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The environmental response of hybrid composites

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Hybrid composite specimens containing a total of 60 or 75 vol % of unidirectional fibre were prepared from HT S-carbon fibre and E-glass fibre, HT S-carbon fibre and Kevlar 49 fibre, and E-glass fibre and Kevlar 49 fibre with a standard anhydride cured epoxide resin. The specimens were divided into four groups and subjected to the following environments: (A) room temperature and humidity; (B) soaked in water for 300 h at 95° C and then oven dried at 60° C to a constant weight; (C) thermally cycled 100 times between − 196 and 95° C; (D) cycled 35 times between − 196 and water at 95° C. The flexural properties of the samples were measured at room temperature after exposure. The modulus of the hybrid materials was not significantly affected by any of the treatments, although thermal cycling with or without water caused a large decrease in the modulus of all Kevlar fibre/resin and to a lesser extent all glass fibre specimens. The flexural strength of the unexposed carbon fibre/glass fibre and glass fibre/Kevlar fibre hybrids showed a positive deviation from the rule of mixtures behaviour at low volume loadings of the lower extension fibre. Wet thermal cycling or soaking in water caused a substantial reduction in the flexural strength of glass fibre/Kevlar fibre specimens. The interlaminar shear strength of all three fibre combinations was not affected by dry thermal cycling, but the effects of soaking in water and especially thermal cycling with water exposure were significant and irreversible.

1. Introduction

Most composite materials experience time varying internal distributions of moisture and temperature during their lifetime which can cause swelling and plasticization of the resin, distortion of laminae, deterioration of the fibre/resin bond etc. These effects, known collectively as hydrothermal degradation, may be reversible on drying out the laminate and returning it to its initial condition, or permanent. Because of the use of high performance laminates and composites, especially in aerospace, the effect of the water/temperature environment has become an important aspect of composite materials behaviour. Some of the literature is reviewed by Hancox [1] and predictive aspects of the work dealt with by Springer [2].

A hybrid composite consists of two or more dissimilar fibre types in a common resin matrix. The fibres or tows may be intimately mixed, arranged in a core/shell structure, or in the form of alternating laminae. The hybrid construction enables engineers to design a material with properties tailored to suit a specific application, often at a reduced cost. Further details of the types and performance of hybrids are given by Hancox [3]. Although this type of composite is becoming of increasing importance no studies devoted solely to its response to the hydrothermal environment appear to have been reported. In this work the behaviour of carbon fibre/glass fibre, carbon fibre/Kevlar fibre and glass fibre/Kevlar fibre composites in several different environments is described. The three types of hybrid specimen chosen represent the fibre combinations most likely to be used in practice. These would be expected to be sensitive to moisture and temperature as the coefficients of expansion of the various fibres are different and the properties of Kevlar fibres and the glass/fibre interface are sensitive to moisture.

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2. Specimens

Three hybrid systems were studied:

1. carbon fibre/glass fibre composite containing up to 36 vol % of carbon fibre,
2. carbon fibre/Kevlar fibre composite containing up to 47 vol % carbon fibre;
3. glass fibre/Kevlar fibre composite containing up to 56 vol % glass fibre.

In the first two cases the total fibre volume content was approximately 60 vol % in the third case approximately 75 vol %. In addition specimens of a single fibre type containing up to 60 vol % of carbon or Kevlar fibre and 75 vol % of glass fibre were used.

The approximately 1 mm thick unidirectional specimens were prepared from Torayca T300 carbon fibre, E-glass fibre and oven dried Kevlar 49 fibre. Tows of the appropriate fibres were mixed together in an attempt to give a random tow dispersion. The resin system comprised 100 parts by weight (pbw) of a liquid DGEBA epoxide (Ciba Geigy MY750), 87 pbw methyltetrahydrophthalic anhydride and 0.55 pbw *N* methyl imidazole. The cure was 4 h at 100° C followed by 4 h at 160° C.

3. Environments

The specimens were divided into four groups and exposed to four environments:

(A) room temperature (20 to 25° C) and humidity. This provided specimens for base measurements;

(B) soaking in water at 95° C for 300 h followed by oven drying at 60° C to a constant weight;

(C) thermally cycling 100 times between liquid nitrogen temperature and 95° C;

(D) cycling between liquid nitrogen temperature and water at 95° C, 35 times, followed by oven drying at 60° C to a constant weight.

The temperatures of cooled and heated specimens were periodically checked by thermocouples inserted into the specimens.

4. Measurements

The flexural modulus, E_f, flexural strength, σ_f, and interlaminar shear strength, τ, were measured in three-point bending at span to depth ratios of 40.1, 40:1 and 5:1, respectively. The crosshead speed was 5 mm min^{-1}. Normally the results are the mean of five determinations. All measurements were made at room temperature on specimens which after environmental exposure, and drying if required, had been left under room temperature and humidity conditions for 7 days. Flexural testing was chosen as it did not involve the waisting of specimens.

