

Effect of Absorbed Water on Undercured Epoxy/Amine Thermosets

P. JOHNCOCK, *Materials and Structures Department, Royal Aerospace Establishment, Farnborough, Hants, England*

Synopsis

The effect of water immersion at 70°C on undercured epoxy thermosets obtained from tris[4-(2,3-epoxypropoxy)phenyl]methane and 4,4'-diaminodiphenylsulphone and from *N,N*-bis(2,3-epoxypropyl)aniline and 1,3-diaminobenzene was investigated. It is concluded from water absorption studies, T_g measurements, and gravimetric data that the predominant reaction is that of additional cure induced by the plasticising and catalytic effect of the absorbed water.

INTRODUCTION

The effect of absorbed water on undercured epoxy thermosets has been referred to in some recent publications. Thompson, Wong, and Broutman¹ reported that the glass transition temperature (T_g) of an undercured epoxy from Epon 828, which is mainly 2,2-bis[4-(2,3-epoxypropoxy)phenyl]propane, and 1,3-diaminobenzene (MPD) increased after the specimens were aged in water at 70°C, and considered that the sorbed water might have induced further crosslinking. Fornes, Gilbert, and coworkers have reported on the effect of water on CIBA-GEIGY MY 720, which is mainly bis[*N,N*-bis(2,3-epoxypropyl)-4-aminophenyl]methane, cured with 4,4'-diaminodiphenylsulphone (DDS) at 177°C. Thus, differential scanning calorimetry and infrared spectroscopy showed² that further consumption of epoxy groups occurred in water at 70°C, and the thermogravimetric data³ was compatible with both water-induced additional cure and reaction of water with epoxy groups. Most recently, however, from sorption studies at 30–70°C, it was concluded⁴ that the decrease in diffusion coefficient that occurred between 55 and 70°C was a result of reaction between water and epoxy groups at these higher temperatures. This raises the interesting question concerning the relative importance of the water-induced amine/epoxy reaction compared with the reaction of water with epoxy groups for an undercured network and, in connection with this, we report here the results of our own investigations.

EXPERIMENTAL

Dow XD-7342, which is mainly tris[4-(2,3-epoxypropoxy)phenyl]methane, and DDS (CIBA-GEIGY HT-976) were used without further purification. MPD, mp 65–67°C, was purified by sublimation. *N,N*-bis(2,3-Epoxypropyl)aniline (DGA), bp 110–111°C/0.13 Torr, was prepared by a literature procedure.⁵ Thin films of about 0.025 cm thickness were prepared as follows: a homogeneous

solution of DGA and a 97% stoichiometric amount of MPD (prepared at 80°C) and of XD-7342 and a 66% stoichiometric amount of DDS (prepared at 130°C) were degassed (vacuum oven) at these temperatures and cured between clamped glass plates that had been pretreated with mould release agent, and were separated by glass fibre-reinforced Teflon shims; cure details are given in the figures. Specimens (3 × 1 cm) for soaking experiments in distilled water were predried at $\sim 10^{-3}$ Torr to constant weight for 1–2 days (undercured DGA/MPD at 60°C; fully cured DGA/MPD and XD-7342/DDS at 80°C). Weighings were made on a Sartorius 4503 Micro balance. Wet samples were gently wiped with soft tissue before being weighed. Average diffusion coefficients for absorption (\bar{D}_a) were calculated using the Fickian approximation for short times.⁶ To roughly compensate for the relaxation of the network with its associated contribution to the water absorption, the value of w_∞ was taken halfway between the intercept on the y axis and the start of the slowly increasing linear region. Tg determinations were made with a Polymer Laboratories DMTA operating at 10 Hz and a heating rate of 5°K/min.

