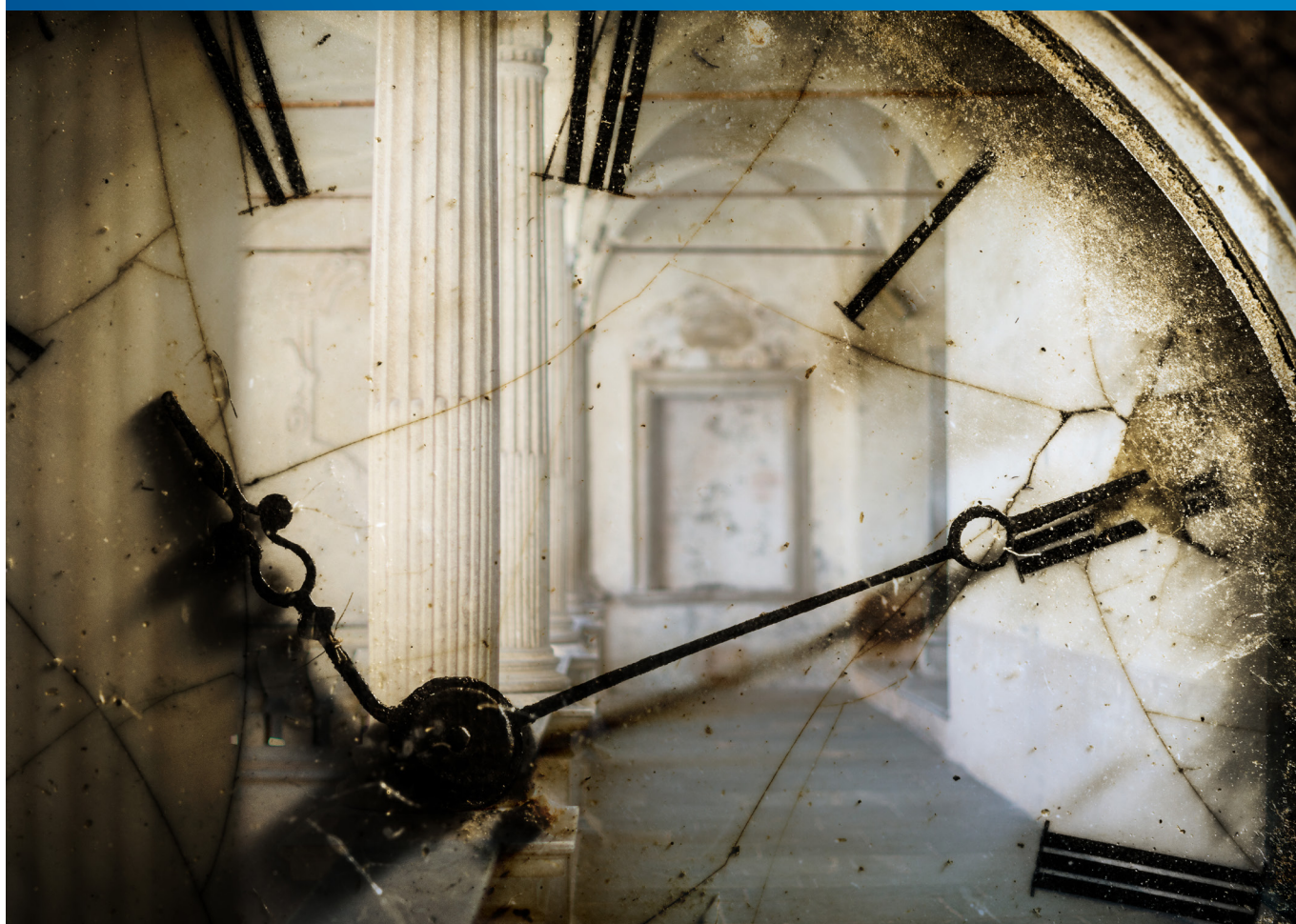


Survey of Long-Term Durability Testing of Composites, Adhesives and Polymers

A.S. Maxwell and W. R. Broughton

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1 INTRODUCTION

Polymer, adhesives and composites are increasingly being used for applications where long-term or critical applications require the use of accelerated ageing regimes to ensure the serviceable life of product and components. A trend that is likely to continue for the foreseeable future due to progressive changes in material procurement strategies that require increased product lifetimes in increasingly harsh environments. As a consequence, there is growing demand on manufacturers to extend the life-time guarantees on products, particularly where inspection can be difficult or failure catastrophic. Regulation and stringent product guarantees are also increasingly being demanded for engineering components in consumer products such as cars and washing machines, where consumers often view extended lifetime warranties as a sign of product quality. Whilst the life expectancy of products in non-demanding applications have traditionally been predicted from previous experience, the use of polymeric materials in long-term or critical applications requires a far better understanding of the failure mechanisms to enable lifetime predictions to be made.

This report summarises the degradation mechanisms found in polymeric materials, the accelerated test methods that have been developed and the techniques used for assessing life-time predictions. The results of an industrial survey to determine current practice and the future needs of industry for long-term testing are also presented. Finally, the report contains a summary of previous NPL publication on durability (Appendix 1) and current ISO and ASTM standards (Appendix 2).

1.1 METHODOLOGY

The aim of durability testing is to assess the effect that ageing processes have on the in-service performance of products and materials. Natural ageing of materials in-service can be assessed either by conducting a programme of condition monitoring using non-destructive testing (NDT) or by examining parts taken out of service. However, the problem with in-service monitoring is that it can only provide information on the current state of components. It does not provide information on how long a component will remain serviceable. To predict future performance some combination of accelerated testing and modelling is required (Figure 1.1). The exact combination of monitoring, accelerated testing and modelling will vary depending on the application and may not include all three elements. For example, when product life-time predictions are required before a new material or design is put into service it is not possible to conduct representative in-service monitoring, in which case the life-time predictions must depend solely on accelerated test results and analytical methods/modelling used to extrapolate the data.

A key component of durability assessments are accelerated tests. The basic concept of these tests is simply to increase the degradation environment, such as temperature or frequency, to levels that are higher than those experienced in service in order to accelerate degradation and reduce the time required for testing. The main restriction to the level of acceleration that can be achieved is that elevated degradation rates may change the mechanisms that occur in the tests from that occurring in-service. The relationship between the degradation agent and time is only likely to be valid over a limited range of acceleration, and regardless of the validity of the mechanisms and extrapolation procedures used the intrinsic experimental uncertainty of the measurements will be magnified the more the results are extrapolated. It is therefore essential that particular attention is paid to the degradation mechanisms and the validity of the predictive techniques used.

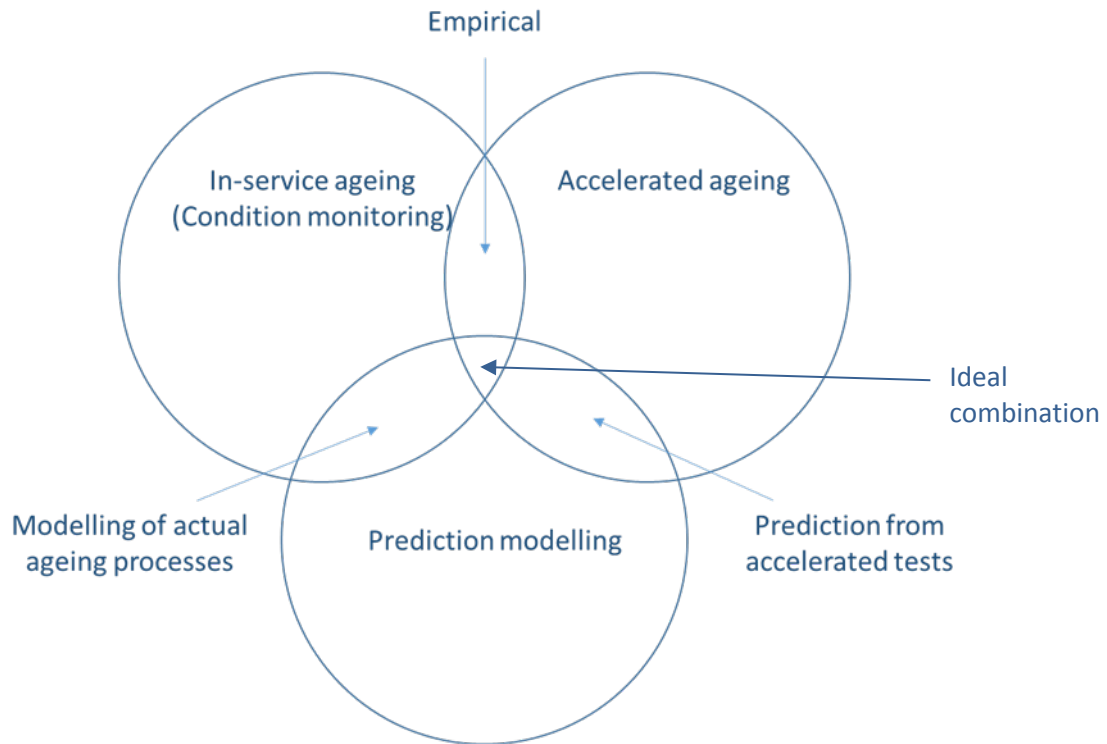


Figure 1.1 Effect prediction of long-term properties requires a combination of condition monitoring

The key steps in conducting an accelerated test programme for a long-term durability assessment are therefore the following:

1. Define the materials, environmental conditions and the serviceable time-scale that the product will experience in-service.
2. Identify the degradation agents/mechanisms and whether there are any synergistic effects (Section 2).
3. Select the parameters that are to be used to accelerate the tests (Section 3), and identify potential for change in mechanisms.
4. Decide on the monitoring parameters and the measurement techniques used to measure them (Section 3).
5. Select the analytical/modelling techniques that will be used to extrapolate the test data to in-service conditions (Section 4).

The testing rational outlined above was that used to develop the questionnaire used to assess current practice and the needs of UK industry (Section 5).

2 DEGRADATION MECHANISMS

Property changes in polymeric materials can be induced by many different degradation agents acting either alone or more commonly in combination. The most common forms of degradation are:

- Thermal - elevated temperatures, sub-zero temperatures and thermal cycling
- Moisture - increased humidity, complete immersion in water, spray or dry/wet cyclic conditions
- Weathering - ultraviolet exposure combined with rain and/or sand erosion
- Chemicals (including acids, alkalis, solvents and oxygen)
- Irradiation- ultraviolet or high-energy radiation
- Biological - micro-organisms
- Environmental stress cracking (combined effect of stress and a plasticiser)
- Stress - static and fatigue loads and residual stresses

In many applications, materials will be exposed to a combination of two or more degradation agents, often resulting in complex synergistic degradation reactions. Accelerated degradation occurring due to the combined action of two or more degradation agents acting together simultaneously or the degradation from one agent reducing its resistance to another, for example biological degradation occurring in an already partially degraded material. The predominant factors in climatic exposure are moisture, temperature and ultraviolet radiation. The severity of these factors will depend on geographical location, and need to be considered when designing with these materials.

2.1 TEMPERATURE

Exposure to elevated temperatures will often produce chemical and physical changes within polymeric materials that lead to degradation of the material. Increasing the temperature accelerates most of the degradation processes that occur in polymeric materials, such as oxidation, chemical attack and mechanical creep. Physical changes include polymer structure shrinkage, pore formation and weight loss through chemical decomposition of the polymer. As the temperature increases, mechanical properties such as stiffness and strength tend to decrease. Oxidation is generally considered to be the most serious problem when using polymers at elevated temperatures with the rate of degradation increasing with the amount of oxygen present [1, 2]. In adhesively bonded joints, the primary path for oxygen diffusion is through the adhesive, which can be relatively rapid at elevated temperatures. Polymer composites are permeable to atmospheric gases, and hence the rate of degradation is considerably higher with the elevated temperatures also degrading the fibre-matrix interface. At extremely high temperatures, as experienced in fires, fibre ablation occurs.

The overall degradation process will often involve a relatively long induction period during which little degradation is observed [1-3]. At the end of this period, there is a rapid increase in degradation leading to a significant reduction in the mechanical properties of the polymer. This induction period is temperature sensitive and is reduced significantly at elevated temperatures. The induction period of the degradation process can normally be regarded as the serviceable lifetime of the polymer.

Other physical changes can occur in polymers because of temperature changes, one of the most common being thermal expansion.

Fibre-Reinforced Plastics (FRPs): In FRPs, differences in thermal expansion between the fibre and matrix can induce stresses, which can degrade the fibre-matrix bond resulting in thermo-mechanical degradation during thermal cycling. The overall degradation process in fibre-reinforced plastics (FRPs) will often involve a relatively long induction period during which little degradation is observed. At the end of this period, there is a rapid increase in degradation leading to a significant reduction in the mechanical properties of the composite. This induction period is temperature sensitive and is reduced significantly at elevated temperatures. The induction period of the degradation process can normally be regarded as the serviceable lifetime of the composite. A sudden brief exposure to high temperatures can result in a phenomenon known as thermal spiking, which can lead to excessive localised stresses with deleterious effects on structural performance. The effects of rapidly driven-off moisture through thermal spiking can also be expected to contribute to damage.

Adhesives: Similar mechanisms can also occur in adhesive joints. A sudden brief exposure to high temperatures can result in excessive localised stresses forming with deleterious effects on structural performance. Conversely, exposure to low temperatures can result in the brittle fracture of plastics, interfacial fibre-matrix cracking in polymer composites and debonding of adhesive joints. Rapid failure can occur in environmentally degraded polymeric materials at sub-zero temperatures, e.g. due to the formation of ice particles from absorbed water initiating internal fractures. Complete interfacial debonding may occur in multiple component systems exposed to cryogenic temperatures through, for example, the combined effects of differential thermal contraction and embrittlement.

2.2 MOISTURE

Most polymeric materials will absorb small, but potentially damaging amounts of moisture from the surrounding environments with the degree of degradation that occurs often being linked directly with the amount of moisture absorbed. Absorbed water may adversely affect polymeric materials in several ways as indicated below:

- Dimensional changes (swelling of the material)
- Surface degradation and damage (colour, gloss, crazing, blistering, etc.)
- Reduction in the glass transition temperature (T_g)
- Reduction in mechanical and physical properties (i.e. stiffness, strength and hardness)

Although the process of moisture absorption and desorption within the surface layers occurs almost immediately on contact with the environment, moisture diffusion into thick systems is usually a slow process. It may take weeks to months before a substantial amount of moisture has been absorbed and considerably longer periods (i.e. 1-2 years) before the material is saturated. The rate of moisture uptake by a material (i.e. its absorption and diffusion properties) is dependent on factors such as the temperature, relative humidity, exposure time and mechanical load. At elevated temperatures, the rate of moisture uptake and material property degradation is accelerated. The moisture absorption kinetics of polymer systems differs widely both between different grades and with chemical ageing.

The presence of tensile loads will also accelerate moisture uptake by opening existing internal cavities or voids, and by contributing to micro-crack formation. A materials system containing micro-cracks will absorb considerably more moisture than an undamaged materials system. This applies equally to polymers, composites and adhesives [4]. Exposing the wet system to sub-zero temperatures can further exacerbate this process. A commonly used test method for polymer composites and bonded adhesives is to subject hot/wet conditioned specimens to thermal cycling in which the composite is exposed to temperatures as low as -55°C for a given number of cycles to assess the laminates crack resistance.

