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ACCELERATED TESTING AND ASSOCIATED PREDICTIVE MODELLING FOR CHARACTERISING DURABILITY OF COMPOSITES: A CRITICAL REVIEW

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1 INTRODUCTION

Composites are increasingly being used for applications where long-term or critical requirements require the use of accelerated ageing regimes to ensure the serviceable life of product and components. This is 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. Consequently, there is growing demand on manufacturers to extend the lifetime 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, such as construction, requires a far better understanding of the failure mechanisms to enable lifetime predictions to be made.

This review is centred on fibre/polymer composites, whereby the polymer matrix is heavily involved in the composite response. However, the durability of both adhesives and polymers are also of interest, in the roles of joining either as the adhesives, or if a polymer component is bonded to a composite component. New standards such as ISO 22838 [1] and ISO 22841 [2], are being published to cover the bonding performance of composites, both thermoplastic and thermoset based, to metallics in short-term tests. Additionally, long-term galvanic attack is an issue for carbon-fibre based composites in direct contact with metals as tested according to ISO 21746 [3].

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. In addition, appendices detail the results of an industrial survey to determine current practices and the future needs of industry for long-term testing (Appendix 1) and a draft proposal for a Joint Industry Project (JIP) to develop and validate methodologies for ageing of composites (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). The exact combination of monitoring the material performance, 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 is accelerated testing. 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 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 those actually 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.

Long-term performance under adverse conditions is an important issue from both health and safety and economic cost perspectives. The repair or replacement of a deteriorated part is both labour and capital intensive. Consequently, there is a growing demand for manufacturers to guarantee the life expectancy of their products, particularly where inspection can be difficult or failure catastrophic. Whilst the life expectancy of products in non-demanding applications has traditionally been predicted from previous in-service experience (i.e. service conditions considered identical or similar to those for which data already exists), long-term or critical applications require a far better understanding of the failure mechanisms and the use of improved accelerated ageing regimes that simulate the degradation mechanisms and failure behaviour of FRPs in hostile environments.

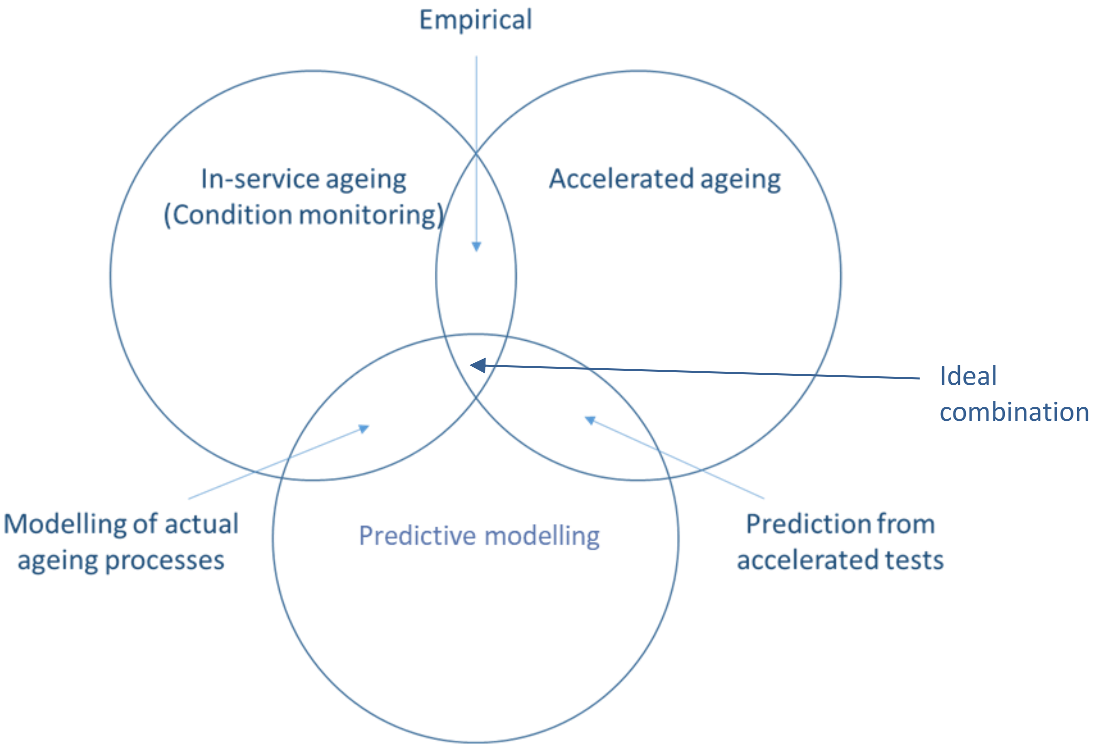


Figure 1 Effect prediction of long-term properties requires a combination of condition monitoring

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 timescale 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 the potential for changes 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 model/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 practices and the requirements of UK industry (see Appendix 1). A further stage of rationalisation of needs/materials/monitoring etc. is expected to be undertaken in a planned joint NPL/Industry project (JIP) (see Appendix 2).

2 DEGRADATION MECHANISMS

In many industrial applications, the operating environments are highly aggressive resulting in a reduction in structural integrity and service life. Prolonged, or even short-term, exposure to environmental agents (e.g. elevated temperature and hostile chemicals) can cause irreversible changes in the chemical and physical properties of FRPs. In some circumstances, only a few hours of exposure may lead to failure or seriously compromise material performance. Conversely, the rate of chemical degradation can be slow and insidious without evident signs of material deterioration. Irreversible property changes 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 shock and cycling,
- Moisture - increased humidity, complete immersion in water, saltwater immersion, or spray, and dry/wet and freeze/thaw cyclic conditions,
- Weathering - ultraviolet exposure combined with rain and/or sand erosion,
- Chemicals - including acids, alkalis, solvents, aviation products and oxygen,
- Irradiation – ultraviolet (UV) and high-energy radiation,
- Electrical - lightning strike and galvanic reactions,
- Biological - micro-organisms (fungal and bacteria),
- Environmental stress cracking - combined effect of stress and a plasticiser,
- Stress – static and fatigue loads and residual stresses.

Although the list of environmental factors is too numerous to elaborate, the common denominator with all these factors is the possible detrimental effect on the material properties, which is exacerbated at elevated temperatures and in the presence of mechanical stress (static and fatigue). 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 occurs 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, analogous to biological systems. For example, 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 composite materials.

Failure of FRPs, insofar as they are no longer fit for purpose, may occur because of cumulative damage to the thermosetting or thermoplastic matrix, fibre-matrix interfacial degradation, chemical or mechanical degradation of the fibres, or a combination of two or more of these processes. Although this review is centred on FRP composites, the durability behaviour of polymers and adhesives is also of interest, in the roles of the composite matrix and in adhesive bonding of composites, respectively. The matrix properties determine the resistance of FRPs to most of the degradative processes that eventually cause failure in composite materials. Adhesives, which are used extensively for joining composites (e.g. advanced aerospace structures), can also be a potential point of failure within a joined structure. Irreversible property changes in adhesive joints can be induced by moisture acting alone or in combination with other environmental and service factors.

This section examines the degrading effects of various chemical environments on failure behaviour and considers the synergistic effects of chemical agents, temperature, and mechanical stress on degradation. Environmental factors, such as humidity, temperature, pressure, seawater, weathering and photo-oxidation, ionising radiation and biological degradation are covered along with the combined effects of stress, temperature, and moisture (i.e. environmental stress corrosion cracking (ESCC)) on material performance. It covers chemicals, such as solvents (including paint strippers), acids and alkalis, and aviation products (jet fuel, hydraulic oil, and de-icing fluids). The section examines the influence of aggressive environmental media on the properties of different types of fibres, resin systems and the fibre-matrix interface and discusses the impact on the failure mechanisms and long-term durability of FRPs. A full list of recognised chemical agents and test methods for assessing the effects of chemical exposure are given in ISO 175 [4].

2.1 THERMAL

Exposure to elevated temperatures will often produce irreversible chemical and physical changes within polymeric materials that lead to degradation of the material. Increasing the temperature accelerates most degradation processes that occur in polymeric materials, such as oxidation, chemical attack, and mechanical creep. As the temperature increases, mechanical properties such as stiffness and strength tend to decrease. Physical changes include polymer structure shrinkage, pore formation and weight loss through chemical decomposition of the polymer. Other physical changes can occur in polymers because of temperature changes, one of the most common being thermal expansion.

The influence of temperature on polymer behaviour will depend on the chemical and physical structure of the polymer itself. Polymers can be categorised into two main groups (i.e. thermosets and thermoplastics) dependent on the response of the polymer to heating. At elevated temperatures, thermoplastic polymers undergo a transition from a crystalline solid to an amorphous liquid, gradually softening and then melting, finally charring (or burning). Precured thermoset polymers do not melt or reflow when heated, unlike thermoplastics, but remain solid until the polymer decomposes (i.e. chars or burns), although thermosets will slightly soften at elevated temperatures. Molecular chain mobility increases with increasing temperature and with sufficient heat thermoset polymers undergo a phase change from a rigid amorphous (glassy) structure to a flexible (rubbery) structure. The transition point is the glass transition temperature, T_g. In fact, T_g is not a discrete thermodynamic transition, but a temperature range over which the molecular mobility increases significantly. Most polymers are semi-crystalline, consisting of a mix of crystalline and amorphous phases; exhibiting a T_g and melt temperature, T_m, with glass transition only occurring in the amorphous phase. As the temperature increases, material properties such as hardness, stiffness and strength tend to decrease with a sudden and marked reduction occurring at T_g for amorphous polymers and amorphous domains in semi-crystalline polymers.

Oxidation is generally considered to be the most serious problem when using polymers at elevated temperatures with the rate of thermo-oxidative degradation increasing with the amount of oxygen present [5, 6]. All polymers are intrinsically susceptible to oxidation. The influence of temperature on the oxidation processes will depend on the chemical structure of the polymer. Thermo-oxidation is usually initiated by the reaction of free radicals ($R^\bullet$) with oxygen (O_2) to form peroxide radicals ($ROO^\bullet$), either by hydrogen abstraction or by homolytic scission of a carbon-carbon bond. All polymers contain free radicals due to their polymerisation and processing history. However, the concentration of free radicals can be significantly increased by interaction with light, ionising radiation or the presence of transition metals. Once formed, the peroxide radicals undergo slower propagation reactions that breakdown the polymer chains. The overall degradation process will often involve a relatively long induction period during which little degradation is observed [5-7]. 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. In adhesively bonded joints, the primary path for oxygen diffusion is through the adhesive, which can be relatively rapid at elevated temperatures. FRPs are permeable to atmospheric gases, and hence the rate of degradation is considerably higher with elevated temperatures also degrading the fibre-matrix interface. At extremely high temperatures, as experienced in fires, fibre ablation occurs.

Fibre-Reinforced Plastics (FRPs): Thermal degradation of FRPs resulting from exposure to high temperatures (referred to as heat damage) involves several mechanisms, including depolymerisation, random chain scission, side group elimination and carbonisation of the composite [8]. The thermal degradation process, which is characterised by various forms of cracks, delaminations and blisters (Figure 2), commences with chemical degradation of the polymer matrix, progressing to include the fibre-matrix interface and fibre reinforcement. As with polymers, the process consists of a relatively long incubation period followed by a rapid and marked reduction in mechanical properties. A sudden brief exposure to high temperatures, a phenomenon known as thermal spiking (shock), can result in irreversible thermodynamic change, deleteriously affecting the physical and/or chemical properties of the composite. Rapid changes in temperature can result in excessive localised stresses and large thermal gradients developing between the surface and the core of thick components.

Extended exposure to heat degrades the resin, resulting in oxidation and/or pyrolysis of the polymer matrix leading to decomposition and eventual charring of the laminate. The effects of rapidly driven-off moisture through thermal spiking can also be expected to contribute to damage. 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. Microcracking and other forms of physical changes induced through thermal cycling, referred to as incipient heat damage, may only become evident at lower temperatures, particularly at sub-zero temperature excursions.

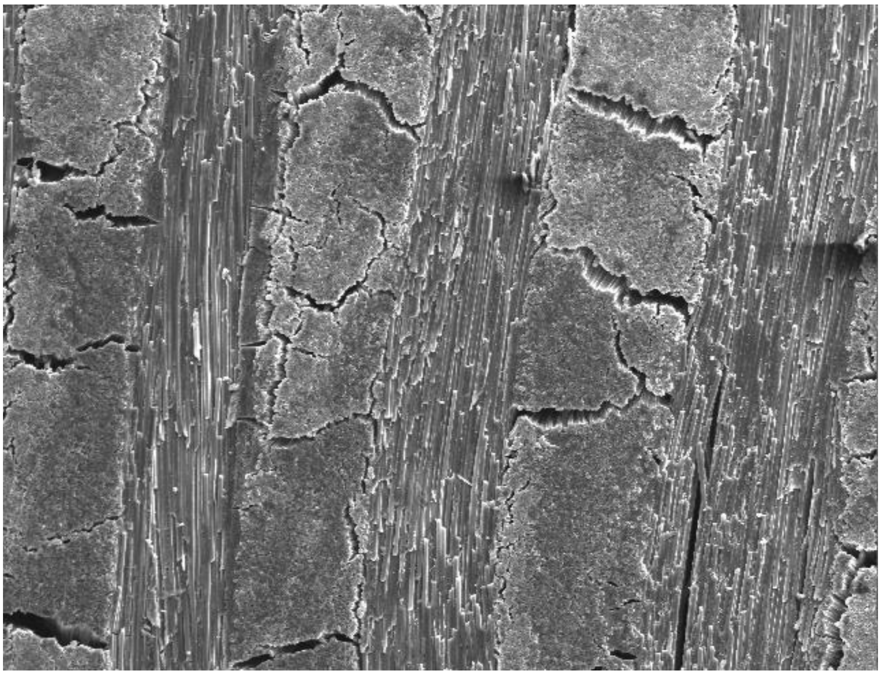


Figure 2 SEM image of heat degraded woven CFRP laminate (Each layer is approximately 0.15–0.2mm in thickness)

The exposure to low (sub-zero) temperatures generally results in an increased embrittlement of the resin, causing an increase in effective stiffness, but a decrease in damage tolerance [9]. At low temperatures, the presence of residual stresses resulting from a combination of resin chemical shrinkage and differential thermal contraction between fibre reinforcement and matrix can result in the formation of microcracks in the matrix and fibre-matrix interface. The degree of micro-damage, the presence of which adversely affects laminate stiffness and strength properties, environmental resistance, dimensional stability and cyclic fatigue resistance, is directly related to residual stresses. Thermal residual stress in the matrix may exceed the yield strength of the matrix and/or the fibre–matrix bond strength causing matrix cracking or fibre–matrix debonding [10]. Microcracks may be readily visible or quite small and difficult to detect - providing failure initiation sites during service. Crack propagation occurs through the matrix for strong interfacial bonding and along the interface for weak interfacial bonding. In general, higher interlaminar residual stresses result in a higher microcrack density in the composite. Residual stresses increase as the temperature is decreased, and consequently the microcrack density increases. In addition, residual stresses may increase the susceptibility of a composite to chemical attack, leading to (environmental) stress cracking (see Section 2.6).

Adhesives: Similar mechanisms can also occur in adhesive joints to those described above. 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 polymers (i.e. adhesives) and debonding of adhesive joints. 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. Residual stress resulting from thermal expansion or contraction are due to the differences in the thermal expansion coefficient between adhesive and adherend and to the temperature distribution in the joint due to differences in thermal conductivity.

At sub-zero temperatures, the difference in thermal expansion between the bonded components plays an important role, especially since the elastic modulus of the adhesive generally increases with decreasing temperature. It is necessary that the adhesive retains some resilience (toughness) if the thermal expansion coefficients of the adhesive and adherend are not closely matched. The adhesive's thermal conductivity is also important in minimising transient stresses during cooling. Adhesive joints with thinner bondlines, particularly in conjunction with adhesives with higher thermal conductivity exhibit better cryogenic properties than adhesive joints with thicker bondlines. Other opportunities for stress concentrations in bonded joints that may be aggravated at low temperature include trapped gases or volatiles evolved during bonding and residual stresses in adherends because of the release of bonding pressure [11]. These internal stresses are amplified when the adhesive or adherend is incapable of deforming to relieve the stress. At cryogenic temperatures, the elastic modulus of the adhesive may increase to a point where the adhesive can no longer effectively relieve the concentrated stresses. Rapid failure can also occur in environmentally degraded polymeric materials at sub-zero temperatures (e.g. formation of ice particles from absorbed water initiating internal fractures).

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 differ widely both between different grades of material and with chemical ageing. Depending on the physical and chemical characteristics of the polymer, considerable quantities of moisture may be absorbed by the material, and both the rate of absorption and the saturation absorption level will depend on the conditions of exposure (i.e. temperature and relative humidity). Moisture ingress in polymeric materials usually follows Fickian kinetics with the amount of moisture absorbed being proportional to $\sqrt{(\text{time})}$ in the early stages of exposure; moisture uptake gradually slows, asymptotically approaching an equilibrium moisture content (i.e. saturation) [12-14]. Although moisture ingress in many polymers follow classical Fickian behaviour, deviation from Fickian behaviour is often observed. Non-Fickian behaviour is associated with moisture induced structural changes, resin degradation, or even simple molecular relaxation – see also Section 4.3.

After prolonged exposure, certain polymeric systems undergo weight loss through chemical degradation of the polymer caused by decomposition of the low-molecular weight constituents resulting in leaching of species (ions) into the water medium. Chemicals leach from polymer fillers and additives (i.e. catalysts, hardeners, pigments, or fire retardants) because of reactions between the additives/fillers and the diffusant (i.e. moisture). Leaching from additives may be 'activated' because of environmental conditions (i.e. temperature and/or moisture concentration). Additives that are 'solids' are less likely to migrate within the polymer matrix unless they undergo dissolution in the matrix (either in the polymer or through ingress of other chemicals) or if the additive size is comparable to the sizes of pores or voids in the polymer (possible issue with nano-particles) [14]. Loss of fillers and additives increases with increasing temperature.

Concentration of dissolved salts in the immersion medium will accelerate moisture uptake, but not necessarily affect the saturation level. Moisture absorption and diffusion rates of polymeric materials are dependent on the previous history of water exposure. The amount of water absorbed at equilibrium and the rate of moisture diffusion usually increases with a previous history of exposure. The increase in moisture uptake is associated with the formation of micro-cavities caused by previous water ingress, which fill with water. The presence of tensile loads will also accelerate moisture uptake by opening existing internal cavities or voids, and by contributing to micro-crack formation. Material systems containing voids and micro-cracks will absorb considerably more moisture than undamaged material systems. This applies equally to polymers, composites and adhesives [15]. Exposing the wet system to sub-zero temperatures can further exacerbate this process. Laminates containing significant amounts of moisture will experience severe stresses if the laminate becomes frozen due to the expansion of water when it freezes (to be discussed in more detail later in this Section).

Water permeates all polymeric materials to a greater, or lesser degree. The moisture absorption kinetics differ widely between resin systems and change with chemical ageing. Absorption of water is known to cause plasticisation (essentially softening) of the polymer, depressing T_g, and lowering stiffness and strength. 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 FRP structures to ensure that the maximum operating temperature is at least 30-40°C below the T_g of the material (considering moisture effects). Elongation to break (strain-to-failure) tends to increase with moisture content (i.e. increase in ductility). The loss of stiffness and increase in ductility can be attributed to structural changes of the resin system resulting from scission of the polymer chains through hydrolysis, leading to a decrease in cross-link density and molecular weight. Hydrolytic degradation is controlled by the diffusion of water in the material, which increases at elevated temperatures. Hydrolysis reactions are generally minimal under ambient conditions. Figure 3 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 different temperatures [15].

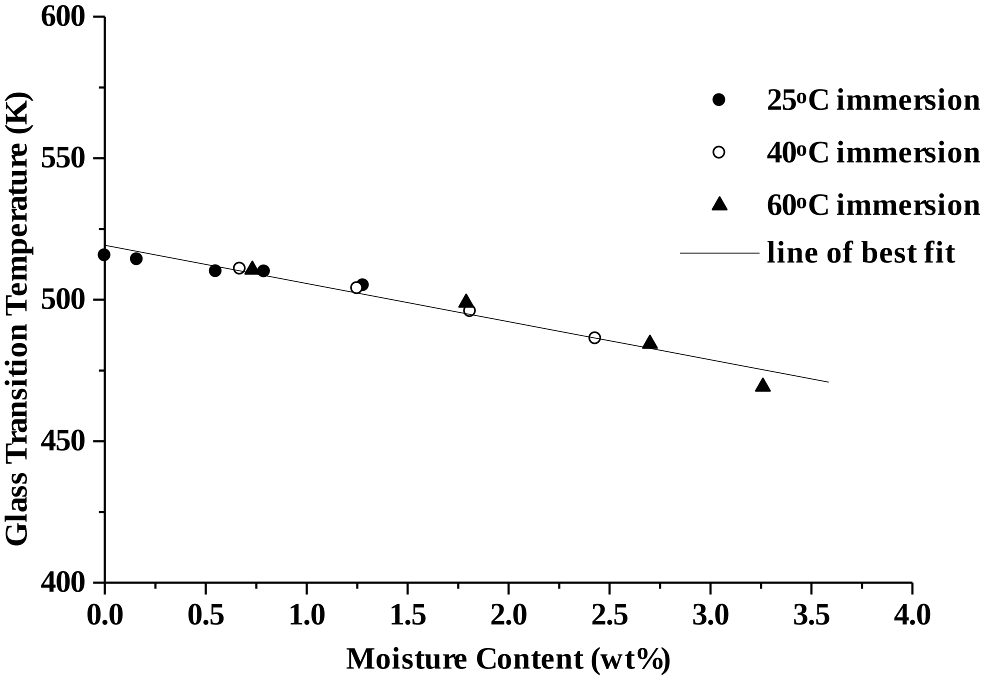


Figure 3 Glass transition temperature of F922 epoxy as a function of moisture content (Immersion in deionised water)

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. Reducing the "free volume" of the polymer will increase the diffusion barrier characteristics and thus increase moisture resistance. This can be achieved by increasing crystallinity content, crystallite size, molecular weight, degree of cross linking and packing density, or adding inert fillers.

Fibre-Reinforced Plastics: Irreversible and reversible degradation mechanisms may occur because of moisture ingress. In many instances water reacts with the matrix and causes irreversible chemical changes and diminished performance. Water diffusing along, or accumulating at, the fibre-matrix interface may cause hydrolytic breakdown of the chemical bond between fibre and matrix, impairing load transfer efficiency between the matrix and fibre reinforcement. Bonds may also be disrupted by moisture induced swelling of the resin. Capillary action along the fibres can account for a significant proportion of initial moisture uptake, although a chemically resistant matrix may encapsulate the fibres [16]. Shrinkage of the resin away from the fibres during curing is a contributing factor to the capillary effect. Another contributing factor is poor adhesion between the fibre and the surrounding matrix due to either chemical incompatibility between the two constituents or degradation of the fibre sizing, as shown by a thin layer with blisters on the surface of the glass fibres in Figure 4.

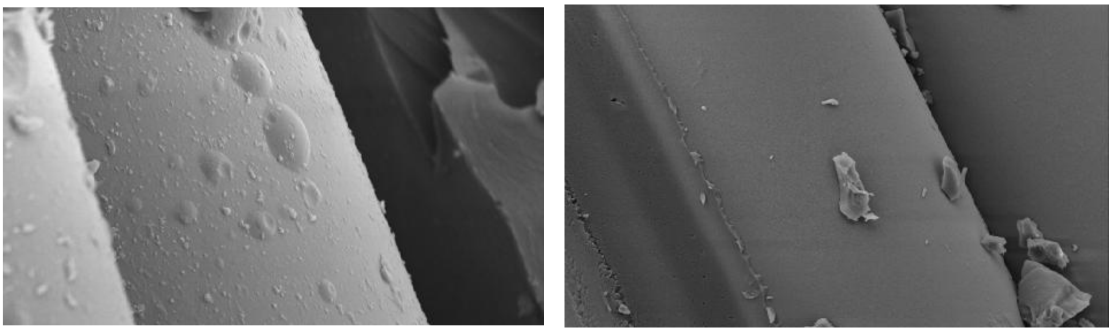


Figure 4 SEM images of E-glass fibre fracture surfaces: poor sizing (left) and good sizing (right) (GFRP pultruded rods subjected to hot/wet conditioning)

If the effect of moisture absorption and desorption are simply physical processes where the chemical and physical properties of the fibre, matrix and fibre-matrix remain unaltered, then strength and stiffness of the composite would be expected to be fully recoverable after drying. Chemical stability and resistance to moisture penetration of the matrix polymer, which depends on the chemical and molecular structure and state of cure, will usually determine the extent of both reversible and irreversible composite damage, although resin void-content and composite fibre-content will also affect damage formation. It is worth noting that for some composite systems a loss in mechanical properties through moisture ingress is not always accompanied by a reduction in T_g. Reductions in flexural strength of the order of 20-40% have been observed for both thin woven glass and carbon laminates with polyester and vinyl ester resin systems immersed for 2 years in sea water at 30ºC [17]. The long-term behaviour of isophthalic polyester composites is particularly poor. Leaching of constituents from the matrix occurs at temperatures approaching 60ºC. The maximum operating temperature of glass fibre-reinforced polyester is close to room temperature.

Hygrothermal (combined moisture and temperature) cycling of FRPs, as experienced by aircraft, can produce transverse matrix cracks in the surface plies, which penetrate deeper into the laminate with accumulating cycles. The rate and severity of transverse matrix cracking is dependent on several conditions, including matrix properties, fibre properties (especially thermal expansion and stiffness), processing conditions, service conditions (including temperature cycle and humidity), ply thickness and ply stacking sequence. Although the overall moisture content may be low, concentration gradients may result from hygrothermal exposure, high moisture levels at the surface to near dryness at the mid-plies. Subsequent desorption in the near-surface plies and redistribution of moisture can lead to significant residual stresses and/or outer-ply delaminations (and possible blistering during rapid heating).