RESULTS AND DISCUSSION

In a previous communication,⁷ a reasonable linear relationship between Tg and the equilibrium water absorption (w_∞) was reported for some 0-glycidyl systems cured with DDS in an inert atmosphere, the slope being dependent on the proportion of hardener employed. When an undercured XD 7342/DDS system having a Tg of 212°C was aged in nitrogen at 160°C and in water at 70°C, an interesting feature was apparent in the plot of w_∞ at 20°C against Tg (Fig. 1): these parameters for the water-aged network fall almost on the line joining those for the unaged network and those after the network was aged in nitrogen at 160°C when additional cure occurred. This indicated that for the water-aged network the predominant reaction was that of amine with epoxy groups induced by the plasticising effect of the absorbed water presumably in association with its well-known catalytic effect on this reaction.⁸ The small gain in weight that occurred during water aging was consistent with this: it corresponded to about 4% reaction of epoxy groups with water but is a minimum figure since some leaching of material by water might have occurred. The \bar{D}_a s for the three states of cure were much the same ($\sim 2.2 \times 10^{-9}$ cm² s⁻¹). The observed deviation from linearity is in the expected direction since the water-expanded network would have a higher w_∞ and possibly, in accordance with data obtained for the other system discussed later in this paper, a lower observed Tg, as a result of the expanded network responding less sluggishly than the relaxed network as the applied temperature rises through the transition region. Choy and Plazek⁹ explained their dilatometric Tg data for a densified epoxy glass in these terms. The slight modification of the network caused by the reaction of the epoxy groups with water might also, of course, affect the Tg. It should be noted that when the undercured system was aged in air instead of nitrogen considerable deviation from linearity occurred because of network oxidation and the \bar{D}_a (0.3×10^{-9} cm² s⁻¹) was significantly lower, but these aspects will be discussed in another publication.

Our conclusion concerning the predominant reaction is as might be expected from the results obtained for the model compound reactions between phenyl-

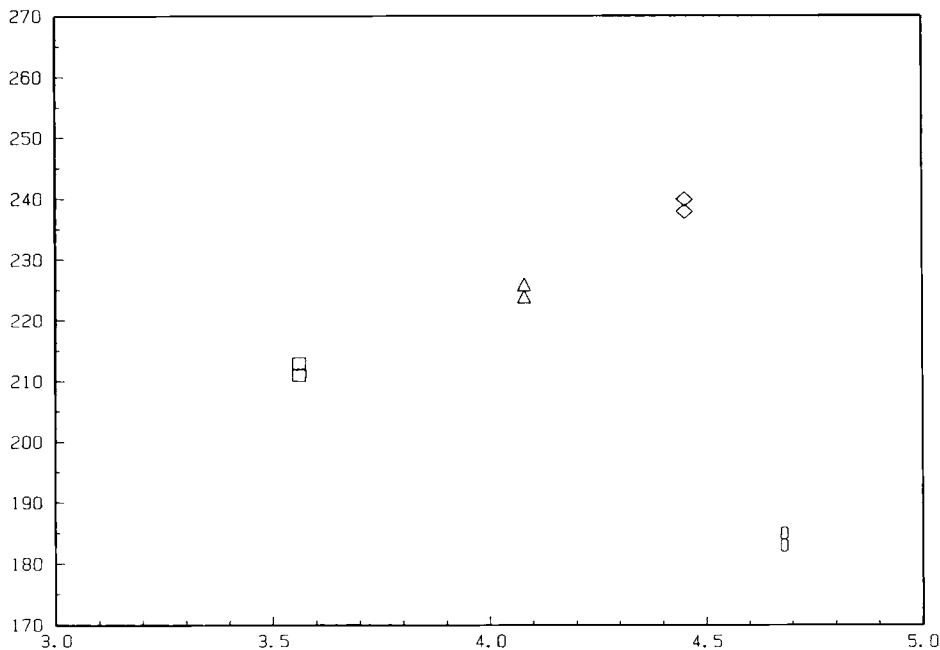


Fig. 1. Effect of air—and water—aging on the T_g and equilibrium water absorption (w_∞) at 20°C of XD 7342 undercured with 66% stoich. amount of DDS (0.025 cm castings) at 150°C/17 h + 180°C/5 h + 200°C/2 h. Aging conditions with \bar{D}_a ($\text{cm}^2 \text{s}^{-1}$) $\times 10^9$ for water absorption at 20°C in parentheses: (□), unaged (2.3); (Δ), 59 days at 70°C in water and desorbed (2.2); (\diamond), 21 days at 160°C in nitrogen (2.1); (○), 21 days at 160°C in air (0.3). Data for duplicate runs shown. Abscissa, w_∞ (g/100 g resin); Ordinate, T_g (°C).