5. Results

5.1. One fibre type specimens

The mechanical properties of one fibre type specimens, in the as-received state, are listed in Table I. Also included are the scaled down results for a glass fibre composite containing 60 vol % fibre, and the flexural stresses in the Kevlar composites at strains corresponding to those for failure in carbon and in glass fibre composites. The weight gains when soaked in water for 300 h at 95° C are noted. The gain for Kevlar composites is particularly high. For hybrid materials the absorption tended to increase with the amount of the more absorbing component, though not evenly.

5.2. Analysis of data

The rule of mixtures, i.e. $X_c = X_f V_f + X_m V_m$, where X is the property, V the volume loading and

TABLE I Mechanical properties of unexposed materials

Carbon fibre composite: 60 vol %
$E_f = 89 \pm 2$ GPa
$\sigma_f = 1563 \pm 68$ MPa
$\tau = 77.5 \pm 7$ MPa
$\epsilon_{fail} = 1 \pm 0.08\%$

Glass fibre composite: 75 vol %
$E_f = 55.7 \pm 0.9$ GPa
$\sigma_f = 1866 \pm 166$ MPa
$\tau = 72.2 \pm 1.7$ MPa
$\epsilon_{fail} = 2.3 \pm 0.04\%$

Scaling to 60 vol % gives
$E_f = 44.6 \pm 0.9$ GPa
$\sigma_f = 1493 \pm 166$ MPa

The stress in the 60 vol % glass fibre composite when the carbon fibre fails is 646 MPa.

Kevlar Fibre Composite: 60 vol %
$E_f = 43.9 \pm 0.2$ GPa
$\sigma_f = 566 \pm 24$ MPa
$\tau = 54.9 \pm 2$ MPa
$\epsilon_{fail} = 2.74 \pm 0.05\%$
σ_f at 1% = 431 ± 8 MPa
σ_f at 2.3% = 545 ± 16 MPa

Weight gains after soaking for 300 h at 95° C and drying to constant weight.

Carbon fibre composite	1.2%
Glass fibre composite	1.3%
Kevlar fibre composite	7.9%

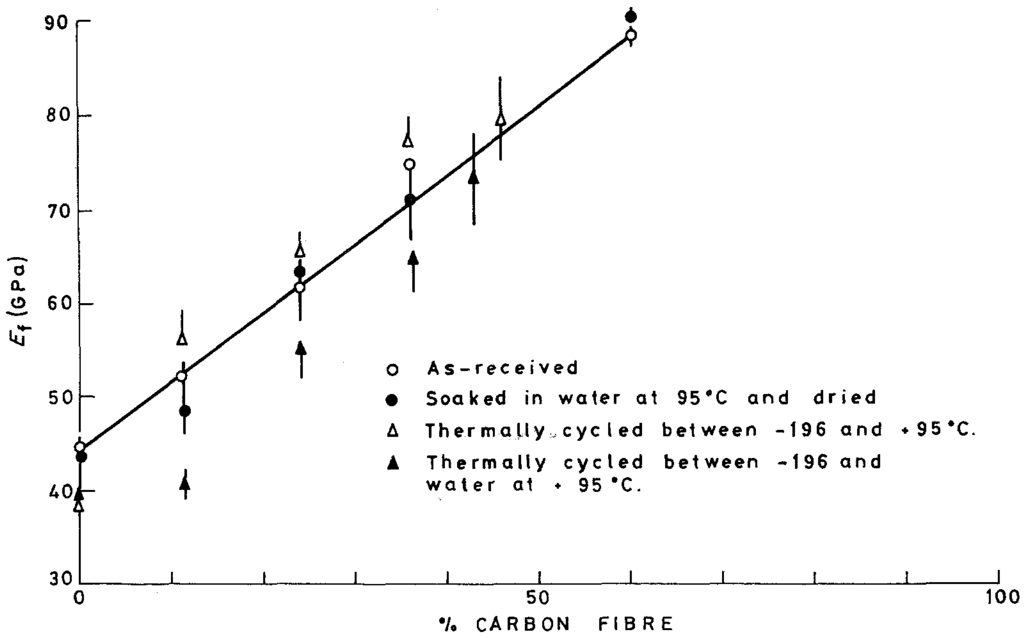

Figure 1 Flexural modulus of carbon fibre/glass fibre specimens.

c, f and m refer to composite, fibre and matrix, respectively, accounts adequately for experimental values of the flexural or tensile modulus and strength of unidirectional, continuous, fibre-reinforced resin composite. It is natural to assume that the same rule will apply to a unidirectional composite containing two or more types of continuous fibre provided that the strength contribution of the higher extension fibre is that appropriate to the breaking strain of the lower elongation component. In practice, it has been observed [3] that the stress or strain at which overall failure occurs in a hybrid composite may differ from that indicated by the modified rule of mixtures, the value often being greater. This deviation is known as the hybrid effect.

The rule of mixtures has been applied to the shear strength [4] in the form $\tau_c = X_i\tau_i + (1 - X_i)\tau_m$, where τ is the shear strength and X_i the interfacial fracture area fraction. Again it may be supposed that a similar relationship would apply to a hybrid composite. The difficulties in applying this equation to an ordinary or hybrid material lie in the complex nature of failure in the short beam shear test, and the determination of X_i and, especially, τ_i.