Figure 5 Osmotic blistering of a GFRP boat hull with inset showing laminate breakdown (Courtesy of Minton, Treharne and Davies Ltd)

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 [18, 19], 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 gelcoat and can lead to a blistering of the surface. Damage can be very extensive requiring major repair or the replacement of the structure (Figure 5).

Osmosis blistering [20, 21] is a 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 (painted or sprayed) to the composite surface where the material is to be exposed for long periods to aqueous solutions. This protective layer (~0.1-0.2 mm thick) acts as a barrier to moisture ingress, thereby protecting glass fibres from moisture degradation. Isophthalic-NPG (neo-pentyl glycol) resin systems are widely used for this purpose. Although the gel coat protects the underlying composite substrate by slowing water ingress, it is not an impermeable layer [22]. The use of gelcoats has been highly successful in protecting GFRP marine structures with few failures due to wet ageing reported. Failures are more likely to result from poor maintenance or inadequate repair following a collision. Other protective measures against natural weathering, such as marine paint and polyurethane coatings 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 [23, 24]. Seawater absorption of FRPs is greatly accelerated by high hydrostatic pressure as experienced in deep sea environs, resulting in increasing absorption rate and saturated absorption. 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, and 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 [23].

Freeze and freeze-thaw exposure are also of concern to engineers and designers of composite structures, particularly in the presence of moisture (see also Section 2.1). 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. 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 lowers the composite's resistance to further moisture ingress. CFRP and GFRP wrap systems used to repair (rehabilitate) corrosion-damaged concrete columns on bridges have been shown to be sufficiently resistant to freeze-thaw cycles, whilst providing protection from corrosion [25]. Freeze-thaw (300 cycles) and wet-dry (190 cycles) conditioning (3% NaCl solution), in the same study, had no detrimental effect on CFRP panels other than a 28% and 36% reduction, respectively, in the ultimate tensile strain. GFRP panels showed 21% and 20% reductions in ultimate tensile strength and ultimate tensile strain due to freeze-thaw conditioning, and 18% and 20% reductions in ultimate tensile strength and ultimate tensile strain due to wet-dry conditioning. Freeze-thaw cycling had no statistically significant effect on the compressive strength of CFRP and GFRP wrapped specimens, although tensile properties degraded because of freeze-thaw and wet-dry cyclic conditioning. Freeze-thaw and wet-dry cycling can also be expected to contribute to deterioration in adhesive joint performance. These processes can induce damage in the form of voids and cracks within the adhesive, and debonds at the interfaces, promoting further moisture ingress. Diffusivity and maximum moisture concentration will gradually increase with exposure time.

Fibre degradation is primarily an issue for glass and aramid fibres, with carbon fibres being stable in most environments (N.B. 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 laboratory 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 [26]. 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 tensile strength. 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 (i.e. 23°C and 50% RH) [26]. The tensile strength is reduced to 3.0 GPa after three weeks exposure to standard laboratory conditions. Immersion in water at the same temperature for the same period results in a 30% reduction (~2.5 GPa). Further strength reduction occurs with increasing exposure time. After 100 days, the strength in air and water is 2.6 GPa and 2.1 GPa, respectively. Exposure to boiling water for 24 hrs results in a 75% loss of strength. As a consequence of handling and moisture, an intrinsic tensile strength of 2.0 GPa is often assumed for design purposes. The original tensile strength of glass fibres can be fully realised, provided the fibres are carefully handled during fabrication to avoid surface damage and are stored in a dry environment.

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 (i.e. environmental stress corrosion). 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 [16, 27]).

Moisture Effect on E-Glass Fibres

- **Leaching of alkali oxides (sodium and potassium oxide) from the fibre surface**

$$\text{— Si —O —R} + H_2O \rightarrow \text{— Si —O —}R^{+} + OH^{-}$$

(R = Na, K, Ca, Mg, Al…)

- **Formation of surface micro-cracks (i.e. stress concentrators)**
- **Glass fibres slowly decompose/dissolve**
- **Permanent loss of strength (even after drying)**
- **Process accelerated with increasing temperature and stress**
- **Deionised water more aggressive than tap water and saltwater**

The mechanical properties of carbon fibre systems when dried will tend to be similar to those observed for unconditioned material provided the chemical composition of the matrix remains unaltered. 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. The effect of moisture on aramid fibre-reinforced epoxy laminates is potentially greater than other composite systems. Substantial hygrothermal strength losses have been observed with these materials, particularly under natural weathering conditions (i.e. combination of moisture and ultraviolet light).

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. In fact, the surrounding environmental conditions are constantly changing (tides, diurnal and seasonal cycles); relative humidity and ambient temperature will fluctuate, thereby changing the diffusivity. After sufficient time, the moisture content within the interior of a bonded structure will remain steady with variations in moisture content generally confined to a narrow region along the exposed edges of the adhesive joint, provided the structure is relatively large. Migration of water to the joint interface will result in permanent loss of adhesion.

Water, being a highly polar molecule, is known to interact strongly with structural adhesive systems containing hydroxyl groups, such as epoxies, polyurethanes, and acrylics [10, 28]. 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. Absorption of water by the adhesive polymer is known to cause plasticisation (essentially softening) of the polymer, depressing T_g, and lowering the modulus and strength (see Figure 6). Elongation to break (strain-to-failure) tends to increase with moisture content. This problem is further exacerbated at elevated temperatures and/or mechanical stress.

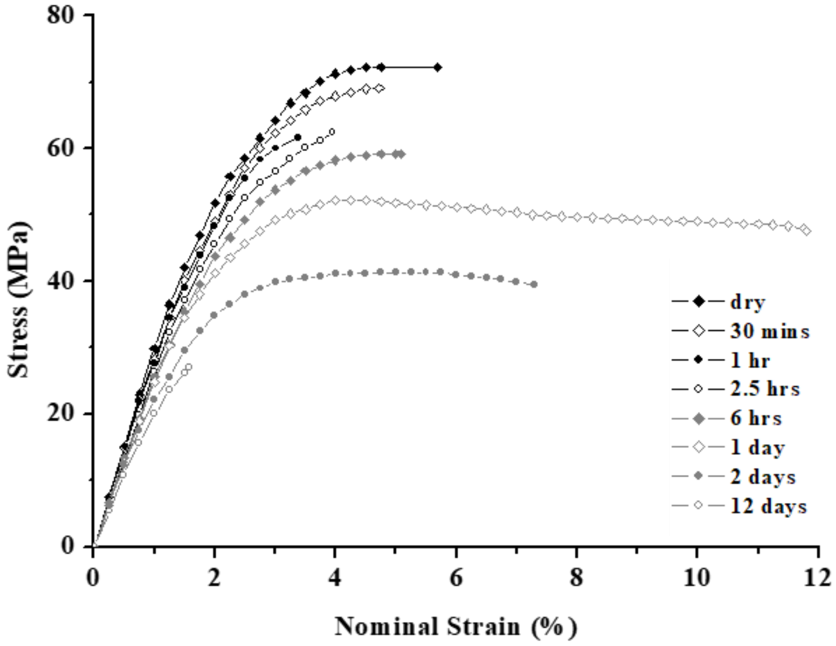


Figure 6 Tensile stress-strain response of an epoxy adhesive as a function of immersion time (Immersion in deionised water)

Osmotic effects have been observed for adhesives, such as epoxies immersed in water [28]. As water diffuses into the polymer it reacts with any hydrolysable components inside the material to form tiny cells of concentrated solution. Under this osmotic process, more water is drawn through the resin to dilute the solution. The water can increase the fluid pressure of the cell substantially, which may eventually cause cracks to form. Concentration of dissolved salts in the immersion medium will accelerate moisture uptake, but not necessarily affect the saturation level. Moisture absorption and diffusion rates of adhesives are dependent on the previous history of water exposure. The amount of water absorbed at equilibrium and the rate of moisture diffusion usually increases with a previous history of exposure. The increase in moisture uptake is associated with the formation of micro-cavities caused by previous water ingress, which fill with water. Moisture absorption of adhesives also increases with increasing stress, with very significant increases and non-linear absorption observed at high stress levels around the yield stress [14].

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. Migration of moisture to the joint interface will result in permanent loss of adhesion. 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.

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 into 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.

Although most structural adhesives, such as epoxies, phenolics, polyurethanes and modified acrylics are highly resistant to moisture at moderate temperatures (< 70°C), the same adhesive systems are susceptible to hydrolysis at elevated temperatures (> 70°C) with considerable loss in mechanical performance. The adhesive bond-line is usually sufficiently thin and well protected from the surrounding environment, especially where the adherends are nonporous and impermeable to the chemicals or solvents present in the surrounding environment. Moisture resistance can be further enhanced through the application of a protective coating and/or sealant (e.g. polyurethanes and silicones) around the edges of the adhesive joint. Fluorosilicones can offer improved chemical resistance compared with silicones; resistance to petroleum-based oils, greases, fuels, oxidation, ozone and weathering is excellent. Surface treatments, such as organosilane primer coatings will bestow joints with improved moisture resistance.

Composite Repairs: The presence of moisture in the composite can adversely affect the properties of the adhesive during the cure process and as a result the joint strength may be compromised. Moisture released from the composite substrate during cure will enter the adhesive and has been known to reduce T_g by as much as 20°C and lower the fracture toughness G_c of a rubber toughened epoxy adhesive by a factor of 10 [29]. With toughened adhesive formulations, the presence of moisture may inhibit phase separation of the rubber-toughening agent, thus preventing the formation of rubber-toughened particles. It is recommended that FRP adherends be dried and then stored in a dry area prior to bonding.

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.

UV radiation can be divided into three groups of wavelengths as described below:

- UVA (315 – 400 nm) - least harmful to polymers, forming 6% of the total solar radiation reaching earth.
- UVB (280-315 nm) - more damaging to polymers, forming 0.1% of the total solar radiation reaching earth.
- UVC (<280 nm) – most harmful to polymers but is filtered out by the earth's atmosphere.

UV radiation below 350 nm is absorbed by window glass, thus eliminating UVB radiation indoors.

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 [7, 27, 30]. 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 ($R^{\bullet}$) have been produced, reaction with oxygen (O_2) generates hydroperoxides (ROOH) [31]. 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 [31].

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 micrometres 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 upper surface layers 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 UV radiation, depending on the chemical formulation. Signs of photo-degradation include embrittlement (surface cracking), discolouration and loss of transparency [18]. Infrared radiation (800 nm to 1000 mm) 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 also added to protect polymeric systems (e.g. adhesives) 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 absorbing UV radiation (protects the polymer chains) and is inexpensive.

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 [32, 33].

Although most forms of high-energy radiation are damaging to polymers because of the relatively low energies required to cause chemical damage, the intensity of ionising radiation on the earth's surface is not normally high enough to significantly affect most plastics and FRPs [13]. Molecular chain scission often causes a lowering of the polymer viscosity and softening temperature, accompanied by a reduction in mechanical strength. In contrast, cross-linking, may lead to an initial increase in strength and ductility, but as cross-linking density increases a limit is often reached beyond which the strength and ductility of the polymer decrease (i.e. polymer embrittlement) [13].

The inevitable long-term effect of irradiation is severe embrittlement of the polymer; surface cracking and erosion, and eventual disintegration, unless the surface is suitably protected. Irradiated surfaces are prone to chemical ingress due to the presence of surface microcracks and internal stresses induced through exposure to high energy irradiation. Environmental stress cracking (ESC) may ensue in the presence of externally applied stresses (see Section 2.6). In composites, most reinforcing fibres will be largely unaffected since the bulk of the fibre reinforcement will be screened by the surface layers of the composite or by a protective coating (e.g. pigmented paints).

2.5 CHEMICAL DEGRADATION

FRPs can face exposure to a range of chemicals and solvents during service life, sometimes inadvertently through maintenance (e.g. cleaning fluids and pain strippers) and accidents. Absorption of any fluid (liquids and gases) plasticises the polymer matrix, lowering T_g and reducing the stiffness and strength of the composite. Other physical changes that can occur include swelling and leaching of soluble constituents (additives) of the composite, thus compromising its chemical resistance. Exposure to chemicals and solvents will often result in degradation of the fibre reinforcement (e.g. E-glass) and fibre-matrix interface. The higher the concentration of absorbed fluid the greater the level of degradation with the process accelerated at elevated temperatures and in the presence of applied stress. The influence of diffusion and absorption of fluids on the rate of chemical degradation and the interaction between factors such as concentration, temperature and stress are key to predicting long-term performance of composite structures under different service conditions. The polymer matrix acts as a chemical barrier to the corrosive effects of water/moisture, but also alkalis and mineral acids. Although polymers, in the main, have good chemical resistance there is free volume between the polymer chains through which chemicals can permeate. Permeation along interfaces may also occur in many applications (adhesive joints, coatings, and laminated structures) [34]. The ingress of chemicals into polymers can have a critical effect on the service performance of a component or structure. The permeation of chemicals within a polymer component may affect the mechanical performance of the material, degrade the material or product that the polymer should protect (e.g. corrosion of coated steel), damage the interface between the polymer and fibres or pollute the environment (e.g. diffusion leakage from storage vessels). As with moisture effects, acid and alkali degradation processes are accelerated at elevated temperatures.

The chemical composition of the polymer matrix will have a strong influence on the solubility and diffusion properties of small molecules in the polymer matrix. Mobility and solubility of small molecules in glassy polymers will depend on the free volume present in the polymer. The free volume depends on the nature of the polymer and on the physical state of the polymer, including molecular orientation, density and physical ageing effects. Molecules will absorb more readily and be more mobile in polymers with high free volumes than in polymers with low free volumes. The greater the free volume, the higher the capacity for absorption and mobility of the molecules within the matrix [34].

Crystalline regions in polymers are more ordered than amorphous regions and free volume will be lower in these regions. It is often assumed that the crystalline region is impermeable and that the sorption depends only on the volume fraction of amorphous phase [35, 36]. For many polymer/gas combinations it has been observed that solubility constants are directly proportional to the volume fraction of the amorphous phase [37]. However, there are systems where the solubilities have been found to be higher than those expected from the volume fraction of the amorphous phase, this has been attributed to the higher probability of denser regions of amorphous material crystallising preferentially leaving the residual amorphous phase with a lower density and higher concentration of 'holes' available for absorption [35]. Structural imperfections, such as voids, can inadvertently be produced in polymeric materials, either during the manufacturing process (entrapped air or volatiles) or generated during the service life of the component (stress generated crazing or chemical swelling).

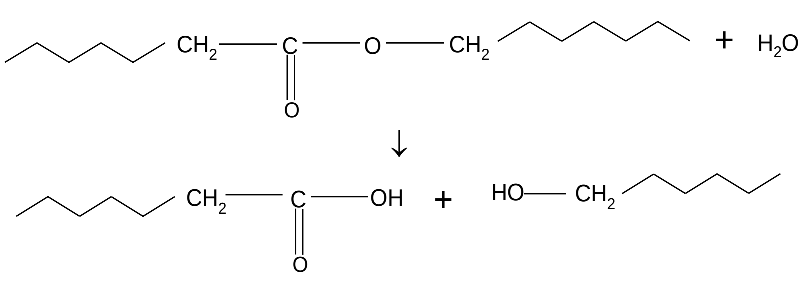
All polymers are ‘porous’ to some degree as the random, entanglements of polymer chains leave very small pores (free volume) into which molecules can diffuse. Voids and pores tend to be on a larger size scale than free volume (i.e. gaps left between entangled polymer chains) and are ‘permanent’ features, independent of polymer chain motion. An increase in porosity results in an increase in both the rate of diffusion (diffusivity) and the level of absorbed moisture at saturation (i.e. an increase in permeability). Diffusion rates are higher when the voids are linked (open pores) and consequently permeation is significantly greater than when the voids are isolated (closed pores).

Voids, like free volume, offer sites into which molecules can absorb and are far less of a barrier to transport than solid polymer. Voids may also provide sites into which liquids and vapours can condense and thereby dramatically increase the uptake. The volume fraction of voids in a sample will depend on the imposed stress state. Hydrostatic tensile stress will tend to open voids whilst hydrostatic compressive stresses will close voids.

Most of the commonly used resin systems employed by the composites industry are far more chemically resistant to strong acids, salt solutions and oxidative agents (e.g. hydrogen peroxide and bleaches) 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.

Polymers with polar chemical groups, such as epoxies, will have a strong affinity for polar molecules, including water. In contrast, the uptake of polar species is much lower in non-polar polymer molecules (e.g. polypropylene). In polar polymer matrices, the diffusion coefficients of polar organic molecules can increase with the absorbed concentration of molecules, due to strong interactions between the molecules and polymer chains that induce structural transformations such as swelling, crazing or partial dissolution of the polymer matrix. Chemical attack of thermoplastics involve specific chemical reactions of the polymer with the fluid with the most common mode of failure being hydrolysis by water, acids, and alkalis [37]. 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. 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.

A general hydrolysis scheme can be summarised as follows:



The higher the concentration of absorbed fluid, the greater the level of degradation with the process accelerated at elevated temperatures and in the presence of applied stress. Stress and elevated temperatures are known to accelerate the chain scission process and the rate of fluid uptake. Metallic and GFRP vessels and pipes are frequently fitted with a thermoplastic lining (e.g. nylon, polypropylene, polyethylene and polyvinylidene fluoride), which acts as a corrosion or permeation barrier to chemical environments.

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.

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 H_2SO_4) and alkalis (e.g. NaOH and KOH) [16, 27]. 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. The dissolution of the supporting network results in a slight enlargement of the fibre diameter and shortening of the fibre length as longitudinal stresses relax, which is resisted by the unaffected core. As the outer layer becomes depleted, tensile stresses imposed by the core of the fibre build up, which significantly decreases the load capability of the fibre and eventually leads to cracks (helical in shape). Exposed fibres gradually lose weight, stiffness and strength with exposure time.

Mineral Acid Attack on E-Glass Fibres

- **Ionic exchange between the metallic cations (e.g. Na^+ ions) at the fibre surface and the H^+ ions in the acid solution**

$$\text{— Si — O — Na} + H^+ \rightarrow \text{— Si — O — H} + Na^+$$

- **Leaching of Na, K, Ca, Mg, B Al from fibre outer layer**
- **Dissolution of the silica network on fibre surface and eventually complete dissolution of fibres**
- **Slight enlargement of fibre diameter/shortening of fibre length as longitudinal stresses relax**
- **Formation of helical and axial cracks**
- **Loss of weight, strength and stiffness**

In the case of alkali attack, the chemical reaction involves a breakdown of the silica network by hydroxide (OH^-) ions and eventually dissolution of all the species in the E-glass. The glass fibres gradually lose weight and strength when they are in contact with strong alkalis. The rate of degradation of glass fibres to alkalis is not determined by the rate of diffusion, but by the active dissolution of the SiO_2 network. The loss of mass is proportional to time.

Alkali Attack on E-Glass Fibres

$$\text{— Si — O — R} + H_2O \rightarrow \text{— Si — O — } R^+ + OH^-$$

(R = Na, K, Ca, Mg, Al…)

$$\text{— Si — O — Si} + OH^- \rightarrow \text{— Si —OH} + \text{— Si —}O^-$$

- **Breakdown of the silica network by hydroxide (OH^-) ions**
- **Dissolution of all the species in the E-glass**
- **Fibres gradually lose weight (proportional to time) and strength**
- **Rate of degradation is not determined by the rate of diffusion, but by the active dissolution of the SiO_2 network**
- **ECR glass is only slightly more resistant than E-glass to strong alkalis**

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. S-2 glass, C-glass and A-glass fibres are known to have superior resistance to mineral acids (e.g. H_2SO_4) than E-glass and ECR-glass fibres with a substantial reduction of fibre dissolution when immersed in solution. ECR (acid corrosion resistant) glass is only slightly more resistant than E-glass to strong alkalis.

Adhesives: As with most materials, adhesives have specific attributes that provide protection against a range of chemicals. Many acids and alkaline agents are known to degrade structural adhesives, although the degree of degradation to specific chemical agents is dependent on the chemical composition of the adhesive, chemical concentration levels, exposure time and temperature. There is no single adhesive that offers a universal solution, protection from all environments. Being impervious to one environment is no guarantee of resistance to other environments. An adhesive with maximum resistance to acids generally has poor resistance to alkaline solutions, and vice-versa. Adhesives with dense cross-linked molecular structures generally have good resistance to chemicals and solvents, and high temperatures. The problem for designers and engineers is selecting an adhesive, which will guarantee the required design life performance when exposed to the chemicals and solvents that the bonded product is expected to experience during service life. This includes secondary environments, such as maintenance activities involving chemical cleaners and paint strippers.

Other Chemical Agents: Several other degradation agents relating to in-service environmental conditions, handling, and maintenance (or even accidental contact – spillage or leakage) 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. In terms of solvent sensitivity of polymers, it is important to prevent solvents encountering the composite during service life. Solvents such as methyl-ethyl-ketone (MEK) and acetone should not be left standing on polymer surfaces.

Epoxy and thermoplastic polyimide adhesives are highly sensitive to organic solvents (e.g. acetone, MEK, ethyl acetate and toluene) even at room temperature. Solvent uptake is rapid and the effects on adhesive strength and T_g are generally irreversible. Solvents tend to have a plasticization (softening) effect on the adhesive and in combination with mechanical stress can result in crazing or cracking of the adhesive (i.e. ESC). Exposure to acetone for short periods (1-3 months) can result in 10% (or higher) tensile strength reduction of structural adhesives, with higher levels of strength loss recorded after exposure to MEK and toluene ($\geq$ 25%).

Aviation Products: Contact with aircraft fuel, gasoline, oil, hydraulic, brake and transmission fluids, lubricants, coolants and de-icing and antifreeze compounds are known to have adverse effects on composite performance through degradation of the polymer matrix [7, 37]. Hydraulic fluid has a similar effect to that of methylene chloride but takes longer. Gasoline (petrol), JP-4 fuel, skydrol, aviation fuel and hydraulic fluid are known to plasticize some structural adhesives and consequently lower joint strength, although the level of degradation induced generally tends to be far less than most other chemicals or solvents [38]. Whilst the de-icing fluid ethylene glycol has been found to have minimal effect on the mechanical properties of structural adhesives, exposure to diethylene glycol monoethyl ether (DGME) can cause severe deterioration of these materials [39]. As previously mentioned, synergistic effects are often observed between the various environmental factors resulting in amplification of the degradation process. As previously mentioned, the combination of JP-4 fuel and water is more aggressive than the two media acting alone. The effect of these highly destructive processes is often evidenced by a degraded surface appearance (i.e. discolouration, cracks and pitting, loss of surface reflectivity, increased surface roughness and exposure of underlying fibres).

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 7 illustrates damage induced in GFRP pipes when exposed to molecular chlorine and hydrogen chloride. Long-term exposure to molecular chlorine is also known to induce embrittlement in acetal resin plumbing fittings and polybutylene water pipes. Chlorine is used in trace amounts as an antibacterial agent in the water supply.

Figure 7 Chlorine degradation (left) and HCl induced blistering (right) of a GFRP pipe (Courtesy of ESR Technology Limited, UK)

Galvanic coupling of metals to carbon composites will cause problems for both the metal and composite materials (N.B. galvanic corrosion occurs when two different conductive materials of different galvanic potential are in contact in the presence of water (electrolyte)) – see also ISO 21746 [3]. Carbon fibre surfaces are electrochemically active supporting chemical reactions. The main reaction is cathodic reduction of dissolved oxygen to form hydroxyl ions. The reaction rate is initially controlled by the diffusion rate of the reactive components through the polymer matrix to the carbon fibre surface with the rate controlled by the type, thickness and quality of the polymer layer and the solution chemistry. Another factor is the retained moisture in the polymer after manufacture. Once the galvanic cell is complete then the cathodic and anodic reactions initiate. The more anodic material will corrode at an accelerated rate resulting in a build-up of corrosion product near the contact area. Metals are susceptible to localized galvanic corrosion (pitting and crevice corrosion) when connected to carbon composites in the presence of moisture/seawater. Hydrogen gas evolution occurring in defect sites (voids and cracks) of the composite will result in the formation of hydrogen-filled blisters. Calcareous (calcium carbonate and other salts) deposits can also form on the composite surface. The galvanic effect will be dependent on moisture content, temperature and electrical and chemical properties of the galvanic cell electrodes and electrolyte.

2.6 ENVIRONMENTAL STRESS CRACKING (ESC)

ESC (combined action of stress and corrosive liquid) 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. The chemical resistance of various thermoset resins is summarised in Table 1.

Table 1 Chemical resistance of thermosetting resins

Polymer	Chemical environment					
	Aliphatic solvents	Aromatic solvents	Esters and ketones	Strong oxidants	Strong acids	Strong bases
Bismaleimides	H	H	L-M	M	M	M
Epoxies	M-H	M-H	M-H	L	M	M
Phenolics	H	H	M-H	L-M	H	M
Polyesters	M-H	M	H	L	L-M	L-M
Polyimides	H	H	M-H	M	M	M
Vinyl esters	M-H	M	H	M-H	M-H	L-M

Code: L = low resistance, M = moderate resistance, H = strong resistance

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 to 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 [40-42]. 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 8). The mechanism of crazing in chemical environments is generally considered to be identical to that in air [40-42]. In general terms, craze initiation is considered to evolve from micro-deformation processes in localised regions about 30 nm in diameter (see Figure 8) [43]. 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 [44].