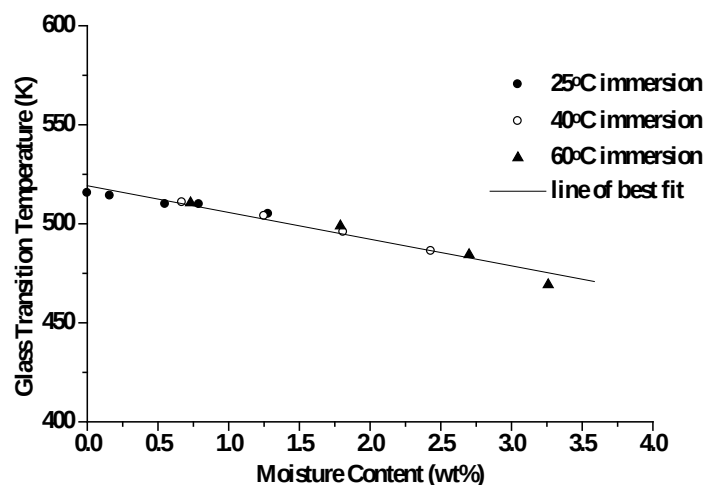


Figure 2.1 Glass transition temperature of F922 epoxy as a function of moisture content

Polymers: Water permeates all polymers to a greater, or lesser degree. Absorption of water is known to cause plasticisation (essentially softening) of the polymer, depressing the glass transition temperature, T_g , and lowering the modulus and strength. Elongation to break (strain-to-failure) tends to increase with moisture content. For example, T_g of a typical polyester resin decreases by approximately 15-20°C for a 2% moisture weight gain. Due to this reduction in T_g it is advisable when using polymeric systems in load bearing structures to ensure that the maximum operating temperature is at least 30-40°C below the T_g of the material (considering moisture effects). Figure 2.1 shows the effect of moisture content on T_g for an epoxy that has been immersed in distilled/deionised water for prolonged periods of time at three different temperatures [5].

The rate of moisture diffusion increases at elevated temperatures. Leaching out of organic additives, such as fillers, catalysts, hardeners, pigments and fire retardants into the surrounding environment can also result in changes in T_g with the loss of fillers and additives becoming more likely with increasing temperature. Permeability is dependent on the structure and chemistry of the polymer. The rate of diffusion in amorphous polymers will depend on the state of the polymer. In the rubbery state ($T > T_g$), there is substantial “free volume” in the polymer mass and considerable molecular segment mobility, which enables easier passage of moisture through the polymer. In the glassy state ($T < T_g$), the “free volume” is far less and molecular segments are immobile, and as a result the diffusion rate is lower. Diffusion rates tend to be higher in amorphous (thermoset) polymers compared with thermoplastics. In semi-crystalline polymers, the crystalline regions are almost impermeable due to the ordered arrangement of molecules and high degree of molecular packing in these regions, with diffusion restricted to the amorphous regions.

Adhesives: Moisture (water) degradation is probably the major cause of in-service failure in bonded structures. The ubiquitous nature of water combined with the ability to penetrate the adhesive structure poses considerable problems for bonded structures. As previously mentioned, water permeates all polymers to a greater, or lesser degree and in the case of bonded joints water will eventually reach the interfaces between adhesive and adherends where its effect is most damaging. Migration of water to the joint interface will result in permanent loss of adhesion. This highly polar molecule is known to interact strongly with structural adhesive systems containing hydroxyl groups, such as epoxies, polyurethanes and acrylics. Hydroxyl groups are hydrophilic and will form hydrogen bonds with water (i.e. hydrolysis). Hydrolysis causes the polymer chains in the adhesive to break into smaller segments (reversion), thus weakening the bond strength of the polymer. This problem is further exacerbated at elevated temperatures and mechanical stress.

Mechanical and thermal properties generally tend to recover on drying, provided irreversible hydrolysis has not occurred. The absorption of moisture by the adhesive may cause the material to swell and deform. Volumetric swelling due to moisture absorption, if significant, may induce additional stresses within the adhesive joint compromising the durability of the joint, and therefore should be included in durability modelling of the adhesive.

It is paramount that the adhesive selected for use in an aqueous environment should have low permeability and diffusion coefficient to water and with good design, it is possible to significantly reduce the rate of moisture diffusing to the adhesive/adhered interfaces. As with most materials, each adhesive has specific attributes that provide protection against moisture. The chemistry of most structural adhesives is a compromise between environmental resistance and mechanical performance with the various classes of structural adhesives possessing different levels of moisture resistance. The problem for designers and engineers is selecting an adhesive, which will guarantee the required design life performance in the service environment to be experienced by the bonded structure. There is no single adhesive that offers a universal solution (i.e. protection from all environments). Being impervious to one environment is no guarantee of resistance to other environments. Highly cross-linked adhesives, such as epoxies and phenolics generally have good resistance to moisture and high temperatures. Most thermosetting adhesives in the presence of moisture are susceptible to hydrolysis at elevated temperatures (above 70°C) with considerable loss in mechanical performance.

Exposure to hot and humid environments can often cause rapid loss of joint strength within a short duration (i.e. less than 2 years) with catastrophic consequences. Failure invariably occurs at the adhesive/adherend interface. The major cause of strength loss in adhesively bonded metal joints is associated with interfacial degradation through water-substrate interaction rather than weakening of the

adhesive. In the case of metallic structures, water can degrade the strength of adhesive joints through hydration of metal oxide layers. Corrosion products, such as rust, at the interface are considered a post-failure phenomenon. The presence of water in epoxy adhesives results in plasticisation (essentially softening) of the polymeric material. At temperatures below T_g , polymer property reduction is reversible upon dehydration, whereas above T_g , matrix properties may be permanently degraded. Surface treatments, such as phosphoric acid anodisation (metallic adherends) and organosilane primer coatings will bestow joints with improved moisture resistance.

FRPs: In many instances, water reacts with the matrix and causes irreversible chemical changes and diminished performance. Capillary action along the fibres can account for a significant proportion of initial moisture uptake, although a chemically resistant matrix may encapsulate the fibres. Shrinkage of the resin away from the fibres during curing is a contributing factor to the capillary effect. The effect of moisture is to cause hydrolytic breakdown of the fibre-matrix interface resulting in a loss in the efficiency of load transfer between the matrix and the fibre reinforcement.

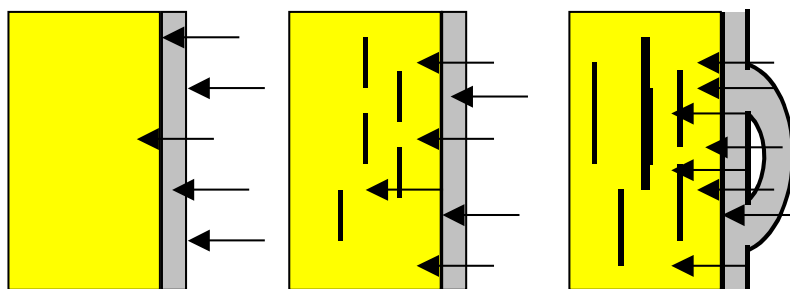


Figure 2.2 Schematic of the osmotic process – leading to delaminations/blistering

All laminates when exposed to marine environments will allow water vapour to permeate the structure. As the water diffuses into the composite it reacts with any hydrolysable components (e.g. ester groups) inside the laminate to form tiny cells of concentrated solution. Under this osmotic process [6-7] (see schematic in Figure 2.2), more water is drawn through the semi-permeable membrane of the laminate, in an effort, to dilute the solution. The water can increase the fluid pressure of the cell by 50 atmospheres, which eventually distorts or bursts the laminate or gel-coat and can lead to a blistering of the surface. Damage can be very extensive requiring major repair or the replacement of the structure (Figure 2.3).



Figure 2.3 Osmotic blistering of a GFRP boat hull with inset showing laminate breakdown
(Courtesy of Minton, Treharne and Davies Ltd)

Osmosis blistering is a very common problem that occurs in glass fibre-reinforced plastics (GFRP) laminated structures that have been immersed for long periods in aqueous solutions and is often observed in GFRP boats, water tanks and swimming pools. A resin rich layer (e.g. gel coat) is often applied to the composite surface where the material is to be exposed for long periods to aqueous solutions. This protective layer acts as a barrier to moisture ingress, thereby protecting glass fibres from moisture degradation. Although the gel coat protects the underlying composite substrate by slowing water ingress, it is not an impermeable layer. Other protective measures against natural weathering include marine paint and polyurethane coatings, which also shield the composite substrate from UV damage and weathering erosion.

Osmotic effects are amplified in the presence of hydrostatic pressure as experienced in sub-sea environments (e.g. submersibles). Simulations of sub-sea conditions have shown that increasing the hydrostatic pressure results in faster diffusion rates. Entrapped air/gas/moisture vapour under pressure expands as the structure is raised from depths (as external pressure decreases), analogous to the effect of the bends experienced by divers. As a result, cracking and delaminations may occur, thus compromising structural integrity. Porous materials can be expected to be far more prone to this effect than well-compacted materials. An increase in porosity results in an increase in both the rate of diffusion (diffusivity) and the level of absorbed moisture at saturation. Other issues to consider in sub-sea applications are the chemical composition and properties of seawater, pressure and depth effects, temperature, salinity, dissolved oxygen content, pH level, oceanic currents and biological attack.

Freeze and freeze-thaw exposure are also of concern to engineers and designers of composite structures, particularly in the presence of moisture. Published information on the effect of freeze-thaw on FRPs is very limited; however, the effects of low-temperature thermal cycling are reasonably well understood. At low temperatures, the presence of residual stresses resulting from a combination of resin shrinkage and differential thermal contraction between reinforcement and resin matrix can result in the formation of micro-cracks in the matrix and fibre-matrix interface. The degree of microstructural damage, whose presence adversely affects laminate stiffness and strength properties, dimensional stability and fatigue resistance, is directly related to the extent of resin shrinkage during cure. Residual stresses increase as the temperature is decreased. Laminates containing significant amounts of moisture will experience severe stresses if the laminate becomes frozen due to the expansion of water when it freezes. This expansion can generate significant pressures in a laminate contributing to the initiation and growth of micro-cracks and delaminations. The resultant damage is associated with free moisture (ice particles) present within voids (cavities) and cracks rather than matrix swelling induced through moisture absorption. The severity of damage and subsequent deterioration of laminate properties increases with thermal cycling. An increase in damage also lowers the composite's resistance to further moisture ingress.

Fibre degradation is primarily an issue for glass fibres and aramid fibres, with carbon fibres being stable in most environments (NB. Carbon fibres are relatively insensitive to moisture, and hence the variability in the tensile breaking stress and strain for carbon fibre tows is noticeably lower than for E-glass fibre and aramid fibre tows). Exposure to humid air (including environmentally controlled laboratories at standard conditions, i.e. 23°C and 50% relative humidity (RH)) will compromise the load-bearing capacity of the fibres, resulting in a loss of strength and an increase in strength variability [8]. For example, the tensile strength of freshly drawn E-glass fibres is typically 3.5 GPa, however exposure to atmospheric moisture can lead to a reduction in strength (tensile strength is typically 2.0 GPa, or less). The loss of tensile strength of E-glass fibres is dependent on exposure time, temperature and degree of humidity. On initial exposure to a humid/water environment, the rate of fibre degradation is relatively rapid, even in benign environments, such as air-conditioned laboratories. The tensile strength is reduced to 3.0 GPa after 3 weeks exposure to standard laboratory conditions. Immersion in water at ambient temperature for the same period results in a 20% reduction (~2.5 GPa). The original tensile strength can be fully realised, provided the fibres are carefully handled during fabrication to avoid surface damage and are stored in a dry environment. An intrinsic tensile strength of 2.0 GPa is often assumed for design purposes. The effect of moisture on aramid fibre-reinforced epoxy laminates is potentially greater than other composite systems.

Degradation of E-glass fibres in water can be mainly attributed to leaching of alkali oxides (sodium and potassium oxide) from the fibre surface resulting in the formation of surface micro-cracks, which act as stress concentrators. The loss of strength can be expected to be permanent at all conditioning temperatures and exposure times. The water surrounding glass fibres evolves into an aggressive alkali solution as the alkali ions dissolve out of the glass, slowly decomposing the glass fibres. Increasing the alkali content of the glass tends to reduce environmental attack from water and alkali solutions. It is worth noting that deionised water is slightly more aggressive than either tap water or seawater. Drying of the composite will remove most of the skin of water adjacent to the fibre, but a small permanent layer with retained water will remain, and the mechanical properties of the fibre will be permanently degraded (for further details on chemical degradation see references [9,10]).

Aramid (e.g. Kevlar® 49) fibres tend to absorb moisture and degrade at room temperature with the rate of degradation accelerating as temperature is increased. Substantial hygrothermal strength losses have been observed with these materials, particularly under natural weathering conditions (i.e. combination of moisture and ultraviolet light).

2.3 WEATHERING

Weathering or more specifically photo-oxidation of polymers refers to the chemical and physical changes that occur when UV radiation is absorbed by a polymer. The UV radiation spectrum comprises wavelengths of between 290 and 400 nm, which corresponds to energies of between 415 and 300 kJ/mol. These energies are in the same range as the bond energies of many organic compounds. Geographical location, seasonal variations and time of day play a significant role in the length, intensity and wavelengths experienced. Equatorial latitudes are particularly hostile in terms of UV exposure, where due to the high solar angle the levels of UV radiation and temperature are higher and the range of wavelengths transmitted by the earth's atmosphere extends even lower (i.e. shorter wavelengths). At higher altitudes, a thinner atmosphere absorbs less UV radiation. The presence of water increases UV degradation, because the dissolved oxygen in water is more active in promoting photo-oxidation than oxygen in the air.

Chemical reactions are induced when specific functional groups absorb the UV radiation. Free radicals liberated in the process will trigger further reactions. The deleterious effect will be dependent on the chemical nature of the material, environmental factors such as temperature and humidity, and exposure time. Material changes include discoloration (yellowing and bleaching), embrittlement, and loss of mechanical and physical properties. Photo-oxidative sensitivity also tends to increase with prolonged exposure to pollutants, such as nitrogen dioxide [3, 10, 12].

Geographical location, seasonal variations and time of day play a significant role in the length, intensity and wavelengths experienced. Equatorial latitudes are particularly hostile in terms of UV exposure, where due to the high solar angle the levels of UV radiation and temperature are higher and the range of wavelengths transmitted by the earth's atmosphere extends even lower (i.e. shorter wavelengths). At higher altitudes, a thinner atmosphere absorbs less UV radiation. The presence of water increases UV degradation, because the dissolved oxygen in water is more active in promoting photo-oxidation than oxygen in the air.

Photo-degradation is initiated by solar radiation, which results in the absorption of UV radiation by chromophores and in the activation of excited states in macromolecules. When a polymer is exposed to solar radiation the energy absorbed by the polymer results in the formation of free radicals within the polymer by the dissociation of the C-H bonds in the polymer chains. The extent of this chemical reaction depends on the radiation exposure that is the quantity of ultraviolet light (<350 nm) to which it is exposed. Once free radicals have been produced, reaction with oxygen generates hydroperoxides (POOH) [13]. These hydroperoxides can dissociate further to produce a series of decomposition products including aldehydes and ketones. The presence of these carbonyl groups in a degraded polymer can be used as a chemical index for degradation. Once formed these free radicals can continue to react via propagation reactions long after the initial UV exposure has ended.

The formation and propagation of free radicals on its own does not seriously affect the mechanical properties of the polymer, as free radicals do not significantly alter the long-chain nature of the polymer molecules. Degradation of the mechanical properties occurs because the free radicals produced are highly unstable and readily undergo chain scission reactions. This results in the formation of two smaller polymer chains, one of which is a free radical and capable of further reactions [13].

The intensity of the UV radiation decreases with increasing depth in the material, so that the reaction tends to be a near surface process. Shorter wavelengths have a far more deleterious effect on material properties than longer wavelengths. Longer wavelengths will penetrate deeper into the material, but are not easily absorbed, whereas the total energy of shorter wavelengths tends to be absorbed within a few micrometers of the surface.

