HYGROTHERMAL EFFECTS ON THE MECHANICAL BEHAVIOUR OF FIBRE-REINFORCED POLYMERIC COMPOSITES

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ABSTRACT: Extensive experimental works have been carried out to study hgyrotetal effects on the mechanical behaviour of glassy/epoxy and carbon/epoxy composites. It is established phenomenon that the moisture/thermal cycles affect certain mechanical properties, which are especially matrix-dominated. Many researchers have so far proved that the percentage of absorbed moisture present in the composites is the sole factor which is responsible for deteriorating the mechanical properties not the mechanism of absorption. The finding of our experiments show that it is the temperature which is the effective controlling factor for changing the mechanism of absorption. The present paper also investigates the effects of strain rate on the interlaminar shear strength (ILSS) of hygrothermally conditioned composite specimen.

Key Words: Hygrothermal, Fibre, Polymer, Composites, Interlaminar shear, Fickian, Non-Fickian, Residual stresses.

1. INTRODUCTION

Composites consist of two or more physically distinct different materials which are combined in a controlled way to achieve a mixture having more useful properties than any of the constituents on their own. In fibre-plastic composites, the most widely used fibre in load bearing applications is glass; for special high performance duties, carbon fibres and aromatic polyamide fibres are also used. Almost all polymers can be reinforced with fibres.

The high specific strength and specific modulus, excellent corrosion and fatigue resistance, ease of manufacture, unique flexibility to tailor the design and several other favourable attributes make composites ideally suited to numerous aerospace applications. A large number of critical structural components in aircraft, rockets, missiles, satellite launch vehicles and satellite structures are currently being manufactured with composite materials. The development of high performance thermo-setting and thermo-plastic resins as well as advanced fibres such as carbon, boron and aramid along with the commonly used glass fibres have been the primary motive in extensive use of composites in these high technology applications. Today more and more structural components are either being designed with composites or being replaced from their metallic counterparts by composites. The present scenario is such that, by the end of this century, the percentage use of composites will increase manifold.

Aircraft during their service life and many other space vehicle components during their fabrication, storage and testing may experience extreme humid and temperature conditions. Polymeric composites are susceptible to this hygrothermal environment. The present paper deals with some aspects of studies carried out by authors in this important area.
The decade of the fifties opened with an uninhibited enthusiasm for the extra-ordinary high strength and stiffness properties primarily available in single-crystal whiskers but also in continuous filament forms. While the realization of the potential of defect-free 'whiskers' in engineering composites has seeped away in the mists of technological reality, striking progress has been achieved in advanced filament reinforcement. Efficient and reliable use of such materials necessitates optimization of a laminated composite with respect to all of its directional properties. The hygroscopic nature of polymeric systems, which find widespread applications as matrices in advanced composite materials, requires that dilatation induced by the absorption of moisture be considered in the stress analysis of composite laminates. Considerable attention has recently been focused upon the reduction in both strength and constitutive properties of fibre-reinforced polymeric composites at elevated temperatures when the composite has been subjected to environments which enhance moisture diffusion. The influence of the thermal/moisture environment upon the behaviour of polymeric composites can be divided into three basic problem areas. First, the physics of moisture diffusion in an anisotropic, heterogeneous medium is not well understood. Second, the absorption of moisture has been shown to reduce the glass transition temperature of the polymer matrix and thereby diminish the matrix influenced strength properties of the components at elevated temperatures. Finally, moisture absorption of the matrix results in swelling of the composites. Since swelling of the composite lamina is restrained in the fibre direction, significant residual stresses are induced in the multi-directional laminate by moisture absorption. Thus deformation is also possible due to change of temperature and absorption of moisture. The hygrothermal deformation affects not only dimensional stability but also safety of structures. The matrix dominated properties, such as interlaminar shear strengths are to a large extent dependent on the deformation characteristics of matrix and adhesivity of matrix/fibre interface.

The presence of absorbed moisture results in a diminution of mechanical properties at elevated temperatures and fatigue life also appears to be reduced by absorbed moisture. Fatigue typically range from a 15-60% loss of interlaminar shear strength and a 0-60% loss of flexural strength for moisture content levels which would be expected to occur in service life.

It should be noted that absorbed moisture reduces the glass transition temperature of a polymeric matrix, resulting in a reduction of the composite strength properties dominated by matrix characteristics such as shear, transverse tension and longitudinal compression.

Hence it is imperative that the hygrothermally induced stresses which is developed due to moisture absorption, as well as the corresponding reduction in composite strength properties be accounted for in the design of advanced polymeric composite structures. The most important conclusion is that the hygrothermal stresses are analogous to thermal stresses; the effect is dilatational and induced stresses are self-equilibrating across the laminate thickness.

2. HYGROTHERMAL RESPONSE

Hygrothermal diffusion usually takes place in presence of thermal and moisture gradients. In many cases water absorption obeys Fick's Law, and diffusion is driven by the moisture concentration gradient between the environment and the material producing continuous absorption until saturation is reached. The atoms diffuse or migrate from the region
Fig. 1. Typical diffusion paths in permeable (Fig. A) and impermeable (Fig. B) fibre based polymer composites.