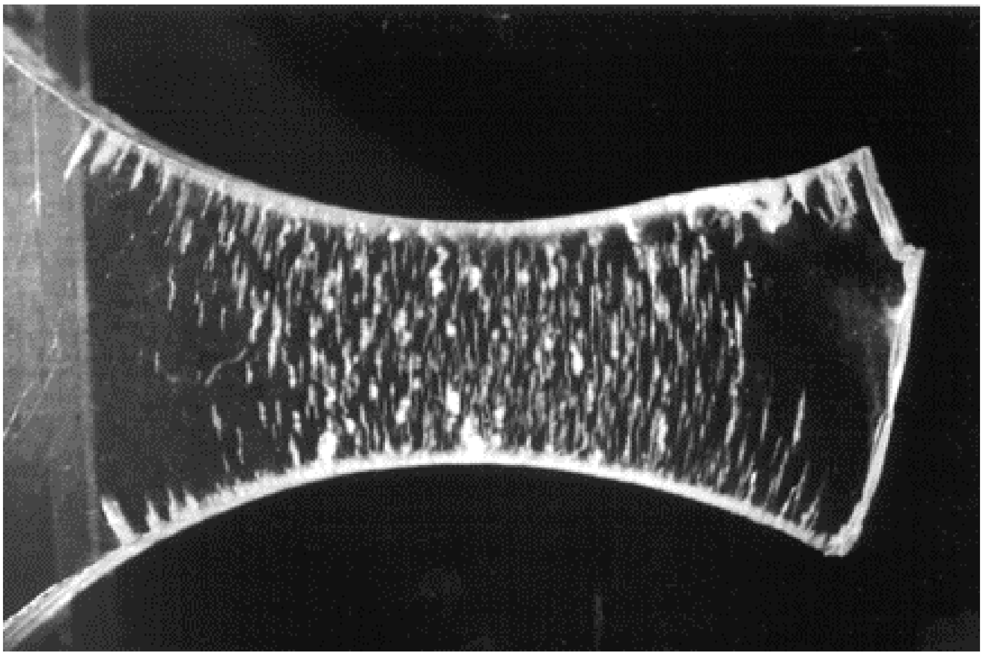


Figure 8 Crazing of PMMA

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 [40, 42]). 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 [39] 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 [40, 45, 46]. 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 may 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.

Fibre-Reinforced Plastics: 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 [16, 47-49]. 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 [50-52]. The timescale involved inducing ESCC failure increases as the initial applied stress is reduced. ESCC is not limited to static loads; it applies equally to dynamic loading conditions. ESCC of glass fibres can be activated by either moisture ingress (weepage) through pre-existing matrix micro-cracks or moisture diffusion through the matrix. The process can be initiated simply by exposure of the composite to humid environments [53]. ESCC of glass fibres is associated with the rupture of Si–O–Si siloxane bonds that form the silicate network and ion exchange reaction between the metallic cations (e.g. Na+) at the fibre surface and the H+ ions (protons) in the surrounding environment. The applied stress contributes to the process through extension of the Si–O bonds, which accelerates the breakage reaction rate of the chemical bonds (see also Section 2.2).

This chemical reaction leads to an increase in the alkaline concentration (pH level) at the tip of a crack or flaw contributing further to the dissolution to alkali ions from the glass fibre; slowly decomposing the glass fibres and causing spiral cracking of the outer sheath of the glass fibres. 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 also occurs in acidic solutions with the rate of degradation dependent on pH level (see also Section 2.5). The consequence is that GFRP laminates suffer delayed brittle fracture in acidic environments, under stress [52].

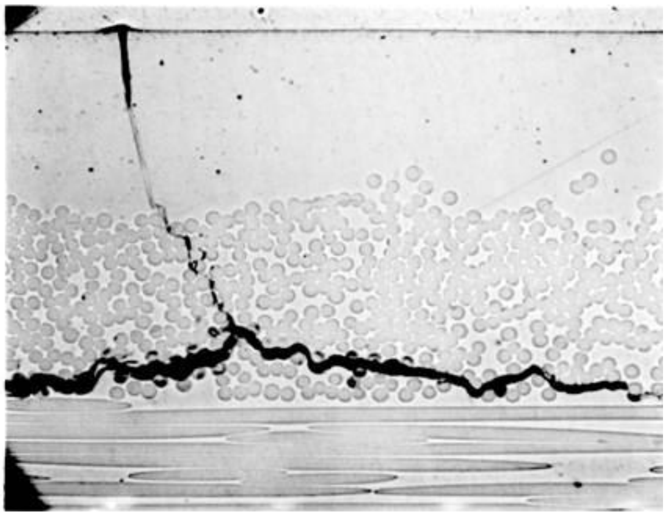


Figure 9 Optical micrograph of a failed GFRP pipe resulting from static fatigue (Courtesy of ESR Technology Limited, UK)

Static fatigue or creep (stress) 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. Creep rupture is an important facet in the design and predictive analysis (i.e. prediction of long-term behaviour or strength) of prestressed structures and for reinforced structures with a high permanent load. Rupture strength is defined as the applied stress under specified environmental conditions required to produce rupture in a fixed amount of time (often in a few hours). Creep failure occurs when the accumulated creep strain results in a deformation of the structure that exceeds the design limits. Figure 9 shows an optical micrograph of a failed GFRP pipe resulting from static fatigue. The less resistant a fibre (or composite) is to a specific chemical environment, the more rapid the drop in the rupture stress time curve. Although obviously apparent for temperature, an increase in chemical concentration or applied stress can also alter the mechanism of degradation. For a given applied load, the stress rupture time decreases with increasing humidity and temperature, or chemical concentration.

Adhesives: The presence of tensile stresses will accelerate moisture uptake by opening existing internal cavities or voids, and by contributing to micro-crack formation. An adhesive joint containing micro-cracks will absorb considerably more moisture than an undamaged bonded system. Absorption increases with increasing stress, with significant increases and non-linear absorption occurring at stress levels approaching the yield stress of the adhesive [14]. Regions of high peel (out-of-plane tensile) stress, such as the ends of bond-lines, are more permeable to moisture than regions of low stress, leading to preferential absorption in these regions and faster degradation.

2.7 BIOLOGICAL DEGRADATION

Biological degradation is not a common form of degradation as many thermoplastics are resistant to microbiological attack by fungi or bacteria. The only cases where biological attack has influenced life expectancy has been with certain polyurethanes and some low molecular weight additives in PVC [7]. 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 [54]. 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.

3 ACCELERATED AGEING TEST METHODS

Safe and reliable design of engineering components/structures for long-term operation in hostile environments depends on the availability of reliable engineering data that can be used for material qualification, and to predict structural integrity and life expectancy. It also requires the designer/engineer to have a good understanding of physical and chemical degradation of surface and bulk properties resulting from exposure to environmental conditions. Whilst the life expectancy of products in non-demanding applications have traditionally been predicted from previous in-service experience (i.e. service conditions considered identical or similar to those for which data already exists), long-term or critical applications require the use of accelerated ageing regimes to generate data to simulate the engineering requirements and life expectancy of the component. This section provides an overview of the test methods and standards for conducting accelerated testing of polymers and composites in hostile environments.

3.1 THERMAL CONDITIONING

Typical service temperatures for FRPs generally range from -55°C to 200°C, although some products may be designed for higher and/or lower values (e.g. space applications). In general, these temperatures relate to continuous or repeated exposure, but occasionally short-term or single-shot capability may be required. ISO 291 [55] and ASTM D618 [56] provide specifications relating to the conditioning (although not necessarily to equilibrium) and testing of all plastics (including FRPs) and test specimen types at constant atmospheric conditions. Special atmospheres applicable to a particular test or material or simulating a particular climatic environment are not included. The most accurate and commonly used condition in test laboratories is 23 ± 1°C, with or without humidity control at 50 ± 5% RH. Ordinary tolerances are ± 2°C and ± 10% RH. Thermal conditioning is generally conducted using a circulatory oven or chamber to maintain a steady flow of air through the oven and to ensure uniform temperature distribution within the test chamber. It is recommended that test specimens should be exposed to air on all sides, unless otherwise specified. The chamber should be significantly larger than the volume occupied by loading fixtures and test specimens. It is good practice to limit the occupied volume to 10% of the free chamber space, and that specimens are separated by 1 to 2 centimetres. The temperature tolerance should be within ± 2°C, or better.

Heat ageing tests [7] should include a minimum of three (preferably five) temperatures for periods of 1,000 hours (~6 weeks), or more in order to generate sufficient data that can be extrapolated to lower (i.e. service conditions). It is important that at the highest temperature the degradation mechanism is the same as experienced at the lower temperatures. The same specimens can be used throughout the test provided the test is non-destructive (e.g. no loss of mass or colour change). If the measurements are destructive then a batch of at least five specimens (preferably more) must be prepared for each combination of duration and temperature. It is advisable to include reserve sets (2 off) in case the threshold of degradation is not reached. The minimum number of durations should be at least five to determine the change of property with time. The spacing of exposure times is usually linear for heat ageing. ISO 11403-3 [57] specifies test procedures for the acquisition and presentation of multipoint data which demonstrate the behaviour of plastics for prolonged exposure to heat, liquid chemicals, environmental stress cracking under a constant tensile stress and artificial weathering.

Thermal Stability Test Methods: A standard procedure for assessing the thermal stability of polymers exposed to elevated temperature for long periods is given in ISO 2578 [58]. The term thermal endurance refers to tests conducted in air under ambient conditions, excluding any other influences including applied stress. It is assumed that a practically linear relationship exists between the logarithm of the time required to cause the predetermined property to change and the reciprocal of the corresponding absolute temperature (Arrhenius Law – see Section 4.1). 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 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 [59] and ASTM D1203 [60] cover the stability of plasticisers in polymers, both standards measuring the amount of plasticiser that is lost due to absorption on activated charcoal. Both standards are essentially used for quality control testing.

Heat Distortion Temperature (HDT) is often the only criterion used in determining a material's "fitness for purpose" at elevated temperatures (i.e. upper limit of safe operating temperature at which the material can support a load for any appreciable time). HDT (or temperature of deflection) tests detect the onset of excessive deformation as a function of increasing temperature. ISO 75-1, 2 and 3 [61-63] and ASTM D648 [64] specify test procedures for determining HDT of polymers and composites. The test procedure for determining HDT, as described in ISO 75-1 [61], consists of three-point loading of a rectangular beam (120 mm long, 3 to 4 mm wide and 10 to 15 mm thick) immersed in a heated mineral oil bath, whose temperature is constantly increased at a rate of 2°C/min. The separation between the test specimen supports is 100 mm. The central deflection is continuously monitored. HDT is reached when the central deflection of the test specimen reaches a specified deflection value for a given nominal surface stress. The standard deflection depends upon the specimen thickness (e.g. 0.32 mm for a specimen thickness of 10 mm and a nominal surface stress of 1.80 MPa). The ISO 75 standard applies to both neat resins (Part 2) [60] and FRPs (Part 3) [61]. HDT test data are only suitable for materials selection and acceptance, and not for design purposes. The results obtained using this method do not necessarily represent maximum use temperatures, because in practice essential factors such as time, loading conditions and nominal surface stress may differ for the different testing conditions. Composite materials are not thermally isotropic and, thick samples, will contain a temperature gradient. HDT records a different thermal transition temperature that is proportional to, but generally lower than T_g. Results obtained using ISO 75 indicate HDT values are higher for unreinforced plastics (measured using Part 2) compared with the corresponding results obtained for the reinforced version measured using Part 3. T_g can also be used to set upper service temperature limits for polymeric systems.

Glass Transition Temperature, T_g of composites is generally measured using DMA (Dynamic Mechanical Analysis) in accordance with either ISO 6721-11 [65] or ASTM D7028 [66]. Whereas T_g of unreinforced plastics is measured using DSC (Differential Scanning Calorimetry) in accordance with either ISO 11357-2 [67] or ASTM D3418 [68]. As DMA data is heating rate dependent, it is recommended tests are carried out at three different heating rates. Linear regression line of best fit of the T_g data when extrapolated to a zero-heating rate will give the true T_g value, coinciding with DSC data.

Sub-Zero Temperatures: The basic principles of elevated temperature testing also apply to low temperatures. Additional time, however, may be required to reach the test temperature and the temperatures achievable may depend strongly on the dimensions and degree of insulation of the environmental chamber. It can be difficult to cool to low temperatures in large chambers. Very low temperature medical freezers and environmental chambers are commercially available - minimum operating temperatures are typically between -40°C and -100°C. Liquid nitrogen-based cooling systems can achieve temperatures of around -150°C, or lower. Even though a liquid nitrogen-based system may be capable of achieving a temperature of -150°C, it takes a considerable time to reach very low temperatures. It is recommended that dry nitrogen gas be circulated through the test chamber to prevent moisture condensation and ice formation on the test specimen and test apparatus. The test apparatus should be constructed from stainless steel to avoid corrosion products forming on the apparatus surface. All moving parts should be coated in molybdenum grease to prevent stiction.

Freeze-Thaw Testing: ASTM D7792 [69] prescribes freeze-thaw conditioning procedures designed to evaluate and compare the effect of 100 freeze-thaw cycles under controlled laboratory conditions on pultruded FRP composites to be used in structural design applications. Freeze-thaw cycle range is typically 23°C to -20°C with a total cycle duration of ~2-5 hours. Maximum cycle rate (cycle duration) will depend on the heating and cooling rate capability of the test chamber. It is recommended that samples are sealed within polyethylene bags throughout testing to minimize interaction with the environment and prevent the moisture conditioned samples from moisture loss [70].

3.2 MOISTURE CONDITIONING

The degree of degradation that occurs in polymeric systems when in service can often be linked directly with the amount of moisture absorbed. Moisture absorption kinetics of polymer systems will differ widely and change with physical ageing. Moisture conditioning can be carried out using either full immersion (where solution chemistry needs to be considered) or in a humid atmosphere (where relative humidity, RH, should be controlled). Absorption and diffusion rates are also temperature dependent. Equilibrium moisture concentrations normally increase with increasing RH. Immersion usually results in a higher equilibrium moisture concentration than atmospheric exposure.

The approach often adopted, is to define a constant exposure environment that will produce a moisture level that is representative of a component or structure that has been exposed to an environment at a particular geographical location. The variability of a natural environment, that is daily, monthly, or seasonal changes in temperature and humidity are known to be a major factor in determining both the final moisture equilibrium level in the material and the distribution of moisture in the outer surface layers. The military consider the worst worldwide environment to be represented by 70°C and 85% RH.

The natural process of moisture absorption in engineering components/structures is normally very slow, and this makes it very difficult to reach an adequate degree of degradation in a structural test element in practical timescales. It has been found necessary, therefore, to speed up the moisture diffusion process by employing an accelerated conditioning technique that can ensure a representative level of degradation in a significantly reduced time.

There are two basic methods of moisture conditioning:

- Fixed-time conditioning, where a test specimen is exposed to a conditioning environment for a specified period; and
- Equilibrium conditioning, where a specimen is exposed until the material reaches equilibrium with the conditioning environment.

Fixed Time Conditioning: This approach is routinely employed for screening purposes and results in non-uniform moisture distribution through the thickness of the test specimen. Test data obtained from specimens conditioned in this manner are only considered suitable for comparing different batches of the same material or for quality control tests. It is essential that test specimens used in this manner are identical in dimensions and have similar surface finishes.

Equilibrium Conditioning: Ideally, comparative studies of water absorption properties of materials should be carried out only using the equilibrium moisture content of polymeric materials exposed to identical conditions. Equilibrium moisture concentration is most likely to indicate ‘worst-case’ material properties. Comparisons between polymeric systems with different moisture absorption characteristics are possible if the materials are preconditioned to equilibrium. The thicker the material the longer the time required to reach equilibrium, hence the use of relatively thin specimens to determine the “through-the-thickness” moisture diffusion coefficient.

An alternative approach to attempting to reach an equilibrium condition, involves altering the acceptance criteria to a given percentage of the chosen equilibrium condition. Conditioning the material to 95% of the full equilibrium state takes a relatively shorter time to reach than the full (100%) equilibrium condition. The time required to obtain the last 5% can take longer than the time taken to reach the 95% level. Clearly a very large saving in time is possible if a 95% of equilibrium level can be justified in terms of a non-significant change in the structural strength and stiffness properties.

Further acceleration can be obtained by increasing the relative humidity to the maximum that can be readily maintained (i.e. 96% RH). It is required that the acceleration method takes full advantage of the high rates of diffusion given by temperature and humidity and still achieve a reasonably realistic moisture absorption. It is not satisfactory to precondition at 96% RH, so that the equilibrium level in the outer surface layers exceeds the bulk equilibrium level obtained due to exposure in service. It is worth noting that the standard controllable temperature/humidity range for most environmental chambers is 5°C to 85°C with 10% to 98% RH, which indicates that the 96% RH requirement is at the upper operating limit of most chambers; it is difficult to accurately control high humidity levels at elevated temperatures.

Moisture Absorption Test Methods: ISO 62 [71], ASTM D570 [72] and ASTM D5229 [73] describe procedures for determining the moisture absorption properties and/or diffusion coefficients in the "through-the-thickness" direction of flat and curved solid plastics, when immersed in water or subjected to humid air under controlled conditions. ISO 62 is suitable for use with thermoset resin (inc. adhesives) and FRP specimens. ASTM D5229 is specific to polymer composites. The three standards assume Fickian diffusion behaviour with constant moisture absorption properties through-the-thickness of the test specimen. Non-Fickian (multi-phase) diffusion behaviour is not covered in either standard.

Conditioning usually consists of exposing pre-dried specimens to a steady-state environment (constant temperature and constant moisture exposure level) and measuring the moisture gain (i.e. average moisture content) for a prescribed period or until the specimen reaches moisture equilibrium. Specimens should be free of voids and surface damage/defects to ensure accurate moisture absorption measurements. Absorption is dependent on the level of porosity with the rate of moisture absorbed and moisture concentration at saturation increasing with the level of porosity. Surface roughness can also affect moisture uptake and drying. Rough surfaces are more difficult to dry and present a larger surface area to the surrounding environment.
The amount of water absorbed by the test specimen is determined by measuring its change in mass (i.e. difference between initial mass and the mass after exposure). All surfaces are in contact with the test environment. It is recommended that when determining moisture absorption properties that square shape specimens be used for homogeneous polymers. In this case, specimen dimensions and tolerances should comply with ISO 294-3 [74]. For FRPs, it is recommended that square specimens also be used with a width, $w \leq 100 \times$ a nominal thickness, d (typically 2 mm). Specimen dimensions need to be accurately measured. Small variations can result in significant errors in diffusivity calculations.

It is recommended that specimens be pre-dried in an oven maintained at 50 ± 2°C until the specimen weight reaches a constant value. The temperature of the drying oven should not exceed the maximum operating temperature of the polymeric system. Specimens are removed at fixed intervals (typically 24 hrs) and allowed to cool to room temperature in a desiccator before being weighed. After weighing, the specimen is returned to the oven and the process is repeated until the mass of the specimen is constant (zero datum level). To minimise moisture uptake prior to preconditioning, specimens are stored in a desiccator (sealed container with desiccant), at room temperature. It should be noted that under standard laboratory conditions many polymeric materials can absorb significant levels of moisture.

Moisture conditioned specimens need to be wiped with a clean cloth to ensure all surface water is removed prior to weighing. Specimens should be weighed immediately on removal from the test environment. When removed from the conditioning environment specimens will immediately dry and lose weight. A significant amount of moisture can be lost within a short period of time, thus compromising measurement accuracy. Damage may accumulate during long-term conditioning, and hence handling and monitoring of test specimens should be minimal. This is particularly pertinent to those specimens used for generating engineering data. Traveller specimens are required to monitor specimen moisture content throughout the environmental history (i.e. manufacture, storage, pre-conditioning and testing). The traveller specimens should have identical material properties, geometry and processing history as the test specimen. It is essential that moisture content prior to pre-conditioning be established.

As conditioning is often carried out at elevated temperature and humidity to accelerate moisture uptake, care should be taken to avoid exceeding the T_g of the material. It is advisable when using polymeric systems in load bearing FRP structures to ensure that the maximum operating (or conditioning) temperature is at least 30-40°C below the T_g of the material (considering moisture effects). The recommended maximum conditioning temperatures are 45°C and 70°C for 120°C and 180°C cure systems, respectively [75]. It is recommended that information on the moisture and temperature response of the material be obtained prior to environmental conditioning.

The rate of moisture uptake is rapid in the early stages of conditioning with the rate of moisture uptake decreasing with time. It is therefore necessary to make frequent weight measurements in the early stages (3-4 measurements on day one) followed by at least two readings per day for the remainder of the first week. At least one reading per day is required for the second week, followed by a gradual decrease in frequency as the rate of weight gain diminishes. It is recommended that weighing be carried out at approximately equal intervals of √(time).

The percentage uptake of water by weight, M, can be determined as follows:

$$M = \frac{\left(W_{wet} - W_{dry}\right)}{W_{dry}} \times 100\% \tag{3.1}$$

where wet and dry weights are denoted by W_{wet} and W_{dry}.

The increase in mass, M, as measured at regular time intervals, is plotted against time 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. Accurate records need to be kept on preconditioning sequence including relative humidity, temperature and time, measured weights, and derived moisture contents. In the case of aramid composites (e.g. Kevlar®), determination of diffusion coefficients can be complicated by the hygroscopic nature of the aramid fibres. For these materials, it is advisable to measure the moisture uptake of both the aramid fibre and resin separately to isolate the constituent contributions. Loss of water-soluble constituents (additives) from test samples may affect results (see Section 2.2). This can be checked by reconditioning (drying) the sample back to constant mass (M_c) and comparing against the original mass (M_0). If there is no loss of water-soluble matter, then $M_c = M_0$. The process would be repeated for different exposures times using traveller specimens. The relative mass uptake is calculated from the moisture content $M(t)$ at time t, initial mass M_0 and the reconditioned mass M_c:

$$M = \frac{M(t) - M_C}{M_0} \tag{3.2}$$

$$M = \frac{M(t) - M_0}{M_0} \quad \text{when } M_C = M_0 \tag{3.3}$$

The recommended procedure for humid environment conditioning is to use an environmental cabinet, which can control the temperature to within ±2°C and the relative humidity to within ±5%. Since diffusion rates depend on temperature it is preferred that the tolerances be smaller. Small changes in temperature or humidity can result in large variations in diffusivity, and hence the need to control the test environment to the utmost accuracy possible. A circulation fan is essential for ensuring uniform temperature and humidity throughout the chamber. It is ill advised to assume that the temperature and humidity settings on environmental conditioning equipment are correct, for example temperature control settings on water baths can be a few degrees in error. Temperature and humidity measurements using calibrated equipment should be carried out to ensure the control settings produce the test conditions required. Checks on control settings should be routinely carried out throughout the duration of testing to ensure environmental test conditions are maintained. Ideally, humidity and temperature of the environmental chamber should be continuously monitored using a data acquisition system with limit alarms. Should a monitoring system be unavailable it is advised to regularly check the temperature and humidity indicators on the equipment. Boiler units of humidity cabinets should be supplied from a deionised/distilled water reservoir to avoid mineral salt deposits on test specimens, and possible corrosion of test equipment and scaling of the plumbing.

Three Stage Conditioning: The approach is to expose the material to the maximum practical humidity that is available (i.e. 96% RH) until the moisture level in the bulk reaches the bulk equilibrium level at the lower humidity/temperature condition (i.e. 70°C/85% RH) [75]. The second stage is to expose the material to a lower humidity level (15% RH), a drying stage, to remove excess moisture in the outer surface layers. The third stage uses a relative humidity that will give the desired final moisture level (i.e. 85% RH). The distribution flattens out across the entire material thickness. The effectiveness of the technique relies on accurate mathematical modelling of moisture diffusion for each stage of moisture conditioning.

3.3 PRESSURISED MOISTURE CONDITIONING

The natural process of moisture absorption in engineering components/structures is normally very slow, which makes it very difficult to achieve saturated moisture content (or an adequate degree of degradation in a structural test element) in practical timescales. Although moisture conditioning of FRPs is often carried out at elevated temperature and/or humidity (e.g. 70°C/85% RH) to accelerate moisture uptake, it still can take considerable time to reach the required moisture content (~1-2 years). An alternative approach is to either immerse specimens in a fluid under pressure at elevated temperature or subject specimens to saturated water vapour at temperatures more than 100°C. Conditioning in both cases is carried out using a sealed pressure vessel.

Supersaturated Water Vapour Conditioning: ISO 22836 [76] specifies accelerated moisture absorption properties and supersaturated water vapour conditioning for FRPs using a sealed pressure vessel at temperatures more than 100°C. The purpose of the procedure is to screen test specimens with moisture by mechanical or thermal properties. ISO 22836 specifies a saturated water vapour condition of 120°C and 0.2 MPa (2 bar). The standard applies to carbon and glass fibre composites and their products with either thermoset or thermoplastic matrices, with a $T_g > 150°C$.

Supersaturated water vapour conditioning using a steam autoclave is an alternative option for inducing accelerated ageing, particularly for those FRPs with a cure temperature more than 120°C [77]. Commercial autoclaves, used for sterilization of medical equipment, are available for this purpose. Exposure to superheated pressurized steam (e.g. 2.2 bar and 136°C) can induce levels of moisture of 2 to 3 weight % in epoxy-based composites within 48 hours. Supersaturated water vapour conditioning is unsuitable for conditioning polyester and vinyl ester resin based FRPs, as these systems will suffer considerable material degradation. Supersaturated vapour conditioning could be useful for assessing environmental durability of thick laminated sections and for providing a worst case-scenario as to material degradation.

Pressurised Fluid Testing: The rate of moisture uptake of specimens immersed in a fluid under pressure, such as deep-sea environments, may be expected to increase with an increase in pressure. Poorly compacted (high porosity) materials tend to absorb moisture more rapidly under pressurized conditions than would occur under atmospheric conditions. Tests simulating deep-sea conditions can be carried out in specially designed pressure autoclaves. High pressure autoclaves can be heated internally using heating elements or externally using a heating blanket. Depressurizing samples back to atmospheric pressure can induce additional damage similar to the bends, particularly in porous materials. Cycling between high and low (atmospheric) pressure can propagate damage in samples.

