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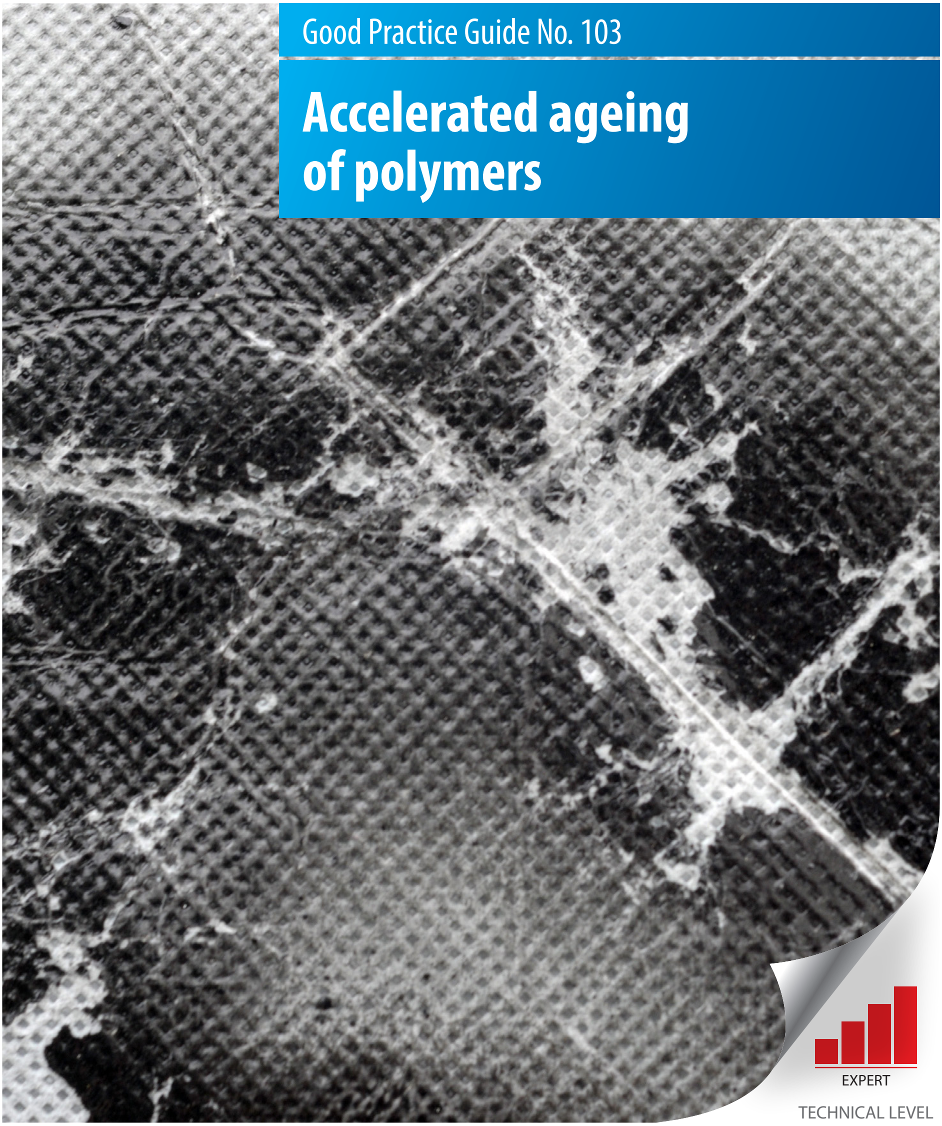

Good Practice Guide No. 103

Accelerated ageing of polymers

EXPERT

TECHNICAL LEVEL

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Abstract

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 to those of which data already exists), long-term or critical applications require the use of accelerated ageing regimes to generate data commensurate with the engineering requirements and life expectancy of the component. This Good Practice Guide is intended to give guidance on accelerated ageing and performance testing of polymeric materials for generating design data and for quality assurance purposes. The document is primarily concerned with polymers (thermosets and thermoplastics) and fibre-reinforced plastics and considers a range of hostile environments including artificial weathering, hot/wet and chemical (inc. solvents, caustic, and acidic solutions) exposure.

Acknowledgements

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Contents

Glossary of Terms (Based on BSI and ASTM Definitions)

Accelerated ageing test: Short-term test designed to simulate the effects of longer-term service conditions.

Adherend: Body that is or intended to be held to another body by an adhesive.

Adherend failure: Failure of a joint in the body of the adherend.

Adhesion: State in which two surfaces are held together by interfacial bonds.

Adhesive: Non-metallic substance capable of joining materials by surface bonding (adhesion), the bonding possessing adequate internal strength (cohesion).

Adhesive failure: Failure of an adhesive bond, such that separation appears to be at the adhesive/adherend interface.

Ageing: Entirety of all irreversible chemical and physical processes occurring in a material in the course of time.

Amorphous regions: Regions within a polymeric material, that, based on X-ray diffraction or other suitable techniques, do not show any evidence of crystalline structure.

Artificial weathering: Exposure to cyclic laboratory conditions involving changes in temperature, relative humidity, and radiant energy, with or without direct water spray, to produce changes in the material similar to those observed after long-term, continuous, outdoor exposure.

ASTM: American Society for Testing and Materials.

Blister: Elevation of the surface of varied contour and dimensions, with a cavity beneath.

Bond: The union of materials by adhesives.

Bond-line: The layer of adhesive, which attaches two adherends.

Bond strength: The unit of load applied to tension, compression, flexure, peel, impact, cleavage, or shear, required to break an adhesive assembly with failure occurring in or near the plane of the bond.

Breaking stress: Stress at the moment of rupture of a specimen.

Brittle failure: Failure in which the fracture surface exhibits no permanent material deformation to the naked eye (e.g., stretching, elongation and necking down).

BSI: British Standards Institute

Butt joint: Joint in which the plane of the bond is at right angles to a major axis of the adherends.

Bulk adhesive: The adhesive unaltered by the adherend.

Cleavage: Mode of application of a force to a joint between rigid adherends, which is not uniform over the whole area, but results in a stress concentrated at one edge.

Cohesion: The ability of the adhesive to resist splitting or rupture.

Cohesive failure: Failure within the body of the adhesive (i.e., not at the interface).

Composite: Solid product consisting of two or more distinct phases, including a binding material (matrix) and a particulate or fibrous material.

Conditioning: A series of operations intended to bring a sample or specimen into a reference state with regard to temperature and humidity.

Coupling agent: Substance (e.g., organosilane) that promotes or establishes stronger bond at the interface of the resin matrix and the reinforcement.

Crack: Fissure that may or may not penetrate the external surface of the material or its entire thickness, the polymeric material being completely separated between the crack walls.

Craze: Defect at or under the surface of a plastic attributable to apparent cracks, bridged by polymeric material of reduced (apparent) density.

Creep: The time-dependent increase in strain resulting from a sustained load.

Crystallinity: Presence of three-dimensional order at the level of molecular dimensions.

Cure: To set or harden by means of a chemical reaction.

Cure time: Time required to affect a cure at a given temperature.

Cure temperature: Temperature at which an adhesive, an assembly or a polymeric composition achieves a state of cure.

Degradation: Change in the chemical structure of a polymeric material involving a deleterious change in properties.

Delamination: Separation of layers (i.e., planar defect) in a laminate because of failure in or near the adhesive joint.

Deterioration: Permanent change in the physical properties of a material evident by impairment of these properties.

Diffusivity: The proportionality constant that describes the ability of chemical species, such as a liquid, to diffuse through a solid. Diffusivity is generally temperature dependent.

Dimensional stability: Consistency of dimensions of a material part or specimen under environmental conditions.

Discolouration: Colour change that involves lightening or darkening and/or change in hue.

Dry strength: Strength of a polymeric material part or specimen after drying under specified conditions.

Ductile failure: Failure in which the fracture surface clearly exhibits permanent deformation with stretching, elongation, and necking.

Durability: The endurance of joint strength relative to the required service conditions.

Elastic limit: Greatest stress, which a material is capable of sustaining without any permanent strain remaining upon complete release of stress.

Electromagnetic radiation: Wave motions of characteristic wavelength, including gamma radiation, X-rays, ultraviolet, visible light, infrared, and radio waves. Elongation: Increase in length of a specimen under tension, usually expressed as a percentage of the original length.

Embedding: Process of encasing completely an article, such as a sensor, in a polymeric material.

EN: European Norm

Environmental test: Test to assess the performance of an assembly under service conditions.

Fibre: Unit of matter of relatively short length, characterised by a high ratio of length to thickness or diameter.

Filler: Relatively inert material (e.g., talc) added to a plastic or resin to modify its strength, fire resistance or other qualities, or to lower costs.

Fillet: Portion of an adhesive that bridges the adherends outside the bond-line.

Glass transition: A reversible change in an amorphous polymer or in amorphous regions of a partially crystalline polymer from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one.

Glass (surface) veil: Thin layer made from glass filaments (continuous or chopped) held together with a binder.

Gloss: Degree to which, a surface approaches perfect optical smoothness in its capacity to reflect light.

Hardness: Resistance of a material to indentation or scratching.

Hygroscopic: Material capable of absorbing and retaining environmental moisture.

Infrared (IR): The region of electromagnetic radiation of wavelengths from 800 nm to 1 mm. IR can be divided into near infrared (800 nm to 2500 nm), mid infrared (2500 nm to 25 μm) and far infrared (25 μm to 1 mm).

ISO: International Standards Organisation.

Laminate: Product made by bonding together two or more layers (plies) of material or materials.

Lap joint: Joint made by placing one adherend partly over another and bonding together the overlapped portions.

Lay-up: Assembly of layers of resin-impregnated material for processing.

Ligament area: Cross-sectional area remaining after notching.

Mat: Product made of filaments, staple fibres, or strands, cut or uncut, oriented, or not, held together in the form of a sheet.

Peel: Mode of application of a force to a joint in which one or both adherends is flexible and which the stress is concentrated at a boundary.

Permeability: Property of a material transmitting gases and liquids by passage through one surface and out at another surface by diffusion and sorption processes.

Plastic deformation: That part of the strain in a stressed plastic, which remains after the applied stress has been removed.

Plasticisation: Increase in softness, flexibility, and extensibility of an adhesive.

Post-cure: Further treatment by time and/or temperature of an adhesive to obtain the required properties by curing.

Porosity: A condition of trapped pockets of air, gas, or vacuum within a solid material. Prepreg: Admixture of resins (with or without fillers), additives, and reinforcements in woven and filamentous form, ready for moulding.

Prepreg: Admixture of resins (with or without fillers), additives, and reinforcements in woven and filament form, ready for moulding.

Primer: A coating applied to a surface, prior to the application of an adhesive, to improve the performance of the bond.

Profile: Extruded or pultruded polymeric product, excluding film and sheet, having a characteristic constant axial section.

Pultrusion: Process of making continuous lengths of reinforced plastic profiles with high unidirectional strength by pulling continuous strands of resin-impregnated rein-forcing material through a heated die and then through a heating chamber, if necessary, to post cure the resin.

Reinforced plastic: Polymer (plastic) with high-strength fibres embedded in the composition, resulting in some strength properties greatly superior to those of the base resin. Roving: Collection of parallel strands (assembled roving) or parallel filaments (direct roving) assembled without intentional twist.

Semi-crystalline: Polymer containing crystalline and amorphous phases.

Size (coupling size): Material applied to fibres or filaments during their manufacture.

Spectrophotometer: An instrument for measuring the transmittance or absorbance/optical density at different wavelengths.

Strain: Unit change due to force in size of body relative to its original size.

Stress: Force exerted per unit area at a point within a plane.

Stress-strain diagram (or curve): A diagram in which the corresponding values of stress and strain are plotted against each other.

Structural bond: A bond, which is capable of sustaining in a structure a specified strength level under a combination of stresses for a specified time.

Substrate: An adherend, a material upon which an adhesive is applied.

Surface preparation (or treatment): Physical and/or chemical treatments applied to adherends to render them suitable or more suitable for adhesive bonding.

Swelling: Increase in volume of a test specimen immersed in a liquid or exposed to a vapour.

Thermoplastic: A material that can be repeatedly softened by heating.

Thermoset: A resin that is substantially infusible and insoluble after being cured.

Toughness: That property of a material by virtue of which it can absorb energy, generally implying absence of brittleness and relatively high elongation to break.

Traveller: A test specimen used for example to measure moisture content as a result of conditioning.

True stress: Stress calculated from the supporting area at the time of measurement rather than from the original area.

Ultraviolet (UV): The region of the electromagnetic spectrum at shorter wavelengths than blue light, generally taken to be between 100 nm and 400 nm. Due to atmospheric absorption UV measurements can only be carried out below 190 nm in a vacuum environment.

Viscoelasticity: Stress response of a material acting as though it were a combination of an elastic-solid and a viscous fluid with flow dependent on time, temperature, load, and rate of loading.

Visible light: The region of the electromagnetic spectrum that can be seen by the human eye, generally taken to be between 400 nm and 800 nm.

Wavelength: The length of the waves associated with the electromagnetic radiation.

Weathering: Effects of exposure of a material to outdoor conditions.

Wet strength: Strength of a polymeric material determined immediately after removal from a liquid in which it has immersed under specified conditions.

Wetting: A surface is considered completely wet by a liquid if the contact angle is zero, and incompletely wet if the contact angle has a finite value.

Yield strain: The strain, below which a material acts in an elastic manner, and above which it begins to exhibit permanent deformation.

Yield stress: The stress (either normal or shear) at which a marked increase in deformation occurs without an increase in load.

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Chapter 1

Scope

Scope

Polymeric materials are increasingly being used for applications where long-term or critical applications require the use of accelerated ageing regimes to ensure the serviceable life of product and components. A trend that is likely to continue for the foreseeable future due to progressive changes in material procurement strategies that require increased product lifetimes in increasingly harsh environments. 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 increasingly being demanded for engineering components in products such as cars and domestic appliances, where consumers often view extended lifetime warranties as a sign of product quality. Whilst the life expectancy of products in non-demanding applications have traditionally been predicted from previous experience, the use of polymeric materials in long-term or critical applications requires a far better understanding of the failure mechanisms to enable lifetime predictions of these materials.

This measurement guide aims to provide guidance to technologists, engineers and designers on accelerated ageing and performance testing of polymeric materials for generating design data and for quality assurance purposes. The document is primarily concerned with polymers (thermosets (including adhesives) and thermoplastics) and fibre-reinforced plastics (FRPs) and considers a range of hostile environments including artificial weathering, aqueous (liquid and vapour) and chemical (i.e., solvents, caustic, and acidic solutions) exposure. Guidance is provided on static and creep rupture testing at ambient and non-ambient temperatures.

The intention of the guide is to provide designers and users with sufficient information, which when coupled with their own expertise and a suitable accelerated test regime can be used to produce design data and enable screening of materials and manufacturing processes (e.g., adhesive/adherend surface treatments). The document provides guidance of the use of test methods that can be used to measure physical changes resulting from exposure to hostile environments, and techniques that can be used to relate laboratory testing to actual service conditions. If the intention is to generate design data, then the guide should be used in conjunction with the appropriate structural design codes and standards.

The guide assumes some basic knowledge of the materials and mechanical engineering and is not intended as a textbook or as a design protocol. There are several published works, which provide a comprehensive coverage of plastics, adhesives, and composites technology, and testing and preliminary design [1-28]. Other NPL Measurement Good Practice Guides [29-36], provide advice on issues relating to the preparation and testing of plastics, adhesives, and adhesive joints. The intention of the guide is to complement these published works.

It is recommended that specialist advice be sought from manufacturers and suppliers on material selection, and use of associated technologies and health and safety requirements. Organisations that can provide specialist advice are listed at the back of the guide along with relevant standards and publications.

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Chapter 2

Ageing mechanisms in polymeric materials

- Introduction
- Temperature
- Moisture
- Natural weathering
- Ionising radiation
- Chemical degradation
- Biological degradation
- Environmental stress cracking (ESC)
- Stress corrosion of fibres

Introduction

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 polymeric materials. In some circumstances, only a few hours of exposure may lead to failure or seriously compromise material performance (see also Measurement Good Practice Guide No. 28 [30]). Conversely, the rate of chemical degradation can be slow and insidious without evident signs of material deterioration.

Irreversible property changes in polymeric materials can be induced by any number of degradation agents (see list below) acting alone or collectively.

- Thermal - static heat ageing, sub-zero exposure or thermal cycling
- Humidity (including hot/wet) exposures
- Complete immersion in water at ambient and elevated temperatures
- Freeze/thaw and dry/wet cyclic conditions
- Continuous or intermittent saltwater immersion or spray
- Weathering (including rain and sand erosion)
- Combined load (i.e., stress) and environmental exposures
- Chemical (including water, fuel, acids, alkalis, solvents and oxygen)
- Ultraviolet (UV) and high-energy radiation
- Electrical stress (e.g., lightning stress and galvanic reactions)
- Micro-organisms (e.g., fungi)

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 in the presence of mechanical stress (static and fatigue).

In many applications, engineering components/structures will be exposed to a combination of two or more factors, often resulting in complex synergistic degradation of the material. Accelerated degradation may be caused by the combined action of two or more vectors (e.g., temperature and humidity). The relative importance of each agent will depend on the agents present and their levels. Degradation from one agent can also reduce resistance to other agents, similar to biological systems. The predominant factors in climatic exposure are humidity, temperature and solar (UV) irradiation. The severity of these factors will depend on geographical location and need to be considered when designing with these materials.

Failure of a FRPs, insofar as it is no longer fit for purpose, may occur because of cumulative damage to the thermoset or thermoplastic matrix, interfacial separation between fibres and matrix, chemical attack of the fibre reinforcement or a combination of two or more of these processes. The net effect is loss of stiffness and mechanical integrity.

It is recommended that when comparing the effects of material systems, surface treatments and processing variables on the durability of components in hostile environments, that all specimens are prepared and conditioned together to account for any variability in the conditioning environment. Also, control specimens are recommended to check changes in systems performance.

Temperature

Prolonged, or even short term, 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 of the degradation processes that occur in polymeric materials, such as oxidation, chemical attack, and mechanical creep. Physical changes include polymer structure shrinkage, pore formation and weight loss through chemical decomposition of the polymer. As the temperature increases, mechanical properties such as stiffness and strength tend to decrease. Oxidation is generally considered to be the most serious problem when using polymers at elevated temperatures with the rate of degradation increasing with the amount of oxygen present [22, 26]. In adhesively bonded joints, the primary path for oxygen diffusion is through the adhesive, which can be relatively rapid at elevated temperatures. Metallic adherends are impermeable to oxygen, thereby providing a barrier to the gas. In contrast, FRPs are permeable to atmospheric gases, and hence the rate of degradation is considerably higher with the elevated temperatures also degrading the fibre-matrix interface. At extremely high temperatures, as experienced in fires, fibre ablation occurs.

The overall degradation process will often involve a relatively long induction period during which little degradation is observed [22-23]. At the end of this period, there is a rapid increase in degradation leading to a significant reduction in the mechanical properties of the polymer. This induction period is temperature sensitive and is reduced significantly at elevated temperatures. The induction period of the degradation process can normally be regarded as the serviceable lifetime of the polymer.

Other physical changes can occur in polymers as a result of temperature, one of the most common being thermal expansion. Thermal expansion is a reversible process, provided no damage occurs as a result of the change in temperature. In FRPs, differences in thermal expansion between fibre and matrix can induce residual stresses, thereby reducing fibre-matrix bond efficiency and resulting in thermo-mechanical degradation during thermal cycling. Similar mechanisms may also occur in adhesive joints. A sudden brief exposure to high temperatures can result in a phenomenon known as thermal spiking, which can lead to excessive localised stresses with deleterious effects on structural performance. The effects of rapidly driven-off moisture through thermal spiking can also be expected to contribute to damage.

Exposure to low temperatures can result in embrittlement of plastics, fibre-matrix interfacial cracking in FRPs and debonding in adhesive joints. Rapid failure can occur in environmentally degraded polymeric materials at sub-zero temperatures (e.g., due to the formation of ice particles from absorbed water initiating internal fractures). Complete interfacial debonding may occur in multiple component systems exposed to cryogenic temperatures through, for example, the combined effects of differential thermal contraction and embrittlement.

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)
- Reduction in the glass transition temperature (T_g)
- Reduction in mechanical and physical properties (i.e., stiffness, strength and hardness)
- Surface degradation and damage (e.g., blistering)

Although the process of moisture absorption and desorption within the surface layers occurs almost immediately on contact with the environment, moisture diffusion into the thick systems is usually a slow process (see Chapter 3). For FRPs, it may take weeks to months before a substantial amount of moisture has been absorbed by the composite, and considerably longer periods (i.e., 1-2 years) before the material is saturated. The rate of moisture uptake by a material (i.e., 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 between resin systems and change with chemical ageing.

The presence of tensile loads accelerates moisture uptake by opening existing internal cavities or voids, and by contributing to micro-crack formation. A materials system containing micro-cracks will absorb considerably more moisture than an undamaged materials system. This applies equally to thermosets (including adhesives) and composite laminates – see also [36]. Exposing the wet system to sub-zero temperatures can further exacerbate this process. A commonly used test is to subject hot/wet conditioned laminates to thermal cycling in which the composite is exposed to temperatures as low as -55 °C for a given number of cycles to assess the laminates crack resistance.

Absorption of water is known to cause plasticisation (softening) of the polymer, depressing T_g, and lowering the modulus and strength. Elongation to break (strain-to-failure) tends to increase with moisture content. For example, T_g for 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, such as glass fibre-reinforced plastic (GRP) products, in load bearing structures to ensure that the maximum operating temperature is at least 30-40 °C below the T_g of the material (taking into account moisture effects). Figure 1 shows the effect of moisture content on T_g for F922 epoxy that has been immersed in distilled/deionised water for prolonged periods of time at three different temperatures [37].

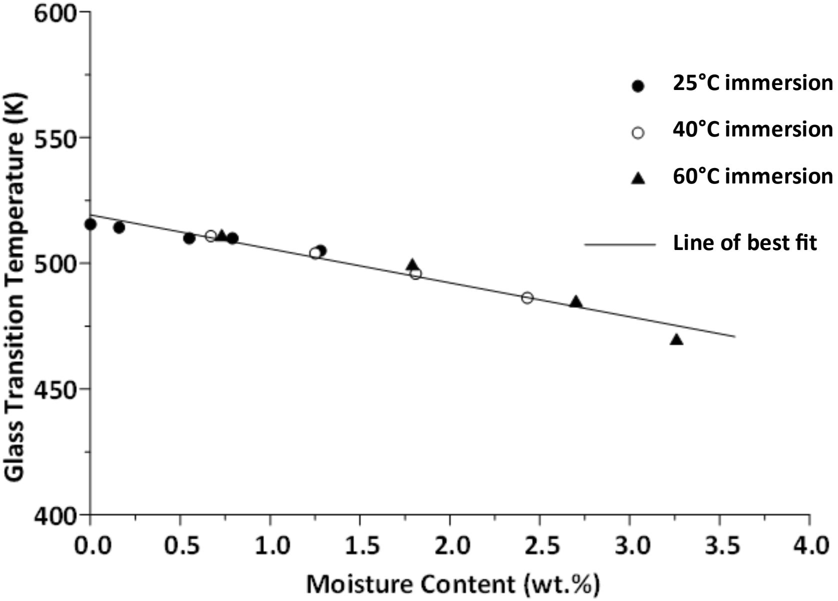


Figure 1. Glass transition temperature of F922 epoxy as a function of moisture content

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.

Adhesive bonded systems

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

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

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

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

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

Note 1: Good surface preparation is crucial to ensuring optimum bond strength and reliable long-term performance of bonded joints, particularly under hostile service conditions. Unsatisfactory surface preparation will result in premature and unpredictable bond failure at the adhesive/adherend interface. Surface preparation is recognised as the most critical step in the adhesive bonding process and considerable effort is often expended in optimising the surface treatment.

Fibre-reinforced plastics

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

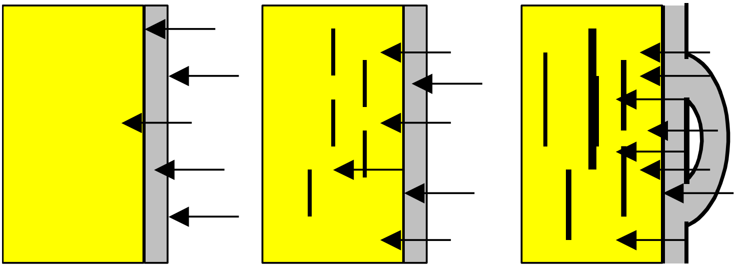


Figure 2. Schematic of the osmotic process – leading to delaminations/blistering

All laminates when exposed to marine environments will allow water vapour to permeate the structure. As the water diffuses into the composite it reacts with any hydrolysable components (e.g., ester groups) inside the laminate to form tiny cells of concentrated solution. Under this osmotic process [38-39] (see schematic in Figure 2), more water is drawn through the semi-permeable membrane of the laminate to dilute the solution. The water can increase the fluid pressure of the cell substantially and increases of 50 atmospheres can occur, which eventually distorts or bursts the laminate or coating and leads to a blistering of the surface. Damage can be very extensive requiring major repair or the replacement of the structure (Figure 3).

Figure 3. Osmotic blistering of a GFRP boat hull with inset showing laminate breakdown (Courtesy of Minton, Treharne and Davies Ltd)

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

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

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

Fibre degradation is primarily an issue for glass fibres and aramid fibres, with carbon fibres being stable in most environments. Carbon fibres are relatively insensitive to moisture, and hence the variability in the tensile breaking stress and strain for carbon fibre tows is noticeably lower than for E-glass fibre and aramid fibre tows. Exposure to humid air (including environmentally controlled laboratories at standard conditions (i.e., 23 °C and 50% relative humidity (RH)) will compromise the load-bearing capacity of the fibres, resulting in a loss of strength and an increase in strength variability [40]. For example, the tensile strength of freshly drawn E-glass fibres is typically 3.5 GPa, however exposure to atmospheric moisture can lead to a reduction in strength (tensile strength is typically 2.0 GPa, or less). The loss of tensile strength of E-glass fibres is dependent on exposure time, temperature, and degree of humidity. On initial exposure to a humid/water environment, the rate of fibre degradation is relatively rapid, even in benign environments, such as air-conditioned laboratories. The tensile strength is reduced to 3.0 GPa after 3 weeks exposure to standard laboratory conditions. Immersion in water at ambient temperature for the same period results in a 20% reduction (~2.5 GPa). The original tensile strength can be fully realised, provided the fibres are carefully handled during fabrication to avoid surface damage and are stored in a dry environment. An intrinsic tensile strength of 2.0 GPa is often assumed for design purposes.

Degradation of E-glass fibres in water can be mainly attributed to leaching of alkali oxides (sodium and potassium oxide) from the fibre surface resulting in the formation of surface micro-cracks, which act as stress concentrators. The loss of strength can be expected to be permanent at all conditioning temperatures and exposure times. The water surrounding glass fibres evolves into an aggressive alkali solution as the alkali ions dissolve out of the glass, slowly decomposing the glass fibres. Increasing the alkali content of the glass tends to reduce environmental attack from water and alkali solutions. It is worth noting that deionised water is slightly more aggressive than either tap water or seawater. Drying of the composite will remove most of the skin of water adjacent to the fibre, but a small permanent layer with retained water will remain, and the mechanical properties of the fibre will be permanently degraded (for further details on chemical degradation see references [27, 41]).

The effect of moisture on aramid (e.g., Kevlar 49®) fibre-reinforced epoxy laminates is potentially greater than other composite systems. Aramid fibres tend to absorb moisture and degrade at room temperature with the rate of degradation accelerating as temperature is increased. Substantial hygrothermal strength losses have been observed with these materials, particularly under natural weathering conditions (i.e., combination of moisture and UV light).

Natural weathering

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

Chemical reactions are induced when specific functional groups absorb the UV radiation. Free radicals liberated in the process will trigger further reactions. The deleterious effect will be dependent on the chemical nature of the material, environmental factors such as temperature and humidity, and exposure time. Material changes include discoloration (yellowing and bleaching), embrittlement, and loss of mechanical and physical properties. Photo-oxidative sensitivity also tends to increase with prolonged exposure to pollutants, such as nitrogen dioxide [9, 23, 27].

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

Photo-degradation is initiated by solar radiation, which results in the absorption of UV radiation by chromophores and in the activation of excited states in macromolecules. When a polymer is exposed to solar radiation the energy absorbed by the polymer results in the formation of free radicals within the polymer by the dissociation of the C-H bonds in the polymer chains. The extent of this chemical reaction depends on the radiation exposure that is the quantity of ultraviolet light (<350 nm) to which it is exposed. Once free radicals have been produced, reaction with oxygen generates hydroperoxides (POOH) [25]. 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 [25].

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 very near surface due to consumption by reaction with the polymer radicals. Since the concentration of these radicals diminishes by termination reaction during the dark period, oxygen ingress can extend to greater depth.

UV radiation is known to degrade polymeric materials (including aramid fibres), although only the outer layer tends to be affected. Glass and carbon fibres tend to be unaffected by UV radiation. Epoxy resins are slightly sensitive to ultraviolet radiation, depending on the chemical formulation. Signs of photo-degradation include embrittlement (surface cracking), discolouration and loss of transparency [39]. 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 added to protect the adhesive system from chemical breakdown caused by heat and UV radiation, whilst UV stabilizers protect against UV degradation and exposure to fluorescent light and filtered daylight. Pigments (e.g., carbon black, titanium dioxide, zinc oxide and barium sulphate) alter the absorption characteristics of the material acting as a screen against UV radiation when compounded with the adhesive. The costs of additives can often be prohibitive and may adversely alter mechanical performance. Carbon black is particularly effective in protecting against UV radiation and is inexpensive. It absorbs UV radiation and protects the polymer chains.

Ionising radiation

Ionising 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 crosslinking 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 [42-43].

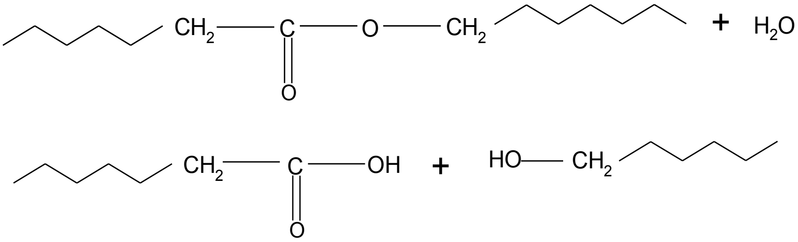
The intensity of ionising radiation on the earth's surface is not normally high enough to significantly affect most plastics and FRPs. Molecular chain scission often causes a lowering of the polymer viscosity and softening temperature, accompanied by a reduction in mechanical strength. In contrast, cross-linking, 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).

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. In FRPs, 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).

Chemical degradation

Chemical attack of thermoplastics involves specific chemical reaction of the polymer with the fluid with the most common mode of failure being hydrolysis by water, acids, and alkalis [11]. Esters, amides, imides, and carbonate groups are particularly susceptible. Where these groups are located within the backbone chain rather than the side chain, chain scission ensues.