5.3. Carbon fibre/E-glass fibre hybrids

5.3.1. Modulus

The results for as-received material fall on a straight line given by the rule of mixtures as is shown in Fig. 1. Soaking and drying causes more scatter but no significant deviation from the straight line. Specimens subjected to temperature cycling without exposure to water tend to have rather higher moduli, while specimens which have been temperature cycled and immersed in water tend to have reduced moduli.

5.3.2. Strength

A straight line derived from the rule of mixtures (see Fig. 2) has been drawn for the as-received material and the other results are compared with this. Firstly for the as-received material there is a slight indication of a positive hybrid effect, which persists after thermal cycling, at a low volume loading of carbon fibre. The two environments involving immersion in water cause a considerable reduction in the flexural strength of all-glass fibre specimens.

In all cases specimens made solely of carbon fibres showed, after testing, compression cracking and tensile failure. The compression damage in specimens exposed to thermal cycling between liquid nitrogen temperature and water at 95° C was particularly severe. The behaviour of all-glass fibre specimens was more complex. Specimens in the as-received state were transparent and failed by tensile cracking with some associated delamination. Exposure to water made the specimens opaque

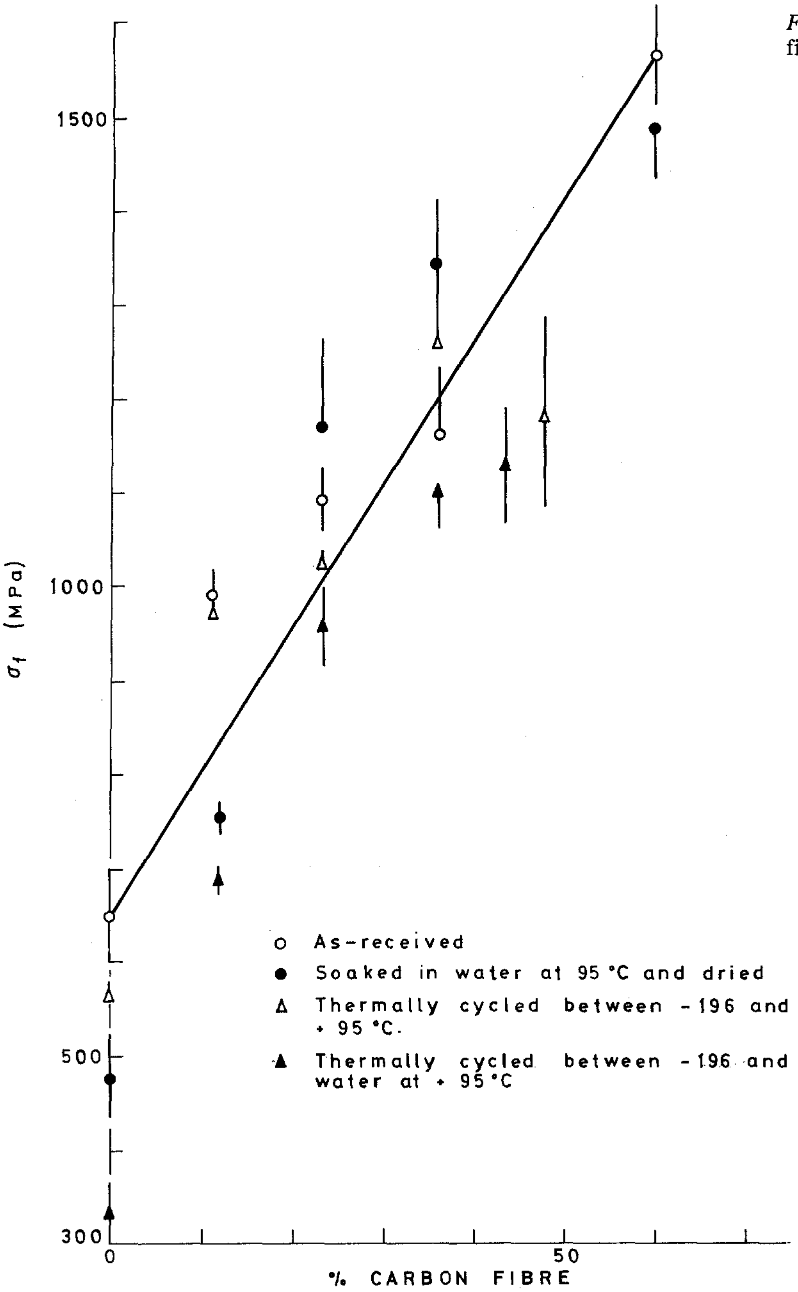

Figure 2 Flexural strength of carbon fibre/glass fibre specimens.

and the combination of thermal cycling and water exposure caused fibres to break away from the surface making it very difficult to determine the type of failure. After thermal cycling, failed specimens showed severe compression damage. Observations on hybrid specimens containing approximately equal proportions of glass and carbon fibre showed evidence of compression damage particularly in specimens exposed to liquid nitrogen and water at 95° C before testing, together with tensile failure.