The equilibrium moisture content \( (M) \) of a composite is related exponentially to the relative humidity \( (\phi) \) term \(^{19}\), i.e.

\[
M_m = a \phi^b \text{ impermeable composite} \quad (4)
\]

\[
M'_m = A \phi^B \text{ permeable composite} \quad (5)
\]

The constants \( (a, b) \) and \( (A, B) \) are to be evaluated experimentally.

Experimental evidence indicates that for most of polymeric composite materials the hygrothermal behaviour is Fickian nature. Thus, the absorption and desorption curves when plotted (time) are always concave towards the (time) axis and asymptotically reach the equilibrium value. But, the diffusion behaviour of glass polymer does not obey the Fick's law. Non-Fickian behaviour is also a material characteristic. Deviation from Fickian's law becomes more pronounced at elevated temperatures and for materials immersed in liquids \(^{19}\).

2.1 Non-Fickian Behaviour

Fickian behaviour is observed in the rubbery state of polymers but often fails to describe the diffusion behaviour in glassy polymers. The deviation from Fickian behaviour occurs when

(i) cracks or delaminations develop
(ii) moisture diffusion takes place among the fibre-matrix interface, and
(iii) presence of voids in the matrix

The nature of diffusion behaviour whether Fickian or non-Fickian depends on the relative rates at which the polymer structure and the moisture distributions change. The relative rates of diffusion and polymer relaxation may be classified into two categories \(^{20}\). When the diffusion rates are much slower than those of relaxation, the diffusion has to be Fickian. Non-Fickian behaviour pertains to the situations when the relaxation processes progress at a rate comparable to the diffusion processes.
of higher concentration to that of lower concentration. The rate of diffusion increases rapidly with the rise of temperature. The concentration gradient of moisture is developed due to non-uniform distribution of moisture. The presence of imperfections and internal stresses also accelerates the process of diffusion.

Epoxy resin absorbs water from the atmosphere with the surface layer reaching equilibrium with the surrounding environment very quickly followed by diffusion of the water into all the material. The water absorbed is not usually in the liquid form but consists of molecules or groups of molecules linked by hydrogen bonds to the polymer. In addition, liquid water can be absorbed by capillary action along any crack which may be present or along the fibre-matrix interface.\textsuperscript{11,12,13,14}

Transport phenomena in polymers are generally explained by a number of free volume-based theories. The free volume is defined as the difference between the measured volume of a polymer and the occupied volume. The latter is the volume occupied by the actual mass of a molecule plus the volume occupied because of thermally dependent vibration. The free volume is a result of 'holes' and 'voids' caused by packing irregularity.

The basic similarity between the thermal and moisture diffusion was earlier recognised by Fick\textsuperscript{16} following the work of Fourier\textsuperscript{16}. The Fickian diffusion process is influenced mainly by two types of factors:

i) the internal (fibre volume fraction and its orientation),

ii) the external (relative humidity and temperature).

The diffusion coefficient and the equilibrium moisture content of the permeable fibre based polymer composite (Jute-epoxy), increases with fibre volume fraction, while a totally opposite trend is noticed in the case of impermeable fibre based composites (Glass-epoxy). The fibre orientation to the diffusion has an insignificant effect on the diffusion coefficient of the permeable fibre composite, while the corresponding effect is produced in the case of the impermeable fibre composite. As described by Mehta et al\textsuperscript{17}, in an impermeable fibre based polymer composite, the diffusion of the moisture takes a distorted path as characterized by the following equation,

\[
K = \frac{1}{\beta \xi}
\]  \hspace{1cm} (1)

where the magnitude of \( K \) called the 'Structure Factor', decides the dependence of the diffusion coefficient on the structure of a given composite, and \( \beta \) and \( \xi \), respectively, represent the tortuosity factor and the polymer chain immobilization factor. Thus in an impermeable fibre polymer composite, the fibre impedes the diffusion process.\textsuperscript{18} The diffusion path for both the composites is shown in Fig.1.

Any activated process can be conveniently characterised by an Arrhenius relationship. The temperature dependence of diffusion coefficients for the respective composite can be represented as,

\[
D_c = D_0 \exp \frac{-E_d}{RT} \hspace{1cm} \text{impermeable composite}
\]  \hspace{1cm} (2)

\[
D_c' = D_0' \exp \frac{-E_d}{RT} \hspace{1cm} \text{permeable composite}
\]  \hspace{1cm} (3)

where \( D_c \) and \( D_0 \) are the diffusion coefficient and the pre- exponential factor respectively, and \( E \) is the activation energy for diffusion. It is clear that the composite diffusion coefficient increases with temperature.
The experimental results \(^{21}\) show that the Fickian behaviour is observed at a low temperatures and for materials exposed to humid air. Glass fibre-epoxy (RP-10/LY-556) composites are exposed to 70°C and 95% relative humidity and it is clear from Fig. 2 that initially for a very short period of exposure time, the moisture absorption is nearly Fickian. It starts deviating from linearity with (time) axis during 2nd stage and at the latter stage (III) the absorption behaviour is totally non-Fickian. This is possibly due to the development of micro-cracks within the material, which enable the moisture to diffuse into the material rapidly. It may be noted that the time of exposure is not extended here so that the specimens absorb moisture to the maximum limit. As the time of exposure is increased, the curve tends to flatten parallel to the time-axis.