A general hydrolysis scheme can be summarised as follows:



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

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

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

Alkali and acidic solutions

As with moisture effects, acid and alkali degradation processes are accelerated at elevated temperatures. Compared with other glass fibre types (e.g., R, ECR and C), E-glass is particularly vulnerable to attack from mineral acids (e.g., HCl and H_2SO_4) and alkalis (e.g., NaOH and KOH) [27, 41]. Dilute mineral acids are not only encountered in the chemical plant industry but are also present in industrial and household effluent and sewage. When E-glass fibres encounter acids, ionic exchange occurs between the metallic cations (e.g., Na^+ ions) at the glass surface and the hydrogen ions in the acid solution, resulting in leaching of sodium, potassium, calcium, magnesium, boron and aluminium from the outer layer or sheath of the fibre. Exposed fibres gradually lose weight, stiffness, and strength with exposure time. Immersion in weak caustic solutions at room temperature can result in strength reductions of 30% within two weeks.

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

Other chemical agents

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

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

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 [11, 23]. 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. Whilst 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.

As previously mentioned, synergistic effects are often observed between the various environmental factors resulting in amplification of the degradation process. For example, the combination of JP-4 fuels 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 4 illustrates damage induced in GFRP pipes when exposed to molecular chlorine and hydrogen chloride.

Figure 4. Chlorine degradation (left) and HCl induced blistering (right) of a GRP pipe (Courtesy of AEA Technology)

Galvanic corrosion occurs when two different conductive materials of different galvanic potential are in contact in the presence of water (electrolyte). The more anodic material will corrode at an accelerated rate resulting in a build up of corrosion product near the contact area. The galvanic effect will be dependent on moisture content, temperature and electrical and chemical properties of the galvanic cell electrodes and electrolyte. Galvanic corrosion can be a problem between carbon fibre-reinforced composite and metallic parts (aluminium alloys and steel), causing corrosion and progressive debonding in the case of honeycomb structures – see also ISO 21746 [44].

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.

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

There is little evidence to suggest adverse structural changes occur in composites through biological (marine organisms and bacteria) attack. Hard (animals with calcium carbonate shells) and soft (algae and animals with soft structures) marine organisms growing on the surfaces of GRP 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.

Environmental stress cracking (ESC)

ESC (the 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, craze formation and crack development all contributing. While crystalline and amorphous polymers are both susceptible to ESC, amorphous polymers are particularly susceptible due to their relatively open structure 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.

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 5). The mechanism of crazing in chemical environments is generally considered to be identical to that in air [13, 15. 45]. In general terms, craze initiation is considered to evolve from micro-deformation processes in localised regions about 30 nm in diameter (see Figure 5) [46]. 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 [47].

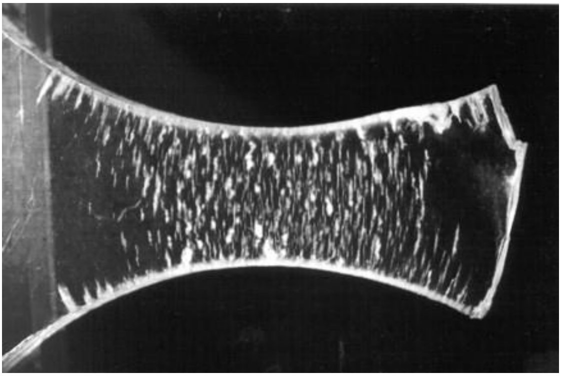


Figure 5. Crazing of PMMA

Exposure to moderate levels of applied stress for extended periods of time can induce crazing and cracking in polymers and is the underlying cause of long-term transition from brittle behaviour for ductile polymers. This mechanism, known as creep (or stress) rupture is a common cause of polymer failure, and consequently has significant ramifications on the chemical resistance of FRPs [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.

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 [15, 45]). However, the particular 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 [45] 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 crazing is thought to occur at a critical level of the inelastic strain, which is independent of the environment and temperature [45, 48-49]. This has significant implications for assessing the durability of a polymer. For example, in polymer-fluid combinations that lead to plasticisation-induced toughening, simultaneous exposure may delay the development of crazes. However, exposure to the fluid after the sample has been stressed in air to attain the critical level of inelastic strain may lead to rapid crazing. It helps explain the very rapid development and growth of crazes in many cases when environment exposure times are relatively short but the time under stress has been long.

Stress corrosion of fibres

The process of environmental degradation of glass fibres is accelerated under mechanical loads with the long-term strength of GRP laminates under hostile environments being controlled by stress corrosion of the fibre-reinforcement [27, 41]. 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. ESC of glass fibres occurs in acidic solutions with the rate of degradation dependent on pH level. The consequence is that GRP laminates suffer delayed brittle fracture in acidic environments, under stress [50].

Static fatigue or creep rupture, which refers to time-dependent failure of the material when subjected to constant load, is used as a measure for gauging the relative resistance of the material (i.e., fibre or composite) to chemical environments. The less resistant a fibre is to a 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.

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Chapter 3

Environmental conditioning and testing

- Introduction
- Temperature
- Moisture conditioning and testing
- Mechanical testing of conditioned specimens
- Fibre bundles and impregnated strands
- Design and planning an accelerated test programme

Introduction

Several techniques have been employed to accelerate testing of polymeric materials. The usual approach for environmental testing has been to increase the temperature, humidity level or pressure (and in the case of chemical exposure the concentration level of the chemical agent). However, there is a temperature limit to which most polymer resins can be raised without affecting a change in the degradation mechanism (e.g., moisture absorption0. Above this critical temperature, there is a strong possibility of altering the degradation mechanism.

An alternative approach to increasing the level of the degradation agent is to increase the frequency of application of the degradation agent. An example is chemical resistance where exposure may be continuous, whereas in-service exposure is intermittent. The concern is that continuous exposure may result in a different response to actual service conditions. The use of relatively small specimens for longer times under less severe conditions could potentially be used. Provided the data generated can be scaled up to predict the long-term performance of more realistic size structures [51-52] to generate durability data provided that allow rapid conditioning under more realistic temperatures, stresses and concentrations reflecting actual service conditions. This Chapter examines temperature and moisture accelerated testing of polymeric materials.

Temperature

High temperatures

Prolonged, or even short term, exposure to elevated temperatures will result in a reduction in the short-term properties and possibly irreversible chemical and physical changes within an adhesive. For polymer systems, high temperatures will rarely exceed 300 °C and will normally be considerably lower.

It is recommended when characterising mechanical properties (i.e., stiffness and strength) at elevated temperatures that testing be conducted in a temperature-controlled chamber [53]. It is important that the load cell is thermally isolated from the chamber and that any sensors within the test environment can operate at the test temperature. It may be necessary to use thermal compensation to ensure accurate sensor measurements. It is common practice for elevated temperature to allow a soak period of 10 minutes at the test temperature prior to testing. The purpose of “heat-soaking” is to eliminate distortion due to non-uniform temperature distributions. The thermal mass of test fixtures can often result in a significant thermal lag in the specimen reaching equilibrium with the surrounding environment. It is recommended that the surface temperature of the specimen be monitored to determine the soak time. This need only be carried out for the initial test for a series of identical tests. Care needs to be taken when testing moisture pre-conditioned specimens to prevent drying of the specimen during the test.

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 temperature is typically between -40 °C and -100 °C. Liquid nitrogen-based cooling systems can achieve temperatures around -150 °C, or better. Although 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 [54] 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 [55].

Thermal conditioning and heat ageing

It is advisable to use 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. 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 smaller.

Heat ageing tests [23] should include a minimum of three (preferably five) temperatures for periods of 1,000 hours (~6 weeks), or more to generate sufficient data that can be extrapolated to lower (i.e., service conditions). It is important that at the highest temperature that 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., 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 5 to determine the change of property with time. The spacing of exposure times is usually linear for heat ageing. ISO 11403-3 [56] 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.

There is no general heat ageing method for polymeric materials, however there are several specific procedures, which are primarily intended for control and comparative purposes (for further details see [23]).

Thermal stability

A standard procedure for assessing the thermal stability of polymers exposed to elevated temperature for long periods is given in ISO 2578 [57]. 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 Chapter 4). 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 [58] and ASTM D1203 [59] cover the stability of plasticisers in polymers, both standards measuring the amount of plasticiser's that is lost due to absorption on activated charcoal. Both standards are essentially used for quality control testing.

Heat distortion temperature (HDT)

HDT is often the only criterion used in determining a material's "fitness for purpose" at elevated temperatures (i.e., upper 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 [60-62] and ASTM D648 [63] specify test procedures for determining HDT of polymers and composites. The test procedure for determining HDT, as described in ISO 75-1 [60], 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) [61] and FRPs (Part 3) [62]. 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 un-reinforced 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.

Moisture conditioning and testing

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, 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 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 - difficult to accurately control high humidity levels at elevated temperatures.

Note 1: Although accelerated ageing is widely used, a full understanding of the effects is not yet available and there is no consensus as to a satisfactory accelerated test.

Moisture absorption test methods

ISO 62 [64], ASTM D570 [65] and ASTM D5229 [66] 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 [67]. For FRPs, it is recommended that square specimens also be used with a width $w \leq 100 \times$ 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. As previously mentioned, 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 absorption effects). The recommended maximum conditioning temperatures are 45 °C and 70 °C for 120 °C and 180 °C cure systems, respectively [68]. 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:

$$M = \frac{\left(W_{wet} - W_{dry}\right)}{W_{dry}} \times 100\% \qquad (1)$$

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. 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:

$$M = \frac{M(t) - M_C}{M_0} \tag{2}$$

$$M = \frac{M(t) - M_0}{M_0} \quad \text{when} \quad M_C = M_0 \tag{3}$$

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) [68]. 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.

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. Moisture conditioning of FRPs is often carried out at elevated temperature and/or humidity, (e.g., 70 °C/85% RH) to accelerate moisture uptake, however, 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 [69] 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 [52]. 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 2-3 wt.% 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: 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 2: 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 [67]. Moisture expansion or swelling can be measured periodically with a micrometer, Vernier caliper, traveling microscope or continuously using strain gauges or embedded sensors, such as optic fibres (I.e., Fibre Bragg Grating) (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. plot of swelling strain versus weight gain will show a change in gradient for high porosity materials.

Fickian diffusion

At temperatures well below the T_g of the conditioned material, water absorption of most polymers correlates well with Fick's laws (see Annex A of ISO 62 [64]). The diffusion coefficient, independent of time and moisture concentration (i.e., humidity level) can be calculated from the Fickian diffusion curve (Figure 6). Figure 7 shows a typical diffusion curve for an epoxy resin sample (see also [36]).

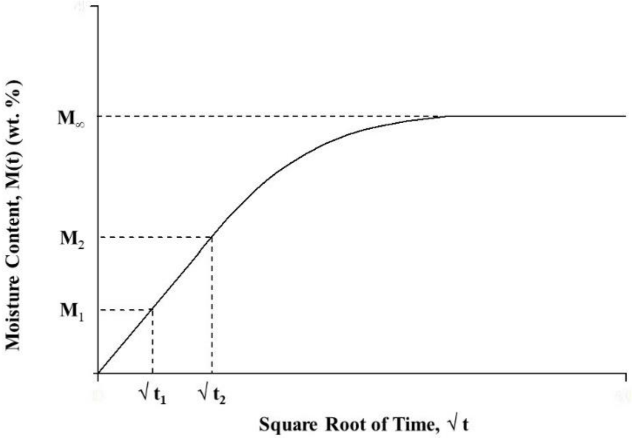

Figure 6. Fickian diffusion curve

The apparent diffusion coefficient D_a (not corrected for edge effects) is determined from the initial linear region of the Fickian diffusion curve using the following relationship [70]:

$$D_a = \frac{\pi}{16}\left(\frac{h(M_2 - M_1)}{M_\infty(\sqrt{t_2} - \sqrt{t_1})}\right)^2 \tag{4}$$

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.

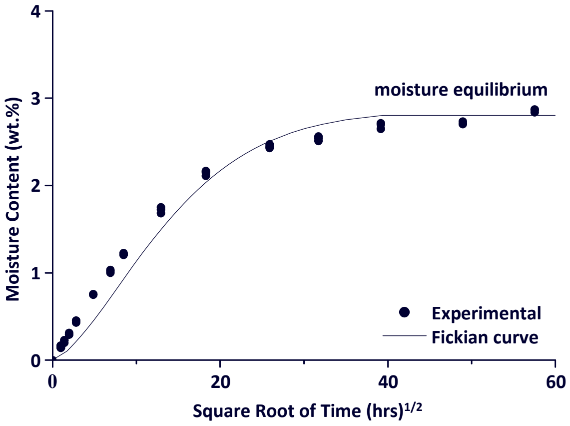

Figure 7. Fickian curve fit of moisture absorption data for an epoxy resin

The fractional moisture content gain *G* can be approximated by [70-72]:

$$G = \frac{M - M_i}{M_\infty - M_i} = 1 - exp\left[-7.3\left(\frac{D_a t}{h^2}\right)^{0.75}\right] \tag{5}$$

M_i is the initial moisture content of the sample and $M = M(t)$ the percent moisture content of the composite at any time t. When only one side of the sample is exposed, the thickness h is replaced by $2h$.

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 [71]:

$$D = D_a\left(1 + \frac{h}{l} + \frac{h}{b}\right)^{-2} \tag{6}$$

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). If the moisture entering through the specimen edges is neglected, then diffusivity of the material $D = D_a$.

Note 3: Diffusion in an adhesive joint may be 10 times as high as that measured for bulk adhesive samples, probably as a result of capillary action along the adhesive/adherend interface. Moisture diffusion may differ between the unstressed and stressed states with the diffusion rate increasing with applied stress.

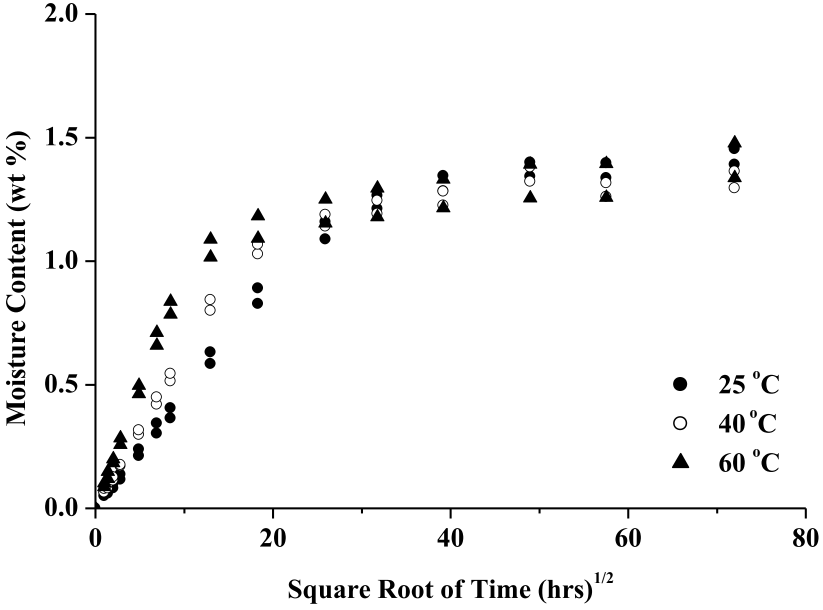

Figure 8. Moisture diffusion curves for UD T300/924 CFRP at three different temperatures (immersion in deionised water)

Diffusion behaviour is temperature dependent (Figure 8) and for ideal systems diffusivity *D* can be expressed as a function of absolute temperature *T* according to the Arrhenius relationship [71]:

$$D(T) = D_0 e^{-(E/kT)} \tag{7}$$

where *k* is Boltzmann's constant. Material parameters D_0 and *E* (energy barrier to diffusion) can be determined from a linear regression fit to loge *D* versus 1/*T* graph (Figure 9).

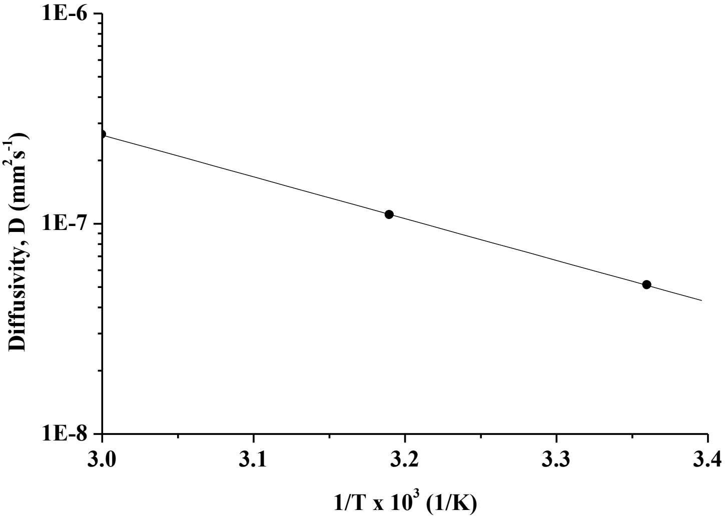

Figure 9. Temperature dependence of diffusivity for UD T300/924 carbon/epoxy (immersion in deionized water)

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 may be estimated by the following relationships [71]:

$$D_{11} = (1 - V_f)D_m \tag{8}$$

$$D_{22} = \left(1 - 2\sqrt{\frac{V_f}{\pi}}\right)D_m \tag{9}$$

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

The diffusion coefficient for a composite is given by the following relationship [71]:

$$D = D_{33}\left(1 + \frac{h}{l}\sqrt{\frac{D_{11}}{D_{33}}} + \frac{h}{b}\sqrt{\frac{D_{22}}{D_{33}}}\right)^2 \tag{10}$$

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 [71]:

$$M_\infty = a\phi^b \tag{11}$$

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

In the case of aramid composites, 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 fibre and resin separately to isolate constituent contributions. After long exposure times, the moisture content may deviate above that predicted by the Fickian analysis, exceeding the saturation level predicted by Fickian theory. This non-Fickian behaviour could possibly be due to defect growth. Thermal spikes and freeze/thaw cycling can result in micro-damage formation, leading to an increase in the rate of moisture uptake and saturation level.

Moisture measurements are sensitive to a number of factors that need to be considered to ensure accurate diffusivity values. These are listed below [36]:

- 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.
- 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.
- Surface roughness can affect moisture uptake and drying. Rough surfaces are more difficult to dry, and also present a larger surface area to the surrounding environment.
- 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.
- Specimen dimensions need to be accurately measured. Small variations can result in significant errors in diffusivity calculations.
- Surface damage and defects must be avoided as these can act as paths for moisture ingress.

Mechanical testing of conditioned specimens

For design purposes, a material test programme should measure both the moisture absorption properties of a material (i.e., diffusion rate and equilibrium content) and the resultant mechanical properties at equilibrium. Mechanical property measurements at intermediate moisture levels (based on average moisture contents) can be used to determine temporal and spatial distributions of stresses and strains within a bonded structure. To evaluate worst-case effects of moisture content on material properties, tests are performed on specimens that have been preconditioned to the design service moisture content (e.g., aerospace worst-case environment is considered to be represented by 70 °C/85% RH).

It should be noted that the material operational limit is influenced markedly by temperature and moisture content. Figure 10 shows tensile stress-strain responses under ambient test conditions for an adhesive that has been immersed in water for periods ranging from 30 minutes to 12 days. There is a significant reduction in tensile stiffness and strength with increasing moisture content. The reduction in material properties will be more severe at elevated temperatures.

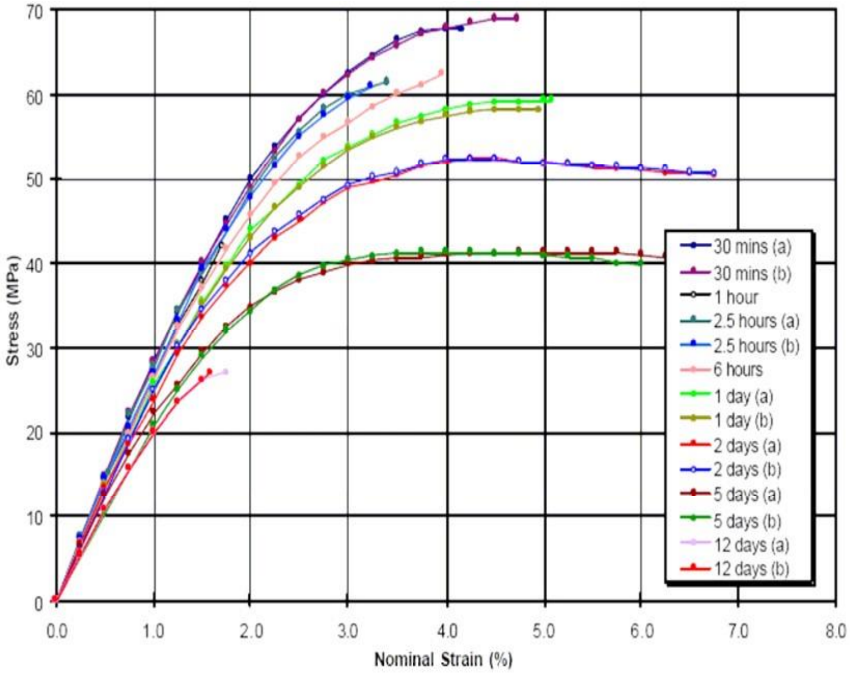

Figure 10. Tensile stress-strain curves for different water immersion periods

A number of contact and non-contact techniques, such as linear voltage displacement transducers (LVDTs), video extensometers, and electronic speckle pattern interferometry (ESPI), strain gauges and crosshead movement are available for measuring strain and displacement. Except for strain mapping techniques (i.e., ESPI and digital image correlation (DIC)), the measured strain will be an average strain. Also, strain gauges only measure strain at the location of the gauge. Further details on these techniques can be obtained from NPL Measurement Good Practice Guide Number 47 [33]. Some thought needs to be given to selecting techniques for the actual tests to be performed. Factors to be considered include:

- Degree of accuracy and resolution required
- Area over which strain is to be monitored
- Suitability of measurement device for testing environment (e.g., calibration for contact extensometers may not be valid at non-ambient temperatures)
- Quality of visual access to specimen (for non-contact techniques)
- Chemical compatibility with any pattern marking or adhesives required
- Likelihood of strain measuring devices (e.g., knife edges on extensometers) damaging specimen and initiating premature failure.

Strain gauges have particular issues that restrict their usefulness in environmental conditioning and testing. Most strain gauge adhesives are sensitive to moisture, which can often preclude bonding of strain gauges to the specimen prior to the preconditioning stage. Moisture attack of the strain gauge adhesive and strain gauges will occur from the top, edges and through the test specimen. It is therefore important to ensure that the adhesive selected for bonding the strain gauges remains unaffected for the entire duration of the test and that strain gauges and associated electrical wiring are suitably encapsulated. Silicone rubber and foil have been placed over strain gauges to isolate the gauges during environmental conditioning. The process is only partially effective, as moisture will eventually penetrate the bond-line. The strain gauge manufacturer should be contacted to obtain advice on adhesive selection and procedures for strain gauge protection. The preferred method is to use either contact extensometers or video extensometers for monitoring strain.

It is important that the moisture content be established prior to testing and that specimens be tested within an hour of removal from the conditioning environment to ensure that minimal water loss occurs. At elevated temperatures, preconditioned specimens tend to dry out during the test, although for static tests the effects are minimal provided testing is completed within 15 minutes of the specimen being removed from the conditioning environment. Methods of inhibiting moisture loss, such as encapsulating specimens with a sealant or enclosing the specimen in a polythene bag containing a salt solution appropriate to the humidity requirements of the test, are not practical.

Traveller specimens are required for monitoring the moisture content loss that occurs during the test. For coupon testing, it is common practice to allow a soak period of 10 minutes at the test temperature prior to testing. The purpose of "heat-soaking" is to eliminate distortion due to non-uniform temperature distributions.

Moisture conditioned specimens can be stored in a refrigerator at a temperature of 4°C for periods of up to six weeks with minimal moisture loss or effect on mechanical properties. Sub-zero temperatures can result in further damage to a material due to ice formation, and hence storage under these conditions should be avoided.

Fibre bundles and impregnated strands

Test methods have been developed for characterising the tensile properties of fibre bundles and impregnated strands under static and cyclic (tension-tension) loads, and/or aggressive environments [51]. These test methods require shorter conditioning times and less manufacturing and testing costs compared with current practices. The use of small diameter composite rods (1.5 to 5 mm), as shown in Figure 11, enables rapid environmental conditioning under more moderate and realistic temperatures and moisture levels compared with those methods used to accelerate ageing in laminates. Degradation effects on the composite rods by the environment are quickly manifested (within 7 days) in terms of strength reduction [51].

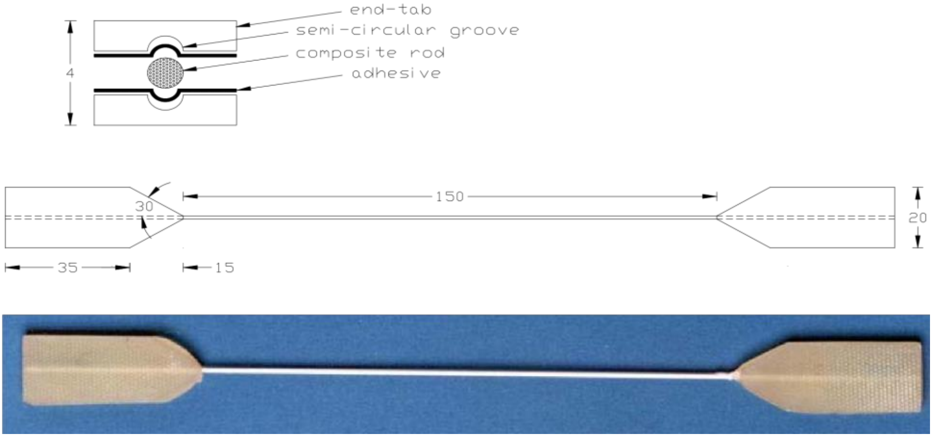

Figure 11. Composite rod specimen with adhesively bonded composite end tabs (dimensions are in mm)

Several test methods exist for measuring the tensile strength and longitudinal modulus of single fibre filaments and fibre tows or rovings (i.e., bundle of continuous parallel filaments). These methods are usually intended for yarns having a diameter of less than 2 mm (typically 0.5 to 0.8 mm), or a linear density lower than 2,000 tex (weight per unit length in g/km). Fibre tow methods include testing of both un-impregnated (i.e., loose, or dry) and impregnated rovings.

ISO 3341 [73] specifies a method for the determination of the breaking force and failure strain of un-impregnated glass fibre rovings, whereas ISO 9163 [74] allows for both un-impregnated and impregnated fibre tows. ASTM D4018 [75] and ISO 10618 [76] specify test methods for carbon fibre tows. Manufacturers will often use in-house quality assurance methods for determining fibre tensile properties. NPL Measurement Note CMMT (MN) 063 [51] gives details on specimen manufacture and testing.

Design and planning an accelerated test programme

In order to conduct an effective accelerated test programme, it is essential to spend time in designing and planning the test program [11, 23]. The process is iterative and will need to be repeated several times to establish a test program that will meet budget and technical requirements. The test program 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 program. 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 accelerated test program to ensure that the test procedures used closely reflect the service conditions [11, 23].

- Clearly define the purpose and aims of the test programme (i.e., product performance assessment, material comparison, quality assurance and design data).
- Specify the service life that needs to be predicted and the level of uncertainty in life expectancy that is acceptable.
- 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/empirical model(s) for extrapolating short-term data to service conditions.
- Timing and sequencing of exposures - where possible, exposure intervals should match these 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.

Although test conditions for quality assurance, material comparison testing, and comparative checks of material performance against design specification, are often limited with respect to the entire spectrum of conditions that may be experienced during service operation, the results still can provide valuable information on material behaviour under extreme conditions. It is important, however, that the test conditions are standardized and reproducible. For design and performance prediction, it is essential that extrapolation relationships from the test conditions to those experienced in service are known and can be used with confidence (NB. Material behaviour (including failure mechanisms) needs to be the same for both the accelerated test and service conditions).

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.

Chapter 4

Static fatigue testing

- Introduction
- Static fatigue testing

Introduction

Testing materials under applied loads further accelerates the onset and accumulation of damage. For static fatigue testing, strain levels in excess of those normally experienced during service are applied to the test component. Although obviously apparent for temperature, an increase in chemical concentration or applied stress can also alter the mechanism of degradation. This Chapter examines static fatigue testing.

Static fatigue testing

Static fatigue (or creep rupture) tests are performed to assess the extension of materials or structures under load in order 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 in excess of 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 (NB. 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 12); and
- Self-stressing fixture where specimens are placed in either a tube equipped with a pre-calibrated spring system (Figure 12) for loading specimens or a circular ring.

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

Figure 12. 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 12), 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 12 is capable of loading 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 in order to accurately determine time-to-failure.

Specimens loaded by springs can often be in an unstressed state for a considerable period of time (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 in order 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 particular 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 13 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).

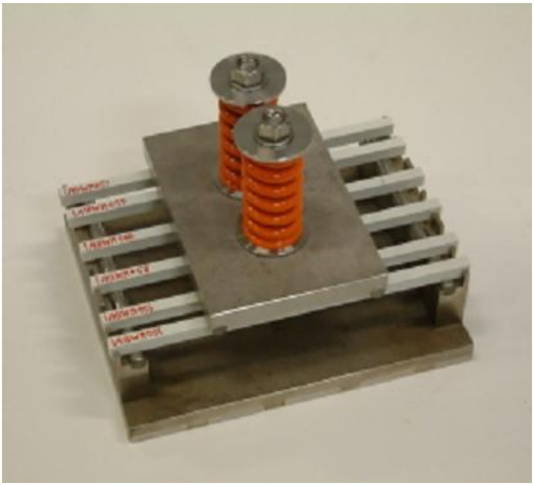

Figure 13. Self-stressing flexure rig with specimens

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 bedding in period at the start of the test and specimens tend to creep rapidly at 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 [77] 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.

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Chapter 5

Environmental stress cracking (ESC) of plastics

- Introduction
- Bent strip tests
- Bent strip for flexible materials
- Ball and pin impression
- Constant tensile deformation
- Slow strain rate testing
- Constant load tests
- C-ring tests
- Strain hardening tests

Introduction

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 products long-term properties. The evaluation of ESC in thermoplastics is covered by several national and international standards [19]. 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 [78])
- Bent strip test for flexible materials (ASTM D1693 [79])
- Ball and pin impression (ISO 22088-4 [80])
- Constant tensile deformation (ISO 22088-5 [81])
- Slow strain rate testing (ISO 22088-6 [82])

Constant Load Tests

- Constant tensile stress (ISO 22088-2 [83])
- C-ring tests (ISO 7539-5 [84] and ASTM G38 [85])

Note 4: ISO 7539-5 [84] and ASTM G38 [85] 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 from NPL Technical Review No.3 [19].

