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The influence of voids on the hydrothermal response of carbon fibre reinforced plastics

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Measurements are reported of the shear modulus, strength and strain at failure of carbon fibre reinforced plastics exposed to the effects of temperature and temperature plus water. Two types of specimen were employed, one with a low void content and one with a high void content. Properties were determined either at room temperature after specimens had been fully dried, or at high temperature* and in some cases at high temperature and under water. For good, low void content specimens, any effects of temperature and water were completely removed by drying. For specimens containing more than 1 vol % voids this was not so. Measurements at high temperature indicated a fall-off in stiffness and strength for either type of specimen, and for void containing specimens an increase in the strain at failure indicative of bond disruption. The added effects of water were complex.

1. Introduction

When high performance fibre reinforced plastics are required to work close to their ultimate mechanical and thermal limits the possible effects of water and temperature exposure on the material become of great importance. Furthermore despite manufacturers' efforts to reduce the void content of composites this can still be as high as 3 vol %, and so the interaction of voids with water at temperature is of considerable interest.

Before describing the experimental work it is useful to survey reported hydrothermal effects in carbon fibre epoxide resin laminates.

Judd [1] has noted that carbon fibres are not attacked by water and so any action of temperature and moisture on composites will involve the resin and interface. Browning [2] concluded that it did not matter if the weight gain of a composite was due to soaking in water or humidity cycling; for the same material the same increase in weight leads to a similar reduction in properties. The effects of water and exposure to elevated temperatures as measured by the tensile, compressive and interlaminated shear performance were found to be fully reversible on the removal of the water. Water is believed to act as a plasticizing agent disrupting hydrogen bonding. The findings on reversibility were confirmed by [1, 4].

However other studies do not support the reversible nature of the degradation. Kaelble *et al.* [5] and Kaelble and Dynes [6] found irreversible changes in interlaminar shear strength and work of fracture of composites, and microcracking associated with permanent changes in strength, failure strain and work of fracture in a pure epoxide. McKague *et al.* [7] noted that a rapid temperature excursion (thermal spike) caused a permanent increase in moisture diffusion behaviour in composites. Other workers [8–10], found that the fatigue life of composites and the incubation period during which failure was not observed in a fatigue test, were both decreased by hydrothermal exposure.

Shen and Springer [11] and Carter and Kibbler [12] concluded that water uptake or loss in a composite or resin can be accounted for mathematically by simple Fickian diffusion theory. Other studies [13–15], indicated more complex behaviour which, it has been suggested, is associated with time dependant microcracking in the matrix.

To summarize: it appears, firstly, that the effects of hydrothermal exposure on composites are

*The term "high temperature" is a relative one: in the present context it refers to a temperature approaching 100° C.

potentially damaging because of matrix microcracking and reduced fatigue life and, secondly, there is conflicting evidence for the reversibility of the effects of hydrothermal degradation on the removal of water. In addition, some of the early studies are open to the criticism that specimens were removed from the conditioning chamber prior to testing, thus allowing an uneven moisture distribution to be set up causing swelling stresses [16] which will further complicate the results.

The present work was undertaken to investigate the reversibility or otherwise of the changes in mechanical properties of carbon fibre epoxide resin composites on exposure to temperature and water, and to determine the influence of voids on this behaviour. Static torsional testing was adopted as a test method because torsional properties are particularly sensitive to the matrix and interface. Care was taken to make measurements on specimens which were under the appropriate exposure conditions during testing, in order that swelling stresses due to partial drying should be absent.

2. Specimens

Specimens, 150 mm length with the centre 100 mm turned to a diameter of 6 mm, were cut from a unidirectional plate made from HT-S pre-impregnated carbon fibre. The resin system used to prepare the pre-impregnated fibre was a liquid bisphenol A epoxide with diaminodiphenyl sulphone hardener. The cure schedule was 3 h at 150° C. To make specimens with an above average void content the following method was finally adopted. The mould was preheated to 40° C and three layers of pre-impregnated fibre sheet laid up. A small quantity of acetone (less than 0.5 ml) was sprayed on to the surface and the whole process repeated until 45 sheets of pre-impregnated fibre had been used. The mould was then closed and pressed to stops within 1 min.

