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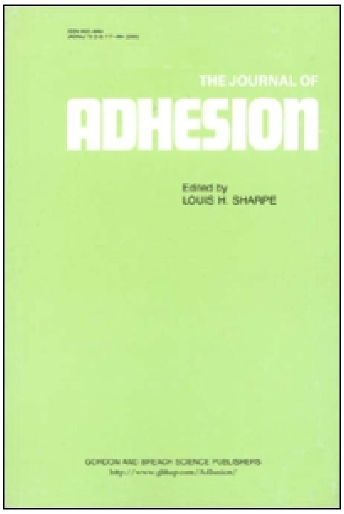

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Modification of Free Volume in Epoxy Adhesive Formulations

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Modification of Free Volume in Epoxy Adhesive Formulations†

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Additives are described which modify the free volume available for segmental motion in epoxy adhesives. Such a mechanism can produce an increase in the tensile modulus of conventional epoxy-amine systems of >60% (*e.g.* to >4.1 GPa) and in tensile strength of >50% (*e.g.* to 125 MPa), while also producing a ductile mode of failure (stress-strain curve has negative slope before failure). At low strains, a reduction in free volume hinders polymer segmental motion and so increases the modulus. However, these materials also exhibit a very low Poisson's ratio and strains of *ca.* 5% cause a sufficient increase in free volume that ductile failure can occur. Improvements in low temperature cure properties (*e.g.* 118 MPa tensile strength at 60°C cure) together with reductions in the coefficient of thermal expansion and water uptake are also reported. These improvements in bulk adhesive properties are shown to translate into improved adhesive joint performance.

KEY WORDS Epoxy; free volume; ductility; adhesive; fortifier; antiplasticization.

INTRODUCTION

Crosslinked epoxy resins remain the most widely-used adhesives in structural applications, where their ease of application, good environmental stability, and adequate creep resistance more than compensate for their perceived shortcomings. For many situations, their mechanical properties are adequate but, for demanding applications, their brittle failure mode and low strength in the presence of defects are viewed with some concern. Several generations of epoxy resins have been developed over the last thirty years in an attempt to alleviate

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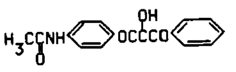
these concerns. For example, reactive rubber additives may be incorporated, and these phase separate on curing to give improved strain to break and fracture energy.[1-3] Unfortunately, there are also some disadvantages associated with rubber addition, such as a loss of modulus, a sensitivity of structure to cure conditions, and a decrease in hygrothermal stability. Therefore, it is reasonable to suggest that alternative routes to mechanical property improvement are of interest. This communication describes one such new route, which involves modification of the free volume and hence molecular mobility of the adhesive.

In a qualitative sense, free volume may be considered simply as the volume unoccupied by the atomic species of the material. This unoccupied volume has a strong influence on the mobility of segments of polymer molecules, and on the permeability of the polymer to gaseous or liquid penetrants. We realize that the whole concept of free volume may be considered as rather simplistic in the light of advances in modern polymer physics, but it has the advantage of ease of visualization and, in this particular case, lends itself to quantitative analysis.

A reduction in free volume as a means of improving adhesive mechanical and physical properties, as proposed here, appears at first sight contrary to conventional wisdom, since for many years plasticizers have been added to brittle polymers to improve their fracture properties *via* an *increase* in free volume. Also, the annealing of polymers at slightly below their glass transition temperature (Tg) can produce a decrease in free volume and sometimes leads to embrittlement.[4,5] The route to property improvement described here is similar in some respects to the use of "antiplasticizers" in glassy thermoplastics,[6-9] where an increase in modulus is achieved at the expense of a decreased strain to break. However, we demonstrate here that for crosslinked epoxy systems, an appreciable increase in modulus (>60%) and strength (*ca.* 50%) of the crosslinked polymer can be achieved with little change in total strain-to-break (*ca.* 5%), and with the occurrence of extensive yielding of the polymer before failure in a tensile test ("ductility"). Fracture toughness (K_{IC}) is also improved but only at low rates of strain.