Bent strip tests

The bent strip test (ISO 22088-3 [78]) involves clamping the test specimen to a semi-circular former to apply a known strain to the specimen. The radius of curvature of former can be varied to induce different levels of strain in the specimen. This strain may be calculated using the following equation:

$$\varepsilon\,(\%) = \frac{d}{2r + d} \times 100 \tag{12}$$

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. The 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 [79]. The technique is suitable for flexible polymers such as polyethylene but should only really be used for quality control purposes. An illustration of the type of apparatus used in this test method is shown in Figure 14. 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.

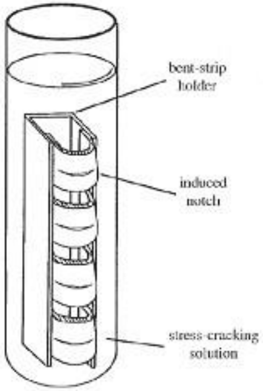


Figure 14. Bent strip technique for flexible polymers [79]

Ball and pin impression

The ball and pin impression test (ISO 22088-4 [80]) 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 (ISO 22088-5 [81]) is a relatively new test. The test method involves applying a constant deformation to the specimen and monitoring the stress relaxation that occurs while it is immersed in the chemical environment. The test is repeated using progressively smaller levels of deformation until the stress relaxation curves of consecutive tests (4 and 5) superimpose on one another (see Figure 15). S_0 is the initial stress and S is the stress at time t. 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.

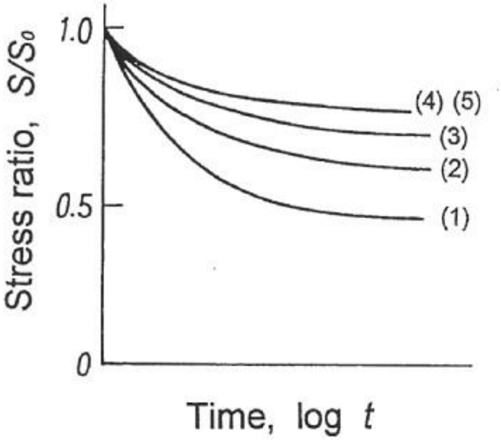


Figure 15. Stress relaxation curves for progressively smaller levels of deformation (1 > 5)

Slow strain rate testing

The slow strain rate method has been used only comparatively recently for characterising the performance of plastics although it is well-established for metals and it has now been developed into a standard as ISO 22088-6 [82]. 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 16. The main advantages of the slow stain rate test are that it is relatively rapid, requires few specimens and can be automated.

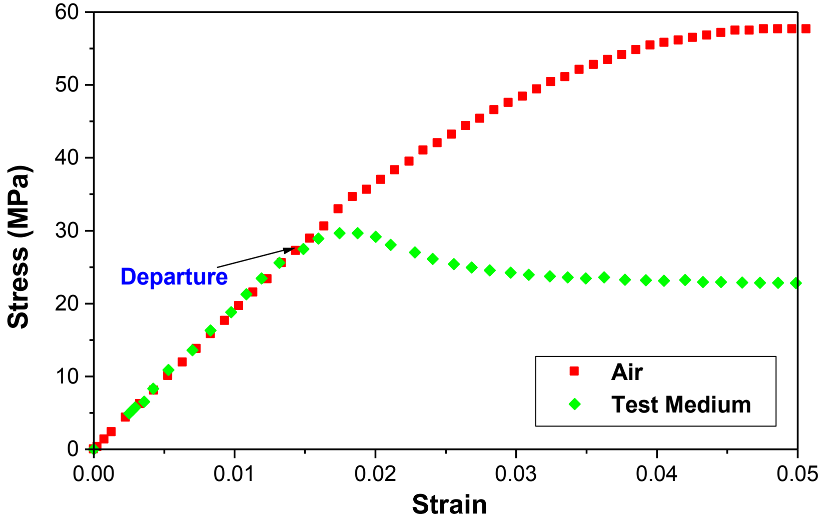


Figure 16. Typical stress-strain plot showing difference in stress/strain profile for material exposed in air and in the test medium

Constant load tests

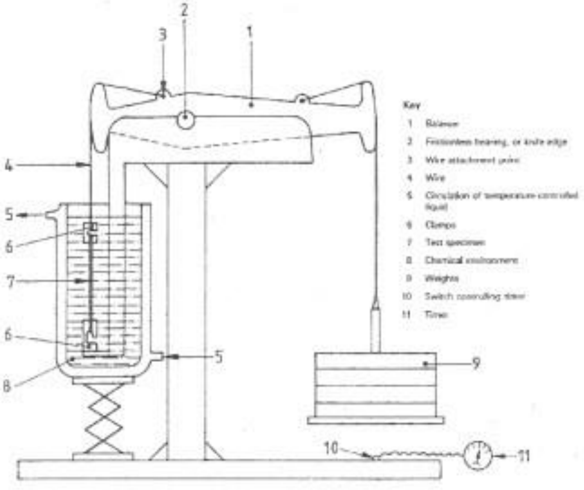
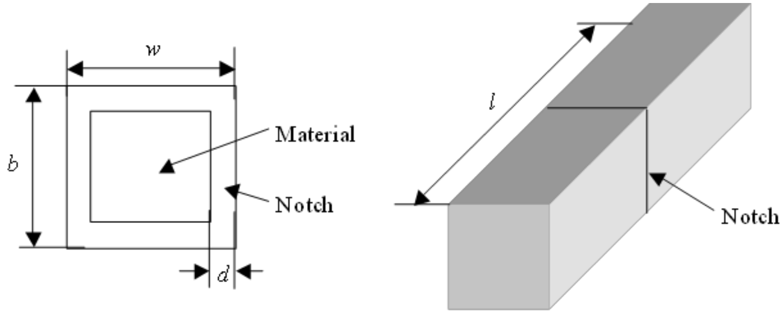


Figure 17. Illustration of typical apparatus used for a constant load test

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 [83]). An illustration of the type of apparatus used in this test method is shown in Figure 17. 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. Environmental cell used for constant load tensile test is shown in Figure 18. 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 1000 hours) can be used as a measure of the ESC resistance.

Figure 18. Typical environmental cell used for the constant load tensile test

Polyethylenes and polypropylenes can also be examined using constant load tests, however due to generally good ESC resistance a more severe test is required. This is achieved by cutting sharp notches on all four sides of the tensile specimen as shown in Figure 19. The procedure used to conduct the tests is similar to that used in the conventional load tests. This tests method is known as the full notch creep test [86].



w = overall length, minimum: 6 ± 0.2 m

b = width at tapered ends: 6 mm ± 0.2 mm

l = length of specimen: 90 ± 0.2 mm

d = notch depth: 1 ± 0.1 mm

Figure 19. Test specimens used in the full notch creep test

The full notch test shows differences in the ESC resistance, but can be misleading if creep tests are not conducted for a sufficient length of time (up to 1 year). Figure 20 compares the time to failure of three grades of linear low-density polyethylene (LLDPE) in which there is a crossover point at approximately 1000 hrs.

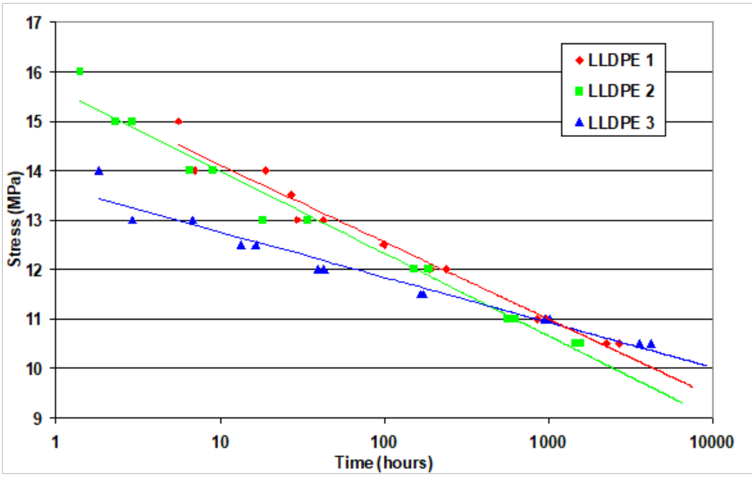


Figure 20. Time to failure of three grades of LLDPE full notch creep specimens

C-ring tests

C-ring specimens are often used for testing of tubing and pipes. 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 [84] and ASTM G38 [85]). An almost constant load can be developed on the C-ring specimen by placing a calibrated spring on the loading bolt.

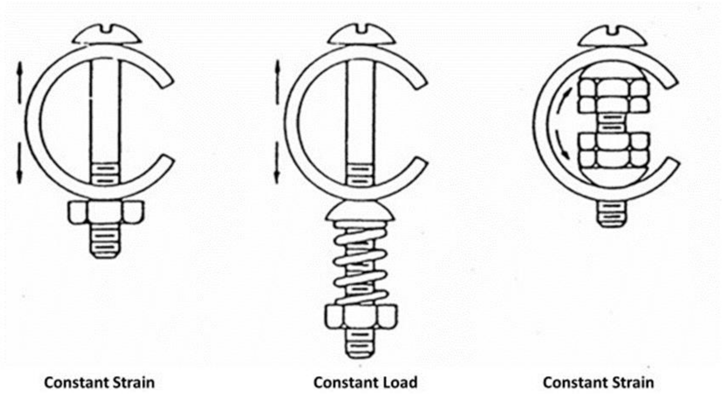


Figure 21. C-ring test methods for assessing ESC in pipe sections

Strain hardening tests

An alternative approach that has been developed for testing the ESC resistance of polyethylenes is to relate the ESC resistance to the creep rate deceleration of drawn polyethylene samples [87-90]. In this approach, it is assumed that the critical step in the ESC of semi-crystalline polymers is the creep of the fibrils. Fibrillar creep is therefore determined by simulating the structure of a fibril using a tensile specimen drawn to its natural draw-ratio. Using this technique Cawood and Rose et al [89-90] showed that for polyethylenes there is a direct relationship between the creep rate deceleration and ESC resistance. Measurement of creep is, however, a slow process and the technique has therefore not been widely adopted.

However, it has been shown recently [91] that the average strain-hardening modulus G_p of high-density polyethylene (HDPE) correlates extremely well with the ESC resistance of the polymer. Typical data obtained from this new strain hardening technique is shown in Figure 22. The strain hardening modulus is given by the average gradient of the completely drawn specimen (draw ratios > 9). In this example, it can clearly be seen that the strain hardening modulus of HDPE 1 is significantly higher than HDPE 2, indicating that HDPE 1 is more resistance than HDPE 2 to ESC.

The advantage of using strain hardening to determine ESC resistance is that the data required may be obtained from simple plots of true-stress again draw-ratio, offering a relatively easy and significantly quicker method of assessing the relative ESC susceptibility of different polyethylene grades.

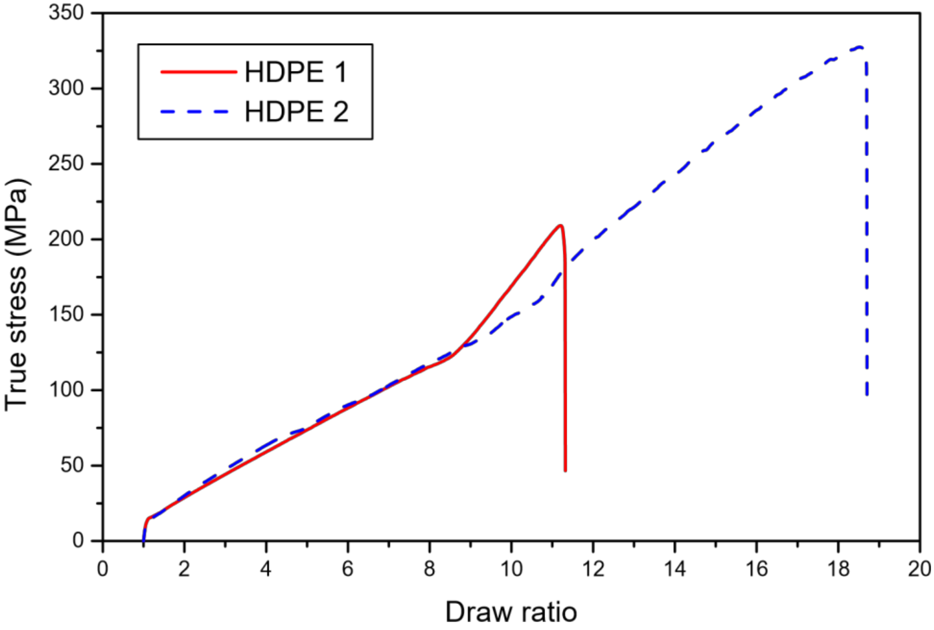


Figure 22 True stress - draw ratio curves used to determine the relative ESC resistance of two polyethylene grades in the strain hardening technique

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Chapter 6

Accelerated weathering

- Introduction
- Artificial weathering apparatus
- Accelerated weathering test procedures
- Ionising radiation
- Performance testing

Introduction

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).

Accelerated weathering procedures [27, 92] generally involve cyclic exposure to a combination of salt spray, elevated and/or sub-zero temperatures, and ultraviolet (UV) radiation. 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) [93]. Whilst mechanical properties and dimensional stability are quantitatively measurable quantities, a number of the 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. This Chapter provides guidance on performance testing and technical requirements relating to accelerated weathering of FRPs.

Artificial weathering apparatus

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 [94] 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 [95-97], ASTM D1435 [98], ASTM D4364 [99] and ASTM G24 [100]. ISO 15314 [101] 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 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, however, 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.

UV lamps

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 [102].

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

- UV-A (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.

- UV-C (<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 UV-B radiation indoors.

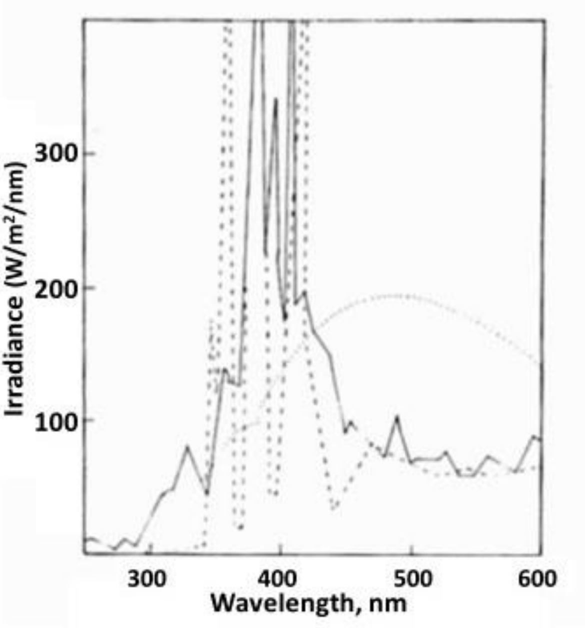


Figure 23. Spectrum of carbon-arc lamp (—), carbon-arc lamp with Cordex D filter (---) and noonday Chicago sunlight (····) [25]

Carbon-arc lamps: Until the 1960's, 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 (<350nm). A typical spectrum from a carbon-arc consists of a series of line emissions that are superimposed on to a continuous background (Figure 23) [25]. 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 there use for plastics is standardised in ISO 4892-4 [103] and ASTM D1499 [104].

Xenon lamps: Xenon-arc lamps give a much better spectral simulation to natural sunlight (Figure 24) 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 [105]. 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 [103] and ASTM D2565 [106].

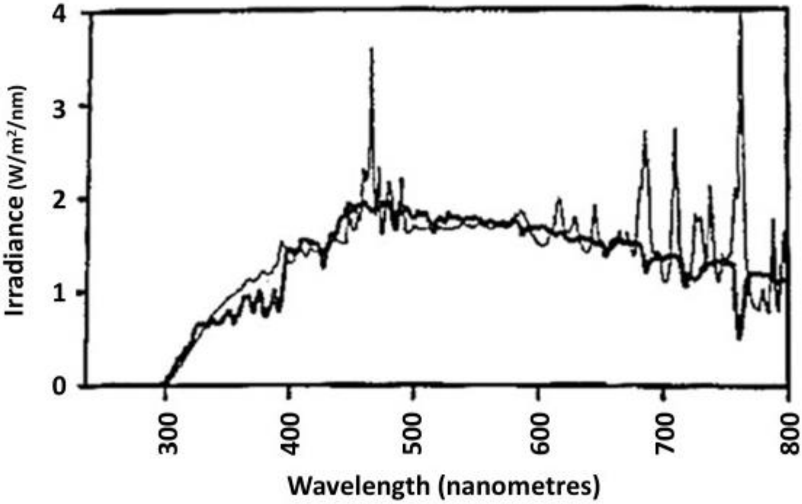


*Figure 24. Spectrum of a xenon lamp (—) compared with noonday Miami sunlight (**—**) [25]*

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 25). 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 [25, 102]). Standard test procedures for the use of fluorescent tube are given in ISO 4892-3 [105] and ASTM D4329 [107].

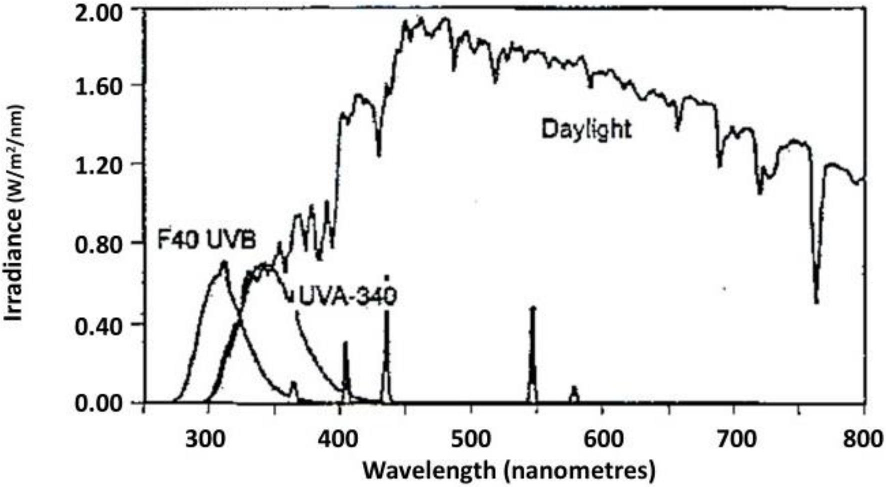


Figure 25. Spectra of UV-A and UV-B fluorescent lamps compared with standard noonday Miami sunlight [25]

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 [108]. Water used for the salt spray must meet the requirements of ISO 4892-1, Clause 5.3 [109]. 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 [109]. 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.

Specimen mounting and handling

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 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 (NB. 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 test 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 of -20°C for 24 hrs has been included in ISO 20340 [110] 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 [92]. 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 16474-1 [111] and ISO 9227 [112]):

- 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

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 [113]. 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 [114] 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 [115] 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 [116] 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.

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.) [117]. 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 Chapter 7).

This section provides guidance on performance testing using data generated from an accelerated weathering study [117] in which glass/polyester pultruded rods were conditioned in accordance with ISO 20340 [110] for a period of six months. Mechanical and physical measurements were conducted on the GRP rods after 0, 1, 2-, 3-, 4- and 6-months exposure (carried out by to assess surface and bulk property degradation. Surface and bulk properties measured include:

- Moisture content (wt.%)
- Glass transition temperature (T_g)
- Barcol hardness
- Gloss
- Spectral reflectance (colour)
- Flexural properties

Moisture content

Moisture content (wt.%) of test specimens should be measured before and after artificially weathering. Prior to conditioning, the material should be dried to a constant weight to provide a zero datum. The drying temperature is typically 50 °C for polyester and vinyl ester based composites, and 70 °C for epoxy based systems. The moisture content of glass and carbon FRPs exposed to standard laboratory conditions is typically 0.2 wt.%. In the case of the glass/polyester, this is equivalent to approximately one month of artificially weathering (see Table 1). The moisture content in accelerated weathered FRPs will reach an equilibrium level (possibly within a few months). Moisture measurement should be conducted in accordance of ISO 62 [64].

Glass transition temperature

An increase in moisture content will generally result in a reduction in T_g. The results presented in Table 1, however, indicate that the moisture content in the glass/polyester remains relatively unaffected by an increase in moisture content. This is probably because the moisture is mainly concentrated in the outer few layers of the composite. Although there may be no changes in T_g, this does not exclude the possibility of material degradation. T_g can be measured using dynamic mechanical analysis (DMA) [118-120]. The recommended DMA standard is ISO 6721 [118].

Material	Moisture Content (wt.%)	T_g (°C)
As received	0.23 ± 0.01	94.70
Dry	0.00	97.01
Exposure (Months)		
1	0.27 ± 0.02	92.20
2	0.34 ± 0.04	95.51
3	0.56 ± 0.04	92.26
4	0.39 ± 0.10	95.20
6	0.54 ± 0.02	96.88

Table 1. Moisture content and glass transition temperature (T_g)

Barcol hardness

Barcol hardness test can be used to measure the surface hardness of FRPs (see BS EN 59 [121] and ASTM D2583 [122]). 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 in order 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. The results shown in Figure 26 indicate that hardness decreases with 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.

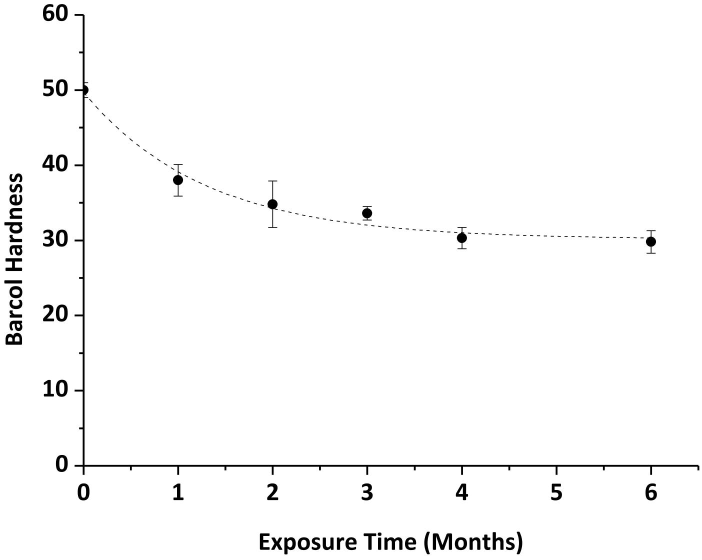


Figure 26. Barcol hardness versus exposure time for artificially weathered glass/polyester rods

Gloss

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 [123, 124], ISO 14782 [125] and BS 2782 [126].

Table 2 presents the 60° angle gloss measurements for different periods of exposure. The gloss measurements clearly show a strong relationship between gloss retention and exposure time (see Figure 27). Gloss retention decreases rapidly with exposure time. After 6 months of artificial weathering, gloss has been reduced by a factor of almost 10.

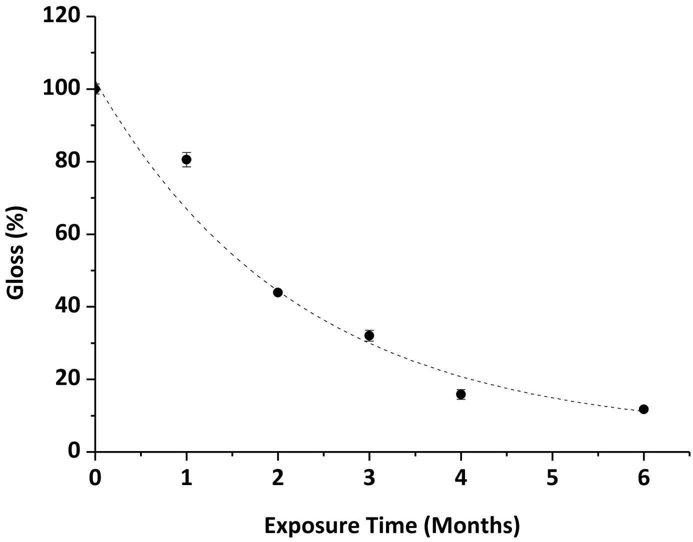


Figure 27. Gloss retention versus exposure time for artificially weathered glass/polyester rods (60° angle measurements)

Material	Gloss Measurement
As received	22.1 ± 0.1
Exposure (Months)	
1	17.8 ± 0.4
2	9.7 ± 0.1
3	7.1 ± 0.3
4	3.5 ± 0.3
6	2.6 ± 0.1

Table 2. Gloss measurements for artificially weathered glass/polyester

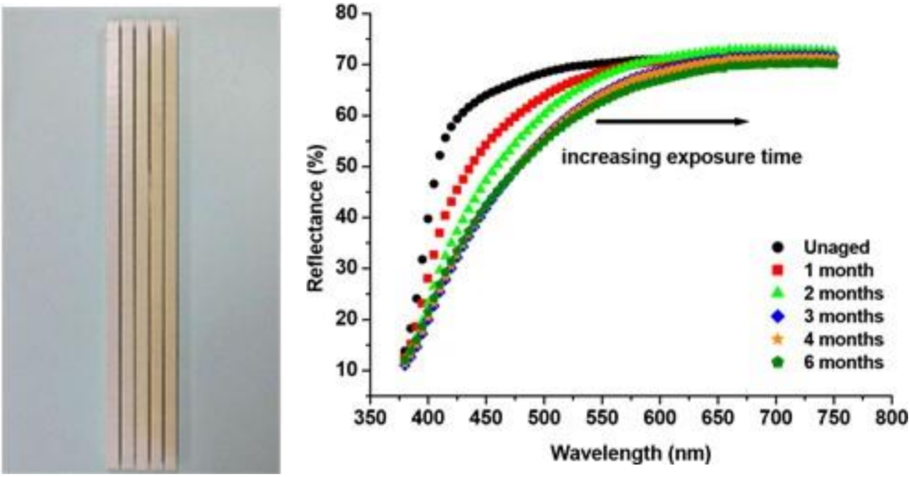
Spectral reflectance (colour)

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 [123-124], and ISO 14782 [125] – see also [127]). 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 [128]. The reflectance of the sample is measured at 1 nm wavelength intervals over the spectral range 380 nm to 780 nm. Two sets of measurements were made on separate occasions on the test specimens and the average recorded. The degree of reflectance decreases with exposure time (see Figure 28), mirroring the changes in gloss measurement. Figure 29 shows a normalised plot of total reflectance over the spectral range 380 nm to 780 nm. The total reflectance data for each specimen (i.e., exposure time) was normalised with respect to the total reflectance data obtained for the unconditioned material.

The discolouration (i.e., yellowing) observed with exposure time, as shown in Figure 28, is due to a reduction in spectral reflectance over the spectral range 380 nm to 600 nm (i.e., blue component). The discolouration can be mainly attributed to exposure to UV radiation (UVA 340 nm).

Note 5: Visual inspection can provide considerable information as to the state of a materials surface (i.e., colour changes, crazing and resin loss).



Discolouration of GRP rods

0 (left), 1, 2, 3 and 6 months

Spectral reflectance versus exposure time

Figure 28. Colour change in glass/polyester rods due to artificial weathering

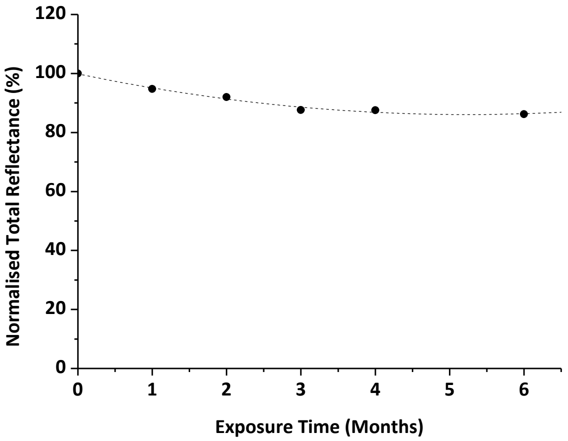


Figure 29. Total reflectance of artificially weathered glass/polyester rods (normalised with respect to the "as-received" material)

Flexural properties

Flexural modulus is relatively insensitive to physical and chemical changes that can occur at the surface or within the bulk of the material, and hence is a poor indicator of material degradation. In contrast, flexural strength is sensitive to material degradation. Any degradation involving the outer layers of the composite will have an amplified effect on load-bearing capacity under flexural loading conditions. The influence of layers on flexural strength increases proportionally to the cube of the distance of the layer from the neutral axis of the beam. Table 3 shows the flexural properties of the artificial weathered GRP rods measured using four-point bend in accordance with ISO 14125 [129] - see also Figure 30. Tests were conducted at a crosshead displacement rate of 5 mm/min under standard laboratory conditions (23 °C/50% RH).

Material	Flexural Modulus (GPa)	Flexural Strength (MPa)
As received	22.5 ± 0.5	442 ± 23
Dry	23.8 ± 1.1	490 ± 11
Exposure (Months)		
1	23.3 ± 1.3	416 ± 38
2	22.7 ± 1.3	404 ± 56
3	21.7 ± 1.3	377 ± 23
4	22.1 ± 1.2	377 ± 24
6	21.3 ± 0.8	371 ± 35

Table 3. Four-point flexure results for artificially weathered glass/polyester rods

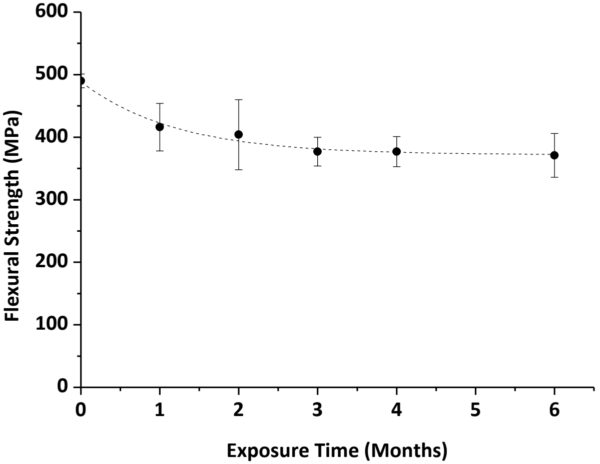


Figure 30. Flexural strength versus exposure time for artificially weathered glass/polyester rods

It is recommended that the displacement at the beam mid-section should be measured using a linear voltage displacement transducer (LVDT). It is recommended where possible to use specimens with dimensions that comply with either ISO 14125 [129] or ASTM D7264 [130]. Tests should be carried out to ensure that non-standard specimens (e.g., narrow rods) produce results equivalent to those obtained using specimens with a geometry that conforms to the standard. Edge effects can cause a reduction in flexural strength in narrow beam specimens.

The question arises as to the use of non-destructive surface measurements, such as Barcol hardness, gloss retention and spectral reflectance, as possible indicators of mechanical property (i.e., flexural strength) reduction. Figures 31 to 33 show that flexural strength tends to be linearly related to gloss, normalised total reflectance and Barcol hardness. The curves shown in Figures 31 to 33 relating to surface reflectance incorporate flexural strength and reflectance data for the “as-received” material and not the “dry” material. Spectral reflectance (i.e., colorimetry) measurements are intrinsically more accurate than specular (gloss) measurements.