Since oxygen is involved in the reaction process, there is an important balance between UV radiation and oxygen diffusion, and of course temperature since that will also determine the kinetics of reaction and the transport of reactive species. Under natural exposure conditions there will be wetting and drying cycles and dark periods. The significance of the latter is that some recovery of the oxygen concentration in the material can occur, which otherwise is confined to the very near surface due to consumption by reaction with the polymer radicals. Since the concentration of these radicals diminishes by termination reaction during the dark period, oxygen ingress can extend to greater depth.

UV radiation is known to degrade polymeric materials (including aramid fibres), although only the outer layer tends to be affected. Glass and carbon fibres tend to be unaffected by UV radiation. Epoxy resins are slightly sensitive to ultraviolet radiation; depending on the chemical formulation. Signs of photo-degradation include embrittlement (surface cracking), discolouration and loss of transparency [7]. Infrared radiation (800 nm to 1000 nm) does not contribute directly to photochemical degradation, however surface heating due to the absorption of the visible infrared radiation has an indirect influence on ageing.

The effects of natural weathering on structural FRPs tends to be confined to the surface (mainly cosmetic) and seldom poses a serious threat to structural integrity. The use of a protective coating (paint or gel coat) is often employed to combat the effects of weathering. UV resistance of the resin can also be improved by including additives, such as antioxidants, thermal and UV stabilizers, and pigments. Antioxidants slow down the process of oxidative degradation, prolonging the life of the product. Thermal stabilizers are added to protect the adhesive system from chemical breakdown caused by heat and UV radiation, whilst UV stabilizers protect against UV degradation and exposure to fluorescent light and filtered daylight. Pigments (e.g. carbon black, titanium dioxide, zinc oxide and barium sulphate) alter the absorption characteristics of the material acting as a screen against UV radiation when compounded with the adhesive. The costs of additives can often be prohibitive and may adversely alter mechanical performance. Carbon black is particularly effective in protecting against UV radiation and is inexpensive. It absorbs UV radiation and protects the polymer chains.

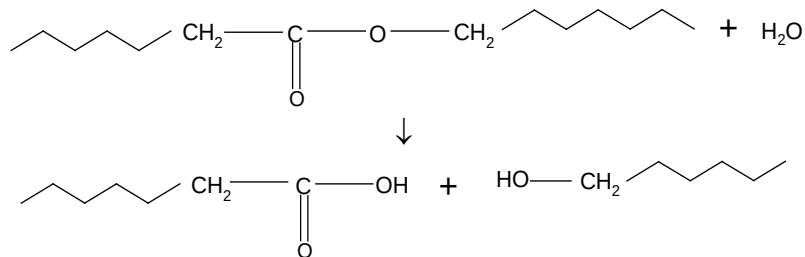
2.4 IONISING RADIATION

Ionising (i.e. high energy) radiation covers a wide range of different forms of radiation including x-rays, gamma rays, neutrons, alpha particles and beta particles. When a polymer is irradiated the ionising radiation induces degradation by the formation of free radicals or ions in the polymer. These reactive intermediates can initiate chemical reactions which occur by free radical or ionic mechanisms and which result in scission as well as in cross-linking reactions. Free radicals with a long lifetime can be present in the bulk of the material after irradiation and still cause changes in properties even a long time after exposure [14, 15]. The intensity of ionising radiation on the earth's surface is not normally high enough to significantly affect most plastics and FRPs. Radiation exposure tests are required for products for use in the nuclear industry and applications where radiation is used (e.g. medical X-rays and sterilisation).

2.5 CHEMICAL DEGRADATION

Chemical attack of thermoplastics involves specific chemical reaction of the polymer with the fluid with the most common mode of failure being hydrolysis by water, acids and alkalis [16]. Esters, amides, imides, and carbonate groups are particularly susceptible. Where these groups are located within the backbone chain rather than the side chain, chain scission ensues.

A general hydrolysis scheme can be summarised as follows:



The reduction in molecular weight consequent upon chain scission can lead to a reduction of toughness and fracture strain. Stress is known to accelerate the chain scission process and enhance the rate of fluid uptake.

Many thermoset resins are susceptible to oxidation by numerous oxidizing agents, from exposure to elevated temperatures (i.e. thermo-oxidation), hydrogen peroxide and bleaches (e.g. hypochlorite). It is often other constituents, such as fillers, catalysts, hardeners, pigments or fire retardants, rather than the resin or fibre reinforcement that are more reactive to these chemicals. Formulators and users, although usually aware of the potential durability problems associated with these additives, often overlook minor constituents such as catalysts, hardeners, pigments and processing aids.

Most of the commonly used resin systems employed by the composite industry are far more chemical resistant to strong acids, salt solutions and oxidative agents than stainless steel or aluminium alloys. However, exposure to secondary solvents, such as paint strippers, can lead to irreversible material damage. The effect of these highly destructive processes is often evidenced by a degraded surface appearance (i.e. discolouration, loss of surface reflectivity, increased surface roughness and exposure of underlying fibres). Composites used in the automotive and aerospace industry may encounter a wide range of chemicals including aircraft fuel, gasoline, oil, hydraulic, brake and transmission fluids, lubricants, coolants and de-icing and antifreeze compounds. Many of these are known to have adverse effects on composite performance through degradation of the polymer matrix, for example the combination of JP-4 jet fuel and water is more aggressive than the two agents acting alone. Synergistic effects are often observed between the various environmental factors resulting in amplification of the degradation process.

Alkali and Acidic Solutions: As with moisture effects, acid and alkali degradation processes are accelerated at elevated temperatures. Compared with other glass fibre types (e.g. R, ECR and C), E-glass is particularly vulnerable to attack from mineral acids (e.g. HCl and H₂SO₄) and alkalis (e.g. NaOH and KOH) [9, 10]. Dilute mineral acids are not only encountered in the chemical plant industry, but are also present in industrial and household effluent and sewage. When E-glass fibres encounter acids, ionic exchange occurs between the metallic cations (e.g. Na⁺ ions) at the glass surface and the hydrogen ions in the acid solution, resulting in leaching of sodium, potassium, calcium, magnesium, boron and aluminium from the outer layer or sheath of the fibre. Exposed fibres gradually lose weight, stiffness and strength with exposure time. Immersion in weak caustic solutions at room temperature can result in strength reductions of 30% within two weeks.

The resistance of glass fibres can be improved by modifying the chemical composition (e.g. using ECR-glass fibres for mineral acids, albeit at a high cost) or by chemical sizing (couplants, such as organosilanes) the fibre during fabrication so that there is a barrier coating, although this has limitations for some chemicals. ECR (acid corrosion resistant) glass is only slight more resistant to strong alkalis.

Other Chemical Agents: Several other degradation agents relating to in-service environmental conditions, handling and maintenance are known to have detrimental effects on the durability of polymeric materials. These are discussed below.

Solvents such as the paint stripper methylene chloride will soften and dissolve epoxy resins. Paint strippers combined with abrasion techniques can cause irreversible material damage. Aircraft, boats and bridges may need to be repainted repeatedly every 2-3 years during a service life, which can extend 20 to 50 years (or more). Hydraulic fluid has a similar effect to that of methylene chloride, but takes longer. Solvents such as methyl-ethyl-ketone (MEK) and acetone should not be left standing on polymer surfaces.

Aqueous Solutions: High modulus carbon fibres are affected by intercalation; chemical molecules (e.g. halogens and many inorganic salts such as ferric chloride) inserting themselves between the graphite layer planes. The result is to induce large changes in fibre dimensions.

Exposure to salt spray or salt water will degrade GFRP systems with the degree of protection depending on the permeability of the resin to diffusion of chloride ions and the ability of the matrix and interface to resist premature cracking, which would allow the environment to come in direct contact with the fibres resulting in corrosion of the reinforcement. Molecular chlorine present in aqueous solutions will cause a gradual reduction in laminate thickness and mechanical properties. The active form of chlorine in an aqueous solution depends on the pH of the solution. Figure 2.4 illustrates damage induced in GFRP pipes when exposed to molecular chlorine and hydrogen chloride.



Figure 2.4 Chlorine degradation (left) and HCl induced blistering (right) of a GFRP pipe
(Courtesy of AEA Technology)

Galvanic corrosion occurs when two different conductive materials of different galvanic potential are in contact in the presence of water (electrolyte). The more anodic material will corrode at an accelerated rate resulting in a build-up of corrosion product near the contact area. Galvanic corrosion can be a problem between carbon fibre-reinforced composite and metallic parts (aluminium alloys and steel), causing corrosion and progressive debonding in the case of honeycomb structures. The galvanic effect will be dependent on moisture content, temperature and electrical and chemical properties of the galvanic cell electrodes and electrolyte. Carbon fibre surfaces are electrochemically active supporting chemical reactions.

Stress Corrosion of Fibres: The process of environmental degradation of glass fibres is accelerated under mechanical loads with the long-term strength of GFRP laminates under hostile environments being controlled by stress corrosion of the fibre-reinforcement [9, 10]. In alkaline solutions, degradation is associated with progressive weakening of the glass fibres rather than a synergism between stress and the environment. This process also occurs when glass fibres are exposed to water vapour or immersed in water. A high alkaline concentration builds up at the tip of a crack, or flaw. Environmental stress cracking (ESC) of glass fibres occurs in acidic solutions with the rate of degradation dependent on pH level. The consequence is that GFRP laminates suffer delayed brittle fracture in acidic environments, under stress [11]. Delayed brittle failure through environmental stress corrosion cracking (ESCC) is known to occur in GFRP structures, such as filament wound pipes transporting oil and gas, and chemical storage vessels because of the combined effect of hostile chemicals and applied stress. The timescales involved inducing ESCC failure increases as the initial applied stress is reduced. ESCC is not limited to static loads; it equally applies to dynamic loading conditions.

Static fatigue or creep rupture, which refers to time-dependent failure of the material when subjected to constant load, is used as a measure for gauging the relative resistance of the material (i.e. fibre or composite) to chemical environments. The less resistant a fibre is to a specific chemical environment, the more rapid the drop in the rupture stress time curve. For a given applied load, the stress rupture time decreases with increasing humidity and temperature, or chemical concentration.

2.6 BIOLOGICAL DEGRADATION

Biological degradation is not a common form of degradation as most commonly used thermoplastics are resistant to microbiological attack. The only cases where biological attack has influenced life expectancy has been with certain polyurethanes and some low molecular weight additives in PVC. No predictive techniques for the life expectancy of conventional polymers due to biological degradation have been developed although there are standards for testing resistance. There is, however, growing interest in the development of deliberately short-lived polymers both for medical applications and for use as disposable packaging.

It is the chemical additives and pigments that are usually susceptible to microbial attack, which tends to occur on exposed surfaces due to oxidation of the additives. Polymers that have good water and weather resistance generally have greater resistance to microbial attack. Geographical location and seasonal effects are important because microorganism growth is more rapid in warm, humid climates than cold, dry climates. Microbial testing generally consists of exposing materials to an outdoor environment in geographical locations where weather conditions are favourable to microbial growth. The angle of exposure to sunlight and weather conditions will influence the extent and duration of microbial attack. An alternative approach (known as soil burial) is to bury specimens for set periods of time and then to exhume and examine the specimens for the effects of microbial attack.

There is little evidence to suggest adverse structural changes occur in composites through biological (marine organisms and bacteria) attack. Hard (animals with calcium carbonate shells) and soft (algae and animals with soft structures) marine organisms growing on the surfaces of GFRP marine vessels have minimal effect on material properties of the composite. Although, these animals may play a role in damage development by increasing load on the structure, altering the composite surface and reducing exchanges (moisture diffusion and leaching) between the composite and the surrounding medium. Removal of marine organisms from the surface of marine vessels is probably more hazardous to the composite than the biological action of the marine organisms.

Resistance to mould, fungi and bacteria can be improved by including antimicrobial additives (also known as fungicides or biocides), uniformly distributed throughout the polymer during the compounding process or alternatively by applying a suitable protective coating (gel coat and anti-fouling treatments in the case of marine vessels). Antimicrobials can provide protection against mould, mildew, fungi and bacterial growth, which can cause discoloration, embrittlement and sometimes failure.

2.7 ENVIRONMENTAL STRESS CRACKING (ESC)

ESC remains one of the most common causes of failure in polymers. The main reason for this is the complexity of the phenomenon, with aspects such as chemical compatibility, liquid diffusion, and craze formation and crack development all contributing. While crystalline (thermoplastic) and amorphous (thermosetting) polymers are both susceptible to ESC, thermosetting polymers are particularly susceptible due to the relatively open structure of amorphous polymers that leads to easy fluid penetration. Once the fluid has penetrated the polymer it becomes locally dissolved promoting cracking and crazing in the polymer. Cracking is normally preceded by the formation of crazes initiated at sites of stress concentration or in regions of local microstructure inhomogeneity. Exposure to moderate levels of applied stress for extended periods of time can induce crazing and cracking in polymers, and is the underlying cause of long-term transition from brittle behaviour for ductile polymers. This mechanism, known as creep (or stress) rupture is a common cause of polymer failure, and consequently has significant ramifications on the chemical resistance of FRPs. It is worth noting that rapid damage formation can occur within the polymer matrix in circumstances where environment exposure times are short, but the time under stress prior to exposure has been long.

Crazes are voids that are held together by highly drawn fibrils, which bridge the void allowing the craze to transmit stress and prevent the craze from propagating (Figure 2.5). The mechanism of crazing in chemical environments is generally considered to be identical to that in air [17-19]. In general terms, craze initiation is considered to evolve from micro-deformation processes in localised regions about 30 nm in diameter (see Figure 2.5) [20]. As the deformation region develops, further localised deformation is induced. The growth and coalescence of such deformed nuclei create a narrow plastic zone. In the presence of dilatational stress, voids develop. The voided structure is considered the precursor of the fibrillated craze structure that ultimately leads to failure [21].

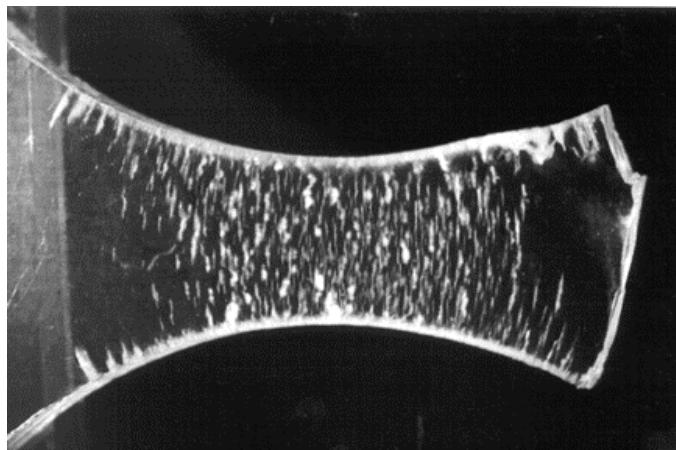


Figure 2.5 Crazing of PMMA

The environment accelerates the craze formation process by local plasticisation (i.e. enhancement of the local relative movement of molecular chains by reduced intermolecular interaction between chains [18, 19]). However, the specific phase of craze precursor development during which acceleration by the environment occurs, and the dependence of this on polymer type, is less clear. It has been proposed [19] that the role of the environment is to determine when the voided precursors break down to form crazes and it has also been suggested that the environment is important in void stabilisation through surface energy reduction.

Stress concentration can be important not only for the development of local deformation zones (although this is not necessarily dependent on stress concentration), but also for concentrating absorbed molecules in response to the presence of dilatational stress. The rapid growth of the craze precursor to a visible craze is thought to occur at a critical level of the inelastic strain, which is independent of the environment and temperature [19, 22, 23]. This has significant implications for assessing the durability of a polymer. For example, in polymer-fluid combinations that lead to plasticisation-induced toughening, simultaneous exposure may delay the development of crazes. However, exposure to the fluid after the sample has been stressed in air to attain the critical level of inelastic strain may lead to rapid crazing. It helps explain the very rapid development and growth of crazes in many cases when environment exposure times are relatively short but the time under stress has been long.