EXPERIMENTAL

The majority of the data here refer to the widely-studied difunctional epoxy resin Epon 828 (Shell Chemical Co., largely the diglycidyl ether of bisphenol A but with some oligomers present), crosslinked with methylene dianiline (MDA, Fisher). The degassing and mixing procedures followed conventional practice[10-12] and, unless stated otherwise, the MDA level was 30 parts per hundred parts of resin (phr). Two additive formulations are described in particular detail here, *viz.* EPPHAA and VCDHAA. The additive EPPHAA was prepared by heating epoxyphenoxypropane (EPP, technical grade, >98% pure) with 4-hydroxyacetanilide (HAA, Eastman) at a 1.05:1 mole ratio to 160°C for 60 minutes in the presence of 0.1 wt% diethylamine hydrochloride catalyst. The product was determined to be largely structure I, and was a glassy solid which became liquid at about 90°C.[11] The additive VCDHAA was prepared by heating vinylcyclohexene dioxide (VCD, Monomer Polymer Labs) and HAA, at a 1.5:1 mole ratio to 120°C for 60 minutes, in the presence of 0.1 wt% diethylamine hydrochloride catalyst. The product was determined to be largely structure II, and was a glassy solid which became liquid at about 100°C. Other additive formulations are described elsewhere.[13–15]



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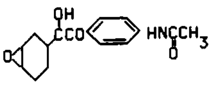

II

After mixing at about 80°C (both the additives and the MDA can be supercooled to 80°C before mixing with the resin), the uncured epoxy system was poured into stainless steel molds and cured, followed by a slow cool at >1°C/min. The 3 mm thick plates were machined into tensile specimens to conform to ASTM D638, type II, for tensile testing at 2 mm/min and 25°C. The volume changes during the tensile test were measured using perpendicularly aligned glue-on strain gauges (Macromeasurements EA-06-062TT-120). Volume changes with temperature were measured using a Dupont 910 thermo-mechanical analyzer (TMA) after annealing at >Tg, then cooling at <1°C/min to remove frozen-in stresses associated with cutting the specimen. In order to determine the extractability of the additives, the cured material was pulverized in liquid nitrogen, 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 for 5 h before each weighing. Densities of cured samples were measured by floatation in water/sodium bromide. The water uptake characteristics of the material were determined by exposure of freshly-dried, 3 mm-thick plaques (polished to remove mold release agent) to 95% humidity at 23°C over a period of several weeks.

A napkin-ring torsional joint geometry was selected for the structural joint study because the stress associated with this geometry is relatively uniform. The adhesive/substrate contact area is also greatly reduced in comparison with the lap shear geometry, with the result that water resistance can be tested over much shorter times.[16] The steel substrates were prepared for bonding using trichloroethylene degreasing followed by ammonium citrate (ammoniated citric acid, pH = 4) treatment at 75°C for 10 minutes. A distilled water bath followed by a methanol bath completed the pretreatment. The surfaces were air dried prior to bonding.

An Epon 828/MDA system with and without additives was used to bond the joints. Exactly 44 mg of the mixture was applied to the annular ring of the joint, using a small disposable syringe with a 21-gauge needle. The two sides of the joint were brought together and placed in a steel sleeve to ensure proper alignment. The joints were cured in a vertical position for one hour at 120°C followed by two hours at 150°C. To test the water resistance, the joints were immersed in 57°C distilled water for known periods of time, with constant bubbling of nitrogen, and then tested on an Instron tensile tester equipped with a torsional test fixture.

RESULTS SECTION

A. Crosslinked Resin Properties

Typical tensile stress–strain curves are shown in Figure 1. The addition of 15 phr and 30 phr of EPPHAA resulted in an increase in tensile strength from about 80 MPa to about 105 MPa and 120 MPa. The tensile modulus was increased from about 2.50 GPa to about 4.0 GPa at 30 phr EPPHAA. The occurrence of a yield point in the tensile stress–strain curve is particularly noteworthy, but it should be pointed out that this was somewhat specimen dependent. If a sufficiently large flaw was present, the specimen would fail in a brittle fashion before reaching the yield point. On the basis of several years experience we concluded that at least 75% of the additive-containing specimens would exhibit a yield point, while none of the control specimens exhibited a yield point (a yield point being defined here as a transition to a negatively-sloping engineering stress–strain curve). The additive VCDHAA gave a similar stress-strain curve, although tensile strengths were 3–5 MPa less (for formulations described here).