The results clearly demonstrate that suitable non-invasive test methods are available that can provide reliable and accurate quantitative data relating the degree of surface degradation to mechanical performance. These test methods make it possible to produce measurable criteria for performance testing for determination of chemical resistance of composite materials. Surface hardness and reflectance measurements could possibly be used to monitor the detrimental effects of service environments on flexural strength. It may also be possible to use these techniques to quantify the level of degradation (i.e., a graduated scale) and provide realistic weighting factors (see Chapter 7).

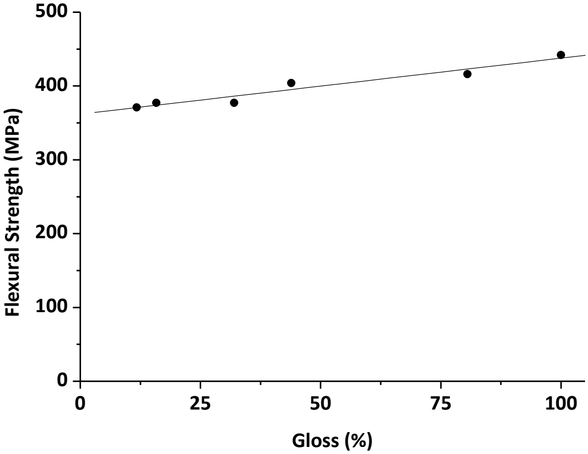


Figure 31. Flexural strength versus gloss measurements for artificially weathered and "as-received" glass polyester rods

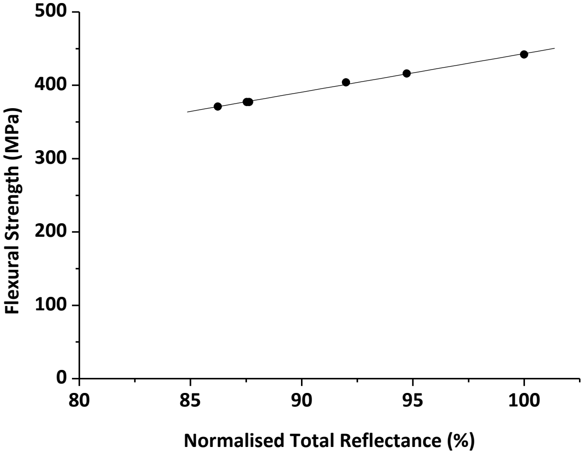


Figure 32. Flexural strength versus normalised spectral reflectance measurementsfor artificially weathered and "as-received" glass polyester rods

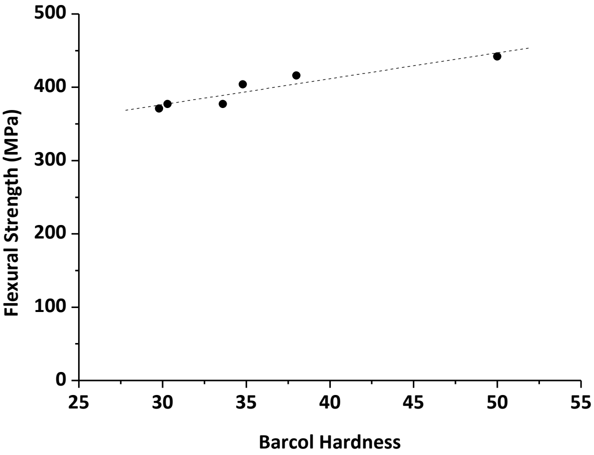


Figure 33. Flexural strength versus Barcol hardness measurements for artificially weathered and "as-received" glass polyester rods

Note 6: Surface measurements, such as hardness and surface reflectance will vary between batches of material and will be affected by surface treatments (i.e., abrasion and solvents), and hence care needs to be taken when carrying out and recording measurements. It is important to compare measurements of the material in the "as-received" condition with measurements obtained on the same material after exposure (i.e., conditioned).

Chemical analysis

Monitoring chemical changes enable direct measurement of the fundamental mechanisms causing degradation. These measurements are essential for understanding the degradation process and rate of chemical degradation that are occurring. The measurement of the carbonyl group is a good indicator of the level of weathering, which can be measured using Fourier Transform Infrared (FTIR) Spectroscopy. Figure 34 compares FTIR spectra for 0, 3 and 6 months of artificially weathered glass/polyester. The set of spectra showed gradual, consistent changes indicating that significant chemical changes have taken place. Some of the more obvious changes are the relative increase in intensity of the absorbance at ~3500 cm and 1640 cm. There are also more subtle changes with an increase in absorbance at ~1775 cm and a change in the absorbance maxima wave number for the absorbance band at ~1725 cm (carbonyl group). The increase in intensity of the absorbance at ~3500 cm and 1640 cm may possibly be attributed to a combination of moisture ingress and oxidation due to UVA radiation.

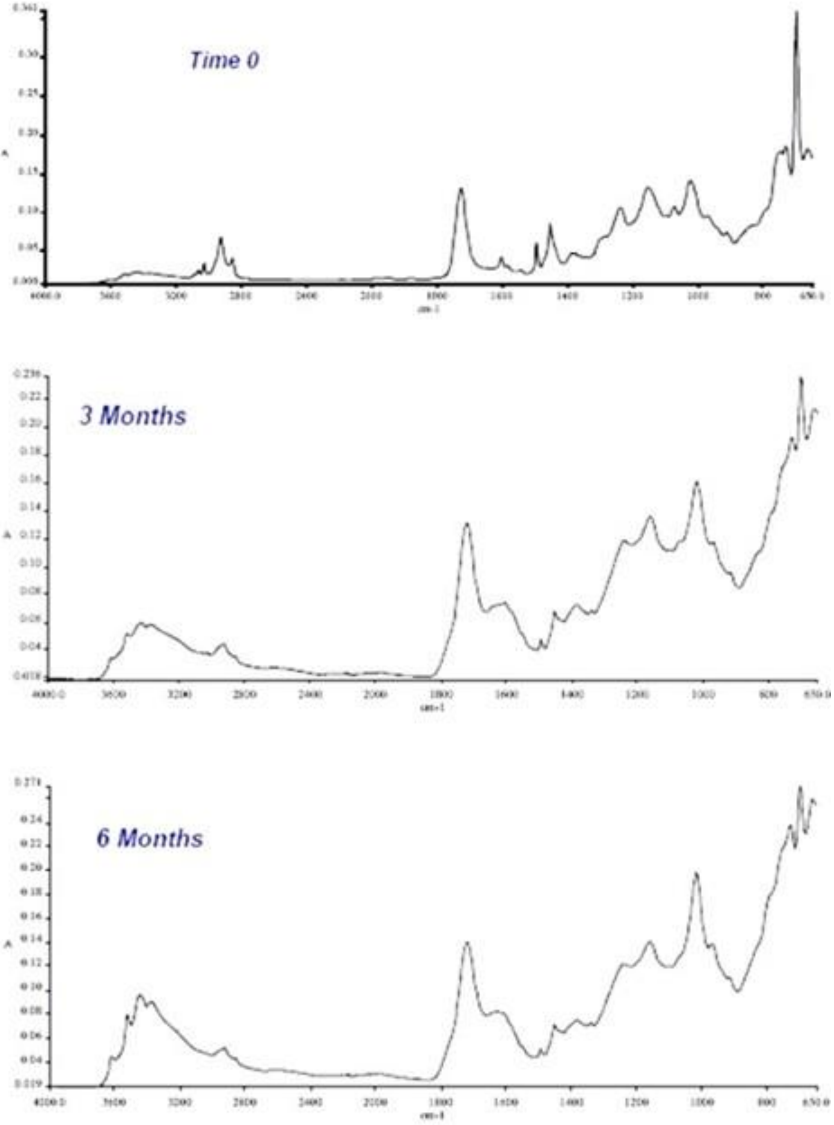


Figure 34. FTIR spectra for 0, 3 and 6 months artificially weathered glass/polyester rods (Courtesy of ElmerPerkin)

Chapter 7

Accelerated testing in aqueous and chemical environments

- Introduction
- Test methods and standards
- Environmental testing
- Test data and analysis

Introduction

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 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 Chapter examines accelerated testing in aqueous and chemical environments (e.g., alkalis and acids).

Test methods and standards

Chemical resistance

An important aspect for composites in many applications is that FRPs are frequently used for their good corrosion resistance (e.g., boats, process equipment, sewage applications). Part 2 of BS EN 13121 [131] 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 4 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 35, where one test plate is in the vapour phase and one in the fluid phase. Assessment is based on a standardised ~3 mm laminate of fixed weight content made by a prescribed method. The tests are undertaken at the design service temperature for a range of exposure times, such as 1, 4, 8, 16 weeks. It is recommended that four exposure units be employed.

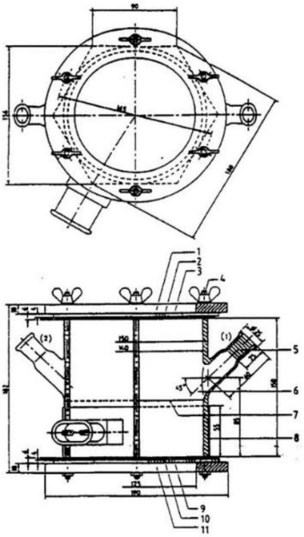


Figure 35. Chemical resistance test (flat plate specimens are numbered 2 and 10)

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 [129]. 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 4). 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.

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
Flexure modulus	20	10	0-10

Table 4. Criteria for chemical resistance

The performance level score from each test should be multiplied by the weighting factor for each criterion (see Table 4), 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:

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

Acceptance of the material for the application should be if the combined score of the test results is ≤ 50% of the total score possible for the tests conducted. 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 5) [131]. The weighting factors are different for single-sided and full immersion. The test can be also be conducted by full immersion of 100 mm x 125 mm plates of the laminate or by testing in-situ within a tank.

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

Table 5. Determination of partial design factor, A_2

British standard BS EN 13121-3 [131] 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 [132] 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 [133] 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 [134] 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 are used in some product test methods. BS EN 14364 [135] and ASTM D3681 [136] 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 36) 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.

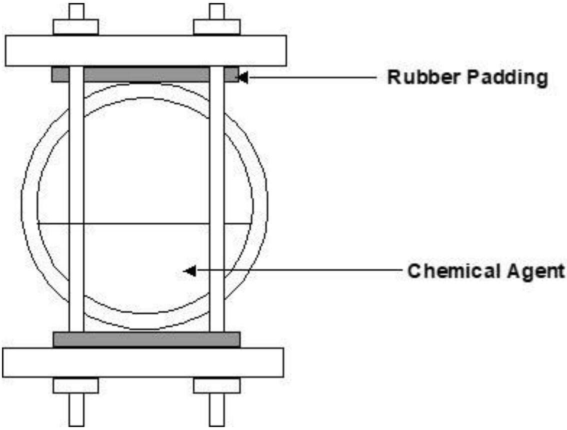


Figure 36. Strain corrosion test apparatus

The American Concrete Institute standard ACI 440.3R-04 “Guide Test Methods for Fibre-Reinforced Polymers for Reinforcing or Strengthening Concrete Structures” [137] 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 [138], BS EN 2489 [139] and ASTM D543 [140] cover the absorption of chemical liquids into polymers.

ASTM C666 [141] 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 [44] 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.

Environmental testing

Treatment tanks

Treatment tanks 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 (see Figure 37) 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.

Note 7: Care needs to be taken when handling, storage and disposal of alkali and acid solutions (see Chapter 8). 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 shown in Figure 13 (Chapter 4) 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.

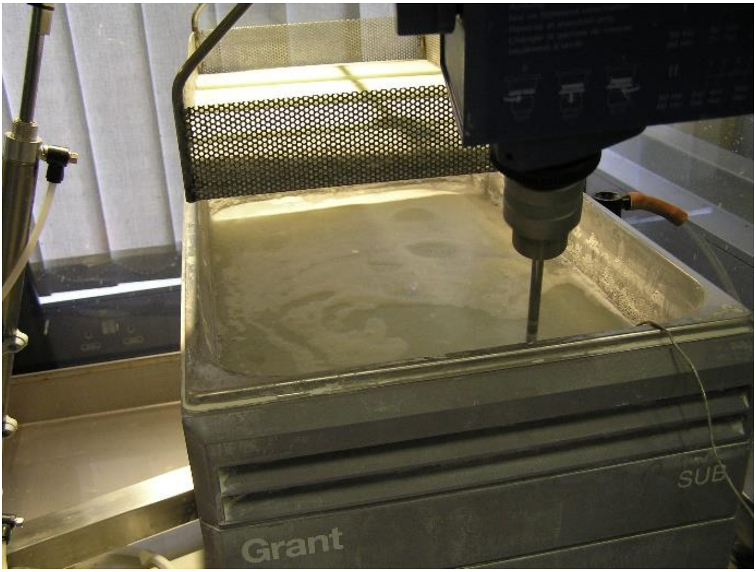


Figure 37 Chemical tank with motorised stirrer
(Courtesy of RAPRA technology Ltd)

Control and monitoring

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.

Warning: Caustic solutions with a high pH level will corrode glass vessels resulting in failure of the vessels.

Care needs to be taken when handling, storage and disposal 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.

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 Chapter 4.

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. Refer to Chapter 6 for further details on specimen mounting.

Simulating chemical spillage (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.

Failure mode

When conducting tests on chemically degraded materials either in-situ or following environmental exposure, a check should be made as to the mode of failure. In the case of tensile tests, failure must occur within the gauge section and not within the gripping region. It is recommended that a suitable structural film adhesive is used to bond the end tabs to the composite specimen in order prevent the possibility of premature failure. There is a possibility that flexure specimens will fail prematurely at the loading point(s) when subjected to flexural loading as a result of high compression and shear stresses acting in the loading regions. This can be avoided through the use of shims placed between the loading rollers and the test specimen. Composites are suitable for short-term ambient and elevated temperature tests, but unsatisfactory for long-term static fatigue tests in chemical environments (including water) because the composite will absorb water and will soften, thus altering the applied stress to the test specimen.

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 the level of degradation agent and exposure time. A potential problem involves changes in the dominant degradation mechanism as the temperature is changed, thus the extrapolated data from accelerated high temperature ageing may not reflect the changes occurring at lower (or ambient) temperature.
- Statistical variability, which generally increases with exposure time, can introduce anomalous effects that make it difficult to differentiate the effects of key variables and determining 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.

Chapter 8

Handling, storage, and documentation

- Handling and storage of materials and chemicals
- Handling and storage of adhesives, resins and prepreg
- Handling and storage of adherends
- Handling, storage, and disposal of chemicals
- Documentation (record keeping)

Handling and storage of materials and chemicals

A number of issues relating to the handling and storage of materials and chemicals need to be considered as many of these factors can affect the performance of the material. Issues to be considered include:

- Health and safety (COSHH)
- Documentation
- Handling and storage (including moisture and temperature effects)

Handling polymeric materials, such as resins and adhesives, can be hazardous to human health, thus COSHH (Control of Substances Hazardous to Health Regulations) procedures should be followed to minimise operator exposure. A safety data sheet should accompany all adhesive samples (Health and Safety at Work Act 1974). The user prior to handling the material must read this document. The safety data sheet supplied with the adhesive identifies:

- Hazardous ingredients and concentrations - includes regulatory information according to legislative directives.
- Hazard statements, such as H225 (highly flammable liquid and vapour), H315 (causes serious eye irritation) and H319 (causes serious eye irritation), and precautionary statements, such as P260 (do not breathe dust/fume/gas/mist/vapours/spray) and P280 (wear protective gloves/protective clothing/eye protection/face protection). Hazard statements are accompanied by classification (e.g., Flammable liquid. 2 – H225 and Eye irritation. 2 – H315).
- First aid measures (including inhalation, ingestion, skin contact and eye contact), and important symptoms and effects, both acute and delayed (e.g., prolonged skin contact may cause redness and irritation). The severity of the symptoms will vary dependent on the concentration and the length of exposure.
- Fire extinguishing/fighting (suitable and unsuitable extinguishing media, and protective equipment and actions) and accidental release (personal and environmental precautions, and methods for cleaning up spillages or discharges) measures.
- Precautions for safe handling and storage including storage precautions (e.g., keep away from heat, sparks, and open flame) and storage class (e.g., flammable liquid storage).
- Control parameters and occupational exposure limits (short-term and long-term exposure limits).
- Exposure controls (includes engineering measures (e.g., adequate ventilation), respiratory protection, eye, skin and body protection, hygiene measures, respiratory protection, and environmental exposure controls).

- Physical and chemical properties (i.e., colour, odour, melting and boiling points, vapour pressure, flammability, etc.), and stability and reactivity of ingredients, and storage and transportation conditions (e.g., temperature).
- Toxicological information (refer to COSHH) – includes potential health effects and hazardous toxicity data.
- Ecological information, disposal considerations and transport information.

Handling and storage of adhesives, resins and prepreg

Polymeric resins may undergo physical and chemical changes when stored for a considerable length of time or under unsatisfactory storage conditions, thus adversely affecting the performance of the adhesive. For example, adhesives may undergo an increase in viscosity, or films a loss of tack and drapeability. Less flow and, thus poorer wetting of the surface, will occur during cure and gel times of epoxy film adhesives could become shorter.

Extended exposure of uncured materials (e.g., adhesives and resins) to temperatures and humidity's above those recommended by the manufacturer will reduce the cohesive and adhesive strength of the material when cured [3]. The overall effect is to reduce the adhesive performance and induce premature failure of the polymeric system.

The safety and product data sheets will provide the user with recommendations regarding storage temperature for an adhesive. Adhesives and composite prepreg should be stored in sealed containers to prevent moisture ingress and contamination, and some cases exposure to light. Opening a storage container exposes the adhesive to oxygen and moisture, which may in some cases severely reduce the shelf life of the adhesive. The shelf (storage) life is generally defined as the time that an adhesive can be stored (unopened) without any adverse affects on the cure properties and bond strength of the adhesive. The product sheet will often specify the shelf life of the adhesive for various temperature ranges. Materials should not be used beyond the expiry date, which will be indicated on the container. The shelf life of an adhesive can decrease significantly with increasing storage temperature. Unless the manufacturer explicitly states that the adhesive must stored or would benefit from being stored at sub-ambient temperatures then adhesives should be stored at ambient temperatures (18°C - 25°C). Materials should not be stored below freezing unless recommended by the manufacturer but for some materials this is essential (e.g., composite prepreg is generally stored in a freezer at -18°C). Adhesives should not be stored below freezing unless recommended by the manufacturer.

Ideally, temperature and humidity in the storage area should be tightly controlled and monitored (i.e., temperature recorders), although this may not always be physically or economically feasible. Standard laboratory conditions are typically 23 ± 2°C and 50 ± 5 % relative humidity (RH).

Refrigerators (or freezers) should be armed with a temperature alarm and the temperature should be monitored continuously to ensure that the temperature remains below the upper temperature limit specified by the adhesive manufacturer. The maintenance of the refrigerator units should allow for regular manual or automatic defrosting.

A refrigerated adhesive or prepreg may be used several times during the shelf life of the product. This will involve the product being taken from a sub-ambient (often sub-zero) temperature and placed at room temperature and allowed to thaw. It is advisable throughout this exercise that the adhesive is enclosed (i.e., remains enclosed in a sealed container) until the temperature has reached room temperature and is ready to be applied to the adherends. Containers that have been opened must be sealed immediately after use. The amount of time at ambient for these adhesives should be minimal, advice on the length of time can be obtained from the manufacturer. Repeated exposure of the adhesive (or prepreg) is a frequent cause of adhesive ageing and deterioration. Sampling of the material before removal from sub-ambient storage may help extend the shelf life of the product, however this may not always be possible for adhesive packed in cartridges.

Exposure to repeated freeze/thaw cycling could limit the shelf life of an adhesive. Exposing a film adhesive that has been stored at sub-ambient temperatures will result in moisture condensing on the surface, which if not allowed to evaporate will compromise the strength and durability of the joint. Entrapped moisture will be released during the cure process, thus compromising the physical and mechanical properties of the adhesive and contribute to the degradation of the bonded surfaces. Routine tests to verify that the physical and mechanical properties of the adhesives are still within specification are recommended, particularly where multiple use of an adhesive has occurred.

Resins, adhesives and prepregs should be stored in an area specifically dedicated to these materials. The area should be suitable for handling flammable and hazardous materials. It may be necessary to segregate materials depending on the hazardous nature of the material. Materials in these areas should be clearly identified and controlled.

Handling and storage of adherends

Before and after machining, adherends sensitive to environmental attack or hygroscopic in nature should be stored in sealed containers to prevent moisture ingress and contamination. It is important that the adherend does not undergo physical or chemical changes whilst being stored. Moisture can alter the chemistry of both the surface and substrate of the adherend, thus compromising the performance of bonded joints. It is recommended that an accurate record of the adherend (including condition and use) be maintained throughout the duration of use the material. Inventory control mechanisms employed for adhesives are also relevant to the storage and handling of adherend materials.

Quality documentation should include details on the material source, manufacturer's code number, batch or lot number, form (i.e., sheet or plate), storage conditions, surface conditions of the adherends (including corrosion products, and surface defects such as scratches present on receipt of the material), and the location of each specimen sectioned from the adherend. The inventory report should also include (where necessary) test data (i.e., strength and stiffness properties) for the adherend. Test certificates are often supplied with metallic materials, such as titanium and aluminium alloys, in which an elemental analysis is supplied along with basic tensile property data. These sheets contain information on the materials condition (e.g., descaled, and annealed titanium). FRP suppliers provide data sheets on processing conditions, fibre volume fractions and mechanical properties of their products. Often elastic and strength properties are quoted for a range of temperatures, and in some cases for hot/wet conditions (e.g., 70 °C and 85% RH) and other environments. It may be necessary to generate mechanical property data for design purposes. This data should be included in the documentation for the material. Variations in material thickness, and elastic and strength properties can be expected between batches of materials.

Handling, storage, and disposal of chemicals

In all cases involving solvents, primers, acid and alkaline solutions, extreme care and good laboratory practice should be followed at all times in storing, handling and disposing these materials (recommended further reading [20]). Personnel need to be trained in handling and using these materials, and should wear appropriate protective clothing as the chemicals can be harmful if they come contact with the skin or eyes. Ventilation and spill containment are particularly important safety considerations. Chemicals treating solutions should be prepared and stored in containers of glass, ceramic, or chemical resistant plastic. Checks should be made to ensure that the containing vessel is resistant to chemical attack from would be contents (e.g., hydrofluoric acid attacks glass). Stirring rods should be made of the same materials. Contact of the chemical solution with metals during preparation and storage should be avoided.

Continuous monitoring and quality control are required for all chemicals employed in chemical conditioning and surface treatments, and all containers with chemical agents should be clearly identified with labels. Labelling should be protected from being damaged through chemical contact or handling. Chemical solutions need to be changed regularly to prevent contamination and ensure repeatable concentration [20]. Quality assurance tests are recommended to check concentrations, and levels of contamination (e.g., opacity for checking particulate content, colour and pH for acidic and alkaline solutions).

Warning: It is important to note that many chemicals, such as acids, alkalis and solvents are toxic and present a risk to both human health and the environment, and that all safety requirements need to be met when handling, storing, and disposing of these materials.

Documentation (record keeping)

It is recommended that an accurate record of the polymeric materials be maintained, and that routine checks are made each month to ensure that the stored materials are within the time limits recommended by the adhesive manufacturer. A record should include details on the material source, manufacturer's code number, batch or lot number, form (i.e., one-or two-part, or film, etc.), shelf life, storage temperature and handling history during the shelf life (i.e., dates of use and length of time at room temperature if refrigerated). The report should include test data from acceptance tests and routine quality checks carried out to assess material performance. Material suppliers will often supply data sheets (material certification) with their materials, and these should be kept as part of the record.

It is recommended that an accurate check as to the quality of the polymeric material be carried out on receipt of the material to ensure that material meets the manufacturers specifications, ensuring the product complies with the purchase order and suppliers test reports (see [20]). The colour, viscosity, shelf life, etc. should be verified. It may be necessary to carry out acceptance tests in-house to ensure mechanical properties are in accordance with the material specification. Acceptance tests should be directed towards assuring that the materials are identical from batch to batch. Accelerated environmental tests (i.e., high temperature and humidity) may also need to be carried out to confirm that the durability performance of the material meets the manufacturer specifications. ISO, BSI, and ASTM list various test methods for quality assurance of adhesives (see Chapter 9).

Standards

ISO Standards

Plastics

Thermal degradation

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

Environmental stress cracking (ESC)

ISO 4599	Plastics: Determination of Time/Temperature Limits after Exposure to Prolonged Action of Heat Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Bent Strip Method.
ISO 4600	Plastics - Determination of Environmental Stress Cracking (ESC) - Ball and Pin.
ISO 6252	Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Constant Tensile Stress Method.
ISO 22088	Plastics - Determination of Resistance to Environmental Stress Cracking (ESC).
ISO 16770	Plastics - Determination of Environmental Stress Cracking (ESC) of Polyethylene - Full-Notch Creep Test (FNCT).

Effects of liquids

ISO 62	Plastics - Determination of Water Absorption.
ISO 175	Plastics - Determining the Effect of Liquid Chemical Including Water

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

Weathering

ISO 877	Plastics - Determination of Resistance to Change upon Exposure under Glass to Daylight.
ISO 2579	Plastics - Instrumental Evaluation of Colour Differences.
ISO 3577	Plastics - Recommended Practice for Spectrophotometry and Calculation of Colour in CIE Systems.
ISO 3558	Plastics - Assessment of the Colour of Near-White or Near-Colourless Materials.
ISO 4582	Plastics - Determination of Changes in Colour and Variations in Properties and Exposure to Daylight under Glass, Natural Weathering or Laboratory Light Sources.
ISO 4607	Plastics - Methods of Exposure to Natural Weathering.
ISO 4892	Plastics - Methods of Exposure to Laboratory Light Sources.
ISO 9370	Guide for the Iinstrumental Determination of Radiant Exposure in Weathering Tests.
ISO TR 9673	Solar Radiation and Its Measurements for Determining Outdoor Weather Exposure Levels.
ISO 11403-3	Plastics - Acquisition and Presentation of Comparable Multipoint Data - Part 3: Environmental Influences on Properties.

Biological attack

ISO 486	Determination of Behaviour under the Action of Fungi and Bacteria - Evaluation by Visual Examination or Measurement of Change in Mass or Physical Properties.

Creep

ISO 899	Plastics - Determination of Creep Behaviour.

Rubbers

Thermal degradation

ISO 188	Accelerated Ageing or Heat Resistance Tests.

ISO 6914	Determination of Ageing Characteristics by Measurement of Stress at a Given Elongation.

Effect of liquids

ISO 1817	Determination of the Effect of Liquids.

Weathering

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

Effect of ozone

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

Biological degradation

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

Mechanical (stress relaxation in compression)

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

Composites

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

ISO 21746	Composites and Metal Assemblies - Galvanic Corrosion Tests of Carbon Fibre Reinforced Plastics (CFRPs) Related Bonded or Fastened Structures in Artificial Atmospheres - Salt Spray Tests.
ISO 22836	Fibre-Reinforced Composites - Method for Accelerated Moisture Absorption and Supersaturated Conditioning by Moisture Using Sealed Pressure Vessel.

Note: *The standards listed in this section refer specifically to fibre-reinforced composites. More general standards covering both plastics and composites are given in the section on ISO plastic related standards.*

Adhesives

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

ASTM Standards

Plastics

Thermal degradation

ASTM D1203	Standard Test Methods for Volatile Loss From Plastics Using Activated Carbon Methods.
ASTM D2115	Standard Practice for Oven Heat Stability of Poly (Vinyl Chloride) Compositions.
ASTM D3045	Standard Practice for Heat Aging of Plastics Without Load.

Effects of liquids

ASTM D543	Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents.
ASTM D570	Standard Test Method for Water Absorption of Plastics.
ASTM D1712	Standard Practice for Resistance of Plastics to Sulfide Staining.

Environmental stress cracking (ESC)

ASTM D1693	Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics.
ASTM F1248	Standard Test Method for Determination of Environmental Stress Crack Resistance (ESCR) of Polyethylene Pipe.

Weathering

ASTM D1435	Standard Practice for Outdoor Weathering of Plastics.
ASTM D1499	Standard Practice Filtered Open-Flame Carbon-Arc Type Exposures of Plastics.
ASTM D2565	Standard Practice for Xenon Arc Exposure of Plastics Intended for Outdoor Applications.
ASTM D4329	Standard Practice for Fluorescent UV Exposure of Plastics.
ASTM D4364	Standard Practice for Performing Outdoor Accelerated Weathering Tests of Plastics Using Concentrated Sunlight.
ASTM G24	Standard Practice for Conducting Exposures to Daylight Filtered Through Glass.
ASTM G156	Standard Practice for Selecting and Characterizing Weathering Reference Materials Used to Monitor Consistency of Conditions in an Exposure Test.
ASTM G178	Standard Practice for Determining the Activation Spectrum of a Material (Wavelength Sensitivity to an Exposure Source) Using the Sharp Cut-On Filter or Spectrographic Technique.

Biological attack

ASTM G21	Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi.

Creep

ASTM D2990	Standard Test Methods for Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics.

Rubber

Thermal degradation

ASTM D454	Standard Test Method for Rubber Deterioration by Heat and Air Pressure.
ASTM D572	Standard Test Method for Rubber—Deterioration by Heat and Oxygen.
ASTM D573	Standard Test Method for Rubber—Deterioration in an Air Oven.

ASTM D865	Standard Test Method for Rubber-Deterioration by Heating in Air (Test Tube Enclosure).

Effects of liquids

ASTM D471	Standard Test Method for Rubber Property-Effect of Liquids.
ASTM D1460	Standard Test Method for Rubber Property-Change in Length During Liquid Immersion.
ASTM D3137	Standard Test Method for Rubber Property-Hydrolytic Stability.

Weathering

ASTM D518	Standard Test Method for Rubber Deterioration Surface Cracking.

Effect of ozone

ASTM D1149	Standard Test Method for Rubber DeteriorationSurface Ozone Cracking in a Chamber.
ASTM D1171	Standard Test Method for Rubber DeteriorationSurface Ozone Cracking Outdoors or Chamber (Triangular Specimens).

Mechanical stress relaxation in compression

ASTM F38	Standard Test Methods for Creep Relaxation of a Gasket Material.

Composites

ASTM C394	Standard Test Method for Shear Fatigue of Sandwich Core Materials.
ASTM C480	Standard Test Method for Flexure Creep of Sandwich Constructions.
ASTM D3479	Standard Test Method for Tension-Tension Fatigue of Polymer Matrix Composite Materials.
ASTM D5229	Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials.
ASTM D6115	Standard Test Method for Mode I Fatigue Delamination Growth Onset of Unidirectional Fiber-Reinforced Polymer Matrix Composites.
ASTM D7792	Standard Practice for Freeze/Thaw Conditioning of Pultruded Fiber Reinforced Polymer (FRP) Composites Used in Structural Designs.

