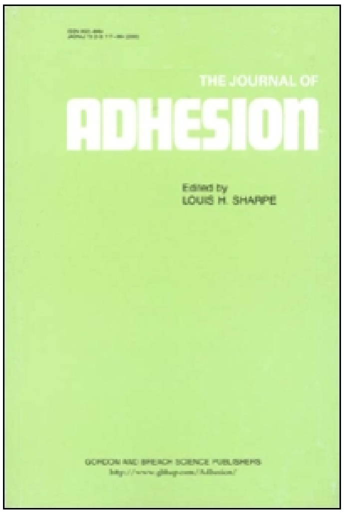

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Moisture in Epoxy Resin Composites

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The effect of external loading on the rate of water uptake by unidirectional composites is examined as a function of the loading angle (θ) with respect to the fibre direction in glass and graphite-reinforced epoxies. The moisture uptake under the effect of the external load increases with θ, suggesting a dependence on the matrix volume increase, itself a function of the strain and of the Poisson's ratio.

INTRODUCTION

Although moisture absorption and its effects on composite properties can be rigorously modeled and systematically tested, an understanding of the relationship between the diffusion coefficient and the stress field is yet unsolved.[1,2]

Water diffusion into composite materials depends on the angle between the diffusion direction and the fibres, and its rate in the direction parallel to the fibre is much higher than in the direction normal to it. The diffusion coefficient at an angle α to the fibre direction is given by[3]:

$$D_x = D_{11}\cos^2\alpha + D_{22}\sin^2\alpha \tag{1}$$

where D_{11} and D_{22} are the diffusivities parallel and normal to the fibres. D_x can also be estimated from the diffusivity of the matrix, D_r, and the volume fraction of the fibres by:

$$D_x = D_r[(1 - V_f\cos^2\alpha + (1 - 2\sqrt{V_f/\pi})\sin^2\alpha] \tag{2}$$

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Equation 2 is based on the assumption that the water molecules diffuse directly into the matrix (the diffusion into the fibres is, in most cases, insignificant), and that the diffusion, therefore, depends on the variation of the matrix cross section with α. A possible penetration by capillary flow along the fibre-matrix interface[4, 5] is disregarded.

Since the diffusion mechanism depends on the free volume within the polymer, the application of an external load is expected to affect both the rate of diffusion and its equilibrium weight gain through changing the free volume of the matrix. The change in the free volume may be determined from the Poisson ratios of the constituents and of the composite, the latter being a function of the fibre direction. Capillarity is expected to be affected by an external load through its action on the fibre-matrix interface, *e.g.*, debonding; it is thought that as the strength of the interfacial bonding is decreased, the rate of water penetration is increased.

For example, in two recent studies the penetration of water into epoxy resins[6] and into cross-ply, graphite-reinforced eopxy[1] was shown to be highly sensitive to the external load. It was found that when these materials were subjected to different stress levels, both the penetration rate and the equilibrium weight gain increased with increasing stress level.

The present work was aimed at examining the effect of external loading on water penetration into composites. This was accomplished by exposing unidirectional composites, loaded at various angles with respect to the fibre direction, to water. Both the Poisson's ratio of the composite and the stress component normal to the fibre were expected to change as a function of the loading angle, thus, having a potential effect on both diffusion and capillarity.

EXPERIMENTAL

Three types of composite materials designated A, B and C were tested: A—an angle ply $\pm 5°$ "S" glass fibre-reinforced epoxy (Scotchply XP-251S, 18 plies, 0.34 mm thick), B—a unidirectional "E" glass fibre-reinforced epoxy (Scotchply SP-315, 9 plies, 0.17 mm thick), C—a unidirectional graphite fibre-reinforced epoxy (Scotchply SP-313, 16 plies, 0.17 mm thick). The latter two composites had the same resin composition. Specimens of 0.9 cm $\times$ 12.0 cm were cut from these composites at angles, θ, of 0, 15, 30, 45, 60, 75 and 90° with respect to the fibre direction ($\theta = 90° - \alpha$). See Figure 1.

Tensile stresses were applied by means of compressed steel springs as shown in Figure 2. The strains were measured by two strain gauges mounted on each side of the specimen.