Note: Pressure vessels must be used with care. Safety tests should be conducted routinely on the equipment to ensure the equipment is within safety specifications.

Moisture Expansion Measurement: Determination of moisture expansion coefficient involves measuring the dimensional change of the material in the principal directions as a function of moisture concentration (i.e. moisture weight gains). Specimen dimensions and tolerances should comply with ISO 294-3 [74]. Moisture expansion or swelling can be measured periodically with a micrometer, Vernier caliper, traveling microscope or continuously using strain gauges or embedded sensors (see [14]). It is assumed that all absorbed moisture is translated into a change in resin volume. In fact, during the initial stages of conditioning, water may also be filling micro-voids and cracks. A plot of swelling strain versus weight gain will show a change in gradient for high porosity materials.

3.4 WEATHERING TEST METHODS

At present, there is no universally agreed performance-based specification for accelerated weathering procedures. Performance based specifications are being developed by several recognized standards bodies including BSI, ISO, NACE, and customer end-users (e.g. NORSOK). The principle aim of these specifications is for the material system to meet a set of pre-determined laboratory performance-based requirements that vary depending on the service requirements. Key to the success of performance testing is the ability of being able to correlate laboratory test data with service performance.

It is important to note that there is no 'foolproof' test that will provide an accurate prediction of service performance and life expectancy. The predominant factors in climatic exposure are humidity, temperature and solar (ultraviolet) irradiation. The severity of these factors will depend on geographical location and need to be considered when designing with these materials. There is no accelerated weathering procedure that can accommodate the wide range of climatic conditions experienced geographically (e.g. Florida, Arizona, Persian Gulf and North Atlantic).

Natural Weathering: As the 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 the length of the life expectancy 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 [78]. Arizona is popular for exposure in hot dry climates and Florida for hot humid climates. Acceleration can also be achieved by using Fresnel mirrors [78] 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 877-1, 2 and 3 [79-81], ASTM D1435 [82], ASTM D4364 [83] and ASTM G24 [84]. ISO 15314 [85] describes methods for the exposure of plastics in a marine environment. Although intended for marine (salt water) exposure, the methodology can be used with outdoor brackish water and fresh-water exposures as well.

Accelerated Weathering: Accelerated weathering procedures involve continuous or cyclic exposure to a combination of salt spray, elevated and/or sub-zero temperatures, and ultraviolet (UV) radiation (artificial light source). An artificial weathering cabinet is used for this purpose. 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 determining synergistic effects (interactions) between the different parameters in the weathering process. The environmentally conditioned material is subjected to a series of tests (i.e. performance testing) to determine the degree of degradation (i.e. chemical resistance) as a function of exposure time. The criteria used to assess chemical resistance include mechanical properties, such as hardness, flexural modulus and strength, dimensional stability (i.e. swelling), weight change and appearance (i.e. colour, gloss retention, crazing, fibre prominence, blister formation, loss of surface resin, etc.). Whilst mechanical properties and dimensional stability are quantitatively measurable quantities, several appearance criteria tend to be assessed in qualitative terms, and hence the question arises as to the reliability of the assessment. A major challenge is to ensure that performance testing for determination of chemical resistance (level of degradation) is based upon a set of "quantitatively" measurable criteria, avoiding qualitative or subjective assessment.

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 UV [86].

Carbon-Arc Lamps: Until the 1960s, the only light source available with sufficient radiation levels were carbon-arc lamps. In recent years, usage of carbon-arc lamps has diminished in favour of xenon-arc and fluorescent UV testing because carbon-arc instruments are expensive, difficult to operate, and the spectrum is not a good match for the solar radiation, particularly at the lower wavelengths (<350 nm). A typical spectrum from a carbon-arc consists of a series of line emissions that are superimposed on to a continuous background (Figure 10) [86]. The UV output primarily consists of two very large spikes of energy (far more intense than natural sunlight) centred around 380 nm and 400 nm. This spectrum has very little output below 350 nm. These high energy, short wavelengths lead to such intensive damage that it bears little relationship to any natural weathering process. It is worth noting that UV light with wavelengths shorter than 320 nm is responsible for nearly all polymer degradation. Despite these deficiencies, carbon-arc lamps are still in commercial use today and their use for plastics is standardised in ISO 4892-4 [87] and ASTM D1499 [88].

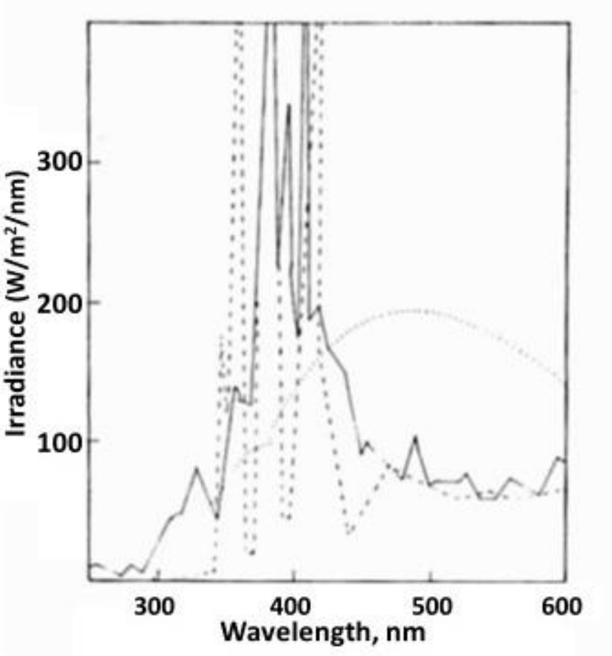


Figure 10 Spectrum of carbon-arc lamp (—), carbon-arc lamp with Cordex D filter (---) and noonday Chicago sunlight (····) [86]

Xenon Lamps: Xenon-arc lamps give a much better spectral simulation to natural sunlight (Figure 11) 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 optical filters can easily remove these shorter wavelengths. Xenon lamps also emit high levels of infrared radiation, which must also be removed to prevent overheating of the specimen. A xenon lamp with an appropriate optical filter (i.e. Daylight filter) provides an excellent spectral reproduction of the full solar spectrum – reproducing both the UV and the light portions of sunlight. Typical xenon exposure equipment such as the Xenon 1200 includes water spray, light/dark cycling, and humidity control [78]. 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 4892-2 [89] and ASTM D2565 [90].

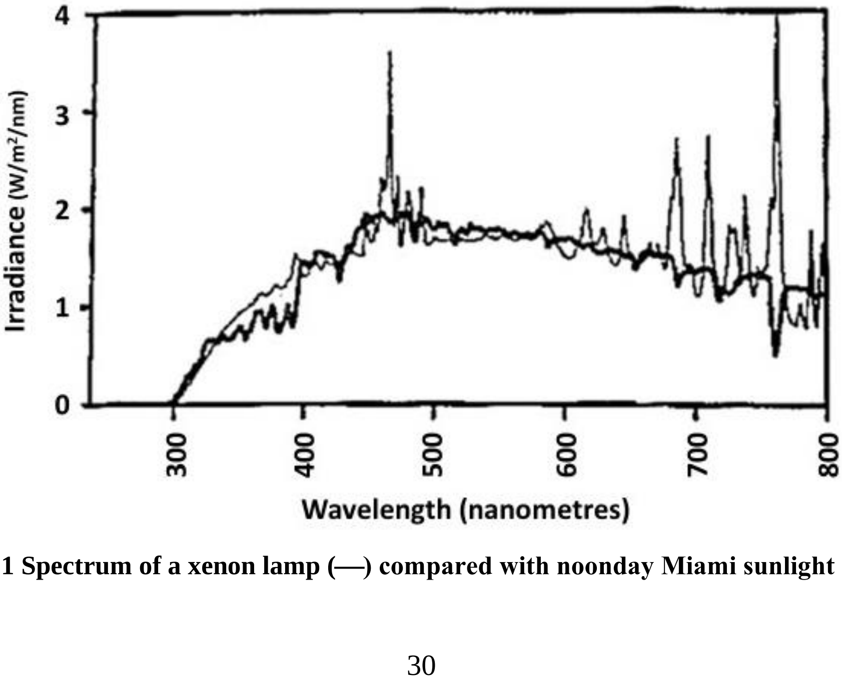


Figure 11 Spectrum of a xenon lamp (—) compared with noonday Miami sunlight (━) [86]

Fluorescent UV 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 12). 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 consequently 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 (further details on photodegradation see [31, 86]). Standard test procedures for the use of fluorescent tube are given in ISO 4892-3 [91] and ASTM D4329 [92].

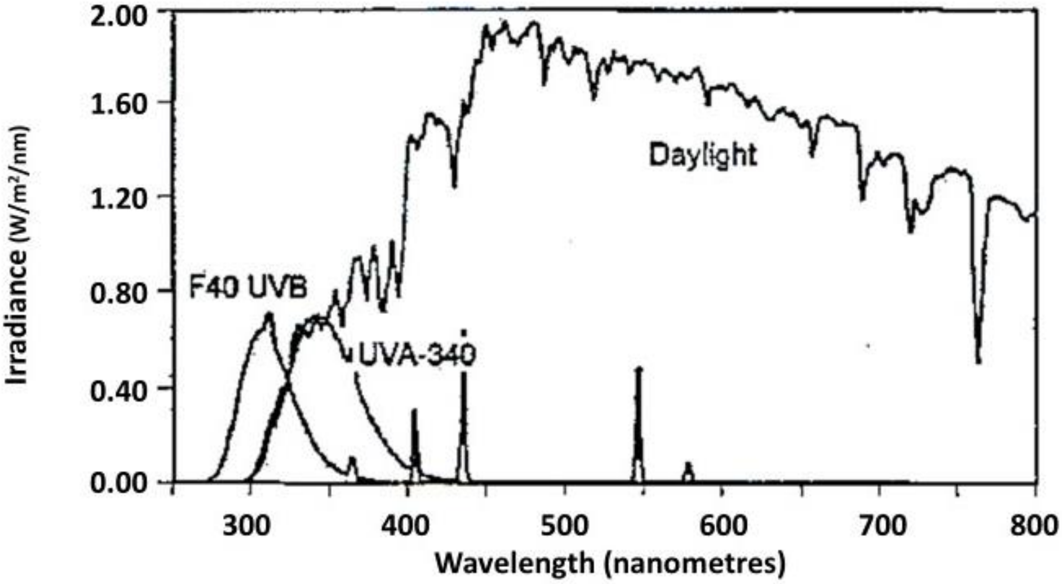


Figure 12 Spectra of UV-A and UV-B fluorescent lamps compared to noonday Miami sunlight [86]

Ionising Radiation: The effect of ionising radiation on degradation of polymeric materials is often accelerated by increasing the radiation dose using gamma radiation from an isotope or electron beam accelerator [93]. The dosage rate can also influence the rate of degradation in polymers, so it is advisable to conduct tests at least at two 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.

ASTM D1879 [94] specifies conditions for the exposure of adhesives in bonded specimens to ionizing radiation prior to determination of radiation-induced changes in physical or chemical properties. The standard covers a range of radiation types (i.e. gamma or X-ray radiation, electron or beta radiation, neutrons, and mixtures of these such as reactor radiation) under ambient (air or other medium), controlled temperature or load, or a combination of two or more of these variables.

The International Electrotechnical Commission (IEC) series IEC 61244 “Determination of Long-Term Ageing in Polymers” developed for evaluation and qualification of electrical insulating materials and systems includes the following technical specifications:

- IEC 61244-1 [95] reviews experimental techniques to quantitatively monitor the effects when oxygen is present during ageing of polymers in various environments including temperature, UV, and other forms of ionizing radiation,
- IEC 61244-2 [96] applies to procedures for predicting ageing of polymeric materials at low dose rates; can be used to extrapolate data obtained from high dose rate experiments to the low dose rates typical of service conditions (see also Section 4.10).

Salt Spray Cabinets: Special cabinets are used for salt spray (and salt mist) exposure in which a spray of sodium chloride solution is produced at specified conditions. This method of conditioning was developed for determining corrosion resistance of metals for marine and offshore applications. The average salt spray output used is 1.6 ml/hour and the concentration of the salt solution being typically 50 ± 10 g/litre. Salt fog (5% NaCl) or artificial seawater as the electrolyte is used for simulating offshore conditions. The drying temperature frequently used is 35 ± 2°C. It is recommended that salt spray exposure be conducted in accordance with ISO 7253 [97]. Water used for the salt spray must meet the requirements of ISO 4892-1, clause 5.3 [98]. The chamber should have a spray system capable of directing an intermittent water spray onto both the front and back surfaces of the test specimens. The water spray must be uniformly distributed over the specimens.

The chamber should be constructed from corrosion resistant material (e.g. stainless steel). In addition to controlling irradiance, the test chamber should have controlled temperature, and if required controlled humidity. When required by the exposure used, the chamber should also include facilities for the provision of salt spray or the formation of condensation on the specimen surfaces, or for immersion of the specimens in water. Irradiance at any position in the area used for the specimen exposure shall be at least 80% of the maximum irradiance. For some materials of high reflectivity, periodic repositioning of specimens is recommended to ensure uniformity of exposures. Requirements and procedure for periodic repositioning of specimens is described in ISO 4892-1 [98]. If the lamp system (one or more lamp(s) is centrally positioned in the chamber, the effect of eccentricity of the lamp(s) on the uniformity of exposure may be reduced by using a rotating frame carrying the specimens or by repositioning or rotating the lamps. It is important that lamps that generate ozone should be isolated from the test specimens and the ozone vented directly to the outside of the building.

Mounting Test Specimens: Specimens should be supported within the test chamber using an open holding frame, which can be adjusted to allow double-sided or single-sided exposure. A solid backing can be inserted into the holding frame for single-sided exposure. Support equipment needs to be constructed using corrosion resistant materials, such as stainless steel (not brass, copper or steel). Consideration needs to be given to the spacing between the backing and the test specimen and ensuring that the holding frame does not introduce stresses into the test specimens. In order to simulate actual topside service conditions, only one surface should be exposed to salt spray and UV radiation. Each specimen should be identified by suitable indelible marking, avoiding areas to be used for subsequent testing. It is advisable to trial all test equipment before carrying out conditioning of test specimens. This is to ensure that the test conditions are met and that all controlling, and monitoring equipment are performing to specification. Maintenance should be planned to avoid disrupting the tests. (N.B. include additional specimens in contingency of unforeseen technical problems and for checks on test conditioning). If it is necessary to remove samples for periodic assessment, such as measuring colour change, avoid handling the exposed surfaces and return to the same position in the test chamber.

Accelerated Weathering Procedures: Accelerated weathering procedures generally involve cyclic exposure to a combination of salt spray, condensation, elevated temperature and UV radiation. These standards tend to exclude the effect of sub-zero temperatures often experienced in practice or in external exposure testing. It is recommended that when selecting a procedure for accelerated weathering, consideration should be given to including a sub-zero temperature excursion. A freeze cycle (-20°C for 24 hrs) has been included in ISO 20340 [99] to produce more realistic results.

The inclusion of the freeze cycle has been shown to produce results much more typical of those seen in practice or external exposure testing [100]. Test procedures excluding a freeze cycle give results not typical of those seen in service. The exposure cycle used in the procedure given in ISO 20340 [99] consists of the following stages (see also ISO 16474 [101] and ISO 9227 [102]):

- 72 hrs exposure to UV radiation and water alternating between:
  - 4 hrs exposure to UV (UVA 340 nm) at 60°C; and
  - 4 hrs exposure to moisture condensation at 50°C
- 72 hrs exposure to salt spray at 35°C
- 24 hrs exposure at -20°C

Performance Testing: Environmentally conditioned material will often be subjected to a series of tests (i.e. performance testing) to determine the degree of degradation (i.e. chemical resistance) as a function of exposure time. The criteria used to assess chemical resistance include material properties, such as hardness, flexural modulus and strength, dimensional stability (swelling), weight change and appearance (i.e. colour, gloss, crazing, fibre prominence, blister formation, loss of surface resin, etc.) [103]. Whilst mechanical properties and dimensional stability are quantitatively measurable quantities, several appearance criteria tend to be assessed in qualitative terms, and hence the question arises as to the reliability of the assessment. A major challenge is to ensure that performance testing for determination of chemical resistance (level of degradation) is based upon a set of “quantitatively” measurable criteria, avoiding qualitative or subjective assessment (see Section 3.5).

3.5 ACCELERATED TESTING IN AQUEOUS AND CHEMICAL ENVIRONMENTS

Safe and reliable design of engineering components/structures for long-term operation in hostile chemical environments depends on the availability of reliable engineering data that can be used for material qualification, and to predict structural integrity and life expectancy. It also requires the designer/engineer to have a good understanding of physical and chemical degradation of surface and bulk properties resulting from exposure to environmental conditions. Whilst the life expectancy of products in non-demanding applications have traditionally been predicted from previous in-service experience (i.e. service conditions considered identical or similar to those for which data already exist), long-term or critical applications require the use of accelerated ageing regimes to generate data to simulate the engineering requirements and life expectancy of the component. This section examines accelerated testing in aqueous and chemical environments (e.g. alkalis and acids).

Chemical Resistance: An important aspect for FRP composites in many applications is that they are frequently used for their good corrosion resistance (e.g. boats, process equipment, sewage applications). Part 2 of BS EN 13121 [104] 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 account for the chemical resistance of the material from which it is constructed. Table 7.1 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:

- Through media lists,
- Resin manufacturer’s data,
- Thermoplastic liner manufacturer’s data,
- Service experience,
- 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:

- The aggressive environments are divided into Categories 1, 2 and 3 media. There are comprehensive instructions depending on service temperatures, type of lining, etc.,
- For materials with a deflection temperature under load (DTUL) 20°C greater than the service temperature, cured according to the manufacturer's instructions, 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,
- Similar approach for thermoplastic liners when used,
- 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,
- Experimental testing is undertaken using the single-sided exposure arrangement shown in Figure 13, 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.
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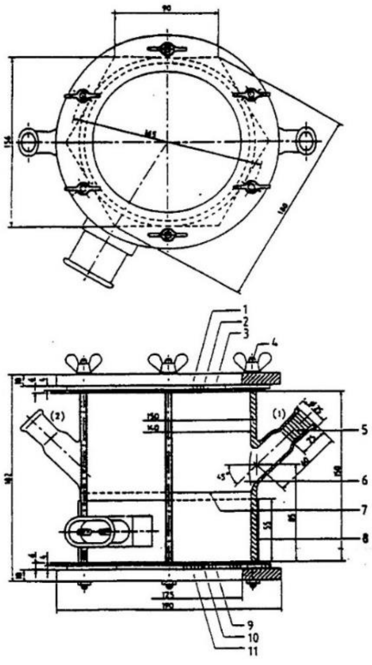


Figure 13 Chemical resistance test (flat plate specimens are numbered 2 and 10)

Degradation is assessed on a combination of appearance changes (10 assessment parameters e.g. gloss), dimensional stability (3 off) and flexural strength/modulus using ISO 14125 [105]. 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 2). 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). The weighting factors are different for single-sided and full immersion. The test can also be conducted by full immersion of 100 mm × 125 mm plates of the laminate or by testing in-situ within a tank.

Table 2 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	3	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 Determination of partial design factor, A_2

% of Total Assessment Score	A_2
≤ 20	1.1
≤ 30	1.2
≤ 40	1.3
≤ 50	1.4
>50	Unsuitable for purpose

The performance level score from each test should be multiplied by the weighting factor for each criterion (see Table 2), which are then combined to give a total score for the tests carried out. The total score is then compared with the maximum total, obtained by summing the product of each weighting for each criterion with the poorest performance rating for each of the tests carried out.

For example, if colour, gloss retention and Barcol hardness are the measured criteria then the maximum (worse) score would be:

$$2 \times 5 + 3 \times 5 + 5 \times 5 = 50$$

Barcol hardness test can be used to measure the surface hardness of FRPs (see BS EN 59 [106] and ASTM D2583 [107]). It may be more appropriate to use the Shore hardness test when assessing thermoplastic-based systems. Measurements need to be conducted at ten locations (or more) on the test surface. The measurements need to be spaced out and cover the entire surface to obtain an accurate indication of surface hardness. Portable hand-held Barcol hardness testers are commercially available and come with calibration discs. When used correctly, the results are generally consistent. Measurements on smooth surfaces should be within ±5% of the average value measured. Hardness measurements will be affected by surface roughness with the degree of uncertainty increasing with surface roughness. Hardness decreases with environmental exposure time; asymptotically approaching a constant value. The disadvantage using Barcol hardness is that it leaves small permanent imprints on the surface, a possible source of environmental ingress and surface damage.

Gloss (or Gloss Retention) can be measured using a portable hand-held meter. It is recommended that surface reflectivity of the weathered and "as-received" materials be made at a fixed angle of 60°. Measurements need to be conducted at ten locations (or more) on the test surface. The measurements need to be spaced out and cover the entire surface to obtain an accurate indication of surface hardness. In the case of highly reflective surfaces, a fixed angle of 20° is recommended. The instrument projects a collimated beam of white light (filtered to give a spectrum response like that of the human eye) onto the target surface at a specific angle and measures the amount of specular reflected light. Surface degradation (e.g. micro-cracking, loss of surface resin and fibre prominence, etc.) causes the incident light to be scattered at other angles, such that the scatter increases with the level of degradation. Gloss retention decreases rapidly with environmental exposure time. Precise measurement of colour change, gloss or light transmission is covered in ISO 13468-1 and 2 [108, 109], ISO 14782 [110] and BS 2782 [111].

Colour change is frequently encountered when a polymeric material has been exposed to UV light for extensive periods of time. The discolouration can be accurately measured using spectrophotometry (see ISO 13468-1 and 2 [108, 109], and ISO 14782 [110] – see also [112]). Portable hand-held colour meters are also available for field inspection. It is important when using these devices in the field that natural light does not impinge on the measurements. The spectral reflectance should be measured for both the conditioned and "as-received" material. The spectrophotometer exposes a 10 mm diameter circular area on the surface to a light source with a daylight colour temperature and compares the percentage reflectance within the visible spectrum (360 - 750 nm wavelength) to that of reference white and black colour tiles [113]. The reflectance of the sample is measured at 1 nm wavelength intervals over the spectral range 380 nm to 780 nm.

GFRP Tanks, Vessels and Pipes: British standard BS EN 13121-3 [114] specifies requirements for the design, materials selection, construction, inspection, testing and erection of vessels and tanks in FRPs. The standard covers a wide range of materials and processing routes and includes design factors to account for the deterioration of the laminated structure due to long-term exposure to combinations of chemical environments, elevated temperature and sub-zero temperatures, and alternating loads. Geometries covered include cylindrical and spherical shells, rectangular tanks, flanges and domes. The document claims that the adoption of a minimum design factor will prevent ESC of the laminated vessels and tanks exposed to aqueous environments.

ASTM C581 [115] was designed for evaluating, in an unstressed state, the chemical resistance of thermosetting resin matrices used in FRPs. This practice provides for the determination of changes in the following properties, of the test specimens and test reagent after exposure of the specimens to the reagent: hardness of specimens, weight change thickness, appearance of specimens, appearance of immersion media, and flexural strength and modulus. ASTM C582 [116] covers composition, thickness, fabricating procedures, and physical property requirements for GFRP thermoset polyester, vinyl ester, or other qualified thermosetting resin laminates comprising the materials of construction for reinforced thermosetting plastic (RTP) corrosion-resistant tanks, piping, and equipment. This specification is limited to fabrication by contact moulding. ISO 10952 [117] prescribes requirements and recommendations for the qualification and design, installation, testing and inspection for the external application of composite repair systems to corroded or damaged pipework, pipelines, tanks, and vessels used in the petroleum, petrochemical, and natural gas industries.

Product Testing: Combined stress and environmental conditions (see also Sections 3.6 and 3.7) are used in some product test methods. BS EN 14364 [118] and ASTM D3681 [119] are often used by industry to determine the chemical–resistant properties of GFRP pipes. Testing consists of exposing the interior of a pipe section to a corrosive solution (Figure 14) while the pipe is subjected to a constant compressive deflection until the structure fails. The test is carried out at several deflections and the time-to-failure is measured for each test. The long-term chemical resistance of the pipe is obtained by extrapolating to 50 years the log-log linear regression line for the initial strain level. This test is appropriate to structures buried underground, such as sewer pipes, which will experience a constant strain throughout the life of the structure.

A self-stressing fixture can be used to apply a constant displacement. Alternatively, a constant load, often in the form of a dead weight, is applied to the pipe section and the creep behaviour is monitored. Time-to-failure is plotted either as a function of stress or as a function of initial strain. This test is appropriate to above ground pipes. Acoustic emission (AE) is often used to monitor the structural integrity of GRP tanks and vessels under pressure.