Adhesives

Thermal degradation

ASTM D1151	Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.
ASTM 4502	Standard Test Method for Heat and Moisture Resistance of Wood-Adhesive Joints.

Chemical resistance

ASTM D896	Standard Practice for Resistance of Adhesive Bonds to Chemical Reagents.

Ageing

ASTM D1183	Standard Practices for Resistance of Adhesives to Cyclic Laboratory Aging Conditions.
ASTM D2295	Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).
ASTM D2918	Standard Test Method for Durability Assessment of Adhesive Joints Stressed in Peel.
ASTM D2919	Standard Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading.
ASTM D3434	Standard Test Method for Multiple-Cycle Accelerated Aging Test (Automatic Boil Test) for Exterior Wet Use Wood Adhesives.
ASTM D3632	Standard Test Method for Accelerated Aging of Adhesive Joints by the Oxygen-Pressure Method.
ASTM D3762	Standard Test Method for Adhesive-Bonded Surface Durability of Aluminium (Wedge Test).
ASTM D4498	Standard Test Method for Heat-Fail Temperature in Shear of Hot Melt Adhesives.

Fatigue

ASTM D3166	Standard Test Method for Fatigue Properties of Adhesives in Shear by Tension Loading (Metal/Metal).

Creep

ASTM D1780	Standard Practice for Conducting Creep Tests of Metal-to-Metal Adhesives.
ASTM D2293	Standard Test Method for Creep Properties of Adhesives in Shear by Compression Loading (Metal-to-Metal).

ASTM D2294	Standard Test Method for Creep Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal).

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Abstract

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 to those of which data already exists), long-term or critical applications require the use of accelerated ageing regimes to generate data commensurate with the engineering requirements and life expectancy of the component. This Good Practice Guide is intended to give guidance on accelerated ageing and performance testing of polymeric materials for generating design data and for quality assurance purposes. The document is primarily concerned with polymers (thermosets and thermoplastics) and fibre-reinforced plastics and considers a range of hostile environments including artificial weathering, hot/wet and chemical (inc. solvents, caustic, and acidic solutions) exposure.

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Contents

Glossary of Terms (Based on BSI and ASTM Definitions)

Accelerated ageing test: Short-term test designed to simulate the effects of longer-term service conditions.

Adherend: Body that is or intended to be held to another body by an adhesive.

Adherend failure: Failure of a joint in the body of the adherend.

Adhesion: State in which two surfaces are held together by interfacial bonds.

Adhesive: Non-metallic substance capable of joining materials by surface bonding (adhesion), the bonding possessing adequate internal strength (cohesion).

Adhesive failure: Failure of an adhesive bond, such that separation appears to be at the adhesive/adherend interface.

Ageing: Entirety of all irreversible chemical and physical processes occurring in a material in the course of time.

Amorphous regions: Regions within a polymeric material, that, based on X-ray diffraction or other suitable techniques, do not show any evidence of crystalline structure.

Artificial weathering: Exposure to cyclic laboratory conditions involving changes in temperature, relative humidity, and radiant energy, with or without direct water spray, to produce changes in the material similar to those observed after long-term, continuous, outdoor exposure.

ASTM: American Society for Testing and Materials.

Blister: Elevation of the surface of varied contour and dimensions, with a cavity beneath.

Bond: The union of materials by adhesives.

Bond-line: The layer of adhesive, which attaches two adherends.

Bond strength: The unit of load applied to tension, compression, flexure, peel, impact, cleavage, or shear, required to break an adhesive assembly with failure occurring in or near the plane of the bond.

Breaking stress: Stress at the moment of rupture of a specimen.

Brittle failure: Failure in which the fracture surface exhibits no permanent material deformation to the naked eye (e.g., stretching, elongation and necking down).

BSI: British Standards Institute

Butt joint: Joint in which the plane of the bond is at right angles to a major axis of the adherends.

Bulk adhesive: The adhesive unaltered by the adherend.

Cleavage: Mode of application of a force to a joint between rigid adherends, which is not uniform over the whole area, but results in a stress concentrated at one edge.

Cohesion: The ability of the adhesive to resist splitting or rupture.

Cohesive failure: Failure within the body of the adhesive (i.e., not at the interface).

Composite: Solid product consisting of two or more distinct phases, including a binding material (matrix) and a particulate or fibrous material.

Conditioning: A series of operations intended to bring a sample or specimen into a reference state with regard to temperature and humidity.

Coupling agent: Substance (e.g., organosilane) that promotes or establishes stronger bond at the interface of the resin matrix and the reinforcement.

Crack: Fissure that may or may not penetrate the external surface of the material or its entire thickness, the polymeric material being completely separated between the crack walls.

Craze: Defect at or under the surface of a plastic attributable to apparent cracks, bridged by polymeric material of reduced (apparent) density.

Creep: The time-dependent increase in strain resulting from a sustained load.

Crystallinity: Presence of three-dimensional order at the level of molecular dimensions.

Cure: To set or harden by means of a chemical reaction.

Cure time: Time required to affect a cure at a given temperature.

Cure temperature: Temperature at which an adhesive, an assembly or a polymeric composition achieves a state of cure.

Degradation: Change in the chemical structure of a polymeric material involving a deleterious change in properties.

Delamination: Separation of layers (i.e., planar defect) in a laminate because of failure in or near the adhesive joint.

Deterioration: Permanent change in the physical properties of a material evident by impairment of these properties.

Diffusivity: The proportionality constant that describes the ability of chemical species, such as a liquid, to diffuse through a solid. Diffusivity is generally temperature dependent.

Dimensional stability: Consistency of dimensions of a material part or specimen under environmental conditions.

Discolouration: Colour change that involves lightening or darkening and/or change in hue.

Dry strength: Strength of a polymeric material part or specimen after drying under specified conditions.

Ductile failure: Failure in which the fracture surface clearly exhibits permanent deformation with stretching, elongation, and necking.

Durability: The endurance of joint strength relative to the required service conditions.

Elastic limit: Greatest stress, which a material is capable of sustaining without any permanent strain remaining upon complete release of stress.

Electromagnetic radiation: Wave motions of characteristic wavelength, including gamma radiation, X-rays, ultraviolet, visible light, infrared, and radio waves. Elongation: Increase in length of a specimen under tension, usually expressed as a percentage of the original length.

Embedding: Process of encasing completely an article, such as a sensor, in a polymeric material.

EN: European Norm

Environmental test: Test to assess the performance of an assembly under service conditions.

Fibre: Unit of matter of relatively short length, characterised by a high ratio of length to thickness or diameter.

Filler: Relatively inert material (e.g., talc) added to a plastic or resin to modify its strength, fire resistance or other qualities, or to lower costs.

Fillet: Portion of an adhesive that bridges the adherends outside the bond-line.

Glass transition: A reversible change in an amorphous polymer or in amorphous regions of a partially crystalline polymer from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one.

Glass (surface) veil: Thin layer made from glass filaments (continuous or chopped) held together with a binder.
Gloss: Degree to which, a surface approaches perfect optical smoothness in its capacity to reflect light.
Hardness: Resistance of a material to indentation or scratching.
Hygroscopic: Material capable of absorbing and retaining environmental moisture.
Infrared (IR): The region of electromagnetic radiation of wavelengths from 800 nm to 1 mm. IR can be divided into near infrared (800 nm to 2500 nm), mid infrared (2500 nm to 25 μm) and far infrared (25 μm to 1 mm).
ISO: International Standards Organisation.
Laminate: Product made by bonding together two or more layers (plies) of material or materials.
Lap joint: Joint made by placing one adherend partly over another and bonding together the overlapped portions.
Lay-up: Assembly of layers of resin-impregnated material for processing.
Ligament area: Cross-sectional area remaining after notching.
Mat: Product made of filaments, staple fibres, or strands, cut or uncut, oriented, or not, held together in the form of a sheet.
Peel: Mode of application of a force to a joint in which one or both adherends is flexible and which the stress is concentrated at a boundary.
Permeability: Property of a material transmitting gases and liquids by passage through one surface and out at another surface by diffusion and sorption processes.
Plastic deformation: That part of the strain in a stressed plastic, which remains after the applied stress has been removed.
Plasticisation: Increase in softness, flexibility, and extensibility of an adhesive.
Post-cure: Further treatment by time and/or temperature of an adhesive to obtain the required properties by curing.
Porosity: A condition of trapped pockets of air, gas, or vacuum within a solid material. Prepreg: Admixture of resins (with or without fillers), additives, and reinforcements in woven and filamentous form, ready for moulding.
Prepreg: Admixture of resins (with or without fillers), additives, and reinforcements in woven and filament form, ready for moulding.
Primer: A coating applied to a surface, prior to the application of an adhesive, to improve the performance of the bond.
Profile: Extruded or pultruded polymeric product, excluding film and sheet, having a characteristic constant axial section.
Pultrusion: Process of making continuous lengths of reinforced plastic profiles with high unidirectional strength by pulling continuous strands of resin-impregnated rein-forcing material through a heated die and then through a heating chamber, if necessary, to post cure the resin.
Reinforced plastic: Polymer (plastic) with high-strength fibres embedded in the composition, resulting in some strength properties greatly superior to those of the base resin. Roving: Collection of parallel strands (assembled roving) or parallel filaments (direct roving) assembled without intentional twist.
Semi-crystalline: Polymer containing crystalline and amorphous phases.

Size (coupling size): Material applied to fibres or filaments during their manufacture.

Spectrophotometer: An instrument for measuring the transmittance or absorbance/optical density at different wavelengths.

Strain: Unit change due to force in size of body relative to its original size.

Stress: Force exerted per unit area at a point within a plane.

Stress-strain diagram (or curve): A diagram in which the corresponding values of stress and strain are plotted against each other.

Structural bond: A bond, which is capable of sustaining in a structure a specified strength level under a combination of stresses for a specified time.

Substrate: An adherend, a material upon which an adhesive is applied.

Surface preparation (or treatment): Physical and/or chemical treatments applied to adherends to render them suitable or more suitable for adhesive bonding.

Swelling: Increase in volume of a test specimen immersed in a liquid or exposed to a vapour.

Thermoplastic: A material that can be repeatedly softened by heating.

Thermoset: A resin that is substantially infusible and insoluble after being cured.

Toughness: That property of a material by virtue of which it can absorb energy, generally implying absence of brittleness and relatively high elongation to break.

Traveller: A test specimen used for example to measure moisture content as a result of conditioning.

True stress: Stress calculated from the supporting area at the time of measurement rather than from the original area.

Ultraviolet (UV): The region of the electromagnetic spectrum at shorter wavelengths than blue light, generally taken to be between 100 nm and 400 nm. Due to atmospheric absorption UV measurements can only be carried out below 190 nm in a vacuum environment.

Viscoelasticity: Stress response of a material acting as though it were a combination of an elastic-solid and a viscous fluid with flow dependent on time, temperature, load, and rate of loading.

Visible light: The region of the electromagnetic spectrum that can be seen by the human eye, generally taken to be between 400 nm and 800 nm.

Wavelength: The length of the waves associated with the electromagnetic radiation.

Weathering: Effects of exposure of a material to outdoor conditions.

Wet strength: Strength of a polymeric material determined immediately after removal from a liquid in which it has immersed under specified conditions.

Wetting: A surface is considered completely wet by a liquid if the contact angle is zero, and incompletely wet if the contact angle has a finite value.

Yield strain: The strain, below which a material acts in an elastic manner, and above which it begins to exhibit permanent deformation.

Yield stress: The stress (either normal or shear) at which a marked increase in deformation occurs without an increase in load.

Chapter 1

Scope

Scope

Polymeric materials are increasingly being used for applications where long-term or critical applications require the use of accelerated ageing regimes to ensure the serviceable life of product and components. A trend that is likely to continue for the foreseeable future due to progressive changes in material procurement strategies that require increased product lifetimes in increasingly harsh environments. 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 increasingly being demanded for engineering components in products such as cars and domestic appliances, where consumers often view extended lifetime warranties as a sign of product quality. Whilst the life expectancy of products in non-demanding applications have traditionally been predicted from previous experience, the use of polymeric materials in long-term or critical applications requires a far better understanding of the failure mechanisms to enable lifetime predictions of these materials.

This measurement guide aims to provide guidance to technologists, engineers and designers on accelerated ageing and performance testing of polymeric materials for generating design data and for quality assurance purposes. The document is primarily concerned with polymers (thermosets (including adhesives) and thermoplastics) and fibre-reinforced plastics (FRPs) and considers a range of hostile environments including artificial weathering, aqueous (liquid and vapour) and chemical (i.e., solvents, caustic, and acidic solutions) exposure. Guidance is provided on static and creep rupture testing at ambient and non-ambient temperatures.

The intention of the guide is to provide designers and users with sufficient information, which when coupled with their own expertise and a suitable accelerated test regime can be used to produce design data and enable screening of materials and manufacturing processes (e.g., adhesive/adherend surface treatments). The document provides guidance of the use of test methods that can be used to measure physical changes resulting from exposure to hostile environments, and techniques that can be used to relate laboratory testing to actual service conditions. If the intention is to generate design data, then the guide should be used in conjunction with the appropriate structural design codes and standards.

The guide assumes some basic knowledge of the materials and mechanical engineering and is not intended as a textbook or as a design protocol. There are several published works, which provide a comprehensive coverage of plastics, adhesives, and composites technology, and testing and preliminary design [1-28]. Other NPL Measurement Good Practice Guides [29-36], provide advice on issues relating to the preparation and testing of plastics, adhesives, and adhesive joints. The intention of the guide is to complement these published works.

It is recommended that specialist advice be sought from manufacturers and suppliers on material selection, and use of associated technologies and health and safety requirements. Organisations that can provide specialist advice are listed at the back of the guide along with relevant standards and publications.

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Chapter 2

Ageing mechanisms in polymeric materials

- Introduction
- Temperature
- Moisture
- Natural weathering
- Ionising radiation
- Chemical degradation
- Biological degradation
- Environmental stress cracking (ESC)
- Stress corrosion of fibres

Introduction

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 polymeric materials. In some circumstances, only a few hours of exposure may lead to failure or seriously compromise material performance (see also Measurement Good Practice Guide No. 28 [30]). Conversely, the rate of chemical degradation can be slow and insidious without evident signs of material deterioration.

Irreversible property changes in polymeric materials can be induced by any number of degradation agents (see list below) acting alone or collectively.

- Thermal - static heat ageing, sub-zero exposure or thermal cycling
- Humidity (including hot/wet) exposures
- Complete immersion in water at ambient and elevated temperatures
- Freeze/thaw and dry/wet cyclic conditions
- Continuous or intermittent saltwater immersion or spray
- Weathering (including rain and sand erosion)
- Combined load (i.e., stress) and environmental exposures
- Chemical (including water, fuel, acids, alkalis, solvents and oxygen)
- Ultraviolet (UV) and high-energy radiation
- Electrical stress (e.g., lightning stress and galvanic reactions)
- Micro-organisms (e.g., fungi)

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 in the presence of mechanical stress (static and fatigue).

In many applications, engineering components/structures will be exposed to a combination of two or more factors, often resulting in complex synergistic degradation of the material. Accelerated degradation may be caused by the combined action of two or more vectors (e.g., temperature and humidity). The relative importance of each agent will depend on the agents present and their levels. Degradation from one agent can also reduce resistance to other agents, similar to biological systems. The predominant factors in climatic exposure are humidity, temperature and solar (UV) irradiation. The severity of these factors will depend on geographical location and need to be considered when designing with these materials.

Failure of a FRPs, insofar as it is no longer fit for purpose, may occur because of cumulative damage to the thermoset or thermoplastic matrix, interfacial separation between fibres and matrix, chemical attack of the fibre reinforcement or a combination of two or more of these processes. The net effect is loss of stiffness and mechanical integrity.

It is recommended that when comparing the effects of material systems, surface treatments and processing variables on the durability of components in hostile environments, that all specimens are prepared and conditioned together to account for any variability in the conditioning environment. Also, control specimens are recommended to check changes in systems performance.

Temperature

Prolonged, or even short term, 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 of the degradation processes that occur in polymeric materials, such as oxidation, chemical attack, and mechanical creep. Physical changes include polymer structure shrinkage, pore formation and weight loss through chemical decomposition of the polymer. As the temperature increases, mechanical properties such as stiffness and strength tend to decrease. Oxidation is generally considered to be the most serious problem when using polymers at elevated temperatures with the rate of degradation increasing with the amount of oxygen present [22, 26]. In adhesively bonded joints, the primary path for oxygen diffusion is through the adhesive, which can be relatively rapid at elevated temperatures. Metallic adherends are impermeable to oxygen, thereby providing a barrier to the gas. In contrast, FRPs are permeable to atmospheric gases, and hence the rate of degradation is considerably higher with the elevated temperatures also degrading the fibre-matrix interface. At extremely high temperatures, as experienced in fires, fibre ablation occurs.

The overall degradation process will often involve a relatively long induction period during which little degradation is observed [22-23]. At the end of this period, there is a rapid increase in degradation leading to a significant reduction in the mechanical properties of the polymer. This induction period is temperature sensitive and is reduced significantly at elevated temperatures. The induction period of the degradation process can normally be regarded as the serviceable lifetime of the polymer.

Other physical changes can occur in polymers as a result of temperature, one of the most common being thermal expansion. Thermal expansion is a reversible process, provided no damage occurs as a result of the change in temperature. In FRPs, differences in thermal expansion between fibre and matrix can induce residual stresses, thereby reducing fibre-matrix bond efficiency and resulting in thermo-mechanical degradation during thermal cycling. Similar mechanisms may also occur in adhesive joints. A sudden brief exposure to high temperatures can result in a phenomenon known as thermal spiking, which can lead to excessive localised stresses with deleterious effects on structural performance. The effects of rapidly driven-off moisture through thermal spiking can also be expected to contribute to damage.

Exposure to low temperatures can result in embrittlement of plastics, fibre-matrix interfacial cracking in FRPs and debonding in adhesive joints. Rapid failure can occur in environmentally degraded polymeric materials at sub-zero temperatures (e.g., due to the formation of ice particles from absorbed water initiating internal fractures). Complete interfacial debonding may occur in multiple component systems exposed to cryogenic temperatures through, for example, the combined effects of differential thermal contraction and embrittlement.

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)
- Reduction in the glass transition temperature (T_g)
- Reduction in mechanical and physical properties (i.e., stiffness, strength and hardness)
- Surface degradation and damage (e.g., blistering)

Although the process of moisture absorption and desorption within the surface layers occurs almost immediately on contact with the environment, moisture diffusion into the thick systems is usually a slow process (see Chapter 3). For FRPs, it may take weeks to months before a substantial amount of moisture has been absorbed by the composite, and considerably longer periods (i.e., 1-2 years) before the material is saturated. The rate of moisture uptake by a material (i.e., 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 between resin systems and change with chemical ageing.

The presence of tensile loads accelerates moisture uptake by opening existing internal cavities or voids, and by contributing to micro-crack formation. A materials system containing micro-cracks will absorb considerably more moisture than an undamaged materials system. This applies equally to thermosets (including adhesives) and composite laminates – see also [36]. Exposing the wet system to sub-zero temperatures can further exacerbate this process. A commonly used test is to subject hot/wet conditioned laminates to thermal cycling in which the composite is exposed to temperatures as low as -55 °C for a given number of cycles to assess the laminates crack resistance.

Absorption of water is known to cause plasticisation (softening) of the polymer, depressing T_g, and lowering the modulus and strength. Elongation to break (strain-to-failure) tends to increase with moisture content. For example, T_g for 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, such as glass fibre-reinforced plastic (GRP) products, in load bearing structures to ensure that the maximum operating temperature is at least 30-40 °C below the T_g of the material (taking into account moisture effects). Figure 1 shows the effect of moisture content on T_g for F922 epoxy that has been immersed in distilled/deionised water for prolonged periods of time at three different temperatures [37].

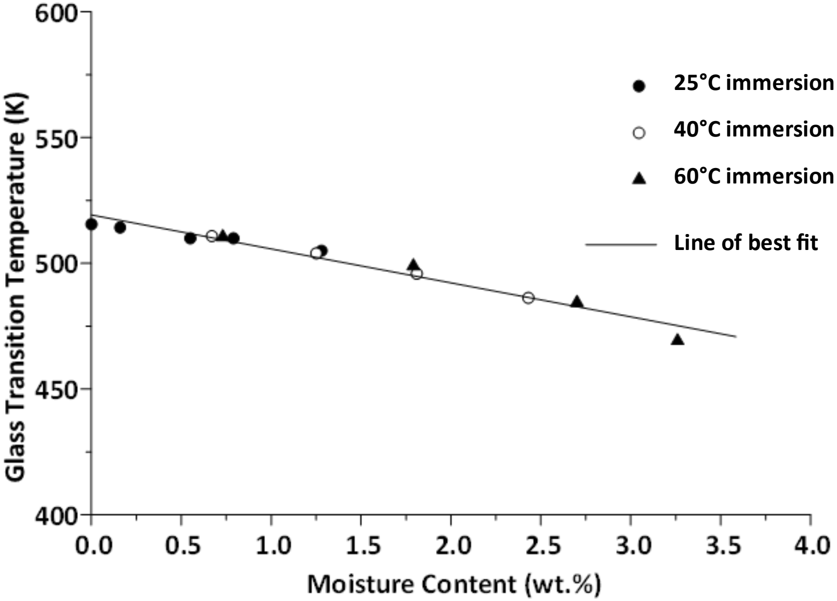


Figure 1. Glass transition temperature of F922 epoxy as a function of moisture content

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.

Adhesive bonded systems

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

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

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

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

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

Note 1: Good surface preparation is crucial to ensuring optimum bond strength and reliable long-term performance of bonded joints, particularly under hostile service conditions. Unsatisfactory surface preparation will result in premature and unpredictable bond failure at the adhesive/adherend interface. Surface preparation is recognised as the most critical step in the adhesive bonding process and considerable effort is often expended in optimising the surface treatment.

Fibre-reinforced plastics

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

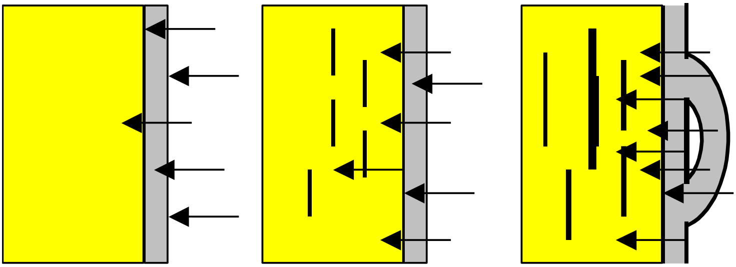


Figure 2. Schematic of the osmotic process – leading to delaminations/blistering

All laminates when exposed to marine environments will allow water vapour to permeate the structure. As the water diffuses into the composite it reacts with any hydrolysable components (e.g., ester groups) inside the laminate to form tiny cells of concentrated solution. Under this osmotic process [38-39] (see schematic in Figure 2), more water is drawn through the semi-permeable membrane of the laminate to dilute the solution. The water can increase the fluid pressure of the cell substantially and increases of 50 atmospheres can occur, which eventually distorts or bursts the laminate or coating and leads to a blistering of the surface. Damage can be very extensive requiring major repair or the replacement of the structure (Figure 3).

Figure 3. Osmotic blistering of a GFRP boat hull with inset showing laminate breakdown (Courtesy of Minton, Treharne and Davies Ltd)

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

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

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

Fibre degradation is primarily an issue for glass fibres and aramid fibres, with carbon fibres being stable in most environments. Carbon fibres are relatively insensitive to moisture, and hence the variability in the tensile breaking stress and strain for carbon fibre tows is noticeably lower than for E-glass fibre and aramid fibre tows. Exposure to humid air (including environmentally controlled laboratories at standard conditions (i.e., 23 °C and 50% relative humidity (RH)) will compromise the load-bearing capacity of the fibres, resulting in a loss of strength and an increase in strength variability [40]. For example, the tensile strength of freshly drawn E-glass fibres is typically 3.5 GPa, however exposure to atmospheric moisture can lead to a reduction in strength (tensile strength is typically 2.0 GPa, or less). The loss of tensile strength of E-glass fibres is dependent on exposure time, temperature, and degree of humidity. On initial exposure to a humid/water environment, the rate of fibre degradation is relatively rapid, even in benign environments, such as air-conditioned laboratories. The tensile strength is reduced to 3.0 GPa after 3 weeks exposure to standard laboratory conditions. Immersion in water at ambient temperature for the same period results in a 20% reduction ($\sim$2.5 GPa). The original tensile strength can be fully realised, provided the fibres are carefully handled during fabrication to avoid surface damage and are stored in a dry environment. An intrinsic tensile strength of 2.0 GPa is often assumed for design purposes.

Degradation of E-glass fibres in water can be mainly attributed to leaching of alkali oxides (sodium and potassium oxide) from the fibre surface resulting in the formation of surface micro-cracks, which act as stress concentrators. The loss of strength can be expected to be permanent at all conditioning temperatures and exposure times. The water surrounding glass fibres evolves into an aggressive alkali solution as the alkali ions dissolve out of the glass, slowly decomposing the glass fibres. Increasing the alkali content of the glass tends to reduce environmental attack from water and alkali solutions. It is worth noting that deionised water is slightly more aggressive than either tap water or seawater. Drying of the composite will remove most of the skin of water adjacent to the fibre, but a small permanent layer with retained water will remain, and the mechanical properties of the fibre will be permanently degraded (for further details on chemical degradation see references [27, 41]).

The effect of moisture on aramid (e.g., Kevlar 49®) fibre-reinforced epoxy laminates is potentially greater than other composite systems. Aramid fibres tend to absorb moisture and degrade at room temperature with the rate of degradation accelerating as temperature is increased. Substantial hygrothermal strength losses have been observed with these materials, particularly under natural weathering conditions (i.e., combination of moisture and UV light).

Natural weathering

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

Chemical reactions are induced when specific functional groups absorb the UV radiation. Free radicals liberated in the process will trigger further reactions. The deleterious effect will be dependent on the chemical nature of the material, environmental factors such as temperature and humidity, and exposure time. Material changes include discoloration (yellowing and bleaching), embrittlement, and loss of mechanical and physical properties. Photo-oxidative sensitivity also tends to increase with prolonged exposure to pollutants, such as nitrogen dioxide [9, 23, 27].

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

Photo-degradation is initiated by solar radiation, which results in the absorption of UV radiation by chromophores and in the activation of excited states in macromolecules. When a polymer is exposed to solar radiation the energy absorbed by the polymer results in the formation of free radicals within the polymer by the dissociation of the C-H bonds in the polymer chains. The extent of this chemical reaction depends on the radiation exposure that is the quantity of ultraviolet light (<350 nm) to which it is exposed. Once free radicals have been produced, reaction with oxygen generates hydroperoxides (POOH) [25]. 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 [25].

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 very near surface due to consumption by reaction with the polymer radicals. Since the concentration of these radicals diminishes by termination reaction during the dark period, oxygen ingress can extend to greater depth.

UV radiation is known to degrade polymeric materials (including aramid fibres), although only the outer layer tends to be affected. Glass and carbon fibres tend to be unaffected by UV radiation. Epoxy resins are slightly sensitive to ultraviolet radiation, depending on the chemical formulation. Signs of photo-degradation include embrittlement (surface cracking), discolouration and loss of transparency [39]. 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 added to protect the adhesive system from chemical breakdown caused by heat and UV radiation, whilst UV stabilizers protect against UV degradation and exposure to fluorescent light and filtered daylight. Pigments (e.g., carbon black, titanium dioxide, zinc oxide and barium sulphate) alter the absorption characteristics of the material acting as a screen against UV radiation when compounded with the adhesive. The costs of additives can often be prohibitive and may adversely alter mechanical performance. Carbon black is particularly effective in protecting against UV radiation and is inexpensive. It absorbs UV radiation and protects the polymer chains.

Ionising radiation

Ionising 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 crosslinking 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 [42-43].

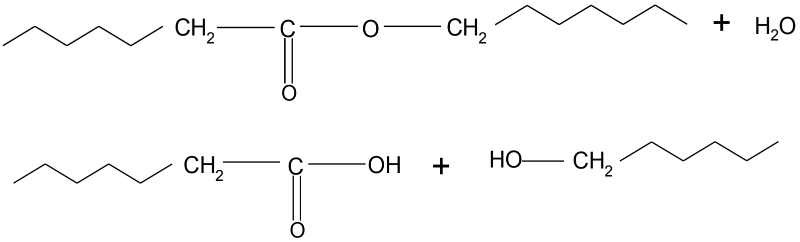
The intensity of ionising radiation on the earth's surface is not normally high enough to significantly affect most plastics and FRPs. Molecular chain scission often causes a lowering of the polymer viscosity and softening temperature, accompanied by a reduction in mechanical strength. In contrast, cross-linking, 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).

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. In FRPs, 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).

Chemical degradation

Chemical attack of thermoplastics involves specific chemical reaction of the polymer with the fluid with the most common mode of failure being hydrolysis by water, acids, and alkalis [11]. Esters, amides, imides, and carbonate groups are particularly susceptible. Where these groups are located within the backbone chain rather than the side chain, chain scission ensues.

A general hydrolysis scheme can be summarised as follows:



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

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

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

Alkali and acidic solutions

As with moisture effects, acid and alkali degradation processes are accelerated at elevated temperatures. Compared with other glass fibre types (e.g., R, ECR and C), E-glass is particularly vulnerable to attack from mineral acids (e.g., HCl and H_2SO_4) and alkalis (e.g., NaOH and KOH) [27, 41]. Dilute mineral acids are not only encountered in the chemical plant industry but are also present in industrial and household effluent and sewage. When E-glass fibres encounter acids, ionic exchange occurs between the metallic cations (e.g., Na^+ ions) at the glass surface and the hydrogen ions in the acid solution, resulting in leaching of sodium, potassium, calcium, magnesium, boron and aluminium from the outer layer or sheath of the fibre. Exposed fibres gradually lose weight, stiffness, and strength with exposure time. Immersion in weak caustic solutions at room temperature can result in strength reductions of 30% within two weeks.

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

Other chemical agents

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

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

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 [11, 23]. 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. Whilst 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.

As previously mentioned, synergistic effects are often observed between the various environmental factors resulting in amplification of the degradation process. For example, the combination of JP-4 fuels 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 4 illustrates damage induced in GFRP pipes when exposed to molecular chlorine and hydrogen chloride.

Figure 4. Chlorine degradation (left) and HCl induced blistering (right) of a GRP pipe (Courtesy of AEA Technology)

Galvanic corrosion occurs when two different conductive materials of different galvanic potential are in contact in the presence of water (electrolyte). The more anodic material will corrode at an accelerated rate resulting in a build up of corrosion product near the contact area. The galvanic effect will be dependent on moisture content, temperature and electrical and chemical properties of the galvanic cell electrodes and electrolyte. Galvanic corrosion can be a problem between carbon fibre-reinforced composite and metallic parts (aluminium alloys and steel), causing corrosion and progressive debonding in the case of honeycomb structures – see also ISO 21746 [44].