glycidyl ether or *N*-glycidylanilines with aniline in ethanol, for which the reaction between epoxy groups and ethanol was negligible.¹⁰ Thus, during epoxy network formation, the reaction of water with epoxy groups should only become significantly competitive when diffusion-controlled factors prevail as might occur in the later stages of cure. To test this further, the reaction between DGA and MPD was chosen since it provided a fully cured network (designated FC) with a T_g of 155°C. It was considered that a partially cured network based on this system would undergo a high degree of additional cure in water at 70°C, and that this might be assessed by water absorption, T_g, and weight gain measurements. The partially cured network (designated UC) had a T_g of 112°C. Water absorption against time plots at 70°C for the FC and UC systems for up to 28 days are given in Figure 2: the FC system shows a good linear initial region but, as observed with other epoxy systems,⁷ continues to slowly absorb water beyond the expected equilibrium point; the plot for the UC system follows the same initial linear path but departs from, and then approaches, the fully cured curve. This behaviour is consistent with the continuation and completion of the cure process during the water immersion. The associated diffusion data supports this interpretation since the \bar{D}_a for the UC system (which has the same initial slope as, but a lower w_∞ than the FC system) is about 30% higher than that for the FC system: this is contrary to what might be expected if the reaction between the epoxy group and water were dominant, the conclusion

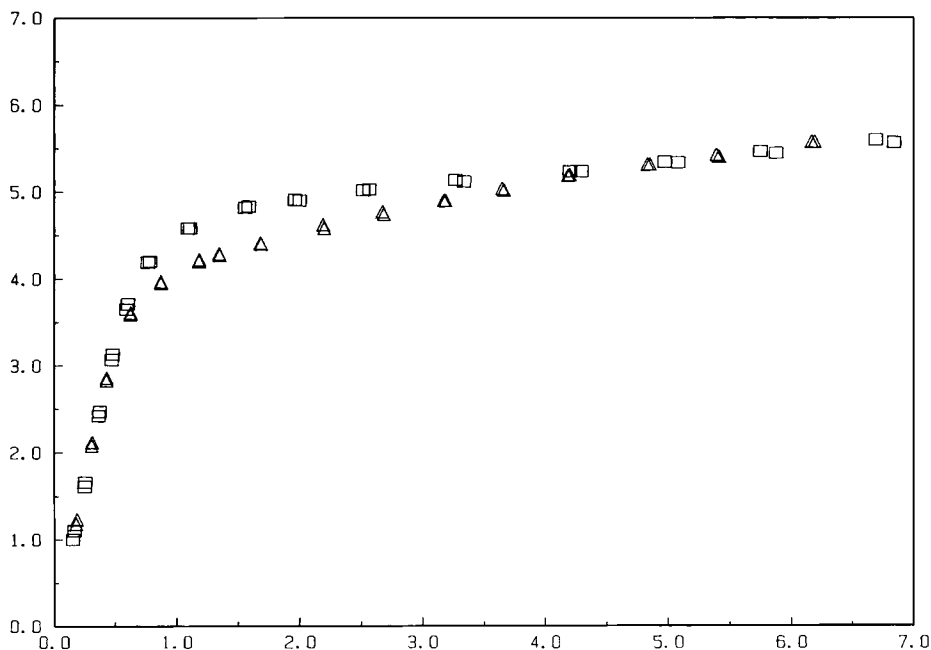


Fig. 2. Water absorption (W_t) at 70°C for DGA cured with stoich. amount of MPD (0.025 cm castings): (Δ), undercured (80°C/17 h) system; (\square), fully cured (80°C/17 h + 160°C/6 h) system. Combined data for duplicate runs is shown. Abscissa, \sqrt{t}/d (s^{0.5}, cm⁻¹); Ordinate, W_t (g/100 g resin).