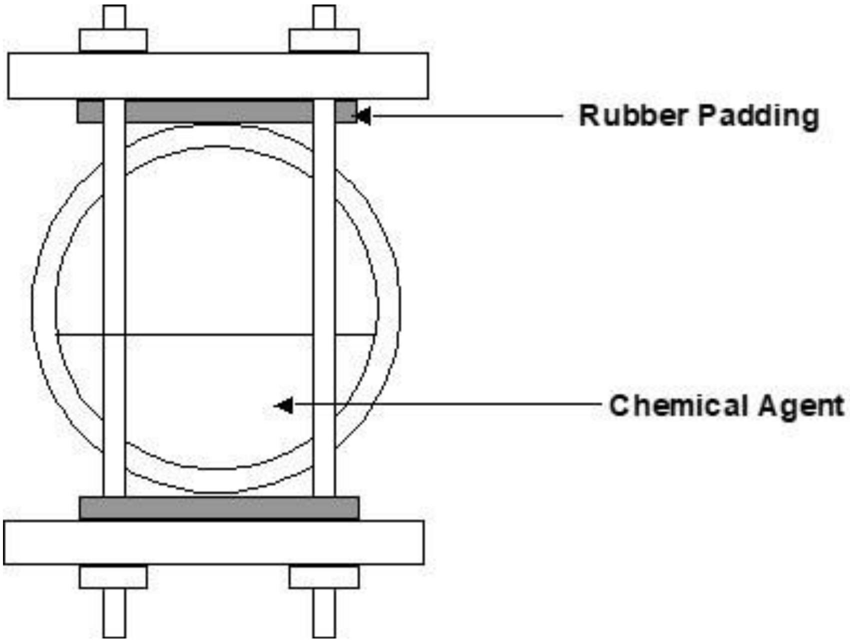


Figure 14 Strain corrosion test apparatus

The American Concrete Institute standard ACI 440.3R-04 "Guide Test Methods for Fibre-Reinforced Polymers for Reinforcing or Strengthening Concrete Structures" [120] specifies environmental conditions representative of porewater in Portland cement for testing GFRP rebars for concrete reinforcement. The requirements of the test solution are listed below:

- $Ca(OH)_2$ – 118.5 g
- NaOH – 0.9 g
- KOH – 4.2 g
- Deionised water – 1 litre
- pH of 12.6 – 13.0 and temperature 60°C

The solution is supersaturated with $Ca(OH)_2$, as a result CO_2 is continually released into solution, thus ensuring the pH level remains within the specified limits of 12.6 and 13.0.

It is quite common for creep tests to be carried out under adverse conditions using standard test coupon specimens (i.e. flexure and tension). ISO 175 [4], BS EN 2489 [121] and ASTM D 543 [122] cover the absorption of chemical liquids into polymers. ASTM C666 [123] developed for assessing the resistance of concrete freezing and thawing is also used to assess the resistance of CFRP and GFRP wrap systems used to repair (rehabilitate) corrosion-damaged concrete columns on bridges. The standard specifies a freeze-thaw cycle temperature range of -17.8°C to 4.4°C (0 to 40°F) and that the heating and cooling rate between the two temperatures should be not less than 2 hours and no more than 5 hours. ISO 21746 [3] specifies the apparatus, the reagents, and the procedure to be used in conducting the neutral salt spray (NSS), acetic acid salt spray (AASS) and copper-accelerated acetic acid salt spray (CASS) tests for assessment of the galvanic corrosion resistance of joints and bonded structures between CFRPs and metallic materials.

Simulating Chemical Spillage Effects (Intermittent Exposure): Chemical spillage can be simulated by cyclic exposure of the material surface through dipping the test specimens into chemical solution using a motorized crane for a short-time duration and then removing. A suggested cycle is 18 minutes exposure followed by 102 minutes of drying. Ideally, the surface should be rinsed after removal from solution and then allowed to dry under ambient conditions. The ratio of immersion/drying time is specified in several accelerated weathering and environmental testing standards. The specimens are clamped in a manner that allows only the top surface to encounter the chemical solution. Care needs to be taken to ensure that there is no overflow due to liquid displacement when immersing the specimens in solution, and that a crust (residue layer) does not form on the test equipment and specimens.

Chemical Test Equipment: Treatment tanks (Figure 15) or containers with chemical solutions should be of sufficient size to accommodate the specimens to be conditioned (i.e. volume of chemical solution should be well in excess of the volume occupied by the component and test fixture in solution). Tests may need to be carried out to determine the minimum volume required to condition a component. Treatment tanks used in chemical etching processes should be equipped with temperature controls and should be regularly agitated or stirred to prevent local overheating and to ensure uniform concentration of the chemical etching solution. The tanks should be suitably lined to prevent reaction between the tank and the chemical solution, thus ensuring no adverse effect on the solution used or the surfaces being treated. Chemical tanks need to be regularly monitored to ensure the temperature, fluid level and pH level remain constant and within the specified range. Ideally, the process of ensuring the fluid level in the test tank remains constant should be automated, but in most cases this a manual operation. In the latter case, it is recommended to use fully sealed containers.

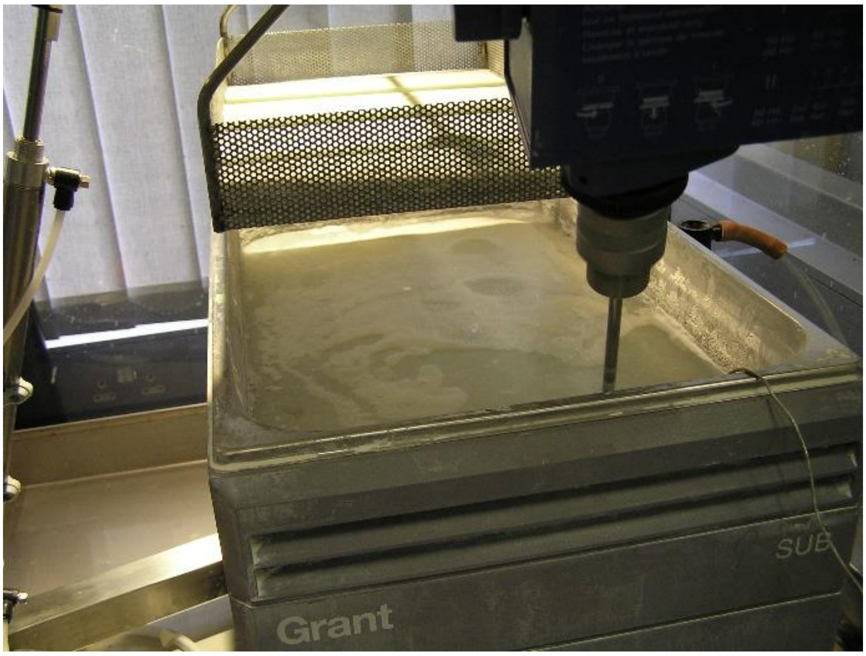


Figure 15 Chemical tank with motorised stirrer (courtesy of RAPRA Technology Ltd)

The temperature of test solution should be checked to ensure it conforms to specification. There may be a few degrees difference between the temperature of the heating chamber or bath and the test solution. In the case of exposure to aqueous solutions, it may be necessary to regularly flush the system with new solution or manually replace when the change in pH level goes outside the specification. The pH level of alkaline and acidic solutions will change with exposure time and is temperature dependent. The pH of alkaline solutions will decrease with increasing exposure time and temperature. Portable hand-held pH meters are available commercially. These devices come with liquid satchels with a known pH level to check that the meter is within calibration. This check should be carried out before testing begins and routinely throughout the test programme.

Care needs to be taken when handling, storing and disposing of alkali and acid solutions. These chemicals are particularly hazardous at elevated temperatures. When handling chemically conditioned specimens it is recommended that the specimens be rinsed in deionised water to remove chemical residue and then dried. Rinse tanks should be large enough to accommodate the specimens that have been chemically conditioned and should be equipped to allow for circulation of clean water to prevent build-up or carryover of residue on the test specimens. Stainless steel or polypropylene tanks or containers can be used for conditioning specimens in alkali solutions. The latter has the advantage of having a low thermal conductivity, and therefore it is easier and safer to handle. If polypropylene boxes are used, then fully moulded construction should be used, and welded seams avoided. Self-stressing fixtures, such as the flexure rig can be quite heavy and cumbersome, and combined with the weight of several litres of fluid the test unit becomes difficult to handle. Glass tanks are ill advised for housing test fixtures. Where loads are applied to test specimens whilst in solution using self-stressing fixtures, then the applied stress needs to be regularly checked and appropriate adjustments made to the mechanical fixture (e.g. tightening springs) – see also Section 3.8.

Specimen Mounting and Handling: It is important to identify each specimen by suitable indelible marking, avoiding areas to be used for subsequent testing, and produce a plan of test specimen positions. Exposure to alkaline or acidic solutions at elevated temperature can quickly degrade identifying marks on the test specimen surface. It may be necessary to mark the samples several times throughout the duration of the test. The spacing between specimens should be sufficient to ensure complete surface contact with the surrounding environment. The location of test specimens in the test environment should be carefully documented in case moisture measurements or non-destructive testing needs to be carried out on the test specimens throughout the duration of the test programme. Accurate records need to be kept on preconditioning sequence including relative humidity, pressure, temperature and time, pH level and applied stress.

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 [124]. 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. ISO 14855-1 [125] method is designed to simulate typical aerobic composting conditions for the organic fraction of solid mixed municipal waste – standard directed towards recycling materials rather than in-service durability.

3.7 ENVIRONMENTAL STRESS CRACKING TEST METHODS

Environmental Stress Crack (ESC) is one of the main causes of failure in polymeric materials accounting for approximately 30% of all in-service failures. Assessing whether a particular polymer/environment combination results in ESC is therefore essential in determining a product’s long-term properties. The evaluation of ESC in thermoplastics is covered by several national and international standards [126]. 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 (ISO 22088-3 [127])
- Bent strip test for flexible materials (ASTM D1693 [128])
- Ball and pin impression (ISO 22088-4 [129])
- Constant tensile deformation (ISO 22088-5 [130])
- Slow strain rate testing (ISO 22088-6 [131])

Constant Load Tests

- Constant tensile stress (ISO 22088-2 [132])
- C-ring tests (ISO 7539-5 [133] and ASTM G38 [134])

Note: ISO 7539-5 [130] and ASTM G38 [134] specify procedures for preparation and use of C-ring stress corrosion test specimens.

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 in [126].

Bent Strip Tests: The bent strip test (ISO 22088-3 [127]) involves clamping the test specimen to a semi-circular former to apply a known strain to the specimen. The radius of curvature of the former can be varied to induce different levels of strain in the specimen. This strain may be calculated using the following equation:

$$\varepsilon(\%) = \frac{d}{2r + d} \times 100 \qquad (3.4)$$

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 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.

Bent Strip for Flexible Materials: This test was developed by Bell laboratories in the USA and has since been standardised as ASTM D1693 [128]. The technique is suitable for flexible polymers such as polyethylene but should only really be used for quality control purposes.

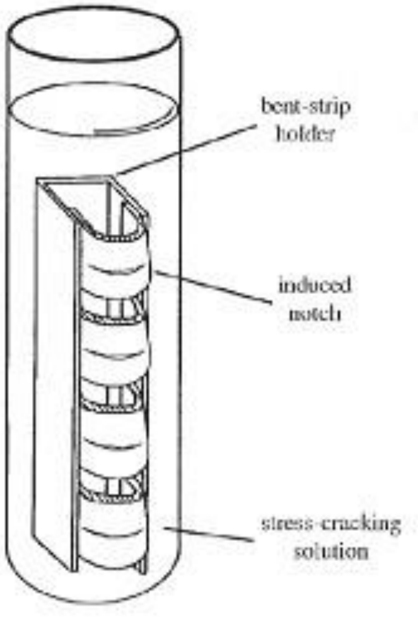


Figure 16 Bent strip technique for flexible polymers [128]

An illustration of the type of apparatus used in this test method is shown in Figure 16. The specimens used in this test are notched rectangular strips (38 × 13 × 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.

Ball and Pin Impression: The ball and pin impression test (ISO 22088-4 [129]) 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.

Constant Tensile Deformation: The constant tensile deformation test method, specified in ISO 22088-5 [130], 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 (4 and 5) superimpose on one another (see Figure 17). 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.

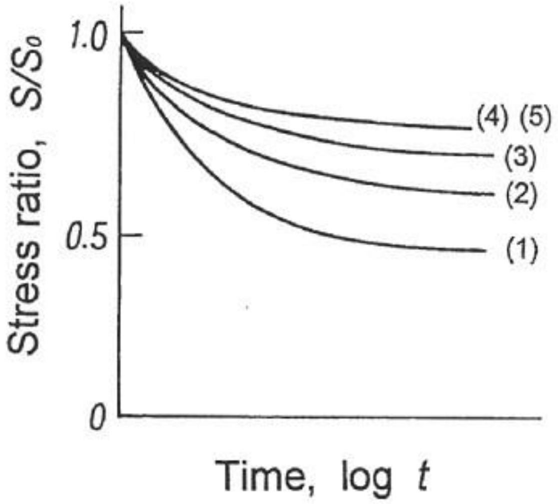


Figure 17 Stress relaxation curves obtained using progressively smaller levels of deformation (1 > 5) [130]
(Note: S_0 is the initial stress and S is the stress at time t)

Slow Strain Rate Testing: The slow strain rate method (ISO 22088-6 [131]) is used for characterising the performance of plastics (and metals). 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 18. The main advantages of the slow stain rate test are that it is relatively rapid, requires few specimens and can be automated.

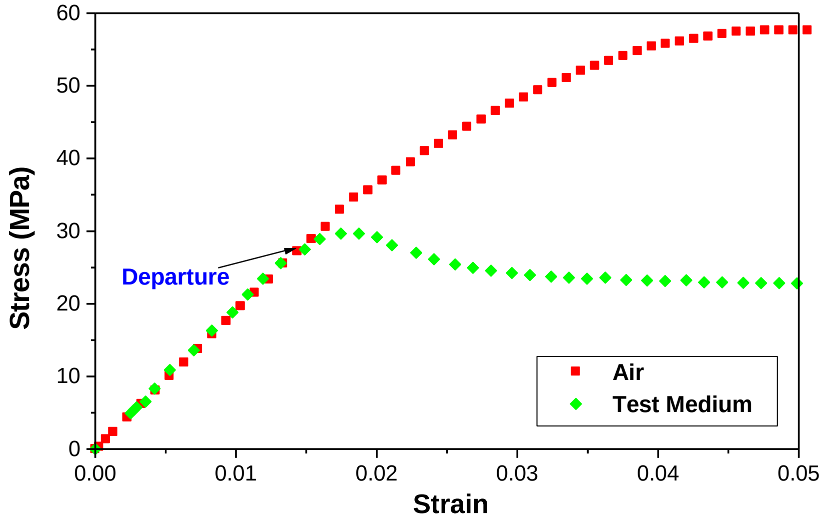


Figure 18 Typical stress-strain plot showing difference in stress/strain profile for material exposed in air and in the test medium

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 (ISO 22088-2 [132]). An illustration of the type of apparatus used in this test method is shown in Figure 19. 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. An environmental cell used for constant load tensile test is shown in Figure 20. 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.

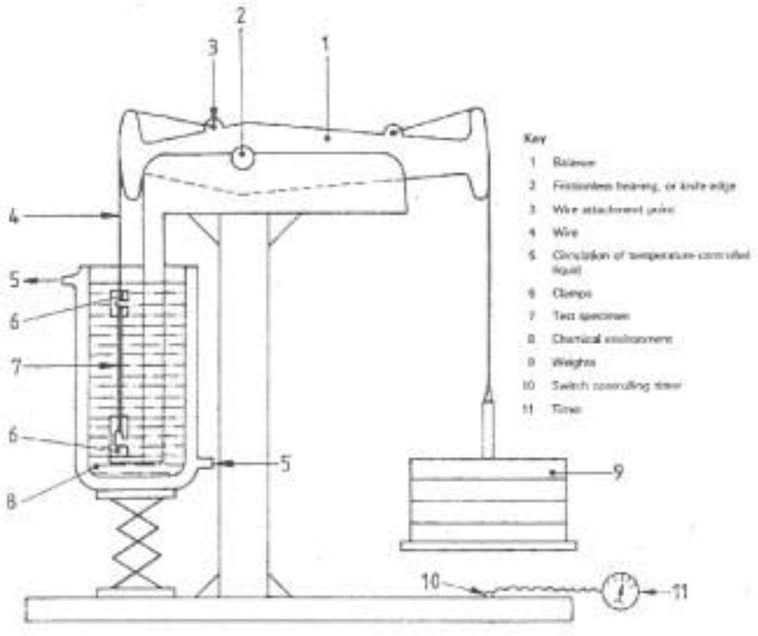


Figure 19 Illustration of typical apparatus used for a constant load test

Figure 20 Typical environmental cell used for the constant load tensile test

C-ring Tests: Typical apparatus for testing C-ring specimens is shown in Figure 21. 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 (see ISO 7539-5 [133] and ASTM G38 [134]). An almost constant load can be developed on the C-ring specimen by placing a calibrated spring on the loading bolt.

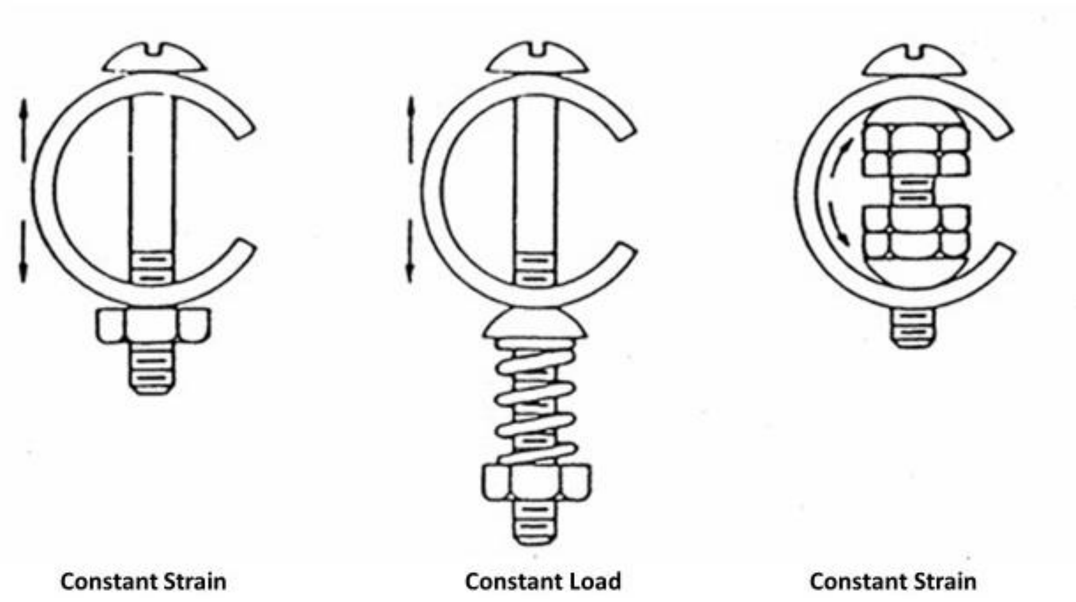


Figure 21 C-ring test methods for assess ESC in pipe-sections

Aviation Product Exposure: An evaluation procedure for assessing the suitability of polymer resin systems for applications involving exposure to harmful fluid environment is presented in military handbook MIL-HDBK-17-1F [135]. The procedure accounts for different exposure levels of aircraft structure to fluids defined as:

- Group I – Fluids that have the potential of pooling or will be in contact with the material for a considerable period (includes JP-4 and JP-8 jet fuels, hydraulic fluids, engine lubricating oil, ethylene glycol de-icer, methylene chloride and salt spray). It is recommended immersing the material in fluid until equilibrium weight gain (saturation) is reached.
- Group II – Fluids that are wiped on and off (or evaporate) or will not contact the material for an extended period (includes alkaline cleaner, polypropylene glycol and isopropyl alcohol de-icers). It is recommended immersing the material for 15 days to determine worst case effects to be followed by tests that a more realistic exposure including accidental extended exposure.

Note: Just because a saturation condition has apparently been reached, it does not automatically follow that further degradation of properties has ceased.

3.8 STRESS (CREEP) RUPTURE

Static fatigue (or creep rupture) tests are performed to assess the extension of materials or structures under load to predict long-term behaviour or to assess the long-term strength of the system under load. The test is performed to determine the performance characteristics and operating limitations of a material, component, or structure. A creep rupture test measures the amount of creep a material can withstand prior to rupture. Strain levels more than those normally experienced during service are applied to the test component. Creep rupture testing differs from standard creep testing in that the test continues until failure (or rupture) occurs. During the test, material deformation and the elapsed time are recorded. High precision extensometry is required to monitor extension and the tests must be performed under stable environmental conditions (temperature and humidity) to avoid artefacts in the measurement.

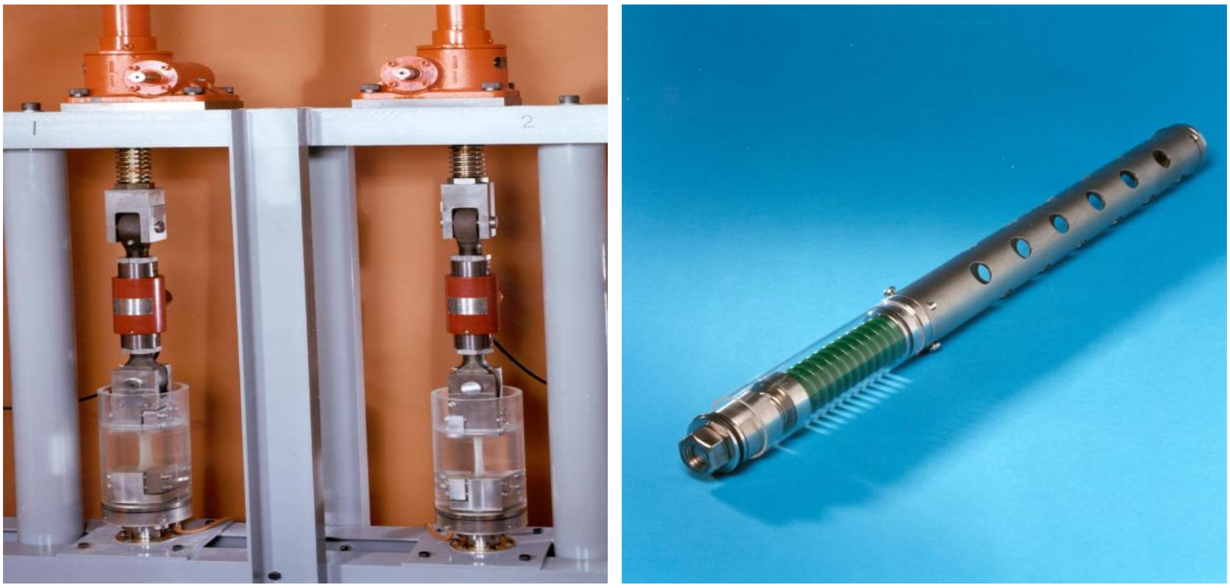
Two approaches have been adopted for assessing the degree of degradation under combined static load and environment:

- **Rate of strength loss with time (i.e. residual strength):** This approach determines the time taken for the strength of the materials system to decline to a design stress limit, below which the joint is no longer considered safe. Specimens are removed at regular intervals to assess strength reduction,

- **Time-to-failure:** This approach attempts to determine the probable average life expectancy of a materials system at a prescribed stress level or to determine the percentage of failures that can be expected to occur within a given exposure period.

Static fatigue tests could, in theory, be performed using any of the loading options outlined below (N.B. the first two options offer the highest accuracy):

- Mechanical (servo-hydraulic or motor driven) test machines,
- Dead-weight and lever creep testing machines,
- A screw jack in series with a load cell (Figure 22); and
- Self-stressing fixture where specimens are placed in either a tube equipped with a pre-calibrated spring system (Figure 22) for loading specimens or a circular ring.



Screw-jack test machines **Self-stressing tubes**

Figure 22 Tensile creep fixtures

The use of a mechanical test machine is not an economic option in most cases. A bank of small creep machines can be assembled at a considerably lower cost compared with the capital outlay involved with purchasing and operating such machines. Self-stressing fixtures (Figure 22), which are light and economic to produce and maintain, are particularly suited for field trials and for large batch testing. Care should be taken to ensure that the thermal mass of the tubes does not exceed the capacity of the conditioning cabinet, thus preventing correct maintenance of humidity and temperature.

Self-stressing tubes have been used to successfully test many different types of specimen (e.g. small single-lap and T-peel adhesive joints). Testing consists of placing specimens in a tube equipped with a pre-calibrated spring system for loading the specimens. The spring system can be compressed and locked in place to apply the required load with the spring stiffness determining the load range. The amount of load is determined by measurement of the spring compression.

The fixture shown in Figure 22 can load a series of 3-6 specimens at a time. The specimens are bolted together with either stainless steel or polyamide bolts. The tubes should be suspended vertically within the environmental cabinet to ensure uniform exposure of the test specimens.

The stress tubes need to be inspected at frequent intervals to check on the condition of the test specimens (i.e. failed or intact). Failed joints are replaced with spacers and the remaining specimens re-stressed. The failure times are measured at which the first three specimens fail. When the third specimen fails, the remaining specimens are removed from the loading tube and tested to failure to determine residual strength. The average lifetime of the failed specimens and the residual strength of the remaining specimens should be recorded. The large uncertainty associated with time-to-failure measurements, especially at the high stress levels will require either electromechanical or optical devices to monitor load or deformation to accurately determine time-to-failure.

Specimens loaded by springs can often be in an unstressed state for a considerable period (overnight or weekends) before the failed joint is replaced (by a “dummy” specimen) and the loading train is re-tensioned. There is also a tendency for surviving specimens to be damaged in the re-stressing process with the probability of occurrence increasing at high stresses. Creep/relaxation histories of specimens will be different due to the replacement of failed specimens and subsequent re-loading. This contributes further to the uncertainty of creep rupture data. For long-term tests over months or years, this effect will probably be minimal. For short duration tests (i.e. static loads close to the maximum load at failure) load relaxation occurs, and it is therefore necessary to continuously adjust the manual screw jack on the creep frame or the loading spring on the self-stressing tube to maintain a constant load. The use of controlled mechanical test frames avoids this problem. Manually operated systems are best suited to long-term testing where loads are relatively low and load relaxation is minimal.

Design limits for load and stress levels need to be established for any system tested. Typically, these are between 10 and 50% of the short-term strength of the polymeric system. It is generally recommended that the sustained stress in an adhesive bonded joint under service conditions should be kept below 25% of the short-term strength of the joint. Some design guides suggest a knockdown factor of 10 (i.e. stress level of 10%). The onset of failure tends to be catastrophic. In general, damage and stiffness loss prior to damage initiation is minimal. In adhesive joints, the time involved in crack formation tends to be far greater than the time associated with crack propagation. Methods for accelerating the testing process that use mechanical loading, tend to use stress levels that are significantly higher than stress levels used in design, thus the limiting design strains are reached in shorter times than in actual service.