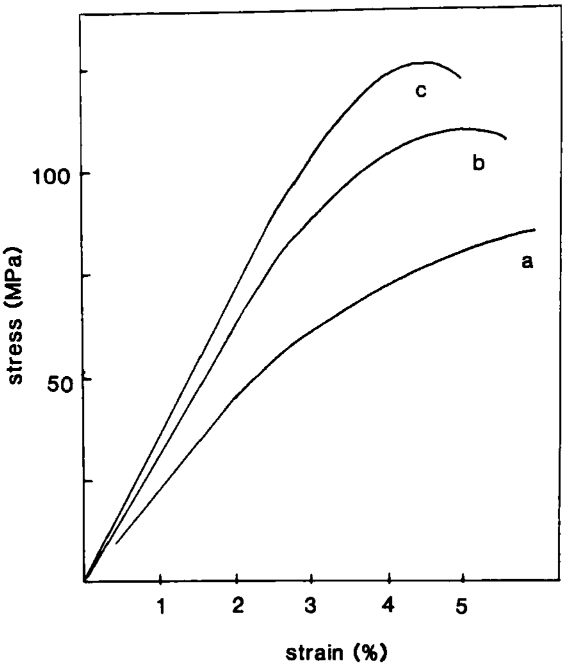

FIGURE 1 Tensile stress versus strain at 25°C and 2 mm/min (a) control (b) +20 phr EPPHAA (c) +30 phr EPPHAA.

The fracture properties of these materials are described in detail elsewhere.[11] Briefly, the fracture surface of additive-containing specimens which failed after yielding bore no resemblance to conventional epoxy fracture surfaces.[5] Instead, almost the entire fracture surface was characterized by shallow cavities of about 100 μm diameter, surrounded by material which had clearly undergone extensive plastic deformation.[11] As an indication of fracture toughness, we also determined K_{IC} using miniature compact tension specimens.[11,17] K_{IC} was strongly strain rate dependent for additive-containing specimens, and was about 60% higher than the control at low strain rates but approximately equal to the control at higher strain rates. It should be noted, however, that the values of K_{IC} ($<2\,\mathrm{MN/m^{3/2}}$) are significantly less than those obtained for rubber-toughened systems, and so it may be misleading to call these materials "tough" in the conventional sense.

Other mechanical properties of the crosslinked resins reported elsewhere include a relative insensitivity of tensile strength to humid aging, and the achievement of high tensile strengths with low cure temperature.[17] Immersion in boiling water of tensile specimens containing a proprietory additive formulation (Fortifier C, Uniroyal) produced almost no change in tensile strength, while 8 days at 75°C and 95% relative humidity produced a constant 10 MPa decrease in strength, independent of the additive concentration. Thus, a specimen containing 30 phr C decreased in tensile strength from 117 to 106 MPa after 8 days at 75°C and 95% humidity, while the control decreased from 85 to about 75 MPa. The improvement in the properties of low-temperature cured systems is illustrated by the fact that a specimen containing 30 phr of EPPHAA had a tensile strength of 118 MPa after a 60°C cure, while in the absence of the additives a cure temperature of at least 90°C was necessary to obtain anything other than a fragile B-stage material.[17]

As will become clear later, the volume expansion under tensile strain is an important physical property. Figure 2 shows that considerable volume expansion occurs, which implies that Poisson's ratio for these materials is appreciably less than 0.5. The volume expansion at constant strain is at least 20% higher for the EPPHAA containing specimen than for the control. The value of Poisson's ratio was dependent upon both strain and time as might be expected for a viscoelastic material but at, for example, 0.5% strain during a 1% min^{-1} tensile test was about 0.42 for the control and 0.38 for 30 phr EPPHAA.[15]

In order to provide a physical basis for these mechanical property changes, we explored the effect of the additives on the chemical and physical properties of the crosslinked resin. One particularly significant observation is that, for additive EPPHAA at least, almost no chemical bonding occurs between the additive and the resin. After pulverization of the polymer, EPPHAA can be solvent extracted from the crosslinked resin almost on a quantitative basis. Additive VCDHAA has residual epoxy functionality (structure II) and, not surprisingly, is less extractable by the solvent after curing (Figure 3).