reached by Fornes and Gilbert (loc. cit.) from their studies with MY 720 cured with DDS. The changes in weight that were recorded after the soaked samples were dried *in vacuo* also indicated that the reaction between the epoxy group and water was slight: after being dried to constant weight at 60°C (72 h), the UC system showed a weight increase of 0.3%, which was reduced to 0.25% after 48 h at 80°C and then to 0.13% after 24 h at 150°C; the FC system had a residual weight gain of 0.1% after 48 h at 80°C and 0.02% after 6 h at 150°C. A 0.3% weight gain corresponds to about 2% consumption of epoxy groups by water.

The water absorption vs. time plots at 20°C for the UC and FC virgin systems, for those after hygrothermal aging at 70°C for 28 days (UC predried 60°C and FC predried at 80°C), and for those after hygrothermal aging at 70°C which had been dried as above and then thermally relaxed at 150°C *in vacuo* (UC for 24 h, FC for 6 h) are given in Figure 3 with that for a control experiment in which the virgin UC system was aged in air at 70°C for a similar period. After immersion at 20°C, all samples essentially recovered their initial weights (< 0.03% gain) after being dried at 80°C (FC) or at 60°C (UC) for 48 h. For the virgin samples, the usual effect⁷ was observed that further cure led to increased water absorption ($w_\infty = 4.6\%$ for the FC compared to 2.7% for the UC system). There was no indication from the sorption profile that the UC system underwent any additional cure in water at 20°C such as was observed at 70°C. After hygrothermal treatment at 70°C, plots for both the UC and FC systems were almost superimposable with the expanded network having a higher water