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.

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

There is little evidence to suggest adverse structural changes occur in composites through biological (marine organisms and bacteria) attack. Hard (animals with calcium carbonate shells) and soft (algae and animals with soft structures) marine organisms growing on the surfaces of GRP 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.

Environmental stress cracking (ESC)

ESC (the 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, craze formation and crack development all contributing. While crystalline and amorphous polymers are both susceptible to ESC, amorphous polymers are particularly susceptible due to their relatively open structure 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.

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 5). The mechanism of crazing in chemical environments is generally considered to be identical to that in air [13, 15. 45]. In general terms, craze initiation is considered to evolve from micro-deformation processes in localised regions about 30 nm in diameter (see Figure 5) [46]. 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 [47].

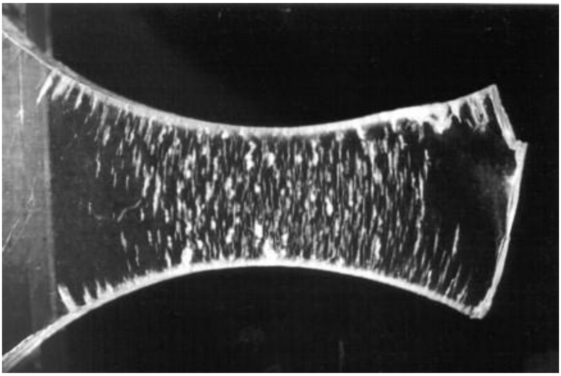


Figure 5. Crazing of PMMA

Exposure to moderate levels of applied stress for extended periods of time can induce crazing and cracking in polymers and is the underlying cause of long-term transition from brittle behaviour for ductile polymers. This mechanism, known as creep (or stress) rupture is a common cause of polymer failure, and consequently has significant ramifications on the chemical resistance of FRPs [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.

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 [15, 45]). However, the particular 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 [45] 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 crazing is thought to occur at a critical level of the inelastic strain, which is independent of the environment and temperature [45, 48-49]. This has significant implications for assessing the durability of a polymer. For example, in polymer-fluid combinations that lead to plasticisation-induced toughening, simultaneous exposure may delay the development of crazes. However, exposure to the fluid after the sample has been stressed in air to attain the critical level of inelastic strain may lead to rapid crazing. It helps explain the very rapid development and growth of crazes in many cases when environment exposure times are relatively short but the time under stress has been long.

Stress corrosion of fibres

The process of environmental degradation of glass fibres is accelerated under mechanical loads with the long-term strength of GRP laminates under hostile environments being controlled by stress corrosion of the fibre-reinforcement [27, 41]. 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. ESC of glass fibres occurs in acidic solutions with the rate of degradation dependent on pH level. The consequence is that GRP laminates suffer delayed brittle fracture in acidic environments, under stress [50].

Static fatigue or creep rupture, which refers to time-dependent failure of the material when subjected to constant load, is used as a measure for gauging the relative resistance of the material (i.e., fibre or composite) to chemical environments. The less resistant a fibre is to a 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.

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Chapter 3

Environmental conditioning and testing

- Introduction
- Temperature
- Moisture conditioning and testing
- Mechanical testing of conditioned specimens
- Fibre bundles and impregnated strands
- Design and planning an accelerated test programme

Introduction

Several techniques have been employed to accelerate testing of polymeric materials. The usual approach for environmental testing has been to increase the temperature, humidity level or pressure (and in the case of chemical exposure the concentration level of the chemical agent). However, there is a temperature limit to which most polymer resins can be raised without affecting a change in the degradation mechanism (e.g., moisture absorption0. Above this critical temperature, there is a strong possibility of altering the degradation mechanism.

An alternative approach to increasing the level of the degradation agent is to increase the frequency of application of the degradation agent. An example is chemical resistance where exposure may be continuous, whereas in-service exposure is intermittent. The concern is that continuous exposure may result in a different response to actual service conditions. The use of relatively small specimens for longer times under less severe conditions could potentially be used. Provided the data generated can be scaled up to predict the long-term performance of more realistic size structures [51-52] to generate durability data provided that allow rapid conditioning under more realistic temperatures, stresses and concentrations reflecting actual service conditions. This Chapter examines temperature and moisture accelerated testing of polymeric materials.

Temperature

High temperatures

Prolonged, or even short term, exposure to elevated temperatures will result in a reduction in the short-term properties and possibly irreversible chemical and physical changes within an adhesive. For polymer systems, high temperatures will rarely exceed 300 °C and will normally be considerably lower.

It is recommended when characterising mechanical properties (i.e., stiffness and strength) at elevated temperatures that testing be conducted in a temperature-controlled chamber [53]. It is important that the load cell is thermally isolated from the chamber and that any sensors within the test environment can operate at the test temperature. It may be necessary to use thermal compensation to ensure accurate sensor measurements. It is common practice for elevated temperature to allow a soak period of 10 minutes at the test temperature prior to testing. The purpose of "heat-soaking" is to eliminate distortion due to non-uniform temperature distributions. The thermal mass of test fixtures can often result in a significant thermal lag in the specimen reaching equilibrium with the surrounding environment. It is recommended that the surface temperature of the specimen be monitored to determine the soak time. This need only be carried out for the initial test for a series of identical tests. Care needs to be taken when testing moisture pre-conditioned specimens to prevent drying of the specimen during the test.

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 temperature is typically between -40 °C and -100 °C. Liquid nitrogen-based cooling systems can achieve temperatures around -150 °C, or better. Although 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 [54] 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 [55].

Thermal conditioning and heat ageing

It is advisable to use 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. 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 smaller.

Heat ageing tests [23] should include a minimum of three (preferably five) temperatures for periods of 1,000 hours (~6 weeks), or more to generate sufficient data that can be extrapolated to lower (i.e., service conditions). It is important that at the highest temperature that 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., 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 5 to determine the change of property with time. The spacing of exposure times is usually linear for heat ageing. ISO 11403-3 [56] 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.

There is no general heat ageing method for polymeric materials, however there are several specific procedures, which are primarily intended for control and comparative purposes (for further details see [23]).

Thermal stability

A standard procedure for assessing the thermal stability of polymers exposed to elevated temperature for long periods is given in ISO 2578 [57]. 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 Chapter 4). 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 [58] and ASTM D1203 [59] cover the stability of plasticisers in polymers, both standards measuring the amount of plasticiser's that is lost due to absorption on activated charcoal. Both standards are essentially used for quality control testing.

Heat distortion temperature (HDT)

HDT is often the only criterion used in determining a material's "fitness for purpose" at elevated temperatures (i.e., upper 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 [60-62] and ASTM D648 [63] specify test procedures for determining HDT of polymers and composites. The test procedure for determining HDT, as described in ISO 75-1 [60], 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) [61] and FRPs (Part 3) [62]. 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 un-reinforced 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.

Moisture conditioning and testing

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, 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 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 - difficult to accurately control high humidity levels at elevated temperatures.

Note 1: Although accelerated ageing is widely used, a full understanding of the effects is not yet available and there is no consensus as to a satisfactory accelerated test.

Moisture absorption test methods

ISO 62 [64], ASTM D570 [65] and ASTM D5229 [66] 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 [67]. For FRPs, it is recommended that square specimens also be used with a width $w \leq 100 \times$ 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. As previously mentioned, 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 absorption effects). The recommended maximum conditioning temperatures are 45 °C and 70 °C for 120 °C and 180 °C cure systems, respectively [68]. 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:

$$M = \frac{\left(W_{wet} - W_{dry}\right)}{W_{dry}} \times 100\% \tag{1}$$

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. 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:

$$M = \frac{M(t) - M_C}{M_0} \tag{2}$$

$$M = \frac{M(t) - M_0}{M_0} \quad \text{when} \quad M_C = M_0 \tag{3}$$

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) [68]. 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.

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. Moisture conditioning of FRPs is often carried out at elevated temperature and/or humidity, (e.g., 70 °C/85% RH) to accelerate moisture uptake, however, 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 [69] 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 [52]. 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 2-3 wt.% 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: 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 2: 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 [67]. Moisture expansion or swelling can be measured periodically with a micrometer, Vernier caliper, traveling microscope or continuously using strain gauges or embedded sensors, such as optic fibres (I.e., Fibre Bragg Grating) (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. plot of swelling strain versus weight gain will show a change in gradient for high porosity materials.

Fickian diffusion

At temperatures well below the T_g of the conditioned material, water absorption of most polymers correlates well with Fick's laws (see Annex A of ISO 62 [64]). The diffusion coefficient, independent of time and moisture concentration (i.e., humidity level) can be calculated from the Fickian diffusion curve (Figure 6). Figure 7 shows a typical diffusion curve for an epoxy resin sample (see also [36]).

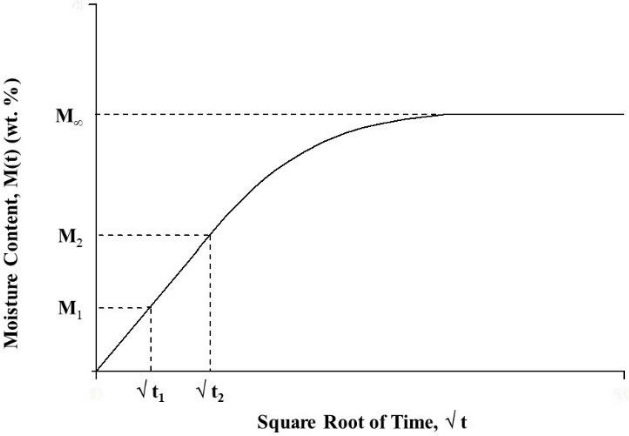

Figure 6. Fickian diffusion curve

The apparent diffusion coefficient D_a (not corrected for edge effects) is determined from the initial linear region of the Fickian diffusion curve using the following relationship [70]:

$$D_a = \frac{\pi}{16}\left(\frac{h(M_2 - M_1)}{M_\infty(\sqrt{t_2} - \sqrt{t_1})}\right)^2 \quad (4)$$

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.

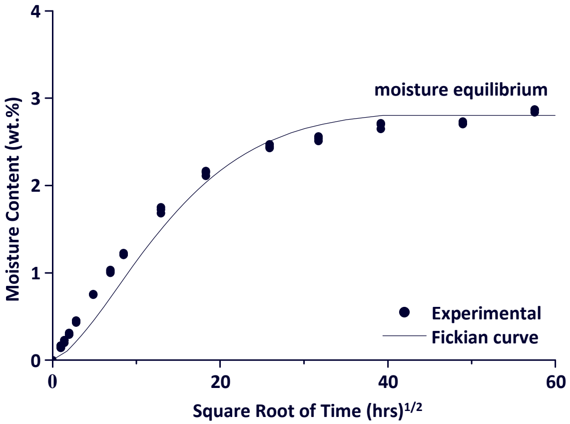

Figure 7. Fickian curve fit of moisture absorption data for an epoxy resin

The fractional moisture content gain *G* can be approximated by [70-72]:

$$G = \frac{M - M_i}{M_\infty - M_i} = 1 - exp\left[-7.3\left(\frac{D_a t}{h^2}\right)^{0.75}\right] \quad (5)$$

M_i is the initial moisture content of the sample and $M = M(t)$ the percent moisture content of the composite at any time *t*. When only one side of the sample is exposed, the thickness *h* is replaced by 2*h*.

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 [71]:

$$D = D_a\left(1 + \frac{h}{l} + \frac{h}{b}\right)^{-2} \quad (6)$$

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). If the moisture entering through the specimen edges is neglected, then diffusivity of the material $D = D_a$.

Note 3: Diffusion in an adhesive joint may be 10 times as high as that measured for bulk adhesive samples, probably as a result of capillary action along the adhesive/adherend interface. Moisture diffusion may differ between the unstressed and stressed states with the diffusion rate increasing with applied stress.

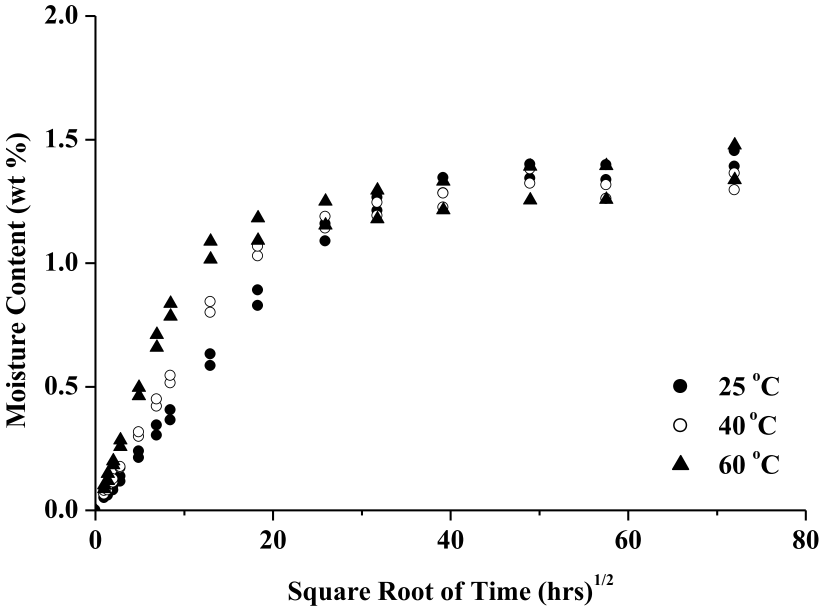

Figure 8. Moisture diffusion curves for UD T300/924 CFRP at three different temperatures (immersion in deionised water)

Diffusion behaviour is temperature dependent (Figure 8) and for ideal systems diffusivity *D* can be expressed as a function of absolute temperature *T* according to the Arrhenius relationship [71]:

$$D(T) = D_0 e^{-(E/kT)} \tag{7}$$

where *k* is Boltzmann's constant. Material parameters D_0 and *E* (energy barrier to diffusion) can be determined from a linear regression fit to loge *D* versus 1/*T* graph (Figure 9).

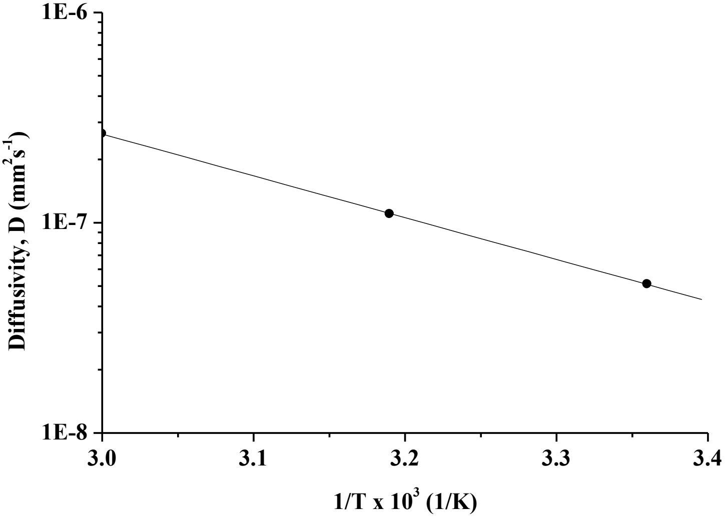

Figure 9. Temperature dependence of diffusivity for UD T300/924 carbon/epoxy (immersion in deionized water)

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 may be estimated by the following relationships [71]:

$$D_{11} = (1 - V_f)D_m \tag{8}$$

$$D_{22} = \left(1 - 2\sqrt{\frac{V_f}{\pi}}\right)D_m \tag{9}$$

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

The diffusion coefficient for a composite is given by the following relationship [71]:

$$D = D_{33}\left(1 + \frac{h}{l}\sqrt{\frac{D_{11}}{D_{33}}} + \frac{h}{b}\sqrt{\frac{D_{22}}{D_{33}}}\right)^2 \tag{10}$$

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 [71]:

$$M_\infty = a\phi^b \tag{11}$$

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

In the case of aramid composites, 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 fibre and resin separately to isolate constituent contributions. After long exposure times, the moisture content may deviate above that predicted by the Fickian analysis, exceeding the saturation level predicted by Fickian theory. This non-Fickian behaviour could possibly be due to defect growth. Thermal spikes and freeze/thaw cycling can result in micro-damage formation, leading to an increase in the rate of moisture uptake and saturation level.

Moisture measurements are sensitive to a number of factors that need to be considered to ensure accurate diffusivity values. These are listed below [36]:

- 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.
- 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.
- Surface roughness can affect moisture uptake and drying. Rough surfaces are more difficult to dry, and also present a larger surface area to the surrounding environment.
- 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.
- Specimen dimensions need to be accurately measured. Small variations can result in significant errors in diffusivity calculations.
- Surface damage and defects must be avoided as these can act as paths for moisture ingress.

Mechanical testing of conditioned specimens

For design purposes, a material test programme should measure both the moisture absorption properties of a material (i.e., diffusion rate and equilibrium content) and the resultant mechanical properties at equilibrium. Mechanical property measurements at intermediate moisture levels (based on average moisture contents) can be used to determine temporal and spatial distributions of stresses and strains within a bonded structure. To evaluate worst-case effects of moisture content on material properties, tests are performed on specimens that have been preconditioned to the design service moisture content (e.g., aerospace worst-case environment is considered to be represented by 70 °C/85% RH).

It should be noted that the material operational limit is influenced markedly by temperature and moisture content. Figure 10 shows tensile stress-strain responses under ambient test conditions for an adhesive that has been immersed in water for periods ranging from 30 minutes to 12 days. There is a significant reduction in tensile stiffness and strength with increasing moisture content. The reduction in material properties will be more severe at elevated temperatures.

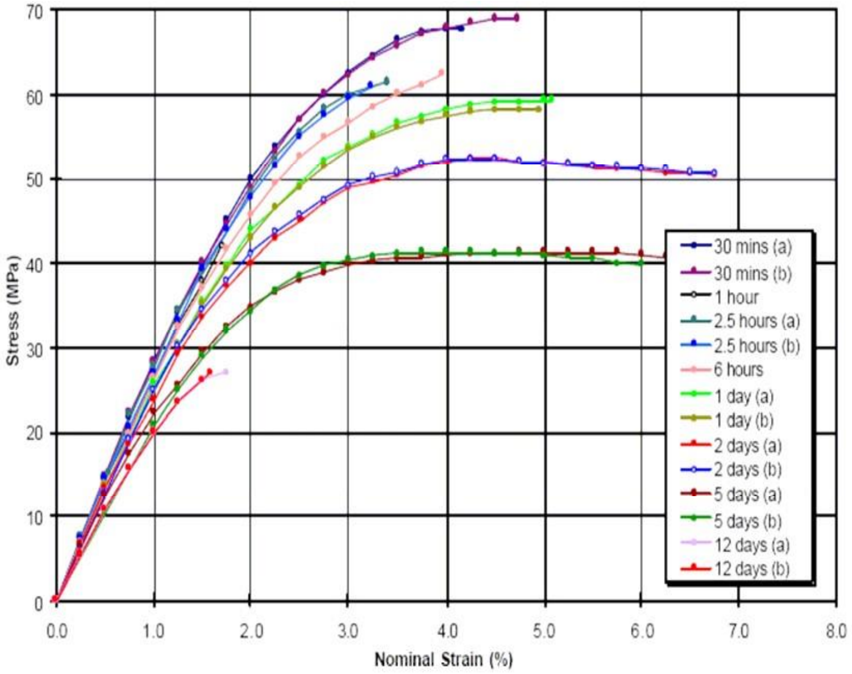

Figure 10. Tensile stress-strain curves for different water immersion periods

A number of contact and non-contact techniques, such as linear voltage displacement transducers (LVDTs), video extensometers, and electronic speckle pattern interferometry (ESPI), strain gauges and crosshead movement are available for measuring strain and displacement. Except for strain mapping techniques (i.e., ESPI and digital image correlation (DIC)), the measured strain will be an average strain. Also, strain gauges only measure strain at the location of the gauge. Further details on these techniques can be obtained from NPL Measurement Good Practice Guide Number 47 [33]. Some thought needs to be given to selecting techniques for the actual tests to be performed. Factors to be considered include:

- Degree of accuracy and resolution required
- Area over which strain is to be monitored
- Suitability of measurement device for testing environment (e.g., calibration for contact extensometers may not be valid at non-ambient temperatures)
- Quality of visual access to specimen (for non-contact techniques)
- Chemical compatibility with any pattern marking or adhesives required
- Likelihood of strain measuring devices (e.g., knife edges on extensometers) damaging specimen and initiating premature failure.

Strain gauges have particular issues that restrict their usefulness in environmental conditioning and testing. Most strain gauge adhesives are sensitive to moisture, which can often preclude bonding of strain gauges to the specimen prior to the preconditioning stage. Moisture attack of the strain gauge adhesive and strain gauges will occur from the top, edges and through the test specimen. It is therefore important to ensure that the adhesive selected for bonding the strain gauges remains unaffected for the entire duration of the test and that strain gauges and associated electrical wiring are suitably encapsulated. Silicone rubber and foil have been placed over strain gauges to isolate the gauges during environmental conditioning. The process is only partially effective, as moisture will eventually penetrate the bond-line. The strain gauge manufacturer should be contacted to obtain advice on adhesive selection and procedures for strain gauge protection. The preferred method is to use either contact extensometers or video extensometers for monitoring strain.

It is important that the moisture content be established prior to testing and that specimens be tested within an hour of removal from the conditioning environment to ensure that minimal water loss occurs. At elevated temperatures, preconditioned specimens tend to dry out during the test, although for static tests the effects are minimal provided testing is completed within 15 minutes of the specimen being removed from the conditioning environment. Methods of inhibiting moisture loss, such as encapsulating specimens with a sealant or enclosing the specimen in a polythene bag containing a salt solution appropriate to the humidity requirements of the test, are not practical.

Traveller specimens are required for monitoring the moisture content loss that occurs during the test. For coupon testing, it is common practice to allow a soak period of 10 minutes at the test temperature prior to testing. The purpose of “heat-soaking” is to eliminate distortion due to non-uniform temperature distributions.

Moisture conditioned specimens can be stored in a refrigerator at a temperature of 4°C for periods of up to six weeks with minimal moisture loss or effect on mechanical properties. Sub-zero temperatures can result in further damage to a material due to ice formation, and hence storage under these conditions should be avoided.

Fibre bundles and impregnated strands

Test methods have been developed for characterising the tensile properties of fibre bundles and impregnated strands under static and cyclic (tension-tension) loads, and/or aggressive environments [51]. These test methods require shorter conditioning times and less manufacturing and testing costs compared with current practices. The use of small diameter composite rods (1.5 to 5 mm), as shown in Figure 11, enables rapid environmental conditioning under more moderate and realistic temperatures and moisture levels compared with those methods used to accelerate ageing in laminates. Degradation effects on the composite rods by the environment are quickly manifested (within 7 days) in terms of strength reduction [51].

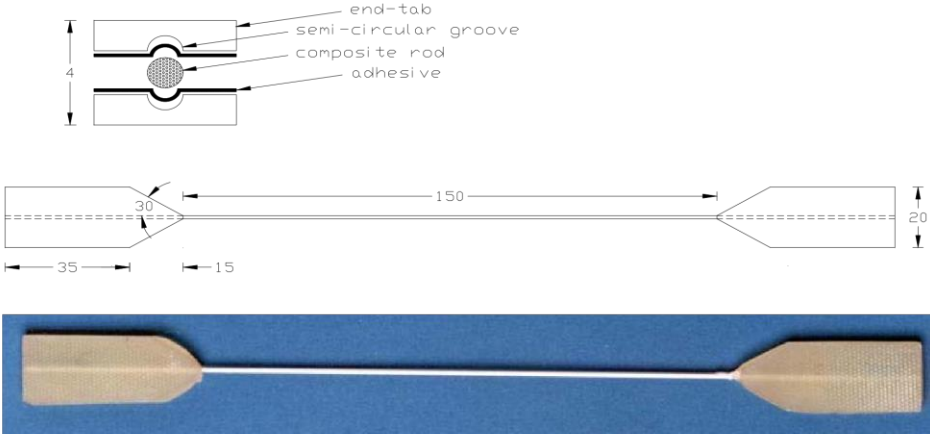

Figure 11. Composite rod specimen with adhesively bonded composite end tabs (dimensions are in mm)

Several test methods exist for measuring the tensile strength and longitudinal modulus of single fibre filaments and fibre tows or rovings (i.e., bundle of continuous parallel filaments). These methods are usually intended for yarns having a diameter of less than 2 mm (typically 0.5 to 0.8 mm), or a linear density lower than 2,000 tex (weight per unit length in g/km). Fibre tow methods include testing of both un-impregnated (i.e., loose, or dry) and impregnated rovings.

ISO 3341 [73] specifies a method for the determination of the breaking force and failure strain of un-impregnated glass fibre rovings, whereas ISO 9163 [74] allows for both un-impregnated and impregnated fibre tows. ASTM D4018 [75] and ISO 10618 [76] specify test methods for carbon fibre tows. Manufacturers will often use in-house quality assurance methods for determining fibre tensile properties. NPL Measurement Note CMMT (MN) 063 [51] gives details on specimen manufacture and testing.

Design and planning an accelerated test programme

In order to conduct an effective accelerated test programme, it is essential to spend time in designing and planning the test program [11, 23]. The process is iterative and will need to be repeated several times to establish a test program that will meet budget and technical requirements. The test program 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 program. 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 accelerated test program to ensure that the test procedures used closely reflect the service conditions [11, 23].

- Clearly define the purpose and aims of the test programme (i.e., product performance assessment, material comparison, quality assurance and design data).
- Specify the service life that needs to be predicted and the level of uncertainty in life expectancy that is acceptable.
- 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/empirical model(s) for extrapolating short-term data to service conditions.
- Timing and sequencing of exposures - where possible, exposure intervals should match these 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.

Although test conditions for quality assurance, material comparison testing, and comparative checks of material performance against design specification, are often limited with respect to the entire spectrum of conditions that may be experienced during service operation, the results still can provide valuable information on material behaviour under extreme conditions. It is important, however, that the test conditions are standardized and reproducible. For design and performance prediction, it is essential that extrapolation relationships from the test conditions to those experienced in service are known and can be used with confidence (NB. Material behaviour (including failure mechanisms) needs to be the same for both the accelerated test and service conditions).

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.

Chapter 4

Static fatigue testing

- Introduction
- Static fatigue testing

Introduction

Testing materials under applied loads further accelerates the onset and accumulation of damage. For static fatigue testing, strain levels in excess of those normally experienced during service are applied to the test component. Although obviously apparent for temperature, an increase in chemical concentration or applied stress can also alter the mechanism of degradation. This Chapter examines static fatigue testing.

Static fatigue testing

Static fatigue (or creep rupture) tests are performed to assess the extension of materials or structures under load in order 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 in excess of 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 (NB. 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 12); and
- Self-stressing fixture where specimens are placed in either a tube equipped with a pre-calibrated spring system (Figure 12) for loading specimens or a circular ring.

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

Figure 12. 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 12), 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 12 is capable of loading 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 in order to accurately determine time-to-failure.

Specimens loaded by springs can often be in an unstressed state for a considerable period of time (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 in order 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 particular 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 13 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).

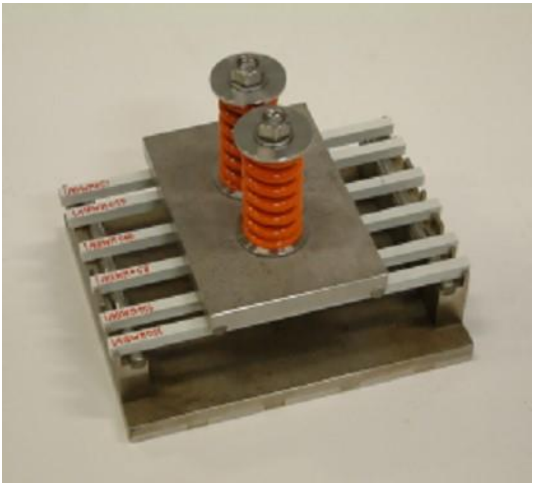

Figure 13. Self-stressing flexure rig with specimens

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 bedding in period at the start of the test and specimens tend to creep rapidly at 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 [77] 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.

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Chapter 5

Environmental stress cracking (ESC) of plastics

- Introduction
- Bent strip tests
- Bent strip for flexible materials
- Ball and pin impression
- Constant tensile deformation
- Slow strain rate testing
- Constant load tests
- C-ring tests
- Strain hardening tests

Introduction

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 products long-term properties. The evaluation of ESC in thermoplastics is covered by several national and international standards [19]. 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 [78])
- Bent strip test for flexible materials (ASTM D1693 [79])
- Ball and pin impression (ISO 22088-4 [80])
- Constant tensile deformation (ISO 22088-5 [81])
- Slow strain rate testing (ISO 22088-6 [82])

Constant Load Tests

- Constant tensile stress (ISO 22088-2 [83])
- C-ring tests (ISO 7539-5 [84] and ASTM G38 [85])

Note 4: ISO 7539-5 [84] and ASTM G38 [85] 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 from NPL Technical Review No.3 [19].

Bent strip tests

The bent strip test (ISO 22088-3 [78]) involves clamping the test specimen to a semi-circular former to apply a known strain to the specimen. The radius of curvature of former can be varied to induce different levels of strain in the specimen. This strain may be calculated using the following equation:

$$\varepsilon\,(\%) = \frac{d}{2r + d} \times 100 \qquad (12)$$

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. The 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 [79]. The technique is suitable for flexible polymers such as polyethylene but should only really be used for quality control purposes. An illustration of the type of apparatus used in this test method is shown in Figure 14. 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.

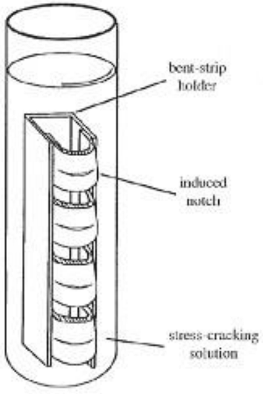


Figure 14. Bent strip technique for flexible polymers [79]

Ball and pin impression

The ball and pin impression test (ISO 22088-4 [80]) 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 (ISO 22088-5 [81]) is a relatively new test. The test method involves applying a constant deformation to the specimen and monitoring the stress relaxation that occurs while it is immersed in the chemical environment. The test is repeated using progressively smaller levels of deformation until the stress relaxation curves of consecutive tests (4 and 5) superimpose on one another (see Figure 15). S_0 is the initial stress and S is the stress at time t. 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.

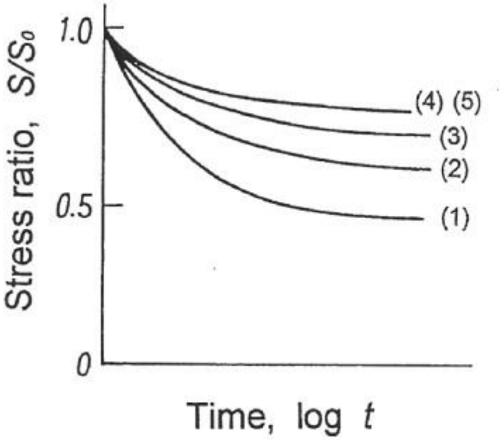


Figure 15. Stress relaxation curves for progressively smaller levels of deformation (1 > 5)

Slow strain rate testing

The slow strain rate method has been used only comparatively recently for characterising the performance of plastics although it is well-established for metals and it has now been developed into a standard as ISO 22088-6 [82]. 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 16. The main advantages of the slow stain rate test are that it is relatively rapid, requires few specimens and can be automated.