The large uncertainty associated with creep test results, especially those obtained under hot/wet conditions, implies that the current approach of conducting three tests per stress level is inadequate and that considerably more data points are required for generating reliable creep rupture curves for engineering design purposes. Five (preferably 10) specimens per stress level with five stress levels per condition should provide a reasonable number of data points. For characterisation purposes it is recommended that specimens are mechanically loaded at each of five stress levels (i.e. 80%, 70%, 55%, 40% and 25% of the short-term tensile strength of the material).

A self-stressing fixture can also be used to produce flexural loading. Figure 23 shows a four-point bend flexural rig capable of loading six beam specimens at a time. Load is achieved through compression of the two loading springs, which are pulled down towards the base when tightened. The springs are calibrated by applying compression loads using a mechanical test machine to determine the load-displacement relationship (Hooke’s law).

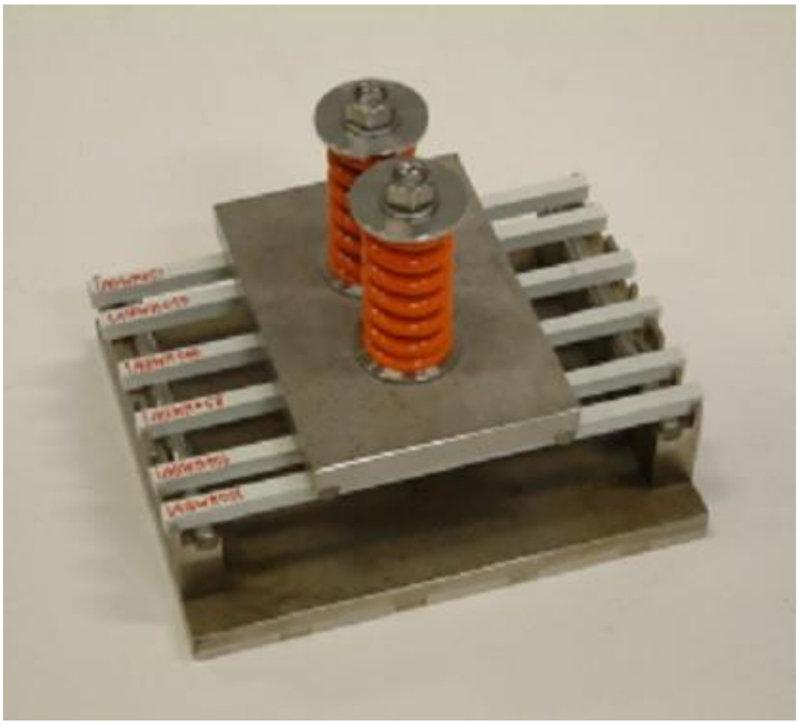


Figure 23 Self-stressing flexure rig with specimens

It is important that three, or more specimens are loaded at any one time to ensure balanced loading. The spring stiffness and strength needs to be selected according to the loads required. It should be noted that the load is equally shared between the two springs, which should have identical mechanical properties and dimensions. The load (spring displacement) needs to be continuously monitored and adjusted to maintain constant load. Load relaxation occurs at all stress levels with relaxation increasing with temperature and stress. Special attention is required at the start and end of testing. There is a bedding in period at the start of the test and specimens tend to creep rapidly towards the end of their life. When a specimen fails the load is rapidly redistributed to the remaining specimens, which can cause the surviving specimens to fail. It is advisable to stop the test and replace all the specimens rather than replace the failed specimen and re-load the fixture.

ASTM D7337 [136] describes a method for measuring the creep rupture time of FRP bars under a given set of controlled environmental conditions and force ratio. Unlike steel reinforcing bars or prestressing tendons subjected to significant sustained stress, creep rupture of FRP bars may take place below the static tensile strength. Therefore, the creep rupture strength is an important factor when determining acceptable stress levels in FRP bars used as reinforcement or tendons in concrete members designed to resist sustained loads. Creep rupture strength varies according to the type of FRP bars used.

3.9 DESIGNING AND PLANNING AN ACCELERATED TEST PROGRAMME

In order to conduct an effective accelerated test programme, it is essential to spend time on designing and planning the test programme [4]. The more consideration given to this process the more likely that the outcome of the exercise will meet expectations. The process is iterative and will need to be repeated several times to establish a programme that will meet budget and technical requirements. The test programme needs to be suitably flexible in case of unexpected results or technical problems occurring. It may be necessary for test parameters to be changed during the test programme. Short-term tests at high stress levels and high temperatures are generally set-up first to check the procedure and to identify technical issues that may not have been apparent prior to testing. It is often possible to establish the timescale of the longer-term tests based on short-term results. This is important where measurements need to be completed within a set period, as specified in several standards.

Several points to consider when designing an environmental test programme to ensure that the test procedures used closely reflect the service conditions [7]:

- Clearly define the purpose and objectives of the test programme,
- Specify the service life that needs to be predicted and the level of uncertainty in life expectancy that is acceptable (N.B. the time to reach saturation depends on the square of thickness, and therefore exposure timescales will need to be considered in in relation to the sample dimensions. A maximum sample thickness of 1 mm is recommended by ISO 62 [71] to ensure that test durations do not exceed one week for typical diffusivity values for polymers (~10-12 m^2s^{-1})),
- Identify critical degradation agents and levels (e.g. temperature, humidity, and pressure) - often dependent on resources and time available. The exposure temperature should reflect the application temperature. Multiple temperature exposures may be needed to build up a picture of the full behaviour of the material. High temperatures may also cause chemical or phase changes in the material, which could limit the possibility of extrapolating behaviour from one temperature to another,
- Environmental and safety issues that need to be considered in relation to handling, storage and disposal of chemicals,
- Specimens and products to be exposed,
- Synergistic effects (e.g. humidity and temperature) - establish requirements and if conditions can be achieved,
- Loading requirements and test parameters to be monitored (e.g. temperature, salt concentration, humidity, pH level, displacement, load, etc.),
- Detailed test conditions and specimen numbers to be tested per condition,
- Environmental and monitoring equipment requirements - include a contingency plan to allow for possible equipment failure,
- Performance tests (destructive and non-destructive) to be performed on the conditioned material,

- Methods for analysing data and predictive model(s) for extrapolating short-term data to service conditions,
- Timing and sequencing of exposures - where possible, exposure intervals should match those in the standards to enable comparability with standard data. If multiple specimens are to be exposed in a study, then the exposure intervals for each of the specimens should be consistent. The start of the exposures may need to be staggered to allow mass measurements to be carried out efficiently,
- Ensure equipment, and labour costs and time agree with budget and available timescale,
- Identify specimen/product machining and preparation requirements.

The two most important criteria when selecting a test method are the availability of a standard test method and the ability of the test method to produce consistent and reliable engineering data for a range of service conditions. When planning a test strategy, the following should be considered:

- Selection of an appropriate test for ranking and screening, design data and quality assurance/quality control (i.e. conformance to design standards/codes) purposes,
- Knowledge of existing standards/legislative requirements,
- An understanding of the material characteristics, test method and the test data generated. An awareness of the mechanical and physical properties of the polymer material is invaluable in understanding the test results and for troubleshooting,
- Cost of fabrication and testing/test facility requirements,
- Knowledge on factors that affect data reliability.

3.10 TEST DATA ANALYSIS

Several 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 (post-curing) 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 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, which describes the relation between rate of reaction and temperature, 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 [7]. 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:

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

where $K(T)$ is the reaction rate for the process, E is the reaction (activation) energy, R is the gas constant (8.314 J/mole/K), T is absolute temperature (in Kelvin) and A is the rate constant.

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

$$\ln(K(T)) = \ln(A) - E/RT \qquad (4.2)$$

An alternative way of using the Arrhenius equation is to consider $E/RT + C$ (where $C = \ln(A)$) 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 needs 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.

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:

$$ln\, K(T) = ln\, K_o + B(T_o - T)/10 \qquad (4.3)$$

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

4.2 TEMPERATURE-STRESS INTERACTION

The temperature and strain-rate dependence of the yield stress in glassy polymers can be modelled using the Eyring theory of viscosity [137]. In this model, the molecular motions associated with flow are represented by thermally activated transitions across an energy barrier separating two different molecular conformations. The application of stress changes the height of the energy barrier (ΔE^*) separating the energy minima for each conformation such that the barrier height increases for one conformation and conversely decreases for the other conformation.

According to Eyring theory, the relationship between strain-rate, $\dot{\varepsilon}$, and applied stress, σ, for high stress regions where yield occurs is:

$$\dot{\varepsilon} = A\, exp\left[-\frac{(\Delta E^* - v^*\sigma)}{RT}\right] \tag{4.4}$$

where A is a constant, R is the gas constant and v^* is the activation volume.

The equation can be rearranged to give the yield stress, σ_y, in terms of the strain-rate $\dot{\varepsilon}$:

$$\frac{\sigma_y}{T} = \frac{\Delta E^*}{v^* T} + \left(\frac{R}{v^*}\right) ln\left(\frac{\dot{\varepsilon}}{A}\right) \tag{4.5}$$

A series of parallel lines can be generated at different temperatures by plotting σ_y/T against $\log_e \dot{\varepsilon}$ using this equation [137]. The activation volume v^* can be determined from the slope of the lines. For glassy polymers, v^* is typically of the order of several nm^3 (i.e. approximately 10 times the size of structural features in the polymer). Although v^* has dimensions of volume, it is not in fact a volume. The quantity σv^* is the work done (i.e. energy) on a mobile segment of the polymer during transition between molecular conformations.

4.3 MOISTURE ABSORPTION

The degree of moisture degradation that occurs in polymeric materials when in service can often be linked directly with the amount of moisture absorbed. Moisture absorption kinetics will differ widely and change with physical ageing. The process of water permeation through polymers is a combination of two interrelated processes, dissolution in the polymer and diffusion through the polymer. There is a limit to the amount of moisture that can be absorbed under any set of conditions (i.e. solubility). Permeability is the product of solubility and diffusion.

Diffusion of moisture within polymeric materials, such as FRPs is a time- and temperature-dependent process and can often be expressed by Fick's second law [138]:

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} \tag{4.6}$$

where C is the moisture concentration of the diffusing species, D is the bulk diffusion coefficient (m^2/s), and x is the direction of diffusion (usually taken as the through-thickness direction for an infinitely long and wide section).

Through consideration of the one-dimensional (1-D) diffusion case, analytical solutions for the temporal and spatial distribution of moisture concentration $M(t)$ at a distance x from the mid-plane in the direction of diffusion can be approximated by the relationship [139]:

$$\frac{M(t)}{M_\infty} = 1 - \frac{4}{\pi}\sum_{j=0}^{\infty}\frac{(-1)^j}{(2j+1)} exp\left[\frac{-(2j+1)^2\pi^2 Dt}{h^2}\right] cos\left[\frac{(2j+1)\pi x}{h}\right] \tag{4.7}$$

where $M(t)$ is the moisture content at time t, M_∞ is the maximum (saturation) moisture content (or equilibrium concentration) and h is the plate thickness.

As point moisture concentrations are difficult to measure experimentally, this expression is integrated with respect to x to generate an expression in terms of mass gain as a function of time [139-142]:

$$\frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{j=0}^{\infty}(2j+1)^{-2} exp\left[-\frac{(2j+1)^2\pi^2 Dt}{h^2}\right] \tag{4.8}$$

The absorbed fluid content $M(t)$, which is often expressed as a percentage of the specimen dry mass, is calculated using either Equation (3.2) or (3.3) – Section 3.2. If there is no loss of water-soluble matter during environmental conditioning, then the mass of the reconditioned specimen $M_c = M_0$ (original mass of the specimen prior to environmental conditioning). In both cases the specimen is dried to a constant weight.

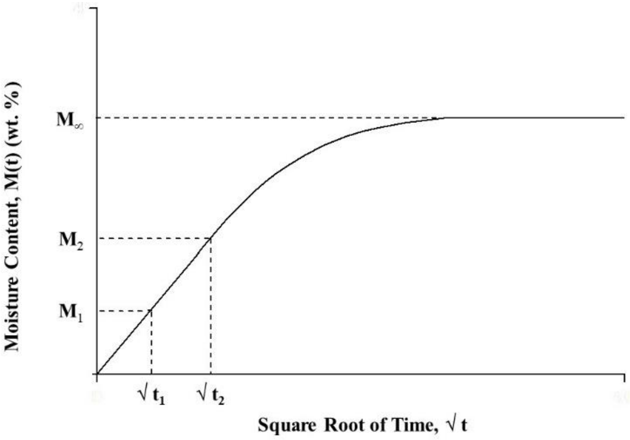


Figure 24 Schematic of a Fickian diffusion curve

The "apparent" diffusion coefficient D_a for a polymer specimen can be determined from the initial linear region of the Fickian diffusion curve (see Figure 24) using the following relationship [139-141]:

$$D_a = \frac{\pi}{16}\left(\frac{h(M_2 - M_1)}{M_\infty(\sqrt{t_2} - \sqrt{t_1})}\right)^2 \qquad (4.9)$$

where M_∞ is the saturation moisture content, M_1 is the moisture uptake after time t_1, M_2 is the moisture uptake after time t_2 and h is the specimen thickness.

If the starting point is a dry sample at $t = 0$, then t_1 and $M(t_1)$ can be eliminated and the fractional mass uptake $M(t)/M_\infty$ plotted as a function of $\sqrt{t}$ has a slope proportional to $\sqrt{D_a}$ [142]. Equation (4.8) can be simplified for short-term and long-term exposure time as follows [142]:

$$\frac{M(t)}{M_\infty} = \frac{4}{\pi^2}\sqrt{\frac{D_a t}{h^2}} \text{ for } \frac{D_a t}{h^2} < 0.04 \qquad (4.10)$$

$$\frac{M(t)}{M_\infty} = 1 - \frac{8}{\pi^2} exp\left[-\left(\frac{D_a t}{h^2}\pi^2\right)\right] \text{ for } \frac{D_a t}{h^2} > 0.04 \qquad (4.11)$$

For Fickian diffusion, this plot is approximately linear until $M(t)$ approaches ~0.6 to 0.7 M_∞. D_a can be calculated from the square of the slope.

The analysis used to derive diffusivity assumes that the specimen is an infinite rectangular plate with no diffusion from the specimen edges. In fact, diffusion occurs from all six surfaces of a rectangular section. A correction factor to account for edge effects has been derived, which enables the true one-dimensional diffusion coefficient D to be determined as follows [140, 141]:

$$D = D_a\left(1 + \frac{h}{l} + \frac{h}{b}\right)^{-2} \qquad (4.12)$$

where *l*, *b* and *h* are the length, width, and thickness of the rectangular specimen, respectively. Based on the above relation, correction factors for 1 mm and 3.2 mm thick squares with 50 mm sides are 0.925 and 0.786, respectively. The reliability of the above relationship was observed to decrease for thicker specimens [14]. This may indicate that edge effects become more influential as the thickness increases (i.e. moisture ingress). For anisotropic materials, the diffusion coefficients vary with direction. The diffusion coefficients parallel and perpendicular to the fibres (D_{11} and D_{22}) for aligned glass and carbon fibre-reinforced systems (see Figure 25) may be estimated by the following relationships [140, 141]:

$$D_{11} = (1 - V_f)D_m \tag{4.13}$$

$$D_{22} = \left(1 - 2\sqrt{\frac{V_f}{\pi}}\right)D_m \tag{4.14}$$

where D_m is the diffusivity of the resin and V_f is the fibre volume fraction.

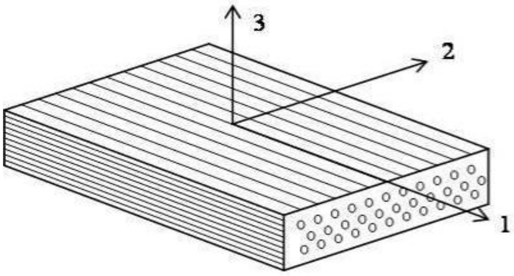


Figure 25 Principal material axis of a unidirectional laminate

The diffusion coefficient for a composite is given by the following relationship [140, 141]:

$$D = D_{33}\left(1 + \frac{h}{l}\sqrt{\frac{D_{11}}{D_{33}}} + \frac{h}{b}\sqrt{\frac{D_{22}}{D_{33}}}\right)^2 \tag{4.15}$$

D_{11}, D_{22} and D_{33} are diffusivities along the length (longitudinal), across the width (transverse) and through the thickness of the material.

The rate of moisture uptake by a composite laminate is dependent on the temperature and relative humidity of the environment. The equilibrium moisture concentration M_∞ is assumed to be independent of temperature, depending only on the moisture content or relative humidity of the environment. M_∞ increases with increasing relative humidity ϕ according to the relationship [140, 141]:

$$M_\infty = a\phi^b \tag{4.16}$$

where *a* and *b* are constants derived from a linear regression fit to the moisture content data.

Diffusion behaviour is temperature dependent (see Figure 26) and for ideal systems diffusivity *D* can be expressed as a function of absolute temperature *T* according to the Arrhenius relationship [140, 141]:

$$D(T) = D_0 e^{-(E/kT)} \tag{4.17}$$

where *k* is the Boltzmann's constant. Material parameters D_0 and *E* (energy barrier to diffusion) can be determined from a linear regression fit to $\log_e D$ versus $1/T$ graph (see Figure 27).

Moisture absorption data presented in Figures 26 and 27 show that the diffusion rate increases with temperature for unidirectional (UD) T300/924 carbon/epoxy laminates immersed in deionized water at three different temperatures (i.e. 25°C, 40°C and 60°C).

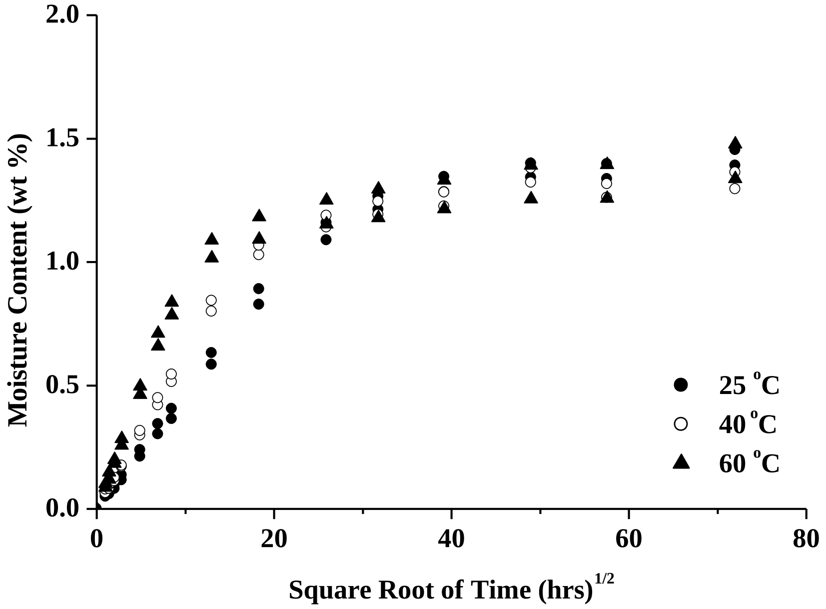


Figure 26 Moisture diffusion curves for UD T300/924 CFRP at three different temperatures (immersion in deionized water)

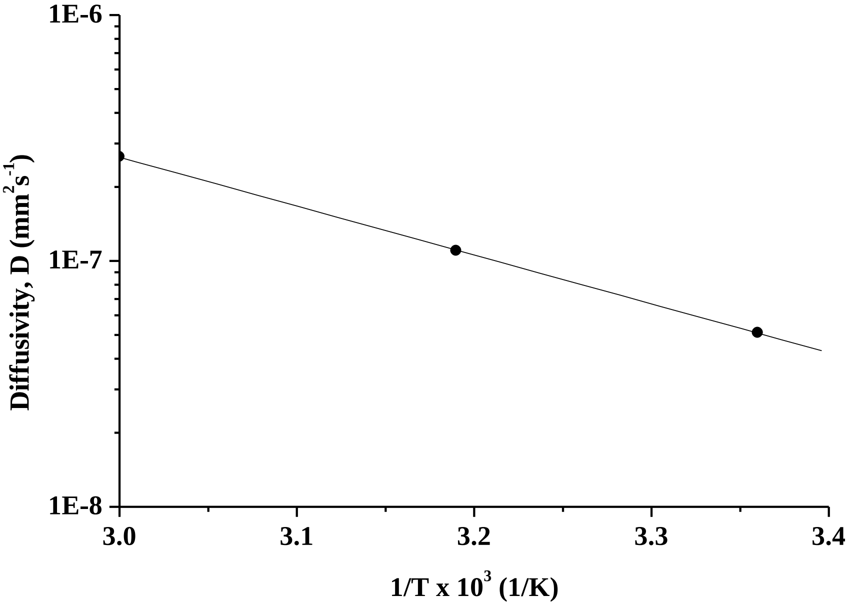


Figure 27 Temperature dependence of diffusivity for UD T300/924 carbon/epoxy (immersion in deionized water)

Non-Fickian Behaviour: The classical 1-D Fickian model, as described above, can be used to accurately predict the moisture absorption behaviour in polymeric materials provided the diffusion kinetics is not highly anomalous (i.e. single diffusion phase with clearly defined Fickian features as shown in Figure 26). In the diffusion process of a fluid through a polymeric material, as for example moisture ingress in FRP, two main phenomena must be considered: the rate of diffusion of the fluid and the change in the internal structure of the material. It is the second phenomena that results in the non-Fickian behaviour that is often observed in polymeric materials. Non-Fickian behaviour being associated with moisture induced structural changes, resin degradation, or even simple molecular relaxation.

Several modelling approaches have been considered to account for non-Fickian behaviour; time-, concentration- and relaxation-dependent based methods or methods that assign dual phase behaviour to either the polymer (i.e. two distinct materials and associated densities), moisture or moisture uptake process [143-145]. Langmuir based models seem to be the preferred route in modelling anomalous (non-Fickian) moisture diffusion behaviour. These models consider the effect of diffusing molecules interacting with the polymer simultaneously with the occurrence of classical unbound diffusion. The two-phase Langmuir-type diffusion model (i.e. 1-D hindered diffusion model) developed by Carter and Kibler [146], a modification of the Fickian diffusion model, considers the chemical binding of water molecules to polymer chains (bound) in addition to mobile or free (unbound) diffusing of molecules of the Fickian model.

The Langmuir-type 1-D hindered diffusion (LHD) model uses the following four material properties: through-the-thickness diffusion coefficient, D; maximum percent mass gain (saturation), M_∞; the probability of bound molecules becoming mobile, β; and the probability of mobile molecules becoming bound, γ. The variables γ and β describe the effect of chemical interaction between the polar water molecules and the polar sites of the polymer resin. The chemical interaction process slows the rate of moisture uptake, and consequently a delay occurs in reaching the equilibrium moisture content when compared to classical Fickian moisture absorption.

The governing equations for this model are as follows [146]:

$$D\frac{\partial^2 n}{\partial x^2} = \frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} \qquad (4.18)$$

$$\frac{\partial N}{\partial t} = \gamma n - \beta N \qquad (4.19)$$

where n and N represents the unbound and bound molecules per unit volume, respectively.

At equilibrium, the relationship between free molecule concentration, n_∞, and bound molecule concentration, N_∞, is:

$$\gamma n_\infty = \beta N_\infty \qquad (4.20)$$

In the LHD model, fluid concentration, C, is summation of concentration of unbound molecules, n, and concentration of bound molecules, N, whereas in Fickian diffusion, the total fluid concentration is given only by C as shown in Equation (4.6). For Fickian diffusion, fluid concentration C is only dependent on diffused, unbound molecules, and thus, the molecular binding probability of the penetrant to the matrix material is not considered. The following relationship is a simplified version of the more exact model developed by Carter and Kibler [146] - see also [143-145, 147].

$$\frac{M(t)}{M_\infty} = \frac{\beta}{\beta+\gamma}e^{-\gamma t}\left[1 - \frac{8}{\pi^2}\sum_{j=1}^{\infty}\frac{e^{-k(2j+1)^2 t}}{(2j+1)^2}\right] + \frac{\beta}{\beta+\gamma}\left(e^{-\beta t} - e^{-\gamma t}\right) + \left(1 - e^{-\beta t}\right) \qquad (4.21)$$

where:

$$k = \frac{\pi^2 D}{h^2} \qquad (4.22)$$

The above relationship is valid for when 2γ and 2β are much smaller than k. The simplified LHD model is similar to the Fickian approximation when $\gamma = 0$.