Stressed and unstressed specimens were immersed in water at 95°C and

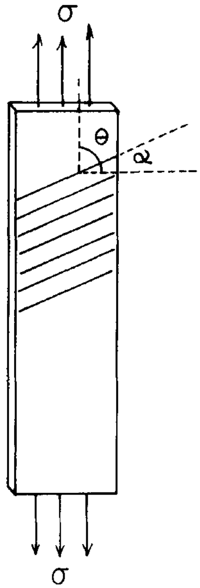

FIGURE 1 A schematic description of the test specimens.

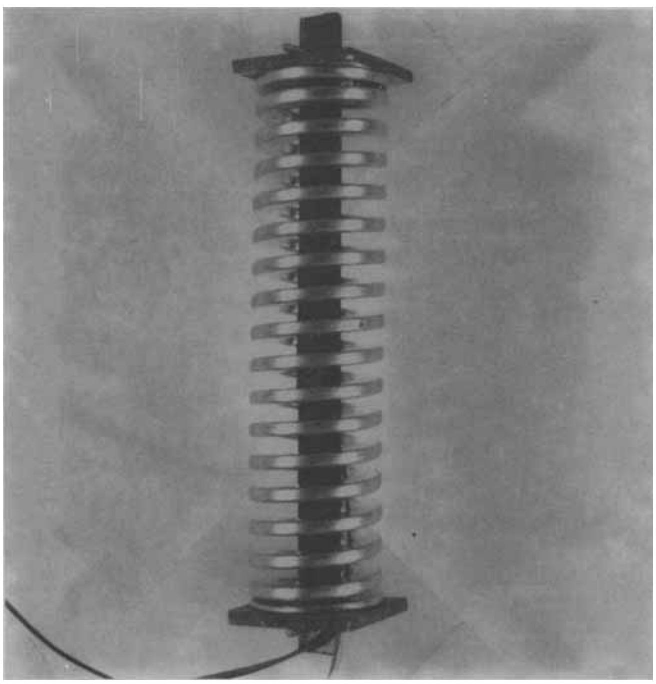

FIGURE 2 A stressed specimen of graphite-epoxy composite.

taken out periodically for recording the weight gain. The stressed specimens were weighed without the loading springs.

RESULTS AND DISCUSSION

The initial results present the effect of external loading on the water absorption behavior of material A. Figures 3–5 show the water gain response to loading at $\theta = 90°$, $\theta = 0°$ and $\theta = 45°$, respectively. While at $\theta = 90°$ the relative water content increases in an approximately linear fashion with the stress level, at $\theta = 0°$ it is stress independent, and probably inversely proportional to stress at higher levels. Loading at 45° also resulted in a positive stress effect, although smaller than that for $\theta = 90°$. Hence, the water penetration behavior clearly depends on the angle between the fibre and the loading directions.

Since the parameters which govern the volume change, *i.e.*, Poisson's ratio and the strain of the composite, vary with θ, thus affecting the diffusion, and as the normal-to-the-fibre stress component controlling capillarity also varies with θ, the question to be considered is how the external loading effect varies

