An Additive for Increasing the Strength and Modulus of Amine-Cured Epoxy Resins*

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Synopsis

The reaction product of 4-hydroxyacetanilide and 1,2-epoxy-3-phenoxypropane, when added at 19 wt % to a conventional epoxy-resin-curing agent mixture, increases the tensile strength of the cured system from 82 MPa to 123 MPa and increases the shear modulus (20°C, 1 Hz) from 970 MPa to 1560 MPa. As well as showing increased strength, the tentile-test specimens also fail in a ductile fashion, i.e., the slope of the stress–strain curve is negative at failure, with appreciable localized deformation occurring during fracture. For notched samples (compact tension specimens), the fracture properties are strongly strain-rate-dependent. At low strain rates the additive-containing sample has a fracture energy ($\mathcal{G}_{I_c}$, critical strain energy release rate) about twice that of the additive-free control, but at higher strain rates $\mathcal{G}_{I_c}$ falls to about 65% of the control value. The critical stress for crack propagation is also strain-rate-dependent and is about 50% higher than the control at low strain rates and about 10% less than the control at higher strain rates. Dynamic mechanical analysis and dielectric loss measurements indicate that the additive causes a decrease in the T_g and a suppression of the β-relaxation. Chemically, the additive accelerates the cure process but does not significantly alter the final extent of reaction of the epoxy resin. After curing, the additive is almost totally extractable by solvent indicating that it is not chemically bound to the polymer. These observations are discussed in terms of the concept of antiplasticization.

INTRODUCTION

We have described previously a family of additives which were given the descriptive name "epoxy fortifiers."[1–3] These additives are mixed with an epoxy resin and a curing agent, prior to curing, and result in an increase in strength and modulus of the cured product. The purpose of this paper is to describe in some detail the mode of action of one particular member of this family, viz. the reaction product (EPPHAA) of 1,2-epoxy-3-phenoxypropane (EPP) and 4-hydroxy-acetanilide (HAA). This system was chosen as a model for detailed examination because the reaction product consists largely of a single chemical compound and also because it does not become chemically bound to the cured epoxy network, thus simplifying analytical procedures. EPPHAA produces strength and modulus properties typical of other members of the family but, because of the reduction it produces in the T_g, has somewhat inferior high temperature performance.[1]

The epoxy resin chosen for this study was a diglycidyl ether of bisphenol A

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(DGEBA) cured with 4,4′-diaminodiphenylmethane (DDM). This resin–curing agent mixture was chosen because it is widely used for structural applications and has been studied extensively.[4,5]

EXPERIMENTAL

Materials. HAA (Eastman) has a melting point of 170°C and contained no detectable impurities by liquid chromatography. EPP was technical grade and was >98% pure as determined by liquid chromatography. The product EP-PHAA was prepared by heating EPP and HAA at a 1.05:1 mole ratio to 160°C for 60 min in the presence of 0.1 wt % diethylamine hydrochloride catalyst. The DGEBA resin (Shell, Epon 828) and DDM curing agent (Ciba-Geigy HT972 flake) were used as received.

Analytical Techniques. Liquid chromatographic analysis of reactants and products was carried out using a Waters ALC 201 equipped with a Rheodyne injection system and a Spectra Physics variable wavelength detector. Separations were achieved by isochratic reverse phase elution, using a 30/70 acetonitrile/water mixture. Infrared (IR) spectroscopic analysis was carried out using a Nicolet 7199 FT-IR. Samples for IR analysis were prepared as thin films on salt discs.

The extractability of the additive from the cured material was determined using finely powdered samples. The cured material was pulverized in liquid nitrogen (Spex mill), passed through a 60-mesh sieve, dried for 2 h at 125°C, weighed, extracted with methyl isobutyl ketone at 116°C for 1 h, redried, and reweighed. The samples were conditioned in a controlled environment (23°C, 65% relative humidity) for 5 h before each weighing. Densities of cured samples were measured by flotation in water/sodium bromide.