The following simplified expression may be used to describe the initial part of the absorption curve (Equation (4.21) at short exposure times [145]:

$$\frac{M(t)}{M_\infty} = \left(\frac{\beta}{\beta+\gamma}\right)\sqrt{\frac{16kt}{\pi^3}} \text{ for } kt \leq 0.7 \tag{4.23}$$

When exposure times are sufficiently long, corresponding to post-linear uptake behaviour, and kt is large compared to 0.7, the moisture uptake behaviour can be approximated by the relation [142]:

$$\frac{M(t)}{M_\infty} = 1 - \frac{\gamma}{\beta+\gamma}e^{-\beta t} \text{ for } kt > 0.7 \tag{4.24}$$

A pseudo saturation level M_S is obtained for $kt \approx 5$:

$$\frac{M_S}{M_\infty} = \frac{\gamma}{\beta+\gamma} \tag{4.25}$$

Absorption is dependent on the level of porosity with the rate of moisture absorbed and moisture concentration at saturation increasing with the level of porosity. Porosity can be interfacial or result from internal or external induced damage. The presence of tensile stresses will accelerate moisture uptake by opening existing internal cavities or voids and by contributing to micro-crack formation (i.e. porosity can alter the kinetics of moisture diffusion). Porosity can alter the kinetics of moisture diffusion. The coexistence of bound and unbound water makes it difficult to identify if the water is linked to pores or voids within the bulk matrix or interfacial voids or cracks. In principle, it should be possible, to detect the presence of pre-existing pores from density changes linked to water absorption in the composite at low to moderate levels of activity (i.e. water concentration). The density of the water-polymer mixture varies between two limits ρ_{min} and ρ_{max} corresponding to the case where water is fully soluble in the polymer (i.e. does not form a separate phase and both volumes are additive) and the case where water is insoluble in the polymer and fills only pores. Assuming the water density is unity (i.e. 1 g/cm^3), ρ_{min} and ρ_{max} can be determined as follows [148]:

$$\rho_{min} = \frac{\rho_m}{1 + M(\rho_m - 1)}, \qquad \rho_{max} = \rho_m\left(1 + \frac{M}{1-M}\right) \text{ for } \rho_{max} > 1 \tag{4.26}$$

where M is the water mass fraction calculated using Equation (3.1) and ρ_{m} is the polymer density in dry state. At low activity, density increases with M when water fills the pores, and decreases when water is dissolved in the matrix. It may be necessary to use different thickness samples to separate the effects of surface adsorption from bulk absorption properties.

At higher activity, clustering can be expected to occur in composite matrices; although clusters will often contain only a few water molecules; particularly for very low hydrophilicity materials (i.e. low molecular polarity polymers). It is understandable since water molecules are considerably more ‘‘attractive’’ to themselves than to polymer segments. In highly hydrophilic polymers, plasticization by water induces a rearrangement of the polymer structure favorable to a hydrophilicity increase. Any physical and chemical changes will impact on material density and diffusion kinetics. Diffusivity will generally increase because of moisture ingress. Permanent changes in diffusion rate can be observed by comparing the original diffusivity with the diffusivity measured for reconditioned (dried) material; original and reconditioned specimens tested under the same environmental conditions. Changes in density resulting from environmental exposure can be determined by measuring the density of dried specimens before and after conditioning. Density can be expected to decrease. The existence of pre-existing microstructural cavities can be detected using other penetrating fluids than water (e.g. nitrogen and helium). A helium pycnometer can be used to measure both density and porosity, as the small inert helium molecules are able to penetrate the sample pores (provided a direct path exists between the surface and internal pores and cavities) occupying the entire free volume of the material.

4.4 MOISTURE EFFECTS

The plasticising effect (i.e. reduction of T_g) of absorption of moisture into a composite laminate can be described by [149]:

$$T_g = \frac{\alpha_m T_{gm}(1 - V_f) + \alpha_f V_f T_{gf}}{\alpha_m(1 - V_f) + \alpha_f V_f} \qquad (4.27)$$

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

The wet glass transition temperature T_{gw} can be determined using the quadratic relationship [150]:

$$T_{gw} = (AM^2 + BM + C)\, T_{gd} \qquad (4.28)$$

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

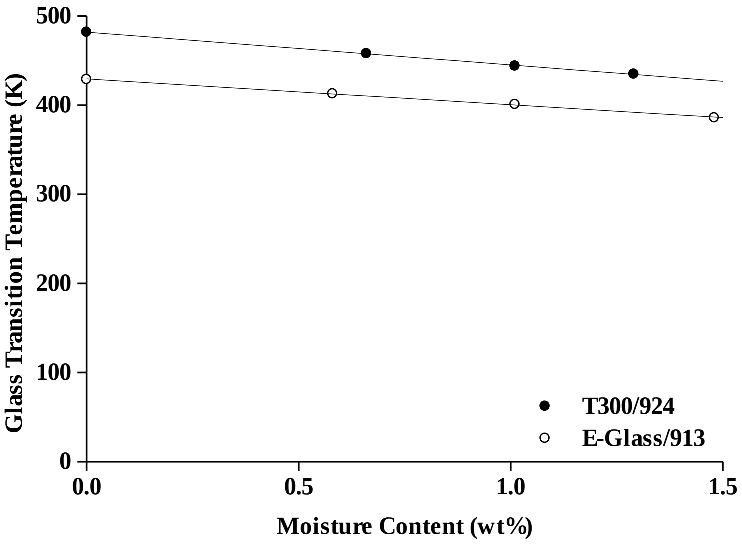


Figure 28 T_g versus moisture content for hygrothermal aged unidirectional laminates

For several materials (see Figure 28), T_{gw} and T_{gd} are related as follows [151]:

$$T_{gw} = T_{gd} - gM \qquad (4.29)$$

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

Strength and stiffness property degradation because of hygrothermal ageing can be approximated using a simple algebraic relationship of the form [150]:

$$\frac{P}{P_0} = \left(\frac{T_{gw} - T}{T_{gd} - T_0}\right)^n \qquad (4.30)$$

P denotes the material property (usually strength) at the test temperature T, P_0 is the initial property (un-aged) value of the dry material at room or reference temperature T_0, 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 $T_{gd} > T_0$ and $T_{gw} > T$.
The good agreement between predicted and measured transverse flexure properties shown in Figure 29 is understandable as the power-law formula was originally intended for estimating hygrothermal-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, 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.

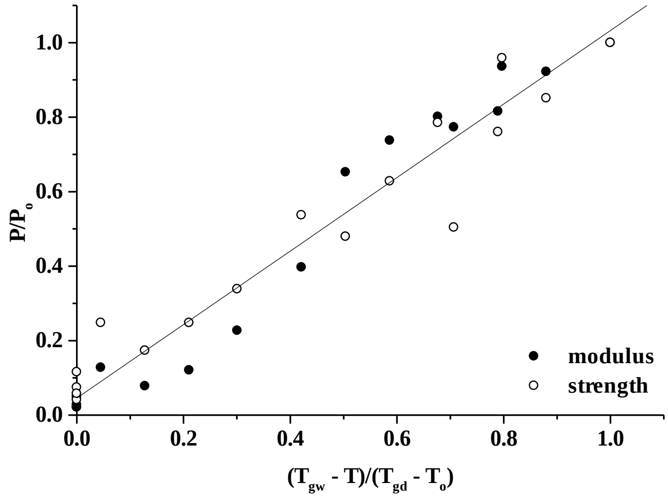


Figure 29 Transverse flexure properties of unidirectional E-glass/913

The matrix and fibre strength and stiffness properties determined using Equation (4.30) 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 [78]. In these cases, residual stresses that have arisen in the laminate during the curing process are relieved through moisture plasticisation of the resin matrix. Changes in T_g due to environmental exposure are not always indicative of material property degradation. There are composite systems where T_g only decreases by a small amount for a large increase in moisture content, although mechanical properties may be severely compromised.

Equation (4.30) can be extended to include a component for cyclic fatigue as shown below [150]:

$$\frac{P}{P_0} = \left(\frac{T_{gw} - T}{T_{gd} - T_0}\right)^n - kTlog_{10}N \qquad (4.31)$$

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.

A model developed by Bowden et.al [152] to predict the yield behaviour of glassy polymers has been expanded and generalised by Kittagawa [153] 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 [154]:

$$\frac{T_0 \tau_y}{T \tau_{y0}} = \left(\frac{T_0 G}{T G_0}\right)^n \qquad (4.32)$$

where T_0 is the reference temperature (in Kelvin), τ_{y0} and G_0 are the shear yield stress and the shear modulus at reference temperature T_0 (usually room temperature) respectively, and the exponent n is a constant.
The values of log $(T_0\tau_y/T\tau_{y0})$ are plotted against those of log (T_0G/TG_0), 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 (wet or dry) of unidirectional carbon/epoxy and glass/epoxy composites [12, 154].

4.5 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 [7, 37, 155, 156]. These are usually of the form:

$$P(t,T) = P(\infty,T) + [P(0,T) - P(\infty,T)]e^{-K(T)t^n} \qquad (4.33)$$

where, K is the reaction rate (or degradation rate), P is the material property (i.e. strength or stiffness), T is the ageing temperature (in Kelvin), 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:

$$log\, P(t,T) = A(T) - B(T) \qquad (4.34)$$

$$P(t,T) = P(0,T)\, e^{[-k(T)\, t]} \Rightarrow P(\infty,T) = 0 \qquad (4.35)$$

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

From a series of tests carried out at different ageing temperatures it is possible to produce logarithmic-linear plots of changes in mechanical properties (stiffness and strength) with time. The time required for the property to decrease 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 at service temperature can be estimated by extrapolation from the plot of ln $t_{1/2}$ versus 1/T (a straight line) or by fitting the data to Equation (4.36).

The half-life $t_{1/2}$ is related to the ageing temperature T as follows:

$$lnt_{1/2} = C + \frac{D}{t} \qquad (4.36)$$

where C and D are material constants.

It is important that the test temperatures are kept moderate (<100°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. It is also possible to relate the rate of strength of degradation with the rate of moisture uptake (i.e. diffusivity D), as shown in Figure 30. The diffusivity D is a function of absolute temperature T and is given by the Arrhenius relation in Equation (4.17).

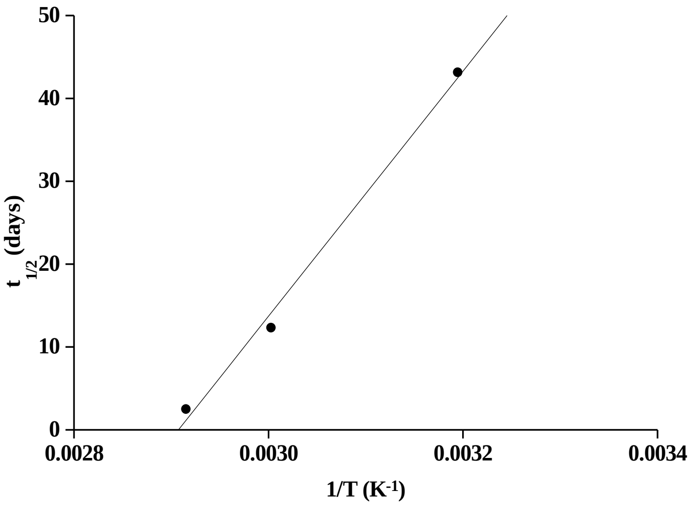


Figure 30 Tensile strength half-life versus temperature for E-glass/polyester

The relationship between half-life $t_{1/2}$ and diffusivity D can be approximated by the following empirical relationship (see Figure 31):

$$lnt_{1/2} = A - BD \tag{4.37}$$

where constants *A* and *B* are derived from linear regression line of best fit.

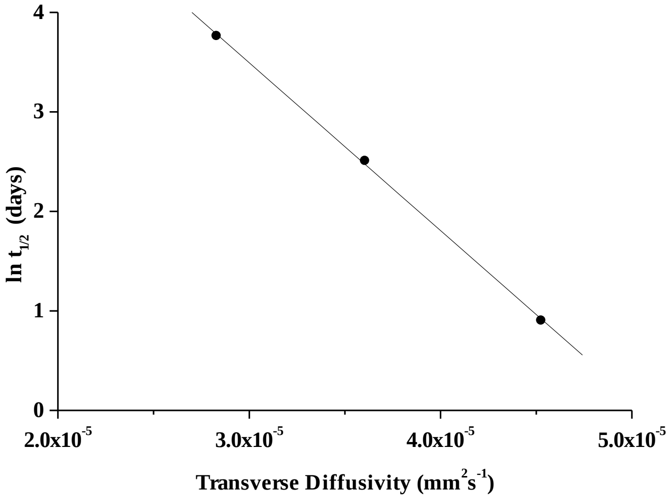


Figure 31 Tensile strength half-life versus diffusivity for E-glass/polyester

The above approach has been extended to determining the combined effect of temperature, moisture, and stress with the failure time t_f given by [155]:

$$log\, t_f = C - log\, T + \frac{E}{2.303\, RT} - b\frac{S}{T} \tag{4.38}$$

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

Several factors may raise 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 difficult to duplicate service conditions using accelerated ageing procedures, particularly as realistic environments include large random variations in temperature and humidity.

4.6 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 [7, 30, 31, 37]:

Linear (without temperature effects)

$$P = P_o + bD \qquad (4.39)$$

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)

$$P = P_o + De^{(-\Delta H/RT)} \qquad (4.40)$$

Power law (without temperature effects)

$$P = P_o + bD^n \qquad (4.41)$$

where n is a constant.

Exponential (without temperature effects)

$$P = P_o + Ae^D \qquad (4.42)$$

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.

4.7 CHEMICAL AND SOLVENT EXPOSURE

Chemical attack of composites often involves specific chemical reactions of the polymer matrix with the penetrating fluid with the most common mode of failure being hydrolysis by water, acids, and alkalis. Thermoplastics are particularly susceptible to hydrolytic degradation. Hydrolysis causes the polymer chains to break into smaller segments (reversion), and thus weakening the bond strength of the polymeric chains. There are two main steps involved in the hydrolysis process. The first involves water (or other chemical species) reacting with the hydrolysable group resulting in an unstable structure and the second, involves rearrangement of this structure with a chain scission. If the first step is the rate controlling factor, then stresses are expected to have no direct influence on hydrolysis kinetics. Whereas, if the second step is the controlling factor, stress can be expected to accelerate hydrolysis (i.e. chain scission process) and enhance the rate of fluid uptake. Hydrolytic degradation also increases at elevated temperatures. Hydrolysis reactions are generally minimal under ambient conditions.

According to the simplest stress assisted reactions, the reaction rate R is related to the stress σ by the following Arrhenius type relationship [148]:

$$R = R_0 \, exp\left[-\frac{(H - v^* \sigma)}{RT}\right] \qquad (4.43)$$

where H is the activation energy of hydrolysis and v^* an activation molar volume, expressing the sensitivity of the reaction to stresses.

Plasticisation of polymers can be attributed to all the processes that contribute to a decrease in the T_g. According to the following relationship, a decrease in T_g leads to a decrease in yield stress σ_y, thus making plastic deformation easier [148].

$$\sigma_y = C(T - T_g) \qquad (4.44)$$

where C is a parameter generally of the order of 1 MPa.K^{-1}. A decrease of 1 K in T_g translates into a decrease in σ_y of approximately 1 MPa. The water molecules associated with clustering exerts no effect on T_g.

For matrix-dominated properties, strength, and stiffness property degradation due to chemical species ingress can be expressed as:

$$\frac{P}{P_0} = \sqrt{\left(\frac{C - C_0}{C_{max} - C_0}\right)} \qquad (4.45)$$

where C is the concentration of ingress species, and C_0 and C_{max} denote initial and saturation concentrations.

Several power law relationships have been used to describe weathering and corrosion behaviour of FRPs [7, 39, 41]. An example is the semi-empirical relationship for uniform corrosion behaviour of FRP in chlorine dioxide environments [157, 158]:

$$\Phi = Bt^{\alpha} CAe^{-E/RT} \qquad (4.46)$$

where Φ is the depth of corrosion (mm), B is a special factor (0 or 1) for the case of protective deposits on the surface, t is the time in service (years), α is a factor (0.5 to 1.0) dependent on the thickness and degree of degradation of the corroded (degraded) surface layer, C is the concentration of chloride dioxide (g/l) and A is a material constant dependent on the type of resin, degree of cure and laminate structure.

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

$$P = f(y_1 + y_2 + y_{3.}\ldots\ldots + y_n) \tag{4.47}$$

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.

Solubility measurements of the polymer matrix (or adhesive) in different solvents are important in assessing the chemical resistance and potential applications for the material. It is also essential to assess the solubility of the different additives, such as plasticizers, antioxidants, and pigments in the adhesive, which can impact on chemical resistance. Although the solubility relations in polymer systems are complex, empirical solubility rules have been derived that enable solubility predictions for several polymer-chemical species combinations. The solubility parameter, δ, is defined in terms of the cohesive energy density in the liquid state $(\Delta E_V/V)$, in which ΔE_V is the molar energy of vaporization and V is the volume of the liquid [159]:

$$\delta = \left(\frac{\Delta E_V}{V}\right)^{1/2} \tag{4.48}$$

Cohesive energy density provides a measure of the intermolecular attraction forces in the material, which approximately equals the heat of vaporization for liquids or sublimation for solids per mol. The total cohesive energy ΔE_t, which holds a liquid together, can be divided into contributions from dispersion forces ΔE_d, polar forces ΔE_p and hydrogen bonding forces ΔE_h [159]:

$$\Delta E_t = \Delta E_d + \Delta E_p + \Delta E_h \tag{4.49}$$

The total solubility parameter can be expressed in terms of solubility parameters δ_d, δ_p and δ_h due to dispersion forces, dipole forces and hydrogen bonding, respectively.

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{4.50}$$

The three parameters, known as Hansen Solubility Parameters (HSPs), have been derived empirically from experiments conducted on many solvents. For each polymer, a three-dimensional spherical volume of solubility in δ_d, δ_p and δ_h space can be defined with an interaction radius, R_0. The distance of the coordinates of any solvent i from the centre point of the spherical sphere of polymer j is [160]:

$$d^2 = \left[4\left(\delta_d^i - \delta_d^j\right)^2 + \left(\delta_p^i - \delta_p^j\right)^2 + \left(\delta_h^i - \delta_h^j\right)^2\right] \tag{4.51}$$

The scale on the dispersion axis is usually doubled, as indicated in the above equation, to improve the spherical nature of the volume. This distance can be compared with the radius R of the solubility sphere of the polymer. If $d < R$, the probability of solvent i dissolving polymer j is high. This approach has proved effective for predicting chemical degradation of structural adhesives [161].

4.8 TIME-DEPENDENT BEHAVIOUR

Findley’s power law model is widely used for describing the viscoelastic behaviour of composite materials under a constant (static) stress [162]. The model has been applied to a range of composite materials and has been included in the ASCE Structural Plastics Design Manual [163].

The time-dependent creep strain $\varepsilon(t)$ is determined using [162]:

$$\varepsilon(t) = \varepsilon_o^{'} + \varepsilon_t^{'} t^n \tag{4.52}$$

where $\varepsilon_o^{'}$ is the stress-dependent and temperature-dependent initial elastic strain, $\varepsilon_t^{'}$ is the stress-dependent and temperature-dependent coefficient, n is a stress-independent material constant and t is the time after loading.

The terms ε_o' and ε_t' are often expressed as a polynomial series as shown below [162]:

$$\varepsilon_o^{'}(\sigma, T) = a_1\left(\frac{\sigma}{\sigma_0}\right) + a_2\left(\frac{\sigma}{\sigma_0}\right)^2 + a_3\left(\frac{\sigma}{\sigma_0}\right)^3 + \cdots \tag{4.53}$$

$$\varepsilon_t^{'}(\sigma, T) = b_1\left(\frac{\sigma}{\sigma_0}\right) + b_2\left(\frac{\sigma}{\sigma_0}\right)^2 + b_3\left(\frac{\sigma}{\sigma_0}\right)^3 + \cdots \tag{4.54}$$

Equation (4.54) can be rewritten in terms of creep compliance as follows:

$$D(t) = D_0 + D_t t^n \tag{4.55}$$

where $D(t)$ is time-dependent creep compliance, σ is stress, D_0 is the instantaneous creep compliance and D_t is the amplitude of transient creep compliance.

Findley's power law can also be used to derive expressions for time-dependent in-plane and through-thickness viscoelastic moduli of composite materials:

$$E_v = \frac{E_0 E_t}{E_t + E_0 t^n} \tag{4.56}$$

where E_v is viscoelastic modulus, E_0 is initial modulus and E_t characterises time dependent behaviour.

When the applied loads are approximately constant for the duration of loading, a "pseudo-elastic" design method may be used. Creep or time-dependent modulus:

$$E(t) = \sigma/\varepsilon(t) \tag{4.57}$$

may be modelled by the following relationship:

$$E(t) = E_0 t^{-n} \tag{4.58}$$

E_0 is initial (or 1 second) modulus and n is the creep index (an experimentally derived constant). The value of E_0 is obtained by extrapolation. This approach can be used for different loading modes and elastic properties. The creep index n is a measure of viscoelastic behaviour and is dependent on the resin type and degree of cure, fibre format, orientation of the fibres with respect to the applied load, fibre volume content, loading regime and environmental effects (i.e. temperature, moisture, and aggressive chemicals). Creep index can be obtained from the gradient of $E(t)$ versus log t. Low values of n can be expected for elastic materials reinforced with continuous aligned fibres. The value of n is lower in the fibre direction for these materials. In fact, loading along the fibre direction is unlikely to result in significant creep deformation. Creep index increases for random fibre formats (e.g. CSM) and unfilled materials. For design purposes, creep modulus and creep index should be obtained direct from experiments on the composite system.

4.9 CREEP RUPTURE

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 composite is to a particular 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. Figure 32 compares the static fatigue curves of glass fibre-reinforced vinyl ester pultruded rods subjected to four-point bending whilst immersed in porewater (alkaline) solution (pH 12.6–13.0) at 40°C, 60°C and 80°C (see American Concrete Institute standard ACI 440.3R-0427) [120]. The self-stressing fixture used in the tests is shown in Figure 23. The rate of moisture diffusion increases with increasing applied stress and temperature; however, the fatigue life was mainly influenced by the applied stress and temperature rather than moisture content. The degradation process is enhanced by capillary diffusion along the fibre–matrix interface. In flexure loading, maximum tensile and compressive stresses occur at the upper and lower beam surfaces, which coincides with regions of maximum moisture concentration.

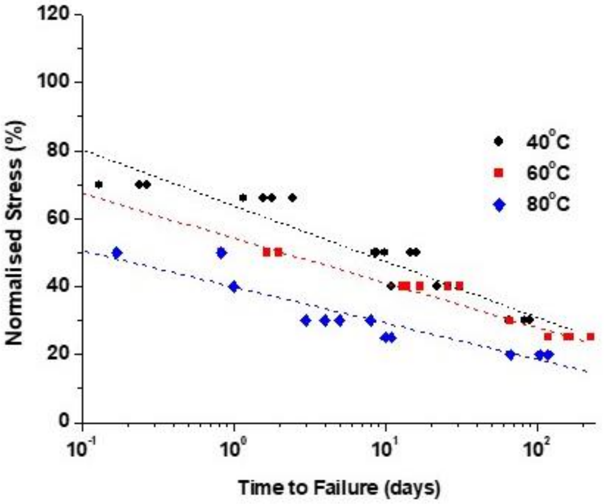


Figure 32 Flexure fatigue curves for GFRP rods in porewater solution at elevated temperatures

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 applications 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.

4.10 IONISING RADIATION

The effects that ionising radiation have on the properties of plastics can be predicted using a time-temperature-dose rate superposition principle [164, 165]. 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 expression for the shift factor a_T:

$$a_T = exp\left[\frac{E\left(T_{ref}^{-1} - T^{-1}\right)}{R}\right] \qquad (4.59)$$

where T_{ref} and T are the reference and service temperatures respectively, E is the activation energy for the process and R is the gas constant. 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 [166].

5 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 [58], 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 GFRP 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.

Although the survey reported in Appendix 1 was undertaken in 2017, it is still considered relevant and meaningful. 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. There is still an absence of good quality comparison exercises of longer-term laboratory tests and products recovered from service. A proposal for a Joint Industry Project (JIP) is outlined in Appendix 2. Companies interested in this project should contact Dr Tony Maxwell at NPL (tony.maxwell@npl.co.uk).

A further NPL report on a review of lifetime predictions [167] for a wider scope of materials (i.e. not limited to composites) by Nilmini Dissanayake, supported by a Daphne Jackson Fellowship held at NPL, will be published at a later date.

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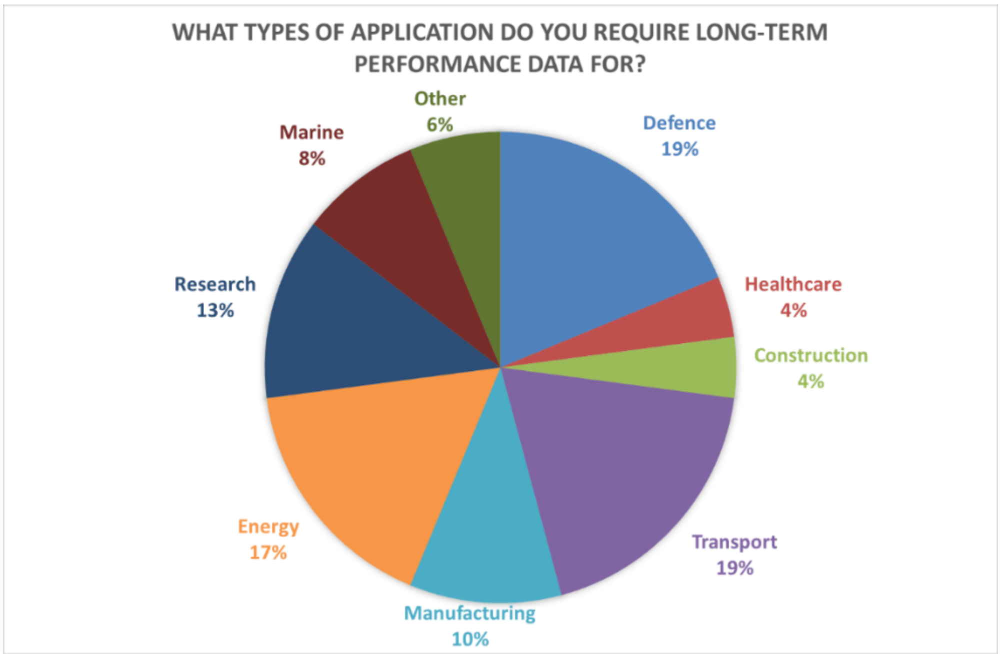
APPENDIX 1 INDUSTRIAL SURVEY ON COMPOSITE LIFETIME PREDICTION

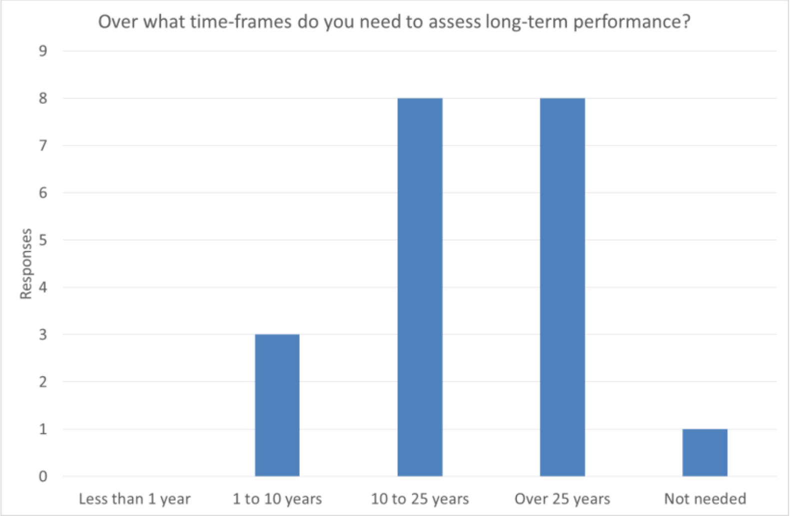
This appendix collates the responses that have been obtained from 23 UK companies that engaged in a survey held at the NPL Composites, Adhesives and Polymer (CAP) Industrial Advisory Group (IAG) concerning their requirements for long-term performance testing.