3 ACCELERATED AGEING TEST METHODS

The following section gives an overview of the standard test methods available for conducting accelerated testing of polymers and composites in hostile environments. Comprehensive lists of the ISO and ASTM standards for the accelerated ageing of plastics, rubbers, composites and adhesives are given in Appendices 1 and 2.

3.1 THERMAL STABILITY TEST METHODS

A standard procedure for assessing the thermal stability of polymers using the Arrhenius expression is given in ISO 2578 [24]. The procedure enables the user to define the highest temperature to which a plastic can be subjected for a chosen length of time before a particular property will have degraded unacceptably. The property of the polymer and the level at which it is considered unacceptable will depend on the particular application. The significance of this standard is that it is the only one to specify the Arrhenius method or any other procedure for making long-term prediction from multi-point polymer ageing data. ISO 176 [25] and ASTM D1203 [26] cover the stability of plasticisers in polymers, both standards measuring the amount of plasticiser that is lost due to absorption on activated charcoal. These test methods are both essentially simple quality control tests.

3.2 LIQUID ABSORPTION TEST METHODS

ISO 175 [27] and ASTM D543 [28] cover the absorption of chemical liquids into polymers and ISO 62 [29] and ASTM D570 [30] the absorption of water. In each of these tests standard sized samples are weighed and then immersed at constant temperature in the test liquid. After an agreed time-period, the samples are removed from the medium and surface liquid wiped off using a dry cloth before weighing. Samples can then be returned to the medium for continuing exposure provided that the time out of the medium is minimised. The balance used should have a resolution of 0.1 mg or better, which can be relaxed to 1 mg if water absorption is greater than 1 %. The increase in mass divided by the initial mass, measured at regular time intervals, is plotted against time in order to define the absorption curve. Results can be reported either as the mass gain after a specific period of immersion or as the mass at saturation defined as the weight gain from three successive measurements that differ in value by less than 1% of the overall weight gain.

3.3 WEATHERING TEST METHODS

3.3.1 Natural Exposure

As the ultimate aim of accelerated ageing is to improve lifetime prediction under service conditions, the most appropriate conditions are those that match the service environment exactly. These are most easily obtained by naturally exposing specimens at outdoor exposure sites. The problem with this is that the exposure period required would have to be at least as long as the life-expectance of the product. Natural weathering is therefore normally accelerated by exposure to climatic conditions that are more severe than those that are expected in service. For this purpose, there are several established test sites in Saudi Arabia, Australia and the southern states of the USA [31]. Arizona is popular for exposure in hot dry climates and Florida for hot humid climates. Acceleration can also be achieved by using Fresnel mirrors [31] that concentrate the sunlight directed on to the specimen.

Standard test procedures for the weathering of polymers in natural daylight, glass-filtered daylight and concentrated sunlight using Fresnel mirrors are given in ISO 877 [32], ASTM D1435 [33], ASTM D4364-02 [34] and ASTM G24-05 [35].

3.3.2 Artificial Exposure

Artificial weathering involves exposing test specimens to an artificial light source in a cabinet in which the temperature, humidity and water spray are controlled. The advantage of artificial weathering is that it is easier to accelerate the testing as all the exposure conditions are controlled. The problem with this approach is to know how these different parameters interact in the weathering process.

The key parameter in all accelerated weathering apparatus is the light source, which should ideally simulate solar radiation. The main types of artificial light sources that are used are: carbon-arc, xenon-arc and fluorescent tube [36].

3.3.2.1 Carbon-Arc

Until the 1960's, the only light source available with sufficient radiation levels were carbon-arc lamps. A typical spectrum from a carbon-arc consists of a series of line emissions that are superimposed on to a continuous background (Figure 3.1). The spectrum is not a good match for the solar radiation, particularly at the lower wavelengths (<350nm). These high energy, short wavelengths lead to such intensive damage that it bears little relationship to any natural weathering process. Despite these deficiencies, carbon-arc lamps are still in commercial use today and their use for plastics is standardised in ISO 4892: Part 4 [37] and ASTM D1499-99 [38].

3.3.2.2 Xenon Lamps

Xenon-arc lamps give a much better spectral simulation to natural sunlight (Figure 3.2) than other light sources, but are considerably more expensive to purchase and maintain. The xenon-arc spectrum contains ultraviolet wavelengths shorter than those found in solar radiation, but filters can easily remove these. Xenon lamps also emit high levels of infrared radiation, which must also be removed to prevent overheating of the specimen. Typical xenon exposure equipment such as the Xenon 1200 described by Davis and Sims [31] includes water spray, light/dark cycling and humidity control. Xenon lamps are now considered to be the preferred source where the total solar spectrum is required. Test procedures for the use of xenon lamps have been standardised in ISO 4892: part 2 [39] and ASTM D2565-99 [40].

3.3.2.3 Fluorescent Tube Lamps

Fluorescent tubes are a considerably cheaper alternative to xenon-arc lamps, capable of simulating the solar spectra in the critical ultraviolet region of the spectra (Figure 3.3). The radiation from a fluorescent lamp is produced by re-emitting the long wavelength spectra from a low-pressure mercury vapour source. This is achieved by a phosphor coating on the inner surface of the bulbs. The spectral distribution of the light radiated by the tubes can vary depending on the type of tube used. For rapid acceleration of the tests UV-B tubes can be used. These have a strong UV peak at around 313 nm, which as a consequence accelerates the degradation process. However, they also transmit intense radiation below 270 nm, which are not found in solar radiation and can lead to degradation not found in normal service. UV-A fluorescent lamps emit radiation at a much higher wavelength producing spectra that are closer to that of solar radiation in the UV region. UVA-340 lamps manufactured by Q-Panel have a UV spectrum (295-350 nm) that is particularly close to that of solar radiation and these are frequently used in weathering studies. Outside the UV region (>350 nm) these lamps do not emit substantial levels of radiation. As most of the degradation processes in polymers occur in the UV region this is not normally a problem. However, this characteristic does have implications for certain polymers. For example, substantial degradation occurs in nylon-6 at a wavelength of 365 nm that is not well represented by fluorescent tubes. Wypych [13, 36] gives numerous examples of other high wavelength degradation processes in his book. Standard test procedures for the use of fluorescent tube are given in ISO 4892 Part 3 [41] and ASTM D4329-99 [42].

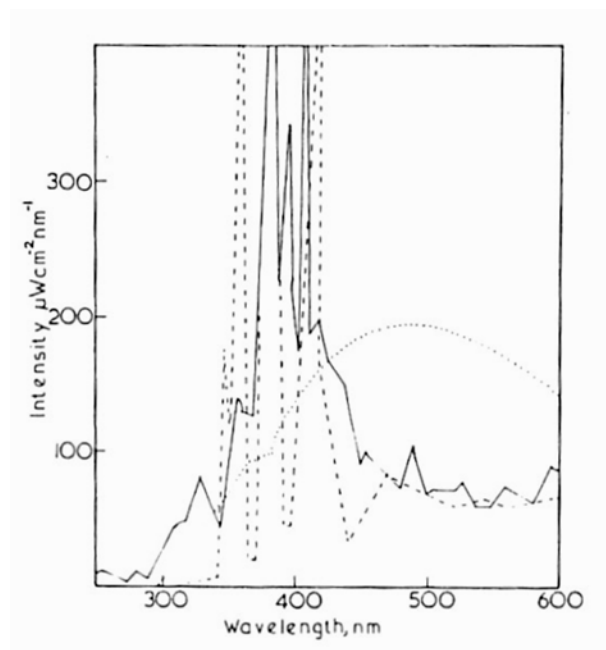


Figure 3.1 Spectrum of carbon-arc lamp (——), carbon-arc lamp with a Cordex D filter (-----) and noonday Chicago sunlight (.....) [36]

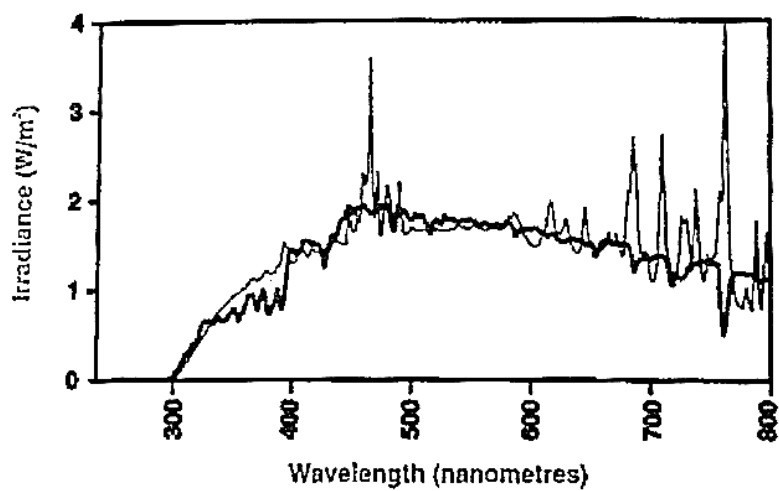


Figure 3.2 Spectrum of a xenon lamp (——) compared with noonday Miami sunlight (——) [36]

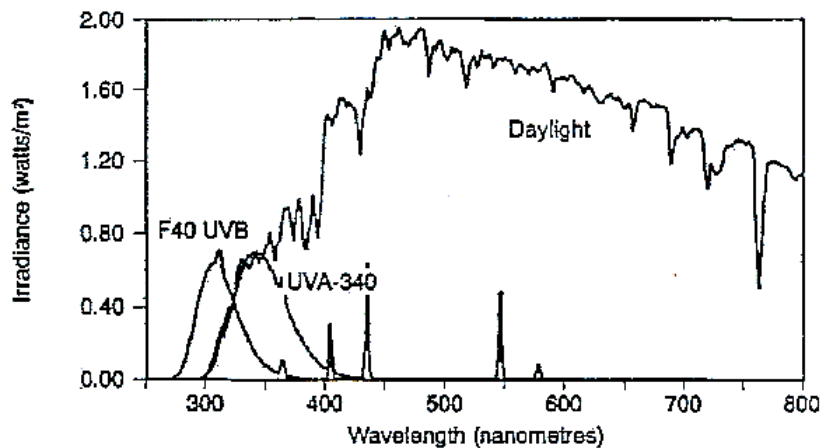


Figure 3.3 Spectra of UV-A and UV-B fluorescent lamps compared to noonday Miami sunlight [36]

3.4 IONISING RADIATION

The effect of ionising radiation on degradation of polymeric materials is most commonly accelerated by increasing the radiation dose using gamma radiation [43] from an isotope or electron beam accelerator. The dosage rate can also influence the rate of degradation in polymers so it is advisable to conduct tests at least at 2 different rates to assess the effect the dosage rate has on the degradation process. A further parameter that needs to be considered when accelerating the irradiation of polymers is the temperature as this will both increase the rate at which oxygen penetrates the specimens and the rate at which the degradation products diffuse through the specimen, both factors that influence the rate of degradation. The penetration depth of radiation particles is also limited so care needs to be taken when examining thicker sections.

3.5 CHEMICAL RESISTANCE TESTING OF GLASS REINFORCED POLYMERS

An important aspect for composites in many applications is that these materials are frequently used for their good corrosion resistance (e.g. boats, process equipment, sewage applications). Part 2 of BS EN 13121 [44] is solely devoted to the determination of chemical resistance as befits a standard on chemical process vessels and aims to provide a partial design factor, A_2 , that can be used in the design of a component to consider the chemical resistance of the material from which it is constructed. Table 3.1 of the standard gives the required thickness for different protective layers, which may be a single protective layer (SPL), a chemically resistant layer (CRL) or one of several thermoplastic linings (TPL).

In accordance with the main philosophy, the design factor A_2 is determined using one of several methods depending on circumstances. Five methods are given for determining the factor:

- i. through media lists
- ii. resin manufacturer's data
- iii. thermoplastic liner manufacturer's data
- iv. service experience
- v. testing in laboratory/in-situ

It is permissible to use the lowest value, if more than one method is used.

In more detail, the methods are:

1. The aggressive environments are divided into Cat 1, 2 and 3 media. There are comprehensive instructions depending on service temperatures, type of lining etc.
2. For materials with a deflection temperature under load (DTUL) 20°C greater than the service temperature, cured according to the manufacturer's instructions, which can be determined using ISO75, partial factors vary between 1.1 and 1.4, and 1.1 and 1.8, for post cured and non-post cured material, respectively, based on the manufacturer's recommendations.
3. Similar approach for thermoplastic liners when used.
4. For service experience greater than 3 years, the same factor may be used, whereas if it has been inspected after this period and found to be satisfactory a reduction not exceeding 0.1 can be made in the design factor. The same factor can be applied for service experience between 6 months and 3 years if internal inspection is satisfactory.
5. Experimental testing is undertaken using the single-sided exposure arrangement shown in Figure 3.4, where one test plate is in the vapour phase and one in the fluid phase. Assessment is based on a standardised ~ 3 mm laminate of fixed weight content made by a prescribed method. The tests are undertaken at the design service temperature for a range of exposure times, such as 1, 4, 8, 16 weeks. It is recommended that four exposure units be employed.

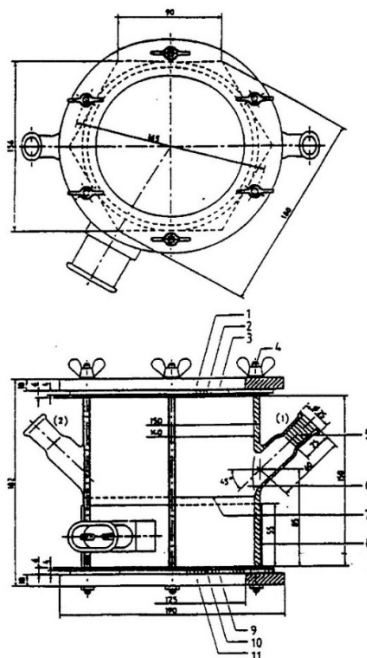


Figure 3.4 Chemical resistance test (n.b. flat plate specimens are numbered 2 and 10)

Degradation is assessed on a combination of appearance changes (10 assessment parameters e.g. gloss), dimensional stability (3 off) and flexural strength/modulus using BS EN ISO 14125 [45]. For each property, a scoring system is used including a weighting system that increases in order of the above text, with mechanical tests the most important to the final score (see Table 3.1). The flexural properties are plotted as a function of the exposure time and extrapolated to the 50% retention point. If this point is obtained before 10 years, then the material should be rejected for this application (e.g. temperature, concentration etc.). Otherwise, the score varies from zero to 10 based on the percentage loss after 10 years, from 0% to 50%, respectively. Depending on the total score for all aspects, as a percentage of the maximum that could be obtained for the parameters assessed, the partial factor A_2 is obtained from a chart within the range 1.1 to 1.4 (see table 3.2). The weighting factors are different for single-sided and full immersion. The test can be also be conducted by full immersion of 100 mm x 125 mm plates of the laminate or by testing in-situ within a tank.