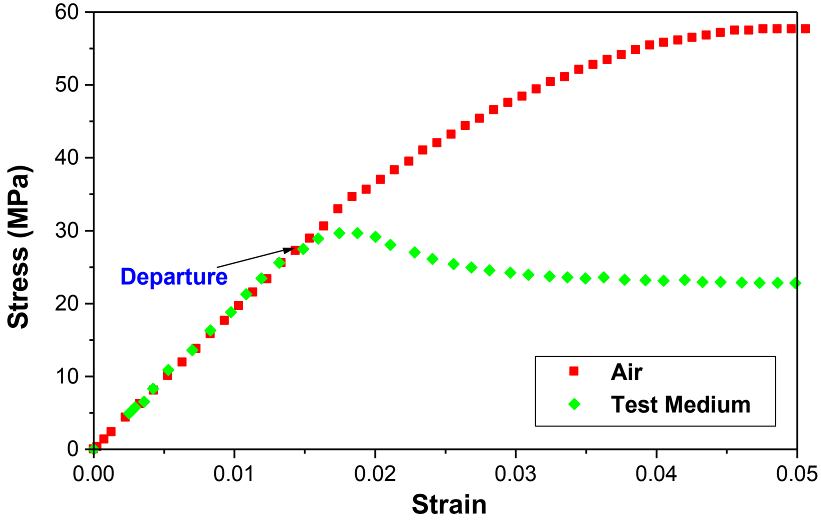


Figure 16. Typical stress-strain plot showing difference in stress/strain profile for material exposed in air and in the test medium

Constant load tests

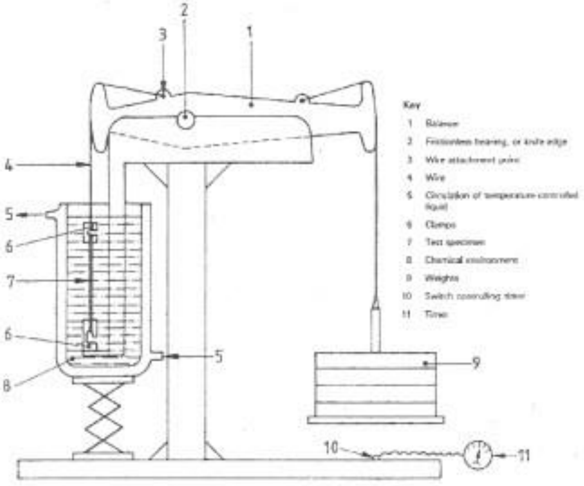
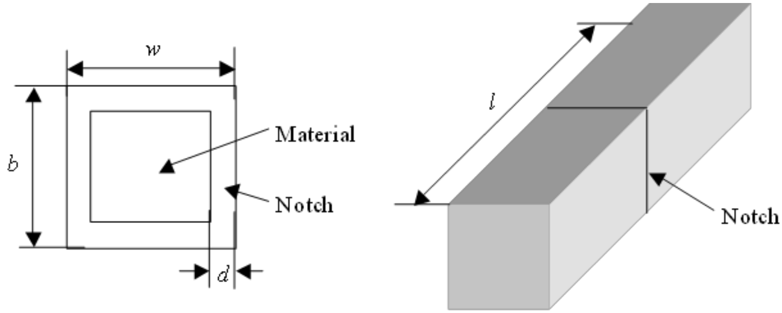


Figure 17. Illustration of typical apparatus used for a constant load test

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 [83]). An illustration of the type of apparatus used in this test method is shown in Figure 17. 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. Environmental cell used for constant load tensile test is shown in Figure 18. 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 1000 hours) can be used as a measure of the ESC resistance.

Figure 18. Typical environmental cell used for the constant load tensile test

Polyethylenes and polypropylenes can also be examined using constant load tests, however due to generally good ESC resistance a more severe test is required. This is achieved by cutting sharp notches on all four sides of the tensile specimen as shown in Figure 19. The procedure used to conduct the tests is similar to that used in the conventional load tests. This tests method is known as the full notch creep test [86].



w = overall length, minimum: 6 ± 0.2 m

b = width at tapered ends: 6 mm ± 0.2 mm

l = length of specimen: 90 ± 0.2 mm

d = notch depth: 1 ± 0.1 mm

Figure 19. Test specimens used in the full notch creep test

The full notch test shows differences in the ESC resistance, but can be misleading if creep tests are not conducted for a sufficient length of time (up to 1 year). Figure 20 compares the time to failure of three grades of linear low-density polyethylene (LLDPE) in which there is a crossover point at approximately 1000 hrs.

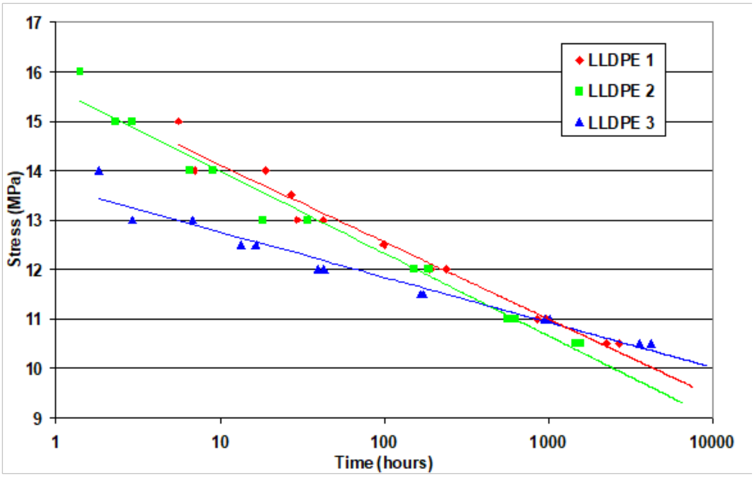


Figure 20. Time to failure of three grades of LLDPE full notch creep specimens

C-ring tests

C-ring specimens are often used for testing of tubing and pipes. 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 [84] and ASTM G38 [85]). An almost constant load can be developed on the C-ring specimen by placing a calibrated spring on the loading bolt.

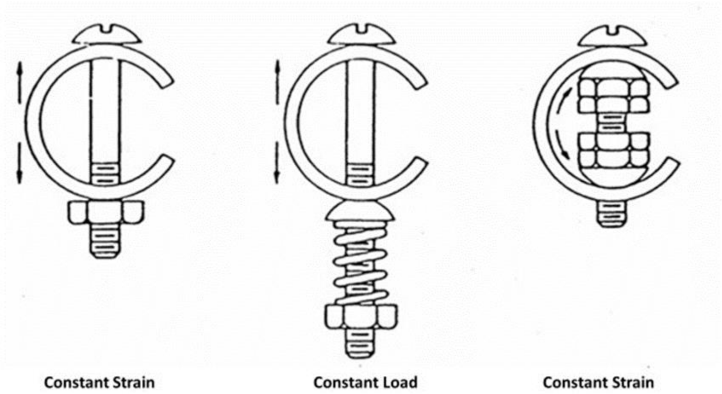


Figure 21. C-ring test methods for assessing ESC in pipe sections

Strain hardening tests

An alternative approach that has been developed for testing the ESC resistance of polyethylenes is to relate the ESC resistance to the creep rate deceleration of drawn polyethylene samples [87-90]. In this approach, it is assumed that the critical step in the ESC of semi-crystalline polymers is the creep of the fibrils. Fibrillar creep is therefore determined by simulating the structure of a fibril using a tensile specimen drawn to its natural draw-ratio. Using this technique Cawood and Rose et al [89-90] showed that for polyethylenes there is a direct relationship between the creep rate deceleration and ESC resistance. Measurement of creep is, however, a slow process and the technique has therefore not been widely adopted.

However, it has been shown recently [91] that the average strain-hardening modulus G_p of high-density polyethylene (HDPE) correlates extremely well with the ESC resistance of the polymer. Typical data obtained from this new strain hardening technique is shown in Figure 22. The strain hardening modulus is given by the average gradient of the completely drawn specimen (draw ratios > 9). In this example, it can clearly be seen that the strain hardening modulus of HDPE 1 is significantly higher than HDPE 2, indicating that HDPE 1 is more resistance than HDPE 2 to ESC.

The advantage of using strain hardening to determine ESC resistance is that the data required may be obtained from simple plots of true-stress again draw-ratio, offering a relatively easy and significantly quicker method of assessing the relative ESC susceptibility of different polyethylene grades.

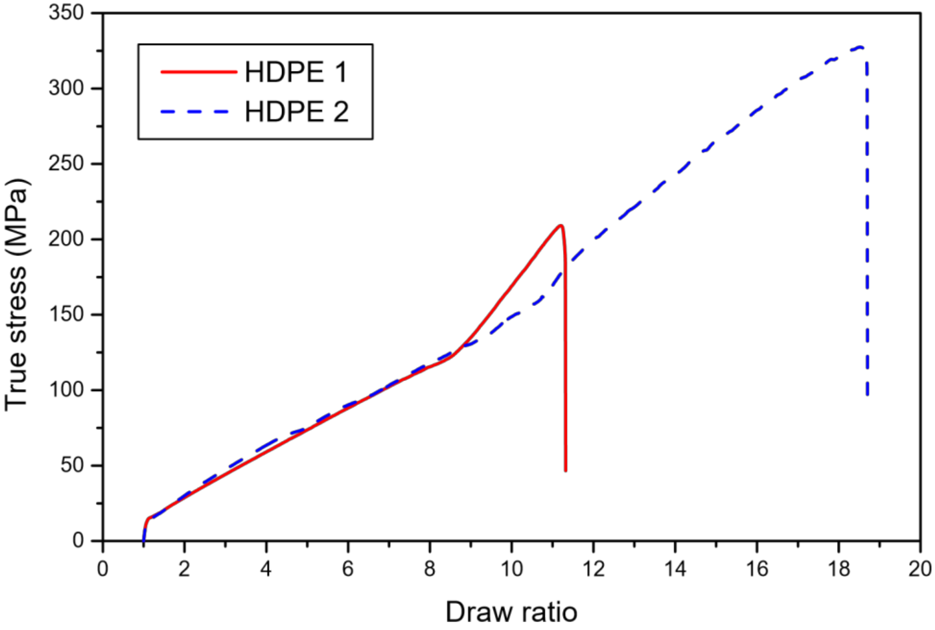


Figure 22 True stress - draw ratio curves used to determine the relative ESC resistance of two polyethylene grades in the strain hardening technique

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Chapter 6

Accelerated weathering

- Introduction
- Artificial weathering apparatus
- Accelerated weathering test procedures
- Ionising radiation
- Performance testing

Introduction

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).

Accelerated weathering procedures [27, 92] generally involve cyclic exposure to a combination of salt spray, elevated and/or sub-zero temperatures, and ultraviolet (UV) radiation. 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) [93]. Whilst mechanical properties and dimensional stability are quantitatively measurable quantities, a number of the 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. This Chapter provides guidance on performance testing and technical requirements relating to accelerated weathering of FRPs.

Artificial weathering apparatus

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 [94] 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 [95-97], ASTM D1435 [98], ASTM D4364 [99] and ASTM G24 [100]. ISO 15314 [101] 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 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, however, 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.

UV lamps

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 [102].

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

- UV-A (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.

- UV-C (<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 UV-B radiation indoors.

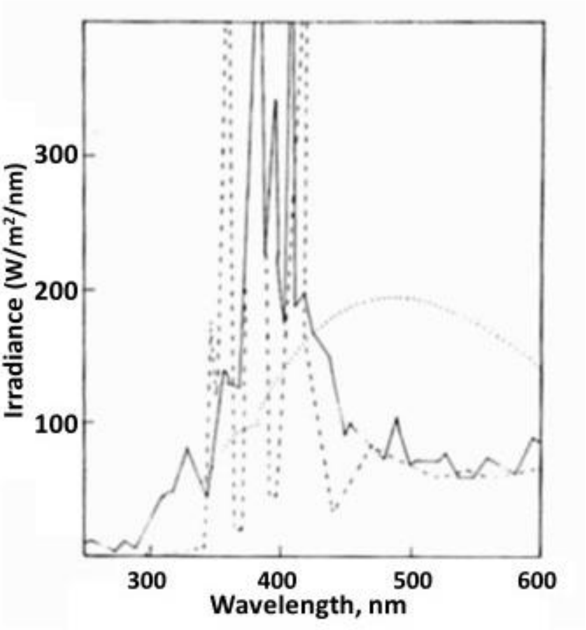


Figure 23. Spectrum of carbon-arc lamp (—), carbon-arc lamp with Cordex D filter (---) and noonday Chicago sunlight (····) [25]

Carbon-arc lamps: Until the 1960's, 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 (<350nm). A typical spectrum from a carbon-arc consists of a series of line emissions that are superimposed on to a continuous background (Figure 23) [25]. 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 there use for plastics is standardised in ISO 4892-4 [103] and ASTM D1499 [104].

Xenon lamps: Xenon-arc lamps give a much better spectral simulation to natural sunlight (Figure 24) 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 [105]. 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 [103] and ASTM D2565 [106].

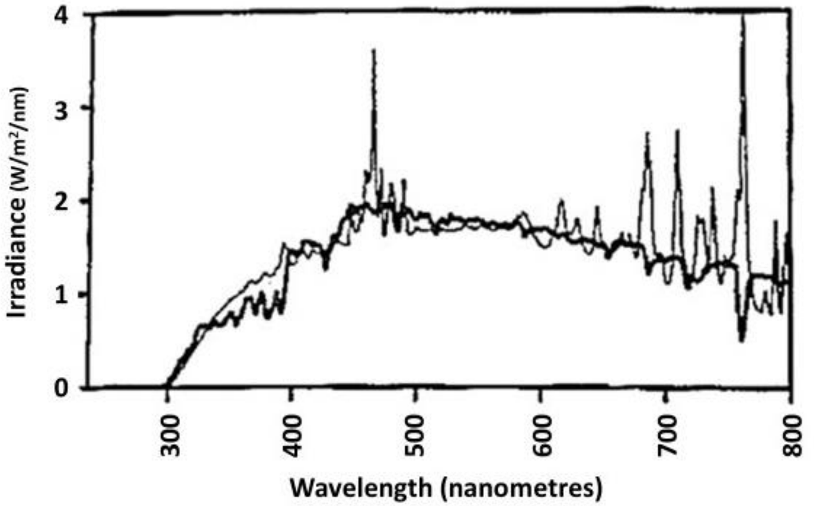


Figure 24. Spectrum of a xenon lamp (—) compared with noonday Miami sunlight (━) [25]

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 25). 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 [25, 102]). Standard test procedures for the use of fluorescent tube are given in ISO 4892-3 [105] and ASTM D4329 [107].

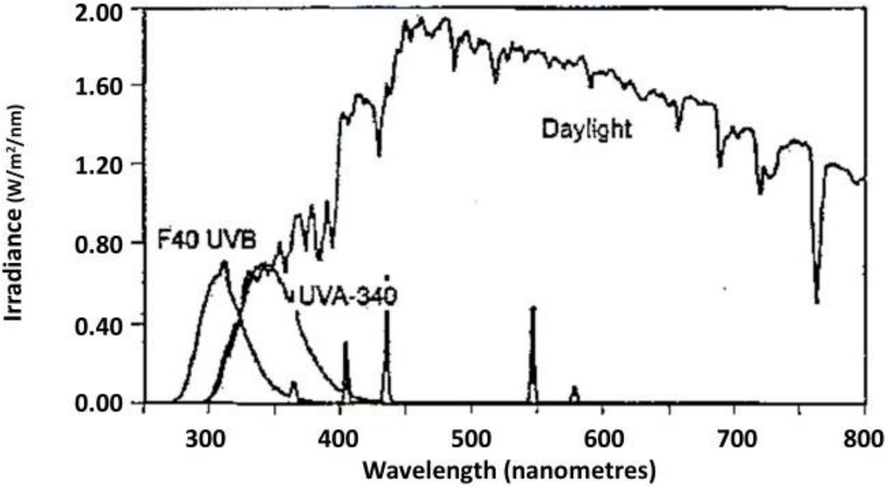


Figure 25. Spectra of UV-A and UV-B fluorescent lamps compared with standard noonday Miami sunlight [25]

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 [108]. Water used for the salt spray must meet the requirements of ISO 4892-1, Clause 5.3 [109]. 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 [109]. 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.

Specimen mounting and handling

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 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 (NB. 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 test 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 of -20°C for 24 hrs has been included in ISO 20340 [110] 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 [92]. 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 16474-1 [111] and ISO 9227 [112]):

- 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

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 [113]. 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 [114] 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 [115] 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 [116] 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.

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.) [117]. 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 Chapter 7).

This section provides guidance on performance testing using data generated from an accelerated weathering study [117] in which glass/polyester pultruded rods were conditioned in accordance with ISO 20340 [110] for a period of six months. Mechanical and physical measurements were conducted on the GRP rods after 0, 1, 2-, 3-, 4- and 6-months exposure (carried out by to assess surface and bulk property degradation. Surface and bulk properties measured include:

- Moisture content (wt.%)
- Glass transition temperature (T_g)
- Barcol hardness
- Gloss
- Spectral reflectance (colour)
- Flexural properties

Moisture content

Moisture content (wt.%) of test specimens should be measured before and after artificially weathering. Prior to conditioning, the material should be dried to a constant weight to provide a zero datum. The drying temperature is typically 50 °C for polyester and vinyl ester based composites, and 70 °C for epoxy based systems. The moisture content of glass and carbon FRPs exposed to standard laboratory conditions is typically 0.2 wt.%. In the case of the glass/polyester, this is equivalent to approximately one month of artificially weathering (see Table 1). The moisture content in accelerated weathered FRPs will reach an equilibrium level (possibly within a few months). Moisture measurement should be conducted in accordance of ISO 62 [64].

Glass transition temperature

An increase in moisture content will generally result in a reduction in T_g. The results presented in Table 1, however, indicate that the moisture content in the glass/polyester remains relatively unaffected by an increase in moisture content. This is probably because the moisture is mainly concentrated in the outer few layers of the composite. Although there may be no changes in T_g, this does not exclude the possibility of material degradation. T_g can be measured using dynamic mechanical analysis (DMA) [118-120]. The recommended DMA standard is ISO 6721 [118].

Material	Moisture Content (wt.%)	T_g (°C)
As received	0.23 ± 0.01	94.70
Dry	0.00	97.01
Exposure (Months)		
1	0.27 ± 0.02	92.20
2	0.34 ± 0.04	95.51
3	0.56 ± 0.04	92.26
4	0.39 ± 0.10	95.20
6	0.54 ± 0.02	96.88

Table 1. Moisture content and glass transition temperature (T_g)

Barcol hardness

Barcol hardness test can be used to measure the surface hardness of FRPs (see BS EN 59 [121] and ASTM D2583 [122]). 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 in order 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. The results shown in Figure 26 indicate that hardness decreases with 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.

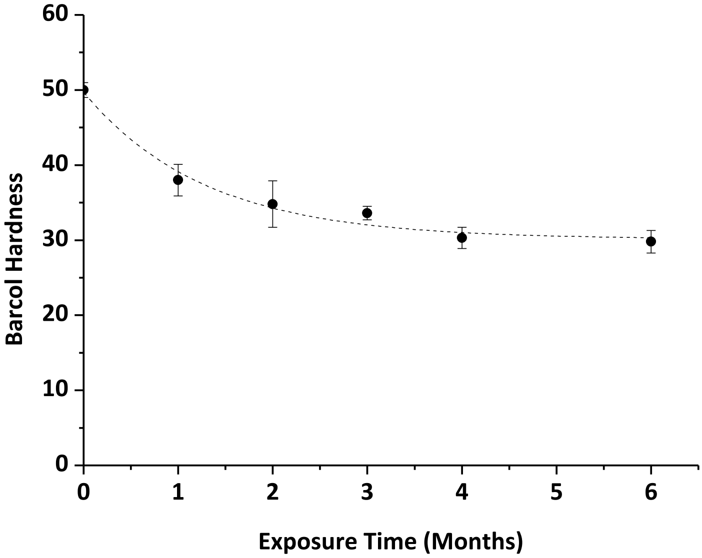


Figure 26. Barcol hardness versus exposure time for artificially weathered glass/polyester rods

Gloss

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 [123, 124], ISO 14782 [125] and BS 2782 [126].

Table 2 presents the 60° angle gloss measurements for different periods of exposure. The gloss measurements clearly show a strong relationship between gloss retention and exposure time (see Figure 27). Gloss retention decreases rapidly with exposure time. After 6 months of artificial weathering, gloss has been reduced by a factor of almost 10.

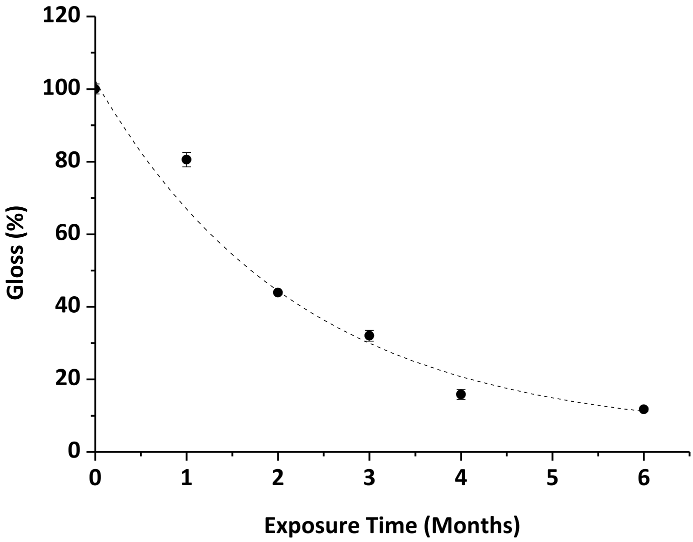


Figure 27. Gloss retention versus exposure time for artificially weathered glass/polyester rods (60° angle measurements)

Material	Gloss Measurement
As received	22.1 ± 0.1
Exposure (Months)	
1	17.8 ± 0.4
2	9.7 ± 0.1
3	7.1 ± 0.3
4	3.5 ± 0.3
6	2.6 ± 0.1

Table 2. Gloss measurements for artificially weathered glass/polyester

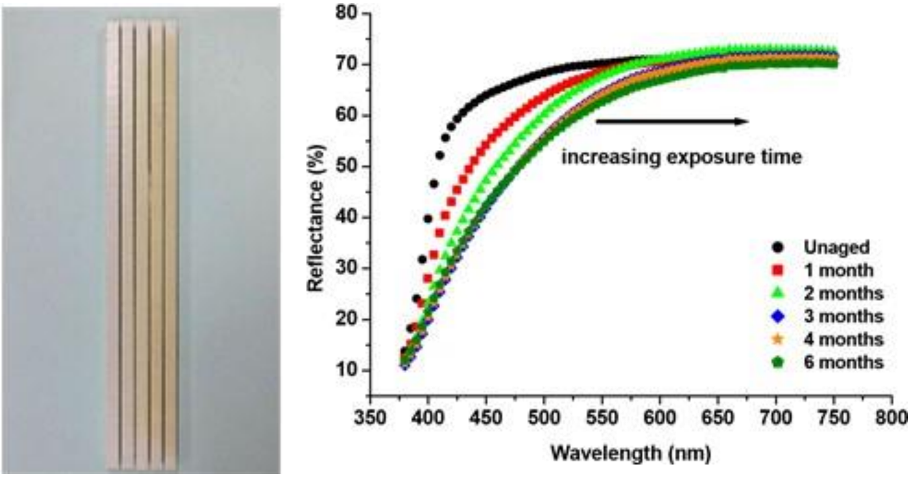
Spectral reflectance (colour)

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 [123-124], and ISO 14782 [125] – see also [127]). 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 [128]. The reflectance of the sample is measured at 1 nm wavelength intervals over the spectral range 380 nm to 780 nm. Two sets of measurements were made on separate occasions on the test specimens and the average recorded. The degree of reflectance decreases with exposure time (see Figure 28), mirroring the changes in gloss measurement. Figure 29 shows a normalised plot of total reflectance over the spectral range 380 nm to 780 nm. The total reflectance data for each specimen (i.e., exposure time) was normalised with respect to the total reflectance data obtained for the unconditioned material.

The discolouration (i.e., yellowing) observed with exposure time, as shown in Figure 28, is due to a reduction in spectral reflectance over the spectral range 380 nm to 600 nm (i.e., blue component). The discolouration can be mainly attributed to exposure to UV radiation (UVA 340 nm).

Note 5: Visual inspection can provide considerable information as to the state of a materials surface (i.e., colour changes, crazing and resin loss).



Discolouration of GRP rods

0 (left), 1, 2, 3 and 6 months

Spectral reflectance versus exposure time

Figure 28. Colour change in glass/polyester rods due to artificial weathering

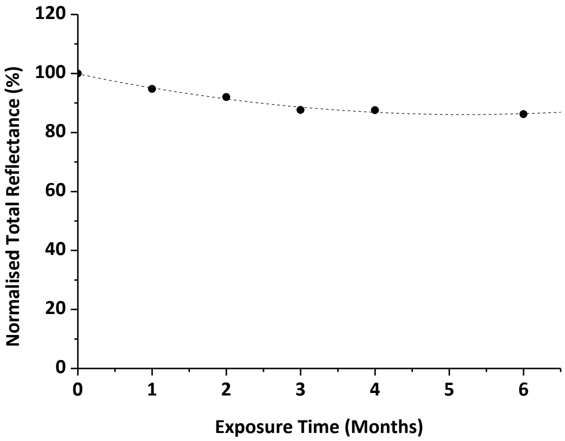


Figure 29. Total reflectance of artificially weathered glass/polyester rods (normalised with respect to the "as-received" material)

Flexural properties

Flexural modulus is relatively insensitive to physical and chemical changes that can occur at the surface or within the bulk of the material, and hence is a poor indicator of material degradation. In contrast, flexural strength is sensitive to material degradation. Any degradation involving the outer layers of the composite will have an amplified effect on load-bearing capacity under flexural loading conditions. The influence of layers on flexural strength increases proportionally to the cube of the distance of the layer from the neutral axis of the beam. Table 3 shows the flexural properties of the artificial weathered GRP rods measured using four-point bend in accordance with ISO 14125 [129] - see also Figure 30. Tests were conducted at a crosshead displacement rate of 5 mm/min under standard laboratory conditions (23 °C/50% RH).

Material	Flexural Modulus (GPa)	Flexural Strength (MPa)
As received	22.5 ± 0.5	442 ± 23
Dry	23.8 ± 1.1	490 ± 11
Exposure (Months)		
1	23.3 ± 1.3	416 ± 38
2	22.7 ± 1.3	404 ± 56
3	21.7 ± 1.3	377 ± 23
4	22.1 ± 1.2	377 ± 24
6	21.3 ± 0.8	371 ± 35

Table 3. Four-point flexure results for artificially weathered glass/polyester rods

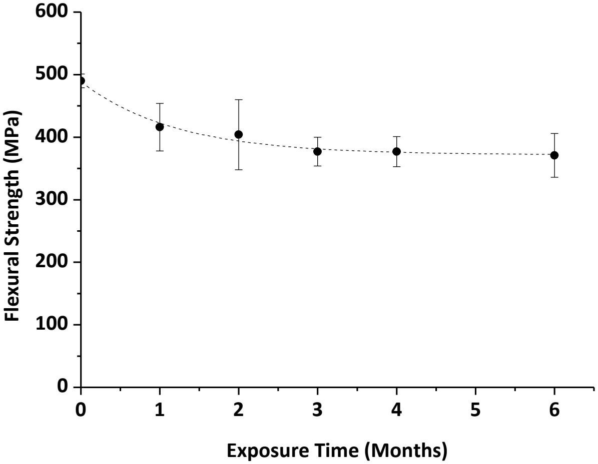


Figure 30. Flexural strength versus exposure time for artificially weathered glass/polyester rods

It is recommended that the displacement at the beam mid-section should be measured using a linear voltage displacement transducer (LVDT). It is recommended where possible to use specimens with dimensions that comply with either ISO 14125 [129] or ASTM D7264 [130]. Tests should be carried out to ensure that non-standard specimens (e.g., narrow rods) produce results equivalent to those obtained using specimens with a geometry that conforms to the standard. Edge effects can cause a reduction in flexural strength in narrow beam specimens.

The question arises as to the use of non-destructive surface measurements, such as Barcol hardness, gloss retention and spectral reflectance, as possible indicators of mechanical property (i.e., flexural strength) reduction. Figures 31 to 33 show that flexural strength tends to be linearly related to gloss, normalised total reflectance and Barcol hardness. The curves shown in Figures 31 to 33 relating to surface reflectance incorporate flexural strength and reflectance data for the “as-received” material and not the “dry” material. Spectral reflectance (i.e., colorimetry) measurements are intrinsically more accurate than specular (gloss) measurements.

The results clearly demonstrate that suitable non-invasive test methods are available that can provide reliable and accurate quantitative data relating the degree of surface degradation to mechanical performance. These test methods make it possible to produce measurable criteria for performance testing for determination of chemical resistance of composite materials. Surface hardness and reflectance measurements could possibly be used to monitor the detrimental effects of service environments on flexural strength. It may also be possible to use these techniques to quantify the level of degradation (i.e., a graduated scale) and provide realistic weighting factors (see Chapter 7).

