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The effect of water on the critical stress intensity factor of unsaturated polyester resins

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The effect of water on the critical stress intensity factor, K_{IC}, of a highly unsaturated isophthalic polyester resin has been measured for periods of immersion of up to 2200 h in water at temperatures of 35, 70 and 80° C. K_{IC} decreased from 0.84 ± 0.1 MN m$^{-3/2}$ to 0.24 ± 0.03 MN m$^{-3/2}$ after immersion for 2200 h in water at 80° C. The observed changes in the critical stress intensity factor indicate that a constant value is eventually reached. This is consistent with the decline being attributable to the leaching of extractable matter from the polyester resin.

1. Introduction

The mechanical properties of glass-reinforced plastics depend not only on the nature of fibre, matrix, interface and fabrication method, but also on subsequent conditions of use. For example, glass-reinforced polyester resins are used in aqueous environments where interfacial damage [1] and matrix cracking [2, 3] can occur. This paper is concerned with the latter. Results are presented of an investigation into the effect of water immersion on the fracture toughness of an unsaturated polyester resin.

Empirical data on the fracture of polymers has been reviewed by Andrews [4] and a subsequent general theory of fracture has been presented [5]. The experimental techniques and standard tests for measuring fracture resistance in polymers have been considered by Bucknall *et al.* [6]. The majority of published data refers to uncross-linked polymers, but Selby and Miller [7] recently investigated the interpretation of experimental data obtained from tapered double cantilever beam fracture toughness tests on epoxy resins to derive a valid numerical value of fracture toughness. The effect of chemical environments on the fracture of amorphous polymers has been investigated for poly(methylmethacrylate) [8–10] and for polyester and epoxide resins [11]. The effect of temperature on environment-stress crack initiation and propagation has also been reported [8].

Internal crack initiation occurs in the absence of applied stress, in glassy polymers immersed in hot water [2, 3] and the question arises whether sustained water exposure affects the propagation energy of the cracks or eventually blunts them. To determine this, the critical stress intensity factor of single edge notched resin cast specimens was measured before and after immersion, using the analysis of Srawley and Brown [12].

2. Experimental method

A brittle polyester resin of high unsaturated: saturated acid ratio and a high heat distortion temperature, 130° C, was chosen to ensure that considerable water-induced crack initiation would occur in a reasonable time at temperatures not exceeding 80° C. The resin was formulated from 3 molar proportions of maleic anhydride, 1 of isophthalic acid, and 4 of propylene glycol. Except for viscosity, it matched the requirements of the B.P.F. resin designation RT4. Styrene content was 36% wt/wt.

Cure was effected by 2 active parts of cyclohexanone peroxide per 100 parts by weight of

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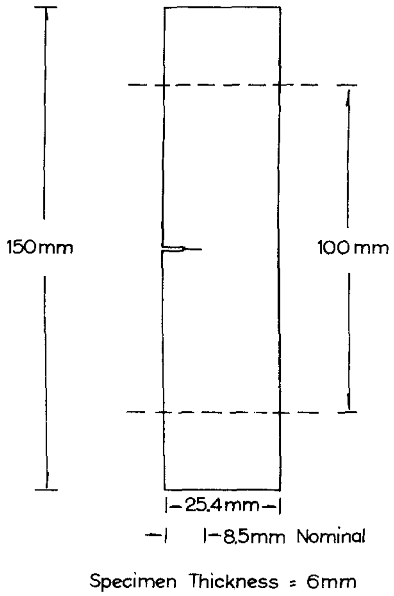

Figure 1 Fracture toughness specimen.

resin, with 0.2 parts of cobalt naphthenate. The resin was cured for 24 h at room temperature and 3 h at 80° C.

Fracture toughness specimens (see Fig. 1) were cut from resin casts with a circular saw having a silicon carbide blade. A manual notching method was used, in which the initial cuts were made with a jeweller's saw and the notch tip sharpened with a serrated razor blade. The specimens were totally immersed in water at 35, 70 and 80° C for periods up to 2200 h, and, when removed, were wiped dry and conditioned at room temperature for 20 h. The specimens were subsequently loaded to fracture in tension using an Instron 1114 test machine. Electrical strain gauge sensors were used in the measurement of Poisson's ratio for the control specimens. The fracture surfaces were examined in an optical microscope and also in a Cambridge 610 scanning electron microscope. Thin films, 0.2 mm thick, of cast resin were immersed in water under identical conditions to those of the fracture toughness specimens and the resulting changes in linear dimensions as a function of time were measured using a travelling microscope.

3. Results

The initial critical stress intensity factor, K_{IC}, was 0.84 ± 0.1 MN m^{-3} and found to be independent of initial crack length up to a value of 12 mm. The effect of water immersion on the critical stress intensity factor is shown in Fig 2. K_{IC} was

Figure 3 Fracture surface of an unexposed, notched resin cast fracture toughness specimen.

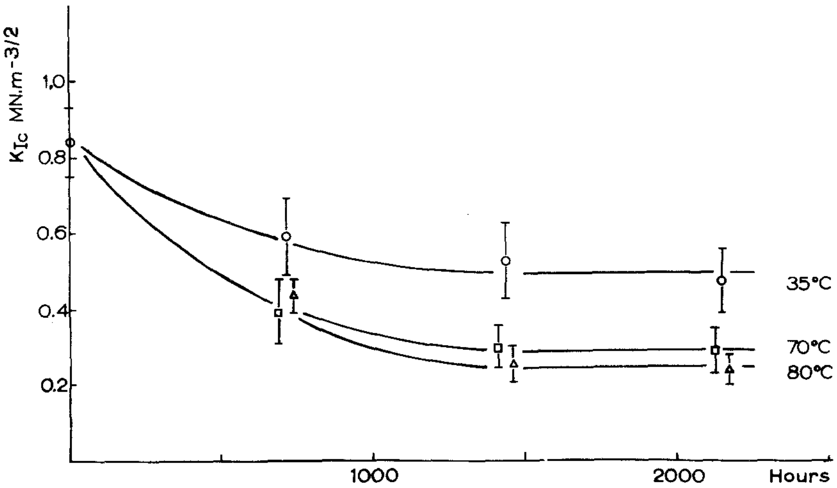

Figure 2 The effect of water temperature and exposure time on the critical stress intensity factor.

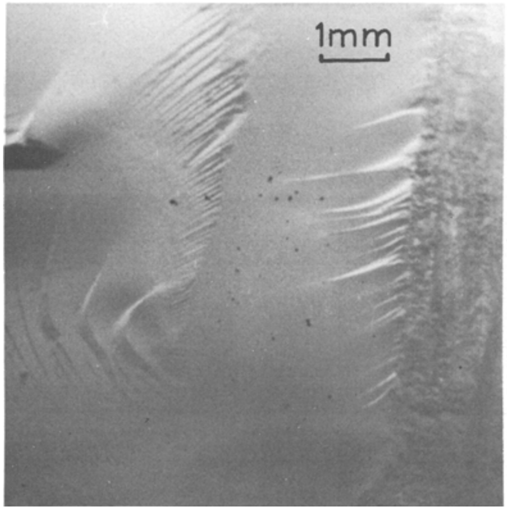

Figure 4 Fracture surface of a notched resin cast fracture toughness specimen exposed for 3 months at 70° C.

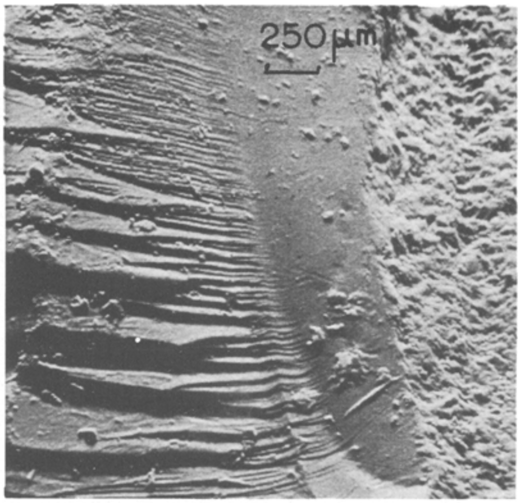

Figure 5 Fracture surface of a notched resin case fracture toughness specimen exposed for 3 months at 80° C.