1.1 Applications



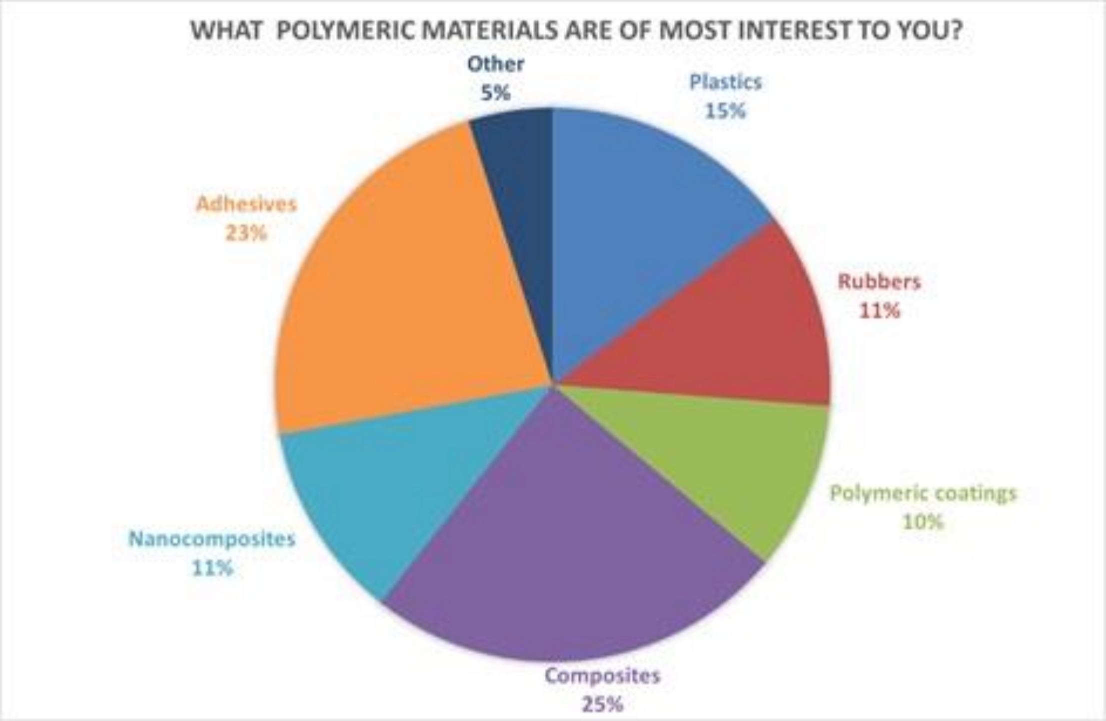
The main sectors requiring long-term performance data were found to be Defence, Transport and Energy. Many of the responses classified under manufacturing and research also came under these sectors. It is noticeable that there was limited interest from either healthcare or construction. In healthcare, 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.

1.2 Time-scales



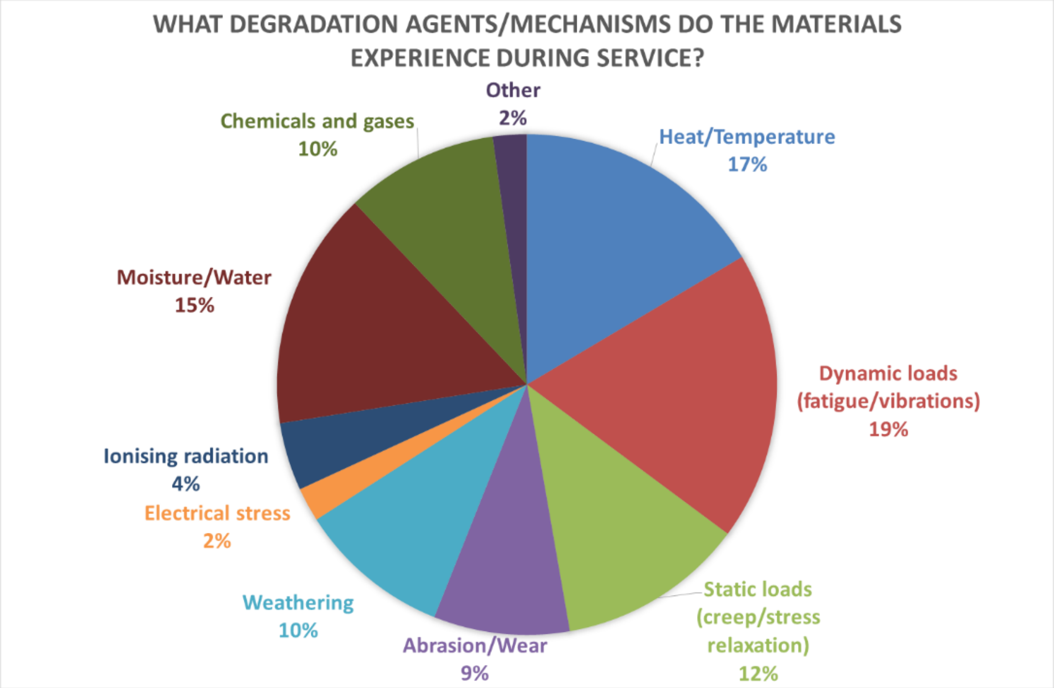
The timescale over which long-term performance of materials is required depends critically on the application of the product. As can be seen from the results, most applications requiring long-term performance measurement need properties predicted to at least 10 years and almost half of responses required 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 timescales 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.

1.3 Materials



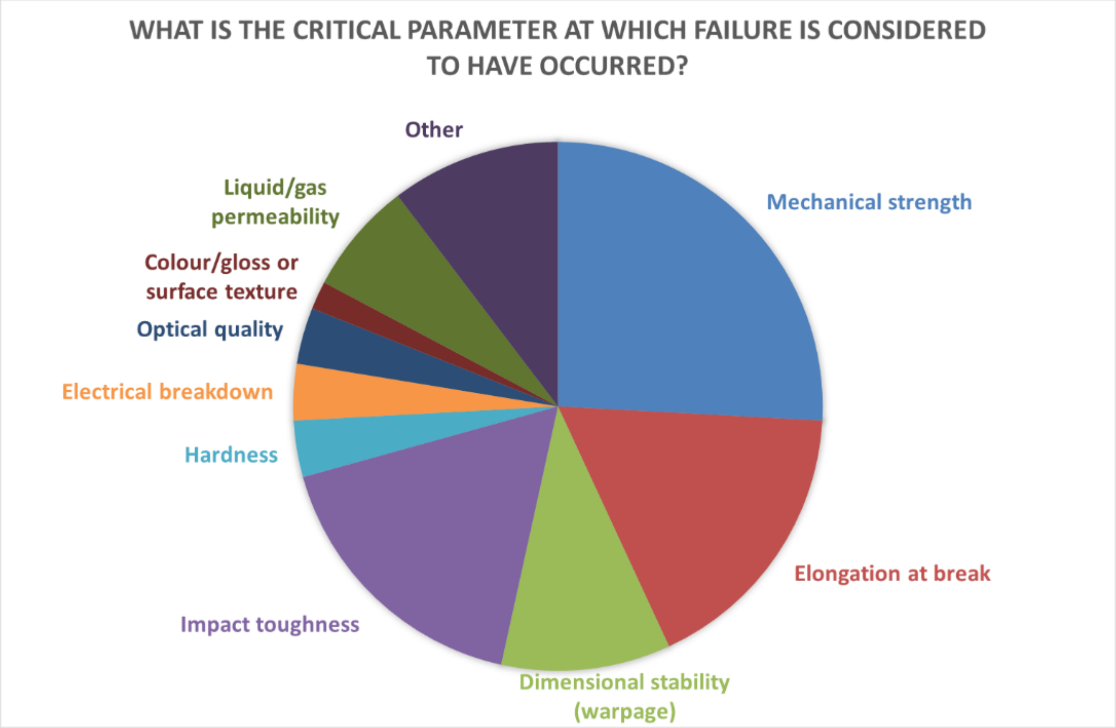
The two main areas of interest in terms of materials were adhesives and composites, where in both cases there is connectivity between the polymer and other materials used in the structure. Detailed examination of the survey results indicated that many of the composite materials are not conventional continuous 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.

1.4 Degradation mechanisms



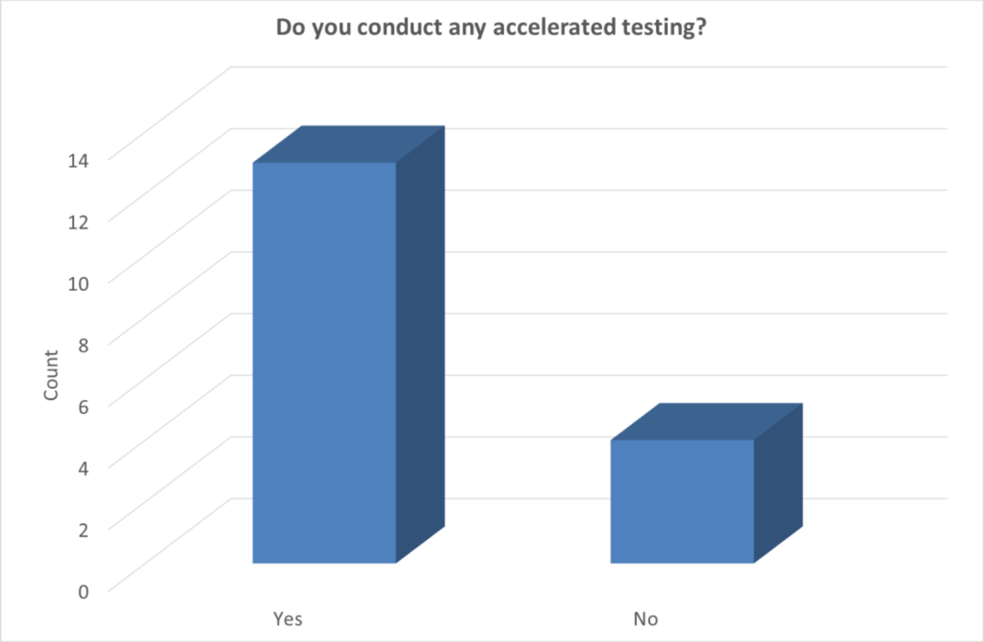
The main degradation mechanism that was identified for the causes of failure were stress (dynamic and static), temperature and moisture. Electrical stress and weathering were not identified as significant causes of concern possibly due to the considerable amount of research that has been conducted in 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.

1.5 Failure parameters



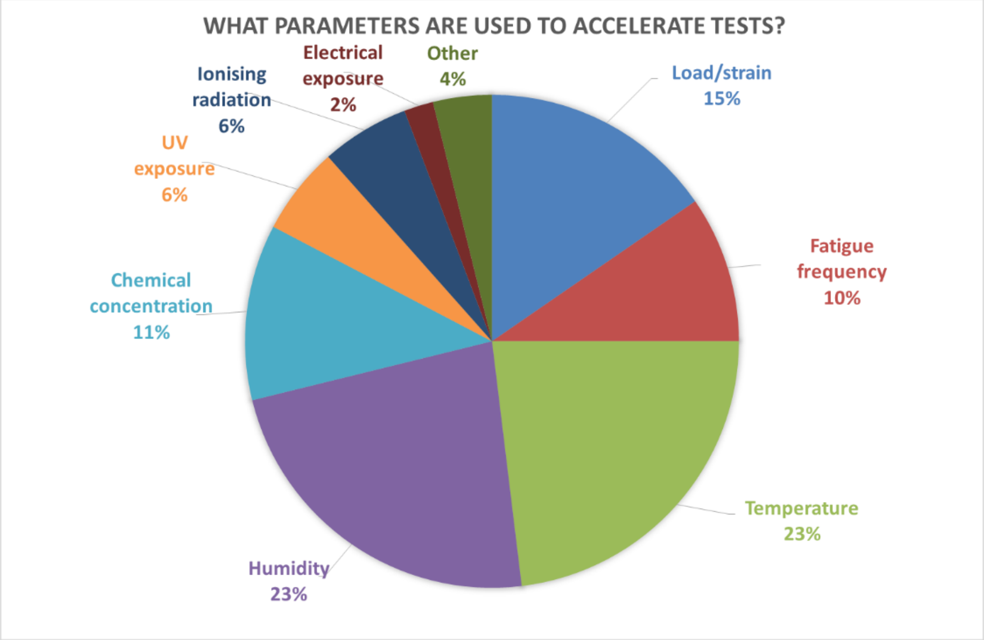
Critical to predicting the lifetime of a product is to define the failure criteria, for example a material can be mechanically intact during its entire service life but may have to be replaced due to loss of gloss if this is critical to its functioning. Identifying the appropriate failure mechanism is 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 cases what causes failure was not unknown at the design stage and sometimes even after failure has occurred.

1.6 Accelerated testing



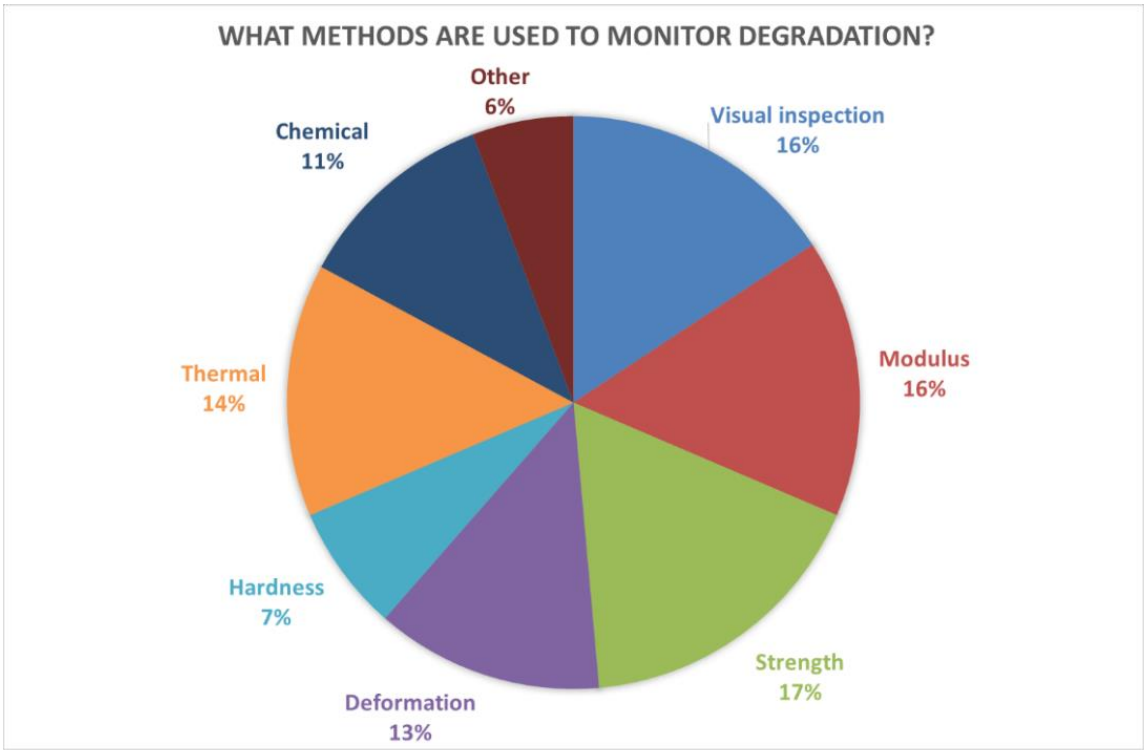
Three quarters of the respondents to the survey confirmed that they conducted accelerated testing and all respondents had an interest in accelerated tests for the prediction of long-term behaviour.

1.7 Methods of acceleration



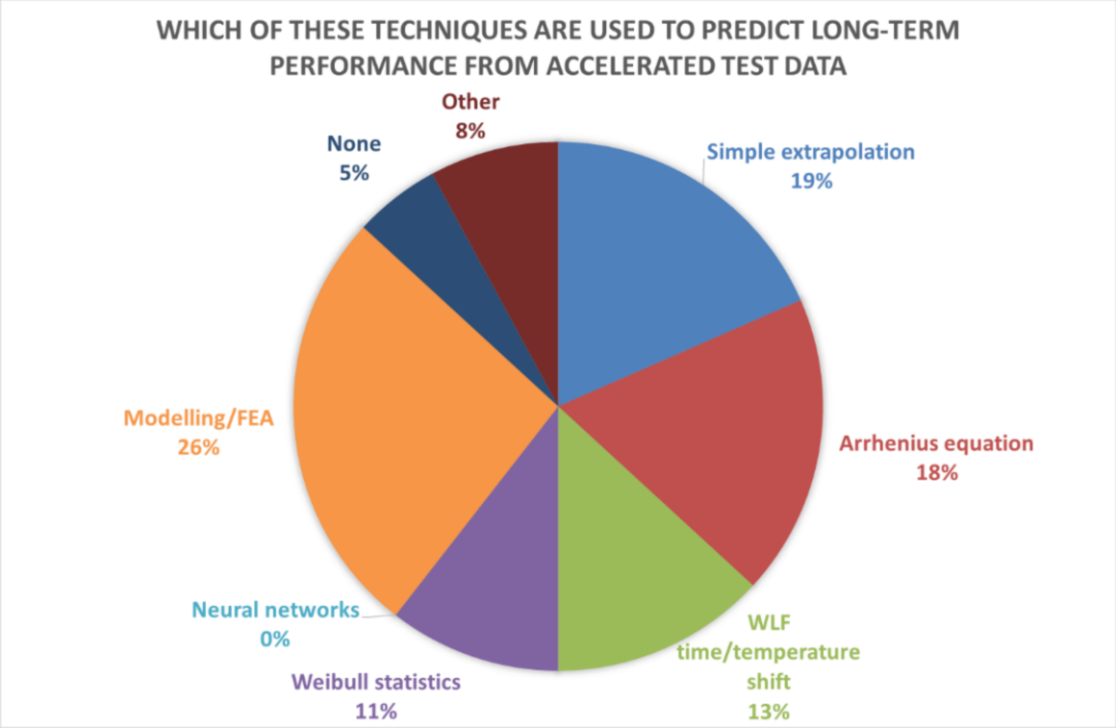
Loading under tension or compression as a function of moisture content and temperature were the most common forms of testing together with fatigue testing. The means of acceleration that were reported reflected the forms of testing being conducted with the most frequently used acceleration parameters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

1.8 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.

1.9 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.

1.10 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?

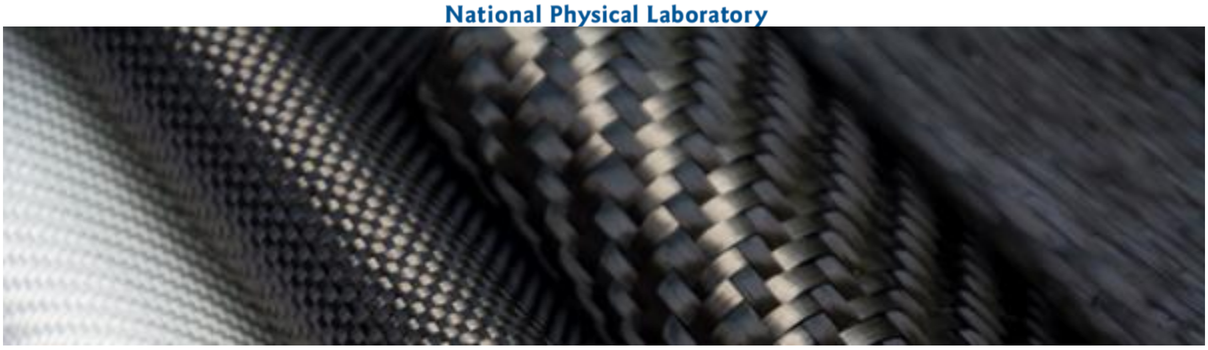
The following list summarises the areas where respondents feel further developments are required:

- 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.

APPENDIX 2 DRAFT JOINT INDUSTRY PROJECT (JIP) ON DURABILITY OF COMPOSITES

National Physical Laboratory



Joint Industry Research Project

Enabling a sustainable future for composite assets in demanding environments

The continuous need for lightweight, corrosion resistance and low maintenance structures in environmentally challenging applications in renewable energy, marine and infrastructure has naturally led to an increased use of advanced polymer composites. Despite their evident advantages, there are yet technical challenges that the sector needs to solve to maximise the benefits composites offer and increase their uptake and sustainable use. A validated methodology for the way composites environmentally age and their properties changes with time under realistic conditions, considering appropriate degradation mechanisms, is yet to be established. This project aims to deliver such methodologies by developing and validating predictive modelling toolsets through realistic lab-based accelerating ageing experiments and demonstrating the approach in scaled down industrially relevant demonstrators.

Approach and Overview

Building on stakeholder consultation and a state-of-the-art review carried out by NPL, where academic and industrially relevant developments in accelerated testing and associated predictive modelling of composites were captured and critically assessed, several technical work packages are proposed. The following description presents an overview of the objectives and the proposed deliverables. Further technical details will be defined and agreed on a collaborative basis via the project board which will be formed when the project commences and will have equal representation of all collaborators. The project comprises a range of activities including reviews, long-term laboratory-based experiments, modelling software toolset development, data analysis, and production of evidence-based good practice guidance and reports.

1 Application requirements and selection of demonstrators

Define industrially relevant demonstrators and in-service relevant performance requirements, leading to selection of associated composite materials and constituents for investigation.

Deliverable: *Project internal technical note articulating materials, in-service relevant test conditions and demonstrator structure*

2 Definition of physical test and predictive modelling approaches

Design-of-Experiment (DoE) to address industrial requirements and materials selected, including validation approach for demonstrators. Define modelling and simulation strategy to maximise the benefit of data obtained from physical tests in lifetime predictive toolsets.

Deliverable: *Project internal technical note to guide experimental programme,* simulation activities *and validation activities*

3 Accelerated ageing methodology – Physical testing

Validate the proposed accelerated ageing methodology through physical tests, in-depth investigation of the ageing mechanisms and the effects of time/environment on material changes.

Deliverable: *Good Practice Guidance document on how to appropriately define and implement an accelerated ageing programme for several composite material classes*

4 Predictive modelling methodology – Simulation tools

Develop and deliver a validated modelling toolset enabling prediction of lifetime of composite assets utilising an online data-informed approach. Utilise data generated through the experimental accelerated methodologies for validating the predictive tools.

Deliverable: *A validated predictive modelling toolset*

5 Demonstrators

Demonstrate relevance of proposed lab-based validated methodologies through scaled-down physical and digitally twinned engineered structures. Demonstrate the mechanics of online data exchange, informing the digital twin about the state of the physical component, and the predictive modelling, enabling asset management through smart maintenance internals and/or life extension.

Deliverable: *Physical and digitally twinned demonstrators*

Funding and Duration

The funding required for this Joint Industry Research Project will be equally spread between project sponsors with further support from NPL's National Measurement System programme. The anticipated duration of the project is 3 years, with an expected start date of October 1, 2021.

For further details please contact Dr Tony Maxwell tony.maxwell@npl.co.uk

APPENDIX 3 MODELLING MATERIALS' LIFETIME ABSTRACT

by Nilmini Dissanayake
(Daphne Jackson Scheme position undertaken at NPL)

Abstract

The evaluation of long-term aging responses of materials using accelerated testing is important to determine the secure working life of polymeric materials for their successful application. An understanding of physical and chemical changes in different polymers when exposed to long-term external factors such as heat, water vapour, humidity, UV radiation has provided models for examining their ultimate lifetime and accelerating degradation reactions. This paper represents an overview of the methods of lifetime prediction of degradable polymers using accelerated ageing tests and methods of extrapolation of data from most common environmental impact factors in degradation processes of polymeric materials.

Degradation of materials is caused by many different factors – singly or combined; both chemical (working environment) and physical (temperature, radiation) and mechanical (stress). Therefore, the mechanism of degradation can be rather complicated. The aim of this paper was to review the models that are used to predict the lifetime of different materials under different environmental conditions such as Arrhenius and Eyring models for temperature, humidity model using Arrhenius and Eyring, Fick's diffusion law for moisture and photodegradation. Mechanical degradation under fatigue and creep loading has also been presented. Models such as the inverse-power relationship, Peck and exponential are used to model the combination of degradation such as temperature and humidity or temperature and moisture for example.