Subsequent examination indicated that the fibre content for either type of specimen lay between 58 and 62 vol% fibre. The void content of the good specimens was less than 1 vol% and that of the others was 5 to 6.5 vol%. In either case the voids were distributed along the interfaces of layers of pre-impregnated fibres.

3. Environments

Apart from control specimens which were maintained and measured under room-temperature

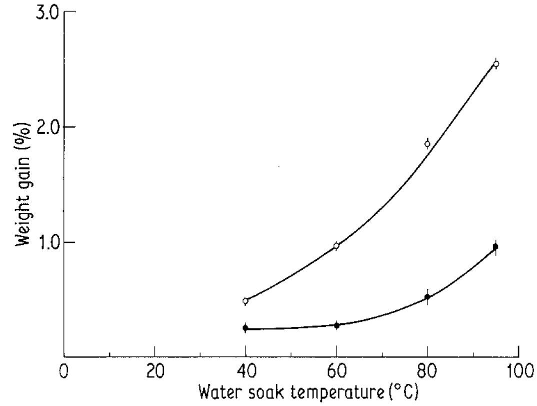

Figure 1 Weight gain as a function of water soak temperature. • good specimens and ○ void-containing specimens.

conditions, specimens were subjected to one of the following environments:

(a) Exposure to high temperature for 100 h, followed by 72 h at room temperature, before making measurements at room temperature.

(b) Exposure to water and high temperature for 100 h, followed by 168 h over silica gel at 60° C, before making measurements at room temperature.

(c) Exposure to high temperature for 100 h, with measurements made at that temperature.

(d) Exposed to water and high temperature for 100 h, with measurements made with the specimen immersed, at high temperature.

In separate experiments on pure resin samples the water uptake to equilibrium was determined and found to be 0.57% at room temperature and 2.42% at 95° C. Assuming that the resin content of composite samples is 40 vol% the water uptake figures agree well with those in Fig. 1 for good (i.e. low void content) specimens.

4. Testing

The torsional shear properties of the solid unidirectional rods were determined as described by Hancox [17]. The fibre direction was along the long axis of the torsional test machine. The modulus is based on the initial slope of the torque twist curve. The strength was determined from the load when failure occurred, as demonstrated by either a sudden drop in torque transmitted or by the angular deflection increasing at constant torque.

5. Results and discussion

The percentage weight gain as a function of

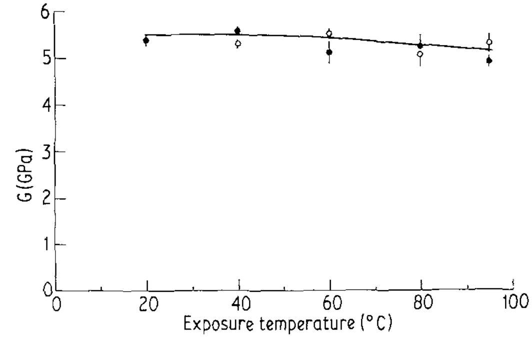

Figure 2 Shear modulus measured at room temperature. • exposed to various temperatures. ○ exposed to high temperature and water. Both were measured dry at room temperature.

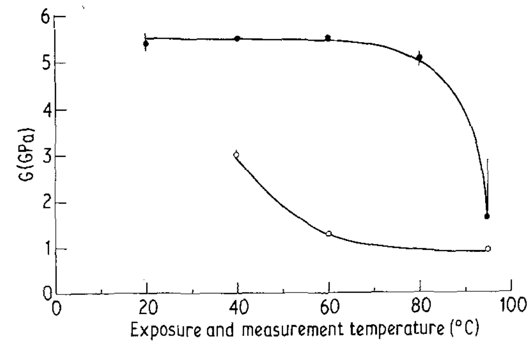

Figure 4 Shear modulus measured at various temperatures. • exposed to various temperatures for 100 h and measured at those temperatures and ○ exposed to various temperatures and water for 100 h and measured at the same temperatures.

soaking temperature for good specimens and those containing more than 1 vol% voids is shown in Fig. 1. As is to be expected, specimens containing a substantial number of voids absorb water more readily than those which do not. The ratio of water taken up by the two types of specimen varies from approximately 2 at 40° C to 2.5 at 95° C, indicating that at neither temperature are all the voids filled with water. When dried for 168 h over silica gel all specimens that had previously been saturated, showed a net loss in weight of 0.1%, or less, compared with their manufactured weight. This may have been due to leaching out of resin or the fact that all samples contained a small quantity of water when made.

The results are shown in three groups, Figs 2 to 5 show the shear modulus of good specimens and those containing more than 1 vol% voids, Figs 6 to 9 the shear strength and Figs 10 to 12 the shear deflection at failure. The temperature scale refers either to the exposure temperature, or the temperature of exposure and measurement. Measurements of the angular deflection at failure for void containing specimens at temperature or in the presence of water at temperature, indicate that in the majority of cases the failure angle was in excess of 160°. In two cases, at temperatures of 40 and 60° C the presence of water caused failure at a deflection of between 35 and 45°.

The effects of the environment on the two types of specimen are not simple though certain generalizations can be made. For good specimens:

(1) Exposure to temperature, and temperature plus water, and then making measurements on dried specimens at room temperature has no significant influence on G (shear modulus), τ (shear strength) and θ_f (angular deflection at failure) in other words the effects are reversible;

(2) Temperature alone can cause G and τ to decrease and θ_f to be more scattered though showing a tendency to increase;

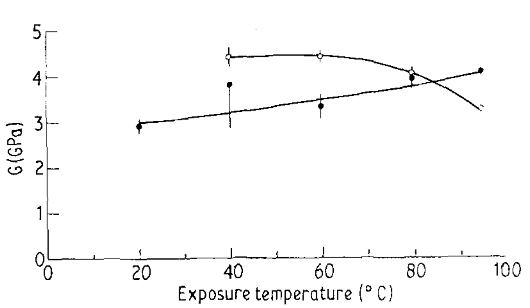

Figure 3 Void-containing specimens. Shear modulus measured at room temperature. • exposed to various temperatures and ○ exposed to various temperatures and water. Both were measured dry at room temperature.

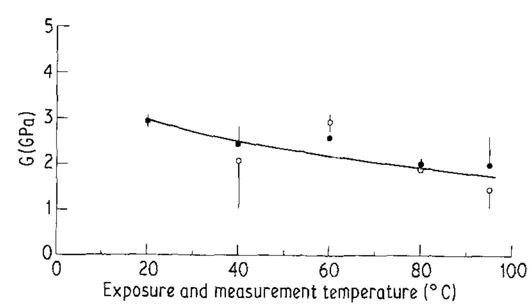

Figure 5 Void-containing specimens. Shear modulus measured at various temperatures. • exposed to various temperatures for 100 h and measured at those temperatures and ○ exposed to various temperatures and water for 100 h and measured under the same conditions.

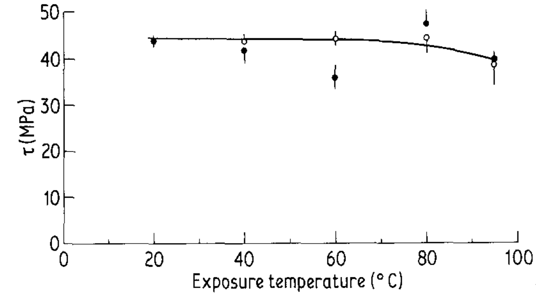

Figure 6 Shear strength measured at room temperature. • exposed to various temperatures and ○ exposed to various temperatures and water. Both were measured dry at room temperature.

(3) Temperature plus water causes a decrease in G and τ, and an erratic increase in θ_f;

(4) By inference, the effect of water as distinct from temperature on τ was minimal, but water caused a marked decrease in G and some increase in θ_f.

For specimens containing voids:

(5) Exposure to temperature or temperature and water, and then returning to room temperature for drying and measurement, has more complicated effects than for good specimens. G increased especially after exposure to water; τ was constant (i.e. the effects were reversible) and θ_f decreased with temperature of exposure, but for both τ and θ_f there was no difference between the effects of temperature and temperature plus water;

(6) Temperature or temperature and water exposure and measurement at temperature indicated some decrease in G and τ, and a change in the failure mode, θ_f being in excess of 160° in many cases. Temperature causes a large increase in θ_f more frequently than temperature and water combined.

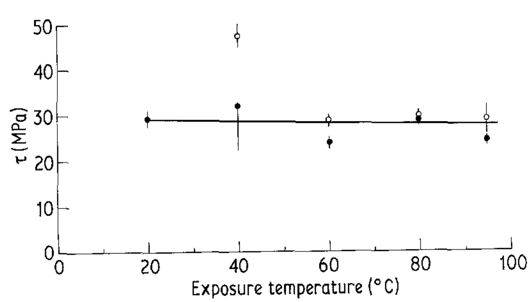

Figure 7 Void-containing specimen. Shear strength measured at room temperature. • exposed to various temperatures and ○ exposed to various temperatures and water. Both were measured dry at room temperature.

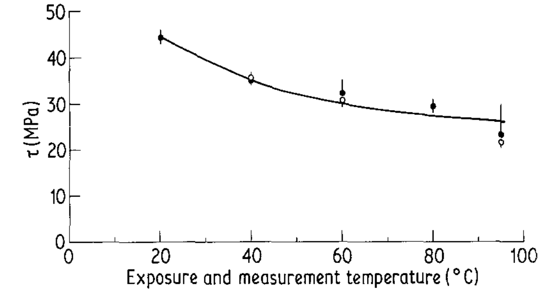

Figure 8 Shear strength measured at various temperatures. • exposed to various temperatures for 100 h and measured at those temperatures and ○ exposed to various temperatures and water for 100 h and measured under the same conditions.

Comparing good specimens and those containing more than 1 vol% voids it is found that:

(a) G and τ measured at room temperature are about 1.5 times as great for good as for specimens containing more than 1 vol% voids and that voids cause no extra scatter in the results for measurements on any specific set of specimens;

(b) For measurements at temperature, G for void-containing specimens is less sensitive to temperature and temperature and water, τ decreases in a similar manner for either good or void-containing specimens, and θ_f is much greater for the latter material.

The effects of temperature and water on the matrix will be to reduce stiffness and possibly strength and increase strain-to-failure. Additionally, there is evidence from previous studies that water probably disrupts the fibre–resin bond. The effects should be reversed when the material is returned to its pre-exposure conditions provided that the temperature has not been high enough to cause degradation of the matrix. Voids will reduce the stiffness and strength of the matrix and may interfere with bonding.

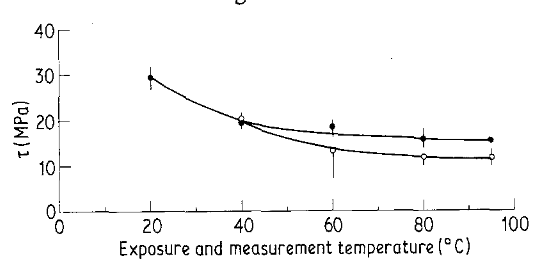

Figure 9 Void-containing specimens. Shear strength measured at temperature. • exposed to various temperatures for 100 h and measured at that temperature and ○ exposed for various temperatures and water for 100 h and measured under the same conditions.

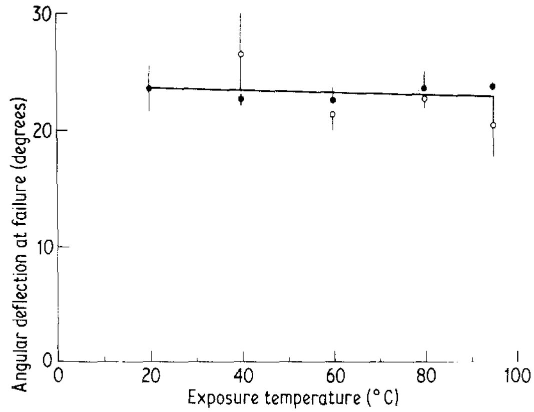

Figure 10 Angular deflection at failure measured at room temperature. • exposed to various temperatures and ○ exposed to various temperatures and water. Both measured at room temperature.

From the results for good specimens it can be seen, as expected, that exposure and return to the original conditions leaves properties unchanged. Measurements at high temperature indicate the expected fall-off in modulus and strength. As θ_f does not increase significantly until 95° C it is probable that below this temperature ultimate failure is governed by the bond strength. The influence of water is marked on stiffness but not on the other properties indicating that the fibre resin bond is not being affected.

Irrespective of the environment, the presence of excessive voids reduces the mechanical properties of a composite. Now, only the shear strength is unaffected after the specimen has been exposed and returned to its starting conditions. For measurements at high temperature on specimens containing more than 1 vol % voids water has no more influence on strength and stiffness than temperature alone. However it appears that the

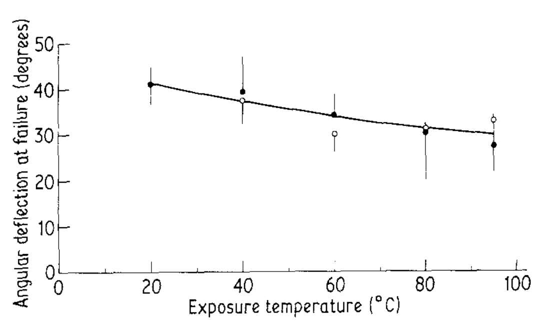

Figure 11 Void-containing specimens. Angular deflections at failure measured at room temperature. • exposed to various temperatures and ○ exposed to water and various temperatures. Both were measured at room temperature.

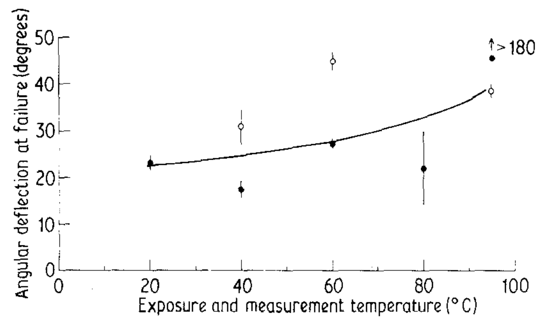

Figure 12 Angular defection at failure measured at various temperatures. • exposed to various temperatures for 100 h and measured at that temperature and ○ exposed to various temperatures and water for 100 h and measured under the same conditions.

combined effect of voids and temperature is to disrupt the bond between the fibre and matrix thus allowing the resin to behave plastically.

Although all specimens were carefully examined after exposure and several sectioned and polished no evidence was found of debonding or resin microcracking. This suggested that the reason for the reversible behaviour noted here for low void content specimens is the absence of resin microcracking. This may be because of the resin/cure schedule employed, the exposure conditions, or both.

6. Conclusion

The work shows that for good specimens with a low void content the effects of temperature and water exposure on the torsional properties are reversible provided the specimen is returned to its starting conditions. Measurements at high temperature show a fall-off in stiffness and strength with water having a severe effect on modulus but not on strength.

The torsional properties of specimens containing more than 1 vol % voids are lower than those of good ones and apart from shear strength the effects of moisture and temperature exposure are not reversed on drying out. Strength and modulus further decrease at high temperature and judging by the angle of twist at failure at temperature fibre/resin debonding occurs.

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