Preparation of Cured Samples. The EPPHAA additive (0–40 parts) was dissolved in the DGEBA resin (100 parts) at 100°C, degassed, cooled to about 80°C and mixed with the degassed molten DDM curing agent (30 parts). The mixture was then poured into stainless steel moulds. The cure conditions were 100°C for 3 h followed by 125°C for 2 h and 175°C for 4 h. Cured sample were in the form of 20 × 10 cm sheets, 0.16 or 0.32 cm thick, which were cut to shape with a high speed band saw and milling tool.

Physical Testing and Characterization. Tensile testing was performed on dumbell-shaped samples according to ASTM D638 (Type II except that gage length was 25 mm) using an Instron Tensile Tester run at 2 mm/min crosshead speed. Fracture energy determinations were made using a rectangular compact tension specimen as described by Ting and Cottington,[6] with the exception that the sample thickness (0.32 cm) was less than the ideal for plane–strain conditions and so the fracture energy values should be used for internal comparison purposes only. Fracture energies are very sensitive to moisture and so the notched samples were dried for 2 h at 105°C before testing in a controlled environment (65% humidity, 23°C). The fracture energy data represent the average of at least five samples per data point because of the appreciable scatter in failure loads (±30%).

A Rheometrics mechanical spectrometer (RMS-605) with a forced torsion test fixture was used to determine the storage modulus (G'), loss modulus (G''), and loss tangent (tan δ) as a function of temperature and frequency. The system

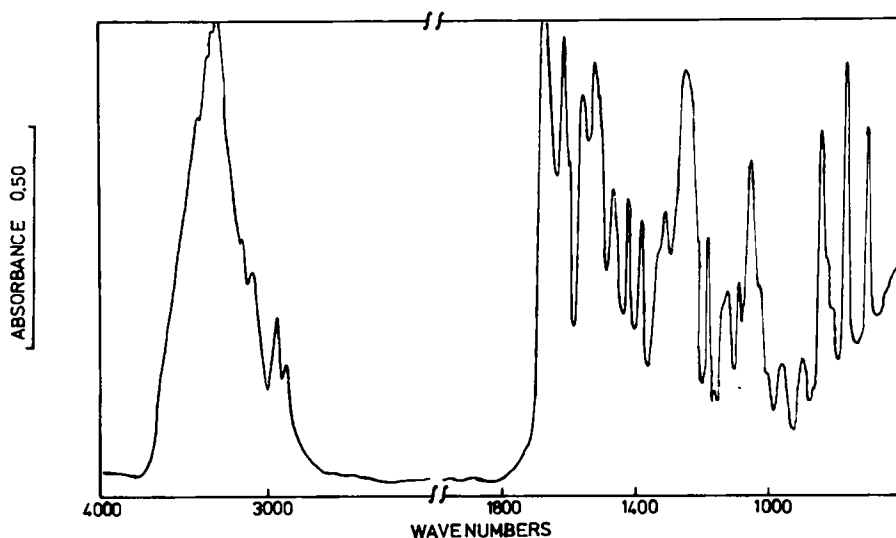Fig. 1. Infrared spectrum of recrystallized EPPHAA.

had a temperature stability of ±0.5°C and an accuracy in frequency of 0.1% of setting. The temperature and frequency dependence of the mechanical data gave information on the position of transition regions and on the apparent activation energies for the various processes.

Dielectric permittivity (ϵ') and loss (ϵ'') values at a constant frequency of 1 KHz were obtained over the range 173–273 K. A three-terminal cell with a guarded electrode was used in conjunction with a General Radio capacitance bridge (Type 1615-A), a Rhode and Schwarz tunable detector (Type UBN), and a Hewlett-Packard signal generator (Model 203A). The use of an auxilliary amplifier (Keithley electrometer) and an oscilloscope as the detector allowed accurate measurements of low loss values. The cell was cooled to 173 K with liquid nitrogen and then heated at 1 K/min.

Fracture surfaces were examined by scanning electron microscopy (SEM) using an AMR-1000 Microscope. Samples were coated with about 500 Å of gold to reduce charging in the electron beam.