5.3.3. Interlaminar shear strength

The results for as-received and thermally cycled specimens (see Fig. 3) are similar and approximately linear. The line, however, has not been drawn on the basis of the rule of mixtures. Soaking in water and drying causes a steady reduction in properties (i.e. the effect is not reversible), while thermally cycling and soaking in water leads to a marked reduction in shear strength especially for all-glass fibre composites.

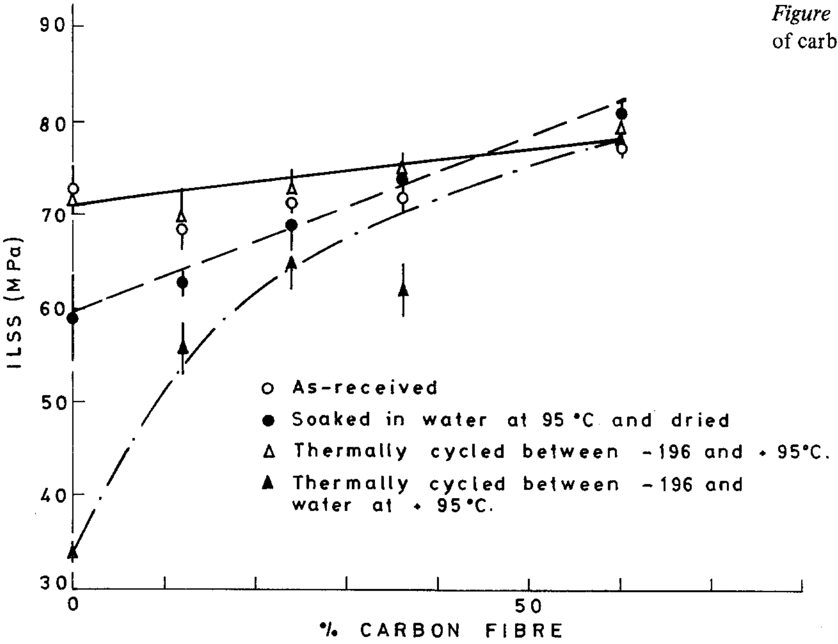

Figure 3 Interlaminar shear strength of carbon fibre/glass fibre specimens.

5.4. Carbon fibre/Kevlar fibre hybrids

5.4.1. Modulus

The results are shown in Fig. 4. With the exception of the all-Kevlar fibre specimens which have been thermally cycled the results lie about the rule of mixtures line. As with carbon fibre/glass fibre composites there is a tendency for dry thermal cycling to lead to slightly higher results.

5.4.2. Strength

There is no evidence of any hybrid effect in Fig. 5. The effect of the various environments is to increase the scatter in the results. Specimens made solely of Kevlar fibres and resin and in the as-received state or exposed to dry thermal cycling failed with minimal compression damage and a tensile fracture. Soaking specimens in water for

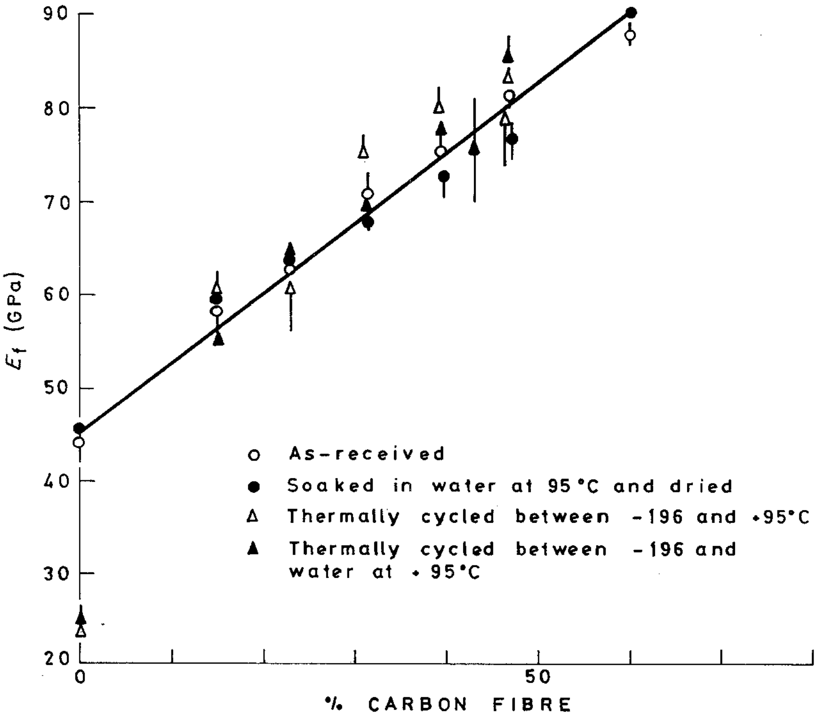

Figure 4 Flexural modulus of carbon fibre/Kevlar fibre specimens.

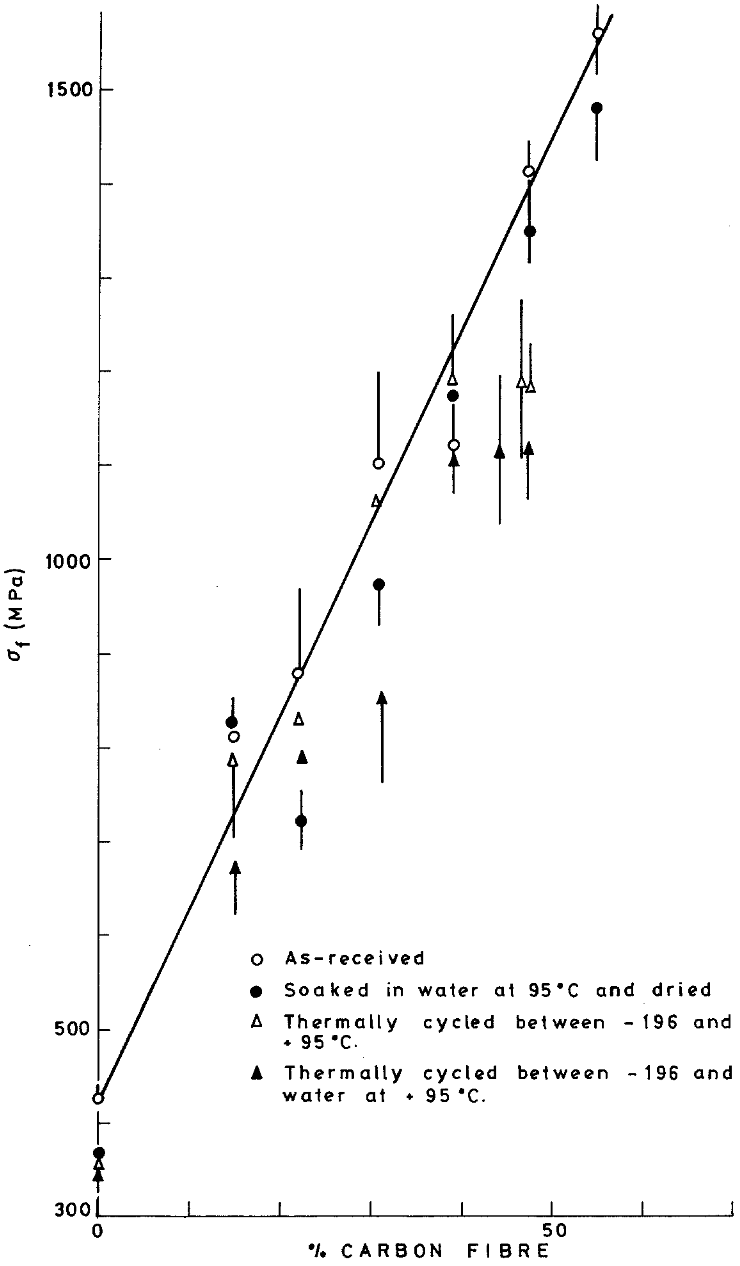

Figure 5 Flexural strength of carbon fibre/Kevlar fibre specimens.

300 h at 95° C led to a loss in colour of the specimens, the upper, compression surface, layers of tested specimens were wrinkled and compression damage extended through to the back of the specimen. After exposure to thermal cycling between liquid nitrogen and water at 95° C all-Kevlar fibre specimens appeared to flow and deform permanently under loading with little localised compression or tensile damage being visible.

5.4.3. Interlaminar shear strength

Shear strengths (Fig. 6) lie about two straight lines, one for as-received and thermally cycled specimens, the other for specimens exposed to water with or without thermal cycling. The lines have not been derived theoretically. The effect of exposure to water and drying out is not reversible.

5.5. Glass fibre/Kevlar fibre hybrids

5.5.1. Modulus

The results are shown in Fig. 7. With the exception of those for all glass and all-Kevlar fibre specimens subjected to thermal cycling with or without

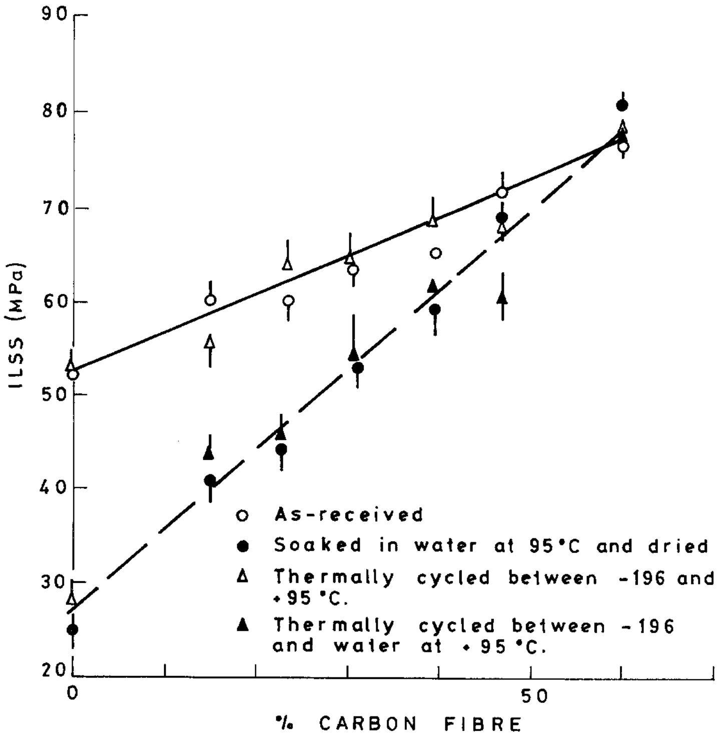

Figure 6 Interlaminar shear strength of carbon fibre/Kevlar fibre specimens.

exposure to water, the points lie approximately about the same theoretical straight line.

5.5.2. Strength

The results for the as-received material shown in Fig. 8 indicate a positive hybrid effect at the lower fibre volume loadings. Apart from all-Kevlar fibre specimens dry thermal cycling has no deleterious effects. Soaking and drying causes some degradation, but thermal cycling combined with water immersion reduces all strength values very markedly.

5.5.3. Interlaminar shear strength

The results shown in Fig. 9 fall into three distinct groups each showing a linear decrease from the all-glass fibre to the all-Kevlar fibre specimens. As-received and thermally cycled specimens have similar properties which for a given glass fibre volume fraction are greater than those for speci-

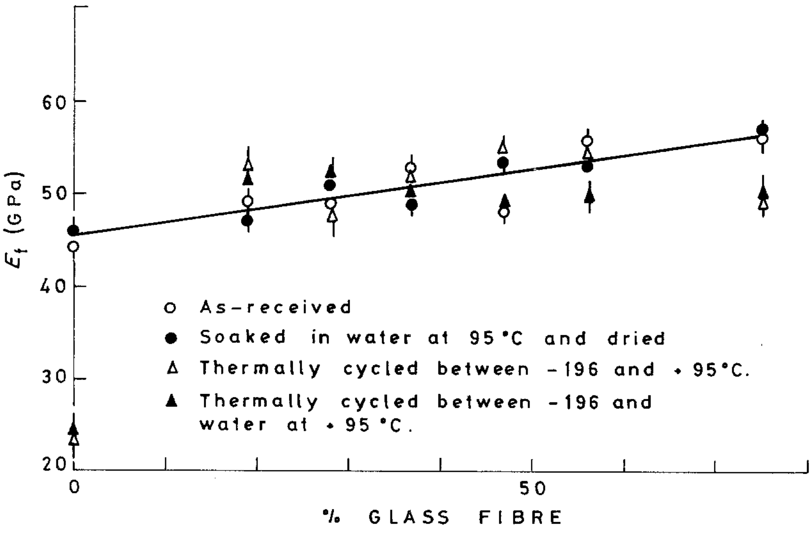

Figure 7 Flexural modulus of glass fibre/Kevlar fibre specimens.

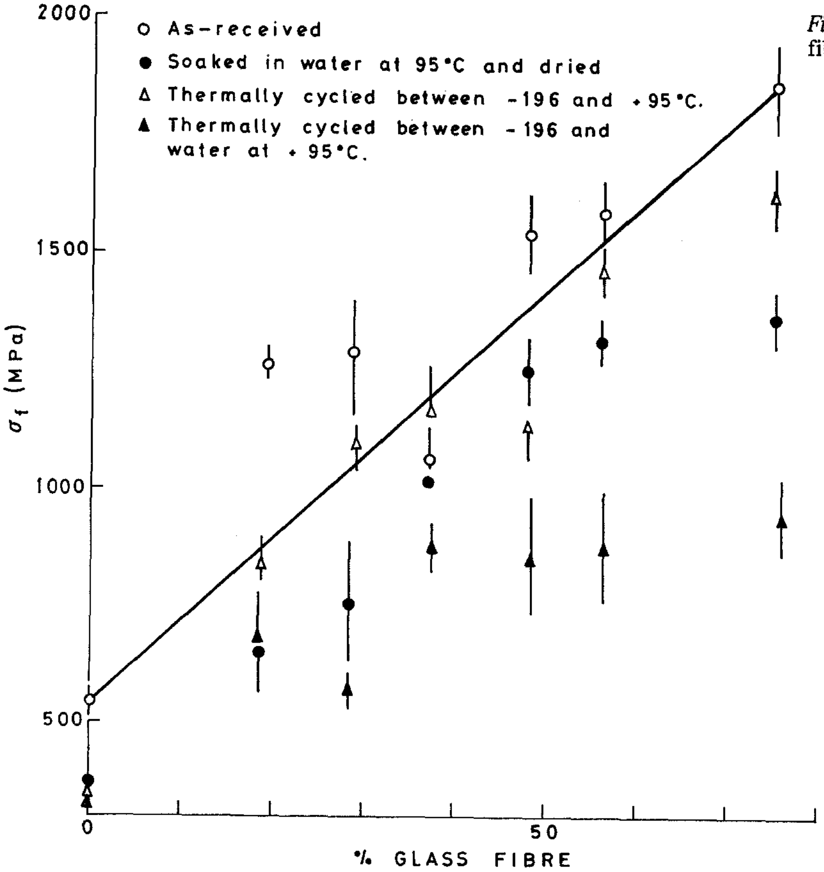

Figure 8 Flexural strength of glass fibre/Kevlar fibre specimens.

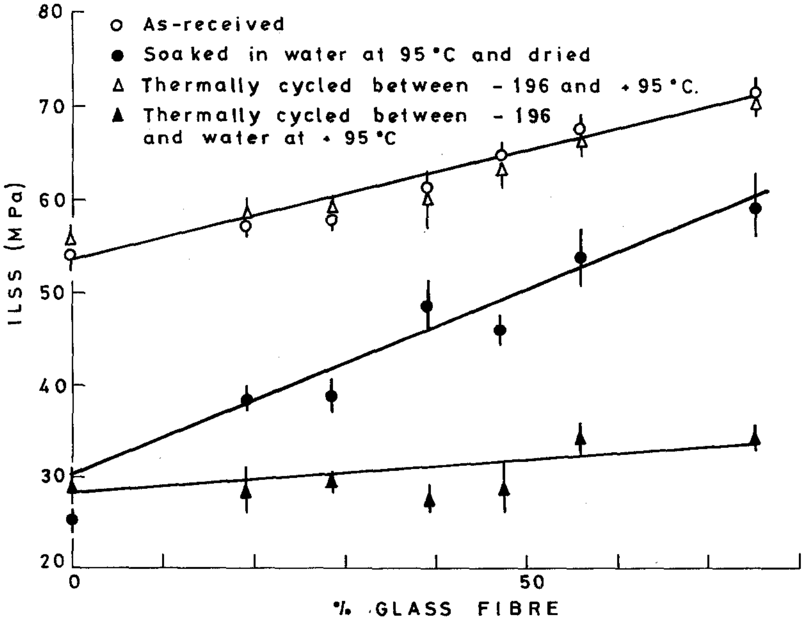

Figure 9 Interlaminar shear strength of glass fibre/Kevlar fibre specimens.

mens soaked in water or thermally cycled and immersed in water. The effects of water soaking are not reversible on drying out the specimens, while the additional effect of large temperature changes on the specimens is especially severe.

6. Discussion

6.1. Possible mechamisms

There are several mechanisms which could influence the results of this work. Firstly, significant shear deflection might occur in the beam specimens used to determine modulus and strength; secondly, because of the differing thermal expansion characteristics of the various components inbuilt thermal stresses exist and thermal cycling will magnify these; and finally, the properties of glass and Kevlar fibres and the interface involving either or both of these fibres are influenced by water.

According to Timoshenko [5] the ratio of the shear to bending deflection in a simple beam loaded in three-point bending is

$$\frac{3}{2}\frac{E}{G}\frac{d^2}{l^2}$$

where E and G are flexural and shear moduli, respectively, d is the depth of the beam and l the span. Evaluating this for all-carbon, all-glass and all-Kevlar fibre composites, taking $d = 1$ mm and $l = 40$ mm, $G = 4.5$ GPa for as-received material and assuming G is proportional to the interlaminar shear strength for exposed specimens, it is found that the maximum ratio of shear to bending deflection is about 2%. Values for hybrids, with intermediate flexural and shear moduli, are less than 2%. The shear, τ, and flexural, σ, stresses in a beam loaded in three-point bending are $\tau = 3W/4bd$ and $\sigma = 3Wl/2bd^2$ where W is the load and b the breadth of the beam. By taking the value of W when flexural failure occurs the shear stress in the beam is found to be $\tau = \sigma d/2l$. The maximum shear stresses in all-carbon, glass and Kevlar fibre composite beams at flexural failure are approximately 20, 18 and 7 MPa, respectively. Values for hybrids, in which the flexural strength is lower, are less.

Thermally induced tensile, compressive and interfacial stresses can be estimated using very simple models, (see Hancox [3, 6]). The compressive stress, σ_L, generated in the lower expansion component of a composite is given by

$$\sigma_L = \frac{-(\alpha_H - \alpha_L)\Delta T E_L V_H}{V_L(E_L/E_H - 1) + 1}$$

while the tensile stress in the higher elongation component can be obtained from

$$\sigma_L V_L + \sigma_H V_H = 0$$

The interfacial stress, τ_i, is given by

$$\tau_i = (\alpha_H - \alpha_L)\Delta T \left[\frac{G_L E_L E_C}{E_H}\,\frac{(V_H + V_L)}{V_L}\right]^{1/2} \times \frac{\sinh(\beta x)}{\cosh \beta l/2}$$

with

$$\beta^2 = \frac{4 G_L E_C}{E_L V_L^2 E_H}\left(\frac{V_H + V_L}{V_H}\right)$$

Subscripts H, L and C refer to the components with the higher and lower coefficients of thermal expansion and the overall composite material respectively, α is the coefficient of thermal expansion, V the volume fraction, ΔT the temperature differential and x the length.

It is assumed that the hybrid material is made of two composite components. For each hybrid system results have been calculated for two cases corresponding to the maximum and minimum quantities of the higher elongation component in the experimental system. The maximum tensile stress in the higher elongation composite component is about 36 MPa with the maximum compressive stress in the lower elongation component having a similar value. The maximum interfacial stress is about 15 MPa for the carbon fibre composite/glass fibre composite and glass fibre composite/Kevlar fibre composite, but rather less, ~ 8 MPa, for the carbon fibre composite/Kevlar fibre composite. In deriving these interfacial stresses the calculated values were reduced by a factor of 3 as it was noted by Hancox [6] that this was required to obtain agreement between theory and experiment for a carbon fibre composite/aluminium specimen. If this factor should not hold here the interfacial stresses might be higher. When specimens are subject to thermal cycling between liquid nitrogen and + 95° C all the stresses will be increased by a factor of about 2 because of the larger value of ΔT.

Water does not affect the properties of carbon fibre but can influence those of glass fibre [7], while Kevlar is hygroscopic. The upper temperature in dry thermal cycling was not high enough to exceed the glass transition temperature, T_g, of the matrix but this might not be so for thermal cycling in the presence of water. If the reduced T_g was exceeded in the latter case then according to

Shyprykevich and Wolter [8] the diffusion coefficient for water in the matrix would be increased. The specimens were essentially void-free but any water present would, depending on its state, freeze and thaw during wet thermal cycling. Because of its interfibrilar nature Kevlar fibre might be especially susceptible to wet thermal cycling.

6.2. Interlaminar shear strength

In the as-received state the shear strength of the carbon fibre composite was greater than that of the glass fibre composite, which in turn exceeded that of the Kevlar fibre material. Thus the steady increase in shear strength as the proportion of the higher performance composite increases is to be expected. Despite the influence of interfacial shear stresses which may be generated between hybrid, composite, components by thermal cycling (up to 30 MPa) it is seen that dry thermal cycling does not disrupt the interfacial bond. As is expected because of the known sensitivity of the glass fibre/resin interface and Kevlar fibres to moisture, a wet environment causes permanent bond disruption even after the specimens have been dried. The effect of wet thermal cycling is pronounced. The periodic interfacial thermal stresses allied to the reduced bond strength presumably cause severe, permanent, disruption especially when two moisture-sensitive components (the glass/resin interface and Kevlar fibres) are combined. It is interesting to note that carbon fibre/Kevlar fibre composites, in which the calculated thermally induced interfacial stress is less than in the other two systems, does not show any added effect when thermal cycling is combined with water exposure.

6.3. Flexural strength

The results for as-received, and, arguably, dry thermally cycled hybrid specimens correlate reasonably well with the prediction of the rule of mixtures. These two sets of results are similar in nature to the corresponding ones noted for interlaminar shear strength and it must be assumed that interfacial stresses generated by thermal cycling are insufficient to cause damage in the abscence of moisture. As-received glass fibre/Kevlar fibre and carbon fibre/glass fibre composites show a slight positive hybrid effect at the lower volume loadings of the lower elongation fibre composite although, due to the scattered nature of the results, no calculation has been made of the magnitude. Generally, flexural strength specimens (most noticeably glass fibre/Kevlar fibre ones) subjected to water exposure or water exposure and thermal cycling showed considerable compression damage on failure and sometimes surface fibre debonding. Calculations show that the maximum tensile and compressive stresses generated by thermal cycling are not significant compared with the strengths of the hybrids. It is possible that the interlaminar stress present when flexural failure occurs and the interfacial stress generated by thermal cycling can, in the presence of water, contribute to failure. Alternatively, reduced compression strength and fibre delamination may be the cause of the lower flexural strength particularly for glass fibre/Kevlar fibre materials that have been thermally cycled.

6.4. Flexural modulus

For each hybrid combination the rule of mixtures gives a reasonable representation of the variation of modulus with fibre content. The effects of soaking in water and drying out are reversible. Because of the small magnitude of the stresses and strains involved in modulus measurements the results are not expected to be very sensitive to the different environments and the stresses and damage they may produce. The shear deflection in all the specimens is negligible. The extreme sensitivity of all-Kevlar fibre specimens to thermal cycling with or without water present is the most noticeable deviation from expected behaviour. This agrees with the flexural strength and interlaminar shear strength results noted for all-Kevlar fibre composites exposed to these two environments may be related to the fibrillar structure of Kevlar fibres. Disruption of the fibre structure could be suppressed by the presence of other fibre composites.

7. Conclusions

1. Allowing for the scatter the flexural moduli of hybrid systems are not affected by any of the environments.
2. The flexural strengths of unexposed carbon fibre/glass fibre and glass fibre/Kevlar fibre hybrids show a positive hybrid effect at low volume loadings of the component with the lower extension to failure.
3. Soaking and drying and thermal cycling with exposure to water reduces the flexural strength of glass fibre/Kevlar fibre hybrids.
4. The interlaminar shear strength of all systems

is not affected by dry thermal cycling but is permanently reduced by soaking in water and drying or by wet thermal cycling.

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