Table 3.1 Criteria for chemical resistance

Criteria	Weighting factor for single sided exposure	Weighting factor for double sided exposure	Performance level
Appearance			
Colour	2	2	0-5
Gloss retention	3	23	0-5
Opacity	3	3	0-5
Tackiness	4	4	0-5
Fibre prominence	4	4	0-5
Loss of surface resin	5	5	0-5
Blister formation	5	5	0-5
Crazing	5	5	0-5
Crack formation	5	5	0-5
Delamination	5	5	0-5
Dimensional stability			
Swelling	8	4	0-5
Weight change	10	5	0-5
Barcol hardness	5	5	0-5
Mechanical property retention			
Flexural strength	20	10	0-10
Flexural modulus	20	10	0-10

Table 3.2 Determination of partial design factor, A₂

% of total assessment score	A ₂
≤ 20	1.1
≤ 30	1.2
≤ 40	1.3
≤ 50	1.4
>50	Unsuitable for purpose

3.6 BIOLOGICAL DEGRADATION

Biological attack of polymers is extremely difficult to accelerate to any great extent as it depends on simulating the activities of living organisms. A standard procedure for assessing the resistance of plastics to bacterial and fungi attack is described in ISO 846 [46]. This laboratory procedure essentially involves exposing the specimens to specific bacteria and controlling the environmental conditions to accelerate biological attack of the specimens. The level of biological activity in the test is assessed by comparing the biological degradation of the polymer to that of a cotton strip.

3.7 ENVIRONMENTAL STRESS CRACKING TEST METHODS

3.7.1 Introduction

The evaluation of ESC resistance is covered by several national and international standards [47]. These test methods can be divided roughly into two groups those that are based on an applied deformation and those based on applied load. The main international standards for testing ESC resistance are:

Constant deformation tests

- Bent strip [48]
- Bent strip test for flexible materials [49]
- Ball and pin impression [50, 51]
- Constant tensile deformation [52]
- Slow strain rate testing [53]

Constant load tests

- Constant tensile stress [54]
- C-ring tests [55]

The following section gives a brief overview of the ESC test methods that have been standardised. More detailed information about these and other non-standard test methods can be obtained from a technical review on ESC test methods produced by Turnbull and Maxwell [47].

3.7.2 Bent Strip Tests

The bent strip test (ISO 4599) [48] involves clamping the test specimen to a semi-circular former to apply a known strain to the specimen. The radius of curvature of former can be varied to induce different levels of strain in the specimen. This strain may be calculated using the following equation:

$$\varepsilon(\%) = \frac{d}{2r + d} \times 100 \quad (3.1)$$

where d is the thickness of the specimen and r is the radius of the former.

Once the specimen has been strained it is brought quickly into contact with the chemical environment. After an agreed time, the specimens are removed from the apparatus and either visually inspected for crazing or mechanically tested to assess their residual strength.

This test is most commonly used for assessing the ESC susceptibility of amorphous polymers. It is not suitable for semi-crystalline polymers, which are susceptible to rapid stress relaxation, as the stress applied to the specimen will decrease during the test.

3.7.3 Bent Strip for Flexible Materials

This test was developed by Bell laboratories in the USA and has since been standardised as ASTM D1693 [49]. The technique is suitable for flexible polymers such as polyethylene, but should only really be used for quality control purposes.

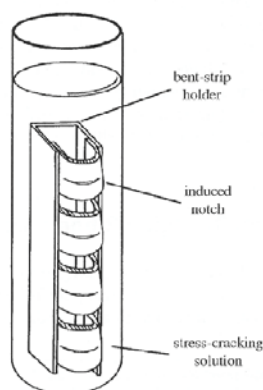


Figure 3.5 Bent strip technique for flexible polymers [49]

An illustration of the type of apparatus used in this test method is shown in Figure 3.5. The specimens used in this test are notched rectangular strips ($38 \times 13 \times 3$ mm) that are clamped in a jig so that the sample folds over on itself at an angle of 180° to produce stress within the specimen. Once loaded into the jig the specimens are immediately exposed to the chemical environment at the required test conditions. The specimens are then inspected visually at given time intervals and the time required for 50% of the specimens to fail is noted.

3.7.4 Ball and Pin Impression

The ball and pin impression test [50, 51] is used primarily for complex finished components. The method involves drilling a series of holes of a specific diameter into the polymer. A series of oversized balls or pins are inserted into the holes to induce a range of different stresses. One hour after the pins have been inserted the specimens are immersed in the environment for 20 hours. The specimens are then dried and visually examined for crazes. The smallest ball to cause visible crazing is used to determine the ESC resistance of the polymer.

3.7.5 Constant Tensile Deformation

The constant tensile deformation test is a relatively new test that is currently being developed as an ISO standard as ISO 22088 Part 5 [52]. The test method involves applying a constant deformation to the specimen and monitoring the stress relaxation that occurs while it is immersed in the chemical environment. The test is repeated using progressively smaller levels of deformation until the stress relaxation curves of consecutive tests superimpose on one another Figure 3.6. The applied stress required to produce this level of deformation is defined as the critical stress. The ESC resistance of the material is determined by comparing the critical stress obtained in the test environment to that obtained in air.

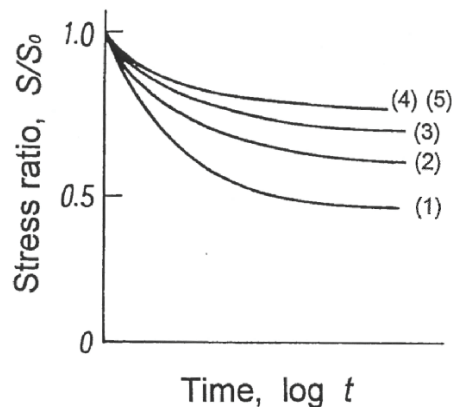


Figure 3.6 Stress relaxation curves obtained using progressively smaller levels of deformation (1>5) until consecutive curves superimpose on one another (4 and 5) [52]. Note: S_0 is the initial stress and S is the stress at time t

3.7.6 Slow Strain Rate Testing

The slow strain rate method has been used only comparatively recently for characterising the performance of plastics although it is well-established for metals and it has been now been developed into a standard [53] as ISO 22088 Part 6. The test method involves subjecting a specimen to a gradually increasing strain at a constant displacement rate whilst it is exposed to the chemical environment. The tests are conducted under uniaxial tension at low strain rates to enhance the influence of the environment on the specimen. Load and displacement are monitored continuously to enable stress-strain curves to be produced.

The development of crazes within the specimen causes the strain to be taken up locally at the crazes such that the stress required to deform the specimen is reduced compared to that in an inert environment. The onset of craze initiation can therefore be detected by the departure of the stress-strain curve in the chemical environment from that in air Figure 3.7. The main advantages of the slow stain rate test are that it is relatively rapid, requires few specimens and can be automated.

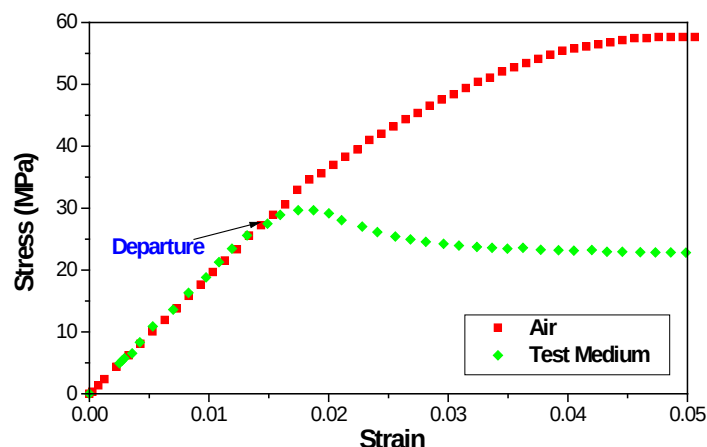


Figure 3.7 Typical stress-strain plot showing difference in stress/strain profile for material exposed in air and in the test medium [53]

3.7.7 Constant Tensile Stress Test

The distinctive feature of this test is that a constant load is applied to the specimens, thereby avoiding the problem of stress relaxation that is found in the constant strain test methods [54]. An illustration of the type of apparatus used in this test method is shown in Figure 3.8. The technique involves subjecting the specimen under investigation to a constant tensile stress at a stress below the tensile yield stress of the polymer. This is usually achieved using a dead weight that is suspended from one end of the specimen. The specimen is then immersed in the stress-cracking agent and inspected at regular intervals to establish the onset of crazing. The time required for crazes/cracks to appear after the specimen has been exposed, or the threshold stress below which no crazes appear in a specific time-period (typically 100 hours) can be used as a measure of the ESC resistance.

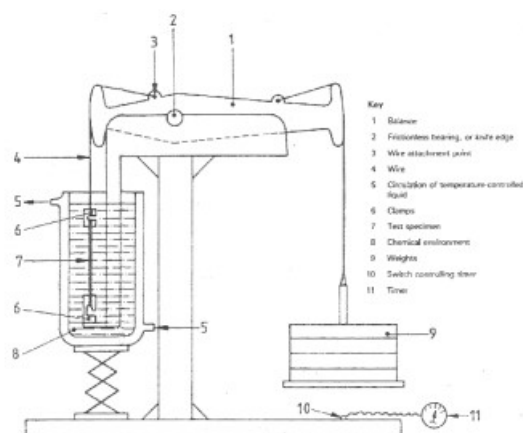


Figure 3.8 Illustration of typical apparatus used for a constant load test [54]

3.7.8 C-ring Tests

C-ring specimens are often used for the testing of tubing and pipe and have been standardised for the testing of polyethylene pipes in ASTM F-1248 [55]. Typical apparatus for testing C-ring specimens is shown in Figure 3.9. Circumferential stress is of principle interest and this stress varies around the circumference of the C-ring from zero at each bolthole to a maximum at the outer surface of the middle of the arc opposite the stressing bolt. C-rings can also be stressed in the reverse direction by spreading the ring and creating a tensile stress on the inside surface. An almost constant load can be developed on the C-ring specimen by placing a calibrated spring on the loading bolt.

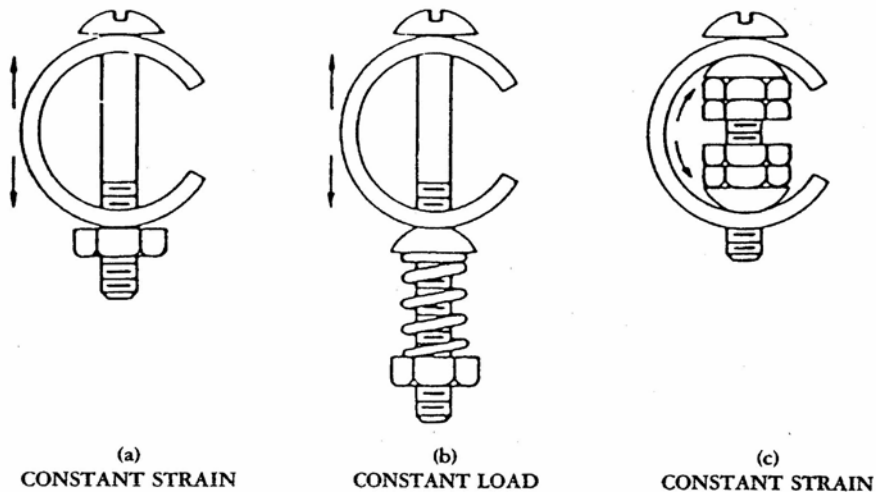


Figure 3.9 C-ring test methods for assess ESC in pipe-sections

4 LIFE PREDICTION

This section considers several non-mechanistic techniques that have been proposed to predict the residual strength and life expectancy of polymers and composites following exposure to combinations of heat, applied loads (static and fatigue) and moisture, or natural weathering.

4.1 THERMAL AGEING

One of the most common situations that a polymer is likely to experience in service is that of prolonged exposure to elevated temperatures. The Arrhenius equation is one of the best-known models for assessing the lifetime of polymers and is commonly used to predict the combined effects of temperature and time [3]. It is particularly useful for the accelerated testing of polymers as it allows short-term tests conducted at elevated temperatures to be used to assess long-term exposures at lower temperatures.

The Arrhenius relationship is:

$$K(T) = Ae^{-(E/RT)} \quad (4.1)$$

therefore

$$\ln t_{1/2} = C + \frac{D}{T} \quad (4.2)$$

where

$K(T)$ is the reaction rate for the process

E is the reaction energy

R is the gas constant

T is absolute temperature

C is a constant

A plot of $\ln K(T)$ against $1/T$ should yield a straight line with slope E/R , which can with caution be extrapolated.

An alternative way of using the Arrhenius equation is to consider $E/RT + C$ as a shift factor when a master curve can be built up from the material's response at different temperatures. This technique has the advantage that no particular measure of the reaction rate has to be chosen nor any form assumed for the change of parameter with time. Considerable care needs to be taken with extrapolation.

The Arrhenius relation is generally the first choice to apply to the effects of temperature, but no general rule can be given for the measure of reaction rate (change of parameter with time) to be used with it. Very frequently the time taken to a given % of the initial value is chosen.

When a form of the change in parameter with time is proposed, a power law is usually tried first:

$$f(X) = X^n \quad (4.3)$$

Combining these gives the Avrami equation:

$$X = X_o e^{-[At^n e^{(E_n/RT)}]} \quad (4.4)$$

There are occasions when the Arrhenius equation does not give a straight line and hence there is clear indication that predictions from it will not be valid. An alternative expression which has improved the linearity in certain cases is:

$$\ln K = \ln K_o + B(T_o - T)/10 \quad (4.5)$$

where K_o is the reaction rate at a reference temperature T_o .

4.2 TEMPERATURE-MOISTURE-STRESS SUPERPOSITION

The modelling of any degradation process requires information on the change in material properties with time, and the rate of change of those properties with the level of degrading agent(s). Several semi-empirical relationships (linear and logarithmic) for property degradation have been suggested [3, 16, 56, 57]. These are usually of the form:

$$P(t,T) = P(\infty,T) + [P(0,T) - P(\infty,T)] e^{-k(T)t^n} \quad (4.6)$$

where, k is the reaction rate (or degradation rate), P is the material property (e.g. strength or stiffness), T is the ageing temperature (in K), t is the ageing time and n is an experimentally determined constant. The strength decays exponentially with time to an asymptotic value (usually zero). This approach assumes only one time-dependent process is occurring when in fact there can be several processes occurring simultaneously.

An alternative approach is to plot material property data against time for one temperature-moisture level with the data represented by one of the following empirical relations:

$$\log P(t,T) = A(T) - B(T)t \quad (4.7)$$

$$P(t,T) = P(0,T) e^{[-k(T)t]} \Rightarrow P(\infty,T) = 0 \quad (4.8)$$

where B is the degradation rate and A is a constant.

Similar data are generated at different temperatures. The time required for the strength to degrade to a pre-determined or limit value (usually half its original value (half-life)) at each temperature is then calculated from the fitted equations. The next step involves plotting the limit value as a function of the reciprocal of the ageing temperature (i.e. $1/T$). The half-life $t_{1/2}$ is related to the ageing temperature T as follows:

$$\ln t_{1/2} = C + \frac{D}{T} \quad (4.9)$$

where C and D are material constants.

The half-life at service temperature can be estimated by extrapolation from the plot of $\log t_{1/2}$ versus $1/T$ (a straight line) or by fitting the data to Equation (4.9). It is important that the test temperatures are kept moderate ($<100^\circ\text{C}$) to ensure that chemical reactions (e.g. thermal oxidation) that occur at higher temperatures are avoided, and that the dominant mode of failure is identical at all temperatures and stress levels.