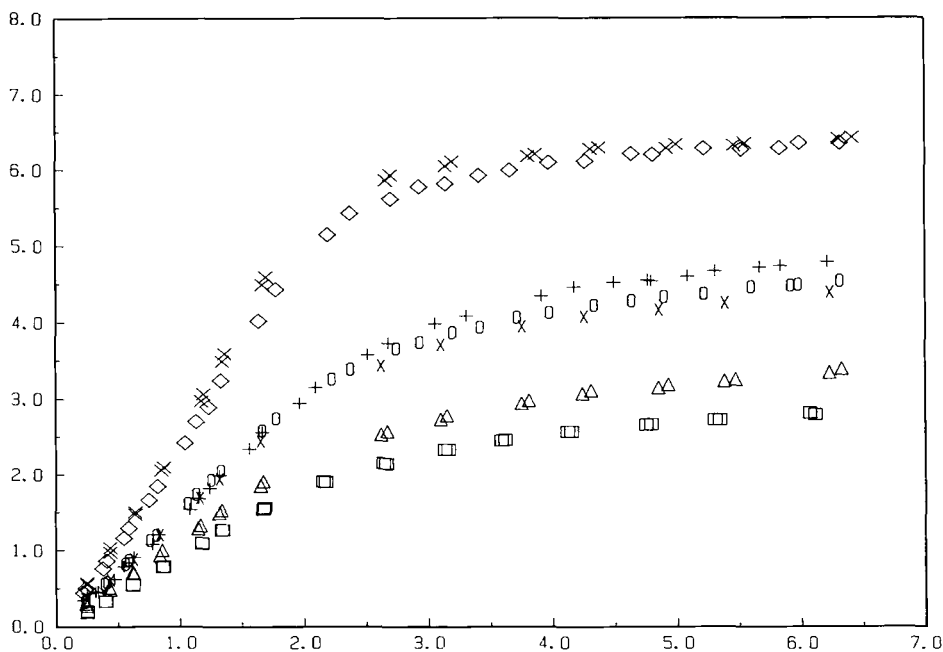


Fig. 3. Water absorption at 20°C showing effect of water at 70°C on DGA undercured (UC, 80°C/17 h) and fully cured (FC, 80°C/17 h + 160°C/6 h) with stoich. amount of MPD. Aging conditions: (□), UC as prepared; (△), UC 28 days at 70°C in air; (×), UC 28 days at 70°C in water, desorbed and thermally relaxed; (○), FC 28 days at 70°C in water, desorbed and thermally relaxed; (+), FC as prepared; (◇), FC 28 days at 70°C in water and desorbed; (×), UC 28 days at 70°C in water and desorbed. Combined data for duplicate runs except for (×) are shown. Abscissa, \sqrt{t}/d ($s^{0.5}$, cm^{-1}); Ordinate, W_t (g/100 g resin).

absorption ($w_\infty \sim 6.5\%$). Relaxation of these expanded networks led to plots that were very similar to that for the virgin FC material. The recorded Tg data were more sensitive to differences in these systems: the dried (80°C) hygrothermally aged FC system in its expanded state had a Tg of 146°C, which was about 10°C lower than that of the virgin FC material, and the probable reason for this was discussed earlier. After relaxation at 150°C and removal of the small amount of residual water (0.1%), the Tg increased to 154°C, essentially the value for the virgin FC material. The Tg of the dried (60°C) hygrothermally aged UC system was 136°C, and this value increased to 150°C when the system was thermally relaxed at 150°C. It will be recalled that this system, unlike the similarly treated FC system, still showed a slight residual weight increase of 0.13%, and the small difference in Tg of 4°C presumably reflects the small amount of reaction (about 1%) that had occurred between the epoxy group and water. The larger difference in Tg of 8°C between the UC and FC systems in their expanded states presumably also reflects an additional contribution from water plasticisation since the residual weight gains at that stage were 0.3 and 0.1%, respectively. It should be noted that in the control experiment, in which the UC system was aged in air at 70°C, some additional cure occurred, as reflected by the slight increase in Tg (121°C) and water absorption ($w_\infty = 3.2\%$).

The \bar{D}_n s at 20°C for both the FC and UC systems that had undergone the water aging treatment at 70°C followed by thermal relaxation at 150°C were much the same (0.32 and $0.31 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, respectively).

It is thus concluded that for this fairly reactive system involving DGA and MPD and, even for XD 7342 and the less reactive DDS, the reaction of water with the epoxy group is far less important than its role as a plasticiser and catalyst in facilitating the reaction of amine with epoxy groups. This conclusion is clearly of some importance in considering the effect of water on prepregs based on epoxy resins that are cured with amines. The role of water at their storage temperatures should be even more specifically confined to advancing the degree of cure and, providing it is removed so as to prevent void formation during the cure process, should have very little effect in modifying the final network structure.

References

1. K. W. Thompson, T. Wong, and L. J. Broutman, *J. Polym. Eng. Sci.*, **24**, 1270 (1983).
2. A. N. Netravali, R. E. Fornes, R. D. Gilbert, and J. D. Memory, *J. Appl. Polym. Sci.*, **30**, 1573 (1985).
3. A. N. Netravali, R. E. Fornes, R. D. Gilbert, and J. D. Memory, *J. Appl. Polym. Sci.*, **31**, 1531 (1986).
4. B. K. Kelly, R. D. Gilbert, R. E. Fornes, and V. T. Stannett, *J. Polym. Sci., Polym. Phys. Ed.*, **26**, 1261 (1988).
5. J. Hayden and M. Balzajak, German Patent 1,206,915 (1965).
6. P. Meares, *Polymers: Structure and Bulk Properties*, Van Nostrand Co. Ltd., London, 1965, p. 320.
7. P. Johncock and G. F. Tudgey, *Br. Polym. J.*, **18**, 292 (1986).
8. B. A. Rozenberg, in *Advances in Polymer Science—75*, K. Dusek, Ed., Springer-Verlag, Berlin, 1986, p. 115.
9. I.-C. Choy and D. J. Plazek, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 1303 (1986).
10. P. Johncock, L. Porecha, and G. F. Tudgey, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 291 (1985).

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