Although it does not become chemically bound to the polymer, the additive EPPHAA does exhibit some catalytic effect on the cure, as was implied by the improved mechanical properties at low cure temperatures. The rate of consump-

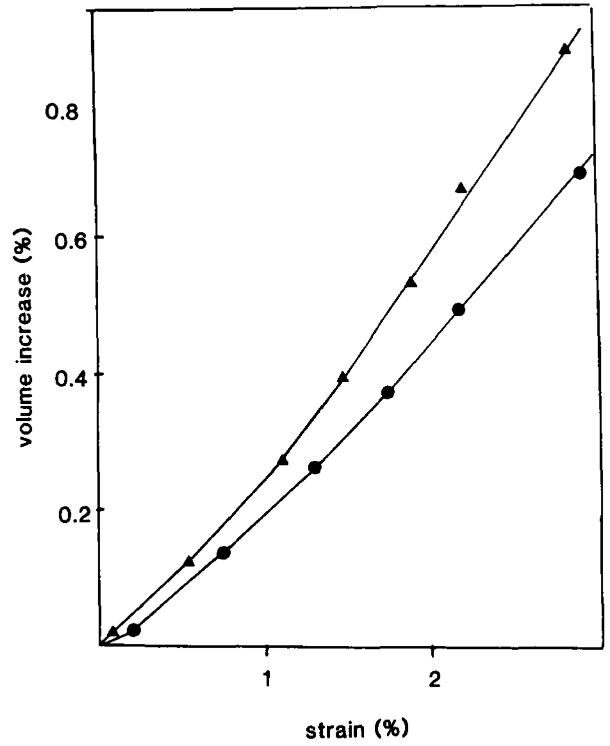

FIGURE 2 Volume change which occurs during a tensile test (●) control (▲▲) +30 phr EPPHAA.

tion of epoxy functionaltiy was increased by EPPHAA, although the low residual epoxy level at the end of a 150°C cure was unchanged from the control.[11]

In spite of having little effect on the final chemical state of the cured polymer, the additives obviously interact strongly with the polymer, as evidenced by an increased density. The data points in Figure 4 represent the density of EPPHAA-containing specimens. The dashed line in Figure 4 was calculated based upon additivity of the density of the polymer and EPPHAA. At 30 phr EPPHAA, an anomalous increase in density of at least 2% has occurred. For VCDHAA, such a simple calculation has less meaning because the additive becomes partially incorporated into the polymer network in a chemical sense.

The volume expansion with temperature is shown in Figure 5. The addition of 20 phr VCDHAA has reduced the coefficient of thermal expansion (CTE) at temperatures below Tg. There is also a significant reduction in Tg, and the magnitude of the effect is greater with EPPHAA than with VCDHAA. Other additive formulations are described elsewhere which produce either only a small decrease in Tg, or even produce a small increase.[13]

Figure 6 shows that the water uptake of the epoxy resin system can be reduced significantly by the presence of 20 phr VCDHAA. Note that the test was