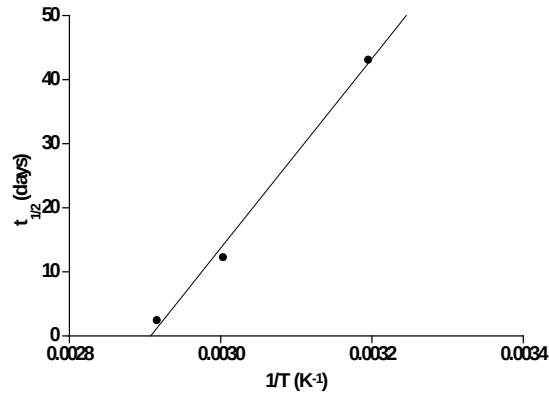


Figure 4.1 Tensile strength half-life versus temperature for E-glass/polyester

It is possible to relate the rate of strength of degradation with the rate of moisture uptake (i.e. diffusivity D), as shown in Figure 4.1. The diffusivity D is a function of absolute temperature T and is given by the Arrhenius relation:

$$D = D_0 e^{-E / RT} \quad (4.10)$$

D_0 is a constant, E is the activation energy of diffusion and R is the ideal gas constant.

The relationship between half-life $t_{1/2}$ and diffusivity D can be approximated by the following empirical relationship (see Figure 4.2):

$$\ln t_{1/2} = A - BD \quad (4.11)$$

where, constants A and B are derived from line of best fit.

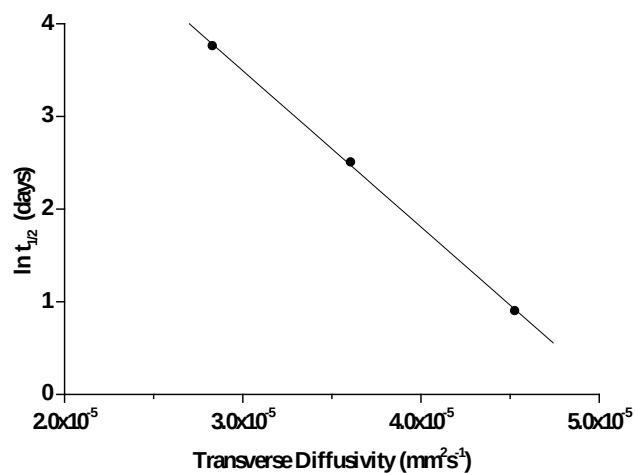


Figure 4.2 Tensile strength half-life versus diffusivity for E-glass/polyester

The above approach has been extended to determining the combined effect of temperature, moisture and stress with the failure time t_f given by [57]:

$$\log t_f = C - \log T + \frac{\Delta H}{2.303 RT} - b \frac{S}{T} \quad (4.12)$$

where, C and b are constants, T is absolute temperature, ΔH is the activation energy, R is the universal gas constant, T is the absolute temperature (in K) and S is the uniaxial stress. At constant temperatures, the $\log t_f$ versus S/T relation is a straight line.

Strength and stiffness property degradation due to the effects of hygrothermal ageing can be approximated using a simple algebraic relationship of the form [58]:

$$\frac{P}{P_o} = \left(\frac{T_{gw} - T}{T_{gd} - T_o} \right)^n \quad (4.13)$$

P denotes the material property (usually strength) at the test temperature T , P_o is the initial property (un-aged) value of the dry material at room or reference temperature T_o , and T_{gd} and T_{gw} are the glass transition temperatures of dry and conditioned (i.e. wet). The exponent n is a constant empirically derived from experimental data. The relationship will only provide a rational solution when $T_{gd} > T_o$ and $T_{gw} > T$.

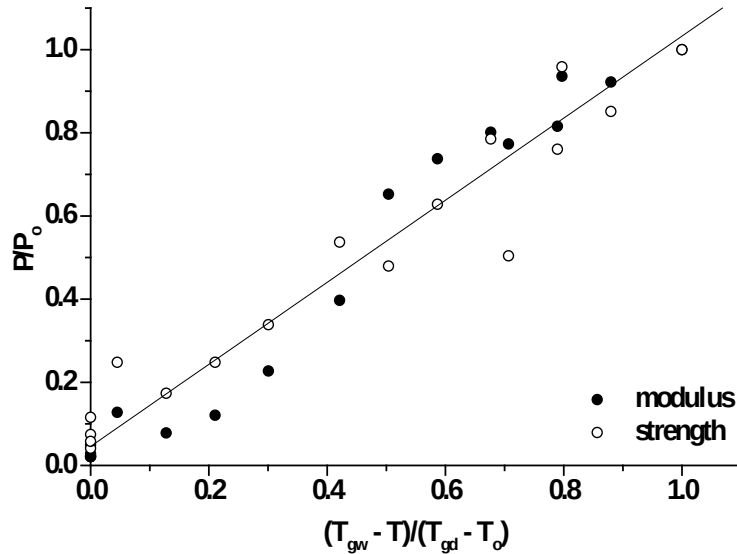


Figure 4.3 Transverse flexure properties of unidirectional E-glass/913

The good agreement between predicted and measured transverse flexure properties shown in Figure 4.3 is understandable as the power-law formula was originally intended for estimating hygrothermally-degraded properties of the resin matrix. Hence, the relationship can be expected to apply to matrix-dominated properties, such as transverse flexure and shear stiffness and strength, provided the integrity of the fibre-matrix interface is not compromised. Fibre dominated properties are less sensitive to changes in matrix properties, and hence there is poorer agreement between experimental data and estimates made using this approach and the value of the exponent n will differ for the stiffness and strength data.

The matrix and fibre strength and stiffness properties determined using Equation (4.13) when incorporated into micromechanics formulas (e.g. Halpin-Tsai equations) could potentially be used to derive ply stiffness and strength properties for laminate analysis. An increase in moisture content generally causes mechanical properties to decrease, although mechanical properties have been known to increase with moisture uptake [31]. In these cases, residual stresses that have been produced in the laminate during the curing process are relieved through moisture plasticisation of the resin matrix.

Equation (4.13) can be extended to include a component for cyclic fatigue as shown below [58]:

$$\frac{P}{P_o} = \left(\frac{T_{gw} - T}{T_{gd} - T_o} \right)^n - k \log N \quad (4.14)$$

where, k is obtained by curve-fitting experimental data and N is the number of cycles. The value of constant A will depend on the resin system, fibre type and orientation, and loading mode.

The wet glass transition temperature T_{gw} can be determined using the following quadratic relationship [58]:

$$T_{gw} = (AM^2 + BM + C)T_{gd} \quad (4.15)$$

where, M is the moisture content (wt %), and A , B and C are constants obtained by curve fitting experimental data.

For several materials (see Figure 3.4), T_{gw} and T_{gd} are related as follows [59]:

$$T_{gw} = T_{gd} - gM \quad (4.16)$$

where, g is temperature shift (in K) per unit moisture absorbed.

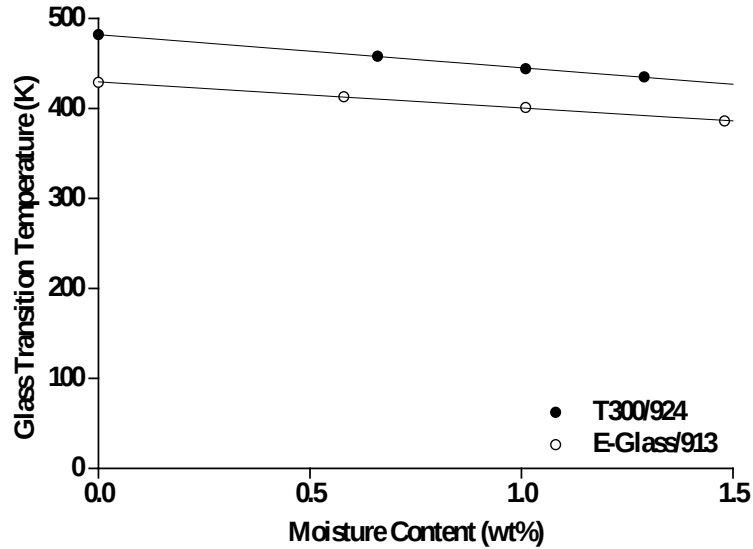


Figure 4.4 T_g versus M for hygrothermal aged unidirectional laminates

The plasticising effect (i.e. reduction of T_g) of absorption of a diluent, such as moisture, into a composite laminate can be described by [60]:

$$T_g = \frac{\alpha_m T_{gm} (1 - V_f) + \alpha_f V_f T_{gf}}{\alpha_m (1 - V_f) + \alpha_f V_f} \quad (4.17)$$

where T_{gm} and T_{gf} are the glass transition temperatures of the fibre and matrix respectively, α_m and α_f are the corresponding thermal expansion values, and V_f is the fibre volume fraction.

A model developed by Bowden and co-workers [61] to predict the yield behaviour of glassy polymers has been expanded and generalised by Kittagawa [62] to provide a relationship between shear yield stress τ_y and shear modulus G . This relationship is in the form of a power law given by [62]:

$$\frac{T_o \tau_y}{T \tau_{yo}} = \left(\frac{T_o G}{T G_o} \right)^n \quad (4.18)$$

where T_o is the reference temperature (in K), τ_{yo} and G_o are the shear yield stress and the shear modulus at reference temperature T_o (usually room temperature) respectively, and the exponent n is a constant.

The values of $\log (T_o \tau_y / T \tau_{yo})$ are plotted against those of $\log (T_o G / T G_o)$, such that the exponent n is the gradient of the linear regression fit through the log-log data. The Kittagawa power-law relationship is applicable to both shear and flexural properties of unidirectional carbon/epoxy and glass/epoxy composites [3, 63].

A number of factors may provide difficulties in interpretation of property-time measurements. These include:

- Strength may increase or decrease upon initial exposure to elevated temperatures. This may result from loss of volatiles, chemical cross-linking or relief of internal stresses.
- Long-term degradation rate may change during the ageing period. The ageing process may also change with temperature and exposure time.
- Statistical variability, which generally increases with exposure time, can introduce anomalous effects that make it difficult to differentiate the effects of key variables and to determine the ageing sequence. Rigorous statistical analysis is required to determine the precision (confidence limits) of the durability data.
- It is virtually impossible to duplicate service conditions using accelerated ageing procedures, particularly as realistic environments include large random variations in temperature and humidity.

4.3 WEATHERING

Weathering is of considerable complexity due to natural fluctuations in temperature, humidity, ultraviolet radiation and other environmental factors, and to the interaction of these factors, and is therefore impossible to simulate. Attempts have been made to determine the rate of degradation of a material property P due to the combined effect of temperature and sunlight in a similar manner to temperature-moisture superposition relations. Several empirical relations have been proposed [3, 12, 13, 16]:

Linear (without temperature effects)

$$P = P_o + bD \quad (4.19)$$

where P_o is the initial property value, D is the ultraviolet radiation dose and b is a constant.

Linear with temperature effects (i.e. Arrhenius relationship)

$$P = P_o + De^{(-\Delta H / RT)} \quad (4.20)$$

Power law (without temperature effects)

$$P = P_o + bD^n \quad (4.21)$$

where n is a constant.

Exponential (without temperature effects)

$$P = P_o + Ae^D \quad (4.22)$$

where A is a constant.

The above relations only apply to one set of conditions, and therefore extrapolating short-term data to long-term property prediction is not advised.

A further approach is to start with a relation of the form:

$$P = f(y_1 + y_2 + y_3, \dots + y_n) \quad (4.23)$$

where y_1 etc. represent the various factors or agents, which may cause degradation (e.g. dosage, intensity, temperature, humidity).

Regression analysis techniques can then be used to find the significant agents and produce a model for the specific data in question. This is essentially an empirical approach. Alternatively, a mathematical form for the data could be found using neural networks or curve fitting without giving consideration for the effect that individual agents have on the process. However, extrapolation of the data is then particularly dangerous.

Modelling

Recent work [64] conducted in the Accelerated Weathering Laboratory at NIST has attempted to combine high quality material testing data with multiscale predictive models to determine the life time of polymers. The data required for the models was obtained using their integrated weathering sphere that uses electrodeless microwave-energised mercury arc lamps to provide stable, intense, highly uniform UV irradiation. The lamp system avoids heating of the system enabling both the temperature and the relative humidity to be controlled independently allowing the underlying degradation mechanisms to be accurately modelled. This multiscale modelling approach has to-date been applied to thermoplastic and elastomeric but has not yet been applied to polymer composites. A similar approach using stochastic modelling is also being applied to composites by a consortium of UK universities led by Warwick University in the Duracomp Project [65, 66, 67, 68, 69]. They are developing a toolkit that combines experimental test data with advanced computational multiscale FEA techniques to assess the durability of composite materials in civil engineering applications.

4.4 IONISING RADIATION

The effects that ionising radiation have on the properties of plastics can be predicted using a time-temperature-dose rate superposition principle [70, 71, 72]. This model is based on the Arrhenius expression and allows plots of degradation versus time obtained at different temperatures to be displaced along the time axis and superimposed upon one another using the following expression for the shift factor a_T :

$$a_T = \exp \left[\frac{E_a (T_{ref}^{-1} - T^{-1})}{R} \right] \quad (4.24)$$

where T_{ref} and T are the reference and service temperatures respectively, E_a is the activation energy for the process and R is the gas constant.

Burnay [72] has shown that a similar shift factor can also be used for the dose rate. Three different methods for extrapolating from high dose rates to those more typically found in service are given in IEC 61244-2 [73].

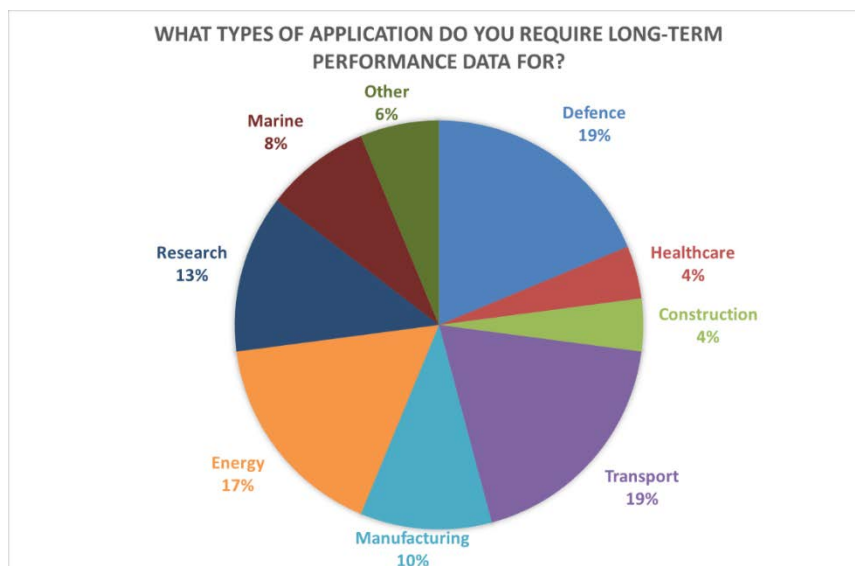
4.5 ENVIRONMENTAL STRESS CRACKING

Environmental stress cracking is essentially an acceleration of the stress cracking that will occur when sufficiently high stresses are applied to the polymer with or without the fluid environment present. The rate at which failure occurs can therefore be predicted using classical creep-rupture equations in which failure at high stresses and short times is extrapolated back to low stresses and long failure times. This is, however, rarely conducted as in most application the material will be considered to have failed as soon as a craze has initiated. The most common procedure is therefore to conduct ESC tests using a series of loads and to detect the threshold load below which crazing does not occur.