3. RESIDUAL STRESSES

Residual stresses in polymeric composites are induced during fabrication and by environmental exposure. The stresses are,

(i) curing stress (due to thermal expansion mismatch during fabrication of composite laminate), and

(ii) swelling stress (by the difference in swelling due to hygrothermal deformation).

The curing stress in certain graphite/epoxy laminates may be large to cause ply failure in the absence of applied stress or premature failure upon tensile loading and it may also cause plastic deformation in the matrix\(^{22,23,24}\).

The analysis of residual stress are formulated under the assumption of elastic behaviour\(^{25,26}\) and within the frame work of the laminated plate theory. When a homogeneous material is subjected to a stress, at temperature \(T\), and with moisture concentration \(H\), the total strain can be expressed as the sum of the mechanical (\(e^M_i\)) and non-mechanical (\(e^N_i\)) strains,

\[
e_i = e^M_i + e^N_i, \quad (i = 1, 2, 6)
\]
A slight increase in the interlaminar shear strength (ILSS) and the axial tensile strength are observed when a small amount of moisture is absorbed, which are shown in Fig. 3 and Fig. 4. This initial increase in the ILSS values could be related to the release of strains, as the swelling strains are opposite in nature to that of curing strains. This means that a certain degree of moisture pick-up can result in an essentially stress-free state in the composite. The ILSS decreases with subsequent moisture absorption when measured at room temperature. It is earlier noted that the ILSS decreases by 25% when it has absorbed a maximum amount of moisture (approximately 2%).

The shear failure mechanism may be explained by a combination of the polymer swelling and plasticization and the lowering of the glass transition temperature of the polymer as it absorbs moisture. As long as there is good bond between the fibre and the polymer, the shear strength is dominated by the plasticization of the polymer even at room temperature.

The ultimate compressive strength of the humidity-conditioned sample is greater than the ambient conditioned part as the curing shrinkage stress has been alleviated. It is suggested that absorbed moisture relieves the compressive curing shrinkage stresses on the 0° fibre but has no plasticizing action on the matrix when the laminate is tested at -40°C. Moisture entering the crack network affects the strength, stiffness and strain capability of the matrix/fibre interface of plies immediately beyond the last cracked ply and thus accelerates the matrix cracking. The material is generally affected by the debilitating cracking of the matrix and a general loss of reverse stress cycling resistance takes place. This effect explains the descent of the S-N curve when the composites are exposed to humid air.

![Graph showing the variation of inter-laminar shear strength (ILSS) with square root of exposure time of glass fibre/epoxy composite](image-url)

*Fig. 5. Variation of inter-laminar shear strength (ILSS) with square root of exposure time of glass fibre/epoxy composite*
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Fig. 5. Variation of inter - laminar shear strength (ILSS) with square root of exposure time of glass fibre/epoxy composite - 0.59
Curtis et al\textsuperscript{32} also suggest that the exposure to a hot/wet environment (75\degree C/95\% RH) has no significant effect on the room temperature static properties, but increasing the test temperature to 100\degree C reduces the static strengths by 9 to 19\%.

The strain rate effect on the hygrothermally conditioned ILSS specimens is carried out by the authors. Fig. 5 demonstrates that this mechanical degradation is less sensitive at higher strain rate for the same level of absorbed moisture. It may be attributed to the fact that this degradation due to absorbed moisture is a diffusion controlled process. The specimens are conditioned at 70\degree C and with 95\% RH and then 3-point bend test is carried out with 1 mm/min and 10 mm/min cross head speeds. This experiment makes it clear that the degradation of ILSS values by moisture is affected by the time during testing, as far the damage of polymer or polymer/fibre interface, the absorbed moisture must have to diffuse to deteriorate the same.

5. CONCLUDING REMARKS

Hygrothermal diffusion in polymeric composites is mostly Fickian type, but non-Fickian behaviour is also the common phenomenon for glassy/epoxy composites. Sometimes, temperatures may be the attributing factor to monitor the mode of absorption mechanism.

Absorbed moisture in the composites certainly deteriorates the matrix-dominated properties, but the effect is more pronounced at higher testing temperatures and at lower strain rates. It is the amount of moisture present in the composites which is the only main factor for deteriorating the mechanical properties, nor the mechanism of absorption by which it has been absorbed. The ILSS values are the worst affected property due to such absorbed moisture.

The research is being carried out in the field of fibre/polymer interface to study the effect of absorbed moisture on the adhesivity of polymer with the fibre by Scanning Electron Microscope (SEM).

The better understanding of such deterioration of mechanical properties may be made, if we can approach to the bond energies and consequently the deformation mechanism of polymer material itself. It can be reasonably assumed that the hygroscopic strains, which are developed due to absorbed moisture, may break the secondary bonds, as they are of weak type Van-der Walls bonds.

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