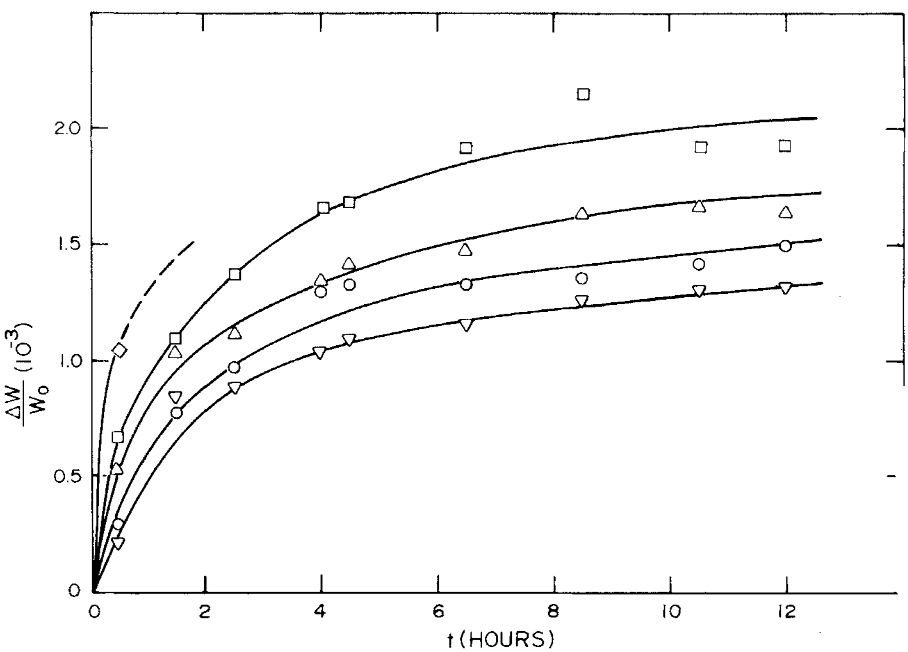

FIGURE 3 The effect of loading at $\theta = 90°$. Unstressed specimen (▽), 3.1 (○), 4.0 (△), 5.5 (□) and 7.6 MPa (◇). Composite A.

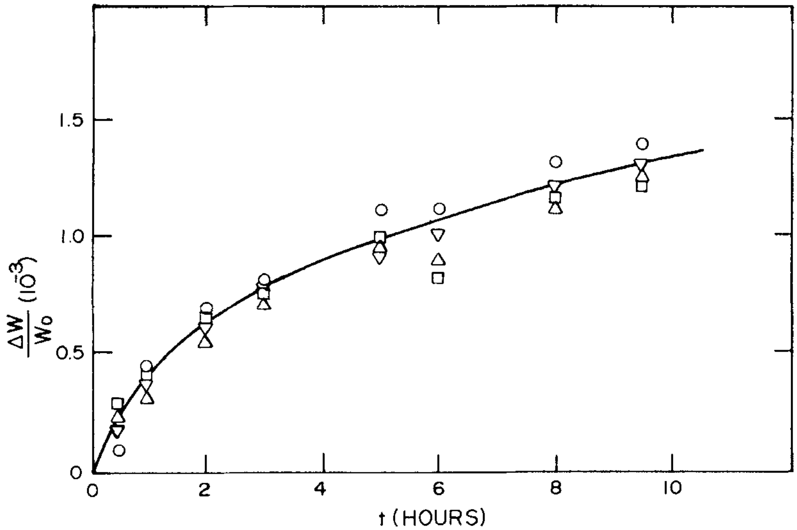

FIGURE 4 The effect of loading at $\theta = 0°$. Unstressed specimen (▽), 6.9 ( ), 11.4 (△) and 17.3 MPa (□). Composite A.

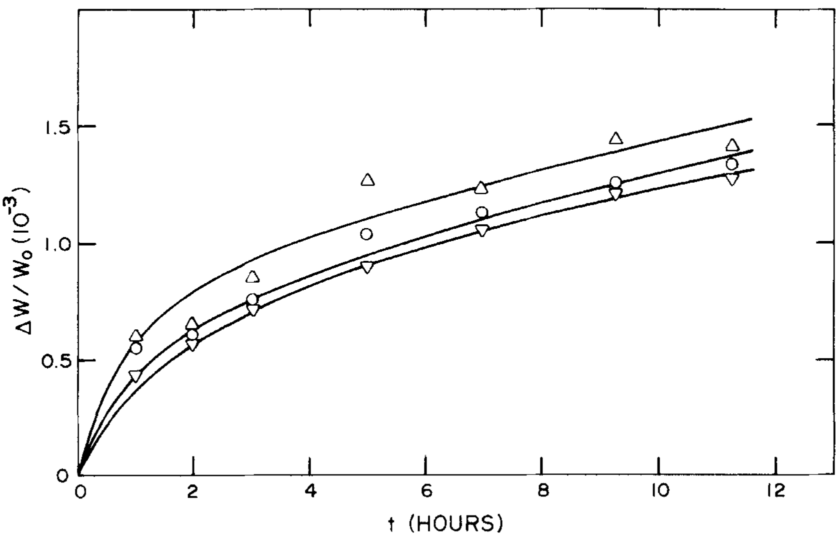

FIGURE 5 The effect of loading at $\theta = 45°$. Unstressed specimen (▽), 3.3 (○), 4.1 MPa (△). Composite A.

with θ. Also, the specimen geometry was uniform, resulting in different fibre lengths as a function of θ, which is expected to have an additional influence on capillarity.