5 INDUSTRIAL SURVEY

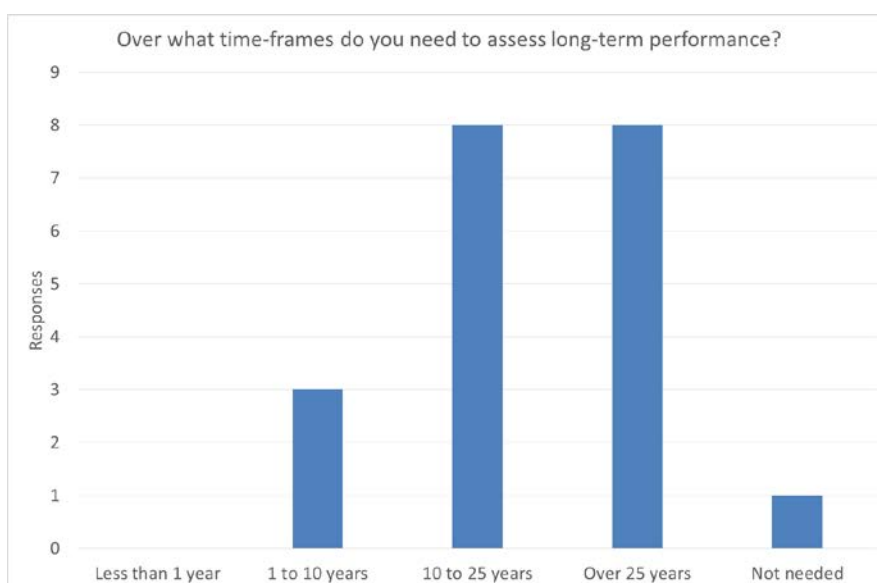
This section collates the responses that have been obtained from 23 UK companies that engaged in a survey held at the Composite, Adhesives and Polymer Industrial Advisory Group concerning their requirements for long-term performance testing.

5.1 APPLICATIONS



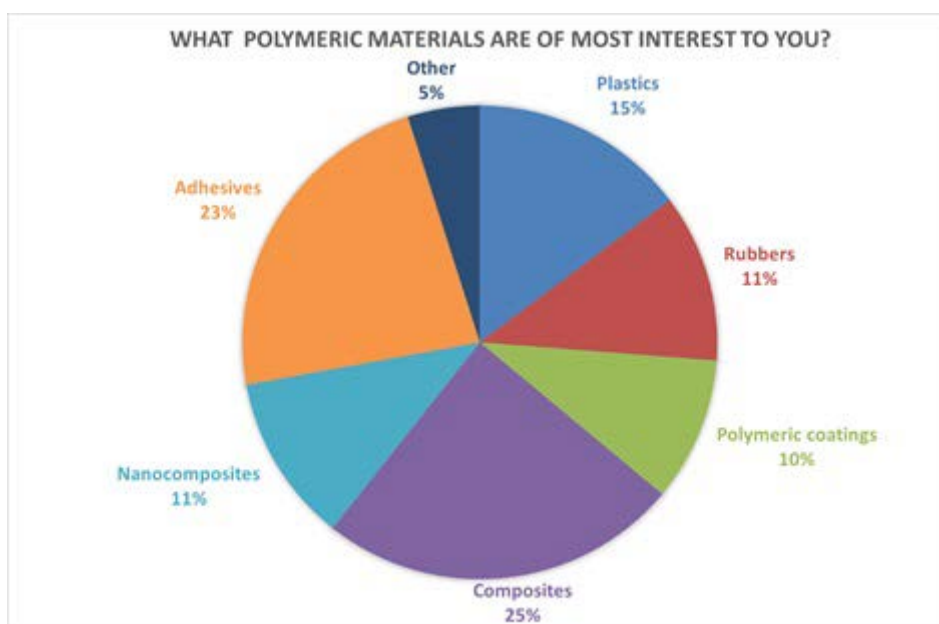
The main sectors requiring long-term performance data were found to be Defence, Transport and Energy. Many of the responses classified under manufacturing and research also came under these sectors. It is noticeable that there was limited interest from either healthcare or construction. In healthcare, this is probably due to the high level of regulation that is already present in this sector that mainly focuses on patient safety and toxicity. Detailed responses from the survey indicated that the three overarching requirements are for applications involving the long-term performance of composites, adhesives joints and elastomers.

5.2 TIME-SCALES



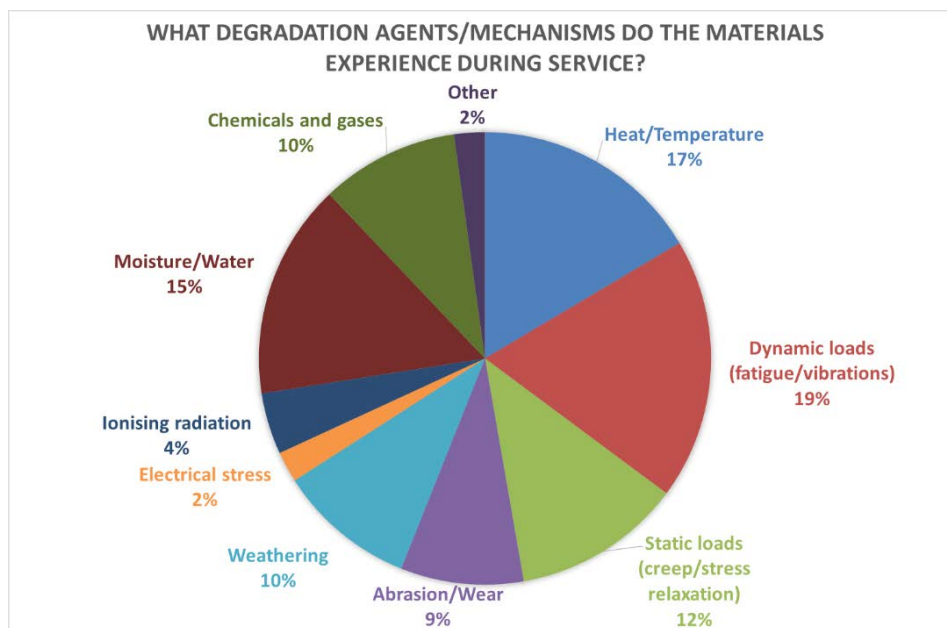
The timescale over which long-term performance of materials is required depends critically on the application of the product. As can be seen from the results most applications requiring long-term performance measurement need properties predicted to at least 10 years and almost half of responses required more than 25 years. The obvious conclusion that can be drawn from this is that it is not going to be possible to prove these products over their design lifetime before production and marketing begins, so some form of accelerated testing and prediction is going to be required. Furthermore, the level of extrapolation in many cases is going to have to be over many decades. The main reasons given for these time-scales are to reduce risk of failure in service and the associated financial, legal, and regulatory aspects (i.e. many civil engineering applications stipulate 60 years). Financial costs include not just the cost of replacing products, but recall costs, litigation, and the loss of reputation and trust.

5.3 MATERIALS



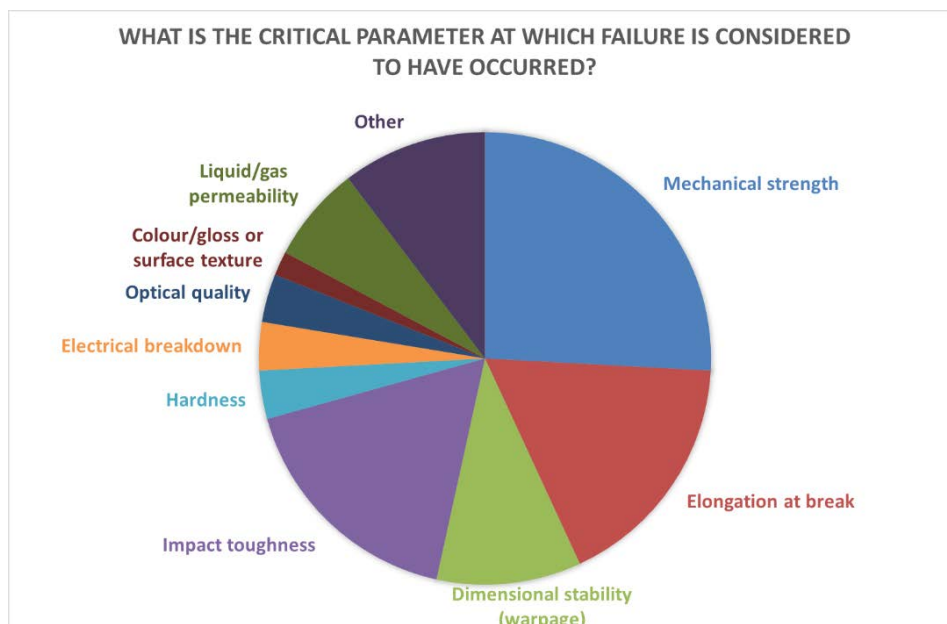
The two main areas of interest in terms of materials were adhesives and composites, where in both cases there is connectivity between the polymer and other materials used in the structure. Detailed examination of the survey results indicated that many of the composite materials are not conventional continuous fibre composites but involve the use of thermoplastics and elastomers. In addition, there is a growing interest in the long-term performance of nanocomposites. Two overarching themes that were identified were the interest in joining/bonding and sealing systems i.e. elastomeric seals.

5.4 DEGRADATION MECHANISMS



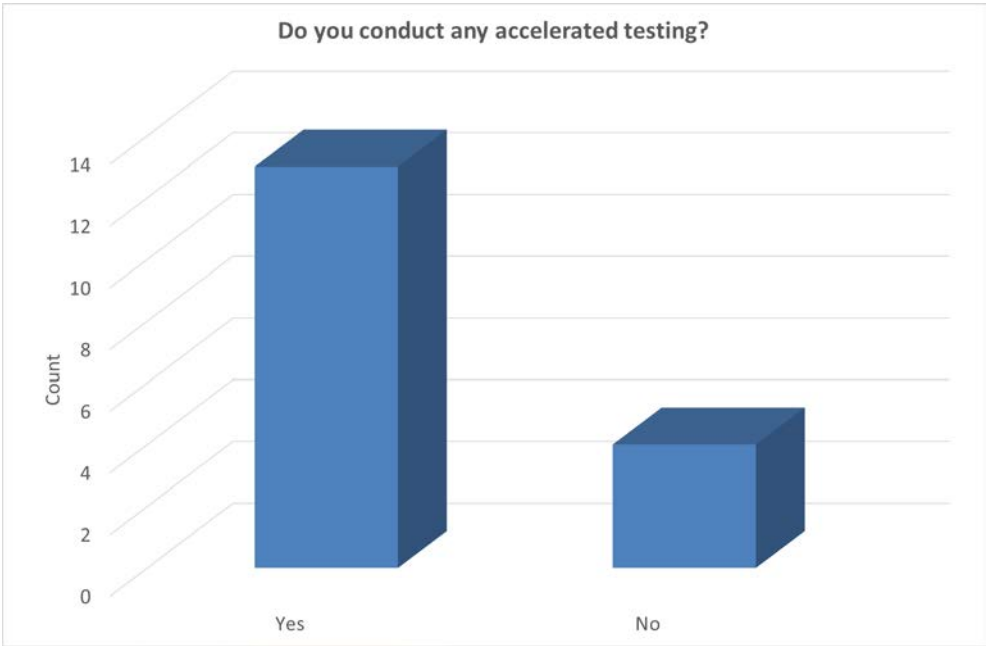
The main degradation mechanism that were identified for the causes of failure were stress (dynamic and static), temperature and moisture. Electrical stress and weathering were not identified as significant causes of concern possibly due to the considerable amount of research that has been conducted in these 2 areas by ERA, PTB and NIST. Specific areas of concern that have been identified by respondents include the effects of moisture and heat on the creep and rupture of adhesive bonds and delamination in composite structures.

5.5 FAILURE PARAMETERS



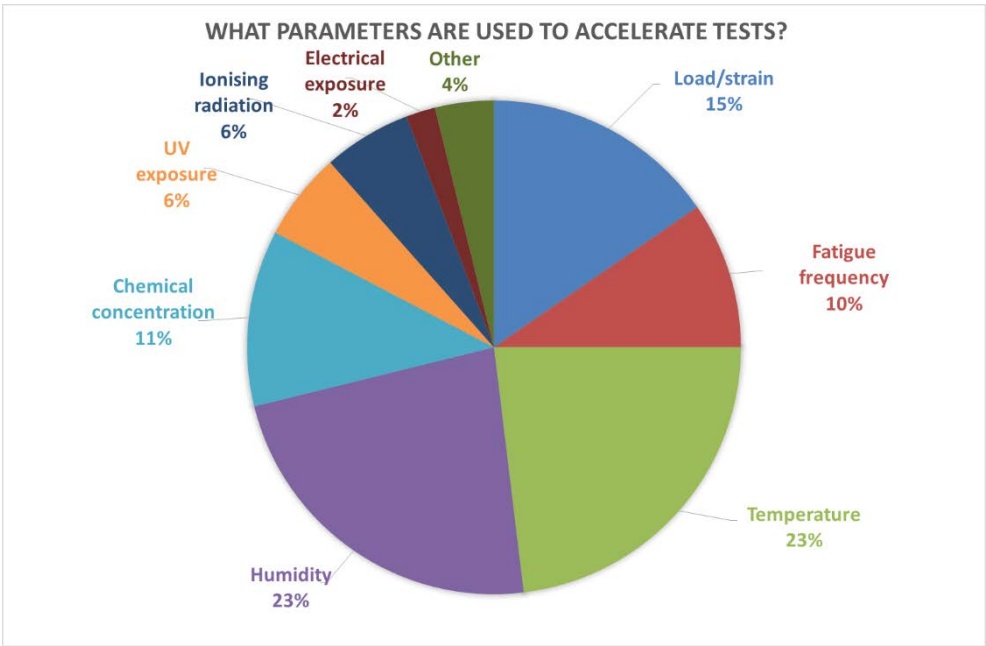
Critical to predicting the life-time of a product is to define the failure criteria, for example a material can be mechanically intact during its entire service life, but may have to be replaced due to loss of gloss if this is critical to its functioning. Identifying the appropriate failure mechanism is therefore essential to long-term testing. Clearly from the responses received mechanical and dimensional stability are critical for most applications. It should, however, be noted that in many case what causes failure was not unknown at the design stage and sometimes even after failure has occurred.

5.6 ACCELERATED TESTING



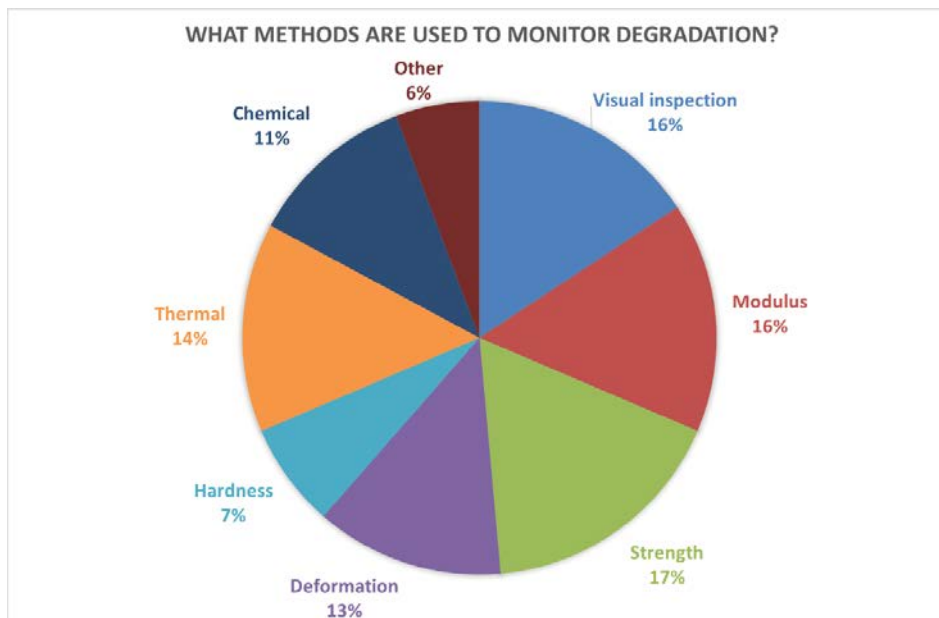
Three quarters of the respondents to the survey confirmed that they conducted accelerated testing and all respondents had an interest in accelerated tests for the prediction of long-term behaviour.