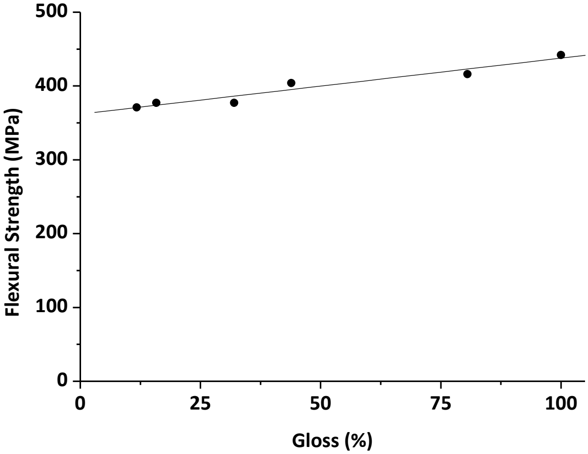


Figure 31. Flexural strength versus gloss measurements for artificially weathered and "as-received" glass polyester rods

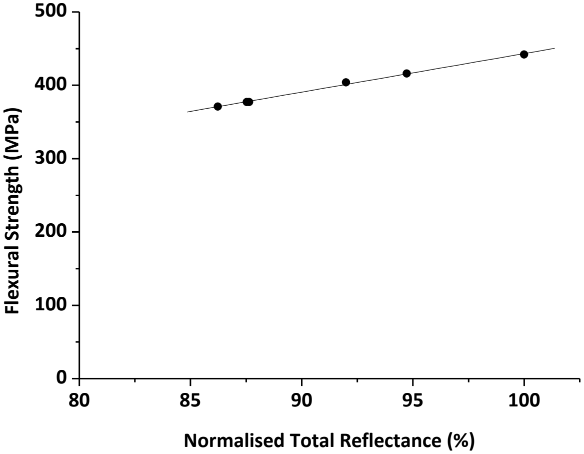


Figure 32. Flexural strength versus normalised spectral reflectance measurementsfor artificially weathered and "as-received" glass polyester rods

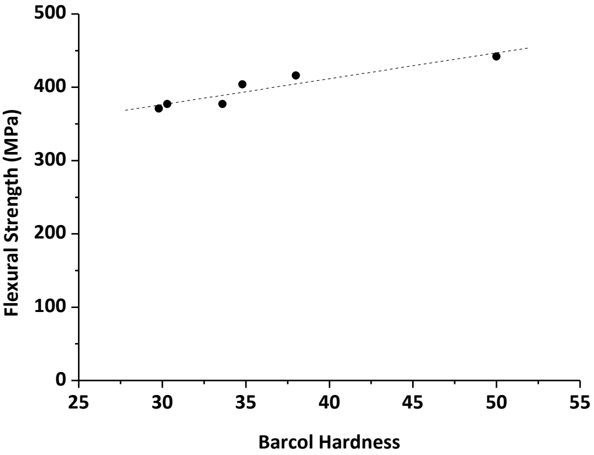


Figure 33. Flexural strength versus Barcol hardness measurements for artificially weathered and "as-received" glass polyester rods

Note 6: Surface measurements, such as hardness and surface reflectance will vary between batches of material and will be affected by surface treatments (i.e., abrasion and solvents), and hence care needs to be taken when carrying out and recording measurements. It is important to compare measurements of the material in the "as-received" condition with measurements obtained on the same material after exposure (i.e., conditioned).

Chemical analysis

Monitoring chemical changes enable direct measurement of the fundamental mechanisms causing degradation. These measurements are essential for understanding the degradation process and rate of chemical degradation that are occurring. The measurement of the carbonyl group is a good indicator of the level of weathering, which can be measured using Fourier Transform Infrared (FTIR) Spectroscopy. Figure 34 compares FTIR spectra for 0, 3 and 6 months of artificially weathered glass/polyester. The set of spectra showed gradual, consistent changes indicating that significant chemical changes have taken place. Some of the more obvious changes are the relative increase in intensity of the absorbance at ~3500 cm and 1640 cm. There are also more subtle changes with an increase in absorbance at ~1775 cm and a change in the absorbance maxima wave number for the absorbance band at ~1725 cm (carbonyl group). The increase in intensity of the absorbance at ~3500 cm and 1640 cm may possibly be attributed to a combination of moisture ingress and oxidation due to UVA radiation.

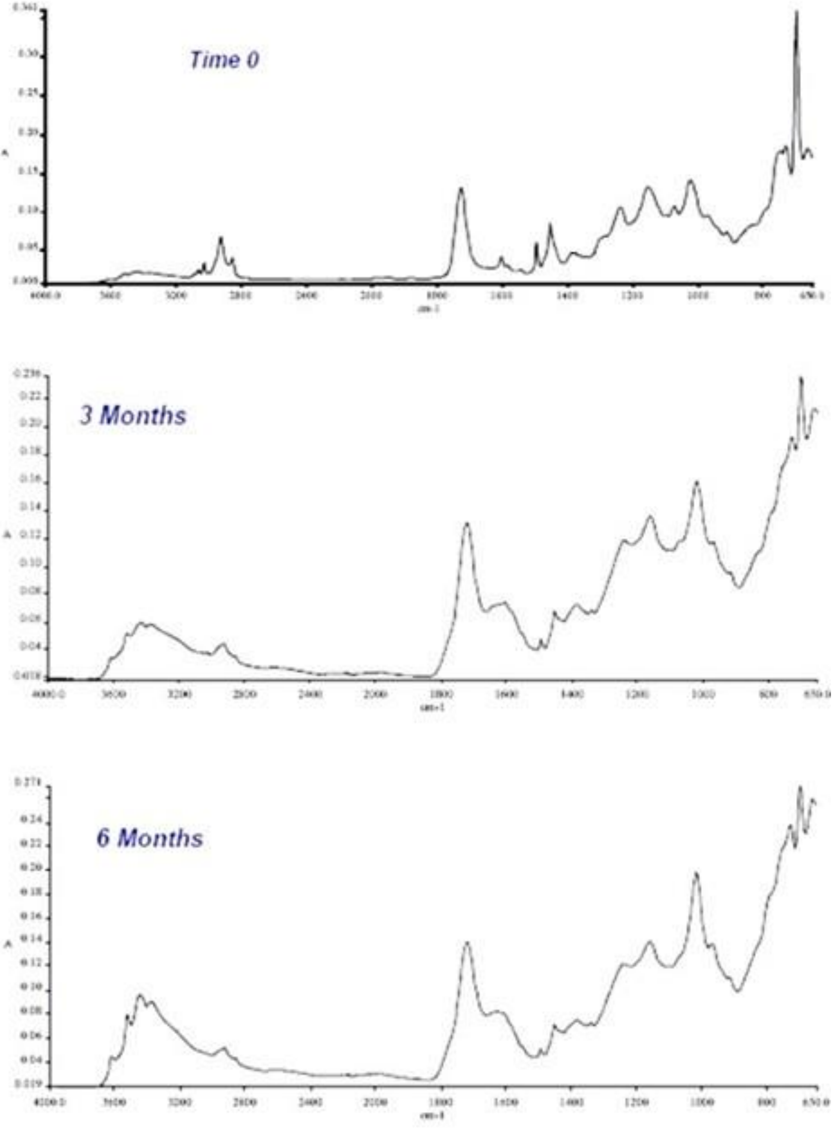


Figure 34. FTIR spectra for 0, 3 and 6 months artificially weathered glass/polyester rods (Courtesy of ElmerPerkin)

Chapter 7

Accelerated testing in aqueous and chemical environments

- Introduction
- Test methods and standards
- Environmental testing
- Test data and analysis

Introduction

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 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 Chapter examines accelerated testing in aqueous and chemical environments (e.g., alkalis and acids).

Test methods and standards

Chemical resistance

An important aspect for composites in many applications is that FRPs are frequently used for their good corrosion resistance (e.g., boats, process equipment, sewage applications). Part 2 of BS EN 13121 [131] 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 4 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 35, where one test plate is in the vapour phase and one in the fluid phase. Assessment is based on a standardised ~3 mm laminate of fixed weight content made by a prescribed method. The tests are undertaken at the design service temperature for a range of exposure times, such as 1, 4, 8, 16 weeks. It is recommended that four exposure units be employed.

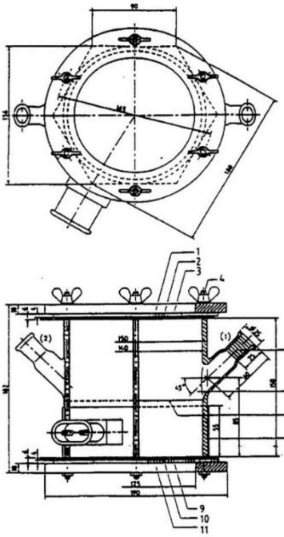


Figure 35. Chemical resistance test (flat plate specimens are numbered 2 and 10)

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 [129]. 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 4). 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.

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
Flexure modulus	20	10	0-10

Table 4. Criteria for chemical resistance

The performance level score from each test should be multiplied by the weighting factor for each criterion (see Table 4), 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:

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

Acceptance of the material for the application should be if the combined score of the test results is ≤ 50% of the total score possible for the tests conducted. 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 5) [131]. The weighting factors are different for single-sided and full immersion. The test can be also be conducted by full immersion of 100 mm x 125 mm plates of the laminate or by testing in-situ within a tank.

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

Table 5. Determination of partial design factor, A_2

British standard BS EN 13121-3 [131] 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 [132] 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 [133] 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 [134] 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 are used in some product test methods. BS EN 14364 [135] and ASTM D3681 [136] 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 36) 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.

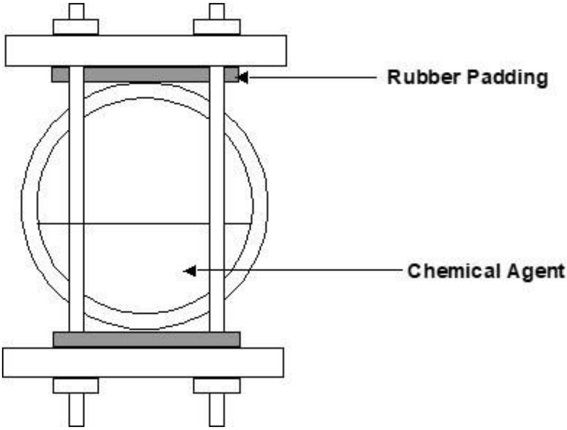


Figure 36. Strain corrosion test apparatus

The American Concrete Institute standard ACI 440.3R-04 “Guide Test Methods for Fibre-Reinforced Polymers for Reinforcing or Strengthening Concrete Structures” [137] 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 [138], BS EN 2489 [139] and ASTM D543 [140] cover the absorption of chemical liquids into polymers.

ASTM C666 [141] 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 [44] 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.

Environmental testing

Treatment tanks

Treatment tanks 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 (see Figure 37) 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.

Note 7: Care needs to be taken when handling, storage and disposal of alkali and acid solutions (see Chapter 8). 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 shown in Figure 13 (Chapter 4) 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.

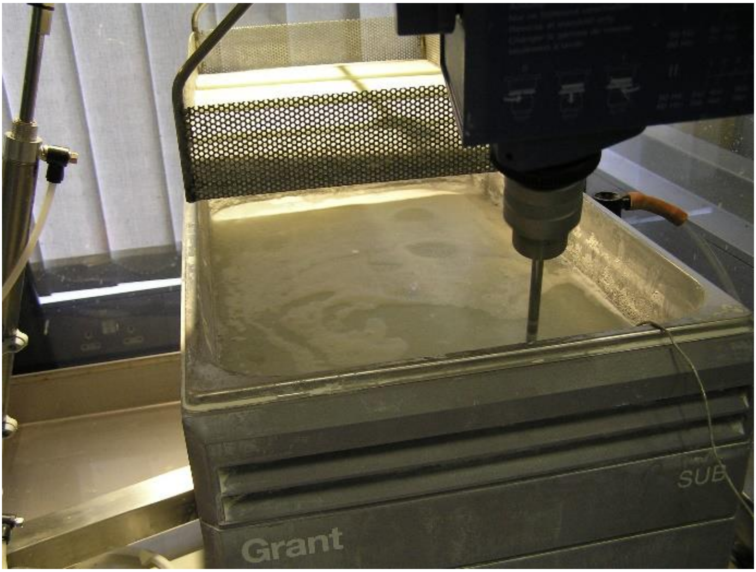


Figure 37 Chemical tank with motorised stirrer
(Courtesy of RAPRA technology Ltd)

Control and monitoring

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.

Warning: Caustic solutions with a high pH level will corrode glass vessels resulting in failure of the vessels.

Care needs to be taken when handling, storage and disposal 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.

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 Chapter 4.

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. Refer to Chapter 6 for further details on specimen mounting.

Simulating chemical spillage (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.

Failure mode

When conducting tests on chemically degraded materials either in-situ or following environmental exposure, a check should be made as to the mode of failure. In the case of tensile tests, failure must occur within the gauge section and not within the gripping region. It is recommended that a suitable structural film adhesive is used to bond the end tabs to the composite specimen in order prevent the possibility of premature failure. There is a possibility that flexure specimens will fail prematurely at the loading point(s) when subjected to flexural loading as a result of high compression and shear stresses acting in the loading regions. This can be avoided through the use of shims placed between the loading rollers and the test specimen. Composites are suitable for short-term ambient and elevated temperature tests, but unsatisfactory for long-term static fatigue tests in chemical environments (including water) because the composite will absorb water and will soften, thus altering the applied stress to the test specimen.

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 the level of degradation agent and exposure time. A potential problem involves changes in the dominant degradation mechanism as the temperature is changed, thus the extrapolated data from accelerated high temperature ageing may not reflect the changes occurring at lower (or ambient) temperature.
- Statistical variability, which generally increases with exposure time, can introduce anomalous effects that make it difficult to differentiate the effects of key variables and determining 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.

Chapter 8

Handling, storage, and documentation

- Handling and storage of materials and chemicals
- Handling and storage of adhesives, resins and prepreg
- Handling and storage of adherends
- Handling, storage, and disposal of chemicals
- Documentation (record keeping)

Handling and storage of materials and chemicals

A number of issues relating to the handling and storage of materials and chemicals need to be considered as many of these factors can affect the performance of the material. Issues to be considered include:

- Health and safety (COSHH)
- Documentation
- Handling and storage (including moisture and temperature effects)

Handling polymeric materials, such as resins and adhesives, can be hazardous to human health, thus COSHH (Control of Substances Hazardous to Health Regulations) procedures should be followed to minimise operator exposure. A safety data sheet should accompany all adhesive samples (Health and Safety at Work Act 1974). The user prior to handling the material must read this document. The safety data sheet supplied with the adhesive identifies:

- Hazardous ingredients and concentrations - includes regulatory information according to legislative directives.
- Hazard statements, such as H225 (highly flammable liquid and vapour), H315 (causes serious eye irritation) and H319 (causes serious eye irritation), and precautionary statements, such as P260 (do not breathe dust/fume/gas/mist/vapours/spray) and P280 (wear protective gloves/protective clothing/eye protection/face protection). Hazard statements are accompanied by classification (e.g., Flammable liquid. 2 – H225 and Eye irritation. 2 – H315).
- First aid measures (including inhalation, ingestion, skin contact and eye contact), and important symptoms and effects, both acute and delayed (e.g., prolonged skin contact may cause redness and irritation). The severity of the symptoms will vary dependent on the concentration and the length of exposure.
- Fire extinguishing/fighting (suitable and unsuitable extinguishing media, and protective equipment and actions) and accidental release (personal and environmental precautions, and methods for cleaning up spillages or discharges) measures.
- Precautions for safe handling and storage including storage precautions (e.g., keep away from heat, sparks, and open flame) and storage class (e.g., flammable liquid storage).
- Control parameters and occupational exposure limits (short-term and long-term exposure limits).
- Exposure controls (includes engineering measures (e.g., adequate ventilation), respiratory protection, eye, skin and body protection, hygiene measures, respiratory protection, and environmental exposure controls).

- Physical and chemical properties (i.e., colour, odour, melting and boiling points, vapour pressure, flammability, etc.), and stability and reactivity of ingredients, and storage and transportation conditions (e.g., temperature).
- Toxicological information (refer to COSHH) – includes potential health effects and hazardous toxicity data.
- Ecological information, disposal considerations and transport information.

Handling and storage of adhesives, resins and prepreg

Polymeric resins may undergo physical and chemical changes when stored for a considerable length of time or under unsatisfactory storage conditions, thus adversely affecting the performance of the adhesive. For example, adhesives may undergo an increase in viscosity, or films a loss of tack and drapeability. Less flow and, thus poorer wetting of the surface, will occur during cure and gel times of epoxy film adhesives could become shorter.

Extended exposure of uncured materials (e.g., adhesives and resins) to temperatures and humidity’s above those recommended by the manufacturer will reduce the cohesive and adhesive strength of the material when cured [3]. The overall effect is to reduce the adhesive performance and induce premature failure of the polymeric system.

The safety and product data sheets will provide the user with recommendations regarding storage temperature for an adhesive. Adhesives and composite prepreg should be stored in sealed containers to prevent moisture ingress and contamination, and some cases exposure to light. Opening a storage container exposes the adhesive to oxygen and moisture, which may in some cases severely reduce the shelf life of the adhesive. The shelf (storage) life is generally defined as the time that an adhesive can be stored (unopened) without any adverse affects on the cure properties and bond strength of the adhesive. The product sheet will often specify the shelf life of the adhesive for various temperature ranges. Materials should not be used beyond the expiry date, which will be indicated on the container. The shelf life of an adhesive can decrease significantly with increasing storage temperature. Unless the manufacturer explicitly states that the adhesive must stored or would benefit from being stored at sub-ambient temperatures then adhesives should be stored at ambient temperatures (18°C - 25°C). Materials should not be stored below freezing unless recommended by the manufacturer but for some materials this is essential (e.g., composite prepreg is generally stored in a freezer at -18°C). Adhesives should not be stored below freezing unless recommended by the manufacturer.

Ideally, temperature and humidity in the storage area should be tightly controlled and monitored (i.e., temperature recorders), although this may not always be physically or economically feasible. Standard laboratory conditions are typically 23 ± 2°C and 50 ± 5 % relative humidity (RH).

Refrigerators (or freezers) should be armed with a temperature alarm and the temperature should be monitored continuously to ensure that the temperature remains below the upper temperature limit specified by the adhesive manufacturer. The maintenance of the refrigerator units should allow for regular manual or automatic defrosting.

A refrigerated adhesive or prepreg may be used several times during the shelf life of the product. This will involve the product being taken from a sub-ambient (often sub-zero) temperature and placed at room temperature and allowed to thaw. It is advisable throughout this exercise that the adhesive is enclosed (i.e., remains enclosed in a sealed container) until the temperature has reached room temperature and is ready to be applied to the adherends. Containers that have been opened must be sealed immediately after use. The amount of time at ambient for these adhesives should be minimal, advice on the length of time can be obtained from the manufacturer. Repeated exposure of the adhesive (or prepreg) is a frequent cause of adhesive ageing and deterioration. Sampling of the material before removal from sub-ambient storage may help extend the shelf life of the product, however this may not always be possible for adhesive packed in cartridges.

Exposure to repeated freeze/thaw cycling could limit the shelf life of an adhesive. Exposing a film adhesive that has been stored at sub-ambient temperatures will result in moisture condensing on the surface, which if not allowed to evaporate will compromise the strength and durability of the joint. Entrapped moisture will be released during the cure process, thus compromising the physical and mechanical properties of the adhesive and contribute to the degradation of the bonded surfaces. Routine tests to verify that the physical and mechanical properties of the adhesives are still within specification are recommended, particularly where multiple use of an adhesive has occurred.

Resins, adhesives and prepregs should be stored in an area specifically dedicated to these materials. The area should be suitable for handling flammable and hazardous materials. It may be necessary to segregate materials depending on the hazardous nature of the material. Materials in these areas should be clearly identified and controlled.

Handling and storage of adherends

Before and after machining, adherends sensitive to environmental attack or hygroscopic in nature should be stored in sealed containers to prevent moisture ingress and contamination. It is important that the adherend does not undergo physical or chemical changes whilst being stored. Moisture can alter the chemistry of both the surface and substrate of the adherend, thus compromising the performance of bonded joints. It is recommended that an accurate record of the adherend (including condition and use) be maintained throughout the duration of use the material. Inventory control mechanisms employed for adhesives are also relevant to the storage and handling of adherend materials.

Quality documentation should include details on the material source, manufacturer's code number, batch or lot number, form (i.e., sheet or plate), storage conditions, surface conditions of the adherends (including corrosion products, and surface defects such as scratches present on receipt of the material), and the location of each specimen sectioned from the adherend. The inventory report should also include (where necessary) test data (i.e., strength and stiffness properties) for the adherend. Test certificates are often supplied with metallic materials, such as titanium and aluminium alloys, in which an elemental analysis is supplied along with basic tensile property data. These sheets contain information on the materials condition (e.g., descaled, and annealed titanium). FRP suppliers provide data sheets on processing conditions, fibre volume fractions and mechanical properties of their products. Often elastic and strength properties are quoted for a range of temperatures, and in some cases for hot/wet conditions (e.g., 70 °C and 85% RH) and other environments. It may be necessary to generate mechanical property data for design purposes. This data should be included in the documentation for the material. Variations in material thickness, and elastic and strength properties can be expected between batches of materials.

Handling, storage, and disposal of chemicals

In all cases involving solvents, primers, acid and alkaline solutions, extreme care and good laboratory practice should be followed at all times in storing, handling and disposing these materials (recommended further reading [20]). Personnel need to be trained in handling and using these materials, and should wear appropriate protective clothing as the chemicals can be harmful if they come contact with the skin or eyes. Ventilation and spill containment are particularly important safety considerations. Chemicals treating solutions should be prepared and stored in containers of glass, ceramic, or chemical resistant plastic. Checks should be made to ensure that the containing vessel is resistant to chemical attack from would be contents (e.g., hydrofluoric acid attacks glass). Stirring rods should be made of the same materials. Contact of the chemical solution with metals during preparation and storage should be avoided.

Continuous monitoring and quality control are required for all chemicals employed in chemical conditioning and surface treatments, and all containers with chemical agents should be clearly identified with labels. Labelling should be protected from being damaged through chemical contact or handling. Chemical solutions need to be changed regularly to prevent contamination and ensure repeatable concentration [20]. Quality assurance tests are recommended to check concentrations, and levels of contamination (e.g., opacity for checking particulate content, colour and pH for acidic and alkaline solutions).

Warning: It is important to note that many chemicals, such as acids, alkalis and solvents are toxic and present a risk to both human health and the environment, and that all safety requirements need to be met when handling, storing, and disposing of these materials.

Documentation (record keeping)

It is recommended that an accurate record of the polymeric materials be maintained, and that routine checks are made each month to ensure that the stored materials are within the time limits recommended by the adhesive manufacturer. A record should include details on the material source, manufacturer's code number, batch or lot number, form (i.e., one-or two-part, or film, etc.), shelf life, storage temperature and handling history during the shelf life (i.e., dates of use and length of time at room temperature if refrigerated). The report should include test data from acceptance tests and routine quality checks carried out to assess material performance. Material suppliers will often supply data sheets (material certification) with their materials, and these should be kept as part of the record.

It is recommended that an accurate check as to the quality of the polymeric material be carried out on receipt of the material to ensure that material meets the manufacturers specifications, ensuring the product complies with the purchase order and suppliers test reports (see [20]). The colour, viscosity, shelf life, etc. should be verified. It may be necessary to carry out acceptance tests in-house to ensure mechanical properties are in accordance with the material specification. Acceptance tests should be directed towards assuring that the materials are identical from batch to batch. Accelerated environmental tests (i.e., high temperature and humidity) may also need to be carried out to confirm that the durability performance of the material meets the manufacturer specifications. ISO, BSI, and ASTM list various test methods for quality assurance of adhesives (see Chapter 9).

Standards

ISO Standards

Plastics

Thermal degradation

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

Environmental stress cracking (ESC)

ISO 4599	Plastics: Determination of Time/Temperature Limits after Exposure to Prolonged Action of Heat Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Bent Strip Method.
ISO 4600	Plastics - Determination of Environmental Stress Cracking (ESC) - Ball and Pin.
ISO 6252	Plastics - Determination of Resistance to Environmental Stress Cracking (ESC) - Constant Tensile Stress Method.
ISO 22088	Plastics - Determination of Resistance to Environmental Stress Cracking (ESC).
ISO 16770	Plastics - Determination of Environmental Stress Cracking (ESC) of Polyethylene - Full-Notch Creep Test (FNCT).

Effects of liquids

ISO 62	Plastics - Determination of Water Absorption.
ISO 175	Plastics - Determining the Effect of Liquid Chemical Including Water

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

Weathering

ISO 877	Plastics - Determination of Resistance to Change upon Exposure under Glass to Daylight.
ISO 2579	Plastics - Instrumental Evaluation of Colour Differences.
ISO 3577	Plastics - Recommended Practice for Spectrophotometry and Calculation of Colour in CIE Systems.
ISO 3558	Plastics - Assessment of the Colour of Near-White or Near-Colourless Materials.
ISO 4582	Plastics - Determination of Changes in Colour and Variations in Properties and Exposure to Daylight under Glass, Natural Weathering or Laboratory Light Sources.
ISO 4607	Plastics - Methods of Exposure to Natural Weathering.
ISO 4892	Plastics - Methods of Exposure to Laboratory Light Sources.
ISO 9370	Guide for the Iinstrumental Determination of Radiant Exposure in Weathering Tests.
ISO TR 9673	Solar Radiation and Its Measurements for Determining Outdoor Weather Exposure Levels.
ISO 11403-3	Plastics - Acquisition and Presentation of Comparable Multipoint Data - Part 3: Environmental Influences on Properties.

Biological attack

ISO 486	Determination of Behaviour under the Action of Fungi and Bacteria - Evaluation by Visual Examination or Measurement of Change in Mass or Physical Properties.

Creep

ISO 899	Plastics - Determination of Creep Behaviour.

Rubbers

Thermal degradation

ISO 188	Accelerated Ageing or Heat Resistance Tests.

ISO 6914	Determination of Ageing Characteristics by Measurement of Stress at a Given Elongation.

Effect of liquids

ISO 1817	Determination of the Effect of Liquids.

Weathering

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

Effect of ozone

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

Biological degradation

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

Mechanical (stress relaxation in compression)

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

Composites

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

ISO 21746	Composites and Metal Assemblies - Galvanic Corrosion Tests of Carbon Fibre Reinforced Plastics (CFRPs) Related Bonded or Fastened Structures in Artificial Atmospheres - Salt Spray Tests.
ISO 22836	Fibre-Reinforced Composites - Method for Accelerated Moisture Absorption and Supersaturated Conditioning by Moisture Using Sealed Pressure Vessel.

***Note:** The standards listed in this section refer specifically to fibre-reinforced composites. More general standards covering both plastics and composites are given in the section on ISO plastic related standards.*

Adhesives

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

ASTM Standards

Plastics

Thermal degradation

ASTM D1203	Standard Test Methods for Volatile Loss From Plastics Using Activated Carbon Methods.
ASTM D2115	Standard Practice for Oven Heat Stability of Poly (Vinyl Chloride) Compositions.
ASTM D3045	Standard Practice for Heat Aging of Plastics Without Load.

Effects of liquids

ASTM D543	Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents.
ASTM D570	Standard Test Method for Water Absorption of Plastics.
ASTM D1712	Standard Practice for Resistance of Plastics to Sulfide Staining.

Environmental stress cracking (ESC)

ASTM D1693	Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics.
ASTM F1248	Standard Test Method for Determination of Environmental Stress Crack Resistance (ESCR) of Polyethylene Pipe.

Weathering

ASTM D1435	Standard Practice for Outdoor Weathering of Plastics.
ASTM D1499	Standard Practice Filtered Open-Flame Carbon-Arc Type Exposures of Plastics.
ASTM D2565	Standard Practice for Xenon Arc Exposure of Plastics Intended for Outdoor Applications.
ASTM D4329	Standard Practice for Fluorescent UV Exposure of Plastics.
ASTM D4364	Standard Practice for Performing Outdoor Accelerated Weathering Tests of Plastics Using Concentrated Sunlight.
ASTM G24	Standard Practice for Conducting Exposures to Daylight Filtered Through Glass.
ASTM G156	Standard Practice for Selecting and Characterizing Weathering Reference Materials Used to Monitor Consistency of Conditions in an Exposure Test.
ASTM G178	Standard Practice for Determining the Activation Spectrum of a Material (Wavelength Sensitivity to an Exposure Source) Using the Sharp Cut-On Filter or Spectrographic Technique.

Biological attack

ASTM G21	Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi.

Creep

ASTM D2990	Standard Test Methods for Tensile, Compressive, and Flexural Creep and Creep-Rupture of Plastics.

Rubber

Thermal degradation

ASTM D454	Standard Test Method for Rubber Deterioration by Heat and Air Pressure.
ASTM D572	Standard Test Method for Rubber—Deterioration by Heat and Oxygen.
ASTM D573	Standard Test Method for Rubber—Deterioration in an Air Oven.

ASTM D865	Standard Test Method for Rubber-Deterioration by Heating in Air (Test Tube Enclosure).

Effects of liquids

ASTM D471	Standard Test Method for Rubber Property-Effect of Liquids.
ASTM D1460	Standard Test Method for Rubber Property-Change in Length During Liquid Immersion.
ASTM D3137	Standard Test Method for Rubber Property-Hydrolytic Stability.

Weathering

ASTM D518	Standard Test Method for Rubber Deterioration Surface Cracking.

Effect of ozone

ASTM D1149	Standard Test Method for Rubber DeteriorationSurface Ozone Cracking in a Chamber.
ASTM D1171	Standard Test Method for Rubber DeteriorationSurface Ozone Cracking Outdoors or Chamber (Triangular Specimens).

Mechanical stress relaxation in compression

ASTM F38	Standard Test Methods for Creep Relaxation of a Gasket Material.

Composites

ASTM C394	Standard Test Method for Shear Fatigue of Sandwich Core Materials.
ASTM C480	Standard Test Method for Flexure Creep of Sandwich Constructions.
ASTM D3479	Standard Test Method for Tension-Tension Fatigue of Polymer Matrix Composite Materials.
ASTM D5229	Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials.
ASTM D6115	Standard Test Method for Mode I Fatigue Delamination Growth Onset of Unidirectional Fiber-Reinforced Polymer Matrix Composites.
ASTM D7792	Standard Practice for Freeze/Thaw Conditioning of Pultruded Fiber Reinforced Polymer (FRP) Composites Used in Structural Designs.

Adhesives

Thermal degradation

ASTM D1151	Standard Practice for Effect of Moisture and Temperature on Adhesive Bonds.
ASTM 4502	Standard Test Method for Heat and Moisture Resistance of Wood-Adhesive Joints.

Chemical resistance

ASTM D896	Standard Practice for Resistance of Adhesive Bonds to Chemical Reagents.

Ageing

ASTM D1183	Standard Practices for Resistance of Adhesives to Cyclic Laboratory Aging Conditions.
ASTM D2295	Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading at Elevated Temperatures (Metal-to-Metal).
ASTM D2918	Standard Test Method for Durability Assessment of Adhesive Joints Stressed in Peel.
ASTM D2919	Standard Test Method for Determining Durability of Adhesive Joints Stressed in Shear by Tension Loading.
ASTM D3434	Standard Test Method for Multiple-Cycle Accelerated Aging Test (Automatic Boil Test) for Exterior Wet Use Wood Adhesives.
ASTM D3632	Standard Test Method for Accelerated Aging of Adhesive Joints by the Oxygen-Pressure Method.
ASTM D3762	Standard Test Method for Adhesive-Bonded Surface Durability of Aluminium (Wedge Test).
ASTM D4498	Standard Test Method for Heat-Fail Temperature in Shear of Hot Melt Adhesives.

Fatigue

ASTM D3166	Standard Test Method for Fatigue Properties of Adhesives in Shear by Tension Loading (Metal/Metal).

Creep

ASTM D1780	Standard Practice for Conducting Creep Tests of Metal-to-Metal Adhesives.
ASTM D2293	Standard Test Method for Creep Properties of Adhesives in Shear by Compression Loading (Metal-to-Metal).

ASTM D2294	Standard Test Method for Creep Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal).

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