To examine these points further, two unidirectional systems of glass fibre-reinforced epoxy (composite B) and of graphite fibre-reinforced epoxy (composite C) were investigated under constant nominal stress levels of 3.6 and 6.7 MPa, respectively, applied at different angles to the fibre direction, resulting in a variation of strain with θ as shown for composite C in Figure 6.

Figures 7 and 8 present some of the water take-up results as a function of the immersion time for composites B and C, respectively. It is seen that in both cases the rate of water uptake increases with θ, and is higher for the stressed composites; since the graphite fibre composites (C) were subjected to a greater stress, they exhibit a stronger effect.

The water uptake behavior as a function of θ is demonstrated in Figures 9 and 10 for stressed and unstressed composites of types B and C, respectively. The trend of the results depends neither on the period of immersion nor on the type of reinforcement, and except at $\theta = 0°$, it is unaffected by the stress. Since water penetration into the unstressed composites in the direction normal to the ply planes is independent of θ, the observed dependence on θ results from penetration through the narrow specimen edges parallel to the ply planes. In other words, this is an edge effect. This trend (except at $\theta = 0°$,

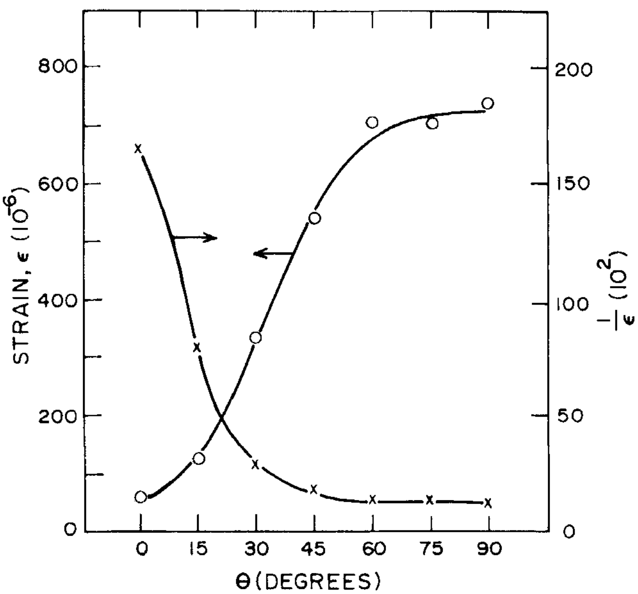

FIGURE 6 The variation of strain with θ for Composite C under a constant stress of 6.7 MPa.

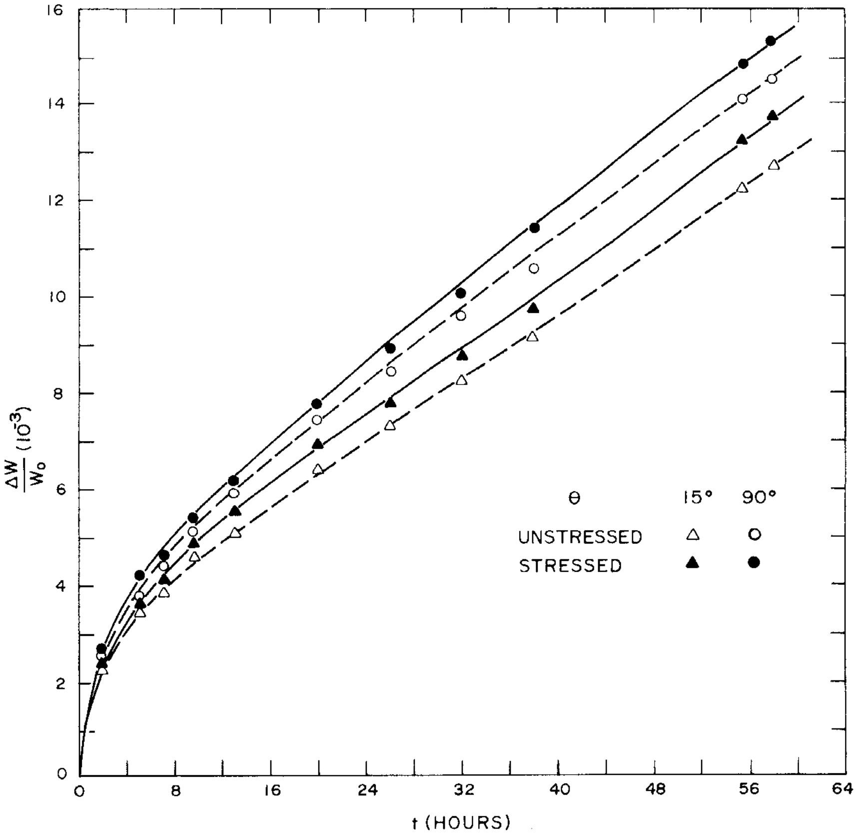

FIGURE 7 Weight gain *v*. time behavior of some type B composites, stressed (3.6 MPa) and unstressed.

where the fibres span the full specimen length) may be explained by the ideas on which Eqs. 1 and 2 are based since at any given time before equilibrium is reached, $\Delta W W_0$ is proportional to $D_x^{\frac{1}{2}}$. This implies that $\Delta W/W_0$ increases with θ because the matrix cross section (across the specimen length) available for direct water diffusion without fibre perturbation also increases with θ.

The results in Figures 9 and 10 indicate also the effect of the external loading reflected in Figure 11 by the difference between water gains of stressed and unstressed specimens of composite C.

Assuming that the diffusion is the prevailing mechanism, then the effect of external loading depends on the volume change as determined by the strain and by Poisson's ratio according to $\Delta V/V_0 = \varepsilon_x 1 - 2\gamma_{xy})$, where $\Delta V/V_0$ is the volume strain, and ε_x and v_{xy} are the strain and Poisson's ratio. Figure 6 shows that ε_x increases by a factor of 10 with θ, and $(1-2v_{xy})$ increases by a

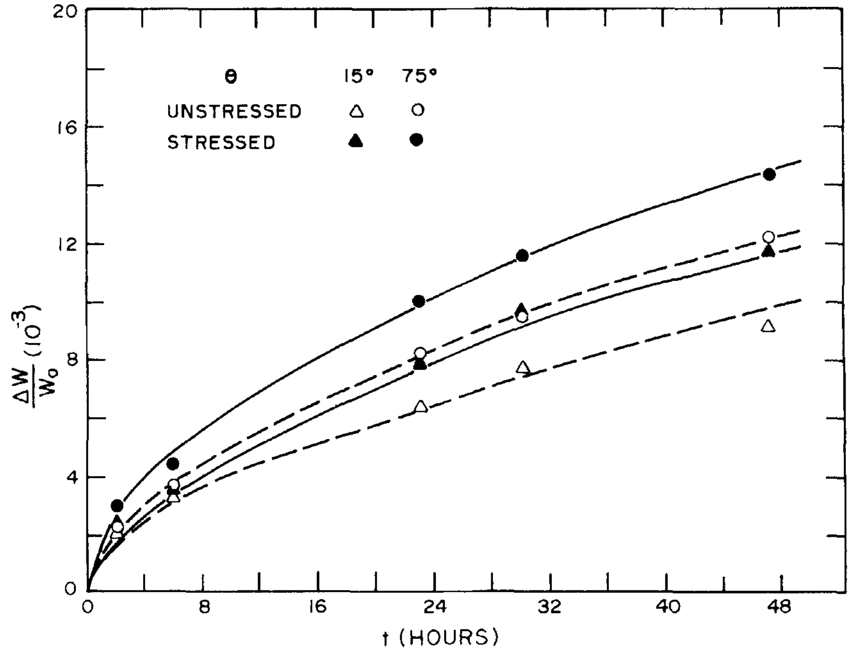

FIGURE 8 Weight gain v. time behavior of some type C composites, stressed (7.6 MPa) and unstressed.

factor of 2.[7] Hence, this should result in a marked change of $\Delta V/V_0$ of the composite with θ, accounting for the big difference between the $\theta = 0°$ and the $\theta = 90°$ results. Furthermore, at $\theta = 0°$, the fibres carry the load, and most of the volume change is confined to them with no bearing on the diffusion, while at $\theta = 90°$, more of the load is carried by the matrix, whose volume increase affects diffusion significantly.

The increase in the stress effect with θ is not monotonic but exhibits a discontinuity between $\theta = 0°$ and $\theta = 15°$. This observation is attributed to the above mentioned edge effect. If the edge effect is disregarded, and an average $\Delta W/W_0$ value is calculated for all specimens of every θ, then the increase in the stress effect will be gradual. The negative effect observed at $\theta = 0°$ is, in fact, explained by a decrease in matrix volume as shown in the Appendix. Finally, the capillary mechanism, if active, will depend on the normal-to-the-fibre stress component, and will therefore result in a $\sin^2 \theta$ dependence of the loading effect, not observed here.

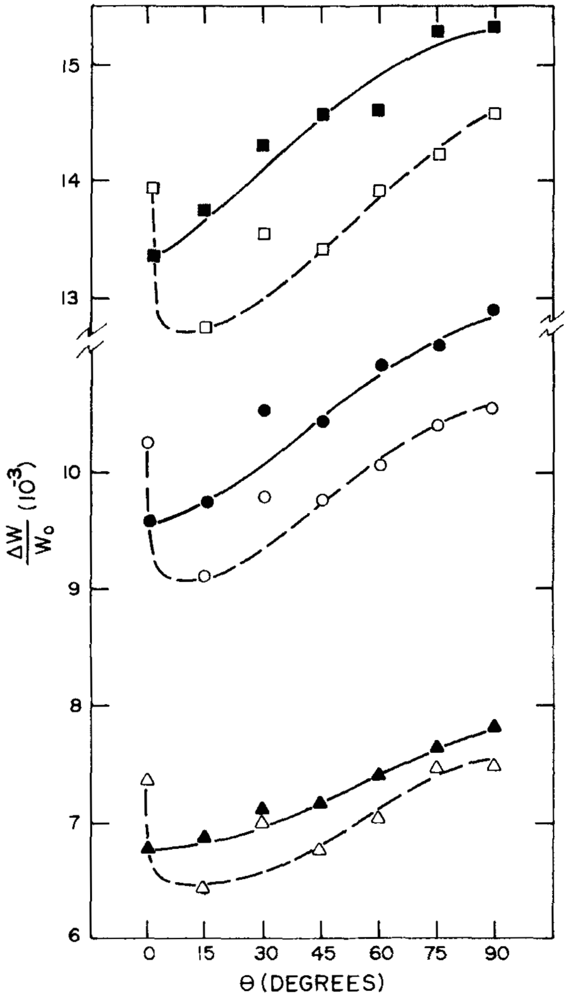

FIGURE 9 Weight gain as a function of the loading angle for type B composites stressed (black symbols) and unstressed (clear symbols) after 20 (△), 38 (○) and 58 hours (□).

CONCLUDING REMARKS

The present work shows that the penetration of water into composite materials increases as the angle between the penetration direction and the fibres decreases. It also indicates that the effect of external loading depends on the angle between the fibre and the loading directions; transverse loading results in a maximum effect. Preference is given to explaining the results assuming

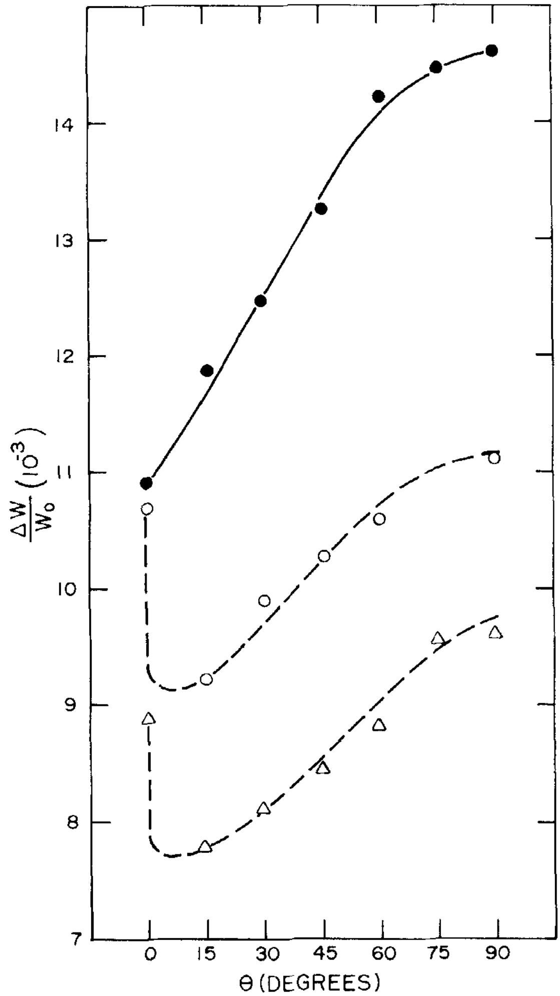

FIGURE 10 Weight gain as a function of the loading angle for type C composites (black symbols) and unstressed (clear symbols) after 30 (△) and 47 hours (○).

