm below the surface. Subsurface cleavage or delamination (a common cause of failure) was initiated at this depth. By microtoming thin (200 micron) slices of gamma irradiated UHMWPE the through thickness profiles of degradation and structural changes were monitored [20]. Of principle interest was the degree of oxidation, as quantified by the carbonyl ratio, using Fourier transform infrared spectroscopy (FTIR), and percentage crystallinity, by differential scanning calorimetry (DSC). Both maximised at 1 – 2 mm below the surface.

It is known that due to a combination of attenuation and Compton scattering, the absorption of radiation maximises just below the radiation exposed surface and it is here that macroalkyl radical concentration maximises. Diffused oxygen stabilises the molecular fragments, reducing the probability of recombination and crosslinking. The net effect is chain scission of the oxygen rich amorphous phase and the tie molecules. The increased molecular mobility promotes crystal growth and this explains the increase in subsurface crystallinity from ~ 50% to 57%. Chain scission of the tie molecules probably accounts for the aforementioned reduction in long term fatigue strength, as it is well established [21] that intercrystalline tie molecule entanglement provides the main resistance to slow crack growth in polyethylenes.

These findings (and others that are supportive) have raised serious doubts about the continued use of radiation sterilisation of such components in the presence of air/oxygen.

Crosslinked Polyethylene (XLPE or PE-X)

XLPE is an important material for cable insulation in nuclear installations. It has been reported [22] that following exposure in air to 100 kGy of radiation at low dose rates, the strain at break (~ 250%) of XLPE was unaffected. After a dose of 1000 kGy, strain at break had declined significantly and was sensitive to dose rate as shown in Table 4.6. The dose rate sensitivity is the consequence of high oxygen permeability within XLPE.

On this evidence and assuming a required life of > 100,000 hours, the critical dose of 100 kGy as listed in Table 4.1 seems reasonable. This would mean a long-term safe dose rate of less than 1 Gy/hour.

Table 4.6 Strain at break of XLPE following exposure to 1000 kGy at various dose rates

Dose rate (Gy/hour)	Dosing time (hours)	Strain at break (%)
300	3,333	12
900	1,111	25
5400	185	110

Polypropylene (PP)

Polypropylene is an attractive choice for many disposable medical products but without modification it should not be radiation sterilised. It suffers from chain scission and severe post radiation oxidative degradation. The critical dose of 10 kGy applies to the unmodified homopolymer.

Resistance is particularly sensitive to the degree of crystallisation. Actions that increase crystallinity such as the addition of conventional nucleating agents, decrease radiation resistance [23]. Actions that decrease crystallinity, such as rapid quenching [24] or copolymerisation [25], increase radiation resistance.

The reduction in resistance with the addition of nucleating agents is of particular concern because many medical products demand transparency, and the addition of such agents (also known as clarifiers) is the conventional method for improving the optical properties of PP. This has been responsible for the mechanical failure (fracture of grip tags) on disposable PP syringes.

The search for clarifying agents that increase radiation resistance has identified some potential candidates. One of the most promising [26] is hydrogenated styrene-butadiene rubber (HSBR). At levels of 10% addition, HSBR reduces haze in PP copolymer from 44% to 29%. The benefits of HSBR addition to three grades of polypropylene can be appreciated from Table 4.7. The critical dose stated is that required to halve the strain at break immediately after radiation exposure (i.e. it does not include post radiation degradation).

The additive also improved post radiation degradation resistance. Figure 4.12 compares the decline in strain at break of a copolymer with storage time following exposure to 25 kGy of gamma radiation. It would be reasonable to anticipate a similar benefit for homopolymers.

Table 4.7 Increase in radiation resistance due to 10% addition of HSBR

Material	Critical dose (kGy)
Homopolymer (MFI = 1)	20
Homopolymer (MFI = 10)	70
Copolymer	48
Homopolymer (MFI = 1) + HSBR	65
Homopolymer (MFI = 10) + HSBR	150
Copolymer + HSBR	150

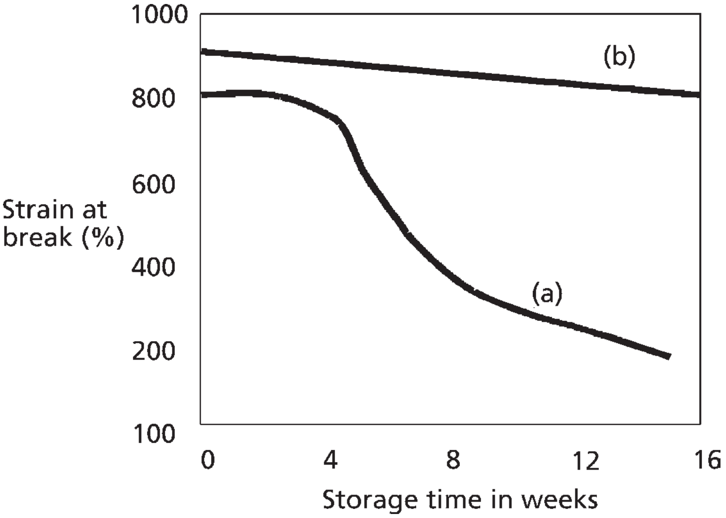


Figure 4.12 Reduction in strain at break with storage time after 25 kGy of gamma radiation, (a) unmodified PP copolymer, (b) PP copolymer + 10% HSBR

4.5 Failure examples

Rapra has no case studies attributable to radiation induced degradation. In addition, although there are some failure examples in the public domain attributable to radiation sterilisation (e.g. polypropylene syringes [27] and UHMWPE hip joints [28]) those that emanate from the nuclear power sector are few and far between. It is probable that there have been significant failures in this sector but the activity is so sensitive and emotive that these have not been publicised.

Early German nuclear power reactors employed ethylene-tetrafluoroethylene (ETFE) cable insulation (Tefzel), after the material had been shown to resist high gamma doses during high dose rate testing. The insulation started to disintegrate after a few years of service and the rewiring costs were enormous. When selected, awareness of dose rate sensitivity was poor. The low oxygen permeability of ETFE ensures that the material's resistance to radiation is very dose rate sensitive.

The corrosion of steel and other metallic components via the products of degradation reactions in polymers and other organics has been openly discussed in public domain literature. It might therefore be surmised that although this is a common, endemic problem, the risks are minor, well known, and safely accommodated. The radiolysis of polymers often leads to the formation of organic acids (carboxylic, acetic, formic, propionic etc.). It was claimed [29] that "no firm evidence exists that organic acids have caused corrosion in turbines, piping, or heat exchangers". However there has been a problem of leaking drums containing transuranic waste [30], that has been attributed to HCl induced pitting corrosion. The waste contained polychlorinated volatile organic compounds (VOCs), which generate HCl as a radiation degradation product. This highlights the risks involved in combining halogen containing polymers with structurally critical metallic components in a radiation rich environment.

References

1. J. W. Hitchon, Radiation Resistance of Plastics and Rubbers, AERE report M3251 Harwell Labs, 1983.

2. D. C. Phillips and S. G. Burnay in, Irradiation Effects on Polymers, Eds., D. W. Clegg and A. A. Collyer, Elsevier, Barking, 1991, p.345.

3. J. Bartko and J. T. Siemon, Journal of Applied Polymer Science, 1991, 42, 6, 20, p.1739.

4. D. J. T. Hill, D. A. Lewis and J. H. O'Donnell, Journal of Applied Polymer Science, 1992, 44, 1, 5, p.115.

5. S. G. Burney and J. W. Hitchon, Journal of Nuclear Materials, 1973, 22, 1, p.27.

6. S. H. Spiegelberg, R. E. Cohen and A. S. Argon, Journal of Applied Polymer Science, 1995, 58, 1, 3, p.85.

7. J. Y. Chung, Proceedings of Antec '96, Vol. III, Indianapolis, p.2784.

8. R. I. Clough, G. M. Malone, K. T. Gillen, J. S. Wallace and M. B. Sinclair, Polymer Degradation and Stability, 1995, 49, 2, p.305.

9. J. L. Stieninger, D. Benderly and M. Rajagopalan, Proceedings of the SPE Vinyl Division, 1990, East Brunswick, NJ, p.133.

10. D. W. Luther and L. A. Linsky, Proceedings of Antec '95, Vol. III, Boston, MA, p.420.

11. S. N. Goyanes, G. M Benites, J. J. Gonzalez, G. H. Rubiolo and A. J. Marzocca, Polymer Testing, 1997, 16, 1, p.7.

12. M. D. Chipara and M. I. Chipara, Polymer Degradation and Stability, 1992, 37, 1, p.67.

13. Z. Zhao, H. Yang, B. Liu, X. Chen and Y. Luo, Journal of Macromolecular Science B, 1993, 32, 4, p.355.

14. I. Novakovic and O. Gal, Polymer Degradation and Stability, 1995, 50, p.53.

15. R. C. Portnoy, Proceedings of Antec '94, Vol. III, San Francisco, CA, p.2614.

16. J. R. de Garavilla, Proceedings of Antec '94, Vol. III, San Francisco, CA, p.2619.

17. M. T. K. Ling, S. P. Westphal, A. Sadik and L. Woo, Proceedings of Antec '96, Vol. III, Indianapolis, p.2842.

18. W. L. Saur, K. D. Weaver and N. B. Beals, Biomaterials, 1996, 17, 20, p.1929.

19. J. P. Collier, M. B. Mayor, J. L. McNamara, V. A. Suprenant and R. E. Jensen, Clinical Orthopedics, 1991, 273, p.232.

20. B. Yoem, Y. J. Yu, H. A. McKellop and R. Salovey, Journal of Polymer Science: Polymer Chemistry, 1998, 36, 2, p.329.

21. N. Brown and Y. Huang, Journal of Polymer Science: Polymer Physics, 1991, 29, p.129.

22. G. Spadaro, E. Calderaro and G. Rizzo, European Polymer Journal, 1992, 28, 3, p.257.

23. Z. A. Kadir, K. Yoshii and L. Ishagaki, Polymer, 1989, 30, p.1425.

24. K. Yoshii, K. Makuuchi and I. Ishagaki, Journal of Applied Polymer Science, 1986, 32, p.5669.

25. J. B. Thorat, C. S. Prabhu, K. Suresh Kumar and M. V. Pandya, Journal of Applied Polymer Science, 1997, 65, p.2715.

26. F. Yoshii, A. Sudradjat, D. Binh, K. Makuuchi and S. Nishimoto, Polymer Degradation and Stability, 1998, 60, 2-3, p.393.

27. A. Tidjani and Y. Watanabe, Journal of Applied Polymer Science, 1996, 60, p.1839.

28. C. M. Rimnac, R. W. Klein, F. Betts and T. M Wright, Journal of Bone and Joint Surgery, 1994, 76-A, 7, p.1052.

29. J. M. Riddle, Effects of Organics on Nuclear Cycles. Final report, Electric Power Research Institute, Palo Alto, July 1992.

30. K. E. Kooda, C. A. Lavery and D. P. Zeek, Drum Corrosion Task Team Report, Lockheed Idaho Technologies Co., INEL – 96/0187, 1996.

5 Chemical Attack

5.1 Introduction

Many degradation phenomena and processes that lead to a deterioration in material properties are grouped under the terms ‘chemical attack’ or ‘chemical incompatibility’. These include oxidation, hydrolysis, halogenation, and other processes involving irreversible modifications to a polymer’s molecular structure by chemical reaction with a fluid. However unlike metals, where chemical attack, irreversible chemical change, and corrosion are virtually synonymous, for polymers some important and purely physical interactions between a material and a fluid are also included. These are dominated by mass transfer phenomena that lead to absorption of the fluid into the polymer or the polymer into the fluid.

Chemical resistance tables as published by material suppliers are conventionally based upon changes in a material’s tensile strength, tensile modulus, surface hardness, elongation at break, and weight due to stress free immersion of the polymer in the fluid for a few weeks at ambient and elevated temperature. If the changes are small the fluid/polymer pair is deemed to be compatible and is awarded a designation of satisfactory (S) or resistant (R). If the changes are large the pair is incompatible and given a designation of unsatisfactory (U) or not resistant (NR). If the changes are modest then the designation fair (F), doubtful (D), or limited (L) is applied. The value judgements can be used to eliminate materials at the selection stage, but they are insufficient to justify selection. Firstly being immersed under stress free conditions, the tests do not identify incompatibilities due to environmental stress cracking (ESC) or (in some cases), stress corrosion cracking (SCC). Secondly a few weeks of immersion is generally insufficient to establish the equilibrium condition.

5.2 Solvation effects

When a solid polymer with low molecular mobility is totally immersed in a fluid, the latter diffuses into the former. For fluids that are transported by Fickian diffusion the weight gain is proportional to the square root of the immersion time and this continues until a static equilibrium condition is reached. In this condition the concentration of the fluid (gas/vapour/liquid) in the polymer is constant and uniformly distributed. The static equilibrium concentration expressed as a percentage weight gain is defined as the solubility

(S). S is independent of product or test piece geometry and is determined only by certain thermodynamic characteristics of the polymer and fluid and by temperature. However the time taken to reach this condition is dependent upon a polymer/fluid parameter (the diffusion coefficient (D)) and the shape factor of the product under test. Thicker bulkier products take longer. Methodologies have been developed [1, 2] to calculate D from immersion tests on one test geometry and to predict the rate of weight gain in other simple geometries.

For the common situation where the polymer is not totally immersed in the fluid but in contact at one surface, a dynamic equilibrium condition is eventually reached when the rate of fluid entering the exposed surface equals the rate of exit at non exposed surfaces. This transport through a material is called permeability (P), and if the interaction is classical then:

$$P = DS$$

The characteristics that most determine solubility (S) are the cohesive forces that bind the materials. For polymers and fluids there are three main types of intermolecular cohesive force, known as dispersive, polar, and hydrogen bonding. The degree of solvation will maximise when the strength of these forces are the same for both fluid and polymer. For fluids these forces can be measured and expressed in the form of partial solubility parameters. They are listed for a wide range of fluids in Table 5.1.

The total (Hansen) solubility parameter $(\delta)_L$ of the liquid is given by:

$$(\delta^2)_L = (\delta_d{}^2)_L + (\delta_p{}^2)_L + (\delta_H{}^2)_L$$

where δ_d, δ_p and δ_H are the dispersive, polar and hydrogen solubility parameters. If the partial solubility parameters for polymers $(\delta_d)_p$, $(\delta_p)_p$ and $(\delta_H)_p$ were also known then the energy required for intermolecular mixing ΔH per unit volume would be given by:

$$\Delta H = ((\Delta\delta_d)^2 + (\Delta\delta_p)^2 + (\Delta\delta_H)^2)\varphi_1(1 - \varphi_1)$$

where $\Delta\delta_d$, $\Delta\delta_p$ and $\Delta\delta_H$ are the differences between the respective partial parameters of the fluid and the polymer and φ_1 is the volume fraction of the fluid in the polymer/fluid mixture. It will be appreciated that the energy required is always positive but will be at a minimum when the difference in the fluid and polymer partial solubilities are minimised. It will also be appreciated that the energy required for a very limited degree of mixing ($\varphi_1 \rightarrow 0$) will be small even if the fluid and polymer characteristics differ significantly. The energy available for mixing is provided by the change in entropy (ΔS) due to mixing. Mixing always increases disorder and therefore ΔS is always positive and the energy available, $T\Delta S$, is always positive. Energy conservation leads to the equilibrium:

$$T\Delta S = ((\Delta\delta_d)^2 + (\Delta\delta_p)^2 + (\Delta\delta_H)^2)\varphi_1(1 - \varphi_1)$$

Table 5.1 Hansen solubility parameters of liquids at 25 °C

Solvent	CAS Number	Molar Volume (cm^3/mol)	Solubility parameters (MPa$^{1/2}$)			
			δ_d	δ_p	δ_H	δ
PARAFFINIC HYDROCARBONS						
n-Butane	106-97-8	101.4	14.1	0	0	14.1
n-Pentane	109-66-0	116.2	14.5	0	0	14.5
Pentane (iso)	78-78-4	117.4	13.7	0	0	13.7
n-Hexane	110-54-3	147.4	14.9	0	0	14.9
n-Heptane	142-82-5	147.4	15.3	0	0	15.3
n-Octane	111-65-9	163.5	15.6	0	0	15.6
2,2,4-Trimethylpentane	540-84-1	166.1	14.3	0	0	14.3
n-Nonane	111-84-2	179.7	15.8	0	0	15.8
n-Decane	124-18-5	195.9	15.8	0	0	15.8
n-Dodecane	112-40-3	228.6	16	0	0	16
n-Hexadecane	544-76-3	294.1	16.4	0	0	16.4
n-Eicosane	112-95-8	359.8	16.6	0	0	16.6
Cyclohexane	110-82-7	108.7	16.8	0	0.2	16.8
Methylcyclohexane	108-87-2	128.3	16	0	1	16
cis-Decahydronaphthalene	493-01-6	156.9	18.8	0	0	18.8
trans-Decahydronaphthalene	493-02-7	159.9	18.8	0	0	18.8
AROMATIC HYDROCARBONS						
Benzene	71-43-2	89.4	18.4	0[a]	2	18.6
Toluene	108-88-3	106.8	18	1.4	2	18.2
Naphthalene[b]	91-20-3	111.5	19	2	5.9	20
Styrene	1-42-5	115.6	18.6	1	4.1	19
o-Xylene	95-47-6	121.2	17.8	1	3.1	18
Ethylbenzene	1-41-4	123.1	17.8	0.6	1.4	17.8
1-Methylnaphthalene	90-12-0	138.8	20.6	0.8	4.7	21.2
Mesitylene	108-67-8	139.8	18	0	0.6	18
Tetrahydronaphthalene	119-64-2	136.0[a]	19.6[a]	0	2.9	20
Biphenyl	92-52-4	154.1	21.5	1	2	21.7
p-Diethylbenzene	105-05-5	156.9	18	0	0.6	18
HALOHYDROCARBONS						
Methyl chloride	74-87-3	55.4	15.3	6.1	3.9	17
Methyl dichloride	75-09-2	63.9	18.2	6.3	6.1	20.3
Bromochloromethane	74-97-5	65	17.4	5.7	3.5	18.6
Chlorodifluoromethane	75-45-6	72.9	12.3	6.3	5.7	14.9

Table 5.1 Continued

Solvent	CAS Number	Molar Volume (cm^3/mol)	Solubility parameters (MPa$^{1/2}$) δ_d	δ_p	δ_H	δ
HALOHYDROCARBONS Continued						
Dichlorofluoromethane	75-43-4	75.4	15.8	3	5.7	17
Ethyl bromide	74-96-4	76.9	16.6	8	5.1	19
1,1-Dichloroethylene	75-35-4	79	17	6.8	4.5	18.8
Ethylene dichloride	107-06-2	79.4	19.0[a]	7.4	4.1	20.9
Methylene diiodide[c]	75-11-6	80.5	17.8	3.9	5.5	19
Chloroform	67-66-3	80.7	17.8	3.1	5.7	19
1,1-Dichloroethane	75-34-3	84.8	16.6	8.2	0.4	18.4
Ethylene dibromide	106-93-4	87	19.6	6.8	12.1	23.9
Bromoform	75-25-2	87.5	21.5[a]	4.1	6.1[a]	22.7
n-Propyl chloride	540-54-5	88.1	16	7.8	2	17.8
Trichloroethylene	79-01-6	90.2	18	3.1	5.3	19
Dichlorodifluoromethane	75-71-8	92.3	12.3	2	0	12.5
Trichlorofluoromethane	75-69-4	92.8	15.3	2	0	15.5
Bromotrifluoromethane	75-63-8	97	9.6	2.5	0	10
Carbon tetrachloride	56-23-5	97.1	17.8	0	0.6	17.8
1,1,1-Trichloroethane	71-55-6	1.4	17	4.3	2	17.6
Tetrachloroethylene	127-18-4	101.1	19	6.5[a]	2.9[a]	20.3
Chlorobenzene	108-90-7	102.1	19	4.3	2	19.6
n-Butylchloride	109-69-3	104.9	16.4	5.5	2	17.4
1,1,2,2-Tetrachloroethane	79-34-5	105.2[a]	18.8	5.1	9.4	21.7
Bromobenzene	222-22-2	105.3	20.5	5.5	4.1	21.7
o-Dichlorobenzene	95-50-1	112.8	19.2	6.3	3.3	20.5
Benzyl chloride	100-44-7	115	18.8[a]	7.2	2.7	20.3
1,1,2,2-Tetrabromoethane[c]	79-27-6	116.8	22.7	5.1	8.2	24.8
1,2-Dichlorotetrafluoroethane[c]	76-14-2	117	12.7	1.8	0	12.9
1,1,2-Trichlorotrifluoroethane	76-13-1	119.2	14.7	1.6	0	14.7
Cyclohexyl chloride	542-18-7	121.3	17.4	5.5	2	18.4
1-Bromonaphthalene	90-11-9	140	20.3	3.1	4.1	20.9
Trichlorobiphenyl[d]	7012-37-5	187	19.2	5.3	4.1	20.5
Perfluoromethylcyclohexane	355-02-2	196	12.5	0	0	12.5
Perfluorodimethylcyclohexane	335-27-3	217.4	12.5	0	0	12.5
Perfluoro-*n*-heptane	335-57-9	227.3	12.1	0	0	12.5

Table 5.1 Continued

Solvent	CAS Number	Molar Volume (cm^3/mol)	Solubility parameters (MPa$^{1/2}$)			
			δ_d	δ_p	δ_H	δ
ETHERS						
Furan	110-00-9	72.5	17.8	1.8	5.3	18.6
Epichlorohydrin	106-89-8	79.9	19	10.2	3.7	21.9
Tetrahydrofuran	109-99-9	81.7	16.8	5.7	8	19.4
1,4-Dioxane	123-91-1	85.7	19	1.8	7.4	20.5
Methylal (dimethoxymethane)	109-87-5	88.8	15.1	1.8	8.6	17.6
Diethyl ether	60-29-7	104.8	14.5	2.9	5.1	15.8
Bis(2-chloroethyl) ether	107-30-2	117.6	18.8	9	5.7	21.7
Anisole[c]	100-66-3	119.1	17.8	4.1	6.8	19.4
Bis-(2-methoxyethyl) ether	111-96-6	142	15.8	6.1	9.2	19.2
Dibenzyl ether[c]	103-50-4	192.7	17.4	3.7	7.4	19.2
Di-(chloro-iso-propyl) ether	108-60-1	146	19	8.2	5.1	21.3
Bis-(*m*-phenoxyphenyl) ether	748-30-1	373	19.6	3.1	5.1	20.5
KETONES						
Acetone	67-64-1	74	15.5	10.4	7	20.1
Methyl ethyl ketone (2-butanone)	78-93-3	90.1	16	9	5.1	19
Cyclohexanone	108-94-1	104	17.8	6.3	5.1	19.6
Diethyl ketone (3-pentanone)	96-22-0	106.4	15.8	7.6	4.7	18.2
Mesityl oxide (4-methyl-3-pentene-2-one)	141-79-7	115.6	16.4	7.2	6.1	18.8
Acetophenone	98-86-2	117.4	19.6[a]	8.6	3.7	21.7
Methyl iso-butyl ketone (2-hexanone)	591-78-6	125.8	15.3	6.1	4.1	17
Methyl iso-amyl ketone	110-12-3	142.8	16	5.7	4.1	17.4
Isophorone	78-59-1	150.5	16.6	8.2	7.4	19.8
Di-iso-butyl ketone (2,6-dimethyl-4-heptanone)	108-83-8	177.1	16	3.7	4.1	16.8
ALDEHYDES						
Acetaldehyde	75-07-0	57.1	14.7	8	11.3	20.3
2-Furfuraldehyde (furfural)	98-01-1	83.2	18.6	14.9	5.1	24.3
Butyraldehyde	123-72-8	88.5	14.7	5.3	7	17.2
Benzaldehyde	100-52-7	101.5	19.4	7.4	5.3	21.5

Table 5.1 Continued

Solvent	CAS Number	Molar Volume (cm^3/mol)	Solubility parameters ($MPa^{1/2}$)			
			δ_d	δ_p	δ_H	δ
ESTERS						
Ethylene carbonate (1,3-dioxolan-2-one)	96-41-9	66	19.4	21.7	5.1	29.5
γ-Butyrolactone (4-hydroxybutryic acid∝-lactone)	96-48-0	76.8	19	16.6	7.4	26.2
Methyl acetate	79-20-9	79.7	15.5	7.2	7.6	18.8
Ethyl formate	109-94-4	80.2	15.5	8.4	8.4	19.6
Propylene carbonate (1,2-propanediol cyclic carbonate)	108-32-7	85	20.1	18	4.1	27.2
Ethyl chloroformate	541-41-3	95.6	15.5	10	6.8	19.6
Ethyl acetate	141-78-6	98.5	15.8[a]	5.3	7.2[a]	18.2
Trimethyl phosphate	512-56-1	99.9	16.8	16	10.2	25.4
Diethyl carbonate	105-58-8	121	16.6	3.1	6.1	18
Diethyl sulphate	64-67-5	131.5	15.8	14.7	7.2	22.7
n-Butyl acetate	123-86-4	132.5	15.8	3.7	6.3	17.4
Iso-butyl acetate	540-88-5	133.5	15.1	3.7	6.3	16.8
2-Ethoxyethyl acetate (Cellusolve acetate)	111-15-9	136.2	16	4.7	10.6	19.6
Iso-amyl acetate	628-63-7	148.8	15.3	3.1	7	17.2
Iso-butyl iso-butyrate	109-21-7	163	15.1	2.9	5.9	16.6
Dimethyl phthalate	131-11-3	163	18.6[a]	10.8[a]	4.9	22.1
Ethyl *trans*-cinnamate	103-36-6	166.8	18.4	8.2	4.1	20.5
Triethyl phosphate	78-40-0	171	16.8	11.5	9.2	22.3
Diethyl phthalate	84-66-2	198	17.6	9.6	4.5	20.5
Di-*n*-butyl phthalate	84-74-2	266	17.8a	8.6	4.1	20.3
n-Butyl benzyl phthalate	85-68-7	306	19	11.3	3.1	22.3
Tricresyl phosphate (tritolyl phosphate)	1330-78-5	613	19	12.3	4.5	23.1
Tri-*n*-butyl phosphate	126-73-8	345	16.4	6.3	4.3	18
Iso-propyl palmitate[c]	2239-78-3	330	14.3	3.9	3.7	15.3
Di-*n*-butyl sebacate	109-43-3	339	14.5	3.9	3.7	15.5
Methyl oleate[d]	112-62-9	340	14.5	3.9	3.7	15.5
Dioctyl phthalate (bis(2-ethylhexyl) phthalate)	117-81-7	377	16.6	7	3.1	18.2
Di-butyl stearate[c]		382	14.5	3.7	3.5	15.3

Table 5.1 Continued

Solvent	CAS Number	Molar Volume (cm^3/mol)	Solubility parameters (MPa$^{1/2}$)			
			δ_d	δ_p	δ_H	δ
NITROGEN-CONTAINING COMPOUNDS						
Acetonitrile	75-05-8	52.6	15.3	18	6.1	24.6
Acrylonitrile	107-13-1	67.1	16.5	17.4	6.8	24.8
Propionitrile	107-12-0	70.9	15.3	14.3	5.5	21.7
Butyronitrile	109-74-0	87	15.3	12.5	5.1	20.5
Benzonitrile	100-47-0	102.6	17.4	9	3.3	19.8
Nitromethane	75-52-5	54.3	15.8	18.8	5.1	25
Nitroethane	79-24-3	71.5	16	15.5	4.5	22.7
2-Nitropropane	79-46-9	86.9	16.2	12.1	4.1	20.7
Nitrobenzene	98-95-3	102.7	20.1	8.6	4.1	22.1
Ethanolamine (2-aminoethanol)	141-43-5	60.2	17.2	15.5	21.3	31.5
Ethylene diamine	107-15-3	67.3	16.6	8.8	17	25.4
1,1-Dimethylhydrazine[c]	57-14-7	76	15.3	5.9	11	19.8
2-Pyrrolidone (2-pyrrolidinone)	616-45-5	76.4	19.4	17.4	11.3	28.4
Pyridine	110-86-1	80.9	19	8.8	5.9	21.7
n-Propylamine	107-10-8	83	17	4.9	8.6	19.6
Morpholine	110-91-8	87.1	18.8	4.9	9.2	21.5
Aniline	62-53-3	91.5	19.4	5.1	10.2	22.5
N-Methyl-2-pyrrolidone (1-methyl-2-pyrrolidinone)	872-50-4	96.5	18	12.3	7.2	22.9
n-Butylamine	109-73-9	99	16.2[a]	4.5[a]	8	18.6
Diethylamine	109-87-7	103.2	14.9	2.3	6.1	16.4
Diethylenetriamine	111-40-0	108	16.8	13.3	14.3	25.8
Cyclohexylamine	108-91-8	115.2	17.4	3.1	6.5	18.8
Quinoline	91-22-5	118	19.4	7	7.6	22.1
Di-*n*-propylamine	142-84-7	136.9	15.3	1.4	4.1	16
Formamide	75-12-7	39.8	17.2	26.2	19	36.6
Dimethylformamide	68-12-2	77	17.4	13.7	11.3	24.8
N,*N*-Dimethylacetamide	127-19-5	92.5	16.8	11.5	10.2	22.7
1,1,3,3-Tetramethylurea	632-22-4	120.4	16.8	8.2	11	21.7
Hexamethyl phosphoramide[c] (hexamethyl phosphoric triamide)	680-31-9	175.7	18.4	8.6	11.3	23.3

Table 5.1 Continued

Solvent	CAS Number	Molar Volume (cm^3/mol)	Solubility parameters (MPa$^{1/2}$)			
			δ_d	δ_p	δ_H	δ
SULPHUR-CONTAINING COMPOUNDS						
Carbon disulphide	75-15-0	60	20.5	0	0.6	20.5
Dimethyl sulphoxide (methyl sulphoxide)	67-68-5	71.3	18.4	16.4	10.2	26.6
Ethanethiol[c] (ethyl mercaptan)	75-08-1	74.3	15.8	6.5	7.2	18.4
Dimethyl sulphone[b] (methyl sulphone)	67-71-0	75	19	19.4	12.3	29.9
Diethyl sulphide (ethyl sulphide)	352-93-2	108.2	17	3.1	2	17.4
ACID HALIDES AND ANHYDRIDES						
Acetyl chloride	75-36-5	71	15.8	10.6	3.9	19.4
Succinic anhydride[b]	108-30-5	66.8	18.6	19.2	16.6	31.5
Acetic anhydride	108-24-7	94.5	16.0[a]	11.7[a]	10.2[a]	22.3
ALCOHOLS						
Methanol	67-56-1	40.7	15.1	12.3	22.3	29.7
Ethanol	64-17-5	58.5	15.8	8.8	19.4	26.6
Ethylene cyanohydrin (hydracrylonitrile; 3-hydroxypropionitrile)	109-78-4	68.3	17.2	18.8	17.6	30.9
Allyl alcohol (2-propen-1-ol)	107-18-6	68.4	16.2	10.8	16.8	25.8
1-Propanol	71-23-8	75.2	16	6.8	17.4	24.6
2-Propanol	67-63-0	76.8	15.8	6.1	16.4	23.5
3-Chloropropanol (trimethylene chlorohydrin)	627-30-5	84.2	17.6	5.7	14.7	23.7
Furfuryl alcohol	98-00-0	86.5	17.4	7.6	15.1	24.3
1-Butanol (butyl alcohol)	71-36-3	91.5	16	5.7	15.8	23.1
2-Butanol	4221-99-2	92	15.8	5.7	14.5	22.1
2-Methyl-1-propanol (isobutyl alcohol)	78-83-1	92.8	15.1	5.7	16	22.7
Benzyl alcohol	100-51-6	103.6	18.4	6.3	13.7	23.7
Cyclohexanol	108-93-0	106	17.4	4.1	13.5	22.5
1-Pentanol	71-41-0	109	16	4.5	13.9	21.7
2-Ethyl-1-butanol	97-95-0	123.2	15.8	4.3	13.5	21.3
Diacetone alcohol (4-hydroxy-4-methyl-2-pentanone)	123-42-2	124.2	15.8	8.2	10.8	20.9
1,3-Dimethyl-1-butanol	105-30-6	127.2	15.3	3.3	12.3	19.8

Table 5.1 Continued

Solvent	CAS Number	Molar Volume (cm^3/mol)	Solubility parameters (MPa$^{1/2}$)			
			δ_d	δ_p	δ_H	δ
ALCOHOLS Continued						
Ethyl lactate	687-47-8	115	16	7.6	12.5	21.7
n-Butyl lactate	138-22-7	149	15.8	6.5	10.2	19.8
Ethylene glycol monomethyl ether (2-methoxyethanol)	109-86-4	79.1	16.2	9.2	16.4	24.8
Ethylene glycol monethyl ether (2-ethoxyethanol) Cellosolve	110-80-5	97.8	16.2	9.2	14.3	23.5
Diethylene glycol monomethyl ether (2(2-methoxyethoxy)ethanol)	111-77-3	118	16.2	9.2	12.3	22.3
Diethylene glycol monoethyl ether (2-(2-ethoxyethoxy)ethanol)	111-90-0	130.9	16.2	9.2	12.3	21.9
Ethylene glycol mono-*n*-butyl ether (2-butoxyethanol) Butyl Cellosolve	111-76-2	131.6	16	5.1	12.3	22.3
2-Ethyl-1-hexanol	104-76-7	157	16	3.3	11.9	20.1
1-Octanol (capryl alcohol)	111-87-5	157.7	17	3.3	11.9	20.9
2-Octanol	123-96-6	159.1	16.2	4.9	11	20.3
Diethylene glycol mono-*n*-butyl ether (2-(2-butoxyethoxy)ethanol)	112-34-5	170.6	16	7	10.6	20.5
1-Decanol	112-30-1	191.8	17.6	2.7	10	20.5
Tridecyl alcohol[d]	112-70-9	242	14.3	3.1	9	17.2
Nonyl phenoxy ethanol[d]	27986-36-3	275	16.8	10.2	8.4	21.3
Oleyl alcohol[d]	143-28-2	316	14.3	2.7	8	16.6
Triethylene glycol mono-oleyl ether		418.5	13.3	3.1	8.4	16
ACIDS						
Formic acid	64-18-6	37.8	14.3	11.9	16.6	25
Acetic acid	64-19-7	57.1	14.5	8	13.5	21.3
Benzoic acid[b]	65-85-0	100	18.2	7	9.8	21.9
n-Butyric acid[c]	107-92-6	110	14.9	4.1	10.6	18.8
n-Octanoic acid[c]	124-07-2	159	15.1	3.3	8.2	17.6
Oleic acid	112-80-1	320	14.3	3.1	5.5	15.8
Stearic acid[b]	57-11-4	326	16.4	3.3	5.5	17.6

Table 5.1 Continued

Solvent	CAS Number	Molar Volume (cm^3/mol)	Solubility parameters (MPa$^{1/2}$)			
			δ_d	δ_p	δ_H	δ
PHENOLS						
Phenol	108-95-2	87.5	18	5.9	14.9	24.1
1,3-Benzenediol^b (resorcinol)	108-46-3	87.5	18	8.4	21.1	28.8
m-Cresol	108-39-4	104.7	18	5.1	12.9	22.7
o-Methoxyphenol (guaiacol)	90-05-1	109.5	18	8.2	13.3	23.7
Methyl salicylate	119-36-8	129	16	8	12.3	21.7
Nonyl phenol^d	25154-52-3	231	16.6	4.1	9.2	19.4
WATER						
Water^c	7732-18-5	18	15.5^a	16.0^a	42.4^a	47.9
POLYHYDRIC ALCOHOLS						
Ethylene glycol	107-21-1	55.8	17	11	26	32.9
Glycerol	56-81-5	73.8	17.4	12.1	29.3	36.2
Propylene glycol (1,2-propanediol)	57-55-6	73.6	16.8	9.4	23.3	30.3
1,3-Butanediol	107-88-0	89.9	16.6	10	21.5	28.8
Diethylene glycol	111-46-6	95.3	16.2	14.7	20.5	29.9
Triethylene glycol	112-27-6	114	16	12.5	18.6	27.4
Hexylene glycol (2-methyl-2,4-pentanediol)	107-41-5	123	15.8	8.4	17.8	25.2
Dipropylene glycol^d	110-98-5	131.3	16	20.3	18.4	31.7

[a] Altered from previously published value
[b] Solid, treated as supercooled liquid
[c] Values uncertain
[d] Impure commercial product of this nominal formula

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where T is the absolute temperature. For a given polymer/fluid pair the volume fraction of the fluid in the polymer φ_1 at equilibrium increases with increasing temperature.

Unfortunately, the total solubility and partial solubility parameters of polymers cannot be measured independently or directly. They may be calculated (with no great precision) via the summation of submolar attraction constants [3] or inferred from the known solubility parameters of fluids that act as the most powerful solvents. Table 5.2 lists the absorption of a wide range of fluids by Nylon 66 taken from Rapra's Chemical Resistance Data Sheets [4]. A number of observations may be made.

Table 5.2 Absorption of fluids by Nylon 66 after 28 days immersion at 70 °C

	δ_d (MPa)$^{0.5}$	δ_p (MPa)$^{0.5}$	δ_H (MPa)$^{0.5}$	δ (MPa)$^{0.5}$	Weight Gain (%)
Phenol	18	5.9	14.9	24.1	dissolved
Meta-cresol	18	5.1	12.9	22.7	dissolved
Acetic acid (glacial)	14.5	8	13.5	21.3	+ 26.8
Benzyl alcohol	18.4	6.3	13.7	23.7	+ 11.8
Methyl alcohol	15.1	12.3	22.3	29.7	+ 11.3
Water	18	15.5	16	42.4	+ 10
Ethyl alcohol	15.8	8.8	19.4	26.6	+ 8.2
Ethylene glycol	17	11	26	32.9	+ 5.8
Aniline	19.4	5.1	10.2	22.5	+ 4.3
Dimethyl formamide	17.4	13.7	11.3	24.8	+ 2.4
Benzaldehyde	19.4	7.4	5.3	21.5	+ 2.1
Ethyl acetate	15.8	5.3	7.2	18.2	+ 1
Ethylene dichloride	19	7.4	4.1	20.9	+ 0.8
Acetone	15.5	10.4	7	20.1	0
Tetrahydrofuran	16.8	5.7	8	19.4	- 0.4
Ethylene dichloride	19	7.4	4.1	20.9	- 0.8
Toluene	18	1.4	2	18.2	- 0.9
Benzene	18.4	0	2	18.6	- 1.1
Oleic acid	14.3	3.1	5.5	15.8	- 1.2
Amyl acetate	15.3	3.1	7	17.2	- 1.7
Carbon tetrachloride	17.8	0	0.6	17.8	- 1.7
Cyclohexane	16.8	0	0.2	16.8	- 1.8
Hexane	14.9	0	0	14.9	- 1.9
Nitrobenzene	20.1	8.6	4.1	22.3	- 10

i) The two most powerful solvents for the polymer are *meta*-cresol and phenol which have similar partial solubility parameters. It could be inferred that the partial parameters of Nylon 66 are in the vicinity of $(\delta_d)_p$ = 18 $(\text{MPa})^{0.5}$, $(\delta_p)_p$ = 5.5 $(\text{MPa})^{0.5}$, and $(\delta_H)_p$ = 14 $(\text{MPa})^{0.5}$.

ii) Glacial acetic acid is the next most powerful solvent with partial parameters that nearly match those of *meta*-cresol and phenol. However with this fluid there is a chemical reaction (hydrolysis) as well as a physical interaction. This gives rise to colour change and embrittlement. Strain at break reduces with fluid absorption because the embrittlement due to chain scission is greater than the plasticisation due to absorption.

iii) The resistance of nylons to alcohols and other highly polar fluids is poor but their resistance to non polar fluids such as aliphatic hydrocarbons (e.g. many fuels, greases, and lubricants) is good.

iv) The correlation between absorption and partial parameters is useful but there are many exceptions to the rule that indicate other hidden influences. Water for example is more aggressive than the simple rule indicates, and oleic acid is less severe than its partial parameters might suggest. These two fluids have the lowest (water = 18 cm^3/mol) and the highest (oleic acid = 320 cm^3/mol) molar volumes of the fluid listed. For the larger molar volume fluids, it would be reasonable to assume that due to reduced rates of diffusion or increased energy for mixing the equilibrium absorption is reduced or not reached during the immersion period.

v) Hydrogen bonding is not just characterised by its strength. The hydrogen bond in Nylon 66 is broken by the addition of a proton and the material can therefore be classed as a 'proton acceptor'. Fluids that are classed as 'proton donors' are more aggressive to Nylon than proton acceptors of equivalent strength. Thus Nylons are more resistant to alkalis (proton acceptors) than acids (proton donors).

vi) Weight loss in Nylon 66 is frequently encountered. This will be due to the extraction of plasticisers, processing aids, low molecular weight oligomers, and other mobile species. Weight loss jeopardises durability by decreasing toughness and strain at break and via volume contraction, by the development of additional tensile stresses.

A similar exercise has been carried out for high density polyethylene (HDPE) and the results are listed in Table 5.3. It is apparent that HDPE is most susceptible to attack by non polar fluids and least susceptible to highly polar fluids such as alcohols. Therefore $(\delta_p)_p$ and $(\delta_H)_p \simeq 0$. In terms of fluid compatibility, Nylons and HDPE are virtually exact opposites.

Again there are exceptions to the rule. Tetrahydrofuran is more aggressive than might be expected towards HDPE, and toluene is less aggressive.

Table 5.3 Absorption of fluids by HDPE at elevated temperatures (1. 70 °C for 28 days, 2. 66 °C for 84 or 90 days, 3. 60 °C for 4 days)

	δ_d $(MPa)^{0.5}$	δ_p $(MPa)^{0.5}$	δ_H $(MPa)^{0.5}$	δ $(MPa)^{0.5}$	Weight Gain (%)
Carbon tetrachloride[1]	17.8	0	0.6	17.8	dissolved
Benzene[1]	18.4	0	2	18.6	dissolved
Cyclohexane[1]	16.8	0	0.2	16.8	dissolved
Tetrahydrofuran[1]	16.8	5.7	8	19.4	destroyed
Amyl acetate[1]	15.3	3.1	7	17.2	+ 17
Dioxane[1]	19	1.8	7.4	20.5	+ 11.8
Ethylene dichloride[1]	19	7.4	4.1	20.9	+ 8.6
Oleic acid[1]	14.3	3.1	5.5	15.8	+ 7.9
Toluene[2]	18	1.4	2	18.2	+ 5.6
Benzaldehyde[2]	19.4	7.4	5.3	21.5	+ 4.6
Nitrobenzene[2]	20.1	8.6	4.1	22.3	+ 3.47
Ethyl acetate[3]	15.8	5.3	7.2	18.2	+ 1.86
Aniline[2]	19.4	5.1	10.2	22.5	+ 1.45
Benzyl alcohol[1]	18.4	6.3	13.7	23.7	+ 1.1
Phenol[2]	18	5.9	14.9	24.1	+ 0.54
Dimethyl formamide[1]	17.4	13.7	11.3	24.8	+ 0.4
Acetic acid (glacial)[2]	14.5	8	13.5	21.3	+ 0.39
Water[2]	18	15.5	16	42.4	+ 0.016
Ethylene glycol[2]	17	11	26	32.9	0

As shown in Table 5.4, and as would be expected from the similarity of their backbone chemistry, polypropylene (PP) is swollen and solvated by the same fluids that attack polyethylene. Even the exceptional response to tetrahydrofuran is shared by both polymers, suggesting that this particular fluid has not been correctly characterised, or more likely, that the solubility model is just too crude to accommodate all fluids.

Table 5.4 Absorption of fluids by PP at elevated temperatures (1. 70 °C for 28 days, 2. 60 °C for 30 days, 3. 100 °C for 30 days, 4. 70 °C for 7 days)

	δ_d (MPa)$^{0.5}$	δ_p (MPa)$^{0.5}$	δ_H (MPa)$^{0.5}$	δ (MPa)$^{0.5}$	Weight Gain (%)
Carbon tetrachloride[1]	17.8	0	0.6	17.8	+ 81
Cyclohexane[1]	16.8	0	0.2	16.8	+ 37.6
Tetrahydrofuran[1]	16.8	5.7	8	19.4	+ 25
Benzene[1]	18.4	0	2	18.6	+ 24.4
Ethylene dichloride[1]	19	7.4	4.1	20.9	+ 15.8
Amyl acetate[1]	15.3	3.1	7	17.2	+ 11
Dioxane[1]	19	1.8	7.4	20.5	+ 9.5
Ethyl acetate[4]	15.8	5.3	7.2	18.2	+ 9.4
Oleic acid[1]	14.3	3.1	5.5	15.8	+ 5.5
Benzaldehyde[1]	19.4	7.4	5.3	21.5	+ 3.8
Acetone[1]	15.5	10.4	7	20.1	+ 2.9
Aniline[2]	19.4	5.1	10.2	22.5	+ 2.3
Phenol[1]	18	5.9	14.9	24.1	+ 1.8
MEK[1]	16	9	5.1	19	+ 1.6
Dimethyl formamide[1]	17.4	13.7	11.3	24.8	+ 1.4
Benzyl alcohol[1]	18.4	6.3	13.7	23.7	+ 1.2
Acetic acid (glacial)[3]	14.5	8	13.5	21.3	+ 0.67
Water[2]	18	15.5	16	42.4	+ 0.2
Methyl alcohol[2]	15.1	12.3	22.3	29.7	+ 0.1
Ethylene glycol[1]	17	11	26	32.9	0

The majority of other plastics exhibit polar and hydrogen bonding levels that lie between the two extremes of high (Nylon and cellulosics) and very low (polyethylene, polypropylene and polytetrafluoroethylene). Acrylonitrile-butadiene-styrene (ABS) and unplasticised polyvinyl chloride (UPVC) are given as examples in Tables 5.5 and 5.6. Generally these polymers are attacked by fluids of intermediate polarity such as ethers, esters, and ketones.

Table 5.5 Absorption of fluids by ABS at ambient temperatures (days immersion in brackets)

	δ_d (MPa)$^{0.5}$	δ_p (MPa)$^{0.5}$	δ_H (MPa)$^{0.5}$	δ (MPa)$^{0.5}$	Weight Gain (%)
Aniline (28)	19.4	5.1	10.2	22.5	Destroyed
Benzaldehyde (18)	19.4	7.4	5.3	21.5	Dissolved
Ethyl acetate (28)	15.8	5.3	7.2	18.2	Destroyed
Nitrobenzene (28)	20.1	8.6	4.1	22.3	Destroyed
Phenol (18)	18	5.9	14.9	24.1	Dissolved
Toluene (365)	18	1.4	2	18.2	Destroyed
Acetone (28)	15.5	10.4	7	20.1	Dissolved
Benzene (28)	18.4	0	2	18.6	Dissolved
Benzyl alcohol (28)	18.4	6.3	13.7	23.7	Dissolved
Amyl acetate (28)	15.3	3.1	7	17.2	Dissolved
Dimethyl formamide (28)	17.4	13.7	11.3	24.8	Dissolved
Dioxane (28)	19	1.8	7.4	20.5	Dissolved
Ethylene dichloride (28)	19	7.4	4.1	20.9	Dissolved
Tetrahydrofuran (28)	16.8	5.7	8	19.4	Dissolved
Carbon tetrachloride (28)	17.8	0	0.6	17.8	+ 103
Diethyl ether (28)	14.5	2.9	5.1	15.8	+ 30
Methyl alcohol (365)	15.1	12.3	22.3	29.7	+ 27
Acetic acid (glacial) (14)	14.5	8	13.5	21.3	+ 23.7
Ethyl alcohol (365)	15.8	8.8	19.4	26.6	+ 13.6
Cyclohexane (28)	16.8	0	0.2	16.8	+ 10
Hexane (28)	14.9	0	0	14.9	+ 6.4
Water (365)	18	15.5	16	42.4	+ 5.2
Ethylene glycol (28)	17	11	26	32.9	0
Oleic acid (28)	14.3	3.1	5.5	15.8	0

Table 5.6 Absorption of fluids by UPVC at ambient temperatures (days immersion in brackets)

	δ_d (MPa)$^{0.5}$	δ_p (MPa)$^{0.5}$	δ_H (MPa)$^{0.5}$	δ (MPa)$^{0.5}$	Weight Gain (%)
Ethyl acetate (28)	15.8	5.3	7.2	18.2	Destroyed
Nitrobenzene (28)	20.1	8.6	4.1	22.3	Destroyed
Amyl acetate (28)	15.3	3.1	7	17.2	Dissolved
Dimethyl formamide (28)	17.4	13.7	11.3	24.8	Dissolved
Dioxane (< 1)	19	1.8	7.4	20.5	Destroyed
Ethylene dichloride (28)	19	7.4	4.1	20.9	Dissolved
Tetrahydrofuran (20)	16.8	5.7	8	19.4	Destroyed
Acetone (< 1)	15.5	10.4	7	20.1	Dissolved
Methyl ethyl ketone (28)	16	9	5.1	19	Destroyed
Toluene (28)	18	1.4	2	18.2	+ 56
Benzene (30)	18.4	0	2	18.6	+ 41
Aniline (28)	19.4	5.1	10.2	22.5	+ 25.5
Acetic acid (glacial) (14)	14.5	8	13.5	21.3	+ 23.7
Diethyl ether (28)	14.5	2.9	5.1	15.8	+ 3
Water (32)	18	15.5	16	42.4	+ 1
Benzaldehyde (28)	19.4	7.4	5.3	21.5	+ 1
Carbon tetrachloride (28)	17.8	0	0.6	17.8	+ 0.7
Phenol (28)	18	5.9	14.9	24.1	+ 0.6
Ethyl alcohol (30)	15.8	8.8	19.4	26.6	+ 0.03
Methyl alcohol (28)	15.1	12.3	22.3	29.7	0
Cyclohexane (28)	16.8	0	0.2	16.8	0
Hexane (30)	14.9	0	0	14.9	0
Benzyl alcohol (28)	18.4	6.3	13.7	23.7	0
Ethylene glycol (28)	17	11	26	32.9	0
Oleic acid (21)	14.3	3.1	5.5	15.8	0

It will also be observed that these two amorphous thermoplastics are destroyed or completely solvated by a greater range of fluids than the three previously listed semicrystalline thermoplastics. The densely packed crystalline phase is far more resistant to fluid penetration than the amorphous phase. This also has a significant bearing on the differences in permeability, diffusion, and ESC resistance between the two material states.

5.3 Oxidation

Plastics have been used extensively for many years by the pulp and paper industries for the process handling of strong oxidising fluids such as chlorine, sodium hypochlorite, chlorine dioxide, and sulphuric acid. These fluids are used to oxidise lignin, the essential bleaching step in the process of turning wood pulp into paper.

An excellent review [5] of the experiences of the Scandinavian paper making industries highlights many successes and failures. This refreshingly honest and open account leads to valuable rules, guidelines, and priorities, and these are summarised here. The only weakness is the lack of in-depth analysis, which is not an oversight on the part of the authors but a reflection of the priorities of the pragmatic culture that is often found in bulk processing industries.

Glass reinforced polyester

Unlined (solid) reinforced pipes and vessels made from HET acid (hexachloroendomethylene tetrahydrophthalic acid) polyester, bisphenol polyester, and vinyl ester are slowly attacked by dry chlorine gas, but should give up to 10 years service at temperatures of up to 70 °C. Two failures are highlighted. After one year of service the resin in a pipeline was corroded away to half the wall thickness of the pipe. Liquid chlorine arising from the condensation of chlorine gas was identified as the culprit. In another example chlorine gas penetration was detected after only six months of operation in a centrifugally cast piping system. The probable cause was cracking of the 3.5 mm thick non-reinforced resin barrier layer. This provided rapid access for the chlorine gas to the glass-rich structural laminate. It was suspected that the ‘corrosion barrier’ may have been pre-cracked due to careless handling during transport or installation. Thick unreinforced layers are prone to impact damage.

High quality glass reinforced plastic (GRP) reactor vessels used to convert sodium chlorate to chlorine dioxide at temperatures of 40 °C exhibit corrosive attack at the rate of about 1 mm per year. GRP pipes transporting concentrated chlorine dioxide at 10 °C corrode at the rate of 0.2 mm per year. In one cited example a 3 years old corroded vessel was repaired by the application of a new barrier layer of 2.25 mm thickness. Within one year corrosion had penetrated the new barrier. The cause of the accelerated rate of attack was initially suspected to be inadequate cure of the repair resin.

GRP vessels have been used successfully for up to 15 years for the storage of concentrated hydrochloric acid at ambient temperatures. In one cited case however, quite rapid penetration of the corrosion barrier was observed over a band that corresponded with the rise and fall of the liquid level. HCl liquid and HCl vapour lead to very modest attack but the repeated absorption and desorption of the fluid increases the rate of attack. Attack at the liquid/gas interface is commonly observed in many material fluid combinations and is due to a combination of increased fluid concentration via evaporation, and the mechanical effects (equivalent to cyclic fatigue) of repeated swelling and contraction. In this case degradation was even more pronounced because the semitransparent vessel was sited outdoors and temperatures in the upper vapour filled part of the vessel could reach 40 °C.

Rules and guidelines

i) The durability of GRP in highly oxidising media depends primarily upon the quality of the inner corrosion barrier.

ii) The resin-rich barrier should be fully cured via post-curing of the structure. Residual styrene content within the laminate should be reduced by this means to less than 0.5%. Slight undercure can double the rate of corrosion.

iii) The thickness of the barrier is a compromise. The thicker the barrier is, the longer it will take for the corrosion to reach the structural laminate. However increasing the barrier thickness renders the product more fragile and susceptible to cracking on impact. A 2.5 mm thick resin-rich barrier lightly reinforced with multiple layers of synthetic or C glass veils is recommended.

iv) Cobalt curing systems should be avoided as these are known to reduce resistance by catalysing the breakdown of hypochlorites to the more aggressive hypochlorous acid [6].

v) Brominated bisphenol vinyl esters are recommended for hypochlorite solutions and novolac modified vinyl esters for chlorine dioxide [6].

Polyvinylidene fluoride (PVDF)

PVDF loose lined steel pipe has been a popular choice for conveying dry chlorine gas. Failures have been reported as being due to the inadvertent condensation of the gas to the more aggressive liquid chlorine phase, the high stresses due to the temperature drop on evaporation of this phase, and collapse of the liner. The latter occurs when the vent holes in the steel pipe corrode and block as exemplified in Case 7.6.5.

Solid PVDF pipe (i.e. without GRP or steel outer reinforcement) used for the handling of dry chlorine gas has resulted in a spate of failures. As exemplified in Case 5.6.1 these were due to the ultraviolet (UV) transparency of the material.

Thick-walled carbon steel is often used to transport concentrated sulphuric acid, but at high turbulent flow rates ‘erosion corrosion’ rates are unacceptably high. Also the resistance of steel to dilute acid is poor. PVDF lined steel is a favoured choice for situations where accidental dilution is possible. However the reaction between the acid and water is highly exothermic and there is at least one reported case of a PVDF lining melting in this circumstance.

Neither solid PVDF nor PVDF lined pipe should be used for handling sodium hypochlorite. Of the many failures reported most are due to environmental stress cracking. There is little evidence of corrosion but cracking can occur within ‘a few weeks’. In lined pipe this most commonly occurs where the liner has been flared or otherwise deformed to form pipe flanges. Fluorinated ethylene-propylene (FEP), ethylene-chlorotrifluoroethylene (ECTFE) and polytetrafluoroethylene (PTFE) are resistant.

The durability of PVDF in contact with chlorine dioxide solutions is reported to be ‘highly variable’. This may be connected with an unusual corrosion effect first observed in 1985. Microcracking occurred within the pipe wall rather than on the surface in contact with the chemical. Chlorine content also maximised within the pipe wall. Although no explanation has yet been found, it would seem reasonable to surmise that differences in the crystalline morphology between the slowly cooled mid wall material and the rapidly cooled pipe surfaces are responsible. If this is the case then processing history would have a profound effect on performance, and this would perhaps explain the highly variable durability of PVDF pipes and linings.

Polyvinyl chloride (PVC)

The visual indications of degradation of PVC in bleaching environments are less obvious than with GRP. Generally the depth of corrosion is assessed by colour change from (say) dark grey to light grey resulting from the bleaching of pigment. On this basis the rate of attack is initially greater than the rate for GRP. However for PVC the rate is linear with the square root of the elapsed time. Thus after 1 year of exposure to 12 grams per litre of chlorine dioxide at 35 °C, the depth of attack is 1 mm, but after 10 years it has only increased to 3 mm.

Therefore (at modest temperatures) PVC outperforms GRP in the longer term, and PVC lined GRP is often regarded as the cost effective option.

Although the depth of corrosion in a PVC product may be only 1 or 2 mm, this embrittled layer is sufficient to convert tough 10 mm thick products to fragile products. Cracks in PVC linings and the fast fracture of solid PVC products are reported to be the major problem. In one unfortunate incident a PVC pipe carrying concentrated sulphuric acid burst when a person leaned on it. Fragility is promoted by high stress at joints, by repeated thermal cycling, and by chance impact loading.

Leakage through solvent-based cemented pipe joints has frequently been reported. The corrosion resistance of the cement in some environments is significantly inferior to that of the pipe material. In well made joints the path length for leakage through the joint is several times greater than the wall thickness of the pipe. Therefore the rate of corrosion of the cement can be several times greater than that of the pipe wall before joint leakage becomes the factor that limits durability. Where joint leakage does occur this is found to be because the joint has not been well made. Such joints contain large cement free voids that drastically reduce the length of leakage path. Failure to bevel pipe ends prior to insertion into a joint fitting has been identified as the cause of the voids and premature leaking.

Polytetrafluoroethylene (PTFE)

PTFE lined steel has been used successfully to contain the most aggressive oxidising fluids, such as chlorine saturated sodium hypochlorite solutions, without corrosion problems. In this sense the material lives up to its claims and reputation.

The material is permeable to all fluids and its permeability is rather more variable than might be expected. This arises from the fact that PTFE is difficult to process. Durability is most often limited by corrosion of the reinforcing steel pipe by permeated fluids. Other problems include vacuum collapse or as already highlighted for PVDF linings, collapse due to the blocking of vents.

One problem is that conventionally manufactured PTFE contains a small amount of free hydrogen fluoride. This will be leached out by the process fluid. One metal, tantalum, although generally very resistant to corrosion, is very prone to attack on contact with even very low concentrations of HF. This very expensive material is frequently used for safety critical parts such as bursting discs, and embrittlement via HF can cause costly process interruptions.

Polyethylene (PE)

Polyethylene bottles are commonly and successfully used for containing bleach-based domestic cleaning fluids. However these solutions are relatively dilute and rarely exceed a hypochlorite content of 5%. At higher concentrations, and particularly under environmental conditions that promote the rapid release of chlorine, severe degradation and product failure can be expected. For example rotationally moulded crosslinked polyethylene storage tanks were introduced in the early 1970s for the bulk dispensing of concentrated (15%) sodium hypochlorite into swimming pools. It has been reported [7] that of 925 tanks supplied to the Florida region, about 200 had failed within 2 years of service. The tanks corroded (with material loss), embrittled, and cracked, with attack enhanced by mechanical stress. It was concluded that product tests had not sufficiently replicated real service conditions in several important respects. The rate of bleach decomposition to chlorine increases by a factor of 4 per 10 °C increase in temperature, and in addition the rate of attack also increases by a similar factor for a given chlorine concentration. Therefore the rate of attack is extremely sensitive to temperature. Metallic contamination of the bleach (e.g. from adjacent stainless steel pipework) was also overlooked. Metallic ions such as iron, nickel, copper, and cobalt at contamination levels as low as 1 ppm promote hypochlorite decomposition to a significant degree. Finally, exposure of bleach to sunlight will typically increase decomposition rates by a factor of 4.

In the same reference the failure of similar tanks used for storing and transporting highly oxidising acids (e.g. chromic and nitric) is discussed.

5.4 Acid induced stress corrosion cracking

With a few important exceptions, polymeric materials offer excellent resistance to inorganic acids. For example, taking sulphuric acid as reasonably representative of the class, Table 5.7 lists the recommended maximum concentrations and temperatures for some common rubbers and plastics. As acids promote degradation via hydrolysis the exceptions include those polymers that are known to be the least hydrolytically stable such as thermoplastic polyesters, Nylons, polyurethanes, silicones, and polycarbonates. The least resistant polymer in common use and the one most likely to suffer from acid induced stress corrosion cracking is acetal. Cases 5.6.4, 5.6.5 and 5.6.10 illustrate the weakness.

The premature failure of GRP products is most frequently traced to the phenomenon known as stress corrosion cracking (SCC) and the fluid responsible is invariably acidic. The principal degradation interaction is between the fluid and the fibres. The composition of glass fibres is as shown in Table 5.8, a mixture of oxides dominated by silicon. E glass

Table 5.7 Maximum service conditions for common polymers in contact with sulphuric acid

Material	Max. concentration	Max. temperature
UPVC	95%	20 °C
UPVC	80%	60 °C
Polyethylene	80%	60 °C
Polypropylene	80%	80 °C
Bisphenol polyester	75%	20 °C
Natural rubber (soft)	50%	60 °C
Ebonite	70%	70 °C
Polychloroprene	50%	75 °C
Butyl rubber	75%	60 °C

Table 5.8 Oxide composition of various glasses used for fibre manufacture together with weight loss due to immersion in water, an alkali, or an acid

	Composition %			
Oxides	**E Glass**	**C Glass**	**ECR Glass**	**S Glass**
Silicon	54	66	58	65
Aluminium	14	4	12	25
Boron	7	5	0	0
Calcium	20	13	20	0
Magnesium	3	3	2	10
Zinc	0	0	3	0
Others	2	9	5	0
	24 hour weight loss (%)			
Water	0.7	1.1	0.6	0.5
10% Na_2CO_3	2.1	24	-	2.0
10% H_2SO_4	39	2.2	6.2	4.1

is the general purpose grade offering good tenacity and good resistance to alkalis at modest cost. However the grade is severely attacked by acids as indicated by the rapid loss of mass due to 24 hour exposure to sulphuric acid. The oxides other than silicon are highly susceptible to extraction via leaching. This is understood to be the result of an ion exchange process. The hydrogen ion in the acid replaces the anion in the glass. This results not only in a loss of glass mass but also the creation of microvoids and surface fissures. Due to its very low fracture toughness, glass has a very low defect tolerance and therefore as a result of acid attack the material is rendered fragile.

C glass is usually reserved as the reinforcement for the resin rich acid corrosion barrier. However it should be noted that C glass veils are not appropriate for alkaline environments. ECR glass and S glass are the preferred alternatives to E glass within the structural part of the laminate for acid environments. The superiority of ECR glass has been clearly demonstrated [8]. In this study stress corrosion cracking was monitored on prenotched material in one molar HCl. The crack growth rate increased with increasing temperature and increasing stress (or stress intensity). At the same temperature the ECR glass reinforced laminate required about twice the stress of that applied to the E glass reinforced laminate to induce the same crack growth rate. At the same stress the inferior laminate at 20 °C suffered the same crack velocity as the superior laminate at 80 °C.

S glass would appear from Table 5.8 to offer even better acid resistance. However in practice this is probably not the case. In 1996 a compressed air cylinder constructed from an inner aluminium liner with overwrapped reinforcement of epoxy and continuous S glass fibres, failed at a fire station in California [9]. The internal pressure of air in the cylinder was 31 MPa (4,500 psi) and therefore the failure caused considerable damage to adjacent fire fighting appliances. As the cylinder was part of a self-contained breathing apparatus (SCBA), then had the appliance been on active duty at the time of failure the consequences would have been far more serious and possibly fatal. An investigation into its recent history revealed that 6 days prior to the failure, the cylinder had probably been exposed to an accidental spillage of aluminium cleaning fluid. This fluid contained a mixture of hydrofluoric, phosphoric, and sulphuric acids, and various organic solvents such as 2-butoxyethanol. It had a pH of less than 1.0. A chemical analysis of the fracture surfaces by thermal desorption gas chromatography/mass spectrometry confirmed the presence of 2-butoxyethanol. This, together with the fact that the fracture surfaces at initiation were macroscopically flat and free from fibre pull-out, was sufficient to confirm the diagnosis of stress corrosion cracking via contact with acids in the aluminium cleaning fluid.

The outer fibres of the composite cylinder would have been very close to the surface. Although thinly coated with a polyurethane-based paint this would not have significantly retarded the rate of acid ingress into the outer load-bearing fibres of the laminate. A similar failure involving the exposure of poorly protected fibres to acid is discussed in Case 5.6.8.

An endemic (rather than accidental) example of acid induced stress corrosion has been well researched and is included here in Case 5.6.9. It involves the failure of high tension composite suspension insulators. These have been employed in preference to traditional ceramic insulators because they offer superior resistance to impact. The composite insulators comprise a pultruded E glass fibre/polyester rod. The rod is covered by a rubber sheath to protect it against water ingress. Metal end pieces are bonded to the ends of the rod for attachment to line and pylon. A typical failure due to acid induced stress corrosion cracking is shown in Figure 5.1. It has been claimed [10] that in-service brittle failures have been a major concern of many utility companies, that the rate of failure has increased with each year of service, and that the failure statistics are rarely made available because of 'commercial pressures'.

One set of statistics reports 14 complete fractures and 200 significantly damaged insulators out of a population of 1,756 after only 4 years in service. There is no doubt that these failures are due to acid induced stress corrosion cracking but there has been doubt (and understandable curiosity) concerning the nature and source of the acid. Acid rain (mainly sulphuric) was for many years the principle suspect and there is good reason to accept that some of the failures are due to this. However more recently attention has been directed towards nitric acid. Nitrogen oxides are generated by corona discharges in air and these combine with moisture to form nitric or nitrous acid. It has been suggested that the discharges occur between the rubber sheath and the rod. Although the sheath is a good barrier to water ingress it is by no means perfect. Small quantities of oxides

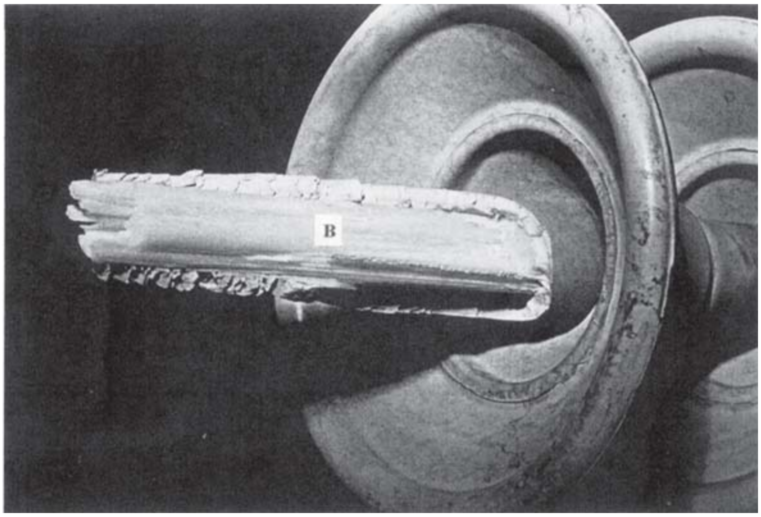


Figure 5.1 a) Brittle fracture zone in a 115 kV composite suspension insulator

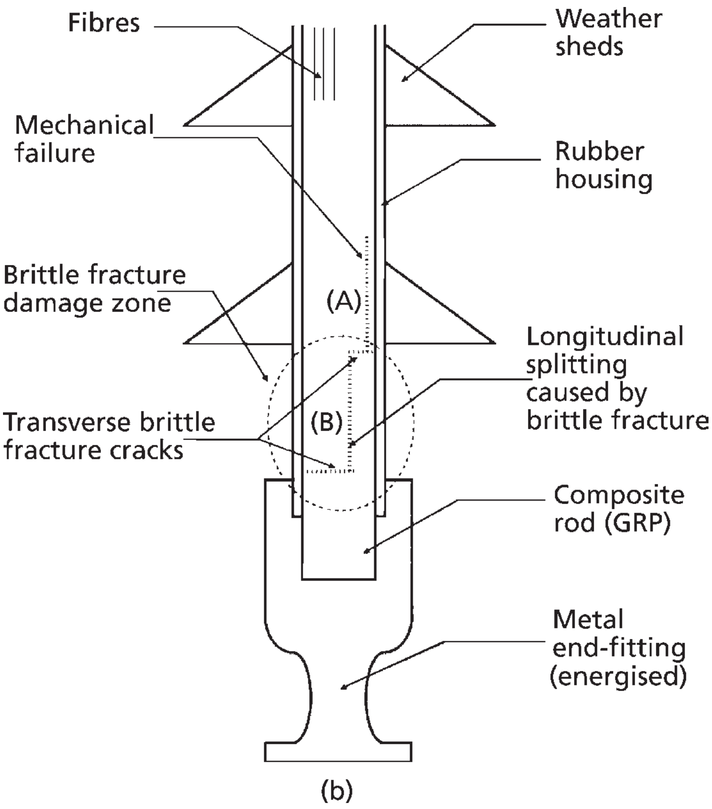


Figure 5.1 b) Schematic of a composite insulator (high energised end) with brittle fracture cracks

(Reprinted from Composites Science and Technology, Vol. 58, A.R. Chughtai, D.M. Smith and M.S. Kumosa, Chemical Analysis of a Field-Failed Composite Suspension Insulator, p.1641-7, Copyright © 1998, with permission from Elsevier Science.)

trapped at the surface of the rod combine with small quantities of moisture to generate small quantities of **concentrated** nitric acid. It has been shown that the acid at a pH of less than 3.5 is sufficient to attack the composite at the rate observed in service.

The examples of stress corrosion above involve attack on glass fibres, that are close to the exposed surface. For applications where composites are purposely exposed for long periods to acid contact (e.g. fluid transport and containment) the essential means of defence is a corrosion barrier. This may be a separate liner usually employing a thermoplastic of proven acid resistance (PVDF, PVC, PP, etc.), or an integral resin rich barrier. The integral barrier approach has been used successfully and extensively in chemical process plant for the transport and containment of very aggressive acids. Nonetheless failures of such products continue to occur.

Intuitively the barrier reduces ingress of fluids by reducing acid permeation, and therefore the thicker the resin rich barrier the better. However, the rate of uptake of 1M hydrochloric acid by thin sheets of cast polyester under zero stress [11] revealed that while water diffuses readily into the resin (diffusion coefficient of 3×10^{-9} cm^2 sec^{-1} at 25 °C) and quite rapidly reaches a saturation level of about 2%, the diffusion rate for the chloride ions is very low. Although very mobile, the diffusion of hydrogen ions is limited to that of the chloride ions because charge separation is energetically unfavourable. The acid concentration is diluted from 1 M to about 10^{-6} M by this process of selective diffusion. Thus it was concluded that normal diffusion processes through resin rich barriers cannot account for the ingress of acid that is known to cause corrosion in these structures.

The most promising explanation is similar to that given for the environmental stress cracking of thermoplastics (see Section 6.2). Under modest stress, microcracks or microvoids are initiated in the resin. In the absence of an aggressive fluid these would remain stable under stress for many years but otherwise they would provide pathways for the bulk transport of fluids through the barrier layer.

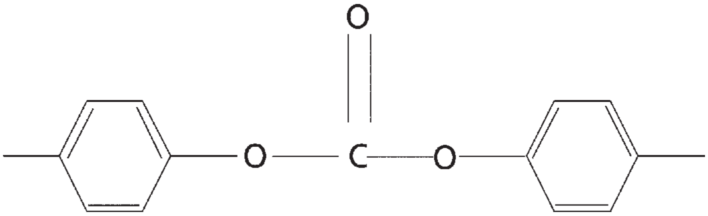
5.5 Hydrolysis

Hydrolysis is a form of degradation resulting from contact with water, or more precisely with the hydrogen ions (H^+) or hydroxyl ions (OH^-) in water. The term is also used to describe similar degradation resulting from contact with other water containing fluids such as acids (increased H^+ concentration) and alkalis (increased OH^- concentration) that may accelerate hydrolysis. Here such terms as acidolysis may be employed to identify the active trigger for the degradation process.

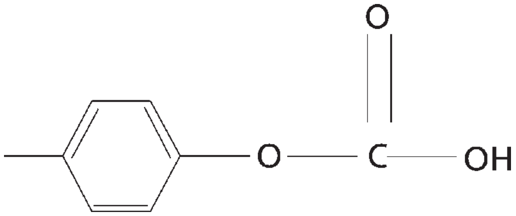
Ester, amide, imide, and carbonate groups are particularly susceptible to hydrolysis and it follows that they are prone to attack by either acids or alkalis or both. Where these groups are located within the main (backbone) chain (rather than side chains) hydrolysis invariably leads to chain scission, a reduction in molecular weight, and consequently, a reduction in toughness and strain at break.

Polycarbonate

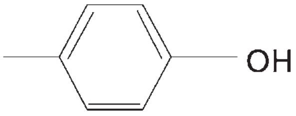
The carbonate group within the main chain of (bisphenol A) polycarbonate is, to a degree, protected by adjacent benzene groups:



and these hydrophobic groups are responsible for the low equilibrium moisture absorption of the material. However at modestly elevated temperatures, hydrolysis proceeds at a significant rate, firstly via chain scission that results in hydroxyl terminated acid carbonates:



and secondly by decarboxylation to:



The reaction rate as determined by the reduction in molecular weight is found to be quite modest, even after stress free immersion in water at 90 °C for 220 days. However, the properties of polycarbonate are potentially very sensitive to modest levels of degradation. This arises from the fact that moulding grades have a molecular weight of typically only 25,000 and a critical chain entanglement molecular weight of about 17,000. Thus a modest level of chain scission can be sufficient to convert a very tough material to a state of fragility. After 60 days exposure to hot humid air (80 °C, 96% RH) the strain at break of polycarbonate film declined to zero, whilst after the same time in dry air (80 °C, 0% RH), 70% of the initial strain at break was maintained [12].

It has also been shown [13] that "in the presence of tensile stresses of a few MPa, the rate of hydrolysis is increased by factor of about 10". Various mechanisms were considered as the cause of this remarkable degree of acceleration. These included stress enhanced diffusion (not sufficient), mechanically induced chain scission (not sufficient) and stress separation of chain ends thus disfavouring chain recombination (possibly sufficient).

It is however a fact that hydrolysis in service is rarely identified as the cause of polycarbonate product failure. This is partly due to the specialist applications that the material is suited for (requiring toughness and transparency) and not suited for (due to poor chemical and ESC resistance). Applications rarely involve hot water or acids and alkalis that promote hydrolysis.

The vast majority of in-service failures (for example see Case 5.6.12) are due to hydrolysis during the hot melt processing of polycarbonate products. Polycarbonate material needs to be thoroughly dried immediately prior to processing. When this is not done down to the limits shown in Table 5.9 then the degree of process induced hydrolysis can cause problems. The appearance of splay marks on injection mouldings (emanating from the sprue or gate), as shown in Figure 5.2, is a clear symptom of inadequate predrying. Significant embrittlement will always accompany visible splay marks, but the absence of splay marks does not preclude embrittlement.

Polyethylene terephthalate (PET)

After 60 days exposure to hot humid air (80 °C, 96% RH) the strain at break of PET film declined by a factor of 5, whilst after the same time in dry air (80 °C, 0% RH), 100% of the initial strain at break was maintained [12]. Thus if the effects of temperature

Table 5.9 Maximum recommended water content of some thermoplastics prior to melt processing

Material	Injection moulding Max water (%)	Extrusion Max water (%)
Nylon 6, 66, 610	0.2	0.1
PMMA	0.08	0.02
SAN	0.08	0.02
ABS	0.08	0.02
Polycarbonate	0.02	0.01
PBT	0.005	0.005
PET	0.002	0.002

Figure 5.2 Splay marks on a polycarbonate moulding due to inadequate drying

alone are ignored, PET is rather less hydrolytically stable than polycarbonate and this is reflected in Table 5.9. Predrying material down to 0.002% water content is an expensive and time consuming operation and failure to do so (as with polycarbonate) is the main cause of defective products and failures in service.

PET fibres are used extensively in geotextiles, but because of their known susceptibility to hydrolysis in alkaline environments there is a general consensus that they should not be employed in ground conditions that exceed a pH of 9. Under conventional immersion testing conditions degradation is essentially restricted to the fibre surface, as might be expected with such a closely packed molecular structure. However when immersed under tensile stress the rate and depth of attack are significantly increased [14] as was also previously observed with polycarbonate. Thus, for example, the breaking load of individual fibres reduced from 0.48 N to 0.41 N following 10 days of stress free immersion in 10% sodium hydroxide at ambient temperature, but went down to 0.17 N when stressed (246 MPa). The increased rate of degradation was tentatively put down to stress enhanced diffusion.

Acid promoted hydrolysis is also a frequent cause of failure. For example PET film wrapping is sometimes used for the primary (inner) insulation of electrical cabling, and also for binding cores together. The acidic byproducts of the degradation of flame retardants in outer insulation or jacketing layers has been shown to embrittle the material. This may occur at elevated service temperatures or, as in one recorded case [15], during cable manufacture. Here the outer insulation was an ethylene-propylene rubber (EP) flame retarded with a brominated additive. During steam crosslinking of the EP, a small amount of HBr was evolved and hence hydrobromic acid came into contact with the film. The problem was solved by improving the control the steam pressure/temperature to minimise the thermal degradation of the flame retardant.

Polyimide

Maintenance problems on US naval aircraft were reported to have increased at an 'appalling' rate due to the frequent failure of polyimide (Kapton) electrical wire insulation. One known weakness of the material was its poor resistance to alkalis. For example [16], 48 hours of immersion in ammonium hydroxide (pH = 11) and sodium hydroxide (pH = 14) at ambient temperature reduced tensile strength by 50% and 99%, respectively. Therefore when cracking of the insulation was first observed it was thought to be due to contact with a highly alkaline cleaning fluid, as it was inconceivable that a material selected to satisfy a rigorous military specification could degrade so rapidly in a natural environment. Eventually it was proved that the material suffered from hydrolytic degradation (main chain scission at the hydrolysis-prone imide groups), in the presence of atmospheric moisture, and that the rate of attack at ambient temperatures was significant. The original specification had overlooked this possibility. Laboratory tests [17] on stressed insulation immersed in water revealed that the time to crack increased with decreasing temperature, being 80 hours at 100 °C, 220 hours at 80 °C and 700 hours at 60 °C. These data fit an Arrhenius relationship predicting cracking after 10,000 hours at 20 °C. This finding was compatible with the rate of failure of naval aircraft insulation (generally in high humidity at ambient temperatures). It also helped to explain the earlier failure of missile components in storage [18]. The store environment had not been humidity controlled.

Polyimide is currently used to insulate wiring in 12,000 civil aircraft. The material was chosen for its strengths such as its resistance to burning aviation fuel and low smoke toxicity. However (and paradoxically) investigative journalists [19] have now made public the possibility that the insulation is responsible for aircraft fires and may have contributed to the crashes of TWA flight 800 and Swissair flight 111. The sequence of events are inferred to be as follows:

i) the material embrittles via hydrolysis.

ii) cracks develop.

iii) electrical arcing at a crack creates a low resistance carbon path.

iv) on completion the carbon path becomes a potential site for 'explosive' flashover generating temperatures (~ 1000 °C) that are sufficient to melt copper wire.

In 1999 [20] the Federal Aviation Administration issued guidance to all carriers urging them to refit all aircraft installed with Kapton insulation.

Another potential contribution to the failure process that seems to have been overlooked in this case is the significant degradation of polyimides that is known to occur as a result of contact with microorganisms. This is discussed in Section 7.3.

Acetal

Acetals appear to offer sufficient resistance to hot water induced hydrolysis to succeed in the domestic kettle market. However as discussed above they (paradoxically) offer pathetic resistance to acids.

Of 600 acetal hot water pipe fittings removed from service, 92% exhibited visible degradation in the form of whitening, and 60% contained visible cracking [21]. The damage was concentrated in areas of high stress generated by crimping forces, and was consistent with a reduction in molecular weight due to thermo-oxidation, hydrolysis, or both in combination. Thermo-oxidation, as experienced with polybutylene (see Section 2.6), would be promoted by the small amount of chlorine in the water, but not to such a significant degree. A low concentration of hypochlorous acid in the chlorinated water would not be expected to hydrolyse polybutylene, but via acidolysis it may be the critical factor for acetals.

This work studied the influence of hydrolysis and stress by comparing cycles to fatigue crack intiation of acetal in air and in dilute acid solutions. Acids such as HCl promote and catalyse hydrolytic degradation (acidolysis) but do not promote oxidation.

In air the acetal resisted crack initiation for at least a million cycles (1 Hz, 35 MPa maximum stress). However this dropped dramatically to 10,000 cycles in 1% HCl and 500 at 6% concentration. Thus very low concentrations of a non oxidising acid in combination with stress dramatically reduces the durability of acetal parts via acid induced hydrolysis. See Case 5.6.4.

5.6 Case studies

5.6.1 Polyvinylidene fluoride in dry chlorine

History

PVDF combines melt processability with the excellent chemical resistance expected of a fluoropolymer. It is readily available in the form of extruded sheet and pipe that can be fabricated by thermal welding techniques. These attributes have made the material very attractive for the construction of process plant for handling corrosive fluids.

In the late 1970s, PVDF extruded pipe of ~ 150 mm diameter and several kilometres in length was chosen to transport dry chlorine gas to various reaction vessels within a large industrial complex. Pressures and temperatures were modest and the pipe was deemed to be structurally adequate without the addition of external reinforcement (e.g. GRP lamination).

Spigot/socket joints were employed as shown in Figure 5.3. The sockets were fabricated by welding.

Within eight weeks the pipe system developed several hundred serious leaks at cracks within the socket collars.

Inspection and analysis

On inspection it was established that all collar cracks had initiated at, or adjacent to, the internal collar weld; that is where the collar is exposed to the chlorine gas. Photographs are shown in Figure 5.4 and 5.5.

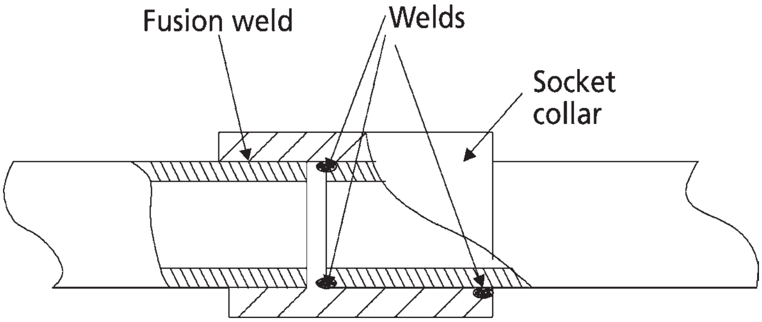


Figure 5.3 Cross-section of a PVDF pipe socket joint

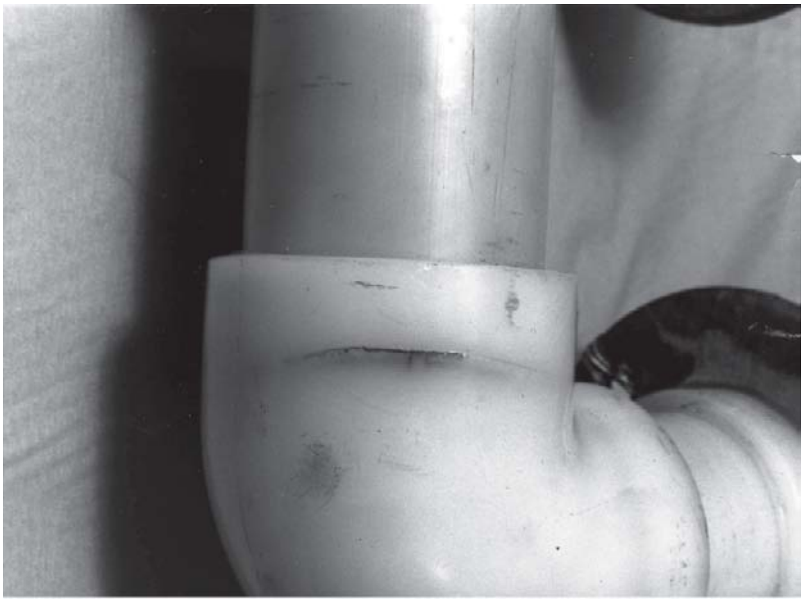


Figure 5.4 External view of a typical leakage crack

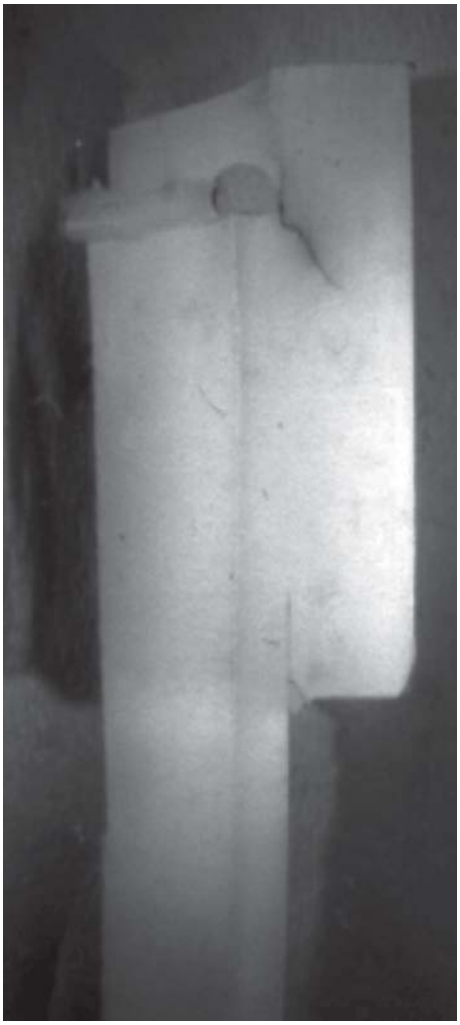
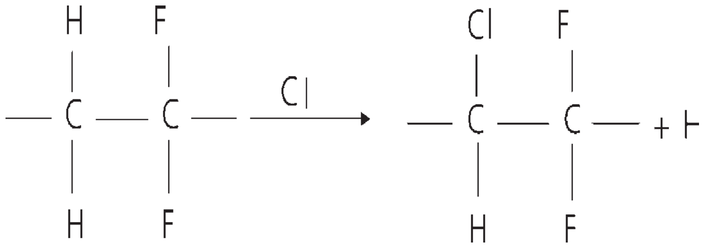


Figure 5.5 Cross-section of a typical leakage crack

The circumferential cracks tended to initiate in the upper quartile (the crown) of the pipe cross-section.

Significant swelling of both the collar and the pipe end was observed.

Electron probe microanalysis of the pipe wall of cracked samples revealed chlorination of the PVDF (hydrogen abstraction/chlorine substitution).



Failure diagnosis

The resistance of PVDF to dry chlorine gas is described as excellent in the supplier's data sheets, yet it was evident that very rapid attack had occurred in this case. The very localised nature of this attack initially suggested that the heat affected zone at or near to the weld may have been rendered prone to chemical attack.

However, it was noted that the degree of attack was most severe in pipe sections that were exposed to outdoor conditions. This combined with upper quartile initiation suggested that sunlight was involved.

It was established that the translucent PVDF pipe was sufficiently transparent to UV to dissociate molecular chlorine:

$Cl_2 \leftrightarrow Cl^{\bullet} + Cl^{\bullet}$

The concentration of highly reactive chlorine radicals maximised in gaps between the pipe ends where gas flow was at a minimum. Hydrogen abstraction and chlorine substitution caused swelling and embrittlement, and cracking at the points of maximum stress concentration (the internal socket weld). As the cracks developed the concentration of chlorine radicals increased at the crack tip (increased UV intensity + reduced gas flow rate). Hence very high rates of corrosion stress cracking were seen.

Lessons and consequences

1. PVDF is severely attacked by atomic (singlet) chlorine radicals.
2. Chlorine radicals can be generated by exposing molecular chlorine to sunlight or artificial lighting with significant radiation in the 300 – 400 nm range.
3. Transparent or translucent polymers should not be used to transport or contain fluids that are prone to dissociation by UV.
4. The installation was replaced with pigmented PVDF and subsequently this proved to be successful.

5. The material supplier gained valuable knowledge from this expensive failure and agreed to bear the cost of the replacement pipe.

6. This was the first of many similar failures involving PVDF and ECTFE with chlorine and chlorinated chemicals (e.g. sodium chlorate). Only three references to this important phenomenon [5, 22, 23], were found in the literature. This highlights the need for very exhaustive searches of public domain literature to minimise the risk of repeated historical failures.

5.6.2 Acrylonitrile-butadiene-styrene in hydrochloric acid

History

A piping system designed for the transport of 36% HCl at ambient temperatures employed a PVDF lined steel construction.

After 18 months of service one of the blanking plates ruptured. 2,500 litres of acid were lost. This caused rapid and severe corrosion of adjacent steel structures.

Inspection and analysis

Fragments from the ruptured blanking plate were not recovered. Fortunately a second plate with a similar service history was available for inspection. The discolouration of the area in contact with the acid was clearly evident. A cross-section of the plate (Figure 5.6) revealed the considerable depth of discolouration, exceeding 5 mm.

A shaving from the blanking plate was ignited. It burned readily with a smoky flame and could not therefore be PVDF.

The plate material was analysed by Fourier transform infrared (FTIR) spectroscopy and found to be ABS.

Failure diagnosis

ABS is not sufficiently resistant to hydrochloric acid and should not have been used in this application. The reasoning behind the choice of ABS for the blanking plates had not been recorded, but the chief engineer was able to recollect that an unnamed person had

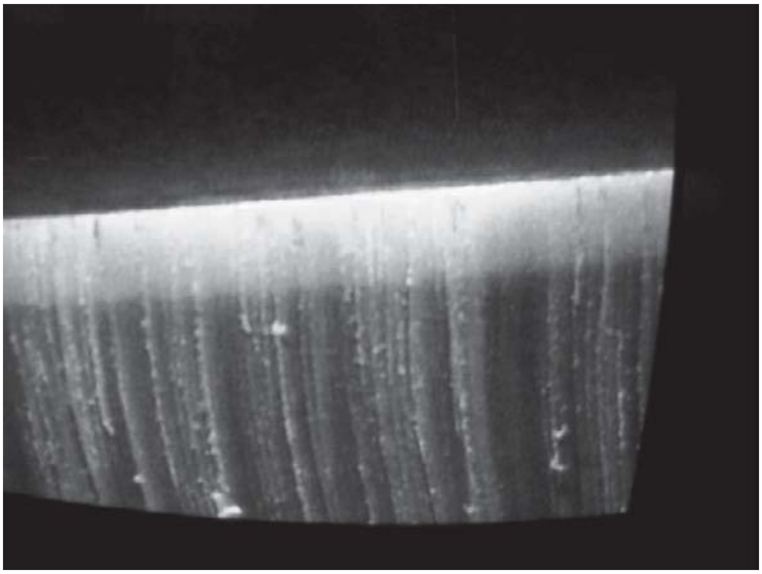


Figure 5.6 Cross-section of the blanking plate showing the depth of attack

checked on the chemical compatibility and advised that this was favourable. He thought that this was based on documented data. On examination of the company's files only two relevant records could be found. The chemical resistance data sheet for Monsanto's Lustran ABS ranked their material as 'resistant' to 38% HCl at 23 °C. The data sheet for Dow Chemical's Magnum ABS admitted 'slight clouding' after exposure to 37% HCl at 23 °C. However these were based on exposure periods of only 7 and 28 days, respectively.

Independent test data [4] were available at that time for the effects of 37% HCl on ABS at 20 °C for an exposure period of 365 days. This recorded a weight gain of 33% and a reduction in Brinell hardness from 570 to 102 kgf/cm^2.

The plate failed as a result of degradation induced material softening in contact with the acid.

Lessons and consequences

1. For applications that demand long-term contact with a fluid, the selection of materials should not rely upon conventional chemical compatibility data sets. Conventionally these are based on short term exposure (7 – 28 days).

2. For such applications candidate materials should be tested for exposure periods and temperatures that in combination match the severity of the intended service conditions. It would be prudent to assume that the rate of degradation increases by a factor of 3 for each 10 °C increase in test temperature. In this case the level of attack in service (18 months at 20 °C) would have been replicated in tests at 50 °C for an exposure period of ~ 2 months.

3. Following inspection by a pressure vessel specialist, an adjacent steel vessel was deemed to be unsafe due to acid corrosion and had to be replaced at considerable cost.

4. The blanking plates were replaced with steel backed PVDF.

5.6.3 Acetal in chlorinated water

History

Acetal copolymers have been used for many years by the water industry. The material is strong, stiff, and hard, and offers excellent wear, creep, and fatigue resistance. One of its major weaknesses is its poor resistance to acids but this is not normally a consideration in potable water applications.

A mains water pipeline system failed via rupture of an injection moulded acetal fitting. To minimise public inconvenience the fitting was immediately replaced. The system failed again within two days by the rupture of an adjacent fitting. A rapid failure diagnosis study was required.

Inspection and analysis

The acetal fittings were black except for the surfaces that were exposed in service to the water. Here the surfaces were white and generally covered with microcracks. In some areas large cracks had formed. All these features as illustrated in Figure 5.7 are indicative of chemical attack. Whitening extended to a surface depth of ~ 250 microns and coincided with material that had microvoided (whitening is due to the light scattering ability of small voids). Fine etching or fine powders would produce the same optical effect.

Enquiries revealed that the fittings had been machined in parts after moulding to satisfy tight dimensional tolerances (thick walled acetal mouldings suffer from high moulding and post moulding shrinkage). All large cracks initiated at machined rather than moulded surfaces. All large crack surfaces exhibited signs of mild degradation (whitening).

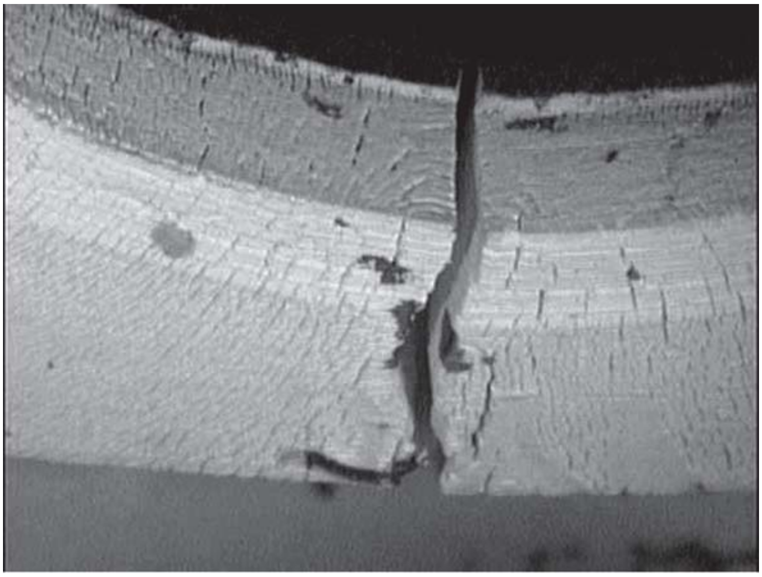


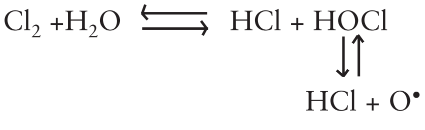
Figure 5.7 Whitening and cracking of an acetal fitting

Material was removed from exterior undegraded and interior degraded surfaces and compared using FTIR to confirm that the white material was acetal rather than an extraneous deposit. A solution viscosity technique [24] revealed that the mean weight average molecular weights of the outer and inner surfaces were 99,000 and 8,000, respectively.

Failure diagnosis

The symptoms are all characteristic of chain scission or depolymerisation. These degradation processes are strongly autocatalytic in acetals because the main by product is formaldehyde and this rapidly oxidises to formic acid.

The initiation step is probably oxidation via contact with chlorinated water. Chlorine (added to domestic water supplies as a disinfectant at typically ~ 1 ppm) accelerates this oxidation by providing a source of highly reactive nascent (atomic) oxygen $O^{\bullet}$:



$$\begin{array}{ccc} Cl_2 + H_2O & \rightleftharpoons & HCl + HOCl \\ & & \downarrow\uparrow \\ & & HCl + O^{\bullet} \end{array}$$

This particular hypochlorous acid (HOCl) dissociation reaction is not dominant, but becomes significant when the chlorinated water is neutral. This is likely if the water source is highly alkaline. Oxidation via this route is limited by oxygen diffusion. This restricts degradation to the surface in contact with the oxidising medium and also concentrates attack within the amorphous phase of the plastics. The increase in molecular mobility due to chain scission in the amorphous phase leads to an increase in crystallinity, and hence microvoiding and whitening.

It was suspected that the water had been overchlorinated, but this would be difficult to prove. The customer was alerted to the probability and an investigation of an upstream chlorine dosing unit was initiated. The control link between water flow rate and chlorine dosing rate was found to be inoperative, leading to the possibility of chlorine concentration levels of 100 ppm at the lowest recorded water flow rates.

Lessons and consequences

1. The sensitivity of acetal to chorine catalysed oxidation and stress corrosion cracking highlighted the need for better control of chlorine concentration.
2. The increased sensitivity of machined acetal surfaces to stress corrosion cracking was found to be significant. The reason for this is probably that injection moulded surfaces are usually under beneficial compressive stress. Compressive stress inhibits diffusion and microvoiding. Removal by machining is detrimental.

5.6.4 Stress corrosion cracking of acetal (1)

History

A cider making plant employed injection moulded acetal parts as a hose locking mechanism. After around 5 years of trouble free service one failed. Loss of confidence rather than the relatively small loss of precious fluid led to replacement of all parts by high quality steel (the traditional material but with a unit cost penalty of x 10). The cider maker was not particularly interested in the cause of the problem. However the upstream supply chain had built up a considerable business with these particular mouldings within the general brewing industry. They were sufficiently concerned to know the cause of the failure and to fund an investigation.

Inspection and analysis

The failed part together with an unused part is shown in Figure 5.8. A more detailed view of the surface of the failed part was shown previously as Figure 1.8. The regular

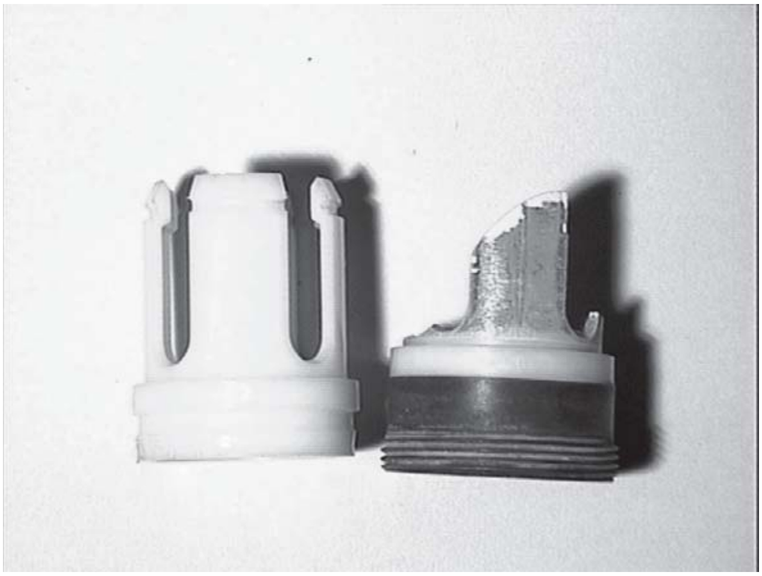


Figure 5.8 An acetal fitting before and after 5 years in a cider making plant

pattern of microcracking reflects the stress pattern arising from the injection moulding process (frozen-in stresses) rather than the applied stress in service.

The part was analysed by FTIR and found to be an acetal homopolymer.

The cider was analysed and found to contain ~ 1% by volume of mixed organic acids. Acetic acid was dominant.

Failure diagnosis

Acids promote hydrolysis (acidolysis) of acetals leading to chain scission, embrittlement, and cracking in the presence of stress.

Normal service temperatures are ambient and this combined with a ~ 1% acetic acid solution would not be expected to result in significant degradation over a period of 5 years. However periodically the plant had been steam sterilised. It seemed likely that during normal operation the surface of the moulding would absorb acetic acid, and acidolysis would commence during the sterilisation period. This was shown to be the case by laboratory simulation. Further investigations revealed the benefits of more careful moulding (higher mould temperatures to reduce moulded-in stress) and a change of material (an acetal copolymer grade formulated for maximum resistance to hydrolysis).

Durability with the improved material was increased by a factor of ~ 3.

Reducing moulded-in stress from 10 MPa to 5 MPa increased durability by a factor of 2.

The absence of acid increased durability by a factor of 10.

Lessons and consequences

1. The parts made from an improved grade of copolymer and moulded with the recommended mould temperature (to minimise stress rather than unit cost) were deemed to be satisfactory for the brewing of most beers and other neutral fluids.

2. Even when optimised, the parts were not deemed suitable for cider manufacturing plants. The suppliers were advised to fund the immediate replacement of such parts.

3. PVDF was suggested as a potential alternative material and worthy of comprehensive testing.

4. The awareness of two facts would have been required to avoid this problem: dilute acids at elevated temperatures will rapidly degrade acetals, and slight acidity is an essential characteristic of cider.

   The part supplier should have known the first but could be excused for not knowing the second, whilst the cider maker knows the second but will not know the first unless clearly warned of the weakness.

5.6.5 Stress corrosion cracking of acetal (2)

History

A manufacturer of domestic cleaning fluids decided to extend its portfolio of products to include a descaling agent for plastic hot water kettles. The company had grown rapidly by concentrating expenditure and expertise on marketing. The technical functions had been allowed to wither to two formulation chemists housed in a prefabricated hut in the shadow of corporate headquarters.

The chemists formulated a mixture of organic acids (acetic/citric/oxalic) that was shown to rapidly dissolve limescale. Two plastic kettles were purchased and trials revealed no deleterious interactions between the fluid and the plastic. The 'back-room boys' were thanked and given their next task whilst the 'front-room boys' took over.

Within days of the product reaching retail outlets, complaints were received. Within a few weeks the product had to be withdrawn.

Inspection and analysis

A photograph of a complainant's kettle is shown in Figure 5.9. Large circumferential cracks together with surface pitting were reported to develop soon after application of the descaling fluid. The cause of the failure and the reason that this had not been detected during testing trials were immediately apparent.

Failure diagnosis

Two materials dominate the plastic kettle market. At the time the fluid was being developed, about 60% were moulded from acetal copolymer and the remaining 40% from polypropylene. The two kettles purchased for compatibility trials were both (by chance) polypropylene. The acid resistance of polypropylene is excellent and it is therefore not surprising that the trials were successful. However the acid resistance of acetal is very poor and the material is particularly prone to stress corrosion cracking.

All complaints came from owners of acetal kettles.

Lessons and consequences

1. Cutting corners improve profits and shortens time to market but only if luck is on your side. In this case it would be fair to say that the manufacturer was slightly unlucky to select two polypropylene kettles at random.

2. Plastics products may appear to be identical but in fact are often made from different plastics with very different properties.

3. In the absence of knowledge about material weaknesses there is no alternative but to engage in comprehensive testing.

Figure 5.9 Stress corrosion cracking of an acetal kettle following exposure to descaling fluid

4. The manufacturer made modest compensation payments to all complainants and by deciding to discontinue the product line wrote off substantial (mainly marketing and promotional) costs. Fortunately for them, the case was not picked up by one of the popular consumer affairs programmes and their reputation was not seriously dented.

5.6.6 Thermoplastic elastomers in hot water

History

Vent and plug washers in central heating hot water radiators have traditionally been made from fibrous material. These were adequate as a long term seal for the relatively low water pressures even at water temperatures of ~ 80 °C.

A supplier of plug and vent assemblies (the product supplier) contacted an injection moulding company (the moulder) with claimed experience of moulding washers. The moulder recommended Hytrel, a co-ether ester based thermoplastic elastomer. It was claimed that the selection was ratified by the material supplier (DuPont).

A large quantity of Hytrel washers were supplied and installed from 1990 but failures started to accumulate from 1993. By 1994 when production ceased, failures were numerous and very widespread. The material supplier was asked to investigate the problem. They reported no problem with the material but suggested that considerable compression set on some washers indicated excessive tightening of assemblies. An engineering consultant suggested insufficient tightening. The product supplier could not accept these as credible explanations for they implied that a whole population of plumbers were either 'ham-fisted' or 'weak wristed'. Legal proceedings against the moulder (and others in the supply chain) were initiated.

Inspection and analysis

Failed washers were inspected and a high proportion was found to exhibit radial cracks.

The compression set of washers was assessed after three weeks in water at a temperature of 85 °C, the degree of compression being approximately that used in service. Under these conditions, 90% compression set was observed. Other tests under the same exposure conditions showed that the torque to undo assemblies fell to less that 10% of the tightening torque and the washers had severely stiffened.

Failure diagnosis

Thermoplastic elastomers are generally known to suffer from high compression set (high stress relaxation/high creep) compared with thermoset rubbers. For this reason they are rarely chosen for elevated temperature, long-term, pressure sealing applications.

It is generally known that polymers with ester groups will offer poor to modest resistance to hydrolytic degradation. Indeed the DuPont trade literature states that even with the addition of a hydrolytic stabiliser, the material is ‘generally suitable’ but not ‘very suitable’ for use in water at temperatures above 50 °C. The washer material contained no such stabiliser.

Leaking occurred due to loss of seal pressure and cracking. Both were accelerated by hydrolytic degradation.

In this case the material cause of failure is less revealing than the human cause of failure. The circumstances that triggered the choice of material are of particular interest.

The moulder had a successful reputation as a supplier of water tap washers moulded from Hytrel. This might suggest that he would be aware of some of the limitations of the material. However tap washers operate either at ambient temperatures or short-term at elevated temperatures and they are frequently recompressed. Thus the moulder was unaware of potential problems with compression set or hydrolysis.

The product supplier was also unaware of these limitations.

Hytrel had approval for contact with potable water, and this was interpreted as Hytrel being ‘approved for use with water’.

As the moulder was confident about the choice of generic material he did not ask the supplier whether Hytrel was the best choice of material but did ask for the best Hytrel grade. The grade recommended (highest hardness, without hydrolytic stabiliser) suggests that the application was inadequately described or understood.

The product was launched without testing.

Lessons and consequences

1. For material selection, product suppliers should not rely upon the advice of a single processor. They should be particularly wary if the processor advises the use of his ‘favourite material’.

2. For functional parts that demand durability, the significance of the product type (e.g. washer, hose, gear wheel, pressure vessel, etc.) should not be overrated or allowed to outweigh the critical factors of time, temperature, stress, and chemical environment. These four factors must be clearly and formally stated if selection advice is sought from material suppliers.

3. New products should always be tested. The resources applied to testing should not be based upon a fraction of the product value (which in this case is quite low) but rather upon a fraction of the consequential costs of endemic product failure (which in this case is very high).

4. The product supplier switched to an EPDM washer. This has proved successful.

5.6.7 Solvent attack: cables in ducts and contaminated soil

History

One of the risks that must be considered with buried cable (and other utility assets such as pipe) is the possibility of contact with aggressive solvents from historical contamination or future (accidental) spillages. In many cases that involve spillage the failures could not have been foreseen. However in this case the risks were predictably high because the cable was installed under a site that was used for respraying cars.

After a few years in service, the ducted cable had disintegrated.

Inspection and analysis

The failed cable was of the construction shown in Figure 5.10.

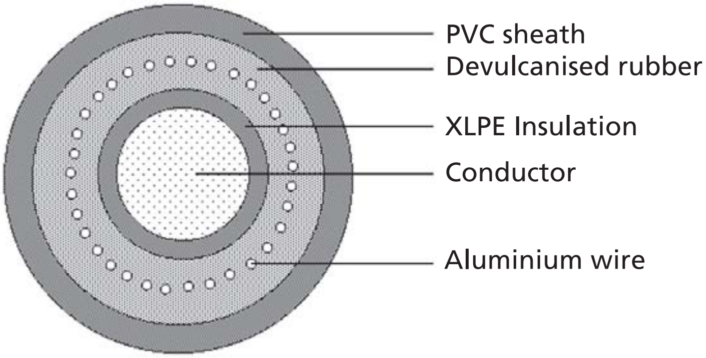


Figure 5.10 Schematic of waveconal cable

An analysis of the duct contents revealed the presence, in addition to water, of a cocktail of solvents, principal of which were toluene, xylene and methyl ethyl ketone (MEK). The PVC sheath was massively swollen and had cracked. Similarly the devulcanised rubber had been attacked. Some swelling of the crosslinked polyethylene (XLPE) insulation had occurred, but this was otherwise undamaged.

Failure diagnosis

Many solvents will attack plasticised PVC. Both toluene and MEK will swell the material significantly, particularly the latter.

Some solvents, e.g. tetrahydrofuran, will actually dissolve PVC, but it would be an unusual occurrence for complete dissolution to occur. Notwithstanding, the effect of massive swelling by toluene and MEK is to reduce the tensile strength of the PVC to a very small fraction of its original value. With a small degree of stress, either induced by differential swelling or still remaining after installation, the outer PVC sheath cracked. These cracks made the ingress of the solvents to the interior easier, although even without cracking steady diffusion would have occurred, albeit over a longer time. The layer encasing the aluminium neutral wires of a waveconal cable is derived by devulcanising (mastication with the addition of a 'peptising' agent) butyl rubber inner tubes. In this state the neutral wire bedding layer can be and was dissolved by the toluene present in the cocktail of solvents. Again, toluene is a swelling agent for XLPE, but the crosslinking, crystallinity and low operating temperature of the cable prevented a massive increase in volume. The MEK component of the solvent mixture is not a severe swelling agent for either XLPE or devulcanised butyl rubber.

In the case of soil contamination, as opposed to a duct spillage, it should be pointed out that just because a swelling agent is known to be present, this does not necessarily mean that the effects will be damaging. Thus MEK is an extremely potent swelling agent for plasticised PVC when it is in a concentrated form. However, it is very soluble in water, so it is very easily dispersed and high concentrations are unlikely to persist. Figure 5.11 shows the effect on PVC of two concentrations of MEK in water. At the 10% level (possible in a duct spillage) swelling is quite severe, but at the 1% level (possible, but high nevertheless, for contaminated soil) it is unimportant.

In contrast to MEK and phenol, solvents such as toluene are insoluble in water. Although they may exist in quite low volume concentrations in the soil they can float as an oily layer on the water table and are easily absorbed by a cable sheath material as the water table rises and falls. Their action on plasticised PVC can be quite complex. As Figure 5.12 shows, toluene initially swells the PVC strongly, but the swelling reaches a maximum.

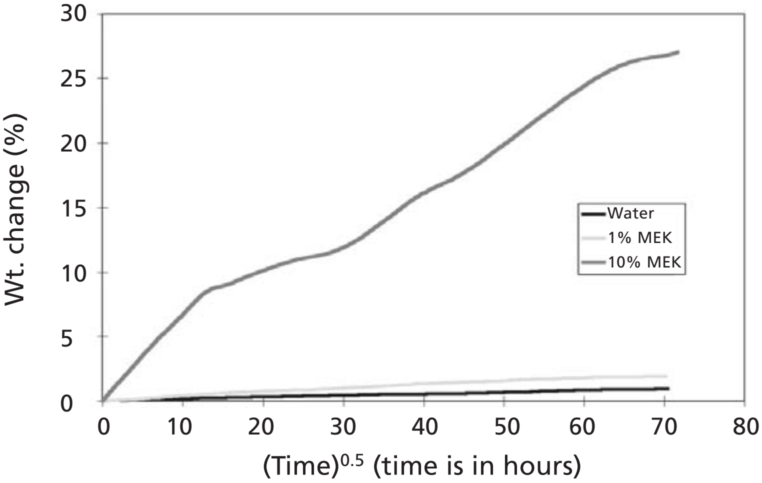


Figure 5.11 Swelling at 20 °C of 3 mm PVC cable sheath in aqueous solutions of MEK

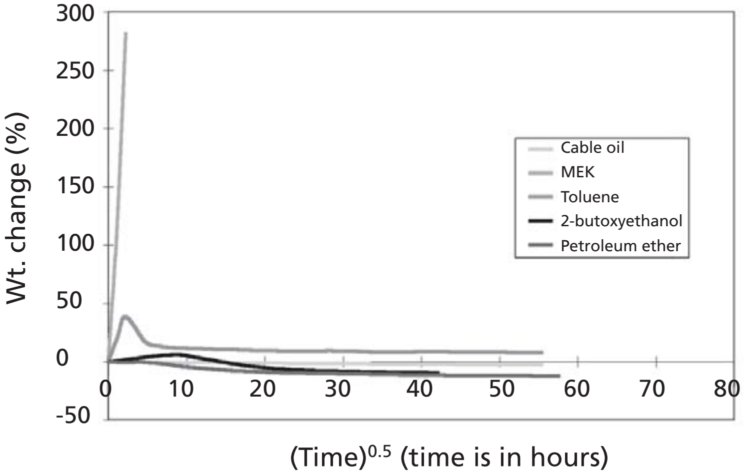


Figure 5.12 Swelling at 20 °C of 3 mm PVC cable sheath in various solvents

At longer times the plasticiser extraction outweighs any additional uptake of solvent. In the case of swelling in 2-butoxyethanol (a paint solvent) there is swelling initially and shrinkage later.

Oil spillages from cables can attack the PVC sheathing of adjacent cables or of the leaking cable itself. However, in this case the long-term effect tends to be embrittlement of the sheath. This is because the oil is a poor swelling agent for the base PVC polymer, but it is very good at extracting the plasticiser. Therefore the PVC shrinks rather than expands and becomes more rigid as more plasticiser is removed by the oil. Figure 5.12 demonstrates that both cable oil and petroleum ether cause weight loss (shrinkage) of the PVC. This process is accelerated and the shrinkage is greater, at higher temperatures.

Lessons and consequences

1. Where exposure to accidental spillage is likely, metal sheathed cables should be used. Polyethylene (PE) generally has better resistance to solvents than PVC. The higher the density of the PE chosen, the better its resistance becomes. However, if the metal sheath is made of lead it is still possible to use PVC. Its 'sacrifice' can be tolerated. Lead sheathed low voltage cables, covered by the EEMUA 133 standard (Engineering Equipment and Materials Users' Association), are widely used by the chemical and oil industries. This is a specification for underground armoured cables to protect against solvent attack. The cables comply with the general requirements of BS 6346 and BS 5467.

2. Where cables are to be laid in contaminated ground it is a wise precaution to have the soil analysed for solvent content. Only rarely are water soluble compounds, such as phenols and ketones, present at high enough levels to constitute a threat, but pure hydrocarbon substances such as xylene and toluene may be present at high concentrations near the water table. This is particularly common in sites where paint spraying has taken place or where there have been gasworks. Here it would be sensible to install metal sheathed cables.

3. If a solvent, or other potentially damaging chemical such as an acid, is likely to come into contact with a cable, then an expert should be consulted on whether it is likely to constitute a threat, and if so, what steps should be taken lessen the impact.

5.6.8 Glass-reinforced plastic in sulphuric acid

History

A PVDF lined GRP pressure vessel containing 250 litres of concentrated sulphuric acid failed catastrophically after 5 years in service. The damage created by high velocity vessel fragments and by the release of acid was extensive. The integrity of similar tanks at the site could no longer be relied upon and the manufacturing operation was suspended pending an investigation.

The operating conditions were as follows:

- Normal working pressure = 0.2 MPa,
- Normal acid temperature = 50 °C,
- Acid concentration ranged from 50 – 80%.

The vessel construction was as follows:

- Horizontal cylinder with domed ends,
- PVDF liner of 6 mm thickness,
- Helically wound inner structural laminate of E glass fibre and epoxy resin,
- Additional hoop reinforcement in the barrel region using hoop windings of E glass and epoxy.

The weight of the vessel was carried by two rubber lined saddle supports.

Inspection and analysis

The fracture surfaces of the epoxy laminate were generally rough due to extensive fibre pull-out. Two evidently contiguous fragments contained planar fracture surfaces which were essentially smooth, these being about 20 cm in length. The PVDF liner was generally distorted and torn but exhibited no evidence of brittle fracture. Fragments were reassembled. The fracture initiation site (A) as shown in Figure 5.13 was traced to that part of the cylindrical section of the vessel adjacent to one of the supports, this being the location of the planar smooth laminate fracture.

A detailed inspection of the planar fracture surfaces revealed that they were smooth to about 90% of the laminate thickness. This would suggest that the fracture initiated at the outside surface and developed parallel to the hoop windings.

Detailed inspection of other similar vessels revealed multiple circumferential microcracking in the external surface adjacent to each saddle support.

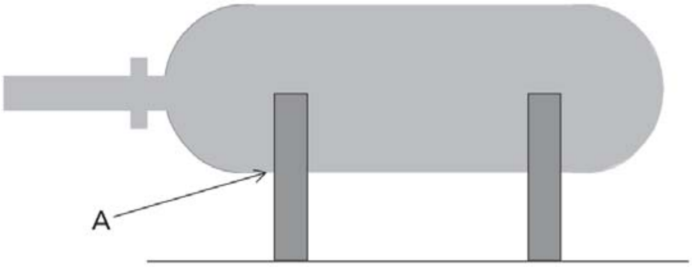


Figure 5.13 Location of fracture initiation on GRP pressure vessel

Failure diagnosis

The circumferential planar fracture surfaces within the hoop windings could be the conventional response to overstressing in the axial direction. The laminate is simply splitting along its weakest plane. However the almost complete local absence of fibre pull in the helically wound part of the laminate could not be explained by overstressing alone. It would suggest that the crack has penetrated the laminate to about 90% of its thickness by slow growth at modest stresses and has then suffered fast fracture. Slow crack growth in GRP is most often linked with acid stress corrosion of the glass fibres. It is mainly for this reason that glass reinforced laminates in contact with acids are protected by a resin rich barrier layer or (as in this case) a solid acid resistant thermoplastic liner.

Chemical analysis of the planar fracture surfaces revealed the presence of calcium sulphate. This is known to be the most abundant reaction product resulting from sulphuric acid attack on E glass fibres. To check whether acid contact following rupture could explain the presence of the sulphate the analysis was repeated on fast fracture surfaces. No calcium sulphate was detected.

The unusual inference in this case is that the corrosion appears to have developed as a result of contact with acid on the external surface of the vessel. The probable cause was eventually traced to a defective flange coupling. Maintenance records revealed that this had been replaced 6 months before the failure because of leakage. The location of the flange could have soaked the external surface of the vessel in the region where cracks first developed.

Therefore the failure sequence was concluded to be as follows:

i) Resin microcracking on the external hoop wound surface due to excessive stress alone. The saddle width was insufficient to carry the weight of vessel and its contents without locally exceeding the resin or resin glass bond strength. Microcracking observed in other similar vessels suggests that this was a basic design error.

ii) The microcracks were in contact with sulphuric acid due to leakage. This would accelerate resin cleavage crack growth in the hoop layers.

iii) Eventually the acid would have access to the stressed helix wound fibres. The fibres would suffer from stress corrosion cracking at modest stresses with local stresses increasing as the crack develops.

iv) When the crack length exceeds a critical length, fast fracture occurs due to fibre pull-out and stress alone.

v) The PVDF liner tears.

Lessons and consequences

1. The weakest cracking plane in a laminate is parallel to the fibre direction. Although in this case the pressure stresses have been efficiently accommodated, the local bending stresses due to support and constraint have been given inadequate attention. This is a common oversight that explains why the vast majority of laminated structures that fail do so at joints, changes in section and other local geometrical features where bending stresses maximise.

2. Once cracked, a stressed laminate is susceptible to stress corrosion cracking if the crack is in contact with an acid.

3. In most industrial environments involving acid transport and containment the risk of external acid contact should not be ignored. The painting of external surfaces with flexibilised epoxy is a cost effective safety measure. In addition, the use of an acid resistant grade of reinforcement is recommended.

4. The remaining vessels were deemed to be safe provided the surface microcracks were removed and the abraded surface recoated with resin, also with the proviso that the saddle widths were doubled.

5.6.9 Corrosion cracking of composite insulators

History

Composite supertension insulators have been available since the 1970s. They consist of a rod of glass fibre reinforced thermosetting plastic surrounded by polymer sheds and with metal fittings at the end. The rod, or core, takes the mechanical load. The sheds, or weather sheds, form a housing that protects the rod from the environment, provides a long surface creepage path with its characteristic profile and is designed to resist erosion of the surface under all weather conditions.

Their low weight and resistance to damage make composite insulators particularly attractive when compared to the traditional materials of glass and porcelain. However, they have been slow to find acceptance in the market, and one of the main obstacles has been the occurrence of failure and a few isolated incidents involving the collapse of high voltage lines.

In typical failures of one type of composite insulator, the epoxy sheds were found to have cracked and brittle fracture of the core had occurred.

Inspection and analysis

The following observations were made on failed composite insulators:

i) Electrical activity started at the interface between the shed and the end fittings, or at cracks formed in the cycloaliphatic epoxy resin shed, allowing ingress of water and pollutants.

ii) Degradation was observed to have proceeded from the end of the core, either along the core-shed interface or within the core material itself, particularly at resin rich sites.

iii) Along these electrical punctures material was found to have melted or to have been totally removed, and crystallites were found. They were identified as containing zinc, presumed to have been transported from the fitting.

iv) Brittle fracture was typically at the ‘hot’ end of the insulator. The fracture surface was characteristically smooth. A microscopic examination of the surfaces generally, and of individual glass fibres, revealed behaviour typical of stress corrosion.

v) The loss of calcium and aluminium from the fracture surface, and their deposition on the surface behind the crack tip, suggests that acids are the stress corroding chemical. These acids could be derived from atmospheric pollution or decomposition of the resin, or nitric acid may arise from the reaction of moisture and oxides of nitrogen derived from electrical discharge in air. Oxalic acid is a known breakdown product of epoxy resins subject to partial discharges and has been shown to be a particularly effective stress corrosion cracking agent for glass.

Failure diagnosis

The process requires an internal cavity or crack, a mechanical stress, and a high dielectric stress, and is promoted by the ingress of moisture. A crack in the external sheds, caused during installation or by faulty design, becomes moist and provides a site for partial discharges to occur. The glass fibre core is corroded by acid produced by the discharges. The stress corrosion crack penetrates the core until the remaining fibres can no longer take the load and the insulator breaks. Other factors such as dynamic loads and diffusing moisture may influence the process, but neither of these alone has been shown in laboratory simulations to produce smooth fracture surfaces.

Lessons and consequences

1. Some failures were probably initiated by mishandling. Thus it is important to avoid severe bending and twisting of insulators during installation. The insulators must, of course, be installed the right way round and they should not be used as ladders.

2. The incidence of failures and their particular nature has highlighted the need for good design of the whole insulator and its fittings. Thus the observation in older composite insulators, that there was easy access of water and pollutants along the resin-metal interface, has led to a radical redesign of the line end of the insulator, including the seal. Manufacturers have improved the materials, so that there is better water repellency of both bond and shed material. The acid resistance of the core glass has been made better by changing its composition and its surface treatment. Attention has been paid to the quality of the shed-core interface, so that excellent adhesion can now be maintained even on exposure to water and acid.

5.6.10 Acetal pipe fittings

History

It has become a common practice to construct plumbing systems using a combination of copper pipe, soldered copper fittings, and acetal compression fittings. The latter are often included at locations where it is anticipated that the pipework will require periodic disassembly.

In this case an acetal fitting failed on the 5th floor of a recently built, and as yet only partly occupied, office block. The exact time of the failure was not known but could have been up to 72 hours before discovery. During that time up to 25,000 gallons of water would have been released. The cost of damage to the lower floors was estimated to be in excess of £100,000. The insurers agreed to the liability but made it quite plain that they would not renew until the risk of a repetition was well and truly established.

Inspection and analysis

The failed fitting is shown in Figure 5.14. It has evidently suffered from severe corrosion and embrittlement.

On the upstream side of the fitting is a soldered copper bend. A viscous deposit was found on the bore surface of the bend. Analysis revealed a high level of zinc chloride in the deposit. The investigators were immediately aware that this was the probable source of the problem but had no idea as to the source of the aggressive deposit. A passer-by remarked that the deposit looked like a run of plumbers' flux.

Conventional plumbers' flux was purchased and found to contain a high level of zinc chloride.

Failure diagnosis

Zinc ions catalyse the initiation of an unzipping (depolymerisation) reaction in acetals. Once initiated the reaction is strongly autocatalytic if the reaction byproducts (e.g. formic acid) are not removed.

In this case the fitting was exposed to a concentrated solution of zinc ions for about 2 years before failure. During this time the system contained static water.

Figure 5.14 The failed acetal fitting

The kinetics of the interaction are particularly complex. The catalytic byproducts are highly mobile so that near surface degradation is retarded. Rapid degradation will occur in the bulk of the material but only after the long delay time required for deep diffusion of the zinc. Long-term immersion testing was required to prove the effect.

It is of interest to note that following this investigation, the failed fitting was stored in a sealed plastic bag. Some years later the contents were needed for reexamination but 90% of the sample had disappeared. The solid acetal, imprisoned in an atmosphere of its own degradation products, had depolymerised to the point of gasification.

Lessons and consequences

1. Unlike the incompatibility between zinc chloride and Nylons (see Case 6.5.5), the incompatibility with acetals is not well known. Many material suppliers claim compatibility. A search of the literature published over the last 10 years reveals no reports of failure and no relevant phenomenological research.

2. Conventional plumbers' flux containing zinc chloride should not be employed in installations that include acetal fittings.

3. The only reason why this type of failure is relatively rare is because in most cases the pipework is well flushed soon after installation.

4. All the acetal fittings were replaced within the building and the system was thoroughly flushed. Reinsurance was granted.

5.6.11 Polyurethane oil seals

History

Brake cylinder and slew seals specified for contact with hydraulic oils at service temperatures of up to 50 °C were moulded from castable polyurethane. The product range prior to distribution had been tested for compatibility by immersion in a selection of commercially available oils. Property retention was assessed as satisfactory.

Seal failures started after about 200 hours of use. 10% of the seal population had failed by 1000 hours of use. A high proportion of the most premature failures was reported from customers in underdeveloped countries. The seal manufacturer suspected that these were caused by local oils that did not meet the necessary standards.

Inspection and analysis

Brake cylinders with seals and residual oil were received for inspection and analysis together with unused seals. The seals were labelled as follows:

- Uganda/failed after 250 hours,
- Germany/failed after 950 hours,
- Pakistan/failed after 910 hours.

Seals had failed by a combination of excessive compression set, wear, and tearing. The used seals were all fragile with low strength and elongation at break. The molecular weights of the failed seals were assessed by gel permeation chromatography to be 7,500 (Uganda), 8,200 (Germany) and 8,500 (Pakistan) compared with 14,500 for unused seals.

Analysis of residual oil in the cylinders revealed the significant differences listed in Table 5.10. The high viscosity of the oil from the Uganda failure together with the higher levels of phosphorus suggest a gear oil. The high levels of copper, magnesium, and iron

Table 5.10 Characteristics of the oils in contact with three failed seals

	Uganda	Germany	Pakistan
Viscosity (m^2/s)	2×10^{-4}	2×10^{-5}	2.2×10^{-5}
Iron (ppm)	230	6	7
Magnesium (ppm)	55	0	0
Phosphorus (ppm)	410	210	200
Copper (ppm)	100	3	2
Water (ppm)	300	230	240
Acidity	0.5	0.2	0.2

further suggest a gear oil that has been degraded and contaminated by pre-use in a severe thermomechanical environment.

Failure diagnosis

All seals have failed due to hydrolytic degradation. The very premature failure in Uganda is probably due to acidolysis catalysed by copper, magnesium, and iron contamination. Other very premature failures could be due to similar instances of oil mismanagement.

The other two failures are more serious for the seal supplier, as they are probably representative of a material/fluid incompatibility that will severely limit the durability of the total population. A prime candidate for the cause of this incompatibility is water contamination of the hydraulic oil. To assess this further, new seals were immersed in hot (dry) oil and hot (water saturated) oil and the decline in tensile strength was monitored as a function of immersion time. The trends are shown in Figure 5.15.

Lessons and consequences

1. Product testing should have been carried out by immersing in used oil rather than new oil because this is a more realistic simulation of the intended service environment. In use, oil absorbs moisture and the medium becomes hydrolytically proactive. With use oil degrades via oxidation, and the degradation byproducts promote oxidation and/or acidolysis of immersed polymer products.

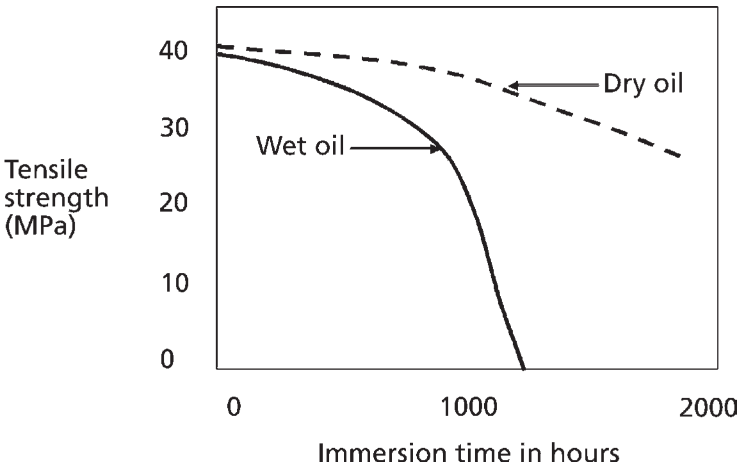


Figure 5.15 Strength reduction of a polyurethane with immersion time in dry and wet oil at 50 °C

2. All polyurethanes are prone to hydrolysis and acidolysis.
3. Users reverted to ethylene-propylene-diene (EPDM) seals.

5.6.12 Degraded polycarbonate mouldings

History

A large consignment of bicycle gear change levers outsert moulded with polycarbonate were found to be fragmented on delivery to south-east Asia. The manufacturer thought it was likely that "something had gone wrong" during the long sea voyage, although the evidence for this suspicion was purely circumstantial. Firstly the products were intact before despatch and in a state of disintegration on arrival. Secondly the product had previously enjoyed a trouble free history and this was the first consignment exposed to a long sea voyage.

Inspection and analysis

A sample of disintegrated products is shown in Figure 5.16.

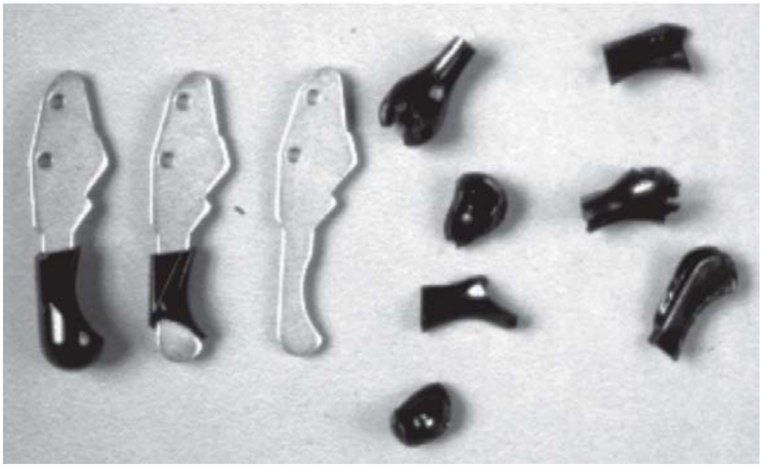


Figure 5.16 Disintegrated outsert mouldings

This case occurred soon after the failure investigation of a consignment of motorised wheelchairs (see Case 6.5.9). Here it was established that disintegration during a sea voyage was due to contact with rust inhibitor vapour. However enquiries revealed that no inhibitor had been added to this consignment. Also a detailed examination of the fractured levers revealed no evidence of ESC, such as multiple crazing or areas of slow craze/crack growth.

The weight average molecular weight of the polycarbonate levers was assessed by gel permeation chromatography and found to be in the region of 15,000.

Failure diagnosis

It was known from many other cases that polycarbonate is fragile if its molecular weight is less than about 16,000. Below this critical level intramolecular entanglement is so weak that strong craze bridging fibrils cannot be formed.

The massive reduction in molecular weight from 25,000 to 15,000 would normally invite the suspicion that the material had not been predried. However the manufacturer was adamant that best practices had been applied. The complete absence of splay marks (silver streaking) on the black mouldings added support for this claim. Therefore, although material degradation was identified as the primary (avoidable) cause of the failure, in combination with the unavoidably high residual stresses associated with outsert moulding, the cause of the degradation could not be traced.

Subsequent internal enquiries by the manufacturer revealed that 'virgin material' had not been used to mould the consignment. In an experiment to reduce costs an employee had purchased material from a new source. The established material had a molecular weight of 25,000 but that of the material from the new source was only about 18,000. The new supplier admitted that a high proportion of their material was recycled.

The material used to mould the levers was already hydrolytically degraded. The mouldings were fragile when despatched but remained intact until post mould shrinkage/physical ageing (see Section 7.5) raised residual stresses to the critical level for spontaneous fracture.

Lessons and consequences

1. Well dried and well processed polycarbonate will suffer a molecular weight reduction of about 15% due to hot melt hydrolysis. If the weight average molecular weight of mouldings is less than about 16,000 the material will be fragile. Therefore following the best practice will still result in products of very poor quality if the stock material has a molecular weight of only 18,000.
2. For highly stressed polycarbonate products the use of regrind should be avoided or very severely limited.
3. The performance of polycarbonate mouldings is so sensitive to material quality that only well established and reputable suppliers should be considered.

5.6.13 Glass-reinforced plastic in hydrochloric acid

History

A nest of 10 rectangular GRP tanks for storing hydrochloric acid gave trouble free service for 5 years until one failed and released 1000 litres. This occurred in an enclosed factory space with poor ventilation. The acid fumes condensed on structural, process, and electronic/electrical metalwork, initiating rapid corrosion and the need for a very expensive, extensive, and intensive clean up operation.

Inspection and analysis

The failed tank is shown in Figure 5.17. A sidewall section of the tank was removed and a polished cross-section inspected. The wall was 12 mm thick including a corrosion barrier of approximately 1 mm thickness. The removed section was submitted to an ashing test. The residue was chopped strand glass mat (CSM) with an inner veil of C glass. Weight loss via ashing indicated that the tank laminate had a glass fibre content of 30% by weight.

The wall thickness and laminate construction, and the size and location of sidewall stiffening struts satisfied all the requirements of BS 4994 (Specification for Design and Construction of Vessels and Tanks in Reinforced Plastics).

The fracture surface was inspected. This was predominantly rough with extensive fibre pull-out. A smooth, semi-elliptical area 100 mm in length at the inner surface and 20 mm in length at the outer surface was identified as the fracture initiation region.

The ashing test was repeated on samples taken from the cracked corner. The C glass veil was found to be absent.

Figure 5.17 The failed GRP tank

Failure diagnosis

The failure is due to acid induced stress corrosion cracking. The C glass veil has two purposes. Firstly it acts to arrest crack growth through the laminate, thus protecting the structural E glass against acid exposure. Secondly it reduces shrinkage strains resulting from resin cure. Unreinforced polyester resin will shrink in volume by at least 4% on curing. Homogeneous volume shrinkage is prevented by the constraint of the male mould and the result is a residual biaxial tensile strain. In this case it is likely that the residual strain plus the applied strain (due to hydrostatic pressure of the contents) exceeded the critical strain for resin cracking (about 2%). The structural reinforcement then suffered rapid stress corrosion via direct contact with the acid.

Lessons and consequences

1. Conventional GRP structures used for acid containment rely upon the protection given by an effective resin rich corrosion barrier.
2. Polyester resins described as rigid or resilient need to be at least lightly reinforced with C glass or synthetic fibre to resist crack initiation and growth. It is essential that the reinforcement is continuous and particular care is needed to ensure that potential discontinuities do not coincide with high applied stress. For processes that cannot incorporate reinforcement in the corrosion barrier (e.g. centrifugal casting), high strain at break ‘flexible’ resins must be selected.
3. An internal inspection of the failed tank and the other 9 tanks revealed all other corners to be free from surface cracking. Subject to detailed annual inspection the remaining tanks were deemed to be fit for service.

5.6.14 Polyvinyl chloride lined rinsing tank

History

A six metre long PVC lined steel tank used for rinsing metallic pipes after degreasing, was observed to be severely affected after only six months in service. The rinsing medium had only been water at ambient temperature.

Inspection and analysis

The affected tank is illustrated in Figure 5.18. The walls of the tank are in pristine condition but the base lining is discoloured and wrinkled. The thickness of the lining was measured

Figure 5.18 Discolouration and wrinkling of a PVC lined tank base

and found to be 10% greater at the base than at the walls. This together with the wrinkles confirms that the base lining has distorted due to an expansion of volume. Surface hardness measurements revealed that the base liner was softer than the wall liner suggesting that the volume expansion was due to the absorption of a plasticising fluid.

The brown discolouration was found to be only a surface effect. FTIR analysis revealed that the discoloured material was oxidised PVC.

Failure diagnosis

The rinsing stage removed a cocktail of acids and hydrocarbons from the pipe surfaces. This eventually created a 'denser than water' sludge that, in the absence of agitation, settled upon the base liner. Degraded and highly oxidised aromatic hydrocarbons would be absorbed causing the liner to soften and expand/wrinkle. Aggressive free radicals absorbed from the sludge would initiate oxidation reactions in the PVC.

Lessons and consequences

1. The benefits of dilution may be lost if fluids are not miscible.
2. In the absence of agitation immiscible fluids may separate under the influence of gravity and thus expose container surfaces to high concentrations of prodegradants.

References

1. J. Crank, The Mathematics of Diffusion, Oxford University Press, 1985.
2. B. Ellis and M. S. Found, Composites, 1983, 14, 3, p.237.
3. P. A. Small, Journal of Applied Chemistry, 1953, 3, p.71.
4. Chemical Resistance Data Sheets Vol. I, Rapra Technology, Shrewsbury, UK, 1993.
5. G. Bergman, Corrosion of Plastics and Rubber in Process Equipment, TAPPI Press, Atlanta, GA, USA, 1995.
6. L. M. Adkins, D. W. Daniel and D. A. Rust, Proceedings of the 49th Annual Conference of the SPI Composite Institute, 1994, p.627.
7. H. F. Wachob et al., Fractography of Modern Engineering: Composites and Metals, 2nd Edition, Eds., J. E. Masters and L. N. Gilbertson, ASTM, West Conshohocken, PA, May 1992, p.132.
8. S. N. Sapalidis, P. J. Hogg and S. J. Youd, Journal of Materials Science, 1997, 32, 2, p.309.
9. R. S. Frankle, Polymers & Polymer Composites, 1998, 6, 5, p.269.

10. A. R. Ghughtai, D. M. Smith and M. S. Kumosa, Composites Science & Technology, 1998, 58, 10, p.1641.

11. B. D. Caddock, K. E. Evans and D. Hull, Journal of Materials Science, 1987, 22, 9, p.3368.

12. M. Edge, N. S. Allen, J. E. He, M. Derham and Y. Shinagawa, Polymer Degradation and Stability, 1994, 44, 2, p.193.

13. I. Ghorbel, N. Akele, F. Thominette, P. Spiteri and J. Verdu, Journal of Applied Polymer Science, 1995, 55, 1, p.173.

14. G. C. East and M. Rahman, Polymer, 1999, 40, 9, p.228.

15. M. Ezrin and G. Lavigne, Proceedings of Antec ‘94, Vol. III, San Francisco, CA, p.3302.

16. T. L. St. Clair, J. F. Dezern and C. I. Croall, Proceedings of Antec ’93, Vol. I, New Orleans, LA, p.650.

17. F. J. Campbell, Report NRL – MR – 5158, US Naval Research Lab., August 1983.

18. Sandia Laboratories, Report SC – TM – 70 – 228, April 1970.

19. G. Byrne, New Scientist, 2000, 166, No.2238, p.24.

20. Fire and Flammability Bulletin, March 1999, p.2.

21. A. Chudnovsky, Z. W. Zhou, S. S. Stivala and S. H. Patel, Proceedings of Antec ‘94, Vol. III, San Francisco, CA, p.3284.

22. M. Barker and L. E. Wylde, Proceedings of Plastics Pipes 6, York, March 26-28, 1985, p.37.

23. B. Schlinquer and C. Tournut, Materiaux & Techniques, 1992, 80, 9/10, p.43.

24. W. H. Stockmayer and L. L. Chan, Journal of Polymer Science, 1966, 4, p.437.

6 Environmental Stress Cracking

6.1 Introduction

Environmental stress cracking (ESC) is the most common cause of plastics product failure. It has been identified as being responsible for ~25% of serious failure cases (see Figure 1.1). 90% of these failures involve glassy amorphous thermoplastics in contact with 'secondary fluids'. Such fluids include the following:

Paints, adhesives, cleaning agents, lubricants, plasticisers, inks, aerosol sprays, antirust agents, leak detection fluids, lacquers, fruit essences and vegetable oils.

These can be applied gratuitously or accidentally by any party within the supply chain. ESC failures due to contact with 'primary fluids' i.e. those that are purposely contained by the plastic product or those into which the product is purposely immersed, are comparatively rare. In the clearly defined situations faced by the industries that handle bulk fluids, materials can be exhaustively tested to avoid the problem.

ESC may be defined as the acceleration of stress cracking by contact with a fluid (liquid or vapour) without chemical degradation. The mechanism is purely physical. The interactions between the fluid, the stress, and the polymer include local yielding, fluid absorption, plasticisation, craze initiation, crack growth, and fracture, without irreversible chemical change (i.e. without change in molecular weight, substitution or abstraction). In this respect ESC may be differentiated from stress corrosion cracking (SCC), which by definition must involve stress and polymer degradation.

It is important to emphasise that the fluid only **accelerates** the mechanism. Stress cracking without chemical degradation will eventually occur in the absence of an active fluid and will therefore eventually occur in air. To fully understand ESC it is necessary to understand craze/crack initiation and growth without fluid interaction.

6.2 Crazing and cracking in air

Modest levels of stress applied over long periods of time induce purely 'mechanical degradation' in the form of crazes and cracks. This is the underlying cause of the long-term transition from ductile to brittle behaviour discussed in Chapter 1. It is a very common cause of product failure yet it is easily overlooked in favour of assumed environmental effects. For example 'camper tops' made from thermoformed coextruded sheets were observed to crack after a few years in service. The sheets were acrylonitrile-butadiene-styrene (ABS) capped with rubber modified styrene-acrylonitrile (SAN). Various unsubstantiated theories were proposed including UV degradation, material ageing, and stress cracking due to contact with inappropriate paints and adhesives. Broutman [1] examined 29 failed tops and measured elongation to failure of strips taken from flat low stress areas. Elongations ranged from 2% to 12%, compared with a pristine value of about 25%. By a process of elimination it was concluded that prestressing at modest levels for extended periods of time was the primary cause of embrittlement. This corresponded with the findings of earlier work [2] on prestress ageing effects in rubber modified thermoplastics. After 250 hours of prestressing the elongation to fail had declined to a degree that depended upon material grade, the level of prestressing and the prestressing temperature. A high melt flow index ABS declined from 43% elongation to 2.1% after 250 hours at a stress level equal to 30% of the material's yield strength. A similar drastic reduction might be expected from the application of lower stress levels for longer periods of time (e.g. several years). Crazing around stress concentrating rubber inclusions and the slow transformation of crazes to cracks were identified as the underlying causes of material embrittlement.

Embrittlement due to sustained prestressing or prestraining in air has also been reported [3] for polycarbonate. The elongation at break without prestraining was 12%. After 175 hours at 0.5% the elongation at break was found to be unaffected but after the same period at 1.5% strain, ultimate elongation was reduced to 2%. There is sufficient evidence to suggest that there is a critical thermomechanical history (or combination of histories) that irreversibly degrades the subsequent structural properties of all glassy amorphous thermoplastics. Furthermore this is induced by the initiation and growth of crazes and cracks.

The sequence that culminates in slow crack growth is illustrated in Figure 6.1. At the microscopic level, polymer surfaces unavoidably contain a high density of stress concentrating defects. Typically these range in stress concentration factor from 1 to ~ 50. Under modest tensile stresses (a few MPa), the yield strength (typically < 100 MPa) will be locally exceeded. The microyielded zones blunt the defect and the feature is initially stabilised. The size and shape of a yielded zone are determined by the yield stress contour of the local stress field. However the yield strengths of all polymers decline with time under stress, and the rate of decline is increased with increasing temperature. Therefore with time under stress, the size of the microyielded zones increases. Thin platelike zones grow in area in a plane normal to the principal tensile stress direction. As they do so the zones increase in thickness. Eventually volume expansion induces cavitation within the zone. The feature can now be described as a craze. In transparent polymers they can be seen under appropriate lighting conditions as 'silver cracks'. The change in refractive index at the craze surfaces gives almost total internal reflection. The effect is illustrated in Figure 6.2.

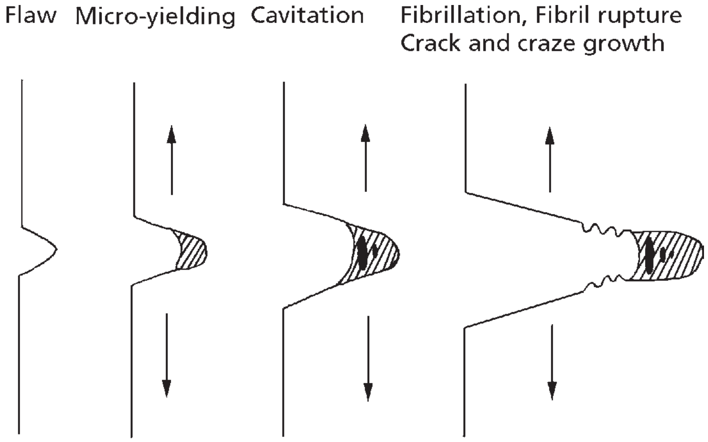


Figure 6.1 Sequence leading to slow crack growth

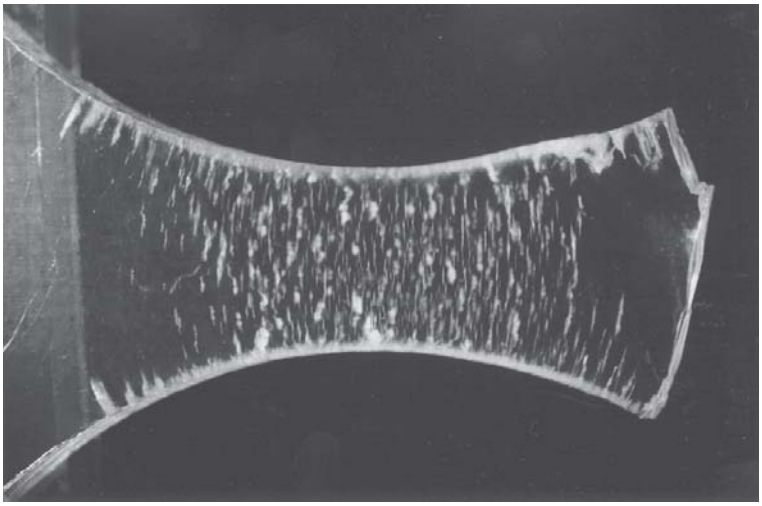


Figure 6.2 Crazes or 'silver cracks' developed in polycarbonate after long term stressing in air

With further growth of the zone and zone cavities, the intercavity material stretches to form highly oriented, load-bearing fibrils. Voids and fibrils are typically of the order of tens of nanometres in diameter. With further growth of the craze, a point is reached when the most highly stretched fibrils (generally those nearest the polymer surface) will rupture. This will lead to an increase in stress at the craze tip, a transient increase in craze growth rate, and an increase in the extension of adjacent fibrils. The sequence is repeated. The now unsupported portion of the craze is called a crack. The crack advances behind a craze of reasonably constant length. The part fractures when the crack reaches a critical length. On examination of fracture surfaces the slow crack growth region (the initial stage up to the critical length) will be macroscopically flat and microscopically 'pimpled'. The pimples are the remnants of ruptured fibrils. The fast crack growth region will be macroscopically uneven (hackle marks, bifurcation etc.) but microscopically smooth. This is illustrated in Figure 6.3. The fracture surfaces that result from cyclic stressing as shown previously in Figure 1.6 also exhibit similar slow and fast growth stages but here in the slow craze growth stage, growth rings may also be observed.

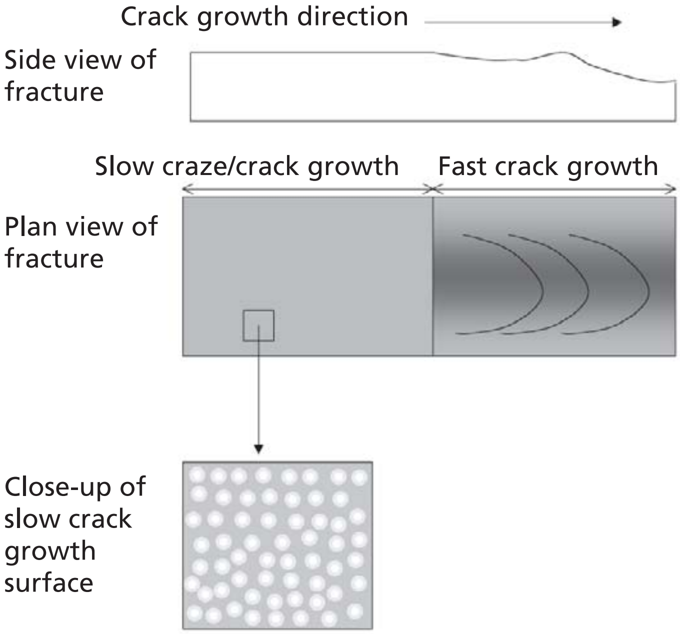


Figure 6.3 Schematic illustration of the slow and fast crack stages under static stress

The progress of slow crack growth (and consequently the durability of the stressed part) depends primarily upon the strength and stability of the craze material, and therefore upon the ultimate properties of the bridging fibrils. Semicrystalline plastics generally form higher tenacity fibrils than amorphous plastics. Higher molecular weight plastics are also superior in this respect. Therefore high molecular weight grades of semicrystalline thermoplastics (see Table 6.1) generally offer the best resistance to slow crack growth and such associated phenomena as ESC, dynamic fatigue fracture, and fretting wear.

To the naked eye, the appearance of crazing in transparent thermoplastics under sustained stress (tensile creep) seems to require an incubation period. At high stresses the 'incubation period' is short, the critical creep strain is high, and the population density of crazes is high. With decreasing applied stress (σ) the incubation period increases, the critical creep strain decreases and the population density decreases. The stress/strain/time coordinates follow the trend shown in Figure 6.4. The trend suggests that there may be a threshold

Table 6.1 Classification of common thermoplastics

Amorphous thermoplastics	**Semicrystalline thermoplastics**
ABS	Acetal
ASA	EVA
Cellulosics	FEP
MBS	Nylons (other than transparent)
PPO/Noryl	PB
PC	PE
PEI	TPX
PMMA	PET
Polysulphone	PBT
Polystyrene	PPS
PVC	PEEK
Polyarylate	PTFE
Polyaryl ether	PVDF
SAN	PU
Transparent Nylon	

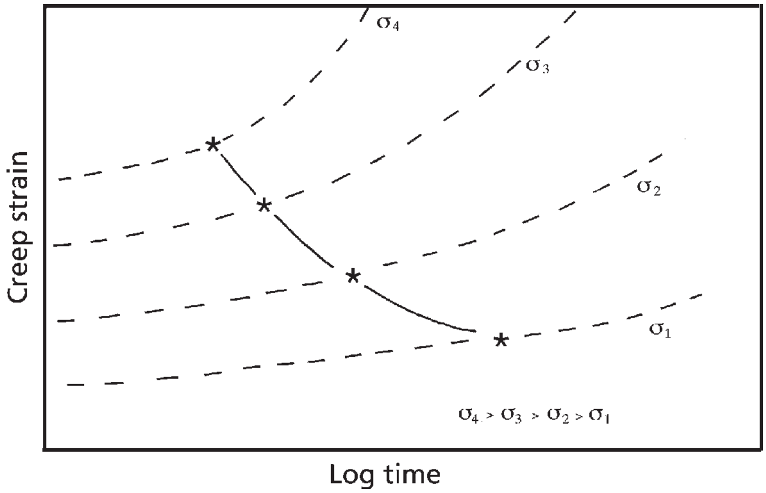


Figure 6.4 Craze initiation under static stress

creep strain below which crazing may never be initiated, and this was proposed by Menges [4] as the most rational engineering design criterion/limit for thermoplastics under long-term stress in air. The limits for polycarbonate, polymethyl methacrylate (PMMA), and unplasticised polyvinyl chloride (UPVC) were all claimed to be about 1% tensile strain regardless of service temperature.

However (and not surprisingly) if the presence of crazes is detected with the aid of a microscope, the 'incubation period' is decreased. The period (and therefore the creep strain) is not a distinct criterion, but rather an indication of the conditions required to grow a craze of detectable size.

Wright [5] developed an indirect method for detecting craze initiation. This could be applied equally to opaque materials. Work on UPVC led to the conclusion that crazes were initiated in air when the inelastic component of the creep strain reached 0.1%. Bruller [6] proposed that the inelastic strain energy density was an even better criterion. For PMMA this would be ~ 0.045 N.mm/mm^3. Such criteria may be employed to predict the stress, strain, time, and temperature combinations that initiate crazing in glassy amorphous thermoplastics in nonaggressive chemical environments.

Brown and co-workers [7] studied the static rupture characteristics of notched medium density polyethylene (MDPE) pipe grade material in air over a range of temperatures. It was found that the activation energies (E) for both ductile failure and brittle failure were the same at 85,500 J/mol. This being similar to the activation energy for the alpha relaxation process would suggest that both modes of failure are controlled by the mobilisation of main chains (e.g. shear flow). With reference to Figure 6.5, if the creep rupture of the material is known at a temperature of T_1 = 80 °C (353 K), then the transition time to brittle failure at another temperature T_2 is given by:

$$\frac{t_c(T_2)}{t_c(T_1)} = \frac{\exp\left(\frac{E}{RT_2}\right)}{\exp\left(\frac{E}{RT_1}\right)}$$

$$\therefore\ t_c(T_2) = t_c(T_1)\exp\left\{\frac{85500}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]\right\}$$

where R is the gas constant (8.3 J/(mol.deg). Therefore, if the transition time at 80 °C is 3×10^4 minutes then transition times may also be predicted at lower temperatures as listed in Table 6.2.

Furthermore, it was established that in the ductile region the time to fail is proportional to σ^{-34}, and therefore if the short-term (1 min) ductile strengths at the above temperatures are known, the minimum stress for ductile failure σ_m can be calculated. For example, if the one minute strength at 20 °C is 11 MPa then:

$$\left(\frac{11}{\sigma_{m(20)}}\right)^{34} = 1.18 \times 10^7 \text{ min}$$

$$\therefore\ \sigma_{m(20)} = 6.8 \text{ MPa}$$

It was also established that in the brittle region the time to fail t_f was proportional to $\sigma^{-3.3}$. Therefore at 20 °C and, say, 4 MPa:

$$\left(\frac{4}{6.8}\right)^{3.3} = \frac{1.18 \times 10^7}{t_f}$$

$$\therefore\ t_f = 6.94 \times 10^7 \text{ min}$$

Consequently the creep rupture characteristics at any temperature can be constructed as shown in Figure 6.6.

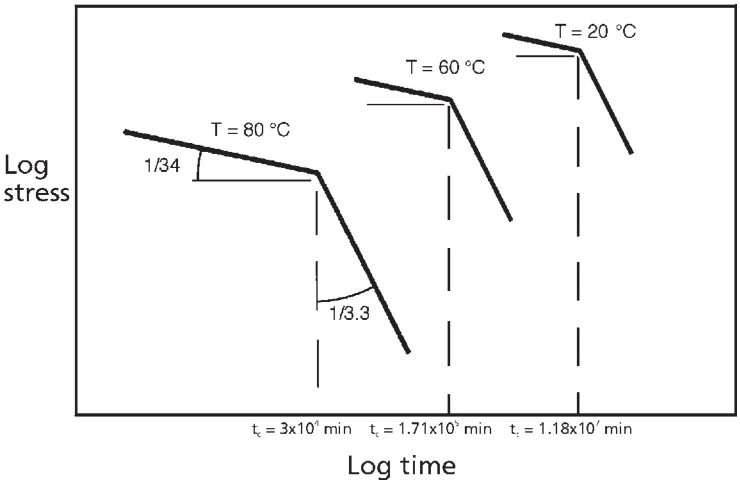


Figure 6.5 Creep rupture of polyethylene (PE)

Table 6.2 Transition time to brittle failure for pipe grade polyethylene

°C	K	t_c (min)
20	293	1.18×10^7
30	303	0.378×10^6
40	313	1.22×10^6
50	323	4.80×10^5
60	333	1.71×10^5
70	343	7.50×10^4

These considerations lead to a single unifying equation:

$$\frac{t_f(T_1)}{t_f(T_2)} = \left(\frac{\sigma(T_2)}{\sigma(T_1)}\right)^n \exp\left\{\frac{85500}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]\right\}$$

Where n = 34 for ductile failure and n = 3.3 for brittle failure.

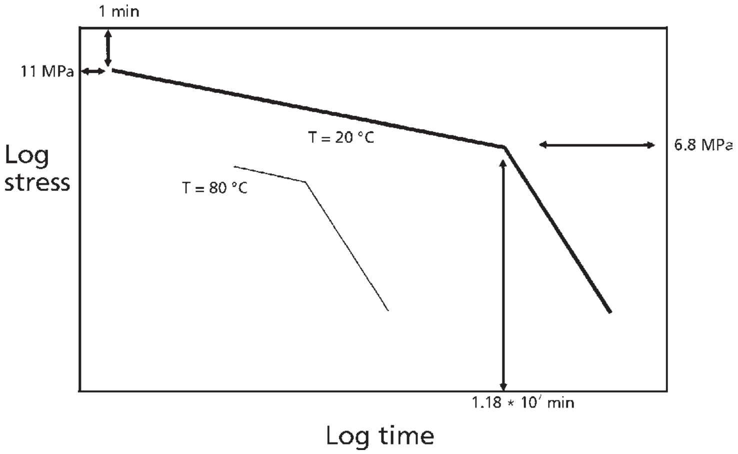


Figure 6.6 Construction of creep rupture behaviour at 20 °C

Brown [8] also studied the initiation and progressive growth of damage at the tip of a notch under constant tensile load as a function of stress intensity and temperature. At very low levels of stress intensity (<0.08 $\text{MPa.m}^{-0.5}$) no damage was detected at the root of the notch. Above ca. 1 $\text{MPa.m}^{-0.5}$ the notch tip was blunted via extensive yielding. Between these limits highly localised damage in the form of microcracking at the root of the notch was initiated as an immediate response to load application. The initial crack opening displacement or COD (U_o), and length of the damaged zone Δ agreed with the predictions of the Dugdale model [9]:

$$\text{Length} = \Delta = \frac{\pi K^2}{\sigma_y^2}$$

$$\text{COD} = U_o = \frac{K^2}{\sigma_y E(1-\eta)}$$

Where K is the stress intensity, σ_y is the yield strength, η is Poisson's ratio and E is the elastic modulus. As the damaged zone was triangular in cross-section with a typical apex angle of 10°, a reasonable estimate of damage length could be calculated by monitoring COD. Manipulation of the above equations reveals that an apex angle of 10° implies that the ratio of σ_y/E is ~ 0.05, i.e. a yield strain of 5%.

Following load application the damage zone length was found to grow at a constant rate until fibril fracture led to crack growth [10], at which point it accelerated. The activation energy controlling this initial damage growth was calculated to be 100,000 J/mol, i.e. similar to that observed for the total time to fracture. The rate of damage growth was proportional to the fourth power of the applied stress. This proportionality and the activation energy are similar to those reported by Williams [11] for crack growth ($\sigma^{4.3}$). It was therefore concluded that crack growth and damage growth are controlled by the same mechanism (microyielding and fibril yield fracture). The dependence of crack growth rate on the power 4.3 of the applied stress can be explained as follows. The velocity of damage growth is determined by the time taken (τ) for the material ahead of the damage zone to change sufficiently, via a decline in strength and stiffness, to extend the damage zone by a given length of Δ (the length of the Dugdale zone). Thus the velocity v is given by:

$v = \Delta/\tau$ and

$$\text{Now}\ \ \Delta = \frac{\pi K^2}{8\sigma_c^{\,2}(\tau)}$$

$$\text{and}\ \ K^2 = U_o \sigma_c(\tau) E(\tau)$$

where U_o is the COD.

The time dependence of strength and stiffness is given by:

$\sigma(t) = \sigma_0 \tau^{-m}$ and $E(t) = E_0 \tau^{-n}$

Therefore:

$$v \propto \sigma_o^{\frac{1}{m+n}}$$

and as m = 0.1 and n = 0.135 for polyethylene [12]:

$$v \propto \sigma_o^{\frac{1}{.235}} \propto \sigma_o^{4.3}$$

This dependency, being based upon the time dependency of the materials' strength and stiffness, is known as 'relaxation controlled crack growth'.

It was established that for a range of test conditions, the growth rate of damage accelerated when the COD reached the critical level of $U_c = 27\ \mu m^{-1}$. Using this value, together with the assumption that a damage length of 1 mm leads to fast fracture, Brown [13] predicted the time to brittle fracture (t_f) using the following simple relationship:

$$t_f = \frac{\alpha a_o + U_c}{\dot{U}_o}$$

Where α is the apex angle in radians, $\dot{U}_o$ is the initial rate of COD and a_o is the notch depth. As shown in Table 6.3, the predictions agree reasonably well with experimental results.

6.3 Crazing and cracking in active fluids

When in contact with certain (mainly organic) fluids the observed sequence of events (craze initiation, craze growth, crack growth and finally fracture) are repeated, but on a shorter time scale and at lower levels of stress and strain than in air. Highly localised

Table 6.3 Comparison of theoretical and experimental times for failure*

a_0 (μm)	σ(MPa)	α(deg)	$\dot{U}_o$ (μm min^{-1})	t_f(theo) (min)	t_f(exp) (min)	t_f(theor)/ t_f(exp)
253	9	7.2	0.11	560	600	0.93
242	10	12.3	0.13	610	515	1.17
240	11	10	0.27	260	310	0.84
241	12	11	0.47	160	195	0.80
135	11	12.9	0.092	630	615	1.02
143	12	12.2	0.148	390	510	0.76
412	8	9	0.146	640	440	1.46
386	9	9	0.142	620	350	1.77
406	10	8.8	0.33	270	240	1.13
407	11	8.8	0.59	150	150	1.01
419	12	10.2	1.11	90	100	0.92

* *$t_f = (\alpha a_0 + Uc)/\dot{U}o$ where Uc = 27 μm, $\dot{U}o$= initial slope of U against t, α = notch angle and a_0 = initial notch depth*

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fluid absorption is probably the mechanism for acceleration. The fluid is preferentially absorbed at sites under high dilational stress such as a stress concentrating defect, a craze, or the tip of a crack. The absorbed fluid locally plasticises the material, reducing its yield strength. Critical strains and stresses for craze initiation with the most active fluids can be as low as 0.1% and a few MPa, respectively. Stresses and strains due to processing and/or assembly can often exceed the critical condition.

For convenience most experimental data in the public domain have been collected at ambient temperatures and test periods of very limited duration (usually ca. 3 hours). Under these conditions, crazing is detected at critical tensile strains of as low as 0.1 to 0.2%. Although by including many fluids, these studies provide an insight into the influence of fluid parameters, the aforementioned restrictions provide little insight into the influence of a plastic's viscoelastic parameters. One exception is the work reported by Crook [14]. Here strips of PMMA and polystyrene (PS) were bent over elliptical straining jigs, immersed in various alcohols, and the minimum strain to craze was established over a temperature range of –40 to +60 °C. The test period was not a constant. As the boundary of the crazed material moved along the strip to lower strains at a decreasing rate, the minimum crazing strain at a time t_R, was defined as that which showed no further strain reduction after a further period equal to three times t_R, that is the apparent asymptotic value. The minimum crazing strain as a function of temperature all had the characteristic form shown in Figure 6.7 (curve A).

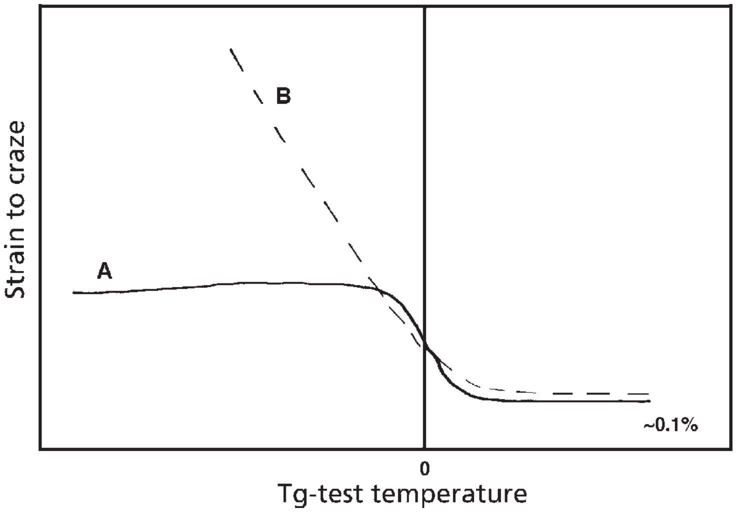

Figure 6.7 Crazing strain as a function of testing temperature

The high temperature minimum values were as follows:

Polystyrene	Methanol	0.2%
	Ethanol	0.15%
	n-Propanol	0.1%
	n-Heptane	0.05%
PMMA	Methanol	0.4%
	n-Butanol	0.1%

The transition temperature between high and low strain was found to be the T_g of the fluid plasticised polymer.

In a similar investigation Kambour [15] reported a different characteristic (curve B in Figure 6.7). Again under conditions where the test temperature exceeded the T_g of the polymer/solvent mixture, the minimum critical strains were around 0.1 to 0.2%, but below T_g the critical strain increased monotonically. The major difference in the test methods is that Kambour employed a constant test period (3 hours).

It is of interest that all the features in Figure 6.7 can be explained using Wright's [5] inelastic strain criterion originally developed for air crazing. This may be expressed as:

$$\varepsilon_c = \frac{x}{\left\{1 - \exp\left(\frac{-t_R}{\tau}\right)\right\}}$$

Where ε_c is the total critical strain to craze, x is the critical inelastic strain, t_R is the test duration, and τ is the relaxation time of a single representative viscoelastic element for the plasticised polymer.

For $T >> T_g$ (according to both Crook and Kambour):

τ is small and therefore for any practical test duration $\left|\left(\frac{-t_R}{\tau}\right)\right|$ tends to infinity and the total strain to craze tends to x (ca. 0.1%) this being independent of temperature. This is consistent with observations.

For $T < T_g$ (Kambour)

As the test period is a constant and as τ increases with decreasing temperature, ε_c will increase with decreasing temperature as observed.

For $T < T_g$ (Crook)

The test period is not a constant but changes to satisfy:

$$\frac{x}{1-\exp\left(\frac{-t_R}{\tau}\right)} - \frac{x}{1-\exp\left(\frac{-4t_R}{\tau}\right)} = \Omega$$

Where Ω is the strain resolution of the experiment. This can only be satisfied if the ratio $\left|\left(\frac{-t_R}{\tau}\right)\right|$ is a constant, and therefore ε_c is independent of temperature and its value is determined by Ω. This is consistent with observations.

The observation that craze initiation in air and in various craze promoting fluids is triggered by the same viscoelastic condition (a critical level of inelastic strain) would be of considerable practical significance if confirmed. Various studies lend support to the thesis and two of these can be referred to. Reference [3] indicated that under constant strain for 175 hours at ambient temperatures, the critical strain for embrittlement of polycarbonate in air was within the range 0.5 to 1.5%. Under the same conditions but in contact with various fluids used in medical applications the transition to brittle failure occurred in the same strain time range. The results are summarised in Table 6.4.

Arnold's [16] more detailed study of the interaction between polycarbonate and ethanol also lends support to the thesis. Conventionally in ESC testing the stress and the fluid are applied

Table 6.4 Elongation at break of polycarbonate following immersion in air and various clinical fluids at two strain levels

	Elongation at break after prestraining for 175 hours at X%	
Environment	X = 0.5%	X = 1.5%
Air	12%	2%
Isopropanol	10%	0.5%
10% Bleach	17%	Fractured
2% Glutaraldehyde	12%	1%
Povidone (polyvinylpyrrolidone-iodine)	11%	3%
Lipid	14%	Fractured

simultaneously. However, Arnold applied the stress for a given time before fluid immersion or contact. He found that the time to detectable cracking depended only upon the time under stress. This is clarified in Table 6.5.

A reasonable interpretation of this finding is as follows. Craze initiation is not accelerated by contact with ethanol, but craze growth is. Crazes are initiated in air or in ethanol at exactly the same combination of time, temperature, stress, and strain as determined by the singular inelastic strain criterion. However, in air the incubated crazes are too small for optical detection. If ethanol is present at initiation (in this case after 100,000 seconds under stress) then, due to accelerated growth, they are almost immediately detected. Further work is needed to confirm or deny that this effect is universal for other fluid/plastic pairs. If confirmed then the durability implications would be very serious. After some months or years in service many amorphous thermoplastic products in contact only with air will exceed the 0.1% inelastic strain condition, and will therefore be damaged via very small quasi-stable crazes. In this state the products would crack soon, or immediately, after coming into contact with moderately aggressive ESC fluids. For example cleaning agents may by traditional testing (simultaneous application of stress and fluid) be classified as modest ESC agents in that they do not trigger cracking for several years at a given stress. However if the product is cleaned after several years under the given stress it will crack very quickly. This may then explain apparently anomalous failures of products that are subjected to fluid contact after many years of service. Cases 6.5.1 and 6.5.3 probably fall into this category.

Table 6.5 Effect of prestressing time on stress cracking time for ethanol in contact with polycarbonate

Prestressing time (s)	Fluid contact time to crack (s)	Time under stress to crack (s)
0	100,000	100,000
50,000	50,000	100,000
100,000	≥ 0	100,000

6.4 Performance of specific materials

Polyethylene terephthalate (PET)

Failures due to ESC are rare unless the material is in the amorphous state. Carbonated beverage bottles are manufactured using injection moulded preforms. Rapid cooling ensures minimal crystallinity. Stretch blow moulding of the preform generates molecular orientation in the plane of the bottle wall and therefore a closely packed highly crystalline structure. However the bottle neck and base are not significantly stretched and these regions, being of low crystallinity, are susceptible to ESC. There have been periodic outbreaks of polyethylene terephthalate (PET) bottle failures due to features called 'smiley cracks' on bottle bases. These failures generally occur after filling but before retail distribution and where this occurs in densely packed warehouses there is some circumstantial evidence to suggest that the rupture of one bottle triggers the rupture of others, leading to large stock losses.

The smiley cracks are in fact crazes that have initiated on the outside wall of the base. It is probable that all bottles are crazed as a result of the blow moulding stresses, but in most cases these are small and cannot be seen with the naked eye. Many factors have been identified as causes for rapid craze growth and reduced durability in storage, including increased warehouse temperatures (and therefore also increased bottle pressures) and high bottle filling speeds. However ESC due to contact with silicone based 'line lubricants' is the most frequently identified culprit.

The candidate mechanisms for the apparent chain reaction of failures in storage are probably as follows. Adjacent bottles are wetted by beverage leakage, which in many cases include in their formulation low concentrations of fruit essences or essential oils. These act as powerful ESC agents when concentrated by evaporation. Alternatively, rosins used in the adhesives to bond cardboard packaging are leached out due to drenching by the first bottle failure. Rosins are ESC agents for amorphous thermoplastics.

Polycarbonate (PC)

A higher than expected proportion of ESC failures involve polycarbonate because the material is selected for applications that demand toughness. It is a premium 'engineering plastic' yet it is as susceptible to ESC fracture as SAN, PVC, PMMA, or many other (supposedly less robust) amorphous thermoplastics. The failure of polycarbonate crash helmets due to paints and adhesives, discussed in Chapter 1 is a good example.

Polycarbonate sheeting was used to construct hermetically sealed chambers for the execution of processes involving dangerous bacterial agents. Transparency and impact toughness were essential. To ensure that the chambers were hermetically sealed they were sprayed with a proprietary leak detection fluid. The fluid stress cracked the polycarbonate and all the chambers had to be scrapped (due to leakage).

Blow moulded polycarbonate baby milk bottles were reported to suffer from 'spontaneous disintegration'. This commonly occurred when the bottle was simply standing empty on a kitchen table. Fragments were found to be severely crazed on the outside surfaces. A considerable amount of detective work was required to identify that an aerosol fly spray was the culprit fluid. This together with excessive processed-in stress (> 8 MPa) was not quite sufficient to explain the phenomenon. Hydrolytic degradation of surfaces due to repeated hot water washing/sterilisation was the additional factor needed to explain the rapidity and severity of ESC attack.

Ignition-proofed fluorescent lighting with polycarbonate glazing fractured in a chemical plant. The cause was traced to toluene vapour.

Retaining bosses in automotive door holder assemblies cracked in service. The problem was traced to oil and phosphite coated self-tapping screws. Zinc chromated screws were recommended to solve the problem.

Case 6.5.4 deals with the failure of polycarbonate instrument housings resulting from contact with dioctyl phthalate (DOP) plasticised PVC film.

Kambour [17] compiled the short-term critical strains for environmental craze initiation in a range of fluids. Minimum critical strains were 0.2%. Henry [18] embarked upon a similar exercise but in addition attempted to correlate the partial solubility parameters of the fluid with the severity of ESC attack. The severity of attack increased as the partial parameters of the fluid approached the following values:

Dispersive δ_D = 18 MPa $^{0.5}$
Polar δ_P = 10 MPa $^{0.5}$
Hydrogen bonding δ_H = 8 MPa $^{0.5}$

and therefore a total solubility parameter of $(\delta_D^2+\delta_P^2+\delta_H^2)^{0.5} = 22$

Polyvinyl chloride (PVC)

Although rigid PVC suffers from ESC in a wide range of fluids, the author is unaware of any cases involving the failure of heavily plasticised PVC. Rigid PVC will stress crack in contact with common plasticisers such as DOP. However these fluids when mixed into rigid PVC to produce plasticised PVC will not cause cracking under stress, whether the material is exposed to air or further DOP contact. ESC is promoted by **localised** fluid absorption, but suppressed by bulk absorption.

The rigid PVC water mains pipeline shown in Figure 6.8 failed at solvent-based cemented joints because the line was pressure tested too soon after jointing. The solvent in the cement had not been given sufficient time to evaporate, and cracking was preferentially observed adjacent to excessive cement residues (which require a longer ‘hardening’ time). The solvents in proprietary cements are powerful stress cracking agents for PVC, and therefore ESC problems can only be avoided by strict compliance with installation rules. A relevant example is covered by case 6.5.14.

Vincent and Raha [19] evaluated the short-term critical strain for craze initiation of PVC in contact with 65 fluids. Minimum critical strains were as low as 0.07%.

Hough and Wright [20] used a constant stressing rate (4 MPa/h) to assess the critical time, stress, and strain for ESC initiation in a selection of 41 fluids. The results are listed in Table 6.6. Many contour plots of ESC severity versus fluid parameters were assessed to establish the best correlation. It is apparent from Figure 6.9 that the rapidity of attack as expressed by the ‘severity index’ of the fluid is dominated by its hydrogen bonding parameter δ_H. Fluids with a δ_H that approached 7.5 MPa $^{0.5}$ were the most aggressive. The molar volume of the fluid had a significant but secondary influence, this being accommodated by the definition of the severity index, SI, where:

$$SI = \frac{\text{critical initiation time (s)}}{(\text{molar volume})^{2/3}}$$

Figure 6.8 ESC failure of a 250 mm diameter PVC water main (the white deposit is excess cement)

Table 6.6 UPVC initiation data at 4 MPa/h and 20 °C

Environment	Initiation time seconds	Initiation stress MPa	Initiation strain %
Methyl ethyl ketone	3.60 x 10^2	0.40	0.02
Chloroform	4.50 x 10^2	0.50	0.02
Acetone	9.00 x 10^2	1.00	0.03
Ethyl acetate	9.00 x 10^2	1.00	0.03
Chlorobenzene	9.90 x 10^2	1.10	0.04
Benzene	1.35 x 10^3	1.50	0.05
Butyl acetate	1.35 x 10^3	1.50	0.05
Dibenzyl ether	1.80 x 10^3	2.00	0.06
Amyl acetate	2.25 x 10^3	2.50	0.08
Di-ethyl ether	2.25 x 10^3	2.50	0.08
Toluene	2.25 x 10^3	2.50	0.08
2-Ethoxy ethanol	2.61 x 10^3	2.90	0.09
Methyl salicylate	2.70 x 10^3	3.00	0.09
N-Butyl lactate	2.70 x 10^3	3.00	0.09
Tri-*n*-butyl-*o*-phosphate	2.70 x 10^3	3.00	0.09
2-Methoxy ethanol	4.05 x 10^3	4.50	0.13
1,1,1-Trichloroethane	4.50 x 10^3	5.00	0.15
Di-acetone alcohol	5.40 x 10^3	6.00	0.17
Di-n-butyl phthalate	5.40 x 10^3	6.00	0.17
Tetrachloroethylene	6.30 x 10^3	7.00	0.20
2-Butoxy ethanol	6.48 x 10^3	7.20	0.21
Benzyl alcohol	7.20 x 10^3	8.00	0.23
o-Xylene	7.56 x 10^3	8.40	0.24
Carbon tetrachloride	9.18 x 10^3	10.20	0.30
Decan-1-ol	1.31 x 10^4	14.50	0.41
Dioctyle phthalate	1.35 x 10^4	15.00	0.44
Propan-2-ol	1.35 x 10^4	15.00	0.44
Dioctyl sebacate	1.53 x 10^4	17.00	0.50
Propan-1-ol	1.80 x 10^4	20.00	0.60

Table 6.6 Continued

Environment	Initiation time seconds	Initiation stress MPa	Initiation strain %
Cyclohexane	2.07 x 10^4	23.00	0.70
n-Butanol	2.07 x 10^4	23.00	0.70
Butan-2-ol	2.16 x 10^4	24.00	0.74
Ethanol	2.16 x 10^4	24.00	0.74
2-Methyl propan-1-ol	2.25 x 10^4	25.00	0.78
Methanol	2.34 x 10^4	26.00	0.80
n-Decane	2.39 x 10^4	26.50	0.83
Cyclohexanol	2.43 x 10^4	27.00	0.85
n-Dodecane	2.61 x 10^4	29.00	0.92
Propylene glycol	3.33 x 10^4	37.00	1.26
Ethane diol	3.38 x 10^4	37.50	1.30
Water	4.59 x 10^4	51.00	2.50

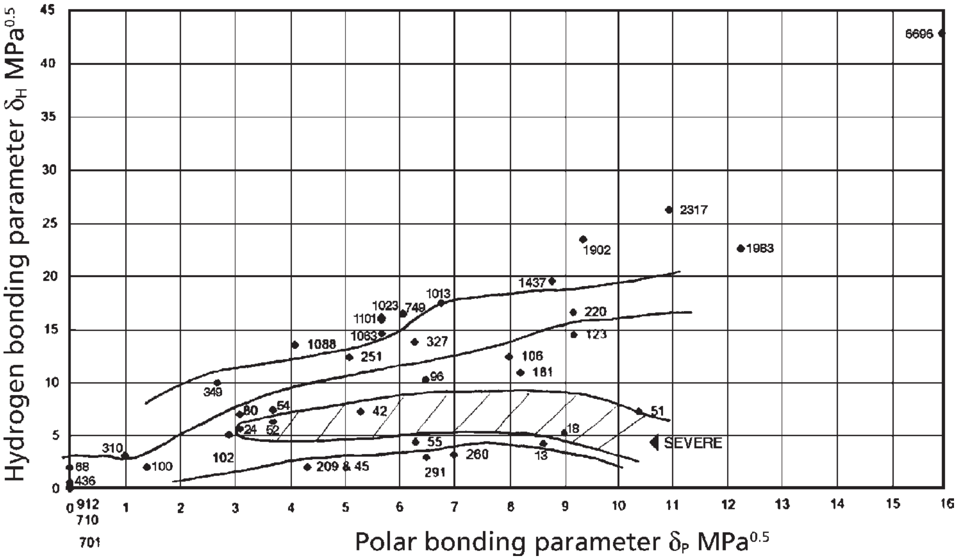

Figure 6.9 PVC severity index for various fluids on the hydrogen bonding vs. polar bonding plot

Polymethyl methacrylate (PMMA)

Cases 6.5.3 and 6.5.15 describe the ESC failure of acrylic sight glasses.

PMMA sheet is used extensively in aircraft glazing. Surface crazing can be readily detected by any observant passenger. Windows are frequently replaced or refurbished. The latter involves surface grinding and repolishing. Although this expensive task has stimulated a great deal of research, the critical environmental parameters that determine durability have yet to be satisfactorily identified. It is known that water absorption reduces crazing stress by 7 MPa/%. It is also known that atmospheric pollution (e.g. the eruption of Mount Helena) can dramatically reduce time to visible crazing. Sulphuric acid is suspected to be the critical pollutant species.

Hough and Wright (20) used a constant stressing rate (4 MPa/h) to assess the critical time, stress, and strain for ESC initiation in a selection of 41 fluids. The results listed in Table 6.7 and the contour plot shown Figure 6.10 reveal a similar pattern to that of PVC. Fluids with a hydrogen bonding parameter δ_H that approached 7.5 MPa $^{0.5}$ were the most aggressive.

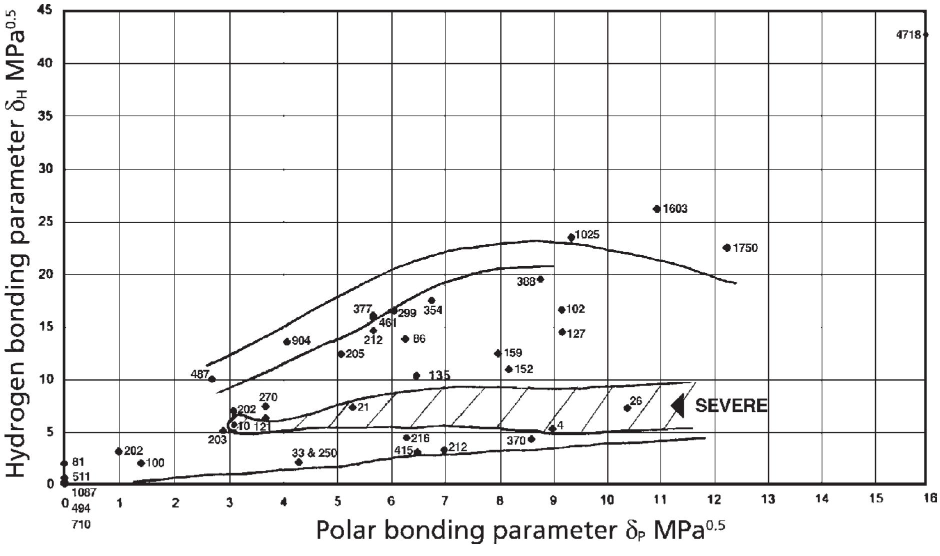

Figure 6.10 PMMA severity index for various fluids on the hydrogen bonding vs. polar bonding plot

Table 6.7 PMMA initiation data at 4 MPa/hr and 20 °C

Environment	Initiation time seconds	Initiation stress MPa	Initiation strain %
Methyl ethyl ketone	90	0.10	0.001
Chloroform	1.80×10^2	0.20	0.01
Acetone	4.50×10^2	0.50	0.02
Ethyl acetate	4.50×10^2	0.50	0.02
Chlorobenzene	7.20×10^2	0.80	0.03
Benzene	1.62×10^3	1.80	0.05
Benzyl alcohol	1.89×10^3	2.10	0.07
2-Methoxy ethanol	2.16×10^3	2.40	0.08
Toluene	2.25×10^3	2.50	0.08
2-Ethoxy ethanol	2.70×10^3	3.00	0.10
Di-acetone alcohol	3.78×10^3	4.20	0.14
n-Butyl lactate	3.78×10^3	4.20	0.14
Butyl acetate	3.87×10^3	4.30	0.14
Methyl salicylate	4.05×10^3	4.50	0.15
Butan-2-ol	4.32×10^3	4.80	0.17
Di-ethyl ether	4.50×10^3	5.00	0.17
o-Xylene	4.95×10^3	5.50	0.19
2-Butoxy ethanol	5.31×10^3	5.90	0.20
Propan-2-ol	5.40×10^3	6.00	0.21
1,1,1-Trichloroethane	5.40×10^3	6.00	0.21
Amyl acetate	5.67×10^3	6.30	0.22
Ethanol	5.85×10^3	6.50	0.22
Propan-1-ol	6.30×10^3	7.00	0.24
n-Butanol	7.65×10^3	8.50	0.30
Dibenzyl ether	9.00×10^3	10.00	0.35
Tetrachloroethylene	9.00×10^3	10.00	0.35
2-Methyl propan-1-ol	9.45×10^3	10.50	0.37
Tri-*n*-butyl-*o*-phosphate	1.06×10^4	11.80	0.42
Carbon tetrachloride	1.08×10^4	12.00	0.43

Table 6.7 Continued

Environment	Initiation time seconds	Initiation stress MPa	Initiation strain %
Dioctyl phthalate	1.11×10^4	12.30	0.44
Di-n-butyl phthalate	1.53×10^4	17.00	0.64
Decan-1-ol	1.62×10^4	18.00	0.66
Dioctyl sebacate	1.62×10^4	18.00	0.66
n-Decane	1.67×10^4	18.50	0.68
Propylene glycol	1.80×10^4	20.00	0.76
Cyclohexanol	2.03×10^4	22.50	0.86
Methanol	2.07×10^4	23.00	0.88
Ethane diol	2.34×10^4	26.00	1.02
Cyclohexane	2.48×10^4	27.50	1.10
n-Dodecane	2.66×10^4	29.50	1.20
Water	3.24×10^4	36.00	1.60

Polyethylene (PE)

Examples of ESC failure are included in Cases 6.5.6, 6.5.11 and 6.5.16.

The term 'Environmental Stress Cracking' was used first in the context of polyethylene cable insulation. It has been subject to enduring attention, but the objective of this attention differs from that applied to amorphous plastics. The intention in this instance has been to optimise material grades for inherent stress crack resistance (in non-aggressive environments such as air and water). In the long term and under stress, polyethylene exhibits slow crack growth and brittle fracture in non-aggressive environments. This is of particular and critical importance because polyethylene is used extensively in applications that demand long-term durability (cable, pipe, landfill linings, geotextiles, etc.). At ambient temperatures for 'high quality' grades the transition to brittle failure will occur after many years under stress. To maintain or optimise material quality accelerated test methods are needed. Increasing the applied stress is not an option because this induces ductile failure. Increasing test temperature is frequently used, but it is known that above temperatures of ca. 50 °C, morphological changes are induced and the method becomes less valid. Certain chemical environments such as Igepal CO-630 (a nonylphenoxypolyethanol surfactant) have been found to accelerate the phenomenon, particularly when combined with elevated temperatures and notching. Notching does not accelerate failures in the ductile region, but it does so in the brittle region. Furthermore, by notching, the failure site is predetermined and precisely characterised, thereby removing the major source of poor reproducibility and high scatter (the unknown severity of inherent flaws).

A large body of archival data of this type is available covering and comparing the response of many material grades to a few chemical environments. This contrasts with the one or two grades of the amorphous plastics usually studied in many chemical environments.

Brown [21] compared the time to brittle fracture in air and in Igepal using a notched specimen geometry for 21 different grades of medium density polyethylene. It was established that at stresses that produced fracture in less than 15 hours, the Igepal did not accelerate the failure. At lower stresses (and hence longer times) the failure time in Igepal was progressively reduced compared with that in air, by up to a factor of 60. The 'order of merit' for grades established in air was reasonably retained by testing in Igepal. It was therefore concluded that testing in Igepal was a valuable method for quality control and grade optimisation. In a subsequent paper Brown [22] provided the following explanation for the delayed influence of the Igepal. The fluid is rapidly absorbed in the amorphous regions at the tip of the notch. This leads to an acceleration of craze growth (typically doubling the rate even below the 15 hour failure condition). However, it would be reasonable to assume that plasticisation of the crystalline regions would take far longer and that the strength of the craze fibrils is determined by the integrity of the crystals. Brown calculates that 15 hours is a reasonable time for Igepal to completely diffuse into a crystalline craze fibril.

The measurement of crack growth as a function of stress intensity, temperature and detergent concentration has revealed interesting insights into the mechanisms responsible for ESC. In general the crack speed is determined by the slowest of 3 competing rate processes. These include the relaxation of material properties such as the yield strength, which declines with time, the rate of diffusion of the fluid into the crystallites, and the rate of flow of the fluid to the crack tip.

As shown in Figure 6.11, Chan [23] observed the following:

i) In distilled water (and indeed air), the crack speed v is proportional to the fourth power (slope = 0.25) of the stress intensity over the complete range of crack speed. This indicates 'relaxation controlled crack growth' as previously discussed in Section 6.2.

ii) In detergent, relaxation controlled crack growth operates up to (in this case) a speed of 10^{-7} ms^{-1}. At any given stress intensity in this range the crack speed in detergent is about twice the crack speed in water, due to plasticisation at the crack tip.

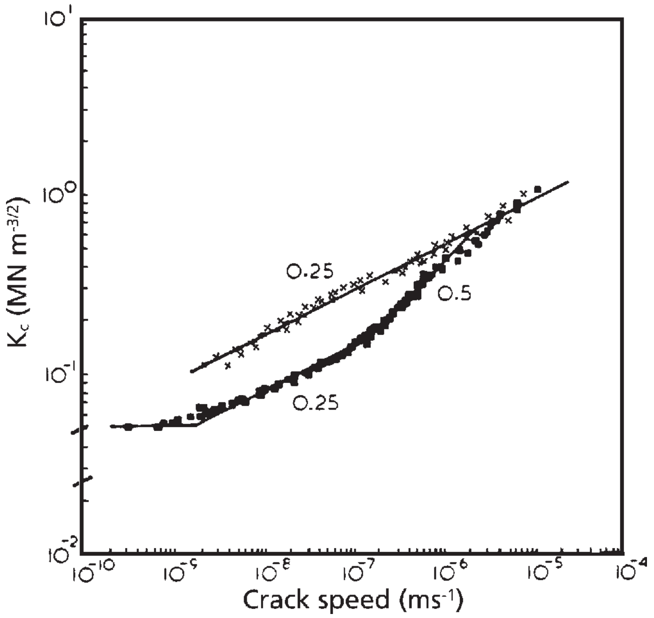

Figure 6.11 Crack growth rates for HDPE in distilled water (x) and 2% Comprox detergent (•)

(Reprinted from Polymer, Volume 24, M.K.V. Chan and J.G. Williams, Slow Stable Crack Growth in High Density Polyethylenes, p.234-244, Copyright © 1983, with permission from Elsevier Science.)

iii) At speeds above 10^{-7} ms^{-1} in detergent, v is proportional to the square of the stress intensity. Here crack growth is controlled by hydraulic flow of the detergent to the crack tip.

iv) At speeds above 10^{-5} ms^{-1} in detergent, hydraulic flow is insufficient to reach the crack tip, and crack growth reverts to relaxation control in the absence of plasticisation (i.e. it coincides with crack growth in water or air).

Ohde [24] also studied various other detergents with increasing molecular size, expressed as the number n of repeat oxyethylene units. The activation energy for crack growth increased monotonically from 45 to 185 KJ/mol as n increased from 8 to 30 (Igepal CO-630 has n = 9).

Tonyali [25] reported some interesting findings of crack growth of low density polyethylene (LDPE) in mixtures of Igepal CO-630 and other fluids. Under the selected test conditions, 10% Igepal in ethanol resulted in a crack speed of only 0.02 mm/hour, whilst the same concentration in water resulted in a crack speed of 0.5 mm/hour. The explanation given for this is that the detergent does not form micelles in ethanol but does so in water. Micelles are structured concentrations of the detergent molecules. It was also established that adding small amounts of solvents to detergent/water mixtures increased crack growth rate. For example, 0.5% xylene increased crack speed from 0.4 to 0.59 mm/hour. The addition of the same amount of nonyl phenol increased the speed rather less. This would seem to be a promising method of accelerating crack growth for testing purposes, by using micelles to deliver small amounts of solvents to the crack tip and thereby avoiding excessive plasticisation and notch tip blunting.

A significant proportion of crack growth studies in the presence of liquids have concentrated on the relatively fast crack growth regime, and considerable effort has been expended in attempts to prove or disprove the hydraulic control mechanism. However, as the conditions for this regime of cracking are so severe (growth rates of ca.1 mm/hour) compared with those encountered in service, they are of limited practical interest.

Isaksen [26] studied the effect of a range of fluids on the time to failure under a static tensile stress of 14 MPa. The high density polyethylene (HDPE) had a relatively low molecular weight (melt flow index (MFI) = 40). He established a 'reasonable correlation' between equilibrium absorption and time to fail. His data together with various fluid parameters are shown in Table 6.8. Inspection of these data reveals that the polar solubility of the fluid correlates better than equilibrium absorption. Evidently polyethylene, which has the lowest polarity of all polymers, is the most rapidly attacked by fluids of (similar) low polarity.

Marshall (private communication) found that for a notched HDPE pipe grade, a range of alcohols actually increase the time to failure but this was only the case at high values of stress intensity. Thus at K=1 MN.m$^{-3/2}$, the following data were reported:

	Av. Failure time (hours)
Air	0.42
Methanol	7.6
Ethanol	12.5
Propanol	18
Butanol	35
Pentanol	25
Hexanol	25
Heptanol	23.5
Octanol	24
Decanol	20
Dodecanol	0.75

Table 6.8 Absorption and time to failure for HDPE in various fluids

	Molar volume cm^3/mol	δ_d	δ_p	δ_H	δ	Absorption %	Time to fail (h)	Log time to fail
Benzene	89.4	18.4	0	2	18.6	74.5	0.77	-0.11351
Xylene	121	17.8	1	3.1	18	60.4	1.1	0.041393
Hexane	131.6	14.9	0	0	14.9	53.2	0.3	-0.52288
Acetone	74	15.5	10.4	7	20.1	50	10.4	1.017033
Toluene	106.8	18	1.4	2	18.2	43	0.85	-0.07058
Butyl acetate	132.5	15.8	3.7	6.3	17.4	22	1	0
Acetic acid	57.1	14.5	8	13.5	21.3	11.3	3.7	0.568202
Amyl alcohol					22	9.8	2.5	0.39794
Ethanol	58.5	15.8	8.8	19.4	26.6	8.7	13.2	1.120574
iso-Propanol	76.8	15.8	6.1	16.4	23.5	5.7	6.5	0.812913
n-Propanol	75.2	16	6.8	17.4	24.6	8.5	1.7	0.230449
Dodecyl alcohol						4.6	3.4	0.531479
Diethylene glycol	95.3	16.2	14.7	20.5	29.9	8.5	28.5	1.454845
Tricresyl phosphate	613	19	12.3	4.5	23.1	0.6	14.6	1.164353
Water	18	15.5	16	42.4	47.9	0.2	55	1.740363

At lower values of stress intensity (K = 0.3 $MN.m^{-3/2}$) the material failed in 943 hours in air but in only 330 hours in methanol. Regardless of the cause, these complexities raise serious doubts concerning the validity of short-term tests on notched specimens.

The influence of alcohols has also been examined in some detail by Ogata [27]. The crack speed over a range of stress intensity (K = 0.5 to 2 $MN.m^{-3/2}$) was measured in methanol, ethanol, propanol, and butanol, at selected temperatures in the range from 7 to 37 °C. As shown in Table 6.9, the time to fail results from Marshall and the crack speed results from Ogata are compatible.

Table 6.9 Comparison of crack speed and time to fail in various alcohols

	Time to fail (h)	Crack speed (mm/s)
Methanol	7.6	1.5
Ethanol	12.5	0.8
Propanol	18	0.5
Butanol	35	0.3

The viscosities of the alcohols increase from methanol through to butanol. Therefore these results would tend to support the theory that, at these comparatively high levels of stress intensity, the crack speed and the time to fail are controlled by fluid flow to the crack tip. However on detailed inspection, Ogata concluded that the process was controlled by diffusion at the crack tip. The rate of diffusion decreases with increasing molecular volume i.e. from methanol through to butanol.

Shanahan [28] concentrated on the correlation between ESC and the absorption of 'weak swelling fluids'. The fluids included silicone oils (covering a range of viscosities), paraffin oil, nitroethane, ethylene glycol, tricresyl phosphate, and diiodomethane. He found that:

i) The higher the equilibrium absorption the less aggressive the ESC agent. This was attributed to the blunting of crack tips.

ii) Under low stress and long time conditions, the higher the viscosity of silicone oil, the shorter the time to failure. This was attributed to the crack tip blunting effect. (The higher the viscosity, the higher the molecular volume and the lower the absorption.)

iii) At high stress the time to failure was increased with oil viscosity, this being due to restricted transport of the fluid to the crack tip.

It can be concluded that depending upon the test method, contact with a particular fluid can extend or reduce the time to failure. With unnotched specimens, the time to failure is reduced by bulk absorption. With notched specimens, highly absorbing fluids can increase the time to failure via notch blunting.

The molecular weight has been established as the most significant and consistent material variable to influence ESC resistance. Increasing molecular weight and therefore decreasing

MFI increases ESC resistance. The following model is generally accepted. Semi-crystalline polyethylene comprises regions of folded chains (lamellae) isolated in a continuous amorphous phase. A proportion of chains in the amorphous phase connect adjacent lamellae directly, or via entanglements. These are called 'tie molecules'. Obviously, to be cohesively effective, tie molecules need to be long enough to bridge the inter-lamellar distance when randomly coiled. This distance is normally taken as twice the lamellar thickness plus the inter-lamellar (amorphous) thickness. The density of effective tie molecules increases with increasing molecular weight and is influenced by both the degree of crystallinity and crystal size.

Brown [29] compared the rate of crack growth in air of HDPE in four grades ranging in weight average molecular weight from 67,000 to 158,000. At 115 kJ/mol, the activation energy was independent of molecular weight but crack growth rates decreased by a factor of 5 from the lowest to the highest molecular weight. The effect on time to failure is even more pronounced, presumably because it includes initiation. For example, Lander [30] reports an increase in time to fail in detergent from 0.1 hours to 1000 hours caused by decreasing the melt flow index from 20 to 0.3.

The molecular weight distribution is also important. For grades with the same weight average molecular weight it has been reported that the preponderance of the high molecular weight fraction has the greatest influence on ESC resistance.

As the yield strength of polyethylene is not particularly sensitive to molecular weight or MFI, it would be reasonable to suppose that the initiation of yielding at defect sites is not the controlling factor for ESC. It has been amply demonstrated by Owen [31] and others that it is the post yield behaviour that has the strongest influence on ESC resistance. Grades that exhibit pronounced strain (orientation) hardening after yielding offer the better resistance. Such grades have higher molecular weights and stronger craze fibrils. ESC in polyethylene is controlled by craze strength rather than craze initiation.

A second important influence is the presence of side chain branches. These suppress crystallisation to a degree, and decrease the lamellar thickness. They also increase resistance to disentanglement. Copolymerisations with alkenes (e.g. butenes, hexanes, and octenes) are particularly effective as a means of enhancing stress crack resistance for this reason. Brown [32] measured crack growth rates as a function of copolymer branch density (expressed in terms of branches per 1000 main chain carbon atoms). Under the chosen test conditions, the homopolymer had a crack growth rate of 0.1 mm/hour. With 2 branches/1000 carbons it had reduced to 0.01 mm/hour and at 5 branches to 0.00001 mm/hour. Further increase in branch density had little effect.

With an increase in branch density from 0 to 4.7 branches per 1000 carbons, Brown was able to list the following findings:

i) Degree of crystallinity reduced from 71% to 52% and the yield strength decreased from 24 MPa to 15.5 MPa.

ii) Lamellar thickness decreased from 33 to 17 nanometres.

iii) The thickness of the amorphous regions increased only marginally (from 13 to 16 nanometres).

iv) The inter-lamellar distance decreased from 78 to 50 nanometres.

v) A statistical analysis indicated an increase in tie molecule density from 1.64 to 92.7.

vi) The decrease in crack growth rates was mirrored by the calculated increase in tie molecule density.

The influence of density and degree of crystallinity is quite complex and often apparently contradictory. For the copolymer reduced density improves performance. Quenching of a copolymer enhances performance by a further reduction in density. ESC resistance therefore increases despite decreasing yield strength. This supports the previous observation that post yield behaviour is the dominant issue. However, for the homopolymer, quenching reduces ESC performance [33]. It can only be surmised that quenching of the homopolymer increases the inter-lamellar distance and therefore decreases the tie molecule density.

It is apparent from the above that for the best ESC resistance, high molecular weight copolymers should be employed. However, there are problems. Firstly, high molecular weight grades have low MFIs and this imposes processing restrictions. Secondly, high molecular weight copolymers are relatively low in density and crystallinity, and hence low in stiffness and ultimate strength. Newer grades offer a solution by employing a bimodal molecular weight distribution [34]. This supplies a sufficiency of long chain molecules for 'tying' without unacceptably low MFIs. Also the degree of crystallinity is increased by restricting copolymerisation to the higher molecular weight fraction. A comparison of a new bimodal grade with a conventional unimodal grade of the same density and MFI revealed that the advanced resin offered a substantial improvement in ESC resistance.

Nylons

An example of ESC failure is given in Case 6.5.5.

Nylons are known to be embrittled by contact with metal halide salt solutions. These include calcium, magnesium, lithium and zinc chlorides, bromides, iodides, and perchlorates. It is now fairly clear that the effects observed are due to ESC, and in particular swelling and plasticisation of the amorphous phase.

Wyzgoski [35] measured craze growth rates of Nylon 6 and 66 in saturated solutions of magnesium, calcium, and lithium chloride over a range of temperatures, and made the following observations:

i) The magnesium salt had the severest effect and the lithium salt the mildest effect. Craze growth rates for Nylon 6 at 55 °C and with a precrack of stress intensity 0.66 $\text{MPa.m}^{3/2}$ were:

LiCl	1 mm/hour
$CaCl_2$	8 mm/hour
$MgCl_2$	30 mm/hour

This ascending order of severity correlated with increasing cation charge density. The cation of sodium chloride has a lower charge density than lithium, and common salt solutions did not generate perceptible craze growth under these test conditions.

ii) Craze growth rates decreased with increasing crystallinity, increasing molecular weight and in Nylons with lower amide group concentrations.

A limited amount of data has also been published [36] on the absorption and critical crazing strain of Nylon 66 in a range of organic fluids. The absorption data correlated very well with the contours of a plot of polar versus hydrogen bonding solubility parameters, with the maximum absorption centred around the $\delta_P = 5.5\ \text{MPa}^{0.5}$ and $\delta_H = 14\ \text{MPa}^{0.5}$ coordinate, this being close to the partial parameters of the two well known solvents for Nylon 66; metacresol and phenol. The crazing strain ranged from a minimum of 1% to a maximum of 4%, but its correlation with partial solubility parameters was less clear. At high levels of absorption the crazing strain was high due to swelling (stress and strain relaxation effects). At low to moderate absorptions the crazing strain was low and at very low levels of absorption, the crazing strain was high. The most severe fluids with crazing strains in the 1% region were:

- 1,4-Dioxane
- Methyl isobutyl ketone
- Diacetone alcohol
- *n*-Butanol
- *n*-Propanol
- Nitroethane

- Acetonitrile

Fluids that generate crazing strains in the region of 2% are:

- Cyclohexanone
- Acetone
- Tetrahydrofuran
- Ethanol
- Dimethyl formamide
- Dimethyl sulphoxide
- Ethylene glycol
- Methanol
- Water

The least severe fluids generating crazing strains in the region of 4% are:

- Carbon tetrachloride
- Toluene
- *n*-Heptane

Polyether ether ketone (PEEK)

PEEK is a high performance thermoplastic normally used in its semicrystalline state. However, because of its high crystallisation temperature, it can quite readily be supercooled to a stable amorphous state. Indeed, the surfaces of injection mouldings will tend to be in this state unless annealed.

Hay [37] compared the equilibrium absorption of selected organic fluids in amorphous and crystalline PEEK. The difference (a factor of between 50 and 150) is a clear testament to the influence of morphology. Testing with a larger range of fluids would be required to identify the most critical fluid parameters for ESC. Indications are that a hydrogen bonding parameter in the vicinity of 5.7 MPa$^{0.5}$ (e.g. chloroform) results in the minimum resistance.

Styrenics

The styrenics encompass polystyrene (PS), high impact polystyrene (HIPS), styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS). Case studies are included in 6.5.8 and 6.5.12.

Of all commercial plastics, general purpose polystyrene (GPPS) suffers from the lowest resistance to crazing in air and therefore, not surprisingly, is lowest ranked in its ESC resistance. Kambour [38] is responsible for the most comprehensive study of the influence of fluid parameters on the initiation of crazing in polystyrene. Using Bergen elliptical straining jigs in contact with 30 selected fluids, the minimum surface tensile strain to craze was visually assessed. Duration of contact was short with no emphasis on control. Three of the fluids (acetone, nitrobenzene, and isoamyl acetate) resulted in solvation, the remainder as shown in Table 6.10 had critical strains in the range 0.1 to 0.42%. Under the same conditions the critical strain to craze in air is reported to be 0.36%.

Together with solvation data from another source [39], and the partial solubility parameters listed in [40], Figure 6.12 shows the influence of the hydrogen bonding parameter δ_H and the total solubility parameter δ. There is a region of solvation centring on $\delta = 19$ and $\delta_H = 6$ MPa$^{0.5}$. These, it might be assumed, are the approximate values of polystyrene's solubility characteristics. Around this region there is an annulus of stress crazing although there is no particular correlation between critical strain and proximity to the solvation centre.

Kramer [41] examined the fatigue life of polystyrene immersed in a selection of alcohols. The results are summarised in Table 6.11. As expected the fatigue life is reduced as the fluid's solubility parameter approaches that of polystyrene (ca. 19 MPa$^{0.5}$). The crazes produced were microscopically examined and found to have a lower fibril fraction for the more aggressive fluids. This would reduce the strength of the craze. The reason given for the reduced fibril volume fraction was slippage of entanglements within the fibrils.

The crazing of polystyrene in contact with various gases at low temperatures [42] identifies another critical fluid parameter. It was found that irrespective of the chemical nature of the gas (argon, nitrogen, methane or carbon dioxide), the ESC effect was controlled by the 'thermodynamic activity' of the gas; this being the ratio of the partial gas pressure and the liquid/vapour equilibrium pressure at the test temperature. Therefore at atmospheric pressures, the efficiency of the gases as crazing agents maximises at the boiling point of the gas. Such conditions would provide for maximum gas absorption. However, the diffusion rates of such gases measured independently were found to be many orders of magnitude lower than that required to significantly plasticise the material. This discrepancy was explained by stress enhanced absorption [43].

Table 6.10 Crazing data for polystyrene

	δ_S (cal/cm^3)$^{1/2}$ [a]	σ_S g/cm^3 [b]	Solvent T_g °C [c]	S_v cm^3/cm^3	T_g °C	ε_o %
Dodecamethylpentasiloxane	5.34	0.88		0.001	104	0.26
Perfluoromethylcyclohexane	6.0	1.79		0.616	90	0.34
Hexamethyldisiloxane	6.0	0.76		0.136	67	0.18
2,2,3-Trimethylbutane	6.95	0.690		0.0426	103	0.24
Pentane	7.02	0.626	-209	0.268	-28	0.10
2-Methylpentane	7.03	0.68		0.182	-32	0.12
Diisopropyl ether	7.06	0.73		0.176	-20	0.13
n-Hexane	7.27	0.654	-203	0.254	-10	0.10
$C_2F_3Cl_3$ (Freon 113)	7.3	1.6		0.132		0.14
n-Heptane	7.50	0.679	-189	0.184	-11	0.12
Diethyl ether	7.53	0.71		0.75	-43	0.27
n-Octane	7.54	0.698	-188	0.151	40	0.17
Cyclohexane	8.19	0.78	-193[c]	0.135		0.13
Isoamylacetate	8.2 (est)	0.870		1.395		[d]
Acetone	9.62	0.792		0.51	-41	[d]
Nitrobenzene	10.0	1.20		1.33		[d]
Triethylene glycol	10.7	1.11		0.028		0.27
Nitroethane	11.1	1.05		0.410		0.24
1-Pentanol	11.12	0.967	-149	0.0766	63	0.21
Cyclohexanol	11.4	0.95		0.0741	100	0.23
N,N-Dimethylformamide	11.79	0.94		0.237		0.42
Dimethyl sulphoxide	12.0	1.1	-120[e]		83	0.18
Benzyl alcohol	12.05	1.05		0.174	51	0.13
Acetonitrile	12.11	0.78		0.140	36	0.17
Ethanol	12.8	0.785	-173	0.055	76	0.27
Diethylene glycol	14.2	1.12		0.032	63	0.21

Table 6.10 Continued

	δ_S $(cal/cm^3)^{1/2}$ [a]	σ_S g/cm^3 [b]	Solvent T_g °C [c]	S_v cm^3/cm^3	T_g °C	ε_o %
Methanol	14.5	0.796	-163	0.067	90	0.29
Ethylene glycol	17.05	1.12		0.027	102	0.36
Formamide	19.2	1.13		0.049	100	0.28
Polystyrene		1.05			105	0.36

[a] *Data of Hoy,* [1] *Burrell and Immergut,* [2] *and Bernier and Kambour.* [3]

[b] *Handbook of Chemistry and Physics.* [4]

[c] *Extrapolated from* T_g *values for alkyl cyclohexanes of Carpenter et al.* [5]

[d] *Rapid softening to jellylike consistency; crazes start to grow in high strain areas but then heal and disappear.*

[e] *Extrapolated from Tg of mixtures with water; data of Rasmussen and MacKenzie.* [6]

1. *K.L. Hoy, J. Paint Technol., 1970, 42, 76.*
2. *H. Burrell and B. Immergut in Polymer Handbook, Eds., J. Brandrup and I. Immergut, Interscience, New York, 1966, pp.IV-341-357.*
3. *G.A. Bernier and R.P Kambour, Macromolecules, 1968, 1, 393.*
4. *Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969.*
5. *M.R. Carpenter, D.B. Davies and A.J. Matheson, J. Chem. Phys., 1967, 46, 2451.*
6. *D.H. Rasmussen and A.P. Mackenzie, Nature, 1968, 220, 1315*

Reproduced from R.P. Kambour, C.L. Gruner and E.E. Romagosa, Solvent Crazing of "Dry" Polystyrene and "Dry" Crazing of Plasticized Polystyrene, Journal of Polymer Science, Polymer Physics Edition, Volume 11, p.1879-1890. Copyright © 1973, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

Table 6.11 Fatigue life of polystyrene in various alcohols

Fluid	**δ ($MPa^{0.5}$)**	**T_g (°C)**	**Fibril vol. fraction**	**Fatigue life (No. of cycles to failure)**
Methanol	29.7	91	0.25	11900
Ethanol	26.6	85	0.18	7530
Propanol	24.6	81	0.12	1230
Butanol	23.1	71	0.09	1170

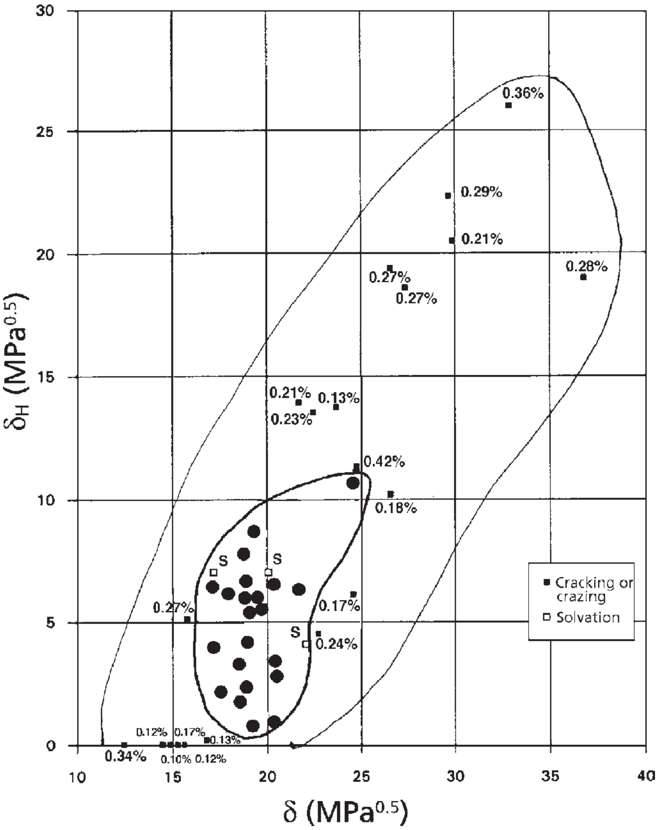

Figure 6.12 Influence of hydrogen bonding on the crazing strain for polystyrene (• fluids that are known to dissolve the material)

The influence of fluid viscosity on crazing has been the subject of several studies. Peredes [44] compared the effect of mineral oils. Over the viscosity range 4 x 10^{-5} to 1.75 x 10^{-3} m^2s^{-1} the crazing stress increased from 15 to 28 MPa. The interfacial tensions of the oils were similar. It was established that the T_g depression in polymer (90%)/oil (10%) mixtures was dependent on oil viscosity. The high viscosity oil depressed T_g by only 8 °C, whilst the low viscosity oil depressed T_g by 22 °C. This would be sufficient to account for the difference in crazing on the basis of plasticisation. However PS did not absorb detectable amounts of oil even after 5 months of stress-free immersion. Again stress induced absorption was proposed to be the enhancing mechanism. In a similar study using silicone oil [45] the crazing stress reduced from 20 to 10 MPa in oils of viscosities of 10^{-3} and 5 x 10^{-6} m^2s^{-1}, respectively.

High impact polystyrene (HIPS) is not transparent and therefore has received less attention. Bubeck [46] investigated the creep rupture of various grades of the material in contact with a 50/50 solution of cotton seed oil and oleic acid. The characteristic has three regions. The short-term high stress region is controlled by 'dry crazing growth' where there is insufficient time for the fluid to maintain contact with the growing craze tip. The intermediate region, which corresponds with the ductile/brittle transition, is controlled by the viscosity of the fluid. Finally there is the low stress long time region (which of course is the most relevant to real service conditions), in which the time to fail is dominated by initiation and is independent of viscosity (sufficient time is always available for transport to the craze tip).

It was established that the logarithm of time to break increased linearly with the weight average molecular weight.

SAN has a higher resistance to crazing than polystyrene. It has a higher total solubility parameter (20 versus 19 $MPa^{0.5}$) and therefore a higher cohesion energy density. This difference is due to the incorporation of highly polar CN groups.

Kambour [47] studied SAN using similar procedures as reported above for polystyrene. His results are listed in Table 6.12. A major difference was that the critical strain/total solubility parameter relationship exhibited two minima; one at $\delta = 16$ and one at $\delta = 24$ $MPa^{0.5}$. These were shown to be the two critical conditions for an equilibrium absorption of 15%, which it was further shown depressed T_g to ambient (test) temperature. Fluids between these limits swell the material excessively which interferes with craze initiation.

Polytetrafluoroethylene (PTFE)

PTFE is known to suffer environmental stress cracking under severe mechanical conditions in the presence of various organic fluids. These include monomethyl hydrazine (in rocket fuel) [48] and kerosene [49]. With a razor notch, stressed specimens in air failed eventually by ductile rupture but similar specimens at the same stress in some fluids failed earlier with little sign of ductility [50]. Carbon tetrachloride reduced the failure time by a factor of 100. The severity of the effect, as indicated in Table 6.13, correlated with bulk absorption.

The non polar fluids (carbon tetrachloride and cyclohexane) are the most aggressive both in terms of plasticisation and ESC severity.

Table 6.12 Crazing data for SAN

	δ (cal/cm^3)$^{0.5}$	ρ_s g/cm^3	S_v cm^3/cm^3	T_g °C	ε_c, max %	ε_c, min %	ε_c, av %	n[a]
Dodecamethyl pentasiloxane	5.34	0.88	0.0254	101±0	0.61	0.26	0.44±0.18	4
Perfluoromethyl c-hexane	5.85	1.79	0.0083	101±1.0	0.64	0.29	0.60±0.14	6
Hexamethyl disiloxane	6.00	0.76	0.025	96.5±1.5	0.54	0.20	0.36±0.14	6
Pentane	7.05	0.62	0.0607	76.5±0.5	0.41	0.38	0.40±0.02	4
Hexane	7.3	0.66	0.171(?)	79±1.0	0.355	0.31	0.33±0.03	6
2,3-Dimethyl pentane	7.3	0.694	0.0316	96.5±1.5	0.52	0.50	0.52±0.02	3
$C_2F_3Cl_3$ (Freon 113)	7.3	1.6	0.00187	100.5±0.5	0.34	0.33	0.35±0.05	6
Heptane	7.4	0.68	0.0130	85[b]	0.39	0.27	0.33±0.06	4
Octane	7.6	0.70	0.0788	84±1.0	0.49	0.34	0.41±0.06	6
Decane	7.7		-	-	0.35	0.35	0.35±0.03	2
Methyl *c*-hexane	7.8	0.77	0.050	89±4.0	0.44	0.31	0.35±0.06	4
c-Hexane	8.2	0.78	0.138(?)	78±2.0	0.35	0.25	0.37±0.05	4
i-Amyl butyrate	8.4 (calc.)	0.86	0.375	20.5±0.5	0.21	0.13	0.17±0.04	4
n-Butyl acetate	8.5	0.88	0.857	-22±0	0.29	0.13	0.20±0.08	5
Methyl ethyl ketone	9.3	0.805	1.630	-15[b]	0.44	0.27	0.35±0.09	4
Methyl acetate	9.6	0.927	1.153	-30±3	0.43	0.24	0.33±0.10	4
Acetone	9.6	0.79	1.784	-18[b]	0.395	0.28	0.34±0.04	6
Dodecanol	9.8		-	-	0.47	0.47	0.47±0.02	2
Nitrobenzene	10.0	1.2	1.001	-42.5±2.5	0.74	0.24	0.49±0.20	5
n-Nonanol	10.3		-	-	0.39	0.38	0.38±0.01	2
n-Pentanol	10.9	0.967	0.0630	63±1	0.24	0.20	0.22±0.02	5
Nitroethane	11.1	1.05	>3.3	-	-	-	-	

Table 6.12 Continued

	δ (cal/cm^3)$^{0.5}$	ρ_s g/cm^3	S_v cm^3/cm^3	T_g °C	ε_c, max %	ε_c, min %	ε_c, av %	n[a]
Triethylene glycol	11.4	1.11	0.0217	96.5±0.5	0.24	0.24	0.24±0.01	2
i-Propanol	11.5	0.79	0.0300	70±0	0.27	0.24	0.25±0.01	4
Dimethyl sulphoxide	12.0	1.1	0.238	31±1.5	0.24	0.14	0.19±0.05	4
n-Propanol	12.0	0.80	0.0947	43[b]	0.15	0.15	0.15±0	4
N,*N*-Dimethylformamide	12.1	0.94	0.730	-18±0	0.48	0.41	0.43±0.06	4
Acetonitrile	12.1	0.78	0.504	-47.5±0.5	0.59	0.25	0.42±0.16	6
Benzyl alcohol	12.1	1.05	0.993	-32±5	0.51	0.25	0.35±0.09	7
Ethanol	12.7	0.79	0.035	76±19	0.30	0.22	0.26±0.03	4
Propylene glycol	13.7	1.04	0.046	88±6	0.45	0.37	0.41±0.04	4
Methanol	14.5	0.79	0.170(?)	74.5±1.5	0.42	0.23	0.30±0.08	6
N-Methylformamide	16.1	1.01	0.965	-25[b]	0.32	0.13	0.22±0.09	4
Ethylene glycol	17.1	1.12	0.039	85±0	0.56	0.47	0.52±0.05	4
Formamide	19.2	1.13	0.0866	87±2	0.61	0.49	0.55±0.06	4
Tyril 767 resin		1.08		102±0.5	0.52	0.47	0.49±0.03	3

[a] *Number of runs*

[b] *Only one interpretable run was made*

Reproduced from R.P. Kambour and C.L. Gruner, Effects of Polar Group Incorporation on Crazing of Glassy Polymers: Styrene-Acrylonitrile Copolymer and a Dicyano Bisphenol Polycarbonate, Journal of Polymer Science: Polymer Physics Edition, Vol. 16, p.703–716, Copyright © 1978 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

Table 6.13 Time to stress rupture of notched PTFE in various fluids, together with fluid absorption data

	Time to fail at 7 MPa (minutes)	% volume absorbed in unstressed state
Air	>100,000	0
Dichloroethane	20000	1.37
Kerosene	7000	-
Chloroform	6000	2.01
Perchloroethylene	6000	2.49
Cyclohexane	3000	3.03
Carbon tetrachloride	1000	3.22

6.5 Case studies

6.5.1 Noryl fire extinguisher head

History

This problem was identified following a fire alarm at a police station. The head of a wall-mounted CO_2 fire extinguisher fractured when manhandled. Fortunately the incident was not a serious one and there was sufficient time to extinguish the fire by other means. However, the fire services were sufficiently concerned to demand a full scale investigation.

The extinguisher together with six others of the same design had been installed for about five years. None of these had seen active service prior to the incident.

Inspection and analysis

A grade of Noryl had been selected for the injection moulded head components. Fracture had initiated at a moulded-in hole. An inspection of the six other extinguishers on the site revealed that one was cracked. The position and orientation of the crack, as shown in Figure 6.13, corresponded with the fracture plane of the failed head. The orientation of the fracture plane coincided with the orientation of the weld/knit line at the moulded-in hole.

The knit line in each case was only about 3 mm in length and therefore could not be classed as severe. Nevertheless it would act as a stress concentrator and evidently had a role to play in the failure. The circumferential tensile stress at the hole could not be calculated with confidence because of the unknown interference between the split pin and the hole. The split pins were crudely manufactured and significant variation in pin diameter, pin/hole interference, and therefore assembly stresses, could be expected. Best estimates of the latter ranged from 4 to 8 MPa.

Three of the five intact heads were removed and dipped in tri-*n*-butylphosphate. Cracking was immediately observed in all cases, and crack orientation coincided with that shown in Figure 6.13.

Failure diagnosis

Tri-*n*-butylphosphate had commonly been used as the medium for assessing the processed-in stress of Noryl mouldings. A 'calibration curve' connecting time to crack with stress was available. Immediate cracking would imply a stress of at least 30 MPa. It was considered very unlikely that such a high stress could have been developed at the stress concentrating knit line.

Recently moulded (unused) heads were pinned, assembled, and subjected to the same dip test. Times to crack indicated that total stresses ranged from 8 – 12 MPa. This

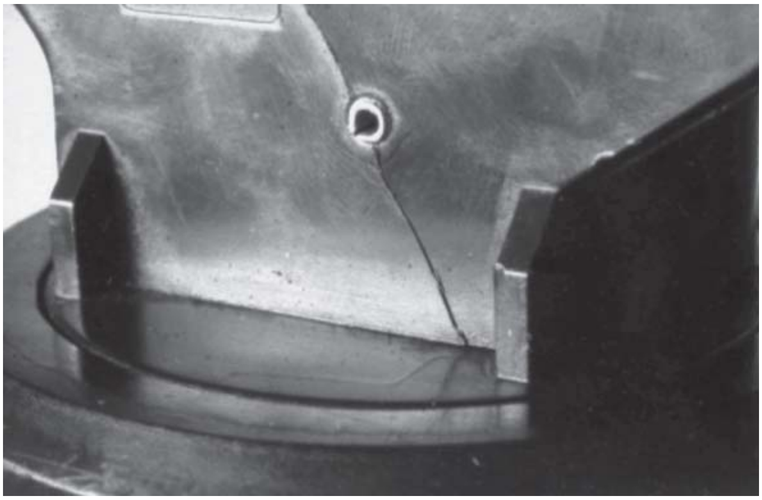

Figure 6.13 The cracked extinguisher head

corresponded reasonably with the calculated values, with a modest stress concentration factor for the knit line.

Various cleaning agents that may have been applied to the extinguisher heads were collected. These included window cleaners, polishes, and surfactants. None of these caused cracking within six months of application when applied to recently assembled heads. However the first two cleaning agents selected caused cracking in the two remaining intact heads from the site within one month of application. It was therefore concluded that any one of a wide range of proprietary cleaning agents could have caused the problem.

The difference in ESC resistance between recently assembled heads and those that had been in service for 5 years is open to a number or explanations including physical ageing (see Section 7.5) or an additional in-service degradation process such as photo-oxidation. However the most rational explanation is as follows. Crazes are initiated in Noryl in air after a few years under a constant stress of about 10 MPa. This is triggered by a critical level of inelastic strain, accumulated by creep or stress relaxation (see Section 6.2 above). If (invisibly) crazed material is exposed to a powerful ESC agent such as tri-*n*-butylphosphate it will crack immediately. If exposed to a weak ESC agent such as a proprietary cleaning agent it will take a few weeks to transform small crazes to large cracks.

Lessons and consequences

1. Holes in mouldings that are to be mechanically stressed should be machined rather than moulded in (to avoid stress concentrating knit lines).
2. Safety critical parts that are exposed to long-term stressing and the possibility of contact with organic fluids should not be moulded from glassy amorphous plastics. A flame retarded grade of polybutylene terephthalate (PBT) would have avoided the problem.
3. It is probable that prestressing for long periods prior to the application of a fluid seriously impairs ESC resistance. Under these conditions weak ESC agents appear to be far more aggressive.

6.5.2 High density polyethylene screw caps

History

Blow moulded HDPE containers (25 litre) were specified for the storage and transport of alcohols for industrial use. The grade of polyethylene for both the container and the screw caps had been fully tested for chemical compatibility and environmental stress crack resistance. The highly polar alcohols (as expected) had no significant interaction with the non polar polymer.

The container supplier started to receive complaints from their principal customer within two months of service use. After 3 months of use approximately 0.5% exhibited signs of cracking in screw caps. Being generally stored in the upright position, no leakages were associated with the cracking and therefore the complaints were of a mild nature. The supplier apologised and gratuitously provided a buffer store of replacement caps. The supplier claimed that their injection moulder had had some initial ‘teething problems’ but these were now resolved.

There was a slight accident in the warehouse owned by a minor customer. A forklift truck shed three pallet loads of filled containers. 60% of the containers failed by cap rupture and a large volume of alcohol drained into a nearby river. Marine life was destroyed.

The supplier was informed and stated that the containers were not designed to withstand drop impact. The supplier did not alert the minor customer to the history of complaints about screw cap cracking. The owner of the warehouse faced the imposition of fines and other costs by various environmental agencies.

Inspection and analysis

A typical rupture failure from the warehouse accident is shown in Figure 6.14. In all cases fracture initiated adjacent to one or both of the cap lugs (as shown). An inspection of caps from intact containers involved in the accident revealed that all caps were partially cracked at the identical points of initiation. An inspection of stored containers in the warehouse revealed that ~ 1% were visibly cracked. Under modest magnification ~ 50% were found to be microcracked; all being located adjacent to the cap lugs.

The crack initiation point was deemed to coincide with the maximum tensile stress due to the screw on torque. It also coincided with the location of a rubber o-ring. The o-ring had been coated with a grease to lubricate the assembly. On analysis the grease was found to be a silicone.

Failure diagnosis

Drop impact could never be justified as the primary cause of failure because:

Figure 6.14 Typical example of a failed cap. Initiation is at the lug

i) The transient stresses due to drop impact would normally maximise in the wall of the container and this is where the majority of impact induced ruptures would be expected. The caps being robustly designed to withstand torquing stresses would be more resistant to transient increases in fluid pressure than the container body.

ii) The presence of subcritical cracks of different length within a population of a product is invariably the result of a slow crack growth process.

iii) Containers should be designed to withstand the modest impact loads experienced in this accident but may be expected to fail under such conditions if they are precracked.

The initial cause of cracking and therefore the primary (avoidable) cause of failure was the combination of sustained and high enclosure stresses and contact with silicone grease. The grease is known to be a mild ESC agent for HDPE, causing slow crack growth at stresses that approach the yield stress of the material. This was proved by comparing the condition of fully torqued caps after 3 months in the presence and absence of the grease.

Lessons and consequences

1. Most ESC failures are due to contact with 'secondary fluids' which are easily and frequently overlooked by the responsible party. In this case the responsible party is

the supplier for applying the grease to all the caps without material tests or effective product tests.

2. The early warning signs were not treated seriously. The true reasons for this are not known but may be inferred to be as follows. If only a small percentage of a product population fails or is deemed to be defective, there is a tendency to regard this as a quality problem, on the assumption that if the problem was more fundamental it would have a higher incidence. In this case it is apparent that the supplier thought that the partial cracking was simply due to excessive stress on the cap lugs. As this stress is mainly controlled by the dimensional interference between the cap and the container, the supplier assumed that variations in the dimensions of the cap and therefore the injection moulding quality were at fault. However the percentage of product failures in this case depends upon the criterion for failure, being only < 1% for visible cracks but 50% for smaller cracks. If the supplier had spent a few hours inspecting assemblies with the aid of a magnifying glass he would have realised that the problem was common and progressive.

3. Petroleum jelly was recommended as a safe lubricant.

4. The supplier was forced to carry all costs. On hearing about the case, the major customer sought and found an alternative source of supply.

6.5.3 Crazing of an acrylic sight glass

History

In-line transparent tubes provide the means of observing the flow of process fluids and are known generically as ‘sight glasses’. Silica glass is the traditional material of construction. However the material is not sufficiently robust in applications where the component is exposed to the risk of impact. In these situations transparent plastics such as PMMA, SAN or polycarbonate are often preferred.

PMMA sight glasses were used in a process cooling system. The coolant was water with a maximum specified temperature of 50 °C. Pressures were modest and capable of generating a maximum hoop stress within the tube of only about 5 MPa.

After 8 years of trouble free service one of the sight glasses failed with severe consequential losses.

Inspection and analysis

Five sight glasses were removed from the process plant, including reclaimed fragments from the failed component. All exhibited the extensive crazing typically as shown in Figure 6.15. The impairment of optical clarity was so severe as to suggest that crazing was recent and sudden (otherwise the damage would have been detected earlier by plant operatives).

Under low magnification and at the critical incidence angle for internal reflection individual crazes ('silvery cracks') can be studied in detail. All craze initiation sites were on the bore surface, suggesting that contact with the coolant was an essential contributor to the failure. This is confirmed by the fact that the bore surfaces adjacent to the ends of the tubes were uncrazed. These areas (see Figure 6.15) were in contact with an end seal.

Failure diagnosis

Crazing in PMMA does not necessarily involve fluid interaction. It can occur as the result of sustained stress alone. The process is accelerated by certain fluids as it is by an increase in temperature.

In this case it is apparent that contact with the coolant fluid rather than excessive temperature is the critical reason for premature crazing. The cooling fluid had been water until about six months prior to failure, but had then changed to a water/corrosion inhibitor mixture.

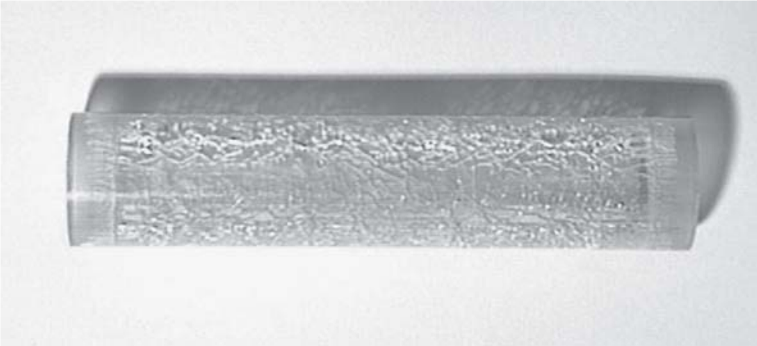

Figure 6.15 Crazed PMMA sight glass

Mild interrogation of the process operatives (in the absence of their managers) revealed that the sight glasses were rarely if ever consulted. Therefore increasing opacity due to craze growth could have gone unnoticed over a long period of time.

The short-term strain to craze of PMMA was assessed in contact with water and with the inhibitor/water mixture at 50 °C using the constant stress rate test (4 MPa/hour) as described in reference [20]. The results are listed in Table 6.14.

The water/inhibitor mixture is a weak environmental stress cracking agent for PMMA. It should take many years to crack under a sustained stress of 5 MPa at 50 °C yet it has failed after about 6 months of exposure. However as revealed by Arnold [16], the time to stress crack is controlled by the stressing time (8 years) and not the fluid exposure time.

Lessons and consequences

1. Applications that demand transparency and ESC resistance are very difficult to satisfy. With only one exception (polymethylpentene (TPX)), all transparent thermoplastics are amorphous. All amorphous thermoplastics are susceptible to ESC.
2. The longer the period under stress before exposure to an ESC agent, the shorter the residual life.
3. As the sight glasses represented a structural weakness regardless of their material of construction, and as they were in any case ignored by process operatives, it was suggested that they be dispensed with and replaced with an audible no flow warning system.
3. The active ingredient in rust and corrosion inhibitors whether oil or water soluble are amines. These can be very aggressive to plastics and rubbers.
4. The supplier of the inhibitor was advised to inform all current and future customers of the incompatibility between the inhibitor and plastic sight glasses.

Table 6.14 Critical conditions for craze initiation in PMMA at 50 °C and 4 MPa/h demonstrating the influence of corrosion inhibitor

	Critical strain (%)	Critical time (s)	Critical stress (MPa)
Water	0.85	18,180	20.2
Water/inhibitor	0.62	11,970	13.3

6.5.4 Polycarbonate instrument housing

History

A company developed an instrument for the remote monitoring of telecommunications systems. The instrument was designed to be portable and could be sited outdoors from time to time. The instrument housings therefore had to be robust, leaktight, and ultraviolet (UV) resistant.

A UV stabilised polycarbonate was chosen for the upper part of the housing (the console) and the lower half (the base). An example of the injection moulded console is shown in Figure 6.16. Considerable effort and ingenuity was expended to ensure that the seal between the console and the base was leak tight against rainwater ingress and remained so for a wide range of climatic conditions.

After extensive testing, 500 instruments were manufactured and distributed worldwide. The first failure arose from an arid tropical site following a rare rainstorm. It was reported that the console had cracked, exposing the electronics to rainwater. Although the instrument had been in service for about two years, records revealed that it had only been exposed to direct sunlight for about 10 days. Thus UV degradation could be dismissed as a contributory factor.

The instrument company informed the customer that the console had failed due to impact abuse. As the warranty had expired their magnanimity extended to a cost price replacement.

Figure 6.16 Console moulded from polycarbonate

Over the next 6 months a further ten failure complaints were received. It was observed that there was an inverse relationship between service life to cracking and the mean climatic temperature of the site.

Inspection and analysis

Five failed consoles were provided for inspection and analysis. All had failed by brittle fracture. The cracks were all adjacent to the siting of a 'company logo' that had been film bonded to the surface of the console. The film was removed and the polycarbonate surface that had been in contact with the film was found to be extensively microcracked, as shown by example in Figure 6.17.

The film was analysed by FTIR and found to be PVC plasticised with dioctyl phthalate (DOP).

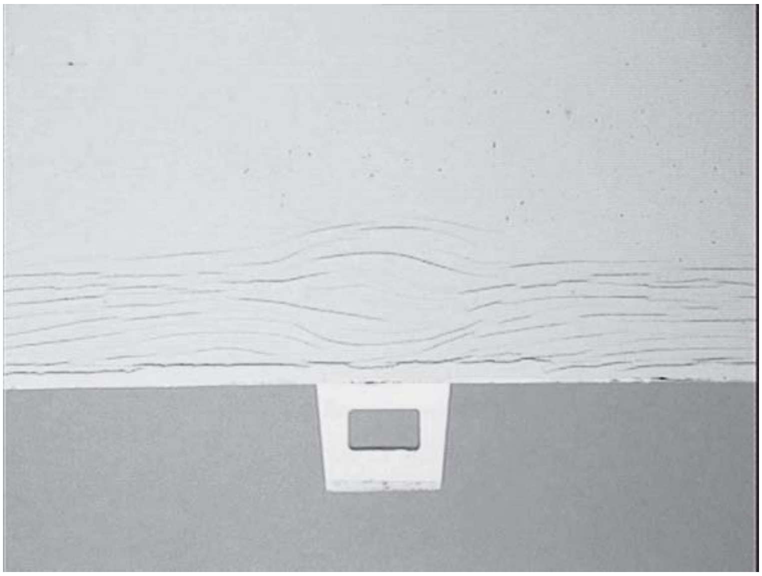

Figure 6.17 Close-up of area attacked by plasticised PVC

Failure diagnosis

The linear and stepped nature of the microcracks in Figure 6.17, without discolouration or other symptoms of material degradation, is characteristic of ESC. The pattern of cracking indicates that moulded-in stress provides the driving force.

DOP is a powerful ESC agent for polycarbonate. The polar solubility and hydrogen bonding parameters for DOP are 7 and 3.1 MPa $^{0.5}$, respectively. According to Henry [18] the short-term critical strain to crack initiation in a fluid with these parameters would be < 0.5%.

DOP is a monomeric plasticiser and therefore is sufficiently mobile to migrate from the film to the surface of the polycarbonate. The rate of migration increases with increasing temperature.

The consoles failed due to stress cracking in contact with DOP.

Lessons and consequences

1. The ‘company logo’ was added after the product had been climatically tested. This case emphasises the penalties that can result from testing products that do not exactly replicate those intended for service.

2. Early brittle failure of products should be treated to serious examination. The ‘head in the sand’ technique is only cost effective if the failures are really due to customer or third party abuse. If a tough material such as polycarbonate fractures in a warm climate, impact failure is unlikely to be the primary cause.

3. All customers were alerted to the problem and provided with replacement consoles (without logo).

6.5.5 Nylon 6 fire hose valve

History

A wall mounted fire hose at a municipal swimming pool failed during a statutory fire drill. The manually operated spool valve had apparently jammed in the closed position. As similar fire fighting systems were known to be employed extensively in other public places the failure stimulated much concern and immediate action.

Inspection and analysis

The hose valve was carefully disassembled. The plastic spool had fragmented as shown in Figure 6.18. The spool remnants were fragile. Other parts (not shown) included rubber o-rings and a brass rod.

Fourier transform infrared (FTIR) spectroscopy confirmed that Nylon 6 had been used to injection mould the spool. Gel permeation chromatography (GPC) revealed only minor differences between the molecular weight distributions of a new spool and the failed spool.

The brass rod was visibly corroded and caked in a white surface deposit. The deposit was analysed and found to be zinc chloride.

Failure diagnosis

Mild interrogation of pool attendants revealed that the fire hose had been used occasionally for cleaning the pool floor and sides. During this operation the hose end would be submerged from time to time in the pool water. This would allow access of chlorinated water to the spool valve assembly. It was possible therefore that for a substantial period

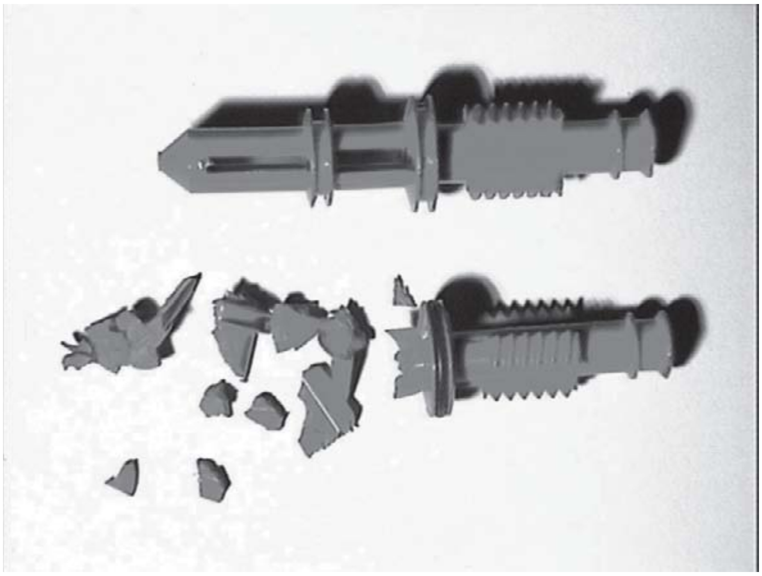

Figure 6.18 An unused and a failed Nylon 6 spool valve

of its service life (~ 5 years) the Nylon spool and the brass rod had been in contact with heavily chlorinated water. During this time the solution, by attacking the brass rod, would convert to a salt solution of predominantly zinc chloride. It is well known that zinc chloride is a powerful stress cracking agent for Nylons.

A high level of cohesion in Nylons relies upon intermolecular hydrogen bonding between amide groups. Bond strengths are typically 33 kJ/mol. Zinc chlorides and other metal halides with high cation charge density form metal complexes with the amide carbonyl thus weakening the hydrogen bonds. The reduction in intermolecular cohesion renders the amorphous phase of the material in particular susceptible to localised swelling and plasticisation in contact with water. In the presence of stress these transform into cracks and crazes.

The rate of attack is known to be rapid even at ambient temperatures. The suppliers of Nylon usually clearly admit incompatibility but only at high salt concentrations. In this case the concentration was not known but could, by slow evaporation over long periods of time, have eventually reached a critical level.

Lessons and consequences

1. It was a relief to all concerned that the failure was proved to be the result of a rare service history, and therefore hoses in most public places were unlikely to suffer from the same problem.

2. The supply chain cannot be held responsible for failing to predict and therefore avoid the problem. If anyone is to blame it is the pool attendant who broke the rules.

3. The supply chain should however be sensitised to the potential dangers of hybrid metal/plastic assemblies. Lithium, calcium, zinc, magnesium in contact with Nylons (or acetals) in a wet environment should be considered very carefully.

6.5.6 Polyethylene agrochemical container

History

Five litre HDPE blow moulded containers had a long and successful history as a means of short-term storage of a particular agrochemical. Typically the containers would be pallet stacked in a warehouse environment for several months, pending distribution to retail outlets.

One consignment of a thousand containers started to leak within two weeks of storage. Leaking containers were buckled as shown in Figure 6.19. The agrochemical in concentrated form was known to be a health hazard, so specialists were deemed necessary to decontaminate the warehouse.

The wholesaler sought recompense from the container supplier. The supplier responded by claiming that the recommended 'top load' on the containers had been exceeded due to overstacking. The buckling of the containers indicated that this was the case.

The wholesaler knew that the top load limits had not been exceeded but could not prove this to the satisfaction of the supplier. Feeling confident that they would be vindicated they agreed to accept the findings of an independent expert specialising in stress analysis.

Whilst awaiting the expert's report, consignments failed in a similar manner in 5 warehouses in other parts of the country. Poor storage practice was relegated as a candidate cause.

Figure 6.19 Buckled PE container

Inspection and analysis

From a plastics technologist's perspective, the most significant feature of the failures was the presence of microcracking in all containers that had buckled and leaked. Figure 6.20 clearly reveals such cracking on the tensile surface of a buckled fold. The 'linear and stepped' appearance of the microcracks is strongly indicative of environmental stress cracking.

However, from the stress analyst's perspective the cracking was of only secondary interest. Common sense and 'intuition' would suggest that the cracking was caused by the buckling.

High powered microscopy revealed the presence of extensive microcracking on the inside surface of all containers including those that had not buckled.

Failure diagnosis

The ESC resistances of material batches were compared using a simple bent strip test. Material from the latest and therefore suspect batches were found to be significantly inferior to material from old batches. Under equal strain, time to crack in the agrochemical was reduced by more than a factor of 10.

Figure 6.20 Close-up showing classical linear stepped microcracking due to ESC

On being presented with this evidence, the blow moulder (ISO 9000 accredited) admitted a change in material supply. He had been offered the 'same grade' in terms of density and melt flow index, at a cost saving of 10%. He was unaware that the premium grade had originally been chosen and formulated for its excellent stress crack resistance (e.g. lightly copolymerised with an enhanced high molecular weight fraction).

The causative connection between ESC and buckling is apparent from Figure 6.21. This compares the creep behaviour of a plastics material in air and in a stress cracking environment. Prior to craze or crack initiation the time dependent stiffness of the material is unaffected by the environment. After initiation the creep rate accelerates and the time to buckle under constant top load decreases from T (in a passive environment) to T* (in an aggressive environment).

Lessons and consequences

1. ISO 9000 and equivalent systems promote but do not ensure the continuity of quality.
2. Apparently small differences in material grade can significantly affect durability.

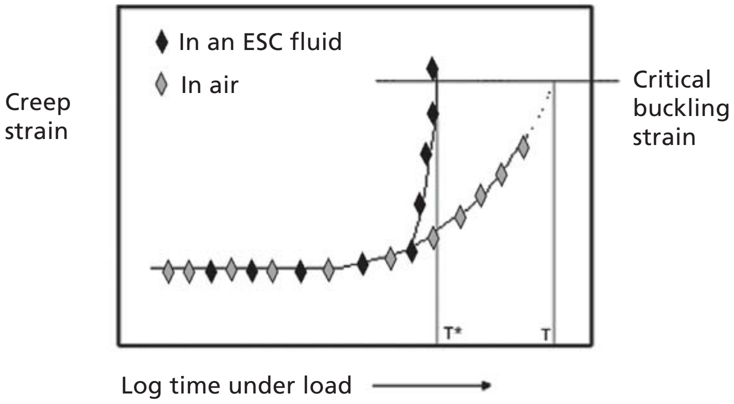

Figure 6.21 Reduction in time to buckle due to environmental stress cracking (schematic)

3. Misdiagnosis is common. Had there been no further consignment failures an incorrect diagnosis would have been made and the wrong party blamed.

4. The blow moulder was insured against consequential losses up to £250,000. This limit was fully exploited in the subsequent settlement.

6.5.7 Noryl electrical plugs

History

Three pin 240 volt plugs were moulded in two parts out of black Noryl (a blend of polyphenylene oxide (PPO), polystyrene, and rubber). The plugs could be assembled at high speeds by ultrasonic welding of the parts. This material and assembly method was preferred for many audiovisual (AV) products for the domestic market. Several proprietary designs had evolved and all had been successful.

A manufacturer introduced a new design with minor dimensional changes. Type approval to various standards was sought and this was given after an extensive testing programme carried out by an independent accreditation laboratory. The product was chosen by three major suppliers of AV equipment, and within two years more than 100,000 plugs had been distributed.

The largest of the AV equipment suppliers started to receive customer complaints. Plugs were cracked and in a few cases the two parts had separated, exposing occupants to the real risk of electrocution. Fortunately for all concerned the two homes included neither curious infants nor blind adults.

The supplier sent the failed plugs to the independent accreditation laboratory where they had, two years previously, been type approved. After inspection it was suggested that failures were all due to 'abuse by impact'. However the credibility of this explanation faded with the subsequent acceleration of the failure rate and the realisation that the two other AV suppliers using identical plugs were experiencing no failures.

As a precaution and at considerable expense, service engineers were despatched to ~4,000 homes (10% of the customer base) to replace and collect suspect plugs. On inspection:

i) ~ 1,880 plugs were found to be visibly cracked.

ii) ~ 100 plugs were deemed to be severely cracked.

iii) 15 plugs had completely separated.

It was now clear to all concerned that regardless of the cause, all 40,000 plugs must be replaced as soon as possible. The cause was then investigated for liability.

Inspection and analysis

Figure 6.22 is a close up photograph of a typical 'visibly cracked' plug. All failed or at risk plugs shared common initiation and growth geometries, implying that 'visibly cracked', 'severely cracked', and 'completely separated' plugs were simply examples of one failure process at progressively later stages of development. The process is evidently one that involves slow crack growth.

All fracture surfaces and part cracks were in the plane coincident or parallel to the ultrasonic weld. In those cases where the weld and fracture were not coincident the plane of the cracks was 1 to 2 mm into the base moulding. This would suggest that the tensile stress that causes the cracking is normal to the plane of the weld, as shown in Figure 6.23.

Several new unused plugs were immersed in tri-*n*-butylphosphate. This fluid is a stress cracking agent for Noryl and had been previously calibrated in terms of stress versus

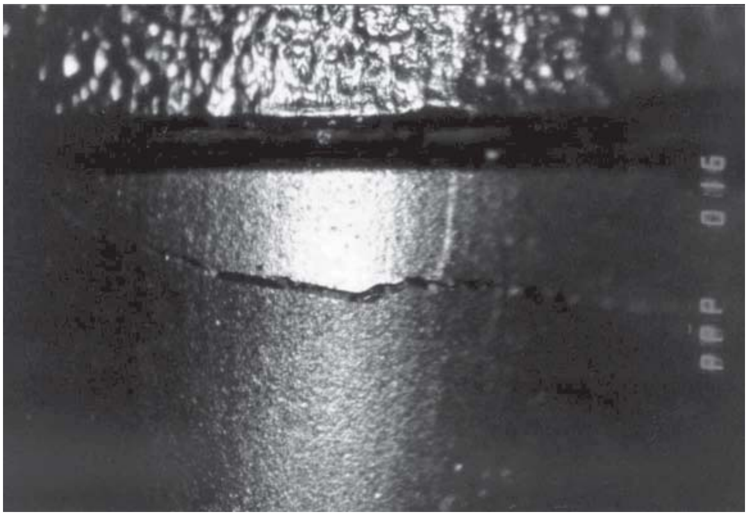

Figure 6.22 Small crack adjacent to a weld

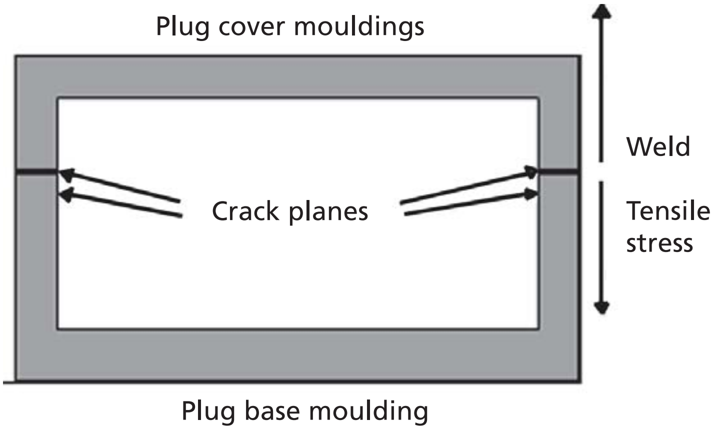

Figure 6.23 Stress direction and crack planes at the weld

time to initiate visible cracking. Cracking was observed to initiate within the weld or adjacent to the weld in a minimum time of 100 seconds, which implied a maximum tensile stress of ~15 MPa.

The source of this unusually high stress was traced to the forces needed to assemble the two parts. Pillars in the base moulding interfered with the cover moulding, and considerable compressive force was required to mate the surfaces for welding. After welding and removal of the compressive restraint, the residual compression on the internal pillars generated a tensile stress of up to 15 MPa across the weld.

The evidence was accumulating to suggest that the single process that led to all the failures was environmental stress cracking. In particular:

i) Noryl is blend of amorphous thermoplastics and it is therefore susceptible to attack by a wide range of (mainly) organic fluids.

ii) 15 MPa applied continuously over many months would be sufficient to render the material susceptible to ESC when in contact with relatively mild proprietary fluids.

iii) The cracks are all ‘stepped’, implying the separate growth, and then coalescence, of linear microcracks within a narrow band. This is clearly seen in the close up shown in Figure 6.24. This is a characteristic of slow ESC development in amorphous thermoplastics.

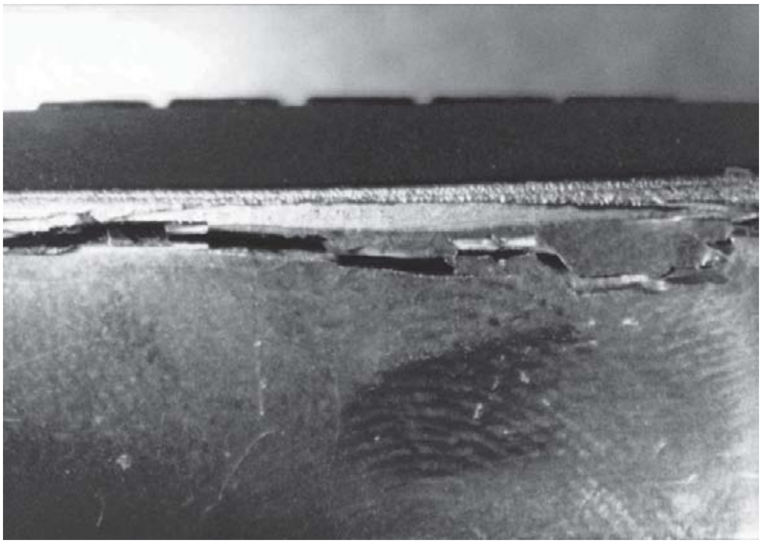

Figure 6.24 Small cracks coalesce

Some detective work was then necessary to trace the culprit fluid or fluids. Evidently this could not have been applied by either the domestic customers, or the plug supplier, for the failures were restricted to only one of the AV suppliers. Attention was focused upon them. Senior staff were interviewed but all were unaware of any fluid being applied. Junior staff were asked the same questions and thankfully one remembered that there had been complaints from retailers concerning loss of gloss and customer appeal due to the accumulation of surface dust on the equipment. This had been solved by a wipe over with an antistatic aerosol foam. For good measure the cable and plug had received the same treatment.

New unused plugs were sprayed with the aerosol and wiped clean. Within one hour visible cracking was detected similar to that shown in Figure 6.24.

Failure diagnosis

ESC failure was due to high assembly stresses plus contact with an antistatic aerosol. No attempt was made to trace the active ingredient. Propellants (e.g. butane) and wetting agents would be prime suspects as both would be classed as mild ESC agents for Noryl (and indeed all other amorphous thermoplastics).

Lessons and consequences

1. Assembly stresses should never be ignored, as they will often exceed processed-in stress or design stress. If significant force is required to assemble parts because of warping, misalignment, or excessive interference then high assembly stresses will result.

2. The stresses in high voltage plugs and other products where safety is paramount should be assessed by dip testing in a calibrated fluid. If the stress is lower than ~ 5 MPa then even amorphous materials will resist all fluids other than the most aggressive organic 'solvents' (e.g. esters, ethers, ketones, halogenated hydrocarbons). If the stress exceeds ~ 10 MPa then there is the risk of failures in the medium to long term by chance contact with a wide range of 'mild' proprietary fluids (including domestic cleaning agents).

3. The fact that exhaustive and expensive accreditation tests do not include ESC susceptibility indicates institutional ignorance of this very common mode of failure.

4. The fact that a specialist test house failed to recognise classic examples of ESC highlights the extent of ignorance. Material suppliers have a responsibility to stimulate awareness, with far more emphasis given to slow crack growth phenomena and issues that limit durability and (if necessary) less given to the 'blowing of trumpets'.

5. The replacement of 40,000 plugs cost the AV equipment supplier well in excess of a million pounds. The plug manufacturer carried the minor cost of modifying the plug base tool. Reducing pillar height by 0.5 mm reduced assembly stresses to less than 5 MPa.

6.5.8 Acrylonitrile-butadiene-styrene pipe fittings

History

A supplier of swimming pools used large quantities of ABS extruded pipe and injection moulded fittings (reducers, bends, and tees). These were used for the pool's water recirculation and filtering systems. Other suppliers also choose ABS for this application in preference to UPVC for cost reasons. Although ABS is the more expensive material, the cost of processing UPVC is higher, and the cost of injection moulding in particular makes the unit price of UPVC fittings higher than similar ABS fittings. Swimming pool pipe systems are compact and complex in geometry and therefore typically the cost of the fittings exceeds the cost of the pipe.

The supplier bought in standard ABS pipe 'off the shelf' but decided for reasons of economy to invest in tooling for the injection moulded fittings. A custom moulder was selected via competitive tender and a significant improvement in margins was achieved.

The pipe systems were constructed by solvent welding using well proven and proprietary ABS solvent-based cements.

Several years after installation, the pipe systems started to fail and the frequency of failure accelerated. The cost of repair for each failure was high as much of the system is buried.

Inspection and analysis

The pipes and fittings removed from two failure sites were inspected. Extensive cracking was observed at each of the ~ 100 fittings but only on internal surfaces. The cracks were all parallel to the cement welds. In addition as shown in Figure 6.25, the cracks followed the perimeter of stray cement blobs or runs but only if these were on the fitting side of the joint.

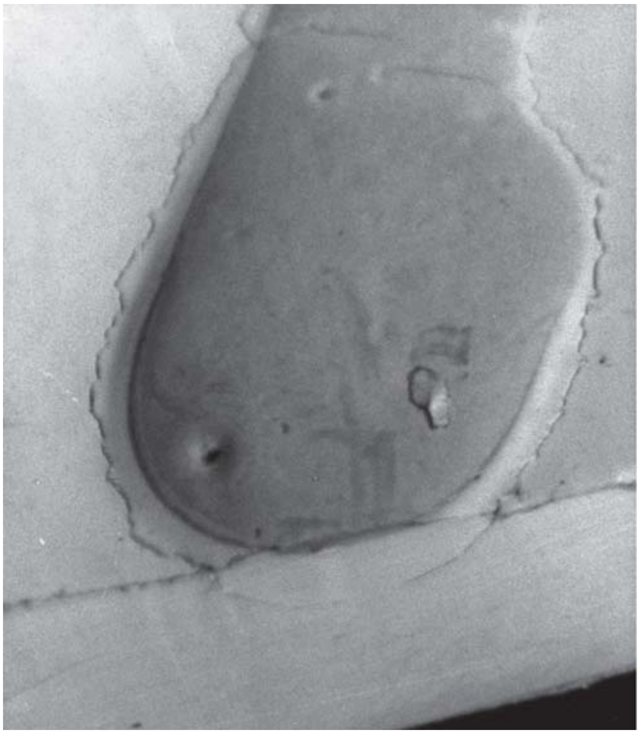

Figure 6.25 Peripheral cracking around an ABS cement blob

The growth of the crack line by coalescence of short linear microcracks is a classic characteristic of ESC. The stress that drives crack initiation and growth is probably due to shrinkage of the cement. The cement is made by dissolving ABS powder in solvent or a mixture of solvents. The cement 'hardens' by loss of solvent to the atmosphere and therefore there is a significant reduction in cement volume (Figure 6.26). Whilst the cement is fluid the volume reduction can be accommodated by surface sinking and cavitation of the interior. However there is constraint against volume shrinkage during the final stage of cement hardening, and this unavoidably induces a triaxial tensile stress in the cement and a peripheral tensile stress in the substrate.

The solvents used in cements are quite powerful stress cracking agents. However, under normal circumstances and with good practice, the shrinkage stresses (and processed-in stresses) are insufficient to induce crack initiation in the time it takes for the solvents to evaporate. Indeed if this was not the case then cement jointing of amorphous thermoplastics would not have gained widespread acceptance.

One departure from good practice that is known to cause 'cement peripheral cracking' is the use of excessive volumes of cement. This is illustrated in Figure 6.8 for a UPVC joint. However for the ABS fittings, cracking occurred regardless of cement line thickness and therefore regardless of the time for solvent evaporation.

Another departure from good practice that is known to cause the same problem is the use of recycled material. In California, ABS pipe and fittings used for domestic waste water plumbing and installed between 1984 and 1990 suffered an epidemic of failures.

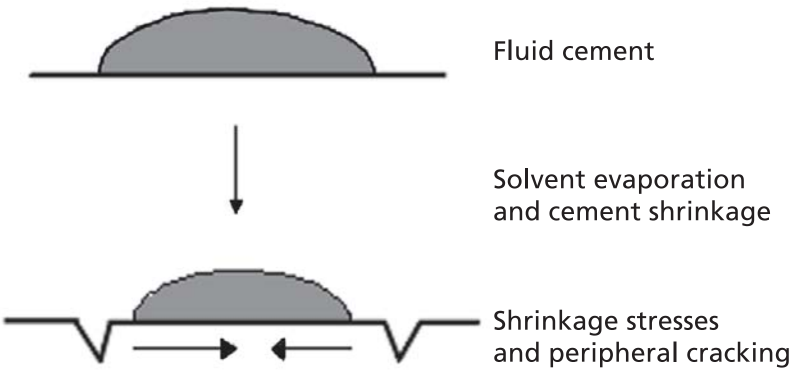

Figure 6.26 Cracking due to cement shrinkage

'Circumferential cracking at the glue line' was observed and the cause traced to substandard (recycled) material. In 1994 the California Senate banned the use of ABS regrind for drain, waste, and vent applications. In 1998 a $73M Class Action suit was set for hearing. There is also evidence that peripheral cracking has been caused by the illicit labelling of SAN and styrene-butadiene rubber (SBR) physical blends as ABS. Such materials are more prone to stress cracking in contact with solvent cements than legitimate graft terpolymers [51]. There is also evidence of the fraudulent practice of mixing ABS with polystyrene [52].

The melt flow rate (MFR) of the materials used in the pipe and fittings were assessed and were found to be in the ranges of:

3 to 4 g/10 min for the pipe
20 to 25 g/10 min for the fittings

This large difference is perhaps sufficient to explain why the pipe was significantly more resistant to ESC than the fittings. The custom moulder was interrogated to establish the source of material used. It was low cost regrind.

Cement blobs were applied to the standard pipe and substandard fitting to establish whether the peripheral cracking phenomenon could be replicated under laboratory conditions. This was unsuccessful until the trial was carried out in an enclosed space. Solvent vapour was essential for the initiation of microscopic crazes at the cement border but these did not develop into visible cracks until the fitting was exposed for extended periods to chlorinated water.

Failure diagnosis

Low molecular weight ABS regrind used to mould the fittings is susceptible to craze initiation whilst in contact with cement solvent vapour. These act as preferential sites for stress corrosion cracking when exposed for long periods to chlorinated water.

Lessons and consequences

1. For structural parts or those requiring reliable durability, always specify virgin materials.

2. For pipe systems with a high linear density of cemented fittings, reduce solvent vapour levels by forced venting.

3. A simple search of public domain information would have alerted the supplier to the potential problems of inadequately specified ABS.

4. The financial consequences were severe. Around 50 swimming pools had to be replumbed and a large stock of fittings destroyed. The reputation of the supplier was so severely impaired that business declined by 50%.

5. Legal action against the custom moulder was considered but abandoned because of the inadequate specification.

6.5.9 Motorised wheelchairs

History

An entrepreneur/engineer set up a company to design, assemble, and market electronically controlled motorised wheelchairs for handicapped children. Materials of construction included steel, glass-reinforced plastics (GRP), rubber and all the thermoplastics normally associated with electrical circuitry. The product was well designed and was the recipient of numerous awards.

The business however did not prosper and the company was in a poor financial state when a large consignment was ordered by a customer in the USA. Champagne was consumed, overdrafts were increased, and the consignment was shipped to the States.

The wheelchairs were shipped in wooden crates. On opening the crates the customer found that all of the polymeric components were either swollen, shrunk, sticky, or fractured. The consignment (valued at ~ £250,000) was rejected.

Inspection and analysis

It was reasonable to suppose that the materials had been subject to attack during the time of crating and shipping. The uniformity of the attack suggested that an aggressive and all pervasive vapour was responsible.

A rubber tube with the most severe swelling and therefore most likely to harbour residual vapour was selected for gas chromatography/mass spectrometry (GC/MS) analysis using a dynamic headspace (purge and trap) injection technique. This revealed the dominant presence of a complex amine.

A sachet of ‘antirust’ agent was belatedly discovered amongst the debris. An unused sachet was acquired and subjected to the same analysis. The same complex amine was identified.

Failure diagnosis

The shipping agent had (gratuitously) added a sachet of a proprietary amine-based antirust formulation to each crate to protect the steel parts during transit. The amine vapour caused rubber parts to swell, extracted plasticiser from PVC, and stress cracked polycarbonate switches, PMMA panel lights, ABS consoles etc.

Lessons and consequences

1. Fluids that are benign or beneficial to metals may be aggressive to polymers. Antirust agents or corrosion inhibitors have been the direct cause of many failures (e.g. Case 6.5.3). The high cost of amine attack on nitrile seals in the offshore oil and gas sector [53] has raised awareness but only within the sector.

2. Most ESC failures involve contact with small amounts of proprietary fluids that are secondary to part function or purpose.

3. The company folded and a well designed product was lost.

6.5.10 Pin hinged polystyrene mouldings

History

A company with a long and successful history as a custom injection moulder decided it was timely to develop and market their own range of products. They chose cosmetic compacts and designed a product that was both ingenious and aesthetically pleasing. Prototype samples moulded from black SAN impressed a national retailer who estimated an annual sales potential of 200,000 units. The moulder invested heavily in tooling and assembly lines and 50,000 units were delivered on schedule.

The retailer sampled the consignment and reported a number of defects and deficiencies including misalignment, sink marks, and fractures. About 500 substandard units were subsequently discarded and the remainder were distributed. Although sales went well, each batch suffered from an increasing reject rate. Eventually the retailer refused a 50,000 consignment, and would order no more until various quality problems were sorted out to their satisfaction.

Inspection and analysis

The compacts comprise a number of individual mouldings connected together by pinned hinges.

The material was analysed by FTIR spectroscopy and found to be impact modified polystyrene.

Inspection with the aid of a hand held magnifying glass revealed that all units were cracked in the vicinity of the pinned hinges. Cracking as indicated in Figure 6.27 invariably initiated at hole bore surfaces in contact with steel pins.

A manual twist of compacts using modest force invariably caused the compacts to disintegrate by fracture at the hinges, as indicated in Figure 6.28.

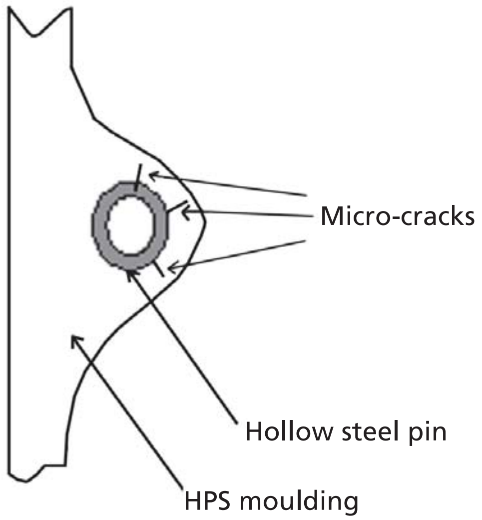

Figure 6.27 Location and orientation of cracks around pinned hinges

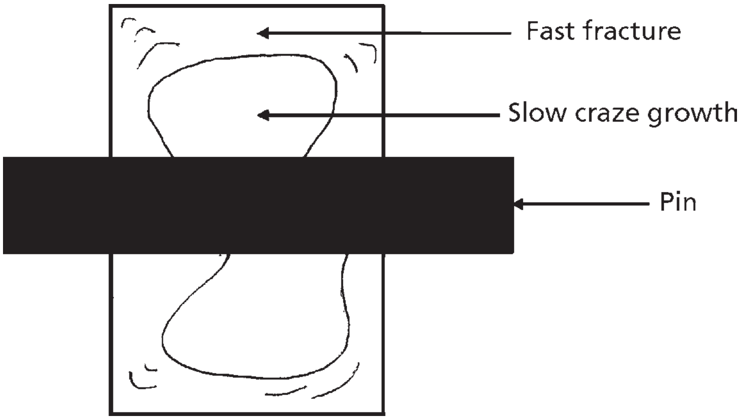

Figure 6.28 Area of slow craze growth and fracture

Failure diagnosis

The multiple initiation and slow growth of microcracks in an amorphous thermoplastic suggests environmental stress cracking. The consistent sites for initiation suggests an aggressive fluid residue on the hinge pins.

The pins and the fracture surfaces were found to be coated with an oil.

The supplier of the hinge pins was well aware (from previous plastic product failures) that the 'processing oil' used in the pin forming operation was 'incompatible' with plastics. It was claimed that the new customer was told to ensure that when pins were ordered the specification should include the designation 'non oiled'. This claim was refuted by the moulder.

During the legal proceedings that followed, the pin supplier claimed that the unannounced change from SAN to HIPS was partly responsible for the problem, and that the high moulding stresses as indicated by excessive mould sinking were a contributory factor. Although SAN is significantly more resistant to the processing oil than HIPS it could be shown that at the time of the initial discussions, this fact was not known by either party. Therefore had the product been originally described as HIPS the quality of advice and the result would have been the same.

Contrary to the claim, it was demonstrated that sinking and moulded-in stress do not go hand in hand. High packing pressures that minimise sinking increase moulded-in stress. Sinking is a visible consequence of the partial relief of such stresses.

Lessons and consequences

1. The retailer's quality reports were shallow. A list of enumerated complaints without any sense of their comparative significance can deflect attention from the critical issue.

2. Product fracture should always attract priority attention. Even if only one in a thousand fails it is prudent to undertake a detailed investigation. In this case a high proportion of the products would have revealed the presence of microcracks.

3. The transition from custom moulder to in house moulder magnifies risks, liabilities, and responsibilities. Success demands a comprehensive knowledge of material phenomena that may lead to premature failure. The moulder did not have this knowledge. The moulder could not interpret the significance of the weak messages from their supplier or customer.

4. The pin supplier was the only party with the knowledge to prevent the problem. As a significant proportion of pin production was destined for contact with plastic components the supplier should have adopted a better (fail-safe) system for avoiding the supply of oiled pins to plastics moulding customers.

6.5.11 Polyethylene wire insulation

History

Low density cellular polyethylene with a dielectric constant as low as 1.4 has been used successfully for many years to insulate high speed communication wire and cable. Intranet systems for interoffice communication are a rapidly growing application. Such systems are expensive and complex and may employ hundreds of bundled wires. These are usually housed in metal conduits or trunking.

In this case the intranet system installed in a large office complex performed perfectly for 2 years. Then problems arose. These included temporary loss of links, and corruption of data during transfer.

An on-site inspection of bundled wires revealed extensive cracking of the insulation. This was considered sufficient to explain system malfunction. The installation contractor and the wire manufacturer disputed responsibility for the failure.

Inspection and analysis

Cracking was generally limited to the outer wires of bundles. As shown in Figure 6.29, the distribution of individual circumferential cracks was not regular but nevertheless was quite discrete, with an average intercrack distance of about 50 mm. Crack opening displacement as shown in close-up (Figure 6.30) was typically 2 mm.

The inside surfaces of the conduit and the outer wires of the bundles were found to be liberally coated with lubricant. This was shown by chemical analysis to be silicone oil.

Failure diagnosis

It is known that silicone oil is a modest to powerful environmental stress cracking agent for polyethylene. It transpired that the installer had used the oil to ease the threading of wire bundles into parts of the conduit system with restricted accessibility.

The ratio of crack opening displacement and the crack interval implies a residual axial strain in the insulation of about 4%. This would then imply a poorly processed product.

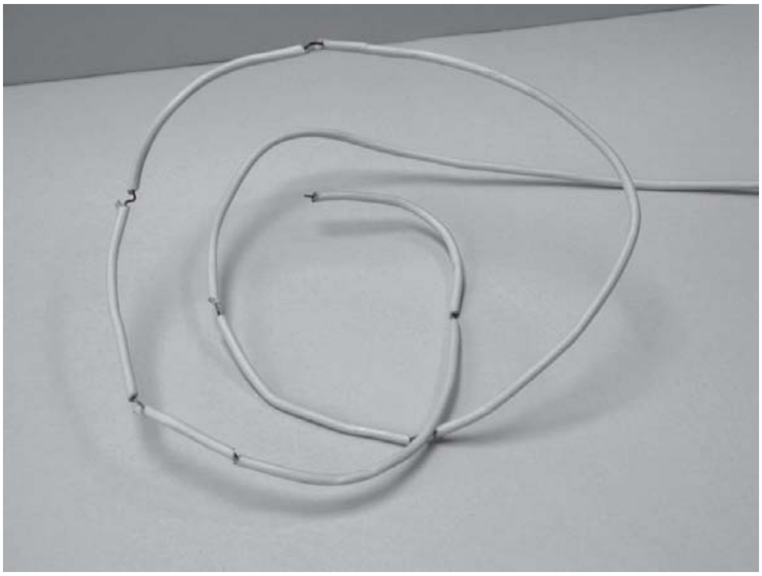

Figure 6.29 Cracking of polyethylene wire insulation (general view)

Figure 6.30 Cracking of polyethylene wire insulation (close-up view)

However cellular materials are prone to contract significantly in volume if softened by heat or the absorption of plasticising fluids. The diameter of insulation in wires that had cracked was found to be significantly reduced. On the assumption that this was due to absorption of the silicone oil, the residual axial strain was calculated to be less than 1%.

On receipt of the report, the findings were accepted by all parties. The installer admitted ignorance and the manufacturer claimed knowledge about the specific interaction between silicone oil and polyethylene.

Lessons and consequences

1. The gratuitous use of silicone oil as a lubricant for polyethylene products is a common cause of failure. This case and Case 6.5.2 are just two examples of many.
2. Although the manufacturer claimed knowledge, there was no documented evidence that any attempt had been made to warn installers against the use of silicone-based lubricants.
3. In these circumstances the installer and manufacturer agreed to share the costs of rewiring. Had the office complex been part of a fully commercial company rather

than part of the public sector, both parties would undoubtedly have faced much heavier consequential costs due to lost production.

6.5.12 Polystyrene scrubbing brushes

History

An importer purchased a consignment of household scrubbing brushes. Samples had been tested and approved by distributing free samples for home trials.

Within a few weeks of receipt the consignment of 50,000 brushes had been distributed to retailers and wholesalers.

Within a month customer complaints were at such a high level that the importer had to concede that the product be withdrawn. Complainants claimed that the product 'disintegrated' or 'shattered' within the first few minutes of use.

Inspection and analysis

A photograph of a failed brush is shown in Figure 6.31. Generally the multiple fracture planes were linear and bisected the bristle retaining holes. On inspection these were deemed to coincide with the position of internal weld or knit lines.

A microscopic examination of the weld lines of an unused brush revealed the presence of crazes.

FTIR analysis revealed that the brush was moulded from general purpose polystyrene and that an epoxy-based adhesive had been used to bond the bristles to the moulding.

Failure diagnosis

Of all plastics, polystyrene has the least resistance to environmental stress cracking. It is therefore not the correct material for a product that will unavoidably come into contact with a wide range of surfactants and other cleaning agents.

The presence of crazes in unused brushes suggests either very high moulded-in stress (resulting in 'air crazing') or an ESC interaction between the adhesive and the polystyrene.

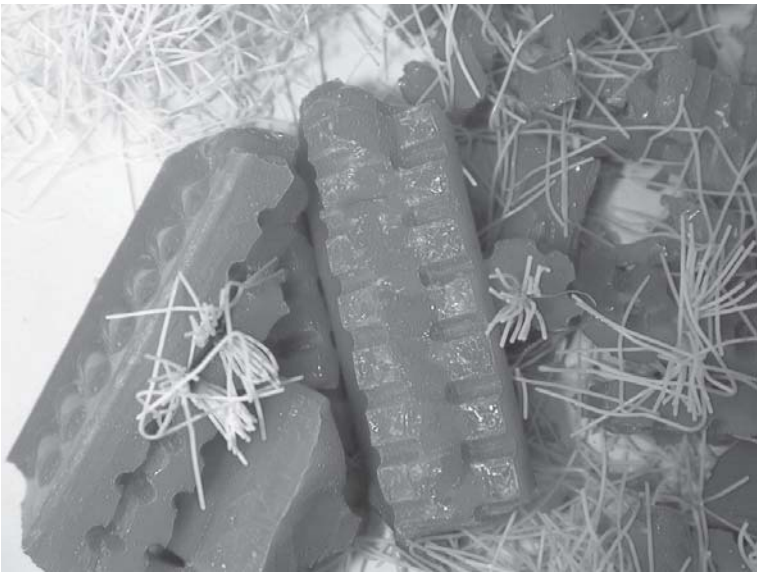

Figure 6.31 Disintegrated scrubbing brush

An original trial sample was inspected and found to be uncrazed. FTIR analysis revealed that the material was styrene-acrylonitrile (SAN).

On being informed of this and of the fact that SAN would be significantly more resistant to ESC than polystyrene, the importer chose to discontinue the investigation.

Lessons and consequences

1. General purpose polystyrene is so susceptible to ESC that the material should only be considered for service where the chemical environment can be precisely predefined.

2. A moulder who is prepared to change materials without informing his customer is unlikely to employ good moulding practices.

3. Poor weld lines plus high residual moulding stress can combine to initiate crazing in the absence of aggressive chemicals. Precrazed mouldings are prone to immediate disintegration on contact with a wide range of (even mild) cleaning agents.

4. The importer was unfortunate but not blameless. It transpired that the ‘initial trials’ were intended only to serve as a market survey. The importer was interested only in

profit and the point of sale attractiveness of the product. Even if the original samples had been moulded from polystyrene rather than SAN it is doubtful whether the problem would have been detected or avoided.

6.5.13 Blow moulded polyvinyl chloride bottles

History

Blow moulded PVC bottles had been used as the container for a particular domestic cleaning fluid for many years without any significant problems. Some customer complaints had been received regarding cracking and leaking but these always applied to old bottles. To limit future complaints and liabilities a senior manager had the ‘bright’ idea of printing a ‘use-by date’ on each bottle.

To stimulate sales, marketing consultants were hired to improve the packaging. They concluded that the shape of the bottle was too similar to that of their major competitor and a radical redesign was needed. Final year undergraduates from a local industrial design college were recommended as the most cost effective source of fresh conceptual designs. Eventually a new design was selected and trial mouldings produced for evaluation. The only performance test to be carried out was a simple drop test.

Ten thousand bottles were filled and distributed. A significant proportion of these failed during transportation.

Inspection and analysis

A typical failure is shown in Figure 6.32. In all cases cracking had occurred in a circumferential area adjacent to the bottle neck. Detailed inspection of the fractures revealed multiple microcrack initiation at the inside surface. Environmental stress cracking of the PVC by the cleaning fluid was clearly the cause of the problem.

Failure diagnosis

The fluid and the grade of PVC had not been changed, but the new bottle design had increased the maximum tensile stress on the bottle during stacking and transport. When stacked the bottles in the lowest layer support the weight of layers above them.

Figure 6.32 ESC failure of a PVC bottle

A major difference between the old and new design was the shape of the bottle shoulder (see Figure 6.33). In the old design the sloping shoulder ensured that the 'top load' applied to the cap was transferred predominantly by axial compression in the wall of the shoulder. In the new design the applied load developed a significant bending moment in the shoulder with tensile stress on the inside surface near the neck (marked * below). This coincides with the fracture initiation site.

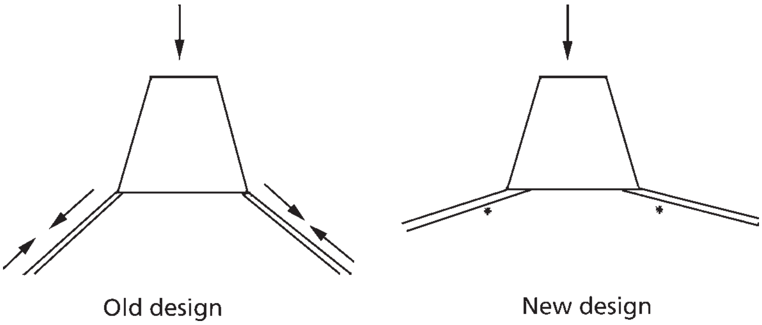

Figure 6.33 Shape of bottle shoulders

New bottles were filled with the cleaning fluid and were subjected to a range of top loads for 24 hours at ambient temperature. Cracking in the shoulder was observed within 24 hours if the applied top load exceeded by 1.5 times that due to the stacking heights used in transportation. Bearing in mind the additional transient dynamic loads and imperfect stacking, the laboratory test result was considered sufficient to confirm the diagnosis. The cleaning fluid is a moderately severe environmental stress cracking agent for PVC, and during transport the maximum stress and time was sufficient to cause cracking.

Lessons and consequences

1. The analysis of in-service failures should be more than a defensive exercise to be applied only when forced to do so by commercial pressures. A positive approach is to regard service failures as the tangible result of a free field trial. In this case an investigation would have revealed that the fluid and the PVC were incompatible in the longer term and therefore that any change in packaging, formulation, or service conditions could render them incompatible in the short-term.

2. All new packaging of this type should have a top load specification.

3. Industrial designers, marketeers and others with a professional interest in style, and fashion should understand that standard product shapes are not accidental. It would be prudent for them to assume that the shape has evolved for good reasons and that any significant departure from the standard involves risks.

4. The company reverted to the old bottle shape and their chemists were given the task of reducing the stress cracking power of the cleaning fluid. This was so successful that the ‘use-by date’ was no longer required. It later transpired that customers and competitors had taken the use by date as an admission of product (fluid) instability. Its removal stimulated sales.

5. The business objectives of the company were achieved via a series of expensive detours up blind alleys.

6.5.14 Polyvinyl chloride pressure pipe

History

PVC pipe competes with medium and high density polyethylene for mains water and waste water distribution. The advantages of PVC compared with polyethylene include:

- Higher design stresses (3 to 4 times those of HDPE at ambient temperature),
- Higher stiffness,
- Jointable by solvent-based cementing.

The disadvantages include:

- Inferior fatigue resistance,
- Inferior damage tolerance,
- Quality inconsistency.

PVC pipe has suffered a higher percentage of failures than PE pipe and the causes have been analysed. In one study of over 300 PVC pipeline failures [54], 23% were due to manufacturing defects such as inclusions, voids, and poor spider lines. 51% were due to laying and jointing defects including 15% for inadequate solvent cementing procedures. 15% were due to operational factors and about a third of these were traced to cyclic or surge fatigue. Most of the pipes in the survey had been manufactured in the late 1960s or early 1970s and since then there has been a significant improvement in material quality, particularly in respect of fracture toughness and the control of gelation/particle fusion levels.

Failures due to environmental degradation have been rare because the environment of a buried pipe transporting water is reliably mild. Those that have occurred are dominated by environmental stress cracking of solvent cemented joints.

Inspection and analysis

A typical joint failure was shown previously in Figure 6.8. This is the socket end of a spigot and socket joint. The white deposit is the excess solvent cement that has been squeezed out of the sliding fit between socket and spigot. Brittle fracture has initiated on the inside surface of the pipe underneath the cement deposit. The fracture surface was partly coated with cement, indicating that during the initial stages of crack growth the cement was fluid.

Failure diagnosis

The solvents used in proprietary solvent-based cements are potentially powerful stress cracking agents. Application instructions stipulate that excess cement is removed, but the reasons for doing this are never stated. When jointing two six metre lengths of pipe it is easy to remove excess cement from external pipe surfaces, but physically impossible to remove the inside deposit that appears to have caused the failure in this case.

It is essential that no stresses are applied to the joint until after the solvent cement has solidified (by solvent evaporation). Pressure testing and handling must be delayed until the hardening process is complete. It is evident that the solvent cement was still fluid at the time that sufficient stress was applied to crack the pipe. The orientation of the fracture plane would suggest the application of flexural stress (possibly vertical jacking of the joint to access and improve the bedding).

Lessons and consequences

1. Instructions and best practice procedures should always give honest reasons; otherwise there is no awareness of the risks involved by failing to abide by them. In this case it was not possible to abide by the instruction to remove excess cement. The implicit reason for the instruction to delay handling is that time is required to develop the full bond strength. This tends to imply that there is a risk of joint displacement if prematurely handled. This is true, but minor displacements are rarely a serious matter and major displacements are obvious and rectifiable. If water companies were aware of the **hidden damage** that could result from departures from best practice then the frequency of failure incidence would decrease.

6.5.15 Fracture of an acrylic sight glass

History

The manufacturer of concrete mixing and dispensing units was informed that an acrylic sight glass had failed ‘explosively’. Although the failure did not cause any injuries, the risk that other units might fail for the same reason was taken very seriously.

The sight glasses had been extruded with a bore diameter of 140 mm and a wall thickness of 5 mm. Pressure relief valves were supposed to limit hydraulic pressures within the tubes to less than 0.025 MPa but these were found to malfunction on the unit that had failed. On the assumption that the unit had been operating at the maximum pump delivery pressure (0.04 MPa) the hoop stresses in the sight glasses would be 5.8 MPa.

Inspection and analysis

Sight glasses in other units were inspected, 19 were considered to be in a satisfactory condition. One contained a single axial craze of 10 mm length and 3 mm depth. This had initiated on the inside surface of the tube.

Fragments from the failed sight glass were inspected. The fracture initiation point was located, and striations similar to those previously shown for polycarbonate (see Figure 1.6) were observed, and deemed to be characteristic of slow craze/crack growth under conditions of cyclic or intermittent stress.

The dynamic fatigue resistance of the acrylic material was assessed at 0.5 Hz under conditions of square wave tension/zero cycling at 23 °C at two stress amplitudes. At a stress amplitude of 8 MPa the material was undamaged after one million cycles. At a stress amplitude of 10 MPa the material was visibly crazed after 300,000 cycles, and failed by fracture after 400,000 cycles.

Proprietary fluids added to the concrete mix, including plasticisers, lubricants, retarders, and waterproofing agents, were investigated as potential stress cracking agents for acrylic. Single cantilever bending beam specimens with a maximum static surface tensile stress of 20 MPa were exposed to each of the eleven fluids for a period of 500 hours. Only one, a plasticiser based on tributyl phosphate, had an adverse effect. The acrylic fractured after 160 hours of exposure. The applied stress level was reduced to 15 MPa and the time to fracture increased to 380 hours. The applied stress was increased to 25 MPa and the time to fracture reduced to 35 hours.

Failure diagnosis

The maximum number of pressure cycles experienced by the failed sight glass was estimated to be 20,000 (7 years at 10 cycles per day). The fatigue resistance of the material assessed (admittedly) at a much higher frequency suggests that 20,000 cycles at 6 MPa is not the cause of failure. There is a need to be cautious with this assumption because:

i) cycles to failure will decrease with decreasing cyclic frequency.

ii) Spider line stress concentrations in the extruded product (but not in the test specimens) may significantly reduce fatigue resistance.

The additive containing tributyl phosphate can be described as a modest environmental stress cracking agent for acrylic. With only 3 points on the stress versus time to fail envelope the durability at 6 MPa cannot be predicted with confidence. However the trend would suggest damage initiation well within 7 years. This together with the established circumstantial evidence (the suspect additive had only been used in the two units that had fractured or cracked) was agreed to be sufficient to identify the primary cause of failure.

Lessons and consequences

1. Pressure relief valves are rarely fail-safe. The significant proportion that are known to malfunction in industrial environments invites diligent and frequent maintenance.
2. Had the relief valves been fully functional the problem would have revealed itself but at a later date.
3. The manufacturers of proprietary fluids will generally only check the compatibility of their products with the plastics used to package them.
4. The manufacturer of the mixing/dispensing units warned all their customers against the use of the culprit fluid. The vendor of the fluid rapidly changed the formulation.

6.5.16 Rotationally moulded polyethylene wine coolers

History

Wine coolers are double skinned boxes made from rotationally moulded high density polyethylene and filled with foamed polyurethane. This wall construction provides a tough and very effective thermal barrier at low temperatures.

After many years of trouble free production a supplier of wine coolers to caterers suffered a rash of complaints and returns. Large cracks had developed within a few weeks of purchase. The supplier blamed the rotational moulder for a lapse in quality.

Inspection and analysis

A failed cooler is shown in Figure 6.34. Cracking was mainly restricted to the top edge, where the tensile stresses due to the foaming process would be expected to maximise.

Figure 6.34 Cracked wine cooler

Cracks had all initiated on the outer surface. It was therefore reasonable to eliminate incompatibility between the polyurethane and the polyethylene as a candidate cause.

The surfaces of several failed coolers were swabbed for analysis. All revealed silicone contamination.

Failure diagnosis

The supplier was informed that failure was due to environmental stress cracking via contact with a silicone-based fluid. A cleaning agent was suspected. It was normal practice prior to dispatch from the supplier's warehouse to clean the coolers with warm soapy water. However for a period a cleaning spray marketed for black polypropylene car bumpers had been used. Exposure tests confirmed that the proprietary fluid was a powerful stress cracking agent for rotationally moulded polyethylene.

The surprising aspect of this case is the rapidity of cracking at such modest levels of stress. An advantage of rotational moulding over competing processes such as injection moulding or vacuum forming is the low level of residual processed-in stress. Therefore if the moulding is of reasonable quality then the driving force for cracking is derived only from the modest hydrostatic pressures generated by foaming.

The same powder used to rotationally mould the product was hot melt injection moulded into tensile bars and exposed under stress to the cleaning fluid. Tensile bars cut from recently manufactured coolers were subjected to the same test. The injection moulded material was significantly more resistant to ESC than the rotationally moulded material.

Lessons and consequences

1. Rotational moulding may, on this evidence, produce products that are particularly prone to ESC under conditions of applied stress. The reason for this is not known. The process involves powder melting with little or no shear, and the more open structure could be responsible for an increased rate of fluid penetration.

2. The gratuitous use of silicone-based fluids is again the avoidable cause of failure in a polyethylene product. The processors, fabricators, and suppliers of such products need to ensure that all staff are aware of the risks.

3. The supplier tightened procedures and banned all unauthorised fluids from the warehouse. Customers were advised to clean the coolers with warm soapy water.

6.5.17 Polycarbonate mixing bowls and jugs

Introduction

The manufacturer of domestic food mixer/blenders had reacted to a low frequency of mild complaints by simply supplying replacements. Customers complained about a deterioration in the appearance of injection moulded polycarbonate mixing bowls and jugs. The manufacturer knew that the problem was surface crazing but did not attempt to identify its cause.

Following an outbreak of food poisoning, health officials traced the source to a small café. One of the items that attracted the attention of the investigating team was a transparent mixing bowl containing “multiple surface fissures that could be the location for colonisation by micro-organisms”. On receipt of this very serious observation, the manufacturer was finally stimulated to investigate the extent and cause of the crazing problem.

Inspection and analysis

100 owners of the mixer/blender were traced and persuaded to return the mixing bowls. 15% were found to be visibly crazed, compared with an historical complaint rate of only

0.2%. Evidently for most customers crazing was either not observed or not considered to be serious enough to justify a complaint.

A typical example of crazing is shown in Figure 6.35. Crazes are invariably oriented in an axial direction. The polycarbonate supplier suggested that the problem was due to the use of aggressive surfactants combined with the high washing temperatures. However

Figure 6.35 Extensive crazing on the internal surface of a polycarbonate mixing jug

this was eliminated by the observation that all crazes had initiated on the inside surface of the bowls. (Surely if aggressive washing was the cause then all surfaces would be equally exposed). The evidence pointed to a reasonably common food/ingredient that was acting as a powerful ESC agent for polycarbonate.

In an attempt to identify the culprit(s), letters of complaint accumulated over several years were studied. Fortunately the letters did provide some valuable clues. Two correspondents observed that the problem occurred soon after fragmentation of pepper corns. Another noted crazing immediately after the bowl was filled with the zest from lemon skins. The common abundant type of constituent in these two foodstuffs are 'essential oils' classified chemically as terpenes. Terpenes are known to be powerful solvents for many polymers and indeed are in common use as tackifiers.

The craze pattern was replicated by exposing new bowls to freshly crushed pepper corns and the zest from orange and lemon peel.

Failure diagnosis

The crazing is due to the combination of residual moulded-in stress and contact with food products that contain high concentrations of essential oils.

Lessons and consequences

1. Customer complaints should be treated seriously as a potential source of valuable information.
2. The frequency of complaints often underrepresents the frequency of the problem.
3. Specific foods and ingredients for human consumption include powerful ESC agents. Polycarbonate and other amorphous thermoplastics are prone to crazing and embrittlement in contact with these including highly flavoured ingredients and spices.
4. The manufacturer was advised to reduce the moulded-in residual stress by increasing cycle time and/or annealing.
5. Eventually the crazed bowl was cleared by investigators as the source of the outbreak of food poisoning. However, the bowl manufacturer could no longer be complacent in the face of potential litigation (past and future) concerning the unhygienic qualities of a crazed product intended for food contact.

6.5.18 Acrylonitrile-butadiene-styrene rotary switches

History

The overhead switch for opening and closing the sunroof on an 'executive saloon' suffered a high incidence of failure. The problem was only identified by the manufacturer 10 years after introduction of the model when the components reserved for spares had been consumed.

The part that failed was an injection moulded ABS dial. This was connected to a rotary switch via a zinc coated metal spindle. The dial was illuminated with a back light. Cracking of the dial decoupled the dial from the spindle and rendered the switch inoperable. Owners may have been irritated by the inconvenience but evidently not sufficiently so to complain. Local dealers failed to observe a trend.

Inspection and analysis

This case is of interest because of the number of candidate causes of failure. The manufacturer identified three, UV exposure from back light illumination, thermooxidation via heat from the back light, and fatigue via repeated use. Of these UV degradation and fatigue were favoured candidates because of the known poor resistance of ABS in these respects.

A failed dial was inspected. Discoloration was minimal, suggesting minimal UV or thermal degradation. This was confirmed by gel permeation chromatography which revealed no significant reductions in molecular weight. Although fatigue striations were observed on the fracture surface these were few and very broadly spaced. Multiple microcracking was detected on surfaces that were in intimate contact with the spindle. These were deep enough to grow rapidly under applied stress, reducing the apparent modulus of the material and inducing structural properties that could be described as 'cheesy'.

Failure diagnosis

Multiple microcracking is symptomatic of ESC rather than fatigue. Spindle surfaces were swabbed and analysis revealed silicone. The manufacturer confirmed that silicone lubricant had been applied to all switches during assembly to improve the smoothness of operation. They were unaware of any incompatibility.

Failure was due to ESC via contact with a silicone lubricant combined with intermittent stresses applied manually during switching.

Lessons and consequences

1. Where possible manufacturers should continuously assess the rate of consumption of spare parts to identify weak components. This should apply to all components regardless of their criticality. Mild but widespread customer irritation is worth avoiding, particularly by those engaged in the highly competitive automotive industry.

2. The lack of awareness on the part of the manufacturer is understandable. At the time the decision to apply the lubricant was taken, it is apparent that ABS suppliers were also generally unaware of the incompatibility. At the time a new ABS cycle lamp cracked for the same reason. The technical services departments of three of the major ABS suppliers expressed surprise that agents other than polar hydrocarbons could stress crack their material.

6.5.19 Vacuum moulded sweets dispenser

History

Thirty sweets dispensers fabricated from solvent welded vacuum formed high impact polystyrene (HIPS) components cracked in service. It was established that all the dispensers that failed had been in contact with a particular sweet called ‘cola bottles’. These were of similar texture to ‘jelly babies’.

Sharp fragments from disintegrating dispensers could have been ingested, and had this occurred the supply chain would have been exposed to the risk of very serious litigation.

Inspection and analysis

Severe attack was concentrated at rectangular depressions in the HIPS mouldings. As shown in Figure 6.36 the uppermost depressions are cracked but mainly intact. The middle depressions have completely disintegrated to leave rectangular apertures. The lower pair of depressions and some of the surrounding material have disintegrated. It would be reasonable to infer that the increased severity of attack with depth is the result

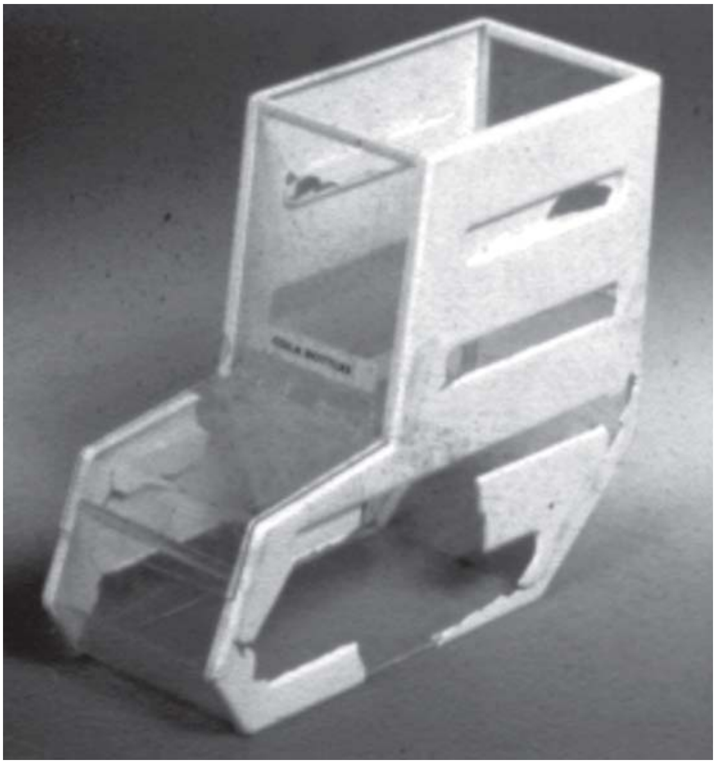

Figure 6.36 Partially disintegrated sweets dispenser

of increasing contact time with the suspect sweets (as the content level varies from full to empty). It would also be reasonable to infer that the attacking fluid is a liquid rather than a vapour.

Various transparent parts made by the hot bending of PMMA sheets were found to be in good condition.

Failure diagnosis

A new HIPS side panel was covered in a single layer of the suspect sweets and placed in an oven at 40 °C. Cracking at the boundaries of depressions was detected after 1000 hours. The test was repeated with the sweet layer under compression at a level chosen to replicate the hydrostatic pressure in a full dispenser. Cracking was detected after 200 hours. The second test was repeated using three other sweets that were known to have been dispensed in service without problems. No cracking was observed after 2000 hours.

The 'cola bottle' sweets contain a stress cracking fluid. The side panels have high residual tensile stress around the periphery of vacuum formed depressions. The lower most depressions were attacked more rapidly and severely for two reasons. Firstly contact time is maximum. Secondly contact pressure is maximum. The latter would imply that slight pressure promotes migration (exudation) of the attacking fluid from the sweet bulk to the sweet surface.

Lessons and consequences

1. Further work would be needed to identify the attacking fluid. The sweet manufacturer would not reveal the precise ingredients other than to confirm a gelatine base with added vegetable oil, artificial flavourings, and organic dyes. Sensitivity to exudation alone would suggest the vegetable oil as the main suspect.

2. The sweet manufacturer was however aware of the risks faced by ignoring the problem. A test methodology was developed for them to confidentially assess the stress cracking power of precursor ingredients.

3. The manufacturer of the dispensers without control or knowledge of the future contents to be dispensed faced the risk of future litigation. To reduce this risk they were advised to change from HIPS to ABS, to eliminate the depressions from the side mouldings (their purpose was only aesthetic) and to generally minimise residual stress by increasing sheet temperature and reducing formed sheet cooling rate.

6.5.20 Acrylonitrile-butadiene-styrene pipe

History

An ABS pipe system was used to convey chilled water (6 – 10 °C) within a factory. The system was essential for many manufacturing operations and in recognition of this, pipe and fittings rated for 1 MPa service were selected even though maximum hydraulic pressures were less than 0.3 MPa.

After 8 years of service the system started to leak.

Inspection and analysis

A leaking pipe section was examined. The bore surface was visibly cracked. The cracks were axially aligned and it would be reasonable to assume they had propagated under the influence of pressure stresses. The cracks as shown in Figure 6.37 were long (~ 10 cm), deep, and virtually straight. At the leakage site a crack had penetrated the pipe wall.

The crack surfaces were flat and devoid of any gross features such as hackle marks, local yielding, or fatigue striations. They did not coincide with the extrusion spider lines.

The water conveyed by the system was known to contain two additives: a corrosion inhibitor and a biocide.

ABS specimens cut from standard sheet were subjected to 3 point bending at 0.9% strain in contact with undiluted inhibitor, undiluted biocide, and water treated with both at the recommended concentrations. No cracking was observed after 600 hours with the undiluted biocide or the treated water but dense microcracking was observed in less than three hours of contact with the inhibitor.

Failure diagnosis

Long, deep, perfectly planar and featureless cracks of this nature are rarely encountered in laboratory tests or in products. They can only be produced by very slow and uniform

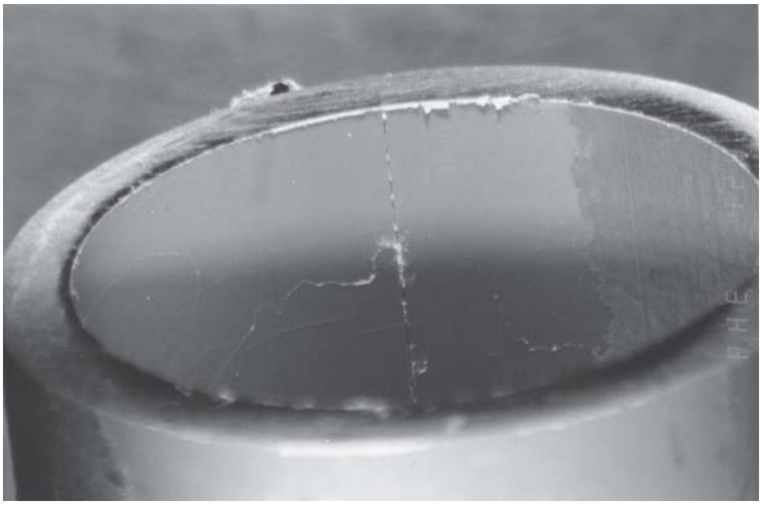

Figure 6.37 An axial crack in an ABS pipe

crack growth rates. Laboratory tests are generally too short and aggressive to reproduce the effect. Products in service are generally perturbed by fluctuations in stress and temperature, or the crack will become unstable leading to fast fracture. ABS offers outstanding fast fracture toughness, and this together with the low and consistent pressure stresses in this application has allowed extensive crack growth over a long period of time and subsequent leaking rather than catastrophic fracture.

Low stresses applied for a long time plus contact with a mild environmental stress cracking agent provide the only possible cause of failure. The inhibitor (containing dimethylamines) is the probable culprit as this was shown to be a powerful stress cracking agent in its undiluted form.

Lessons and consequences

1. Many proprietary corrosion inhibitors (see for example Case 6.5.3) are stress cracking agents for many plastics.

2. In this case it transpired that the current inhibitor had only been used for two years. Prior to that, another inhibitor had been used which was no longer commercially available. On the evidence of very slow crack growth, it was surmised that both inhibitors contributed to the failure.

3. The factory owners were advised that as the whole pipework system was severely structurally impaired it should be replaced. Polypropylene copolymer was recommended in place of ABS.

4. Inhibitors are used in capital plant without awareness of risks or adequate information from the supply chain. A very serious failure is probably the only event that will change the situation.

6.5.21 Polycarbonate filter bowls

History

An airline filter bowl moulded from polycarbonate fractured and an assembly worker was injured by high velocity fragments. The airline system, which had been installed for 2 years included many more filter bowls of the same type. The risk of further failures and injuries forced the plant to suspend production pending the outcome of an initial investigation.

Inspection

All the fragments from the failure were not recovered. The crack initiation site was not located. The fracture surfaces on all recovered fragments were the result of fast crack growth.

Intact bowls were inspected at the site. A cluster of seven in the vicinity of the failed bowl were found to be visibly crazed. All crazes as exemplified in Figure 6.38 were aligned with the axis of the bowl and had initiated on the outside surface.

Failure diagnosis

The hoop stress on the bowls was calculated to be only 5 MPa and this had been applied intermittently for only 2 years. This history is not severe enough to initiate visible crazing in air.

A solvent cleaning bath was located within the cluster. It contained a large volume of toluene. The solvent in liquid form is generally known to be a powerful stress cracking agent for polycarbonate. In vapour form it would be expected to be less powerful. Insufficient time was available to quantify the interaction. However it was recalled that sealed safety lighting glazed with polycarbonate had in the past failed when exposed to a toluene rich atmosphere. Residual and assembly stresses had been in the region of 7 MPa.

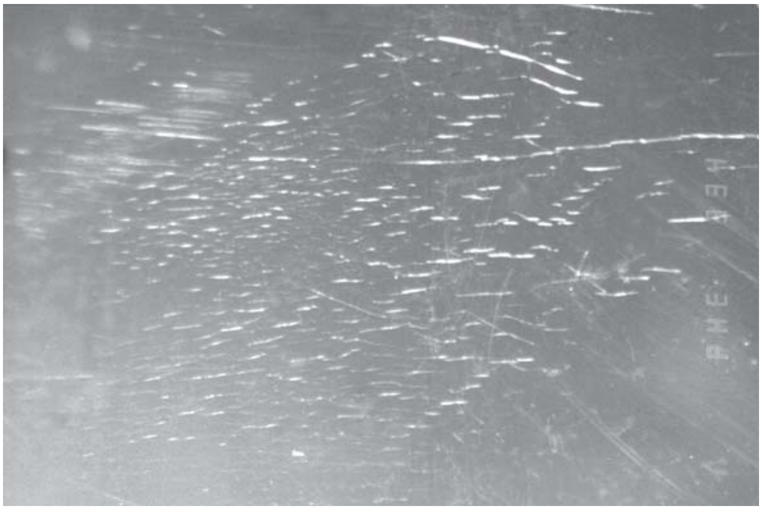

Figure 6.38 Crazing on the outside surface of a polycarbonate filter bowl

Lessons and consequences

1. Amorphous thermoplastics are susceptible to ESC when exposed to aggressive vapours as well as liquids, if conditions allow for condensation on the surfaces of the product. All other factors being equal the most aggressive condition is a condensate at a temperature just below its boiling point.

2. Forty filter bowls a good distance from the cleaning bath were pronounced as structurally sound and safe.

3. Ten bowls in the vicinity of the bath were replaced after improved ventilation had effectively isolated the bath from the surrounding atmosphere.

4. The injured worker received substantial compensation.

6.5.22 Noryl rotary switches

History

Noryl rotors in power isolation switches cracked within a year in service. The component (and assembly) had previously been approved by testing to replicate the number of switching operations expected over a service life of 10 years.

Inspection and analysis

Figure 6.39 reveals that cracking is possibly associated with grease on the surfaces.

The fracture surfaces of larger cracks that were near to areas under high cyclic stress amplitude were striated indicating crack growth via fatigue. Otherwise smaller cracks were planar and featureless and indicative of slow crack growth under static stress conditions.

The proprietary grease used was from the Electrolube range but there was some doubt as to whether this was (as designated here) type A or B. Two other greases (types C and D) which were claimed to be ‘less detrimental to polymers’, were acquired and the four greases were assessed for their compatibility with Noryl (SE1 grade). The times to visible cracking with the plastic exposed to grease at several levels of applied strain are listed in Table 6.15. All are stress cracking agents and Type A is the most aggressive.

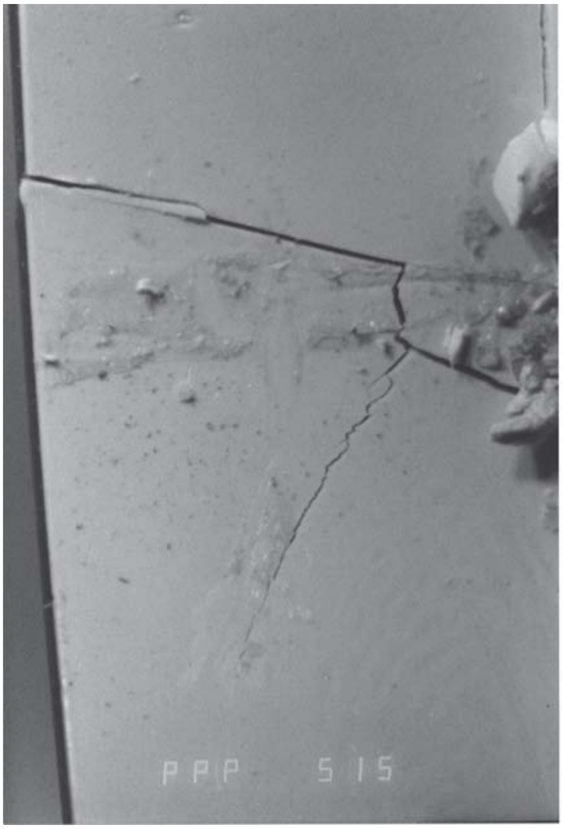

Figure 6.39 Cracking in a Noryl moulding adjacent to surface grease

New Noryl mouldings were dip tested to establish levels of residual stress/strain. In tri-*n*-butyl phosphate at 20 °C the material supplier states that if cracking is observed in less than 10 minutes then the residual stress is at least 9.31 MPa. The rotor mouldings cracked after an immersion time of between 100 seconds and 400 seconds. According to our calibration data this implied a maximum residual stress of about 15 MPa. With a modulus of 2,500 MPa this equates to a maximum residual tensile strain of 0.6%.

Failure diagnosis

The very high residual strains in the Noryl mouldings are responsible for rapid crack initiation when in contact with any of the four greases. The applied torque generates comparatively modest stresses which are calculated to be only about 3 MPa. Although this is insufficient to initiate cracks it is sufficient to propagate them. Thus large cracks exhibit classical fatigue striations.

Table 6.15 Environmental stress cracking of Noryl SE1 in contact with Electrolube greases

Grease	Applied strain (%)	Time to crack (s)
Type A	1	70
	0.7	150
	0.5	1000
Type B	1	200
	0.7	1000
	0.5	12000
Type C	1	200
	0.7	1500
	0.5	12000
Type D	1	150
	0.7	1300
	0.5	11000

The switch manufacturer selected the product testing conditions on the assumption that durability would be limited by cyclic fatigue. Although this assumption turned out to be incorrect, the testing procedure should nevertheless have identified ESC as the primary problem. Gross differences in the quality of the test components and the production components is the most likely explanation for the oversight. Unfortunately the test components had been discarded so this could not be directly proved. The only records of value indicated a significant difference in dimensions between test components and production components; the former being smaller than the latter. Longer cooling times lead to increased shrinkage and reduced residual stress and therefore this supports the probable explanation.

Lessons and consequences

1. The high residual stresses in the rotor mouldings could only arise if the process parameters were well outside the recommended ranges. Lower than optimum melt

and mould temperatures are the major culprits and the means by which a moulder can reduce cycle times and maximise profit.

2. The tributylphosphate dip test should have been applied to the original (test) mouldings and periodically to production mouldings. This would probably have revealed a deterioration in moulding quality.

3. A nonaggressive grease was found (Mobiplex). This together with a stipulated maximum residual stress of ~ 4 MPa would be regarded as a safe combination.

References

1. L. J. Broutman, D. B. Edwards, L. R. Nylander and P. K. So, Proceedings of Antec '98, Vol. III, Atlanta, GA, p.3516.

2. R. S. Dave, C. J. Chen, D. A. Smith and M. C. O. Chang, Proceedings of Antec '94, Vol. III, San Francisco, CA, p.3266.

3. N. J. Hermanson, P. A. Crittenden, L. R. Novak and R. A. Woods in Medical Plastics, Ed., R. C. Portnoy, 1998, PDL, Norwich, NY, p.117.

4. G. Menges and H. Schmidt, Kunststoffe, 1967, 57, p.885.

5. D. C. Wright, British Polymer Journal, 1978, 10, p.60.

6. O. S. Bruller, Polymer Engineering and Science, 1978, 18, p.42.

7. N. Brown and X. Lu, Journal of Materials Science, 1990, 25, p.29.

8. N. Brown and X. Lu, Journal of Materials Science, 1990, 25, p.411.

9. D. S. Dugdale, Journal of the Mechanics and Physics of Solids, 1960, 8, p.100.

10. N. Brown and S. K. Bhattacharya, Journal of Materials Science, 1985, 20, p.4553.

11. J. G. Williams and M. K. V. Chan, Polymer, 1983, 24, p.234.

12. J. G. Williams and G. P. Marshall, Proceedings of the Royal Society of London, A, 1975, Vol. 342, p.55.

13. N. Brown and X. Lu, Journal of Materials Science, 1986, 21, p.2423.

14. H. Crook, B. L. Earl, J. H. T. Johns and R. J. Loneragan, Polymer Engineering and Science, 1973, 13, p.390.

15. R. P. Kambour, E. E. Romagosa and C. L. Gruner, Macromolecules, 1972, 5, p.335.

16. J. C. Arnold, Journal of Materials Science, 1995, 30, p.655.

17. R. P. Kambour, C. L. Gruner and E. E. Romagosa, Macromolecules, 1974, 7 p.248.

18. L. F. Henry, Polymer Engineering and Science, 1974, 14, p.167.

19. P. L. Vincent and S. Raha, Polymer, 1972, 13, p.285.

20. M. C. Hough and D. C. Wright, Polymer Testing, 1996, 15, 5, p.407.

21. N. Brown, A. Ward and X. Lu, Polymer Engineering and Science, 1990, 30, p.1175.

22. N. Brown, Y. Huang and A. Ward, Polymer, 1991, 32, p.2172.

23. M. K. V. Chan and J. G. Williams, Polymer, 1983, 24, p.234.

24. Y. Ohde and H. Okamoto, Journal of Materials Science, 1980, 15, p.1539.

25. K. Tonyali, C. Rogers and H. R. Brown, Polymer, 1987, 28, p.1472.

26. R. A. Isaksen, S. Newman and R. J. Clark, Journal of Applied Polymer Science, 1963, 7, p.515.

27. N. Ogata, T. Yanagawa and K. Yoshida, Journal of Polymer Science: Polymer Physics, 1986, 24, p.89.

28. M. E. R. Shanahan and J. Schultz, Journal of Polymer Science: Polymer Physics, 1980, 18, p.19.

29. N. Brown and Y. Huang, Journal of Materials Science, 1988, 23, p.3648.

30. L. L. Lander, SPE Journal, 1960, 16, p.1329.

31. D. R. J. Owen, R. N. Haward and A. Burbery, British Polymer Journal, 1978, 10, p.98.

32. N. Brown and Y. Huang, Journal of Polymer Science: Polymer Physics, 1991, 29, p.129.

33. N. Brown and X. Lu, Polymer, 1987, 28, p.1505.

34. L. L. Bohn, H. F. Enderle and M. Fliebner, Advanced Materials, 1992, 4, p.234.

35. M. G. Wyzgoski and G. E. Novak, Journal of Materials Science, 1987, 22, p.2615.

36. M. G. Wyzgoski, Organic Coatings and Plastics Chemistry, 1981, 45, p.246.

37. J. N. Hay and D. J. Kemmish, Polymer, 1988, 29, p.613.

38. R. P. Kambour, E. E. Romagosa and C. L. Gruner, Journal of Polymer Science: Polymer Physics, 1973, 11, p.1879.

39. Chemical Compatibility and Environmental Stress Crack Resistance, PDL, New York, 1990.

40. J. Brandrupp, E. H. Immergut and E. A. Grulke, Polymer Handbook, 4th Edition, Wiley-Interscience, New York, USA, 1999, VII/698-701.

41. E. J. Kramer and M. B. Yaffe, Journal of Materials Science, 1981, 16, p.2130.

42. N. Brown and J. C. B. Wu, Journal of Materials Science, 1982, 17, p.1311.

43. H. G. Olf and A. Peterlin, Journal of Polymer Science: Polymer Physics, 1974, 12, p.2209.

44. E. Peredes, A. Bustamante and R. Rivas, Polymer Engineering and Science, 1983, 23, p.498.

45. C. C. Chen, D. R. Morrow and J. A. Sauer, Polymer Engineering and Science, 1982, 22, p.451.

46. R. A. Bubeck and C. B. Arends, Polymer Engineering and Science, 1981, 21, p.624.

47. R. P. Kambour and C. L. Gruner, Journal of Polymer Science: Polymer Physics, 1978, 16, p.703.

48. E. F. Cuddihy, Organic Coatings and Plastics Chemistry, 1972, 32, p.245.

49. A. I. Soshko, A. N. Tynni, N. G. Kalinin, Y. V. Sytyi and M. M. Gudimov, Soviet Plastics, 1971, 4, p.31.

50. W. W. C. Hart and D. H. Ender, Proceedings of Antec ‘82, San Francisco, CA, p.123.

51. M. Ezrin, Plastics Failure Guide: Cause and Prevention, Hanser, 1996, p.380.

52. C. H. Braithwaite, Proceedings of Antec ’93, New Orleans, LA, p.338.

53. G. C. Sweet, Offshore Engineering with Elastomers, PRI, Aberdeen, June 1985, p.16/1.

54. P. Kirby, Proceedings of the International Conference on Underground Plastic Pipe, ASCE, New Orleans, 1981, p.161.

7 Other Miscellaneous Effects

7.1 Electrical treeing and water treeing

7.1.1 Introduction

When low and high density polyethylene (LDPE and HDPE), and (later) crosslinked PE (XLPE) were introduced in the 1950s and 1960s, respectively, for insulating high voltage distribution and transmission cable, a 40 year service life was both specified and expected. However the incidence of premature insulation breakdown (particularly in North America) was observed to accelerate after about 7 years in service. As the replacement cost of (underground) cable is very high (e.g. £60 billion for complete replacement throughout North America [1]), these early failures stimulated the electricity and polymer supply sectors to engage in intense research activity to isolate the causes of failure.

By 1969 a consensus had been reached that the vast majority of LDPE and XLPE cable failures were associated with the initiation and growth of highly localised dendritic (tree- or bush-like) structures. The 'trees' were observed to initiate at adventitious points of high electric field such as voids, inclusions, agglomerated additives, and interfacial protuberances, see Figure 7.1. Although 'bow tie' trees, initiating within the bulk of the insulation, were most common, unless the initiation density is very high (leading to growth by coalescence), the faster growth rate of 'vented' trees initiating at the interface between the conductor and the insulation implicated them as the main culprit.

Two distinct types of vented tree were identified: electrical and water.

Electrical treeing

This can occur in all polymers at relatively high local electric fields (usually > 100 kV/mm). The structure is relatively coarse and can be detected with the naked eye. The volume of an electrical tree grows linearly with time and hence its length is approximately proportional to elapsed time raised to the power of 1/3. Growth is definitely associated with partial discharges (transient ionisation of the gas filled tubular tree branches) which

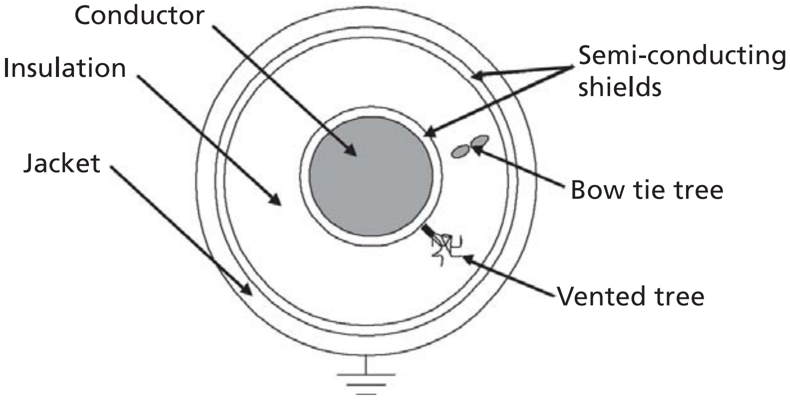

Figure 7.1 Vented and bow tie trees in cable insulation

generate material degradation at the branch tips. The divergent electrical field at the branch tips generates a dilational mechanical stress (Maxwell forces). These stresses applied to the degraded tips cause the material to locally rupture and hence extend the branch. The tree growth mechanism shares many of the characteristics and sensitivities of classical slow crack growth as discussed in Section 6.2. It is observed [2] for example that applied mechanical stress will retard tree growth if this is compressive and accelerate it if this is dilational (tensile). It has been shown [3] that increasing the molecular weight decreases tree growth rate. Growth rate increases with increasing temperature and electrical frequency.

The mechanisms responsible for electrical tree initiation has proved to be more complex and elusive. The role of photodegradation in tree initiation was investigated [4]. It had been known that some polymers emitted ultraviolet (UV) radiation and visible light when subjected to divergent electrical fields. In polyethylene this was put down to electroluminescence. Without light absorbing stabilisers the UV portion of the radiation spectrum increased dramatically with increasing electric field strength, with significant radiation in the 250 nm to 350 nm portion. All polymers are prone to UV degradation within this range (see Section 3.2). However it was established that with light absorbing stabilisers, tree initiation was not retarded unless the insulator was also degassed. With all oxygen removed and with photostabilisation, the tree initiation voltage was increased by a factor greater than 2.

Water treeing

An example of water treeing is provided in Case 7.6.1. This is restricted to low polarity, hydrophobic polymers such as polyethylene and other polyolefins, and may occur at relatively low electric fields (a few KV/mm) when the insulator is in contact with (even small amounts of) water. The tree structure is finer than that of electrical trees and can generally only be detected by a combination of staining and microscopy. Water tree growth is not due to partial discharges, but local material degradation is involved. Water trees most commonly lead to failure by late conversion to an electrical tree when, due to partial bridging, the local electric field exceeds a critical level.

The degradation mechanisms involved in water tree initiation and growth are many and complex and have yet to be reliably confirmed. The nature and concentration of ionic impurities in the water plays a significant role. It is reported [5] that the rate of oxidation associated with water treeing in XLPE is reduced by a factor of 10 with a copper sulphate solution compared with a sodium chloride solution of the same molar concentration. Various theories have been proposed and these are reviewed [6]. A five step process would now appear to be reasonable:

1. Electrolysis of water producing metal ion catalysts and oxidising agents such as ionic oxygen. The latter is a very aggressive reactant particularly in the presence of water.
2. Initiation of polymer degradation.
3. Catalysis by metal ions.
4. Chain scission.
5. Ketone degradation products converted to carboxylate ions.

The detection of carboxylate ions by chemical analysis thus confirms that degradation has resulted from the effects of electricity and water, rather than other agents.

7.1.2 Minimising the risk of failure

Human factors

It is certainly the case that the high incidence of cable failure with the first generation of LDPE and XLPE insulation was due to a combination of poor processing and compounding, poor design, and inadequate testing.

Agglomeration of antioxidants was a major source of electrical stress concentration in early cable. The employment of extruders with superior dispersive mixing efficiency, and the use of lower melting point additives minimised problems from this source. Another problem area in early designs concerned the semiconducting shield between the conductor and the insulator. It was common practice to use helically wound tape. This created surface irregularities and capillary channels for water ingress. (Joints were not sufficiently watertight and in some cases the cable was unjacketed.) Also the semiconducting tape contained carbon blacks of the furnace black type with high levels of ionic impurities, which promoted water treeing.

The extrusion processing of high voltage cable is now much more carefully controlled and sophisticated. Materials of high purity and processing strategies to avoid contamination and degradation are obligatory. Coextrusion avoids the use of tape.

Design improvements include metal (aluminium and copper) foil to minimise through-wall moisture ingress, hygroscopic powders to trap water, and the injection of gap filling fluids such as silicones to block axial water transmission.

However it must be said that the most serious error of judgement was to introduce such a strategically important product, with such a demanding durability specification, without exhaustive testing. Accelerated testing (at elevated temperatures) in a dry environment cannot be excused simply because it is known that polyethylene (PE) is hydrophobic. It was known that water could get into the cable (e.g. at cable joints). It was also known that although water absorption in PE has little effect on its bulk electrical properties, water can for example, leach out antioxidants (see Section 2.3). Thus although water treeing was unknown of at the time, the best practice of testing under the most demanding combinations of structural and environmental conditions would have revealed the phenomenon much sooner.

Material factors

Considerable effort has been expended, mainly by material suppliers, to develop compounds, grades, and modifications that offer demonstrable superiority in terms of treeing resistance. These are rarely described in any detail for commercial reasons and the claims made for them may be optimistic. Apart from high purity grades and grades with superior combinations of antioxidants and UV stabilisers, it would appear that the current offerings fall into two broad categories.

1. Decreased hydrophobicity

Polyethylene homopolymer is the most hydrophobic and least polar of common plastics. Any modification, whether this be via copolymerisation, grafting, blending or compounding, will increase polarity and reduce hydrophobicity. The apparent increase in water tree resistance in materials of reduced hydrophobicity is an interesting effect, and although the beneficial mechanism is not clearly understood the following explanation may be of some value.

The very fine structure of water trees indicates that the initiation and growth mechanism involve very localised interactions between water and the polymer. It may be assumed that a polymer with high bulk hydrophobicity contains micro regions of hydrophilicity (contaminants, free radicals etc.). These regions will absorb water, and constraints against swelling will generate localised dilational stress fields at the hydrophobic/hydrophilic boundary. The stress intensity will be proportional to the local equilibrium differential water absorption. The stress is therefore increased for insulators with higher bulk hydrophobicity. This is similar in concept to the explanation given for the increase in environmental stress cracking (ESC) resistance of polymers via fluid preplasticisation of the bulk (see Section 6.4 on PVC).

In one patent [7] polyethylene glycol (PEG), a fluid of very high polarity, was dispersed into PE and was claimed to provide substantially improved water tree resistance. In another [8] ethoxyacrylates were grafted. In another [9] ethylene oxide/propylene oxide (EO/PO) were grafted. Table 7.1 summarises the performance of these modified materials compared with an equivalent unmodified XLPE. Ageing conditions were as follows:

- Electrical stress = 5 kV/mm at 50 Hz,
- Temperature = 70 °C,
- Tap water,
- Test method 'for accelerated growth of water trees' IEEE, 1990.

Table 7.1 Reduction in dielectric strength of various XLPE grades after electrical ageing [9]

Material	Electrical breakdown strength (kV/mm)			
	Without ageing	After ageing for		
		10 days	30 days	180 days
Unmodified	105	50	45	—
PEG added	107	83	70	—
Ethoxyacrylate grafted	124	82	80	—
EO/PO grafted	110	110	98	85

The benefits of polar additives and grafts are assumed to arise from the ability of the modified material to 'trap and bind' free water. However this facility requires restriction; increasing polarity increases the electrical loss factor, and this is exacerbated by absorbed water.

The tree resistance of ethylene-propylene (EP) rubber and ethylene-propylene-diene (EPDM) rubber-based cable insulation may in part be associated with the slightly reduced hydrophobicity of these materials compared with polyethylene homopolymer. In Tennessee, a survey of underground cable failures [10] revealed that EP rubber insulation was 50 times less likely to suffer from insulation breakdown than XLPE and a massive 250 times less likely than uncrosslinked PE.

2. Molecular weight distribution

As noted already, the resistance to tree growth may be increased by increasing the molecular weight of polyethylene. This also increases the melt viscosity and therefore the difficulty of processing, particularly at high speeds. The same opportunity/problem was faced by the polyethylene pipe sector where resistance to slow crack growth and long-term brittle fracture under continuous mechanical stress was known to improve with increased molecular weight and therefore decreased melt flow index (MFI). As discussed in Section 6.4 on polyethylene, alkene copolymers and grades with a bimodal molecular weight distribution were introduced to increase the density and entanglement of intercrystalline tie molecules without increasing average molecular weight or increasing MFI. The same strategy has probably been adopted for tree resistant cable grades of polyethylene.

7.2 Electrochemical degradation

It is of interest to note that treelike degradation features have also been observed to develop in EPDM rubbers under very low voltage conditions (<12 V). The phenomenon has yet to be satisfactorily explained but it is likely that this will be achieved before a full understanding of water treeing.

Automotive cooling hoses are conventionally made from aramid or polyester fibre reinforced EPDM. The hose bore is exposed to a mixture of water and ethylene glycol (antifreeze) at temperatures of up to ~ 90 °C. Flexural strains due to hose bending can be as high as 50%. These conditions are severe but, as would be expected for a product of such commercial importance, it has been the subject of intensive product development and testing. It was therefore surprising when hoses failed prematurely by cracking and leaking after (in some cases) only 15,000 miles of use. Microcracking together with treelike features (see Figure 7.2) developed at the hose bore and allowed ingress of hot water to the reinforcing fibres. The fibres were rapidly weakened, having very poor resistance to hydrolysis. The apparent degradation of the EPDM could not be simulated until the tests were modified to include a small applied voltage (~ 10 V). In practice the voltage may arise from the difference between the electrochemical potentials of the coolant and metals in contact with the coolant.

In one study [11] it was first established that EPDM degraded and cracked far more rapidly as an anode than as a cathode in a 50/50 water/glycol mixture. It was then observed that:

i) The rate of attack increased for compounds of higher electrical conductivity (carbon black type and loading).

ii) The rate of attack was higher for sulphur cured and lower for peroxide cured compounds.

iii) The rate of attack was highest at parts of the EPDM anode exposed to the fluid/air interface. Under complete immersion degradation was minimal.

iv) Under constant voltage the electrical current through the EPDM anode increased with time as it degraded. In addition peak current discharges were detected (reminiscent of the 'partial discharges' that correlate with the growth of electrical trees).

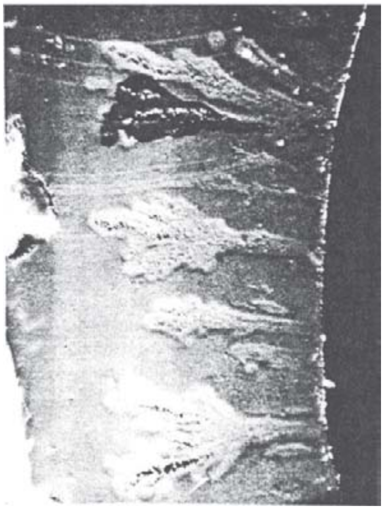

Figure 7.2 Close-up of a crack surface in an EPDM cooling hose showing treelike dendritic structures

Near the anode, water is subject to the following reaction:

$$2H_2O \rightleftarrows O_2 + 4H^+ + 4e^-$$

It is therefore an acidic environment.

Near the cathode the reactions are:

$$2H_2O + 2e^- \rightleftarrows H_2 + 2OH^-$$

$$H_2O + 2e^- + O_2 \rightleftarrows HO_2^{\ -} + OH^-$$

and this is therefore a basic environment. The hydroperoxide ion ($HO_2^{\ -}$) is a very powerful oxidising agent, and although formed at the cathode it is electrostatically attracted to, and absorbed by, the anode.

This evidence and the common understanding of galvanic corrosion would suggest that this phenomenon is likely to be restricted to conductive or semiconductive materials. However this does not appear to be the case. Nonconductive polyetherurethane, polyethylene and polysiloxane are used as protective insulation over metal conductors for pacemaker leads (and other implanted devices). The durability of the insulation has been the cause of serious concern, as significant degradation has been observed after only 2 years of use. As described in the next section, the *in vivo* environment is quite an aggressive oxidation and hydrolysis medium, and initially these conventional forms of degradation were thought to be responsible. However standard immersion tests were never able to simulate the rapidity of attack until a small voltage (6 V) was added as a test condition [12]. Here the electrolyte was a 0.9% saline solution at 37 °C. Degradation was assessed with and without an applied voltage by molecular weight determinations after 69 days of immersion. The results are given in Table 7.2. It will be observed:

i) The reduction in molecular weight in saline solution alone is significant.

ii) The negative polymeric electrode under electrical stress degrades to a similar extent as the electrically unstressed material.

iii) The positive polymeric electrode suffers severe degradation. Fourier transform infrared (FTIR) spectroscopy indicated oxidative chain scission.

The first observation is rather surprising considering the mildness of the test conditions. It is however reminiscent of a much earlier finding [13]. It was reported that significant oxidation of polyethylene had occurred after immersion in (common) salt water for 80 days at 60 °C. However in tap water under the same conditions there was no detectable

Table 7.2 Molecular weight of a polyetherurethane film subjected to various test environments

Sample	Molecular weight
Original	183,000
69 days in saline at zero volts	131,000
69 days in saline at 6V (cathode)	137,000
69 days in saline at 6V (anode)	48,000

degradation. It was suggested that contact with salt solutions even in the absence of high voltage may, by oxidation, be the precursor to water treeing.

Alternatively, it may be suggested that in tests involving the immersion of materials in an electrolyte, voltage is always induced due to differences in the electrochemical potentials of the materials involved (including those used for fluid containment). If by this means significant electrochemical degradation can occur in the absence of applied voltage, then this may help to explain i) above and the similar finding for polyethylene. More generally it would imply that for all polymers in a wide range of fluids, the rate of degradation in service and in tests depends upon a factor that is rarely if ever considered; this being the induced electrochemical potential.

The second observation supports the suggestion that the same degradation mechanism is involved with insulating and semiconducting (carbon black filled EPDM) polymers.

7.3 Biodegradation

7.3.1 Body fluids

The *in vivo* failure of implanted polymeric products justifiably receives a great deal of attention and diagnostic resources. However understanding of the critical issues has been slow to develop because of the difficulty of replicating the complex chemical environment *in vitro*.

Environmental stress cracking of implanted polyurethane (PU) devices including pacemaker leads [14] has been a problem for at least 15 years. Oxidation of the polymer was detected, so the cracking could be better described as stress corrosion cracking (SCC). The oxidising agents found *in vivo* include molecular oxygen, superoxide, and hydroxyl radicals and an effective *in vitro* test has been developed [15] to replicate this oxidising medium and therefore provide a convenient means of screening materials. The method involves the immersion of prestressed material in glass wool soaked in an unstable mixture of hydrogen peroxide and cobalt chloride. The gaseous products are trapped by the wool and therefore remain in intimate contact with the material. The same ether-based polyurethane (Pellethane 2363) as was used previously by Dillon [12], and described in Section 7.2, was found to be the most susceptible to oxidation stress cracking. The condition of the material after 25 days at 37 °C and 100% strain is illustrated in Figure 7.3. The most resistant to stress cracking was an ether and ester free PU (Corethane).

Most recently [16] the same problem has been addressed in terms of classical (non-degrading) ESC. Steroids such as cholesterol, cholesteryl acetate, and cortisone were the

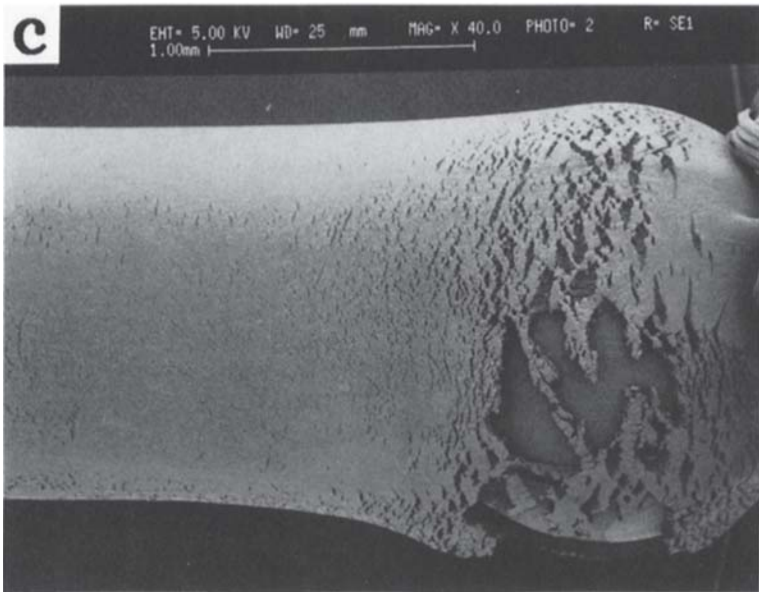

Figure 7.3 Degradation of stressed polyurethane after 25 days immersion in simulated body fluids

(Reproduced from Q. Zhao, J. Casas-Bejar, P. Urbanski and K. Stokes, Glass Wool-$H_2O_2/CoCl_2$ Test System for in Vitro Evaluation of Biodegradative Stress Cracking in Polyurethane Elastomers, Journal of Biomedical Materials Research, Vol.29, p.467-475, Copyright © 1995 John Wiley & Sons, Inc., Reprinted by permission of John Wiley & Sons, Inc.)

candidate suspects. It was established that all the steroids are environmental stress cracking agents and that the more polar cholesteryl acetate is the most powerful. Twelve days at 37 °C with an imposed strain of only 50% was often sufficient to induce cracking in a solution of this steroid. If we compare these findings with those of the previous study on the effect of oxidisers, it is apparent that steroids could be the primary cause of premature cracking in implanted polyurethane devices.

7.3.2 Micro-organisms

Micro-organisms (e.g. algae, fungi, actinomycetes, protozoa, and bacteria) populate most natural environments, and are responsible for the degradation and decay of organic materials. If they have access to water (or moisture) and nutrients they will attach themselves to most surfaces and will multiply. The result is a highly hydrated layer of living and dead micro-organisms, and their metabolic by-products. These are called biofilms, and the mixture of micro-organisms within the film will depend upon such factors as temperature, pH, light intensity, access to oxygen and the types of nutrient that are available. The equilibrium thickness of biofilms is typically of the order of 100 microns, but under very favourable conditions such as waste water treatment plants, film thickness can reach several centimetres. The detrimental effects include the following:

i) Consumption of plasticisers and other low molecular weight additives.

ii) Impairment of electrical properties due to surface and bulk hydration.

iii) Staining and chemical attack by metabolic by-products.

Biofilms will nucleate and multiply even on material surfaces that do not provide nutrients, providing such nutrients are available in the surrounding media. High molecular weight synthetic polymers cannot be directly digested, but lower molecular weight additives such as plasticisers can be consumed. In laboratory tests [17] fungal spores were incubated in a humid environment whilst in contact with plasticised polyvinyl chloride (PVC) film of various formulations. In general the resistances of phthalate-based plasticisers were good compared with phosphates, adipates, and soya bean oil. Of the phthalates tested the most resistant was di-isononylphthalate (DINP), followed by dihexyl phthalate (DHP), di-isooctyl phthalate and dioctyl phthalate (DOP). The least resistant in the class was dibutyl phthalate (DBP). In another study [18] 21 formulations of plasticised PVC were buried for 4 years at various sites. The deterioration in properties due to burial was principally due to the loss of plasticiser via leaching and consumption by micro-organisms. The change in properties was found to depend mainly upon the type and concentration of plasticiser, rather than the burial site or depth of burial. Also there was significant disagreement between the order of merit of plasticisers as assessed in laboratory tests and their performance in contact with soil. For example DOP was relatively immune to attack on agar in petri dish tests, but was rapidly attacked in soil.

Several unexpected electrical failures due to surface hydration are summarised in the literature [19]. In one case the crew of a German freight vessel were lost in a gale when emergency radio units failed to operate. A biofilm on the plastic isolators was found to be the cause of the problem. The failure of printed circuit boards in tropical environments due to the impairment of surface resistivity by surface hydration appears to be the most common problem. Microbial penetration is less common. Fungal hyphae have been observed to grow through and eventually penetrate polyethylene terephthalate (PET) film [20]. Fungal hyphae were also reported [21] to be responsible for the failure of electrical systems at Zurich Airport. Penetration of polyurethane insulation caused closure of the airport whilst the entire facility was rewired. The hyphae are fine filamental dendritic structures that are reminiscent of water trees and 'electrochemical degradation'. The growth mechanism is not clear. Growing organisms can create hydrostatic pressures (Turgor pressures) but these rarely exceed 8 MPa, and are therefore unlikely to be sufficient to locally rupture a high strength polymer. The possibility that these three phenomena share a common mechanism does not appear to have been investigated. Engineers, chemists, and physicists rarely design their experiments to accommodate microbiological effects. In the absence of sterilisation these could be significantly additive in the longer term.

An inspection of various studies related to the impairment of the electrical properties of polyimide clearly reveals the lack of communication between the technical disciplines. Polyimide is the frequent choice of insulating material for integrated circuits. It is known that its electrical properties are impaired by moisture, and that the material is susceptible to hydrolysis. However these factors alone did not appear to explain the high incidence of insulation failure in ambient moist environments. Suspecting microbial attack [22] the following work was carried out. Polyimide film (Kapton) was inoculated with a mixture of 3 common fungal spores (*aspergillus versicolor*, *cladosporium cladosporioides*, and a species of *chaetomium*). The electrical impedance of the inoculated film and a sterile film were monitored in salt solution over a period of 122 days. The absorption of electrolyte reduced the low frequency impedance of both films over a period of 17 to 24 days. After this initial decline the sterile film stabilised but the inoculated film continued to decline. After 122 days the impedance of the sterile film was a factor of 10 greater than the inoculated film at a frequency of 100 Hz. The micro-organisms have a very significant effect, but no attempt was made to isolate the mechanism or to establish whether for example it is a physical process that promotes electrolyte penetration (via hyphae) or a chemical process involving degradation. It is of interest to note that the problem of hydrolysis in Kapton aircraft insulation previously discussed in Section 5.5 did not seem to consider the possibility of microbial attack. Indeed there is no crossreferencing between the two problem solving groups. This is surprising since both involve the failure of polyimide insulation in humid environments and particularly so because both investigations were sponsored by the US Military!

The staining of polymers by lipophilic pigments is a common aesthetic problem in bathrooms and other warm and humid environments. Shower curtains and seals are prone to be stained red or pink. The pigments are capable of diffusing into the material bulk and therefore cleaning is impossible. The erratic incidence of pinking of UPVC window frames may also be due to this mechanism.

High molecular weight polymers can be broken down and consumed by biofilms and can therefore provide a source of nutrients for micro-organisms. With the notable exception of polyurethanes this is a very slow process. Microbes generate esterase enzymes and these catalyse the hydrolytic scission of ester or ether linkages within the urethane chain. The products of degradation (e.g. alcohols) are digestible.

Polyurethane footwear is particularly prone to rapid degradation because of the conducive conditions (warm, moist, and unsterile). Cracking and delamination are visible consequences of microbial attack. The best defence against attack is the incorporation of biocides and antimicrobial agents. Figure 7.4 illustrates the benefits of such additives. Currently however, more research and development work is being applied to finding the means of promoting attack (i.e. for the biodegradation of polymer waste).

7.4 Diffusion, permeation, and migration

Diffusion is the fundamental rate determining process for most forms of environmental attack. Thus:

i) The rate of diffusion of oxygen into polymers in many cases determines the rate of degradation due to thermo-oxidation, photo-oxidation, and ionising radiation.

ii) The rate of diffusion of hydroxyl or hydrogen ions in many cases determines the rate of hydrolytic degradation.

iii) The rate of diffusion of water into adhesive joints has a strong influence on the rate of joint strength decline.

iv) Diffusion is essential for ESC and SCC.

v) Defence strategies that employ mobile additives (antioxidants, UV stabilisers, biocides, etc.) rely upon optimum rates of diffusion.

Figure 7.4 Polyurethane shoe soles after 90 days of soil burial under stress, with and without a biocide

(Reproduced with permission from M. Robeers and K. Mullin, Polyurethane Degradation, Athletic, Safety and Leisure Shoes are Susceptible to Microbial Attack, World Footwear, November/December 1989, published by Shoe Trades Publishing Co.)

vi) Other failure processes that rely upon diffusion include fluid loss or migration (see Cases 7.6.2, 7.6.3, 7.6.4), osmotic blistering (see Case 7.6.8), and explosive decompression (see Case 7.6.13).

The rate of diffusion of a fluid into or out of a polymer depends upon many factors and is increased by:

- Increasing temperature,
- Increasing liquid or vapour pressure,

- Increasing equilibrium solubility of the fluid in the polymer (see Section 5.1),
- Decreasing molar volume of the fluid,
- Mechanical stress in the polymer.

The equilibrium solubility of fluids in polymers increases with the application of tensile stress and decreases under the influence of compressive stress in the polymer. The sensitivity to tensile or dilational stress is responsible for the local plasticisation ahead of intrinsic defects, crazes, and cracks, and therefore an essential stage in the process of environmental stress cracking. The loss of plasticiser due to compression is partly responsible for the decline in performance of gaskets and seals. The rate of loss can be surprisingly high even under modest compression. In one recorded example involving DOP plasticised PVC catheters [23], the pressure of shrink wrap packaging film caused such a high rate of exudation that drops of DOP were visible to the naked eye and the product was unsaleable. In another example, shrink wrapped acrylonitrile-butadiene-styrene (ABS) telephones were rendered unsaleable by surface marring and loss of gloss, where the plasticised PVC cordage made pressure contact with the moulded casings [24]. On this evidence it would be prudent to assume, until proved otherwise by testing, that fluid absorption and desorption is 'spongelike', i.e., a significant proportion of the absorbed fluid is not intimately mixed with the polymer but contained within interconnecting pores.

The diffusion of water through gel coated glass fibre reinforced laminates is the first step that leads to surface blistering. This is the most common cause of environmental degradation in glas reinforced plastic (GRP) boat hulls and other marine products. Water diffuses through the gel coat and dissolves oxides in the glass, emulsions used to size and bind the glass, residual catalysts, etc. The concentrated solution behind the semipermeable gel coat promotes increased diffusion of water via osmosis and the increase in the hydraulic pressure of the solution eventually results in fluid filled surface blisters. These demand removal and repair not only for aesthetic reasons but also because they represent a breach in the resin rich corrosion barrier. Water will only slowly attack glass fibres and the bond between fibres and resin. However the water-based solution is generally acidic and the rate of internal attack following blistering can be very rapid (see Section 5.4).

The time in service to develop blisters can be as short as a year and as long as 30 years. It is known to depend significantly upon the quality of workmanship, and in particular on maintaining a well cured gel coat of sufficient thickness. Laminating with damp glass fibre is also known to reduce the time to blistering. Material qualities are important. Water soluble emulsions (e.g. polyvinyl acetate) used to bind glass mat will accelerate the problem, as will standard resins (whether these are *ortho-* or isophthalic polyesters) that have not been formulated for marine applications.

Structural adhesives formulated from epoxies and other thermosetting resins are more sensitive to moisture pick-up than is generally appreciated. Storage for a few months in high humidity air at 50 °C is sufficient to reduce the lap shear strength of such adhesive joints by 50% [25]. The reduction is due to a combination of phenomenological effects, some of which are reversible, so on drying strength improves but does not completely recover. The two most important reversible effects are plasticisation (by the absorbed water) and the weakening of bond strengths that rely upon interfacial ion pairs.

7.5 Physical ageing

Time and temperature have primary roles in all degradation processes. Increasing temperature increases the rate of reaction and also the rate of purely mechanical and physical processes such as diffusion, equilibrium absorption, creep, stress relaxation, heat reversion, impact strength, and fatigue. With the exception of Cases 7.6.10 (heat reversion and 7.6.11 (low temperature impact), this book does not attempt to cover the latter mechanical effects, for these are arguably outside the scope, and important and distinct enough, to be the subject of a second book with a similar objective. There is however one physical effect due to time and temperature that justifies inclusion. This is the phenomenon of physical ageing.

When an amorphous material has been cooled from a temperature above its glass transition temperature (T_g) to below its T_g, the density of the material will be lower than its equilibrium density. With time at the sub-T_g temperature, the density will marginally and gradually increase, and the properties of the material and dimensions of the product will change accordingly:

- The yield strength will increase with time,
- The material will become stiffer with time,
- The strain at break (ductility) will reduce with time,
- The impact strength will reduce with time,
- The product will reduce in volume and shrink dimensionally.

Thus some properties are apparently degraded by time alone, hence the adoption of the term ‘ageing’. The rate of ageing increases with temperature and maximises just below the material’s glass transition temperature. If this temperature is exceeded then the recooled material will be ‘refreshed’ or ‘reborn’; the change in properties due to prior ageing will be eliminated, and the ageing process reinitiated. For most products and service conditions however ‘rebirth’ is not an option and the tangible symptoms of physical ageing will continue indefinitely.

The magnitude of the ageing process can be assessed by comparing properties on specimens that have recently been rapidly quenched from above T_g (representing a ‘new product’) with specimens that have been very slowly cooled or annealed at temperatures just below T_g (representing an ‘old product’). It has been recorded [26] for unplasticised polyvinyl chloride (UPVC) that the ‘new product’ has a tensile impact strength of 600 kJ/m^2 whilst the ‘old product’ (cooled at 5 °C/hour from 94 °C to 20 °C) has a tensile impact strength of only 320 kJ/m^2. The embrittlement of polymers in service, which is the cause of most failures, is always partly due to this ageing process, although for amorphous thermoplastics it is rarely the dominant factor.

It will be appreciated therefore that the performance of a material depends on its thermal history, sometimes to a significant degree. This fact is known by material suppliers and exploited by some for commercial advantage. Impact tests may be carried out immediately after moulding, whilst heat distortion temperature (HDT), strength, and stiffness tests may be carried out after sub-T_g annealing or long periods of storage at ambient temperatures. For example the yield stress of UPVC increases from 55 MPa when tested one hour after moulding to 57 MPa when tested 85 hours after moulding. Recent initiatives (ISO 10350) will eventually restrict such abuse.

For semicrystallines the equivalent phenomenon, usually referred to as post moulding crystallisation, can be far more significant both in terms of dimensional changes and property degradation. Most products during their melt processing will have been cooled at a high rate and the degree of crystallisation will be significantly less than at thermodynamic equilibrium. With time the degree of crystallisation will increase, and because of the much higher density of the crystalline phase, the volume contraction with time can be as high as 0.5% (compared with only about 0.1% for amorphous materials). Volume contractions of this magnitude will, if constrained, generate significant tensile stresses, and in combination with a decline in ductility they have been known to be the primary cause of product failure. An example is given in Case 7.6.6. Other effects include induced buckling. A particular type of optical fibre cable used in telecommunications suffered excessive attenuation after only eight months in service (27). The problem was traced to compressive stresses induced in the fibre by volume contraction of the thermoplastic elastomer jacket material. Cooling rates during processing had been excessive and the elastomer suffered significant in-service crystallisation even at ambient temperatures.

The maximum rate of post moulding crystallisation occurs at a temperature between T_g and the crystalline melt temperature T_m. The T_gs of some semicrystalline thermoplastics are listed in Table 7.3. Polyethylene, which has a low T_g and a low T_m, is virtually at an equilibrium level of crystallinity immediately after cooling from the melt. In physical

Table 7.3 Glass transition temperatures of some semicrystalline thermoplastics

	T_g (°C)
Polyethylene	-20
Polybutylene	-20
Acetal	-13
Polypropylene	0
PBT	22 - 43
Nylon 6	50
PCTFE	52
TPX	55
Nylon 66	60
PET	67
PPS	85 - 150
PTFE	115
PEEK	145

ageing terms the material is mature immediately after cooling from the melt and subsequent changes in dimensions or properties due to post mould crystallisation will be minor. Acetals have a low T_g and a high T_m. As a consequence the degree of crystallinity is low immediately after cooling, but when stored even at ambient temperatures post moulding crystallisation will proceed very rapidly. An additional shrinkage of 0.5% within two days of moulding is not uncommon. Acetal parts should not be assembled immediately after moulding.

For materials with glass transition temperatures well above ambient the degree of crystallinity can be very low immediately after moulding. For crash cooled polyether ether ketone (PEEK) and polyethylene terephthalate (PET) it can be zero. Subsequent storage or service at ambient temperatures will induce minimal post moulding crystallisation and the material will appear to be stable both in terms of dimensions and properties. However, if as is often the case the material is exposed to temperatures that well exceed T_g in service, the material will no longer be stable. Slow cooling from the melt using high mould temperatures is the conventional means of minimising this problem. However this is generally expensive and in addition it can be ineffective for thin walled products. The alternative is to anneal the product prior to assembly. If the maximum anticipated service temperature is known, the parts should be annealed for a few hours at least 30 °C above this temperature.

Slow cooling and or annealing exhausts the ageing process. In effect the material is pre-aged and its toughness properties are at a stable minimum, whilst other properties such as hardness, wear resistance, stiffness, impermeability, and dimensional stability are at a stable maximum. In addition slow cooling or annealing minimises residual stress via the promotion of stress relaxation. Therefore these practices are to be generally recommended even though the benefits are not universal.

One important source of the decline in toughness that results from slow cooling or post moulding crystallisation is the increase in crystallite or spherulite size. The strain at break of two polypropylenes with identical degrees of crystallinity were 700% and 200% with spherulites of 50 and 200 microns, respectively. For some semicrystalline thermoplastics such as polypropylene and Nylons it is common practice to use grades with nucleating agents, which increase the rate of crystallisation, resulting in the formation of smaller spherulites. To achieve a high density of nucleation (typically $> 10^{10}$ nuclei per cm^3) it is important that the agent is finely divided and well distributed. Initially with this in mind, oxides of silicon (silicates) and other fine inorganic powders such as titanium, aluminium, and zinc oxides, were regarded as effective nucleating agents, as the process was interpreted as essentially physical. Indeed it was observed that other additives including solid pigment, talc and glass fibre also gratuitously act as nucleating agents. However it is now apparent [28] that for the maximum effect there needs to be a chemical interaction between the agent and the polymer.

One measure of the effectiveness of a nucleating agent is the degree by which it raises the temperature for the maximum rate of crystallisation (T_{cc}) in a differential scanning calorimeter (DSC) on cooling at a standard rate. Table 7.4 lists a range of nucleating agents for polypropylene and their effectiveness in these terms.

7.6 Case studies

7.6.1 Water treeing failure of crosslinked polyethylene power cable insulation

History

In the 1960s polymers began to be specified in significant quantities as insulation for high voltage power cables. Growth in use has been strong ever since. In the USA, where large lengths of cable were installed, without jacketing, often with poor quality insulation,

Table 7.4 Effectiveness of nucleating agents for polypropylene expressed as the temperature T_{cc} for maximum rate of crystallisation. The cooling rate is 12.5 °C /minute

	T_{cc} (°C)
Unnucleated	106
Titanium oxide	111
Aluminium oxide	111
Silica	113
Sodium benzoate	121
Sodium methyl benzoate	132

and with taped screens, the early experience was of frequent failures. Such a scenario was not expected, given the excellent dielectric properties of polyethylene (low loss factor and tan d) and its highly hydrophobic nature.

An example of such a premature failure occurring in the UK involved a 11 kV single phase XLPE insulated cable with an 800 mm^2 aluminium conductor. Failure occurred after 7 years in service. Both the inner and outer semiconducting screens (used to contain the electric field within insulation and to eliminate any electrical discharges arising from air gaps adjacent to the insulation) were of tape and lacquer construction.

Inspection and analysis

Unfortunately failure of an 11 kV cable usually results in the destruction of the evidence at the point of breakdown. However, a sample of the cable taken just 100 mm from the failure position exhibited clear evidence of the likely cause of its demise. Extensive 'vented' water treeing, i.e. the presence of tree-like growths connected to and emanating from the insulation surface, was observed. Trees had grown from both the outer and inner insulation surfaces. Lengths of tree from the inner screen were up to 0.5 mm, whilst from the outer screen they were up to 2 mm. Typical water trees observed in this cable are shown in Figure 7.5. Figure 7.6 shows more detail of one of the vented water trees.

A further relevant observation was made concerning the outer screen. When the wound tape screen was removed it was found that there was very little lacquer adhering to the outer insulation surface.

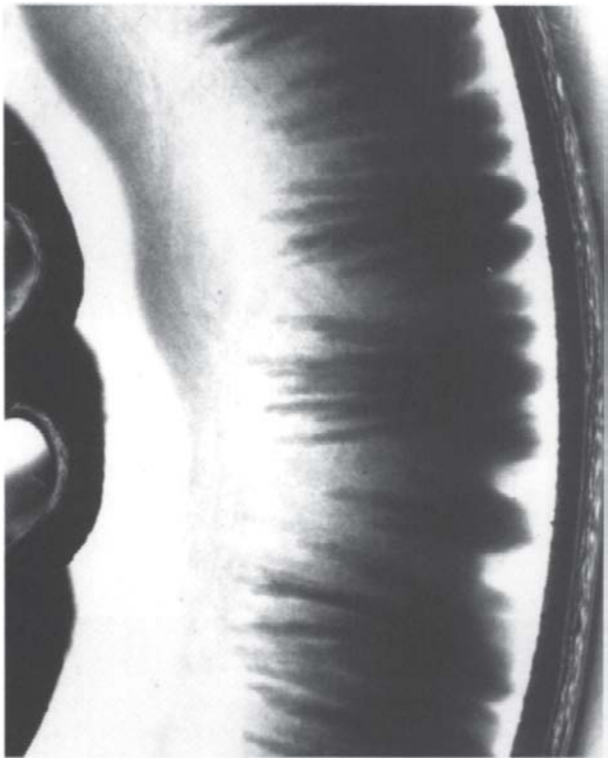

Figure 7.5 Cross section of a failed XLPE power cable

Several lengths from the failed cable were removed and subjected to laboratory testing. One length (1.5 m), having few vented trees in it, was immersed in water for 3 weeks at 70 °C and energised at 8.8 MV/m. No failure occurred after 9 hours. Another length (3.5 m), close to and on the other side of the failure, contained many large vented trees. Having been subjected to the same immersion treatment (to ensure that water diffusing out during transit to the laboratory was replaced), this length failed after just 21 minutes at 8.8 MV/m.

Failure diagnosis

Failure of the cable was caused by the growth of vented water trees. It is now known that when taped screen cables are exposed to moist environments they are particularly susceptible to the growth of vented water trees. The poor adhesion of the screens, and

Figure 7.6 Detail of a vented water tree

other factors such as contaminants and protrusions from the screens, provide regions of enhanced electric stress conducive to the inception and propagation of water trees.

When the vented trees grow towards the full width of the insulation, electrical treeing (not requiring the presence of water) begins, and failure follows shortly afterwards. One may assume that trees bridging the insulation would have occurred at the actual point of failure, but, as mentioned earlier, the failure itself destroys the evidence. However, the great length of the trees just 100 mm away from the point of breakdown, and the much lower time to breakdown in the more heavily treed length of cable examined in the laboratory, are strongly indicative of the failure mode.

Lessons and consequences

1. The scale of the problem of water treeing was not anticipated when polymeric insulated cables were introduced in the 1960s. It was assumed that because polyethylene is a highly hydrophobic material, it could operate under high electric stress and in the presence of water with no problems. The consequences of that attitude, i.e. the premature and frequent failure of these early high voltage LDPE and XLPE insulations, which were often of poor quality, is a salutary lesson in the need to conduct extensive testing before committing wholesale to a new technology.

2. As the result of the poor early experience, and continuing uncertainty concerning the long-term performance of later cables, there has been extensive research and development by material and cable suppliers to isolate the causes of failure and to improve the quality of polymeric cables. Three changes have resulted in significantly longer life. Taped screens have been superseded by triple extruded screens and more recently by super smooth compounds giving extruded screens with hardly any interfacial defects. There has been investment in high purity compounds and cleanliness of the manufacturing process, both of which reduce the incidence of tree-inducing defects. Chemical modifications have been introduced to make the insulation more intrinsically water tree retardant, e.g. graft copolymers.

3. Clearly, if all water can be excluded from the cable then water treeing cannot occur. Therefore many utilities are adopting designs of cable that incorporate polymer/metal foil laminates to prevent radial moisture transfer from the soil, blocking powders and tapes to prevent longitudinal water flow, and measures to ensure dryness of the various polymeric layers at and after manufacture. Inevitably such improvements increase the cost of the cable, but often this can be justified because of the very high cost of replacing failed cable.

7.6.2 Loss of polyvinyl chloride plasticiser

History

Outdoor isolators are required on rural distribution networks for isolating sections of overhead lines, small transformer substations, etc. The 11 kV rocking-type isolator switch uses three insulators for each pole. The outer two insulators are fixed and the central insulator can move about a hinge. The moving contact is between one of the outer insulators and the central mobile insulator. The other outer insulator is connected to the moveable insulator by two flexible black PVC-covered stranded conductors, each about

0.7 m in length. Compression sockets of the ring palm type are fitted at each end of the conductors. The flexible cable conductors (many fine wires) are usually 35 or 50 mm^2 nominal cross-sectional area overall, and are plain or tinned copper, more frequently the latter.

As the rocker isolator is a mechanical device, it is important that the PVC compound is flexible at low temperatures and that this flexibility is retained over the service life, as it may be called upon to work in the depths of the British winter when temperatures of -10 °C or lower may be reached.

After 10 – 15 years of operation many of the PVC coverings of these devices were found to have stiffened and many were cracked, in particular close to the crimped connector. Sometimes the stiffening prevented efficient operation of the switches. Where cracking had occurred, the underlying wires were corroded. In certain cases the corrosion was so severe that there was complete loss of conductor cross section.

Inspection and analysis

Some of the PVC coverings were stiff at an ambient temperature of 20 °C, but there was variability in stiffness, not only between different leads but also with position in each lead. The PVC compounds selected had been specially formulated for their flexibility at low temperature. The PVC colouration is black (a small percentage of carbon black is added) to give good resistance to weathering.

It can be reasonably assumed, and was confirmed by the large number of failures occurring in winter, that the stress imposed upon the PVC covered leads during operation (sudden movement) at a time of low temperature was responsible. One particular formulation of PVC was implicated in the failures. The composition was unknown in terms of exact percentages of components when new (it would have contained more plasticiser initially), but typical measured values of PVC from service are shown in Table 7.5.

It is clear that loss of plasticiser is the key to embrittlement of the PVC. Furthermore, stiffening is more pronounced, and consequently failures occur more often, near the compression sockets where kinking of the PVC is also common. A series of experiments was conducted to find out the contributing factors.

i) **Exudation.** Non-failed PVC and other PVC compositions for comparison were remoulded into 1 mm thick sheet, from which samples were folded through 180° into loops. These were placed for 24 hours in a Xenotest Weatherometer with the black panel temperature set at 50 °C and with a weathering cycle of 5 minutes water spray on, 25 minutes water spray off. The loss of mass was recorded with time.

Table 7.5 Composition of various samples of one PVC compound

Ref. No.	Description	Plasticisers	Filler	Heat stabiliser	Composition %		
					Plasticiser	Filler + heat stabiliser	PVC + carbon black
D1-A	PVC from non-failed conductor - near middle	Dioctyl phthalate/ butyl epoxystearate	Chalk	Basic lead carbonate	20.2	25.6	54.2
D1-B	PVC from failed conductor - near middle	Dioctyl phthalate/ butyl epoxystearate	Chalk	Basic lead carbonate	18.0	26.3	55.7
D1-C	PVC at point of failure - near crimp	Dioctyl phthalate/ butyl epoxystearate	Chalk	Basic lead carbonate	15.9	27.0	57.1

ii) **Extraction.** Samples of 1 mm thickness were placed in water at 50 °C. The loss of mass, principally caused by plasticiser loss, was monitored as a function of time.

iii) **Evaporation.** Samples of 1 mm thickness were heated in a circulating air set at 113 °C and loss of mass was monitored against time.

All three factors are probably involved in the stiffening process. Thus, significant exudation was observed in the loop test (mimicking to some extent the kinking close to the compression sockets) when applied to composition D1-A of Table 7.5. Furthermore, loss of plasticiser by evaporation and by water extraction was high for this PVC compound when it was compared with other compositions.

The weakness of the D1 composition is the presence of the butyl epoxystearate secondary plasticiser, which operates as a costabiliser and an improver of low temperature flexibility. As shown in Figure 7.7, the secondary epoxystearate plasticiser has been removed in preference to the primary phthalate plasticiser.

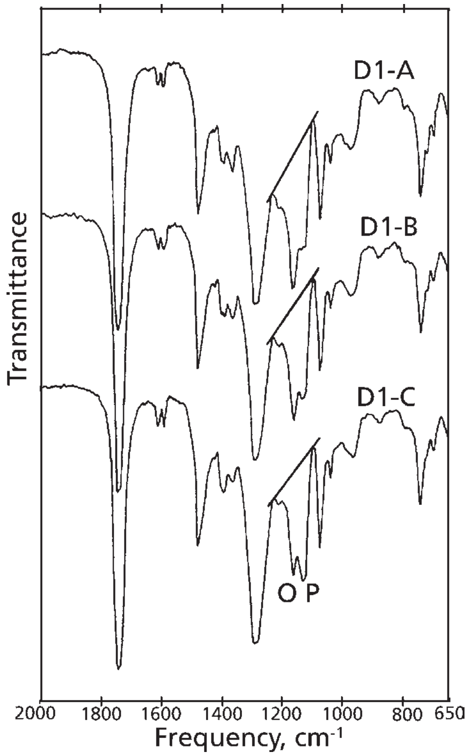

Figure 7.7 Infrared spectra of PVC samples (P = phthalate; O = butyl epoxystearate)

Failure diagnosis

Stiffening is the result of plasticiser loss by the following mechanisms: evaporation (at super-ambient temperatures arising from absorption of solar radiation by the black PVC); extraction and hydrolysis (particularly in the region of the compression socket, where liquid water can accumulate); and exudation (again near the compression socket where kinking tends to occur).

Failure is almost certainly because of rapidly applied mechanical stress on the stiffened PVC coverings at low temperatures.

Lessons and consequences

1. If plasticised PVC is to be used outdoors, and maintenance of mechanical properties is essential, then the plasticiser system needs to be chosen carefully to ensure that undue extraction, volatilisation or exudation does not occur.

2. PVC compounds should be tested thoroughly first to ensure that they will survive extended weathering. It is not sufficient just to specify an ‘arctic’ grade of material.

3. Tests on alternative plasticisers for PVC showed that phthalate plasticisers (without additions of secondary plasticisers) were more effective than alkanoates, e.g. butyl epoxystearate, adipates and sebacates, in all-round resistance to plasticiser loss. Compounds containing high concentrations of both phthalate and chlorinated paraffin performed badly in the loop exudation test, because the latter component is a secondary plasticiser which pushes the composition beyond the compatibility limit. This tendency is exacerbated by the uptake of a third plasticiser, namely water. Additions of polymeric plasticisers yielded materials that were too stiff for the application.

4. Alternatives to plasticised PVC should also be considered for arduous outdoor usage. These may include various rubber compounds, including materials such as Hypalon (chlorosulphonated PE), Neoprene, silicone rubber and EPDM. They do not rely on plasticiser retention for maintenance of flexibility, but they are more expensive than PVC.

7.6.3 Marring in contact with polyvinyl chloride covered wiring

History

Plasticised PVC compounds frequently come into contact with other polymers. When contact is prolonged, transfer of plasticiser occurs across the interface. Marring, which may take the form of softening, cracking, staining or other disfigurement, or combinations of some or all of these, is often the result.

Materials that are prone to marring include polystyrene, ABS, polycarbonate and polymethyl methacrylate. Rigid PVC has been successfully used for ducting wiring covered by plasticised PVC, but in other situations, where there is a bending or tensile stress on the rigid PVC, failure can sometimes occur because of environmental stress cracking (where small amounts of plasticiser act as the environmental agent).

Marring by PVC covered wiring can manifest itself in many ways:

i) Softening and disfiguring of paint at point of contact.

ii) Softening of natural rubber grommets.

iii) Softening of polystyrene cable clips.

iv) Pools of sticky fluid forming on preservative treated wood.

v) Cracking of ABS instrument consoles.

vi) 'Melting' of expanded polystyrene loose fill and tiles.

The last mentioned is singled out for attention because it the one that causes most concern to customers.

Inspection and analysis

Close inspection of every example of 'melted' polystyrene showed that the PVC covered circuit protective conductor (CPC) wiring was coated by a sticky, transparent, semisolid layer, usually less than a millimetre in depth. The expanded polystyrene (XPS) in contact with the PVC had collapsed, giving the appearance that it had melted. To either side of the wiring was a narrow strip of partially collapsed XPS, but outside this zone there was no sign of damage to the XPS foam.

To simulate the damage to the XPS samples of double sleeved single strand conductor and CPC wiring were embedded in polystyrene foam. The assembly was then heated in an oven set at 60 °C. Samples of the PVC covered wiring without XPS were also aged in a circulating air oven with vent. After 36 days it was observed that there was a sticky layer surrounding the wiring embedded in the XPS. The foam had also begun to collapse. Some small degree of stiffening of the outer PVC sleeves could also be detected. The plasticiser loss results are shown in Table 7.6.

It is clear that, under the conditions of the experiments, loss of plasticiser is significantly faster by migration than it is by evaporation. The probability is very high that at longer times the marring/stiffening would have been much worse.

Infrared spectroscopy of an ether extract from the outer sheaths showed that the plasticiser was a mixture of a dialkyl phthalate and chlorinated paraffin, which is highly typical of PVC used as sheathing for wiring.

Table 7.6 Effect of medium (air or XPS) on loss of plasticiser from PVC

Cable type	Sheath colour	Surrounding medium	Mass loss of outer sheath at 60 °C (%)	
			9 days	36 days
2.5 mm^2 concentric insulation and sheath	Red	Air	0.72	1.44
2.5 mm^2 concentric insulation and sheath	Red	Expanded polystyrene	1.14	2.89
2.5 mm^2 (CPC)	Grey	Air	0.68	1.36
2.5 mm^2 (CPC)	Grey	Expanded polystyrene	1.00	2.51

Failure diagnosis

Marring is caused by migration of plasticiser from the PVC sheathing to the expanded polystyrene, which has a high affinity (higher even than PVC itself) for plasticisers such as dioctyl phthalate. The effect of the addition of the plasticiser to XPS is to lower the glass transition temperature of the polymer. In the pure material this is about 100 °C, i.e. it is normally necessary to exceed this temperature to soften XPS. When sufficient plasticiser has been absorbed, however, the glass temperature falls below room temperature, the polystyrene softens and the foam cell structure collapses. As time goes on more and more plasticiser is transferred, so that the end result is a highly viscous, sticky fluid adhering to the PVC. The further away from the PVC surface, the less obvious is the softening because of the large diffusion path.

Lessons and consequences

1. Careful consideration should be given to the consequences of contact of plasticised PVC (or other plasticised polymers) with other materials, including paints, varnishes and structural polymers, so that problems can be avoided before installation.
2. In some cases barrier materials, such as tapes can be used to prevent migration and marring.

3. Where the additional cost can be borne, so called 'monomeric' (actually low molecular weight) plasticisers, e.g. dioctyl phthalate, can be replaced by polymeric plasticisers, which do not migrate and therefore cannot give rise to marring.

4. Alternative materials to plasticised PVC should be considered in critical applications.

7.6.4 Shrinkage of ethylene-propylene-diene hose

History

A 6 metre pleasure cruiser burst into flames in a crowded marina. The craft had been moored and unused for 2 years. Fortunately the occupants were able to extinguish the fire before it could spread to adjoining vessels. However the cruiser suffered extensive damage and an insurance claim of around £20,000 triggered an investigation into the cause of the conflagration.

The fire started in the engine compartment and it was noted that the rubber hose between the deck filler port and the petrol tank was not securely connected at the tank spigot (see Figure 7.8). However it was not obvious whether this was a cause or effect of the fire.

Inspection and analysis

The hose material was analysed by FTIR and it was identified as an EPDM rubber containing mineral oil as a processing aid.

The oil content was assessed by TGA and found to be generally 8% (between the connectors) and 36% in samples taken from above the filler port jubilee clip.

The hardness of the rubber was 80 IRHD and 45 IRHD below and above the filler jubilee clip, respectively.

Failure diagnosis

The hose originally supplied was listed as a nitrile. It had been replaced at some unknown point in the cruiser's history.

EPDM is not recommended for contact with petrol or indeed most aliphatic fluids. Petrol swells EPDM to an equilibrium level of ~ 100% with an attendant reduction in hardness.

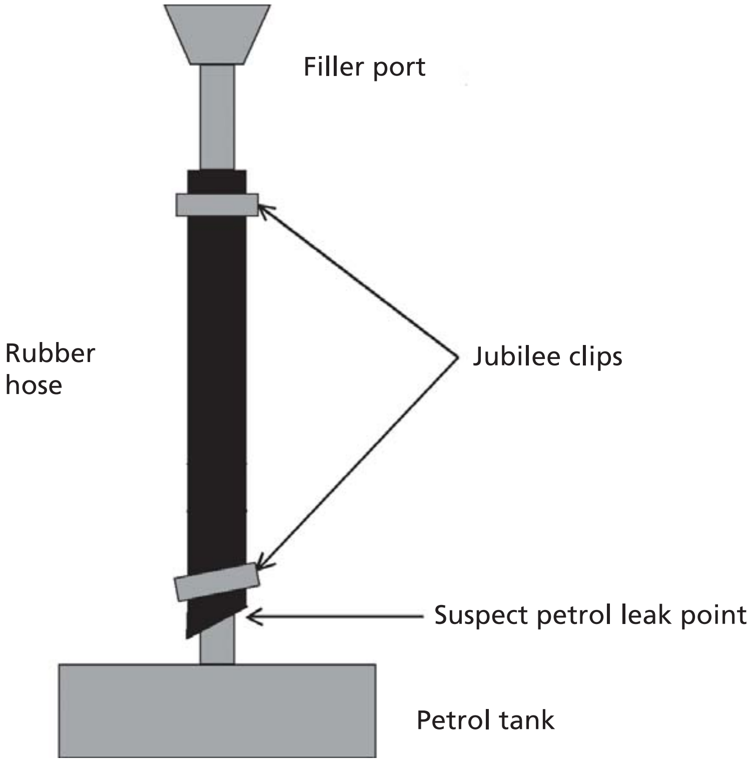

Figure 7.8 Connection of rubber hose to the filler port and petrol tank

Mineral oil is not a recommended additive for elastomers in contact with petrol. Mineral oil will be leached out by the petrol, leading to shrinkage of the rubber and an increase in hardness.

The mineral oil content in the as-manufactured hose was not known but it could reasonably be assumed to exceed 36%. On contact with petrol the following sequence of events was initiated.

1. Petrol is absorbed and the hose swells by increasing in diameter, wall thickness, and length.

2. Petrol extracts most of the processing oil and the swelling effect is moderated by a volume shrinkage of > 28%.

3. After several years without use and with the fuel tank emptied (for reasons of safety!) the petrol absorbed by the hose migrated out of the rubber, leading to a net reduction in hose length and wall thickness.

4. The reduction in hose wall thickness combined with increased compressive stress relaxation under the jubilee clips whilst swollen reduced the clip retaining force.

5. The reduction in hose length generated an axial pull out force that led to the partial disconnection at the fuel tank spigot.

6. On refuelling, petrol leaked into the engine compartment.

7. Ignition!

Lessons and consequences

1. The fact that rubber hoses look alike and are of conveniently similar cross section does not justify the assumption of equivalence.

2. Replacement hoses should at best be genuine spare parts or at worst they should be parts that are rated for similar duties.

3. As the craft had several previous owners and had been maintained by several boat yards, it was impossible to trace the responsible party.

4. The insurance claim was fully settled.

7.6.5 Diffusion of chlorine through polyvinylidene fluoride

History

This concerns a polyvinylidene fluoride (PVDF) lined steel piping system for the transportation of dry chlorine gas in a chlorine electrolysis plant. Pressures were modest but temperatures were high (up to 90 °C).

After about 2 years of service, external corrosion of the steel was deemed to threaten the structural stability of the system. It was isolated for inspection.

Inspection

The corrosion of the steel was very localised and was concentrated at vent holes of 3 mm diameter drilled at intervals along the pipe. The PVDF liner was found to be intact.

Failure diagnosis

Chlorine gas which permeated through the liner reacted with moisture in the ambient air, and a strong chlorinated water condensate collected at or near the vents. Chlorine water corrodes steel.

Lessons and consequences

1. All polymers are to a degree permeable to all fluids.
2. Although vents are an obvious means of limiting the accumulation of permeated fluids (and minimising the risk of liner collapse on decompression) they can actually cause failure as in this case.
3. The line was replaced but this time with vent holes capped with tight fitting polytetrafluoroethylene (PTFE) nipples (see Figure 7.9). Condensed chlorine water was no longer in contact with the steel and the line performed well for many years.

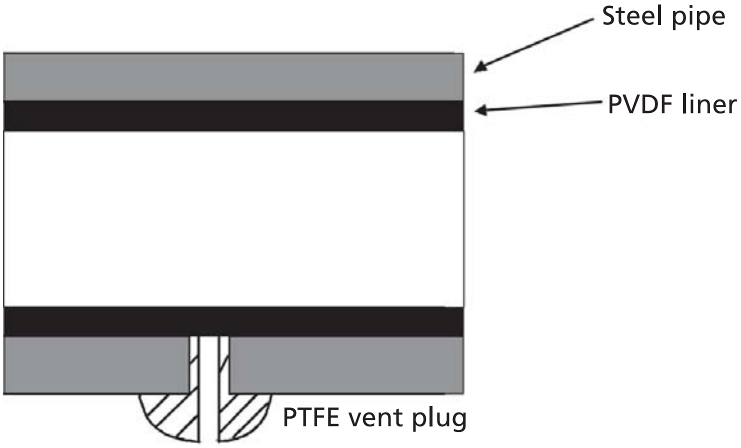

Figure 7.9 Structure of pipe

7.6.6 Cracking of a Nylon 6 outsert moulding

History

The component in this case was a circular magnetic ring of 50 mm outside diameter encapsulated in Nylon 6. Encapsulation was achieved by outsert injection moulding, i.e. by locating the magnet in a mould cavity and injecting the plastic around it. The plastic moulding provided a convenient means of assembly, accurate location, and protection of the relatively fragile (rare earth) magnet against shock loads.

The component was supplied to original equipment manufacturers (OEMs) for incorporation into sophisticated electrotechnical devices. No failures were experienced for about 10 years and by that time the population had grown to over 10,000. Then during the first annual maintenance check, one OEM found that a high proportion of the Nylon mouldings were cracked and could not be reassembled to the required accuracy. Also one of the magnets had cracked.

Inspection and analysis

A photograph of a cracked ring is shown in Figure 7.10. Cracks have initiated at the rectangular and circular retaining features. Crack opening displacement would indicate the relief of about 1.5% of tensile hoop strain. There were no visible signs of material degradation.

There are three candidate causes for high levels of strain:

1. Residual strain due to the moulding process.

2. Contraction of the Nylon due to loss of water.

3. Physical ageing or post moulding crystallisation.

Residual strain in this case will be dominated by the mismatch between the thermal expansion/contraction coefficients of the magnet and the Nylon. On cooling from the melt temperature to ambient temperature the linear shrinkage of the Nylon will be about 2%, and during the same cooling process the thermal contraction of the magnet will be about 0.4%. The difference matches the implied level of residual strain in the failed mouldings. Indeed, if the magnet was not preheated prior to outsert moulding, the residual strain could approach 2%. However a significant proportion of this ‘strain’ would relax during cooling.

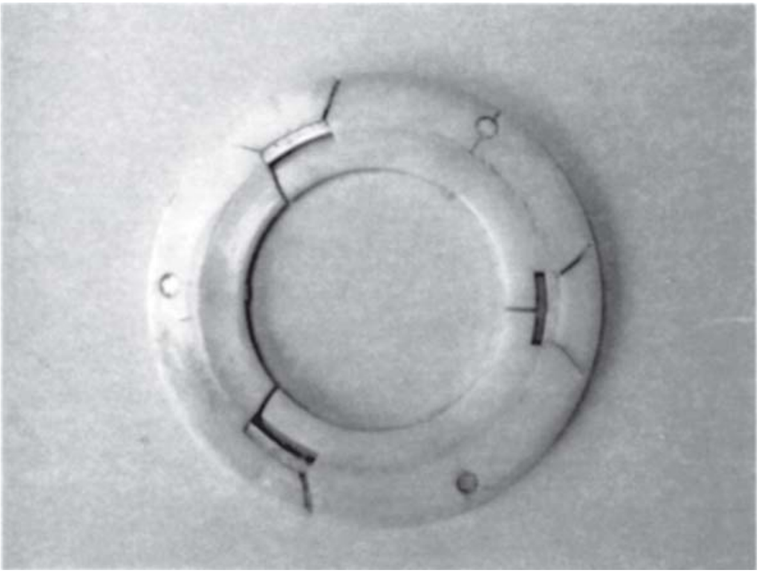

Figure 7.10 Nylon 6 encapsulated ring magnet that has cracked after one year in service at 80 °C

Unused samples from current production were assessed for residual stress using an acetic acid dip test. This indicated a residual stress of 5 MPa, equivalent to a residual elastic strain of only 0.2%.

Nylon 6 is hygroscopic. At ambient temperatures in air at 50% relative humidity (RH), equilibrium water content will be about 3%. The material is moulded dry, and post moulding equilibration will initially generate compressive stresses and strains, which would counteract the residual cooling stresses to a degree. Significant tensile stresses could only develop if the component was then operated in a dry atmosphere. The failed components had been exposed to the normal range of climatic humidity.

All semicrystalline plastics experience post mould crystallisation and therefore post mould shrinkage. This will continue until the degree of crystallinity achieves thermodynamic equilibrium. The potential amount of post mould shrinkage is increased if the moulding has an initial low level of crystallinity, and the rate of post mould shrinkage will increase with increasing temperature. In this case the maximum service temperature was 80 °C.

The degree of crystallisation of new and failed mouldings were 48% and 65%, respectively (compared using DSC).

Failure diagnosis

It can be inferred from the DSC analysis that as-moulded components from current production have uncharacteristically low levels of crystallinity. If the failed components were initially in this condition then it can also be inferred that a considerable degree of in-service crystallisation had been accumulated and this would generate significant tensile stresses due to constrained volume contraction.

To confirm this as the prime candidate for failure, unused mouldings were aged for 3 months at 90 °C to simulate the thermal history of the failed components (about one year at 80 °C). The aged components were subjected to an acetic acid dip test. The cracking pattern that developed was very similar to that observed in the failed components, and the time to crack indicated stress levels of between 15 and 25 MPa.

Records revealed that the cycle time for moulding had been progressively reduced over the past 3 years by aggressive mould chilling. This would explain the low levels of crystallinity in current production. It would also explain the trouble free performance of earlier production batches.

Lessons and consequences

1. Significant tensile stresses can be developed in service as a result of physical ageing/post mould crystallisation. Stresses are maximised for semicrystalline plastics, high mould cooling rates, high service temperatures, and high levels of geometrical constraint.

2. There is a tendency for moulders to maximise profitability by maximising production rate. This may continue until the customer complains about defective products.

3. Nucleated grades of semicrystalline plastics would reduce the risk of fracture via post moulding crystallisation.

4. Nylon 6 was not the optimum material for this component. A heat resistant amorphous thermoplastic with low shrinkage and low moisture absorption (e.g. polycarbonate) would be preferable to maximise dimensional stability and minimise induced stresses.

5. Sharp corners should be avoided.

7.6.7 Nylon 66 drive coupling

History

A splined coupling moulded from Nylon 66 failed after 2 years in service. The coupling connected an electric motor drive shaft to a gear shaft. The coupling, shafts and gears operated whilst totally immersed in oil. Similar couplings of various sizes and power transmission ratings were widely distributed, and therefore it was important to establish whether the cause of this failure could be responsible for limiting the durability of the entire population.

Inspection and analysis

The failed product is shown in Figure 7.11. The splines on the motor side of the coupling appear to have melted. This was the initial conclusion of the component manufacturer. However the customer insisted that during its operating life the oil temperature was stable at around 90 °C. Also the splines on the gear side of the coupling were not only intact but free of any precursor symptoms of meltdown (e.g. permanent deformation). These splines were subject to the same oil temperature and the same mechanical power input as the failed splines.

The component was inspected in some detail. The short spline remnants on the failed side of the coupling provided an insight into the failure mechanism. After careful removal of debris and melt strings, the failure surfaces (marked * in Figure 7.12) were revealed. All had failed by brittle fracture, and not by high deformation shear or melting.

Failure diagnosis

Gross melting has occurred but this is an effect of failure and not its cause. A spline has fractured, transferring higher stresses to remaining splines, which sequentially fractured. After failure of the last spline, frictional heat from the rotating shaft melted and smeared the spline fragments.

The cause of the initial spline fracture is the critical issue. The maximum recommended 100,000 hour operating temperature for Nylon 66 in air is 80 °C (see Table 2.1). In oil and therefore starved of oxygen, one year at 90 °C should not result in significant

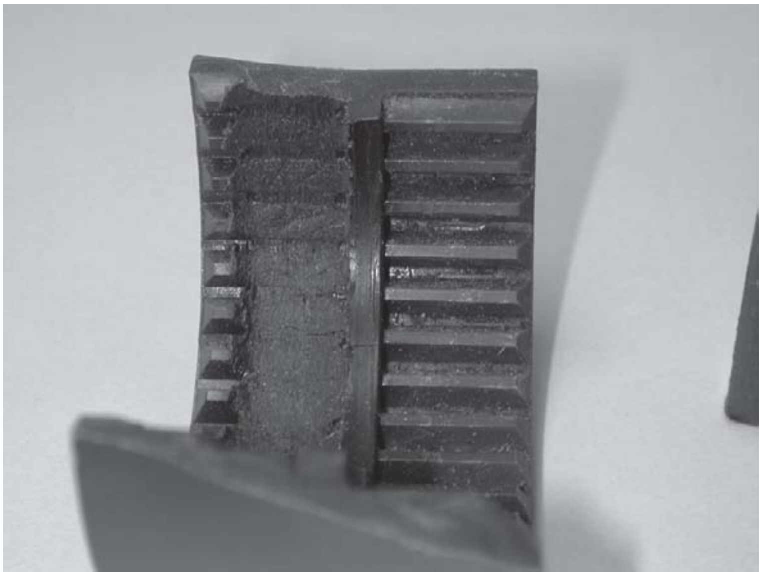

Figure 7.11 Failed Nylon 66 drive coupling

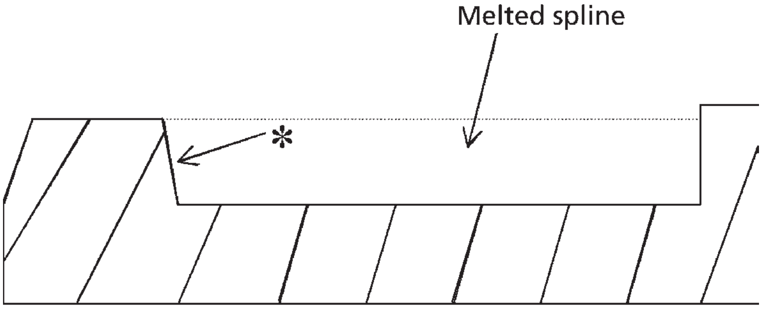

Figure 7.12 Cross section of the failed half of the coupling and location of the fracture surfaces*

embrittlement via thermo-oxidative degradation. However this could not be ruled out, because it was revealed that a high proportion of the heat that raised the oil temperature to 90 °C was transmitted down the motor drive shaft, and the local service temperature of the splines could be significantly higher.

Another potential cause of embrittlement is drying of the Nylon. At temperatures in excess of 100 °C, moisture in the material would be driven off and the oil would preclude reabsorption from the atmosphere during rest periods.

To appraise the contribution of the two candidate causes of embrittlement the following test procedure was carried out. Nylon 66 test bars were conditioned in oil at 120 °C for 3 months, then cooled to ambient in the oil. The Izod notched impact strength of the material was then assessed (A) immediately after removal from the oil, (B) after one month of further conditioning at 20 °C and 65% RH, and (C) prior to any conditioning. The energy to break for specimens (A) averaged at 10% of specimens (C). The energy to break for specimens (B) averaged 90% of specimens (C). Thus degradation due to heat is only responsible for ~ 10% of the embrittlement, whilst the reversible effects of drying are the dominant factor.

Lessons and consequences

1. Careful inspection and a knowledge of the material are required in order to differentiate between cause and effect.
2. Nylon 66 is an excellent bearing material with good fatigue, wear, and oil resistance. However if the operating environment is such that the material is allowed to dry out, its resistance to shock loading is seriously impaired. This is further aggravated by stress concentrations; in this case due to the unnecessarily small spline root radius.
3. Subject to the results of more comprehensive tests, the manufacturer was advised to ensure that maximum local temperature should not exceed 90 °C (for example by the inclusion of a thermal break on the motor drive shaft, or forced cooling of the oil, or reducing the maximum recommended power rating of the couplings.

7.6.8 Blistering of a glass-reinforced plastic laminate

History

A company specialising in open mould glass-reinforced plastic (GRP) laminations for the automotive industries (e.g. lorry cabs) decided to diversify into small marine craft. With a short but demonstrably successful history they were subcontracted to supply hull mouldings for the military. These were moulded by hand lamination using chopped strand mat (CSM) and an unspecified grade of *ortho*phthalic polyester resin. Pigmented marine grade isophthalic polyester was used for the external gel coat.

Within two years of service use, a small fraction of the hulls were observed to be severely blistered. Service records revealed a correlation between fresh water, hot climates and blistering.

Inspection and analysis

In the hull provided for inspection, blisters under the external gel coat ranged in size from a few mm to 25 mm in diameter. Blistering was restricted to the area of the hull below the water line. A cross section of a typical blister reveals a wall thickness of about 1 mm. This is the thickness of the gel coat.

The blister fluid was extracted with a hypodermic syringe and was analysed using various techniques. Gas liquid chromatography was used to identify organic solutes. In ascending order of concentration these were established as diethylene glycol, methyl ethyl ketone (MEK), acetic acid, styrene, benzaldehyde. The fluid had a pH of 4.5.

Atomic absorption spectroscopy was used to identify and quantify cations. Calcium ion concentration was 1500 ppm, aluminium was at 200 ppm, as was cobalt.

Failure diagnosis

Polyester resins are generally formulated with a glycol. Diethylene glycol or polypropylene glycol tend to be used in standard formulations, whilst others such as 2,2,4-trimethyl-1,3-pentanediol or 2,2-dimethyl-1,3-propanediol are preferred for marine grade resins. It is probable therefore that the main laminating resin is a standard *ortho*phthalic polyester containing excess diethylene glycol.

Acetic acid, which is mainly responsible for the low pH of the blister fluid, is a by-product of the hydrolysis of polyvinyl acetate. The high concentration would suggest that emulsion bound CSM has been used as the reinforcement.

Benzaldehyde is a by-product of the oxidation of styrene. The standard reactive diluent for these resins is styrene monomer.

The higher than expected concentration of MEK and cobalt ions is significant. MEK is a soluble breakdown product of methyl ethyl ketone peroxide (MEKP), and MEKP/cobalt (II) is the standard catalyst system for these polyester resins. It is probable that an excess of the catalyst has been used, either by mistake or to facilitate an increase in the cure rate.

The high concentration of calcium and aluminium ions is not unusual. E glass contains calcium and aluminium oxides, and these are leached out of the fibres by water and more rapidly by acids.

Slow permeation of water through the gel coat is inevitable. Whether this is sufficient to cause eventual blistering depends on many factors. The most important is the availability of water soluble species under the gel coat. Concentrated solutions will trigger an increase in the rate of water permeation by osmosis. In this case the immediate availability of excess cobalt salts and MEK probably initiates the process. The next phase is sustained by the hydrolysis of the polyvinyl acetate emulsion to acetic acid. The final stage is the acid leaching of water soluble metal salts from the glass fibres. These reactions, if sufficiently vigorous, will lead to a solute concentration, increased osmotic pressure, and eventually to blistering.

Lessons and consequences

1. Although the gel coat blistering phenomenon cannot be predicted with confidence, the service conditions, material variables and the fabrication procedures that promote it are reasonably well known within the marine construction industry. However in this case the fabricator had insufficient experience within the sector to avoid the risk of blistering. This should be born in mind when selecting a supplier. Suppliers with a short but successful history of fabricating products for a particular service environment should not be treated as equivalent to those whose products have (demonstrably) stood the test of time. Customers should insist that representative laminates be subjected to accelerated testing to assess blistering resistance. Typically this involves exposure of the gel coat to condensed water at 60 °C for several hundred hours. Resin suppliers will advise as to the level of resistance required for any given application.

2. Warm fresh water is the most detrimental service environment for GRP craft.

3. To defend against blistering in such an environment a powder bound reinforcement mat should have been employed rather than an emulsion bound reinforcement mat. Marine grade resins should have been used for the structural laminate as well as the gel coat. More consideration should have been given to catalyst levels.

7.6.9 Polysulphone filter bowl

History

A coffee making machine manufacturer selected polysulphone for a filter bowl that had to be transparent and resistant to boiling water. Brittle fractures of the injection moulded components were reported after about 5 years of service. Poor processing was suspected (as is usual) as the cause of the problem. However, during protracted efforts to optimise the process, it became apparent with an increasing number of failures that there was a consistent limit to the durability of the component, based upon its frequency of use. Up to about 10,000 heating and cooling cycles there were no failures, but above this threshold the probability of failure increased dramatically with further service. This observation did not eliminate imperfect processing as a candidate cause, but it did promote the thesis that a more fundamental (material) limit was being exceeded.

Inspection and analysis

Gel permeation chromotography of material removed from new and failed components revealed no significant changes in molecular weight as a result of service history. Thermo-oxidative, photo-oxidative and hydrolytic degradation were eliminated as the cause of the durability limit.

Detailed inspection of the fracture surfaces revealed that cracking initiated within the wall of the bowl and typically about 1 mm below the inside surface. This suggested thermal cycling fatigue. As illustrated in Figure 7.13 initiation sites were typically of an elongated lozenge shape with peripheral parallel growth rings, indicating incremental craze growth as shown similarly in Figure 1.6.

Failure diagnosis

In use the internal surface of the bowl was subjected to repeated and rapid excursions to 100 °C. During contact with hot water, a severe temperature gradient is created across

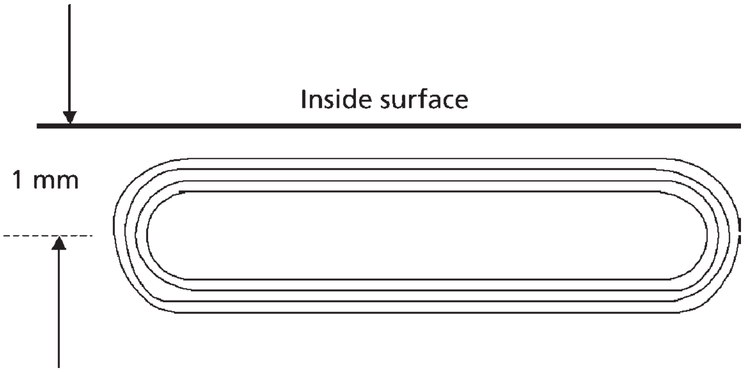

Figure 7.13 Initiation site

the wall. Thermal expansion is constrained to that of the mean wall temperature. Therefore when hot, the inside surface skin is under compression and the bulk of the wall is under tension. The tensile stress maximises near to the compressed skin, its precise position being dependent upon the severity of the temperature gradient, see Figure 7.14.

The dynamic fatigue resistance of polysulphone is very poor. It will fail after one million cycles under a strain amplitude of 0.3%. The material has a thermal expansion coefficient of 0.005% per °C and therefore if unconstrained it will expand by 0.4% for a thermal excursion of 80 °C (ambient to boiling water). If fully constrained, repeated thermal cycling over this range will develop compressive and tensile strain amplitudes of up to 0.4%. This exceeds the safe long-term fatigue limit of the material.

Lessons and consequences

1. Thermal cycling fatigue is a common cause of failure in products made from glassy amorphous thermoplastics.
2. It would be prudent to assume that due to shape effects, or thermal gradients, or the use of metallic fasteners, that the thermal expansion of all products will at some point be fully constrained. This assumption together with an equally prudent assumption

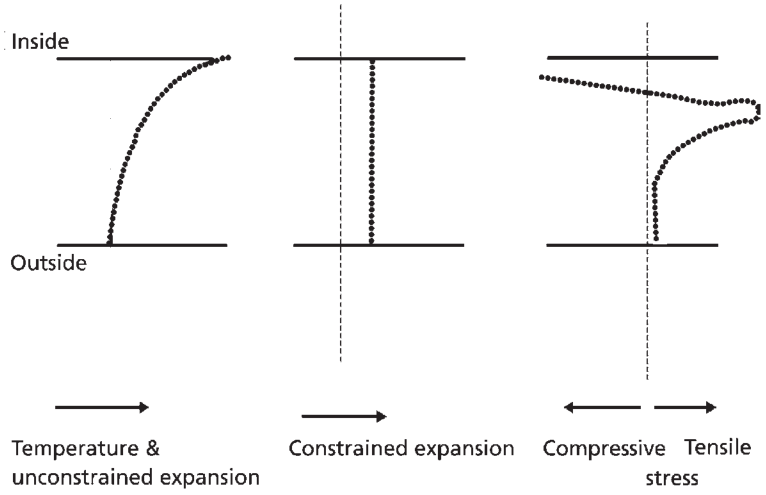

Figure 7.14 Effect of temperature gradient

that the safe long-term strain amplitude will not exceed 0.2% determines the safe temperature excursions for amorphous thermoplastics.

3. In this application, transparency was required and therefore the material could not be replaced with a semicrystalline. The thermal excursion was also fixed.
4. By filling (with boiling water) at a slower rate, the thermal gradient, the degree of constraint, and therefore the maximum strain amplitude were reduced. By this means the manufacturer was able to increase the durability of the component by a factor of two.

7.6.10 Polyvinyl chloride skylights

History

During a period of high winds and rainfall an office complex suffered serious disruption and consequential losses as the result of water damage. Entry was via six skylights that had been installed for five years.

Inspection

The skylights had been manufactured by vacuum forming PVC sheet. Severe discoloration and reduced transparency indicted advanced photo-oxidative degradation. A lack of discoloration of material protected by the peripheral gasket confirmed the diagnosis.

As shown in Figure 7.15, the product has also suffered from distortion. An edge has retracted and this is the entry point for rain water.

Failure diagnosis

The distortion is due to heat reversion, which is a ‘memory effect’. The sheet has been moulded at modest temperatures and the significant residual stresses are distributed in such a manner as to promote reversion back to a flat sheet. However this will only occur at elevated temperatures, or more specifically as temperatures approach the glass transition temperature (T_g) of the material. The claimed T_g of rigid PVC is ~ 80 °C.

The surface temperature of a failed skylight was measured on a cloudless day. With an air temperature of 29 °C the surface temperature of the PVC reached 63 °C. This high

Figure 7.15 Discoloured and locally distorted PVC skylight

temperature is due to solar energy absorption, greatly enhanced by the UV induced opacity of the material.

Although 63 °C is comfortably below the claimed T_g it should be emphasised that T_g reduces with increasing test or exposure period. Most published data result from short-term tests (a few minutes) whilst problems in service can accumulate over months or years. It is likely that the effective T_g of the PVC is less than 70 °C over a time-scale of months.

Lessons and consequences

1. The critical temperature for heat reversion decreases with exposure time. Therefore at constant temperature the distortion of products may not occur in the short-term but may develop in the longer term.
2. In this case and in addition, the service temperature increased with exposure time due to discolouration and a reduction in transparency. The accumulation of dust and dirt would have induced a similar effect.
3. Separate tests to determine thermal and UV stability would not have revealed the antagonistic synergy between the two.
4. Polycarbonate with its higher heat reversion resistance was recommended as the replacement.

7.6.11 Polypropylene scooter wheels

History

Scooters imported from Thailand attracted the attention of various Regional Trading Standards (RTS) offices in the UK. The common complaint was collapse of the plastic wheels. This occurred when the front wheel was impacted at modest speed against (for example) roadside kerbing. Children suffered cuts and abrasions.

The scooter, classified as a toy, satisfied all the detailed safety requirements of the relevant standards. Therefore the RTS could only dissuade further importation by way of the trade description acts. The scooter was claimed in advertising literature to be ‘robust’ and this would be contested in a court of law. The need to do this was stimulated by a more serious failure. A scooter had been purchased as a Christmas present for a child. On Christmas Eve the father decided that the tyres needed more inflation and, having no pump of his own, took the scooter to the local garage and used a high flow rate airline. A wheel rim fractured and the father lost an eye.

Inspection and analysis

The wheel had been injection moulded from polypropylene homopolymer with a weight average molecular weight of about 350,000. Although the moulding contained several radial knit lines these were not critical. Fracture had initiated and grown circumferentially along a line of maximum rim bending stress resulting from pressure in the tyre (Figure 7.16).

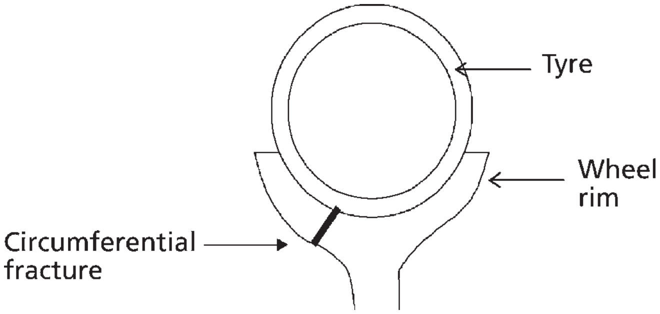

Figure 7.16 Location of fracture

Failure diagnosis

Polypropylene homopolymer exhibits very high sensitivity to impact damage over the temperate climatic range. Under standard Izod notched impact conditions (with a notch radius of 0.25 microns) the material is tough at 20 °C or above and brittle at 0 °C and below. The critical 'brittle temperature' depends upon the molecular weight of the material, being in the region of +15 °C for easy flow grades and 0 °C for stiff flowing grades.

The ambient temperature according to meteorological records was –5 °C at the time of failure. Failure was due to impact/impulse fracture.

Lessons and consequences

1. Polypropylene homopolymer is not an appropriate material for applications that demand impact toughness at temperatures that are significantly below 20 °C. Polypropylene copolymer with a brittle temperature of –20 °C would be a satisfactory choice for the temperate climate of the UK.

2. The scooter manufacturer had chosen the homopolymer because this was the most cost effective material for the local environment. Here creep and buckling of the wheel at elevated temperatures provided the critical durability issue, and the homopolymer satisfies this demand more cost effectively than the copolymer or polyethylene, which have significantly lower stiffness.

3. Plastics products appropriate for one climatic extreme may be deemed unfit for purpose in another environment.

4. The jury were not convinced. However it was clear to them that the scooter tyre should not have been inflated with a high flow rate airline. The case was lost but the importer remained exposed to future litigation and was dissuaded from further importation.

7.6.12 Epoxy flooring

History

Fragile and softened samples of a cast polymeric flooring material were taken from a food factory that had been damaged by fire. The polymer was said to be polyurethane, selected to resist the aliphatic oils and fats being processed at the site. The processing area had suffered smoke damage and because of this the floor had been in contact with liberal amounts of various cleaning materials, including steam.

Inspection and analysis

Examination of the samples showed that the flooring had a base level of resin filled with fine aggregate topped by a thin resin coating layer. Softening (symptomatic of liquid absorption) of both base and surface had taken place. Although a strong soapy smell was evident it could not be positively identified. Apart from the softening, there was no visible evidence of surface scorching or blistering. However detailed inspection did reveal dense microcracking when the flooring was subjected to modest flexural deformation. This would explain the fragility of the material.

Analysis of samples was carried out by extraction in methanol followed by drying and weighing. Infrared spectra were then obtained both of the dried extracts and of the pyrolysis condensates of the extracts. Thermogravimetric analysis (TGA) was also carried out by heating in a nitrogen atmosphere to 550 °C, cooling to 300 °C and heating in air to 850 °C. Samples were dissolved in distilled water and the pH of the resulting solution measured.

The amounts extracted with methanol varied with sample but were up to 11%. The TGA gave inorganic contents of the order of 40% for the coating and 85% for the base. The most badly affected sample had about 60% low molecular weight species/polymer content in the coating and 17% in the base.

The results of the pyrolysis infrared analysis indicated that the polymer was in fact an epoxy and there was no evidence that it had been thermally degraded. The methanol extract infrared spectra were complicated but it was possible to find evidence for aliphatic ester/acid. The pH was about 6.

Failure diagnosis

The floor was in very bad condition with low strength. Assuming it was satisfactory before the fire, the poor condition must be attributable to the treatment received. It was deduced from records obtained that steam, phosphoric acid, alkaline detergents and organic solvents had come in contact with the floor, plus the possibility of hydrochloric acid and other by-products from the burning of cables, etc. From the pH measurements, the acids appeared to have neutralised the detergents.

The extraction figures were regarded as more reliable than the TGA as a guide to low molecular weight species absorbed. The presence of aliphatic ester/acid is consistent with detergent/soap products. The resin had not chemically degraded.

It was concluded that the microcracking was probably caused by thermal shock resulting from the fire or fire fighting activity. Chemicals used in subsequent cleaning operations were then absorbed by the damaged material. Swelling would partially heal the microcracks.

Lessons and consequences

1. Material specifications are frequently ignored.
2. The flooring supplier was exposed to litigation. However it could be claimed in defence that the epoxy flooring was superior, and would have resisted the cocktail of chemicals and steam far better than the specified urethane product.
3. Fluid absorption is normally taken to be the **cause** of microcracking (as in ESC) but in this case the causality is reversed.

7.6.13 Valve sleeves

History

Nitrile rubber sleeves of valves used in the conveyance of mains gas at a pressure of 5 MPa had been operated successfully in many installations. However, in one particular application premature failures occurred frequently. This involved only one size of valve and the pressures were not abnormal, although the temperature was 38 °C as opposed to the more usual 10-20 °C.

It was expected that valves in these applications would suffer ‘explosive decompression’ due to the expansion of absorbed gas on depressurisation. However, the failures in this case occurred at operating pressure, and took the form of splits on the outer side of the sleeve and what appeared to be foaming at discrete spots around the inside of the sleeve.

Inspection and analysis

The damage on both surfaces was located on a narrow circumferential band, with splitting on the outside surface facing foaming on the inside surface (Figure 7.17).

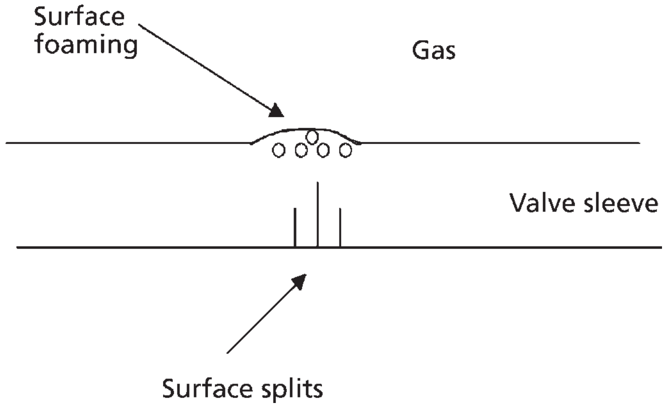

Figure 7.17 Damage on both surfaces

The splits and foamed regions were sectioned and examined under a low power microscope. Ultrathin sections of the rubber were also taken and examined for dispersion under higher power. TGA was carried out on material from the foamed spots, and from an undamaged part of the component. Tensile stress/strain properties were measured at 23, 40 and 70 °C using dumbbells cut from undamaged regions.

Details of the formulation used were available, which showed that the material had not been optimised for fatigue resistance, and included an oil-based softener/extender which may not have been fully compatible.

The chemical analysis showed that the material from the foamed region was a badly dispersed material of the same composition as the bulk, and did not contain agglomerates of filler or foreign material.

Tensile strength and elongation were very variable, with strong indication of local flaws. Both deteriorated sharply at the highest temperature. Dispersion was judged to be rather less good than desirable for a dynamic application.

Failure diagnosis

From the examination it was concluded that the splits were fatigue cracks. It was concluded that the foamed areas were due to expansion of absorbed gas. The circumferential band of damage coincided with the region of highest gas velocity. Gas pressure distributions here would shift and vary significantly with time. The fluctuating stresses due to the expansion of absorbed gases initiated fatigue cracks within the sleeve wall, which propagated in directions dictated by the very complicated strain distribution in the sleeves. This problem was related primarily to the imperfect formulation and the level of dispersion, probably coupled with the quality of moulding for the particular size of sleeve, and the particular operating conditions.

It was not possible to be precise about the main cause of the foaming type of flaw, but it could be deduced that they started from particularly weak areas which were situated in the region of greatest localised dynamic strains. The weak areas could result from a combination of the formulation, dispersion, mould filling and degree of cure defects that preferentially absorb gas. The moulding of this particular size of sleeve and the particular operating conditions resulting in more severe local temperature rise could account for failures in the particular installation.

Lessons and consequences

1. If failures had been more widespread in different installations they would have been simply attributed to the formulation, mixing and moulding being inadequate for the combination of dynamic strain, local temperatures and gas absorption encountered in the application. In fact, failures only occurred in one installation where the conditions were apparently only marginally more severe. It would appear that even a modest change in operating conditions resulted in sufficient increase in local conditions of temperature, dynamic strain and gas absorption to expose the inadequacies of the material.

2. The material formulation should have been optimised for fatigue performance by optimising the dispersion of solid additives.

References

1. J. J. Xuu and S. A. Boggs, Trends in Polymer Science, 1995, 3, 7, p.234.

2. J. V. Champion, S. J. Dodd and G. C. Stevens, Journal of Physics D: Applied Physics, 1994, 27, 1, p.142.

3. Y. Poggi, J. C. Filippini and V. Raharimalala, Polymer, 1988, 29, 2, p.376.

4. S. Bamji, A. Bulinski and J. Densley, Die Makromolekulare Chemie: Macromolecular Symposia, 1989, 25, p.271.

5. D. K. Das-Gupta, A. Svatic, A. T. Bulinski, R. J. Densley, S. Bamji and D. J. Carlsson, Journal of Physics D: Applied Physics, 1990, 23, 12, p.1599.

6. J. J. Xuu and S. A. Boggs, Trends in Polymer Science, 1995, 3, 7, p.234.

7. Y. Kawasaki, K. Igarashi and S. Taniguchi, inventors; Nippon Unicar Company Limited, assignee; US 4,305,849, 1981.

8. K. Soma, S. Kuma, H. Sakaguchi, H. Shirai, R. Ito and T. Shiina, inventors; Hitachi Cable Limited, assignee; US 4,370,517, 1983.

9. F. Peruzzotti, L. Castellani, L. J. Dagal and V. Garcia, inventors; Pirelli Cavi, Spa, assignee; EP 0814 485 A1, 1997.

10. E. Rogers, IEEE, 88th Meeting, Charleston, 1991, p.VB –2.

11. G. Vroomen and H. Verhoef, Kautschuk und Gummi Kunststoffe, 1995, 48, 10, p.749.

12. J. G. Dillon, Polymer Degradation and Stability, 1992, 37, 3, p.183.

13. J. Rye, P. Brown and W. T. Eeles, Journal of Physics D: Applied Physics, 1975, 8, p.L16.

14. K. B. Stokes and M. W. Davis, Advances in Biomedical Polymers, ACS Polymer Science & Technology Series, Volume 35, Plenum Press, NY, 1987, p.147.

15. O. Zhoa, J. Casas-Bejar, P. Urbanski and K. Stokes, Journal of Biomedical Materials Research, 1995, 29, 4, p.467.

16. K. Hughes-Dillon and L. W. Schroeder, Polymer Degradation and Stability, 1998, 60, 1, p.11.

17. E. Bessems, Journal of Vinyl Technology, 1988, 10, 1, p.3.

18. J. B. Decosta, I&EC Product Research and Development, 1968, 7, 4, p.238.

19. H-C. Flemming, Polymer Degradation and Stability, 1998, 59, 1-3, p.309.

20. R. J. Howard, M. Ferrari, D. H. Roach and N. P. Money, Proceedings of the National Academy of Sciences., 1991, 88, p.11291.

21. E. H. Pommer and G. Lorenz in Biodeterioration and Biodegradation of Plastics and Polymers, Ed., K. J. Seal, The International Biodeterioration Society, Kew, UK, 1985.

22. G. Ji-Dong, T. E. Ford and R. Mitchell, Journal of Applied Polymer Science, 1996, 62, 7, p.1029.

23. M. Ezrin and G. Lavigne, Proceedings of Antec '94 Volume III, San Francisco, CA, p.3302.

24. A. J. Duke, Proceedings of Plastics in Telecommunications VI, London, September 1992, p.28/1.

25. J. Comyn, Proceedings of Diffusion in Polymers III, February 1991, p.25/1.

26. L. C. E. Struik, Physical Aging in Amorphous Polymers and Other Materials, Elsevier, New York, 1978.

27. P. C. Warren, Proceedings of Plastics in Telecommunications VI, London, September 1992, p.29/1.

28. J. P. Mercier, Polymer Engineering and Science, 1990, 30, 5, p.271.

Abbreviations and Acronyms

6PPD	*N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine
ABS	acrylonitrile-butadiene-styrene
ACM	ethylene acrylate rubber
AO	antioxidant
ASA	acrylate-styrene-acrylonitrile
AU	ester urethane rubber
AV	audiovisual
BHT	2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene)
BIIR	bromobutyl rubber
BS	British Standard
CA	cellulose acetate
CAB	cellulose acetate butyrate
CB	carbon black
CEE	coether-ester thermoplastic elastomer
CIIR	chlorobutyl rubber
CO	epichlorohydrin rubber
COD	crack opening displacement
CP	cellulose propionate
CPC	circuit protective conductor
CPE	chlorinated polyethylene
CR	chloroprene rubber
CSM	chlorosulphonyl rubber
CTFE	chlorotrifluoroethylene
DAIP	diallyl isophthalate
DAP	diallyl phthalate
DED	dose to equivalent damage
DMC	dough moulding compound
DOP	dioctyl phthalate

DSC	differential scanning calorimeter
DTI	Department of Trade and Industry (UK)
ECR	acid resistant glass fibre
ECTFE	ethylene-chlorotrifluoroethylene
EDAX	energy dispersive x-ray analysis
EEA	etherester-amide thermoplastic elastomer
EEMUA	Engineering Equipment and Materials Users' Association
EMMA	equatorial mount with mirrors for acceleration
EMMAQUA	EMMA + water spray
EO	ethylene oxide
EP	ethylene-propylene rubber
EPDM	ethylene-propylene-diene rubber
ESC	environmental stress cracking
ETBP	1,2-bis(tetrabromophthalimido)ethane
ETFE	ethylene-tetrafluoroethylene
EU	ether urethane rubber
EVA	ethylene-vinyl acetate
EVM	ethylene-vinyl acetate rubber
FDA	Food and Drug Administration (United States)
FEP	fluorinated ethylene-propylene rubber
FFKM	perfluoroelastomer
FPM	fluoroelastomer
FTIR	Fourier transform infrared spectroscopy
FVMQ	fluorosilicone rubber
gfr	glass fibre reinforced
gp	general purpose
GPC	gel permeation chromatography
GPPS	general purpose polystyrene
GRP	glass reinforced plastic
HALS	hindered amine light stabiliser
HDPE	high density polyethylene
HDT	heat distortion temperature
HET acid	hexachloroendomethylene tetrahydrophthalic acid

HI-PMMA	high impact polymethyl methacrylate
HIPS	high impact polystyrene
HNBR	hydrogenated nitrile rubber
HSBR	hydrogenated styrene-butadiene rubber
IIR	butyl rubber
IR	isoprene rubber
IRHD	international rubber hardness degree
KBS	knowledge based systems
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
MbOCA	methylene bis-orthochloroaniline
MCUT	maximum continuous use temperature
MDPE	medium density polyethylene
MEK	methyl ethyl ketone
MF	melamine-formaldehyde
MFI	melt flow index
Mg-EBDC	magnesium ethylenebisdithiocarbamate
MIC	microbiologically influenced corrosion
M_w	weight average molecular weight
NBR	nitrile rubber
NR	natural rubber
OEM	original equipment manufacturer
OIT	oxidative induction time
OLTPE	olefinic thermoplastic elastomer
PA	polyamide
PAI	polyamideimide
PB	polybutylene
PBT	polybutylene terephthalate
PC	polycarbonate
PE	polyethylene
PEEK	polyether ether ketone
PEI	polyetherimide
PEN	polyethylene naphthalate

PES	polyethersulphone
PET	polyethylene terephthalate
PE-X	crosslinked polyethylene
PF	phenol formaldehyde
PFA	perfluoroalkoxyethylene
PMMA	polymethyl methacrylate
PNBR	nitrile rubber/PVC blend
PO	propylene oxide
PP	polypropylene
PPE	polyphenylene ether
PPO	polyphenylene oxide
PPS	polyphenylene sulphide
PPVC	plasticised polyvinyl chloride
PS	polystyrene
PSul	polysulphone
PTFE	polytetrafluoroethylene
PU	polyurethane
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
PVDC	polyvinylidene chloride
PVDF	polyvinylidene fluoride
PVF	polyvinyl fluoride
RH	relative humidity
RIM	reaction injection moulding
RTS	regional trading standards
SAN	styrene-acrylonitrile
SBR	styrene-butadiene rubber
SBS	styrene-butadiene-styrene thermoplastic elastomer
SCC	stress corrosion cracking
SEBS	styrene-ethylene-butylene-styrene thermoplastic elastomer
SI	severity index
SMA	styrene-maleic anhydride
TAPDT	2,4,6-tris-(*N*-1,4-dimethylpentyl-*p*-phenylenediamino)-1,3,5-triazine

TBA	tetrabromobisphenol A
TBNPP	tris(tribromoneopentyl)phosphate
T_g	glass transition temperature
TGA	thermogravimetric analysis
T_m	crystalline melt temperature
TPX	polymethylpentene
UF	urea formaldehyde
UHMWPE	ultra high molecular weight polyethylene
UL	Underwriters Laboratories
UPVC	unplasticised polyvinyl chloride
UV	ultraviolet
VA	vinyl acetate
VOC	volatile organic compound
XLPE	crosslinked polyethylene
XNBR	carboxylated nitrile rubber
XPS	expanded polystyrene

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