5.7 METHODS OF ACCELERATION



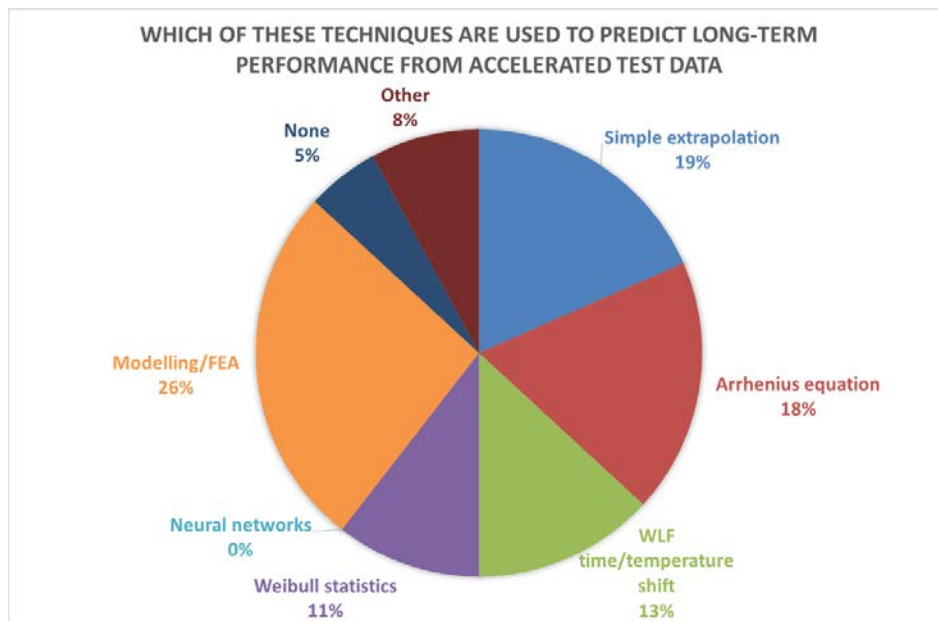
Loading under tension or compression as a function of moisture content and temperature were the most common forms of testing together with fatigue testing. The means of acceleration that were reported reflected the forms of testing being conducted with the most frequently used acceleration parameters reported being temperature and moisture followed by load and strain.

5.8 MONITORING TESTS



The most common monitoring techniques reported were mechanical however these were extremely varied including: Modulus tensile strength, compression modulus, compression set, stress relaxation, creep, tear strength, toughness and hardness. In addition to mechanical monitor there is also changes in dimensions, mass, solvent swell and glass transition. The wide range of monitor techniques is probably related to the wide range of different applications and hence possible failure modes involved in accelerated testing. However, a common issue that has been raised with monitoring is the difficulty of detecting degradation in the material as the tests proceed without interrupting the tests.

5.9 PREDICTION



Two thirds of the respondents in the survey reported that they used predictive techniques to extrapolate accelerated testing data to extended service-lives. Most noticeable from the responses is that the majority of responders use a wide range of different predictive techniques from simple extrapolation to FEA modelling. The main concern expressed is the lack of confidence users have in these methods and the concern that the accelerated tests may not relate to real life situations.

5.10 FUTURE WORK

What improvements in long-term performance testing would you like NPL to address in future research and how would you like it delivered?

The following list summarises the areas where respondents feel further developments are required.

- General accelerated ageing protocol to validate predictive methods including Arrhenius kinetics and time-temperature correlations.
- Multiphysics approaches to correlate physical ageing with permeation/diffusion through materials and its effect on mechanical properties.
- Atomistic modelling and micro scale damage growth models to predict macro scale failure.
- Standardisation of accelerated environmental ageing techniques including creep and fatigue.
- Sensors to monitor degradation during accelerated tests.
- Validity of applying ageing results from laboratory specimens to large scale components.
- Prediction of very long term in-plane properties for composites and adhesive joints.
- Long term performance methodology for assessing hybrid joints and complex structures.

The main deliverables that respondents are looking for are good practice guides and standardisation.

6 SUMMARY

A wide range of mechanisms for the degradation of polymers and composites have been identified; including thermal degradation, weathering, chemical attack, ionising radiation, biological degradation, and environmental stress cracking. Generally, there is a good scientific understanding of the mechanisms involved in these degradation processes, but this has not been formalised into procedures or standards. The only standard that describes how data can be extrapolated for long-term prediction is ISO 2578, which uses the Arrhenius equation to determine long-term thermal stability. Even in this standard the degree of extrapolation is modest, recommending that results are not extrapolated more

than a factor of four in terms of time. In addition, the wider impact of degradation would appear to be less well understood, in particular the influence that more than one mechanism may have on the overall degradation of the material.

Examination of standards revealed that most of the test methods for measuring the degradation of polymers examine a single degradation mechanism in isolation. However, this can be misleading. The one exception to this is the standard on the evaluation of chemical resistance in GPR composites, which uses de-rating factors to assess chemical resistance. The main concern with de-rating factors is that their validity in assessing the long-term performance of the material is not always apparent.

The industrial survey attracted a diverse range of companies demonstrating the need for reliable accelerated test methods for polymer-based materials. Although most correspondents used accelerated test methods very few of them considered that the test methods had been validated to their satisfaction. In particular, there is an absence of good quality comparison exercises of longer term laboratory tests and products recovered from service.

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APPENDIX 1 NPL PUBLICATIONS

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APPENDIX 2 STANDARDS

The following lists summarises the ISO and ASTM standards that exist for testing the long-term performance of polymers, rubbers, adhesives and composites. It should be noted that although many of the standards will describe means by which ageing maybe accelerated there are few references to how data can be used to predict life-expectancy, most of the tests only providing comparative performance between different materials. One exception, is ISO 2578 which describes the principles of how to apply the Arrhenius technique to plastics for examining the resistance of plastics to prolonged exposure to heat.

ISO standards**Plastics*****Thermal Degradation***

ISO 176	Determination of Loss of Plasticisers - Activated Carbon Method
ISO 177	Plastics - Determination of Migration of Plasticiser
ISO 291	Plastics - Standard Atmospheres for Conditioning and Testing.
ISO 305	Determination of Thermal Stability of Polyvinyl Chloride Related Chlorine Containing Polymers, and their Compounds - Discoloration Method
ISO 554	Standard Atmospheres for Conditioning and/or Testing - Specification.
ISO 1137	Plastics: Determination of Behaviour in a Ventilated Tubular Oven
ISO 1599	Cellulose Acetate- Determination of Viscosity
ISO 2578	Plastics: Determination of Time/Temperature Limits after Exposure to Prolonged Action of Heat
ISO 3671	Determination of Volatile Matter of Amino-plastics Moulding Materials
ISO 3205	Preferred Test Temperatures

Environmental Stress Cracking (ESC)

ISO 4599	Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Bent Strip Method
ISO 4600	Plastics - Determination of Environmental Stress Cracking (ESC) - Ball and Pin
ISO 6252	Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Constant Tensile Stress Method
ISO 22088	Plastics - Determination of Resistance to Environmental Stress Cracking (ESC)
ISO 16770	Plastics - Determination of Environmental Stress Cracking (ESC) of Polyethylene - Full-Notch Creep Test (FNCT)

Effect of Liquids

ISO 62	Plastics - Determination of Water Absorption
ISO 175	Plastics - Determining the Effect of Liquid Chemical Including Water
ISO 483	Plastics - Small Enclosures for Conditioning and Testing Using Aqueous Solutions to Maintain Relative Humidity at Constant Value.
ISO 4611	Plastics - Determination of the Effect of Exposure to Damp Heat, Water Spray and Salt

Weathering

ISO 877	Plastics - Determination of Resistance to Change upon Exposure under Glass to Daylight
ISO 2579	Plastics - Instrumental Evaluation of Colour Differences
ISO 3557	Plastics - Recommended Practice for Spectrophotometry and Calculation of Colour in CIE Systems
ISO 3558	Plastics - Assessment of the Colour of Near-White or Near-Colourless Materials
ISO 4582	Plastics - Determination of Changes in Colour and Variations in Properties and Exposure to Daylight under Glass, Natural Weathering of
ISO 4607	Plastics - Methods of Exposure to Natural Weathering
ISO 4892	Plastics - Methods of Exposure to Laboratory Light Sources
ISO 9370	Guide for the Instrumental Determination of Radiant Exposure in Weathering Tests
ISO TR 9673	Solar radiation and its measurements for determining outdoor weather exposure levels
ISO 11403-3	Environmental Influences on Properties

Biological Attack

ISO 846	Determination of Behaviour under the Action of Fungi and Bacteria - Evaluation by Visual Examination or Measurement of Change in Mass or Physical Properties
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Mechanical (Creep)

ISO 899	Plastics - Determination of Creep Behaviour
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Rubbers***Thermal Degradation***

ISO 188	Accelerated Ageing or Heat Resistance Tests
ISO 6914	Determination of Ageing Characteristics by Measurement of Stress at a Given Elongation

Effect of Liquids

ISO 1817	Determination of the Effect of Liquids
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Weathering

ISO 4665-1	Assessment of Change in Properties after Exposure to Natural Weathering or Artificial Light
ISO 4665-2	Methods of Exposure to Natural Weathering
ISO 4665-3	Methods of Exposure to Artificial Weathering

Effect of Ozone

ISO 1431-1	Resistance of Ozone Cracking - Static Strain Test
ISO 1431-2	Resistance to Ozone Cracking - Dynamic Strain Test
ISO 1431-3	Determination of Ozone Concentration

Biological Degradation

ISO 846	Determination of Behaviour under the Action of Fungi and Bacteria - Evaluation by Visual Examination or Measurement of Change in Mass or Physical Properties
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Mechanical (Stress Relaxation in Compression)

ISO 3384	Determination of Stress Relaxation in Compression at Normal and High Temperatures
ISO 6056	Determination of Compression Stress Relaxation (Rings)

Composites

ISO 75 Part 3	Plastics - Determination of Temperature of Deflection under Load. Part 3: High-strength thermosetting laminates and Long-Fibre-Reinforced plastics
BS EN 2378	Fibre reinforced plastics - Determination of Water Absorption by Immersion in Demineralised Water.
BS EN 2489	Fibre reinforced plastics - Determination of the Action of Liquid Chemicals.
BS EN 2823	Fibre reinforced plastics - Determination of the Effect of Exposure to Humid Atmosphere on Physical and Mechanical Characteristics.
ISO 13003	Fibre-Reinforced plastics - Determination of Fatigue Properties under Cyclic Loading Conditions

Adhesives

ISO 9142	Adhesives - Guide to the Selection of Standard Laboratory Ageing Conditions for Testing Bonded Joints
ISO 9664	Test Methods for Fatigue Properties of Structural Adhesives in Tensile Shear
ISO 10354	Adhesives - Characterisation of Durability of Structural Adhesive Assemblies - Wedge Rupture Test
ISO 10363	Hot Melt adhesives - Determination of Thermal Stability
ISO 14615	Adhesives - Durability of Structural Adhesive Joints - Exposure to Humidity and Temperature under Load

ASTM STANDARDS**Plastics*****Thermal Degradation***

D 1203	Standard Test Methods for Volatile Loss from Plastics Using Activated Carbon Methods
D 2115	Standard Practice for Oven Heat Stability of Poly (Vinyl Chloride) Compositions
D 3045	Standard Practice for Heat Aging of Plastics Without Load

Effect of Liquids

D 543	Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents
D 570	Standard Test Method for Water Absorption of Plastics
D 1712	Standard Practice for Resistance of Plastics to Sulfide Staining

Environmental Stress Cracking (ESC)

D 1693	Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics
F 1248	Standard Test Method for Determination of Environmental Stress Crack Resistance (ESCR) of Polyethylene Pipe

Weathering

D 1435	Standard Practice for Outdoor Weathering of Plastics
D 1499	Standard Practice Filtered Open-Flame Carbon-Arc Type Exposures of Plastics
D 2565	Standard Practice for Xenon Arc Exposure of Plastics Intended for Outdoor Applications
D 4329	Standard Practice for Fluorescent UV Exposure of Plastics
D 4364	Standard Practice for Performing Outdoor Accelerated Weathering Tests of Plastics Using Concentrated Sunlight
G 24	Standard Practice for Conducting Exposures to Daylight Filtered Through Glass
G 156	Standard Practice for Selecting and Characterizing Weathering Reference Materials Used to Monitor Consistency of Conditions in an Exposure Test
G 178	Standard Practice for Determining the Activation Spectrum of a Material (Wavelength Sensitivity to an Exposure Source) Using the Sharp Cut-On Filter or Spectrographic Technique

Biological Attack

G 21	Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi
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Mechanical (Creep)

D 2990	Standard Test Methods for Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics
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Rubber

Thermal Degradation

D 454	Standard Test Method for Rubber Deterioration by Heat and Air Pressure
D 572	Standard Test Method for Rubber—Deterioration by Heat and Oxygen
D 573	Standard Test Method for Rubber—Deterioration in an Air Oven
D 865	Standard Test Method for Rubber-Deterioration by Heating in Air (Test Tube Enclosure)

Effect of Liquids

D 471	Standard Test Method for Rubber Property-Effect of Liquids
D 1460	Standard Test Method for Rubber Property—Change in Length During Liquid Immersion
D 3137	Standard Test Method for Rubber Property—Hydrolytic Stability

Weathering

D 518	Standard Test Method for Rubber Deterioration-Surface Cracking
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Effect of Ozone

D 1149	Standard Test Method for Rubber Deterioration-Surface Ozone Cracking in a Chamber
D 1171	Standard Test Method for Rubber Deterioration-Surface Ozone Cracking Outdoors or Chamber (Triangular Specimens)

Mechanical (Stress Relaxation in Compression)

F 38	Standard Test Methods for Creep Relaxation of a Gasket Material
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Composites

C 394	Standard Test Method for Shear Fatigue of Sandwich Core Materials
C 480	Standard Test Method for Flexure Creep of Sandwich Constructions
D 3479/D 3479M	Standard Test Method for Tension-Tension Fatigue of Polymer Matrix Composite Materials
D 5229/D 5229M	Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials
D 6115	Standard Test Method for Mode I Fatigue Delamination Growth Onset of Unidirectional Fiber-Reinforced Polymer Matrix Composites

Adhesives***Thermal Degradation***

D 1151	Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds
D 4502	Standard Test Method for Heat and Moisture Resistance of Wood-Adhesive Joints

Chemical Resistance

D 896	Standard Practice for Resistance of Adhesive Bonds to Chemical Reagents
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Ageing

D 1183	Standard Practices for Resistance of Adhesives to Cyclic Laboratory Aging Conditions
D 2295	Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal)
D 2918	Standard Test Method for Durability Assessment of Adhesive Joints Stressed in Peel
D 2919	Standard Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading
D 3434	Standard Test Method for Multiple-Cycle Accelerated Aging Test (Automatic Boil Test) for Exterior Wet Use Wood Adhesives
D 3632	Standard Test Method for Accelerated Aging of Adhesive Joints by the Oxygen-Pressure Method
D 3762	Standard Test Method for Adhesive-Bonded Surface Durability of Aluminium (Wedge Test)
D 4498	Standard Test Method for Heat-Fail Temperature in Shear of Hot Melt Adhesives

Fatigue

D 3166	Standard Test Method for Fatigue Properties of Adhesives in Shear by Tension Loading (Metal/Metal)
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Creep

D 1780	Standard Practice for Conducting Creep Tests of Metal-to-Metal Adhesives
D 2293	Standard Test Method for Creep Properties of Adhesives in Shear by Compression Loading (Metal-to-Metal)
D 2294	Standard Test Method for Creep Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal)