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Determining the Influence of Immersion on Polymeric Composites

Theory and Testing Standards

Royale S. Underhill
DRDC – Atlantic Research Centre

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Scientific Report
DRDC-RDDC-2016-R195
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Abstract

Fibre reinforced polymer matrix composites are used because they are lightweight, durable, corrosion-free materials. Before they can be chosen for an application, an understanding is needed of their long-term durability. This report discusses potential degradation mechanisms, how to simulate them in an accelerated timeframe and how to measure the resulting change in material properties in a laboratory setting. The goal of this overview is to educate the reader on how to evaluate, and possibly predict, the degradation of composite materials in a marine environment.

Significance for Defence and Security

Polymer matrix composites have been used for over fifty years in marine applications. They are used in everything from major structures (e.g. hulls and propellers) to smaller components (e.g. sensor windows and composite patches). With life extension projects being the norm for Naval assets, it is important to be able to measure and understand the ageing of composites in a seawater environment. This report reviews the main degradation mechanisms possible in polymer matrix composites and explores the current testing standards and equipment available to monitor the resulting changes in material properties.

Résumé

Les composites à matrice polymère renforcée de fibres sont utilisés parce que ce sont des matériaux légers, durables et anticorrosion. Avant de les choisir pour une application, il faut bien comprendre leur durabilité à long terme. Le présent rapport traite des mécanismes potentiels de dégradation, des façons de les simuler de manière accélérée et des moyens de mesurer en laboratoire les nouvelles propriétés des matériaux. Le but de ce survol est d'informer le lecteur sur la façon d'évaluer, et possiblement de prédire, la dégradation des matériaux composites en milieu marin.

Importance pour la défense et la sécurité

Les composites à matrice polymère sont utilisés depuis plus de cinquante ans dans toutes sortes d'applications navales, allant de structures majeures (les coques et les hélices, par exemple) jusqu'aux plus petits composants (fenêtres de capteur et pièces de matériau composite, par exemple). Comme les projets visant une durée de vie prolongée constituent la norme pour les ressources navales, il est important de pouvoir mesurer et comprendre le vieillissement des composites dans l'eau de mer. Le présent rapport examine les principaux mécanismes possibles de dégradation des composites à matrice polymère et explore les normes et le matériel actuellement disponibles pour suivre les changements de propriété des matériaux.

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1 Introduction

Due to an increasing interest in using fibre reinforced polymer matrix composites for the construction of marine parts, DRDC Atlantic Research Centre, Dockyard Laboratory (Atlantic) has undertaken experiments to evaluate composite degradation in seawater. This Scientific Report explores the applicable mechanisms of degradation, how to simulate them in an accelerated timeframe and how to measure the resulting change in material properties in a laboratory setting. The goal of this overview is to inform the reader on how to evaluate the degradation of composite materials in a marine environment.

Fibre reinforced polymer matrix composites have been used for over fifty years in marine applications [1], typically as fibreglass hulls. Knowledge about long-term durability has been based on empirical evidence, and large safety factors have been incorporated into designs to account for the unknown. A qualitative study of degradation and coupling it with physical models is a relatively new field of research.

In this document, “composite” is defined as an assembly of parts: reinforcing fibre, interface and polymer matrix. Examples of polymer matrix materials for marine applications are epoxy or polyester. Fibre reinforcements are typically glass, but can be carbon fibre, and occasionally aramid. Typical fibre contents are 20–40% by volume [2]. The interface consists of a coating on the fibres, called sizing. Sizing is a mixture of various chemicals used to coat (size) the fibres to make them easier to produce and process. Sizing also improves the interfacial properties between fibre surface and composite matrix. Typical constituents may include polymers, a coupling agent, a lubricant, surfactants, plasticizers, anti-static agents, adhesion promoters, anti-foaming agents and rheology modifiers. Sizing tends to be a manufacturer trade secret and little is known about it.

2 Environmental Degradation

Material ageing is a result of environmental degradation, which is a change in material properties brought on by exposure to factors such as temperature, light, moisture, chemicals or mechanical load. These changes are typically viewed as undesirable because they limit operating life.

Environmental degradation originates at the surface or edge of a specimen and progresses inwards; as such it is diffusion controlled. It can be anisotropic and both temperature and load dependent, making ageing prediction in detailed geometries difficult. There are two primary degradation mechanisms: chemical and mechanical [3]. They act at different scales and often interact. The degradation mechanisms of interest are those caused by environmental factors found within the use environment.

2.1 Chemical Degradation

Chemical ageing results in irreversible changes to the polymer matrix, such as crosslinking or chain scission. Degradation can be via thermo-oxidative, thermal, UV or hydrolytic mechanisms.

As stated previously, the most important environmental degradation factors are those that would be seen in the use environment. If the composite part in question is used on a ship's superstructure then it may be exposed to elevated temperatures, oxygen and ultraviolet radiation. These factors may lead to thermo-oxidative, thermal and UV degradation. Conversely, the exposure temperatures of marine composites immersed in the ocean are significantly lower than the glass temperature (T_g) of the composite matrix, thus thermo-oxidative and thermal degradation mechanisms tend not to be a concern. For example, typical epoxies can have a T_g in the range of 50–250°C [4], while the surface of the world's oceans range -1.7 to 32.8°C [5]. However, the near continual immersion in water makes hydrolytic degradation of major importance.

2.1.1 Glass Transition Temperature

In semi- and non-crystalline polymers the range of temperatures upon cooling, at which the polymer transitions from a rubbery to a glassy state, is the glass transition temperature (T_g). Convention defines the T_g as the mid-point in the range of temperatures. A polymer will show a dramatic change in properties at its T_g, for example when an amorphous polymer is cooled below its T_g it exhibits a sharp increase in stiffness. Conversely, this sudden change in properties can be used to determine the glass transition temperature (T_g) of a polymer. The three main techniques for measuring T_g are Differential Scanning Calorimetry (DSC), Thermal Mechanical Analysis (TMA) and Dynamic Mechanical Analysis (DMA). The T_g is specific to the type of measurement used, as well as the rate of heating (DSC, TMA and DMA) and the frequency (DMA). When comparing between DSC, DMA and TMA, the T_g can vary. For example polypropylene has a T_g reported between -15 and -3°C [6] depending on testing method and conditions. As long as the T_g is determined using the same method throughout a study, it can be used to track changes in the matrix. For example, an increase in T_g indicates a degradation mechanism resulting in crosslinking, while a decrease in T_g indicates chain scission or plasticization.

2.1.2 Diffusion

Diffusion is the net movement of molecules from an area of high concentration to one of low concentration. The motion is in response to a thermodynamic force arising from a concentration gradient. Fick's second law of diffusion (Equation 1, in one dimension) relates the rate of change of concentration at a specific point in time to the spatial variation of the concentration.

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2} \tag{1}$$

where c is concentration, t is time, x is distance and D is diffusivity. Fick's second law can be solved to give the simple diffusion equation (Equation 2).

$$\frac{M_t}{M_\infty} = 1 - \sum_0^\infty \frac{8}{(2n+1)^2\pi^2} exp\left(-\frac{D(2n+1)^2\pi^2 t}{L^2}\right) \tag{2}$$

where M_t is the percentage mass increase at time t, M_∞ is the mass increase at the end of the experiment and L is the thickness of the specimen. For the special case of dilute solutions ($\frac{M_t}{M_\infty} < 0.5$), Equation 2 simplifies to Equation 3.

$$\frac{M_t}{M_\infty} = \left(\frac{4D^{\frac{1}{2}}}{\pi^{\frac{1}{2}}}\right)\frac{t^{\frac{1}{2}}}{L} \tag{3}$$

thus a plot of $\frac{M_t}{M_\infty}$ as a function of $t^{\frac{1}{2}}$ will be a straight line if the diffusion is Fickian, where the slope gives the diffusivity. Multiple samples can be normalized by dividing the time by the thickness ($\frac{t^{\frac{1}{2}}}{L}$). If the diffusion is purely Fickian, then the data will all collapse onto the same line. When the gradient no longer exists, the plot will plateau (Figure 1).

Simple diffusion theory does not always accurately describe moisture diffusion in composites. Long term moisture absorption experiments have given anomalous results. Carter and Kibler [7] have proposed a model which links simple diffusion theory and Langmuir adsorption isotherms. This theory takes into account two types of water inside the composite: bound and unbound. Simple diffusion theory assumes there are no surfaces for adsorption, whereas Carter's model includes the ability of the water to become bound to the matrix. The mobile phase diffuses with a diffusion coefficient of D, is bound at a probability per unit time of γ, and released at a probability per unit time of β. This yields Equation 4, where $y(t)$ is Equation 2 as given by simple diffusion [7]. In the case where there is no adsorption (γ is 0 and β is 1), then Equation 4 simplifies to Equation 2.

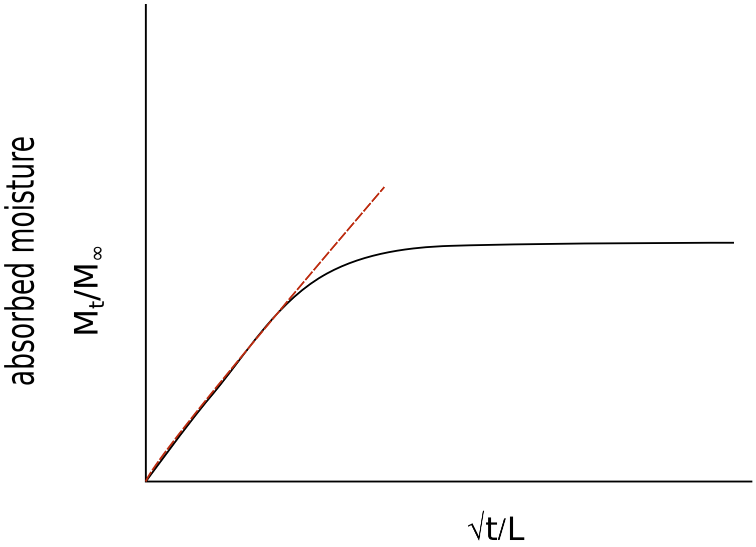

Figure 1: *Fickian style absorption curve. The red dashed line represents Fickian diffusion. The black line plateaus when the sample saturates (i.e. the gradient no longer exists).*

$$\frac{M_t}{M_\infty} \cong \left\{ \left(\frac{\beta}{\gamma+\beta}\right) e^{-\gamma t} y(t) + \left(\frac{\beta}{\gamma+\beta}\right) \left(e^{-\beta t} - e^{-\gamma t}\right) + \left(1 - e^{-\beta t}\right) \right\} \tag{4}$$

2.1.3 Hydrolytic Degradation

Once water has entered the polymer matrix of the composite, it can plasticize the polymer, or cause hydrolysis. Small molecules, such as water, can increase the plasticity or fluidity of a material. Hydrolysis refers to the reaction between the polymer and water, resulting in cleavage of the polymer chain. Cleavage can occur in the backbone or on the pendant groups. The former affects the mechanical properties of the polymer. In general hydrolysis of a molecule A-B is:

$A - B + H_2O \longrightarrow A - H + B - OH$

This can be a problem for esters, anhydride cured epoxies, amides and imides. Although hydrolysis can be reversible, it is not a symmetric reaction. This is because hydrolysis is not diffusion controlled, and can occur relatively quickly, while the opposite condensation reaction is diffusion controlled and occurs relatively slowly.

It is important to note that while small molecules can diffuse into the polymer, they can also diffuse out. These small molecules could be water, but they could also be degradation products, unreacted chemicals from the polymerization reaction, or other additives in the matrix material. If an experiment relies on weight differences (to indicate degradation), such as in Equation 2 or 4, then the mass lost through the diffusion process may obscure the absorption results.

2.2 Mechanical Degradation

Mechanical degradation most often involves wear or mechanical stresses and the degradation is generally irreversible. Mechanical degradation of wet aged composites is usually caused by plasticization, swelling, static loading, fatigue, or thermal cycling. These manifest as matrix cracking, delamination, interface degradation, fibre breaks and inelastic deformation.

Plasticization incorporates all the processes that result in a decrease in the T_g. Typically plasticizers are small molecules that, when added to a polymer, increase the segmental mobility of the chains, giving the material increased flexibility. Industrial polymers have plasticizers added intentionally to change their mechanical properties, but on occasion plasticization will occur unintentionally when small molecules such as water diffuse into a polymer (or matrix).

When composites absorb fluid they undergo dimensional change, typically a volume expansion (i.e. swelling). The absorbed fluid is rarely uniformly distributed, which can lead to internal stresses. Swelling stresses can lead to osmotic cracking (blistering) at the surface of the composite, or micro-cracking in the fibres when deeper in the composite. Fibre micro-cracking is a result of swelling in the polymer matrix inducing a pressure on the undeformable fibre reinforcements. The micro-cracks, in turn, provide additional diffusion paths for the fluid, compounding the problem.

Marine structural composites are always under load, whether it be static (buoyancy, cargo load) or cyclic (waves, slamming, machinery vibration). The two types of load result in two types of fatigue. The first is static fatigue (creep), from resisting static loads over a long period of time. The second is dynamic or cyclic fatigue caused by varying loads. Fatigue is the accumulation of stress-induced failures that gradually increase in size until large enough to cause fracture. Cyclic fatigue tends to cause more damage.

Thermal cycling is the repeated shift of a material between two temperatures with a sufficient dwell time at either to allow thermal equilibrium to be reached. Examples of thermal cycling include diurnal cycling and seasonal cycling. Degradation due to thermal cycling is a result of the differing coefficients of thermal expansion of the matrix and fibre. Thermal cycling in a wet environment can produce transverse (through thickness) matrix cracking that initiates at the surface of the composite but progress deeply into the bulk when the transverse tensile strength is exceeded, and delamination if the shear strength is exceeded.

3 Accelerated Ageing

3.1 Theory

While long-term, real-time exposure is required to fully understand the durability of materials, accelerated ageing can be a cost-effective, timely screening tool to help in determining material suitability. Ageing methodologies are validated by comparing mechanical properties and damage mechanisms determined from accelerated ageing with those from real-time ageing. The most important requirement is that the accelerated ageing must replicate the degradation mechanisms at play in the sample during real-time ageing. There are three common ways of accelerating ageing: increasing the exposure temperature, raising stress levels or reducing sample thickness [8]. Increased temperature is the most commonly used procedure, however it is important to ensure that by elevating the temperature, degradation mechanisms additional to those found in long-term ageing are not introduced. For example, if the composite temperature is raised above the T_g, there will be increased segment mobility in the polymer chains which may influence the rate of water absorption. Likewise, increased temperature tends to result in lower activation energies for endothermic degradation reactions such as hydrolysis (see Section 2.1.3), making them more likely to occur.

If it is assumed that composites immersed in sea water will only experience physico-chemical stresses, it is possible to define the rate of ageing as an Arrhenius relationship (Equation 5) where k is the rate of the phenomenon (in this case diffusion), A and B are constants, and T is the absolute temperature.

$$k = Ae^{\frac{-B}{T}} \tag{5}$$

$$a_T \propto e^{\left(\frac{1}{T_1} - \frac{1}{T_R}\right)} \tag{6}$$

As can be seen by the Arrhenius equation, increasing the temperature results in an increase in k, the rate of diffusion. In other words, the rate of ageing is increased. As a rule-of-thumb, a ten degree increase in the temperature approximately doubles the rate.

In linear viscoelastic materials such as polymers, the effect of increased temperature on mechanical properties can be explained by the time-temperature superposition principle (TTSP) [3]. The TTSP states that the mechanical properties of a material at different temperatures are related by a simple shift on the log time scale (Figure 2). At temperatures below the matrix T_g, Equation 6 can be used to determine the shift factor (a_T), where T_R is a reference temperature (T_g is often used) and T_1 is the elevated temperature being used for accelerated ageing [3].

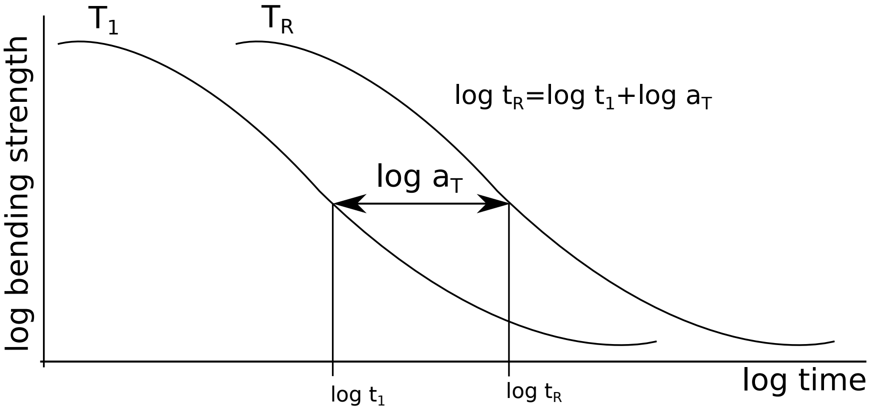

Figure 2: *Time-temperature superposition shown as a simple shift on the log time scale.* t_R *and* T_R *are the reference time and temperature;* t_1 *and* T_1 *are the starting time and elevated temperature and* a_T *is the shift time.*

3.2 Experimentation

There is a wide variety of literature that explores the ageing of composites in marine environments (for example: [2, 9, 10, 11, 12]). Most use immersion in water at varying temperatures for varying lengths of time, and rely on TTSP to extrapolate long-term exposure properties. The results are unique to the materials tested and methodologies used, and there are no testing standards such as ASTM to normalize efforts.

Some of the variables to be considered are:

- water composition (e.g. distilled water, synthetic sea water, natural sea water);
- circulating vs. still water;
- whether water is refreshed/replaced, and frequency;
- temperature profile (e.g. static vs. varying);
- moisture absorption/immersion with or without concurrent mechanical loading; and
- mechanical experiments performed while the sample is either immersed in water or in air.

4 Quantifying Ageing: Physico-chemical Testing

Changes to the chemical properties of the composites can be measured using a number of techniques.

4.1 Fourier Transform Infrared Spectroscopy

Molecules absorb specific infrared frequencies that are characteristic of their structure. Fourier transform infrared spectroscopy (FTIR) measures these absorbances to identify the chemical components of a composite. If measured over time one can track any changes in matrix chemical composition that could result from degradation such as chain scission.

4.2 Thermogravimetric Analysis

The change in mass of a specimen during immersion testing can indicate the absorption of water, or loss of material. Changes in mass can be measured using thermogravimetric analysis (TGA), where a sample is weighed as a function of temperature. The sample can be heated in an oxygen rich (air) or poor (nitrogen) environment, thereby changing how it decomposes. As well as decomposition, TGA can see the desorption of compounds such as water.

4.3 Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) is another thermoanalytical technique used to study the mechanical properties of viscoelastic materials. A sinusoidal stress is applied and the strain in the material is measured, allowing for the determination of the complex modulus. The technique can vary either the temperature of the sample or the frequency of the applied stress. The key properties which can be determined are storage modulus, loss modulus and T_g.

4.4 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) determines the difference in the amount of heat required to increase the temperature of a sample and reference material, as a function of temperature. The output from a DSC experiment is a plot of heat flux versus temperature or versus time. These data are then used to calculate enthalpies of transitions, such as T_g, melting (T_m), and crystallization (T_c) temperatures.

5 Quantifying Ageing: Mechanical Testing

There are three principal mechanical failure modes for composites: fibre failure, matrix cracking and delamination. These failure modes result in changes to the physical properties which characterize a composite, such as elastic moduli, Poisson's ratio, failure strains, shear moduli, and failure stresses. In determining the effect of ageing (both real-time and accelerated), the following characterization techniques are used and the properties followed as functions of time.

5.1 Flexural Tests

Flexural strength is a measure of the greatest stress a material experiences at the moment of rupture in a bending mode. Flexural strength is expressed as stress, σ, in units of pascal (N/m^2). Flexural (or bend) strength and stiffness are results of the combined effects of a composite's tensile, compressive and shear properties (Figure 3). To minimize the shear component, the specimen length is made long relative to its thickness. Typically ratios of 16:1 and 32:1 are used, and the specimens are straight-sided (i.e. not dogbone), with a constant cross-section. ISO 14125 (Fibre-reinforced plastic composites: Determination of flexural properties) and ASTM D 7264 (Standard Test Method for Flexural Properties of Polymer Matrix Composite Materials) are the main standards testing flexural properties, specifically written for composite materials [13, 14]. Both three-point and four-point simply supported loading configurations can be used (Figure 4). The ASTM standard interrogates long beam specimens (32:1 ratio) and is meant for quality control or material specification purposes. The ASTM procedure can be used for the evaluation of multiple environmental conditions, such as temperature or humidity effects, to determine which are design drivers and may require further testing.

Davies and Choquese [2] have shown that there is a correlation between the decrease in flexural modulus in accelerated ageing tests and real-time ageing at sea. One month of accelerated ageing corresponded to real time ageing of one year. After the one year mark, the flexural modulus in real-time ageing plateaus while after the one month mark, the accelerated ageing modulus continues to decrease. Thus using accelerated ageing for longer periods overestimates the amount of degradation.

5.2 Tensile Tests

Composite in-plane tensile tests follow standard NF T 57 101 (Methods of Testing Reinforced Plastics: Glass Reinforced Plastics – Determination Of Tensile Properties) ([15], superseded by ISO 527), ISO 527 (Determination of Tensile Properties) [16], or ISO 37 (Tensile Stress-Strain Properties of Rubber, Vulcanized or Thermoplastic) [17]. They are used to determine the Young's modulus as well as the tensile strength of the material. ASTM D3039 (Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials) can also be used [18]. It allows for building up the gauge section, presumably preventing grip failure. The specimens are straight-sided (i.e. not dogbone), with a constant cross-section. ASTM D3039 also allows for the determination of the Poisson's ratio of the composite. These test specifications are intended to yield data for use in material specification, quality assurance, and structural design.

Davies and Choqueuse [2] have shown a similar correlation for tensile modulus as that seen in the previous section on flexural modulus. That is, that accelerated ageing for periods longer than one year can overestimate the amount of degradation.

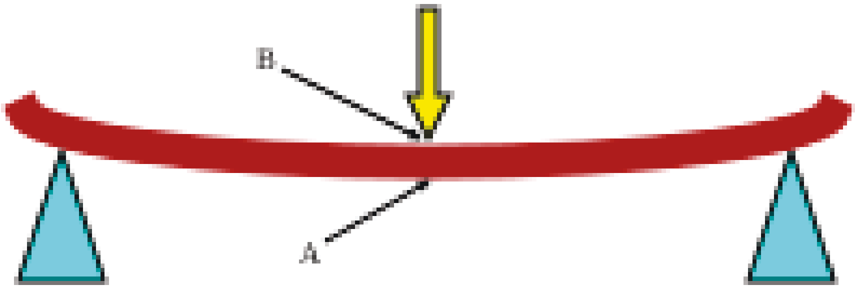

Figure 3: *Illustration of three-point load configuration showing the side under compression (B) and tension (A).*

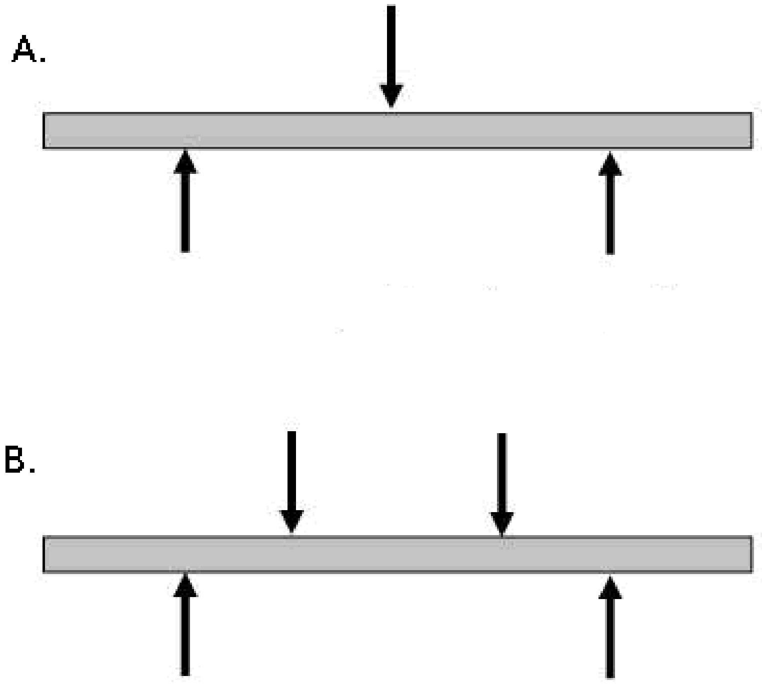

Figure 4: *Illustration of simply supported load configuration for A. three-point bend test and B. four-point bend test.*

5.3 Interlaminar Shear Strength

Interlaminar shear strength (ILSS) is a measure of the shear strength between the composite plies, and is dominated by matrix/fibre interfacial interactions. Shear strength is determined by short beam shear testing (three-point bending). Typical methods are ASTM D2344 (Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates) [18], ASTM D3846 (Standard Test Method for In-Plane Shear Strength of Reinforced Plastics) [19] or ISO 14130 (Fibre-reinforced plastic composites: Determination of apparent interlaminar shear strength by short-beam method) [20]. Since the internal stresses in the specimen are complex and include tension, compression and shear, a variety of failure modes can occur. Generally it is not possible to relate the short-beam strength to any one material property, however the test results have been found to be repeatable for specific specimen geometries, material systems, and stacking sequences. Short-beam strength determined by these test methods can be used for quality control and process specification purpose, as well as comparative, provided that failures occur consistently in the same mode.

The three-point bending set-up was shown in Figure 4A, although the specimen is shorter (span-length-to-thickness ratio of 4:1) for these tests than for the previously described flexural tests. Apparent shear strength (τ) is determined using the force at failure F in the expression:

$$\tau = \frac{3}{4}\frac{F}{BW} \tag{7}$$

where B is the width of the beam and W is the depth of the beam (i.e. thickness), and their product describes the cross-sectional area of the beam.

Figliolini [21] has shown that absorbed water reduces shear strength by affecting the bond between the fibres and the matrix. However the quality of the fibre/matrix interface is also strongly influenced by sizing [21], thus the quality of the sizing will also play a role influencing the shear strength.

5.4 Fracture Toughness

Fracture toughness is the property of a material which quantitatively describes the ability of the material resist brittle fracture once a crack has formed. Another way to think about it is that fracture toughness measures the amount of stress required to propagate a pre-existing flaw. Fracture toughness can be determined using three point bend tests on notched beam specimens according to standard test method ISO 13586 [15] or ASTM D5045 (Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials) [22]. Specimens are parallel sided, notched, with thickness W and width B (Figure 5), meeting the following constraints:

- $4W \geq B \geq 2W$
- span length = 4W
- notch length a such that $0.45 < a/B < 0.55$

It is important to note that these tests are dependent on testing speed and temperature.

5.5 Fatigue Life

Fatigue is the weakening of a material due to repeated loading and unloading and the accumulation of discrete microdamage. A composite's response to cyclic fatigue is important to evaluating a dynamically loaded structure. ASTM defines fatigue life, as the number of stress cycles until failure of a specified nature occurs [23], and is usually reported as a S-N plot (peak load as a function of number of cycles). For homogeneous materials, such as metals, the process is relatively well established. Composites are inhomogeneous and anisotropic, hence both the fibre and the matrix, as well as their lay-up affect the fatigue life. Fibres such as carbon and glass are relatively fatigue resistant as long as the matrix is not extensible and can support the fibres [24]. This is usually the case for unidirectional fibres. As the cyclic loading continues, small viscoelastic movements in the matrix allow a redistribution of stress which results in localized fibre breakage. Damage levels will accumulate until failure occurs.

The weakest point in a composite is the matrix and interface with the fibres [24]. Fatigue failure of composites is usually dominated by matrix effects (e.g. fibre/matrix debonds, matrix cracking). The plasticization of composites by absorbed water can result in further weakening the interfacial bond, reducing fatigue life.

The general procedure for fatigue testing of polymer matrix composites under cyclic loading at constant amplitude and frequency is given by ISO 13003 (Fibre-reinforced plastics: Determination of fatigue properties under cyclic loading conditions) [25]. This standard can be applied to most geometries and materials. Fatigue loading can be performed in tension, compression, flexure or shear, although the tension and flexion testing are the most popular. The mode most applicable to the end use of the composite should be chosen. A constant ratio of minimum to maximum load is applied, in excess of 10^8 cycles. Fatigue life is determined by the number of cycles survived prior to failure. Like ageing experiments, fatigue life can take a long time to conduct. It should be noted that fatigue life is extremely dependant on materials, fabrication route, specimen conditioning, and testing variables including loading rate.

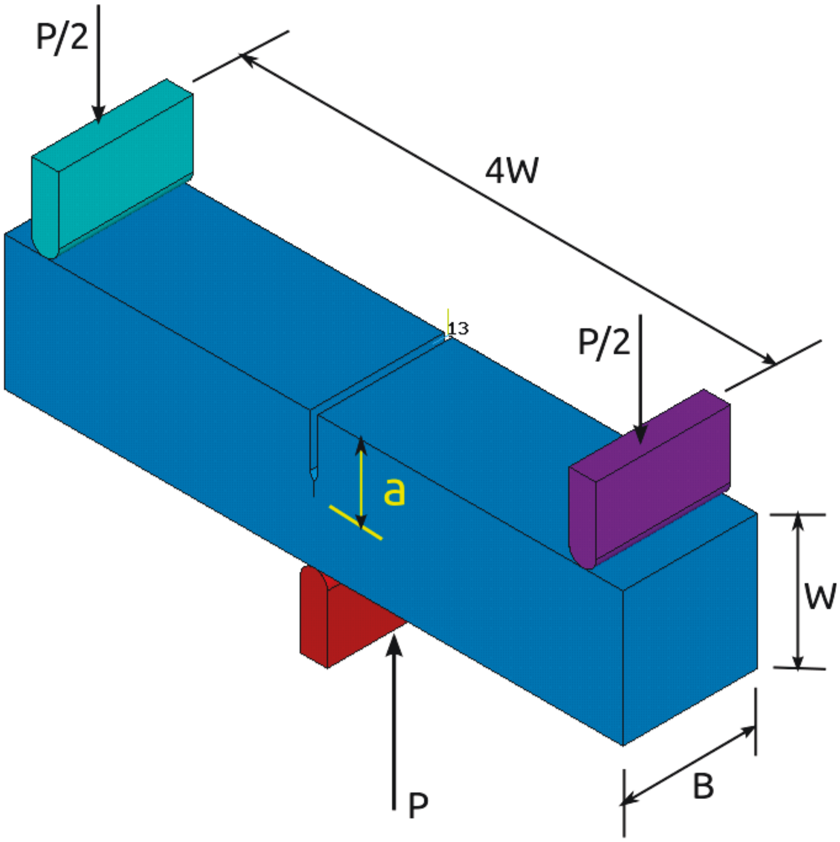

Figure 5: *Single edge notch bending specimen for fracture toughness testing.*

ASTM D3479 (Standard Test Method for Tension-Tension Fatigue of Polymer Matrix Composite Materials) is a standard which is restricted to tensile, unnotched samples only [26]. ASTM D6115 (Standard Test Method for Mode I Fatigue Delamination Growth Onset of Unidirectional Fiber-Reinforced Polymer Matrix Composites) is a standard test method to measure delamination in composites as a result of fatigue [27]. This standard applies to tension-tension fatigue loading of continuous fibre-reinforced composite materials and is limited to unidirectional carbon fibre tape laminates with single-phase polymer matrices.

In general, when performing fatigue life testing on composites, it is important to: reduce test frequencies to avoid sample heating, monitor specimen property changes, avoid buckling situations in compression, avoid fretting in flexure, and limit tensile grip pressures.

6 Fouling and Ageing

Many materials exposed to the marine environment will be affected by fouling organisms, composites are no different. Biofouling is a complex process, and the effects of fouling have not been considered in accelerated ageing methodologies reported in the literature. In order to get a true understanding of composite ageing in the natural environment, biofouling must be considered.

There are three main categories of biofouling organisms: slime, hard fouling, and soft fouling [28]. Slime causes microbiological damage. Hard fouling is caused by animals with hard, calcium carbonate shells, while soft fouling is a result of algae or animals with soft structures. As a result of the attachment of microorganisms and macrofoulants, the composite experiences physical and chemical changes. Such biofouling can result in an increased load or surface alteration of the composite.

There are a number of ways to deter marine organisms, or displace them once they have attached [29]:

- toxic formulations (e.g. cuprous oxide paints), many of which are banned or being examined for toxicity (e.g. tributyl tin)
- self-exfoliating surfaces
- low surface energy coatings (e.g. silicone, PTFE)
- pulsed high-strength electric fields
- biomimetic (low surface energy) materials (e.g. shark skin, lotus leaf)

The key component to understanding biofouling and bioadhesion is the material surface energy. Low surface energy solids are not wetted by liquids (hydrophobic), while increasing the surface energy improves its wettability (hydrophilic). The first step in biofouling is the adhesion of a biofilm to the surface. Muthukumar et al. [30] studied the fouling of composites in a marine environment and determined the main macrofoulants after one year immersion in seawater were barnacles, hydroids and bryozoans. Their work showed an initial positive correlation between surface energy and fouling load. In short terms of 2 months, hydrophobic materials are fouled less than hydrophilic ones. At the end of one year there was no difference in the fouling on substrates with different surface energy, indicating that the later fouling was governed by the initial conditioning biofilm and not the initial surface energy of the substrate [30]. The study by Muthukumar et al. [30] showed that biofouling affects both physical and mechanical properties of the composite. They observed thermogravimetric weight losses, tensile strength losses, surface energy increases, and a decrease in the hardness of the composite [30].

7 Conclusions

This report has discussed the main mechanisms behind the environmental degradation of polymer matrix composites. The theory and methodology behind accelerated ageing was also outlined. Accelerated ageing, while providing fast answers to long-term degradation, must reproduce the mechanisms present in a regular lifecycle. There are many variables to address, contributing to the inability to directly compare experiments between different labs. There is a need for a standard accelerated ageing methodology, which would allow for comparison of data across the literature.

An important component of polymer matrix composites is the interface between the fibre and the matrix. The interface can play a major role in mechanical ageing such as debonding and delamination. Sizing contributes to strengthening the interface, but due to its proprietary nature it is not well covered by the literature.

Biofouling is another mechanism by which degradation may occur. Due to the complexity of a biological system, it is very difficult to simulate biofouling at an accelerated rate. Real-time immersion studies show that biofouling degradation can be mitigated by periodic cleaning of the composite surface, although the same studies do not address whether cleaning would introduce its own defects.

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Fibre reinforced polymer matrix composites are used because they are lightweight, durable, corrosion-free materials. Before they can be chosen for an application, an understanding is needed of their long-term durability. This report discusses potential degradation mechanisms, how to simulate them in an accelerated timeframe and how to measure the resulting change in material properties in a laboratory setting. The goal of this overview is to educate the reader on how to evaluate, and possibly predict, the degradation of composite materials in a marine environment.

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