RESULTS

Characterization of EPPHAA. The crude EPPHAA product was a viscous oil which solidified on standing. Liquid chromatography indicated that the product contained about 90% of a single chemical compound, with the major impurity being unreacted HAA. A sample of EPPHAA was recrystallized from acetone to isolate the major product. This compound, a white powder of melting point ~130°C, was shown by mass spectrometry to have a molecular weight of 301. IR spectroscopy showed that the product retained the secondary amide group of HAA and that the epoxy group of EPP was destroyed (Fig. 1). A comparison with the spectra of model compounds indicated that the major product in EPPHAA resulted from the opening of the epoxide ring of EPP by the phenolic group of HAA:
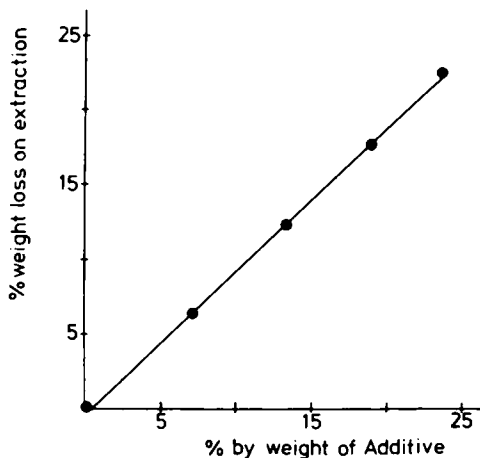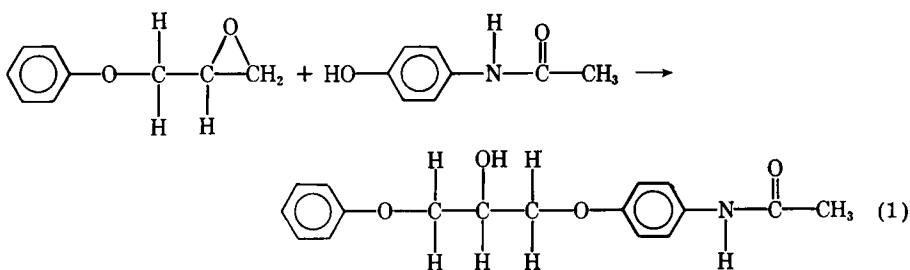
Fig. 2. Extractability of EPPHAA from pulverized polymer.

The product EPPHAA was used in its crude, 90% pure state in the subsequent experiments to modify epoxy resin properties, because of its easier processibility (lower melting point, more readily soluble) in the epoxy resin as compared to the recrystallized product.

Effect of EPPHAA on the Cure Process and Cured Polymer Properties. The cure process was monitored by following the loss of the characteristic epoxy ring IR absorption at 915 cm^{-1}. In the DGEBA–DDM control after 30 min at 160°C, about 6% of the epoxy groups were unreacted while for an identical sample containing 19 wt % EPPHAA, <2% of the epoxy groups were unreacted after 30 min at 160°C. A similar degree of cure (<2% epoxy groups) was only achieved by the DGEBA–DDM reference after 2.5 h at 160°C. It may therefore be concluded that EPPHAA accelerates the cure process but does not alter the final degree of reaction of the epoxy resin (within the limits of precision of the FT-IR technique).

It was possible to extract the EPPHAA almost totally from the cured epoxy resin. The control sample had, however, negligible weight loss on solvent extraction. Figure 2 shows the weight loss on solvent–extraction of the finely powdered material. IR spectroscopy of the extract showed that the composition of the extracted material (after removal of the solvent) was identical to that of the additive. It may therefore be concluded that EPPHAA does not become chemically bound to the epoxy resin during curing.

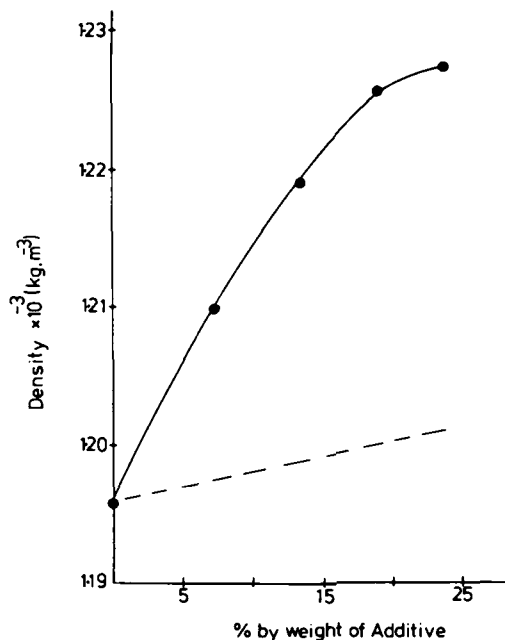Figure 3 shows that the density of the cured material was increased by the

Fig. 3. Density of the cured polymer. Dashed line denotes density calculated assuming additivity of densities of polymer and EPPHAA.

presence of EPP4HAA significantly more than would have been expected from a simple rule of mixtures calculation. Since the additive does not apparently react with the curing resin (see above), the anomalous increase in density implies that some form of molecular interaction is taking place, resulting in a negative volume of mixing.

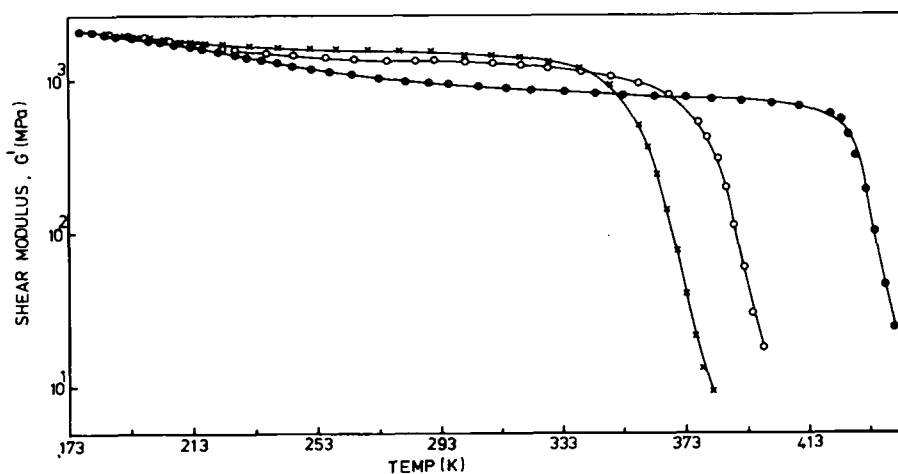Any characterization of a polymer–additive system must also address the

Fig. 4. Shear modulus at 1 Hz vs. temperature: (●) DGEBA–DDM control; (○) containing 10% EPPHAA; (✕) containing 19% EPPHAA.
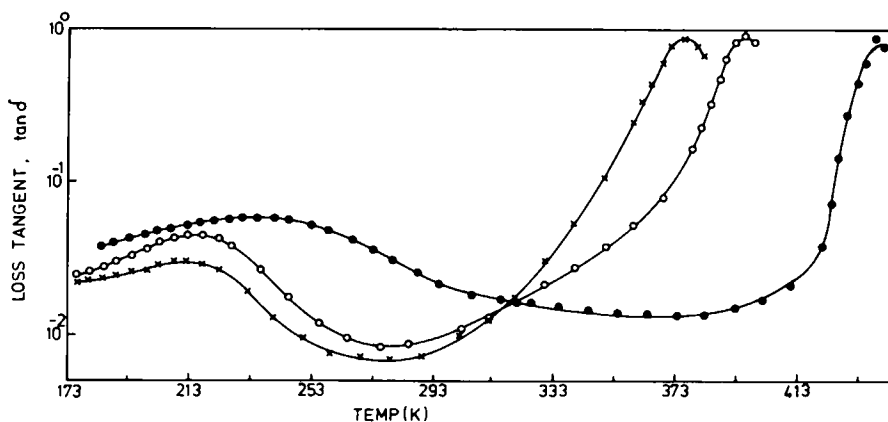
Fig. 5. Loss tangent at 1 Hz vs. temperature. Symbols as in Figure 4.

homogeneity of the system, because phase separation occurs frequently in polymer-containing mixtures. The EPPHAA-containing samples were transparent and exhibited one T_g (albeit a very broad transition, see below). Transparency and a single T_g are frequently taken as criteria of homogeneity in polymer mixtures, and so by these criteria the samples were homogeneous. No attempt was made to characterise the small-scale "nodular" texture claimed to exist[7] in cured epoxy resins.

Effect of EPPHAA on Moduli and Relaxation Processes. Figures 4 and 5 show the shear modulus (G') and loss tangent (tan δ) data for the DGEBA–DDM control and two additive-containing samples. The shear modulus is increased by more than 50% at 20°C by the presence of 19 wt % EPPHAA (Table I). At lower temperatures, the stiffening effect of the additive diminishes, but the moduli still appreciably exceed that of the blank even at −100°C. At elevated temperatures the modulus of the EPPHAA-containing samples drop below the DGEBA–DDM blank as the T_g is approached. The tan δ data (Fig. 4) show that the T_g of the cured polymer is decreased by as much as 60°C by the EPPHAA and that the β-relaxation is suppressed in amplitude. It is not clear whether the apparent downward shift in the position of the β-relaxation in the presence of EPPHAA (Fig. 5) is simply caused by the preferential suppression of the higher temperature components of the β-relaxation or whether it indicates the presence of a new relaxation process. The much lower activation energy of the β-transition in the EPPHAA containing sample implies, however, that the relaxation process is very different in character from the β-relaxation in the

TABLE I

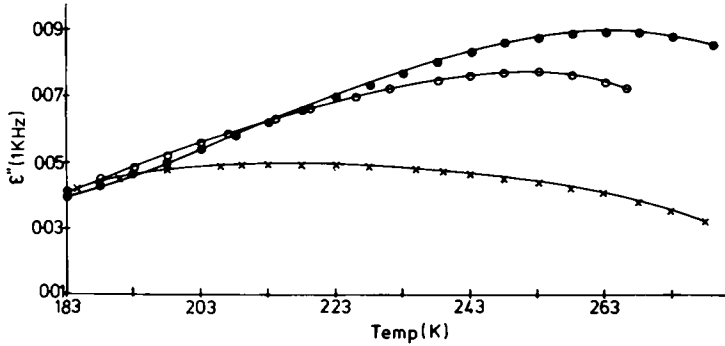| Sample	α-Transition		β-Transition		Shear modulus at 293 K (MPa)
	T_α (K)	Activation energy (kJ·mol^{-1})	T_β (K)	Activation energy (kJ·mol^{-1})	
DGEBA/DDM	438	743	234	91	969
DGEBA/DDM/10% EPPHAA	395	265	213	33	1414
DGEBA/DDM/19% EPPHAA	376	238	211	29	1561

Fig. 6. Dielectric loss at 1 kHz vs. temperature. Symbols as in Figure 4.

control. As was mentioned earlier, the α-relaxation (T_g) is very broad in the presence of EPPHAA. This may indicate that some inhomogeneity exists on a very small (hundreds of Angstroms) scale.

The dielectric loss data (Fig. 6) confirm the low temperature dynamic mechanical data (Figs. 4 and 5). Relaxation maxima occur at higher temperatures than in the dynamic mechanical data because of the higher frequency of the test, but it is clear from the magnitude of the dielectric loss that the β-relaxation is suppressed by the presence of EPPHAA.

Effect of EPPHAA on Strength and Fracture Properties. Typical stress–elongation curves are shown in Figure 7. The elongation axis is expressed
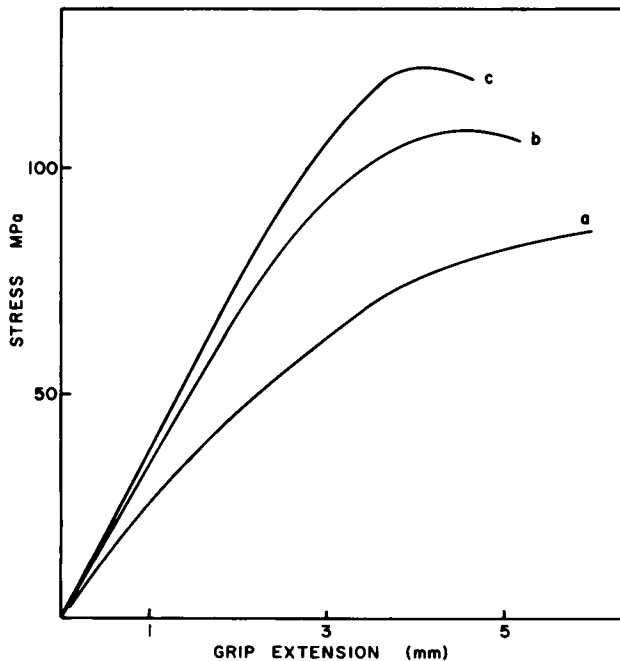

Fig. 7. Stress–elongation curves for cured polymer samples: (a) DGEBA–DDM control; (b) containing 10% EPPHAA; (c) containing 19% EPPHAA.
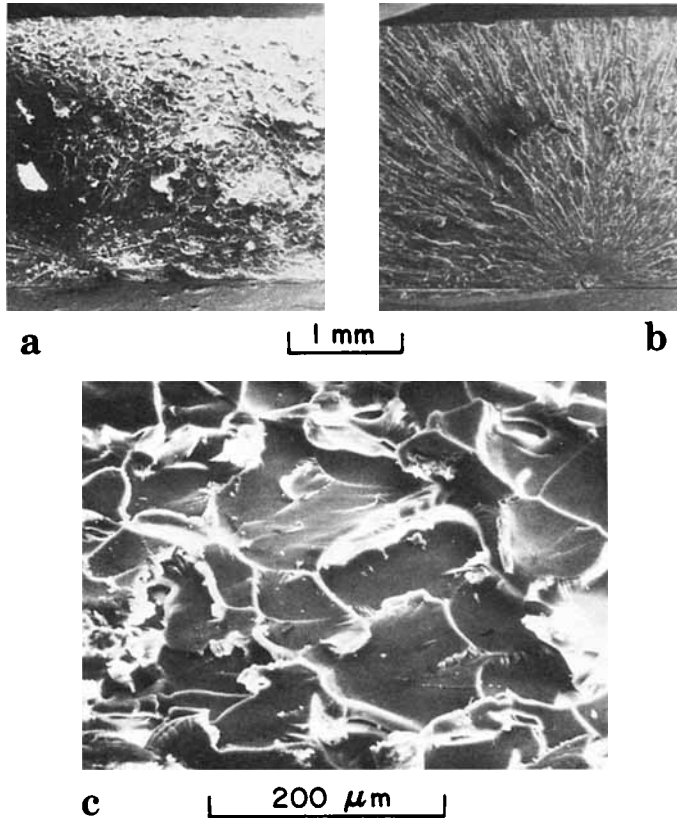
Fig. 8. SEM of fracture surfaces of tensile test specimens: (a, c) sample containing 19% EPPHAA; (b) DGEBA–DDM control.

simply as extension of the grips because of the complex dumbell shape of sample prescribed by ASTM D638. The stress is defined on the basis of the initial cross-sectional area at the narrowest point of the sample.

It is clear from Figure 7 that the tensile modulus is increased markedly by the presence of EPPHAA as would be expected from the shear modulus data (Table I). Tensile strengths are increased proportionately, and the slope of the stress–elongation curve at failure becomes negative, indicating that some localized yielding must occur before fracture.

The fracture surfaces of the tensile bars (Fig. 8) clearly show that EPPHAA modifies the mode of fracture. The DGEBA–DDM control sample [Fig. 8(b)] shows conventional epoxy fracture behavior, with a small smooth region of slow crack growth close to the fracture-initiation point, and a larger rough region of catastrophic crack growth. The EPPHAA-containing sample has a completely different fracture surface [Figs. 8(a), (c)]. A relatively smooth region is again located around the initiation point, but the remainder of the fracture surface is characterized by a series of shallow cavities about 100 μm diameter surrounded by ridges of material which have clearly undergone extensive plastic deformation.

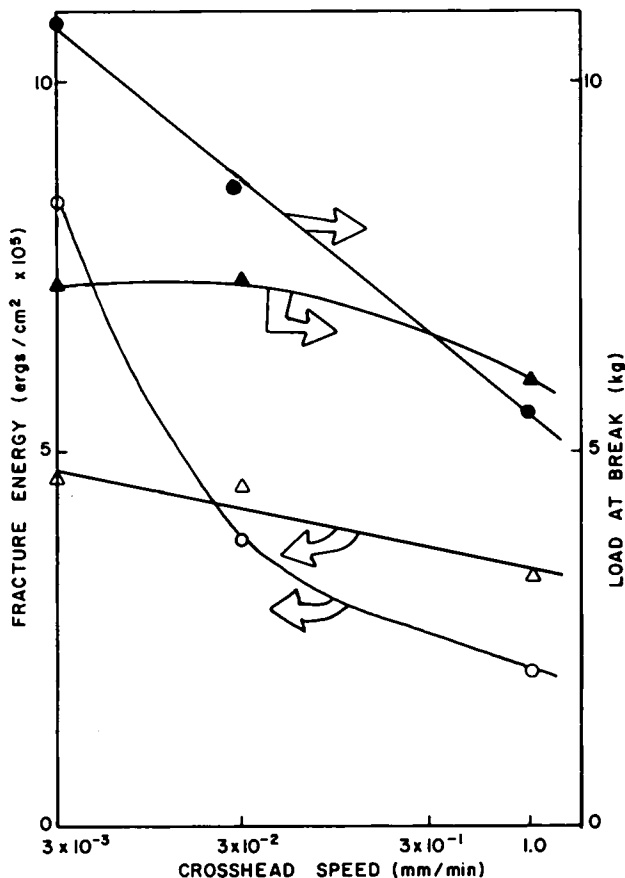Fracture energy measurements were made on notched samples to ensure the

Fig. 9. Fracture data from compact tension specimens: (△, ▲) DGEBA–DDM control; (○, ●) sample containing 19% EPPHAA.

presence of a single dominant defect capable of reproducibly initiating fracture. Two parameters are necessary to describe the fracture behavior of a glassy material. The fracture energy $\mathcal{G}_{I_c}$ describes the ability of the crack to dissipate strain energy, while the critical stress, defined here simply as the load at break, describes the ability of a preexisting crack to resist applied stress (Fig. 9). Using the fracture energy criterion, the EPPHAA-containing samples perform poorly at all but very slow strain rates. However, the EPPHAA-containing samples are able to withstand higher applied stress than the control material over a wide range of strain rates. This strain rate dependence of the fracture process was also evidenced in the fracture surfaces of the notched samples (data not shown), which were shiny at high strain rates but showed increased evidence of plastic deformation at lower strain rates.

DISCUSSION

The addition of EPPHAA to a DGEBA–DDM epoxy resin–curing agent mixture results in:

(a) an increase in modulus and strength (Figs. 4 and 7, Table I);

(b) an increase in density, a depression in T_g and a suppression of the β-relaxation (Figs. 3–6);

(c) an increase in the rate of cure but with no effect on the ultimate degree of cure and without the EPPHAA becoming chemically bound to the polymer (Fig. 2);

(d) a change in the mode of fracture such that the slope of the tensile stress–strain curve is negative at failure (Fig. 7) and appreciable local deformation occurs during fracture (Fig. 8);

(e) a strain rate dependent change in the fracture energy and fracture stress of notched samples (Fig. 9).

These observations may be explained in terms of the concept of antiplasticization, although the magnitude of the effects, particularly on the tensile strength, are larger than those previously reported for antiplasticizers in epoxy resins. The term "antiplasticization" was proposed by Jackson and Caldwell in 1965 to describe the stiffening effect of certain low molecular weight compounds when added to bisphenol-A polycarbonates, and subsequently to other stiff-chain polymers such as poly(sulphone ethers).[8–10] The concept of antiplasticizers being stiff polar additives which reduce the free volume available for molecular motion in stiff-chain, polar polymers evolved in the late 1960s and early 1970s.[10–13] In terms of the free volume concept, when a small molecule (volume fraction V_1, fractional free volume f_1) is added to a polymer (volume fraction V_2, fractional free volume f_2) the free volume of the mixture is given by[14]

$$f = V_1 f_1 + V_2 f_2 + K V_1 V_2 \qquad (2)$$

where K is an interaction parameter. For most polymer/additive systems, K is generally negative but small ($\sim 10^{-2}$) and so the free volume of a polymer (low f) is generally increased by the addition of a small (high f) molecule; hence plasticization occurs. The principle of antiplasticization is that the interaction parameter between the polymer and additive is negative and large. The free volume is then decreased by the additive resulting in an increase in modulus. One apparent anomaly is that while the antiplasticizer decreases the free volume of the system, it also decreases the T_g (Fig. 5). This results from the temperature dependence of the interaction parameter and the fractional free volume of the additive. With increasing temperature, the additive becomes more mobile, thus increasing f_1 and decreasing K. At high temperature, therefore, an antiplasticiser functions as a plasticizer. The prior use of antiplasticizers in epoxy systems has been described by several authors.[15–18] Previously, however, the most effective antiplasticizers have been polychlorinated biphenyls (PCB's). The environmental unpopularity of PCB's, together with the relatively modest increase they produce in material strength, has resulted in a decline of interest in this area.

Two aspects of the data presented here are particularly characteristic of antiplasticisation, vis., the negative volume of mixing (Fig. 3) and the suppression of the β-relaxation (Fig. 5). The negative volume of mixing results from the decrease in free volume predicted by eq. (2). A suppression of the β-relaxation will also be caused in part by the reduction in free volume, in the sense that it will inhibit the short range backbone motions which make up the β-relaxation. Inhibition of backbone motion will result, in turn, in an increase in modulus on a macroscopic scale.

The discussion so far has centered on the effect of EPPHAA on the modulus.

The ultimate tensile strength of the material, however, is also increased by the presence of EPPHAA. Fracture in glassy materials is controlled by the presence (intentional or accidental) of flaws, around which stress concentration occurs. The strength of a material is governed by its ability to dissipate strain energy without catastrophic propagation of these flaws. According to the Griffith failure criterion, if the largest flaw in a material is a sharp crack of length L, the ultimate tensile strength (σ_f) will be given by[19]

$$\sigma_f = (2WE)^{1/2}/(\pi L) \qquad (3)$$

where W is the work done generating unit area of fracture surface and E is Young's modulus. An increase in modulus will therefore only result in an increase in strength if there is no corresponding decrease in fracture energy.

Equation (3) was exploited indirectly when using compact tension specimens to measure fracture energies ($\mathcal{G}_{I_c}$, critical strain energy release rate, Fig. 9), where a large controlled flaw was introduced into the material. Figure 9 shows that the decrease in molecular mobility, which is responsible for the increased modulus, does not lead to a catastrophic decrease in fracture energy, particularly at low strain rates, and so the material has the potential for attaining high strengths, ultimately governed by the natural distribution of defect dimensions in the sample. No attempt was made to compare the fracture surfaces of the compact tension specimens with those of the tensile dumbbells because of the very different amounts of strain energy being dissipated in the two fracture processes.

Finally, it is necessary to comment upon the mechanism for dissipating fracture energy in the additive-containing polymer, where molecular mobility is low. Figure 8 shows that the mode of fracture is entirely different from conventional epoxy resin failure. The zone of rapid crack propagation [Fig. 8(b)] is replaced by a region where cavitation apparently occurred at a large number of sites and failure eventually occurred through this weakened area. A reasonable analogy is with the crazing processes which occur in glassy thermoplastics and have been proposed to occur in some epoxy systems,[20,21] but more detailed study, for example, by transmission electron microscopy, would be required to confirm this hypothesis.

In conclusion, the effects of one particular additive, EPPHAA, on the properties of a cured epoxy resin have been described in some detail. This additive is a model for a family of additives known as "epoxy fortifiers." By extensive modification of the additive formulation, it has been possible to improve some of the commercially unattractive characteristics of EPPHAA (low T_g, affinity for water, low fracture energy) while retaining the more attractive features (strength, modulus, ductile failure mode). Details of these other additive formulations and the results of using these additives in fiber-reinforced epoxy composites will be presented elsewhere.

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