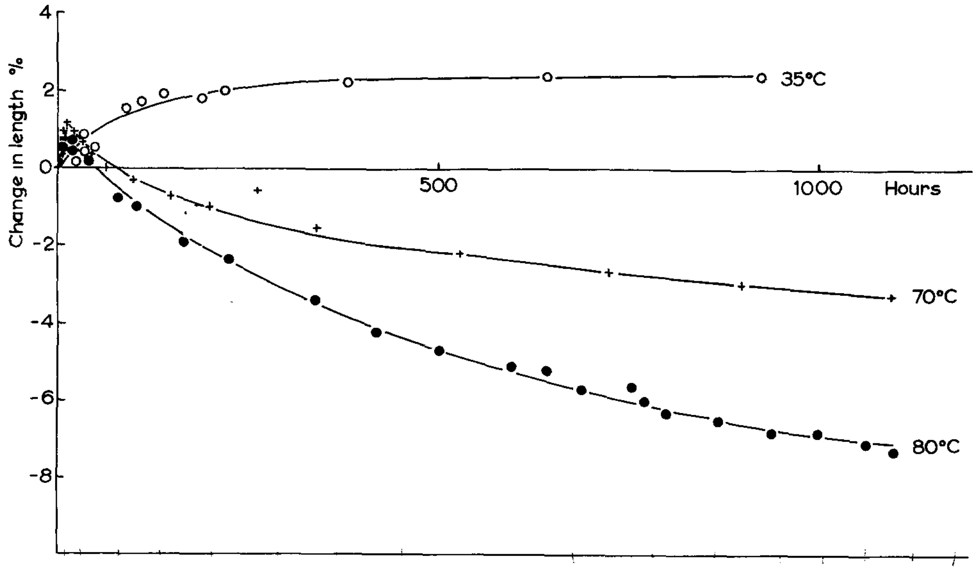

Figure 6 The effect of water temperature and exposure time on the percentage change in length of resin casts.

reduced to approximately half its initial value after immersion for 2160h at 35° C, and even greater reductions occurred after exposure in water at 70 and 80° C.

A typical fracture surface of an unexposed notched resin cast specimen is shown in Fig. 3. Fig. 4 shows part of the fracture surface of a resin cast after three months' exposure to water at 70° C, and Fig. 5 shows a fracture surface after three months exposure at 80° C. The extent of linear shrinkage in thin resin films as a function of immersion time and temperature is shown in Fig. 6.

4. Discussion

K_{IC} is the plane strain critical stress intensity factor and is related both to the fracture surface energy and the strain energy release rate for linearly elastic materials.

$$K_{IC}^2 = EG_{IC}/(1-\nu^2) = 2E\gamma/(1-\nu^2)$$

where E is Young's modulus, ν is Poisson's ratio, G_{IC} is the strain energy release rate, γ is the fracture surface energy. The initial value of K_{IC} compares with a reported value of $0.72\,\mathrm{Mn\,m^{-3/2}}$ for a polyester resin [13], $0.55\,\mathrm{MN\,m^{-3/2}}$ for Dow DER

332 epoxy resin [14] and 0.73 to 0.90 MN m$^{-3/2}$ for Epikote 828 epoxy reisn [7].

Water uptake causes an initial increase in volume (see Fig. 6) which is countered by shrinkage, caused by (a) further cross-linking, (b) leaching [15]. At temperatures high enough to cause a large increase in molecular free volume and in the energy available for segmental motion, leaching is sufficient to produce a large net reduction in volume. This removes the small, mobile, non-bound molecular species capable of contributing to energy dissipation through internal friction.

Exposure at 35° C does not produce sufficient thermal activation and free volume for larger non-bound molecules to be released. Monomeric styrene, propylene glycol, isophthalic acid, maleic anhydride, and propylene isophthalate are among the smallest non-bound molecules present, which could be exchanged to a limited extent with water, causing a net increase in volume, but allowing the possibility of local network distortion. The larger structures, capable of being leached at higher temperatures are the higher saturated ester, and attempts at a quantitative estimate of their expected concentration in Flory distribution polyesters have been made [16, 17]. K_{IC} may, therefore, fall during exposure because of leaching of low molecular weight constituents, but if this mechanism operates it clearly does not require a net volume reduction.

Another possible cause of the changes in K_{IC} may be considered. The effect of water-induced disc cracks and other defects on K_{IC} is complex. However, the fact that K_{IC} values tend to become constant suggests that a cause must be sought which ceases to operate at long exposure times. Disc cracks continue to develop during very long immersion periods, but leaching must decrease, and eventually cease, because the quantity of non-bound matter is limited, and some is trapped by entanglements of a virtually permanent kind. (This assumes that hydrolytic cleavage of ester groups is minimal). Fig. 5 shows a fracture surface in which an internal disc crack had formed, adjacent to the notch, during immersion in water, but had not modified the fracture surface characteristics of the main crack. The curved edge of the disc crack is the feature in the central region of the photograph.

Diggwa [11], using a cleavage method, measured the fracture energy of cast polyester and epoxide resins before and after water immersion. 12 days' immersion in water at 30° C produced only a small (5%) reduction in fracture surface energy. A larger change (an actual increase) was observed when water was injected into the notch tip during the fracture process. This did not occur when the specimen was fully immersed during the test. It was suggested that injection provides effective intimate contact between water and crack tip, and increases the crack propagation energy.

From these studies, it seems necessary to understand the mechanism by which water affects fracture energy more clearly. Polyester and epoxide resins are not pure compounds; they vary (even when formulations are apparently identical) in the important matters of molecular weight distribution, catalyst nature and uniformity of cross-link density [18, 19]. Thus there is a need for careful specification both of material parameters and of test methods.

5. Conclusion

The critical stress intensity factor of an unsaturated polyester resin has been measured and found to fall significantly after exposure to hot water. The reduction in critical stress intensity factor is attributed to the water extraction of non-bound matter present in the resin.

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