water penetration by direct diffusion into the resin according to Chen and Springer's[3] approach. It is thought that external loading results in higher weight gains due to a matrix volume increase (depending on θ). It is proposed that, in order to express the loading effect quantitatively, $\Delta V/V_0$ (being a function of ε_x and ν_{xy}) should be related to the diffusion coefficient D_x. An extension of the research along this line is on its way.

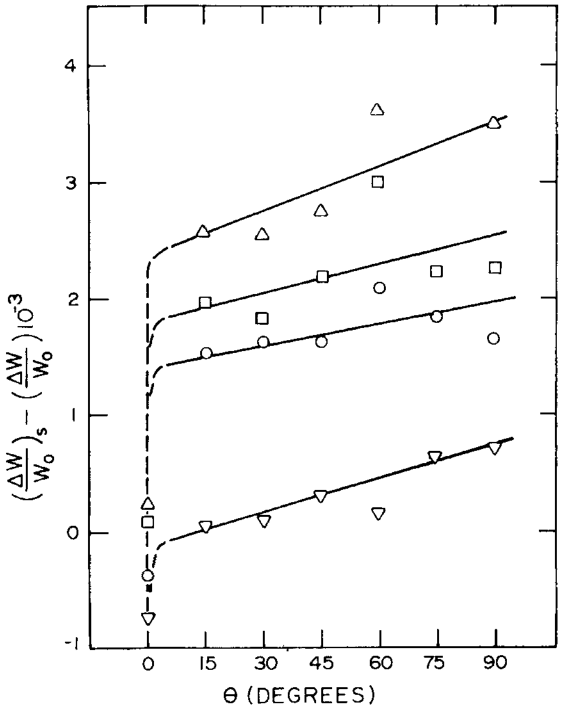

FIGURE 11 Differences between water gains of stressed and unstressed type C composite as a function of θ after 6 (▽), 23 (○), 30 (□) and 47 hours (△).

APPENDIX

The total volume strain of the composite material subjected to external stress is given by

$$(\Delta V/V_0)_c = (\Delta V/V_0)_m + (\Delta V/V_0)_f \tag{A–1}$$

where the subscripts c, m, and f denote composite, matrix, and fibre, respectively. In the longitudinal case ($\theta = 0°$) the fibre volume chance can be written as follows:

$$\left(\frac{\Delta V}{V_0}\right)_f = \frac{\sigma_f}{E_f}(1-2v_f) \approx \frac{\sigma_L}{E_L}(1-2v_f) \tag{A–2}$$

where σ is the stress and E is the modulus, and L denotes a longitudinal composite property.

Also,

$$\left(\frac{\Delta V}{V_0}\right)_c = \frac{\sigma_L}{E_L}(1-2\nu_{LT}) \tag{A-3}$$

and thus

$$(1-2\nu_{LT})-(1-2\nu_f) = \frac{E_L}{\sigma_L}\left(\frac{\Delta V}{V_0}\right)_m$$

or,

$$2(\nu_f-\nu_{LT}) = \frac{E_L}{\sigma_L}\left(\frac{\Delta V}{V_0}\right)_m \tag{A-4}$$

For a glass fibre composite of $V_f = 0.50$, $\nu_{LT} = 0.25$ and $\nu_f = 0.2$, a negative value of -0.1 results for the left hand side of Eq. (A-4). Since $E_L/\sigma_L > 0$, $(\Delta V/V_0)_m < 0$, and moreover, the higher the value of σ_L, the more negative $(\Delta V/V_0)_m$ becomes.

For a graphite fibre composite of $V_f = 0.50$, $\nu_{LT} = 0.30$ and $\nu_f = 0.30$, implying $(\Delta V/V_0)_m = 0$, which is in reasonable agreement with the weight gain observations.

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