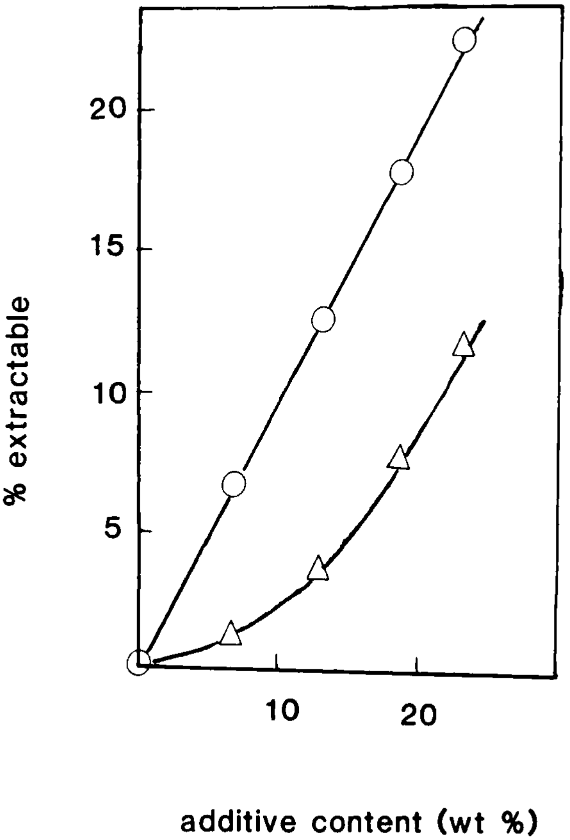

FIGURE 3 Extractibility of EPPHAA (○○) and VCDHAA (△△) from pulverized polymer.

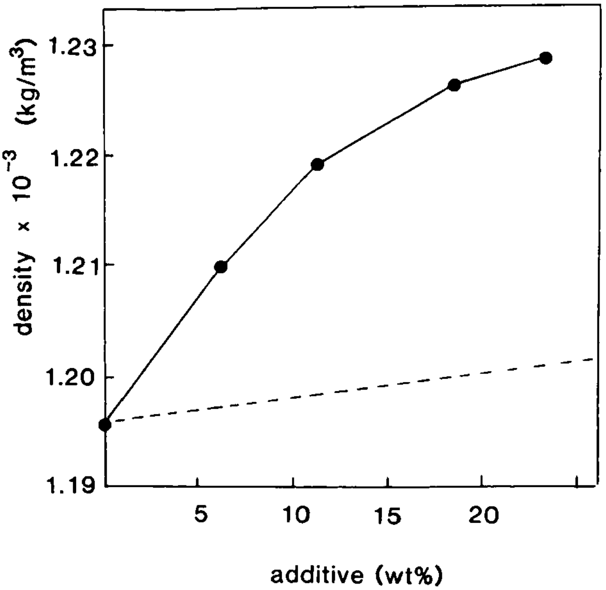

FIGURE 4 Density of the cured polymer. Dashed line denotes the density calculated assuming additivity of the densities of the polymer and of EPPHAA.

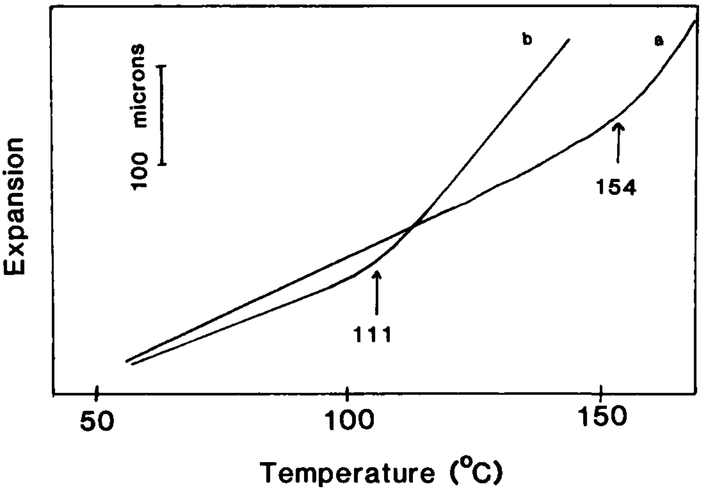

FIGURE 5 Thermal expansion by TMA. Heating rate 5°C/min (a) control (b) +20 phr VCDHAA.

conducted at room temperature over a prolonged period, rather than the more conventional immersion in boiling water, because we wished to distinguish between the effects of free volume reduction and the effect of a reduced Tg.

The dynamic mechanical properties of the crosslinked resin are reported elsewhere.[11,15] Briefly, the shear modulus (G') is increased by the additives at room temperature, as would be expected from the tensile data. At very low

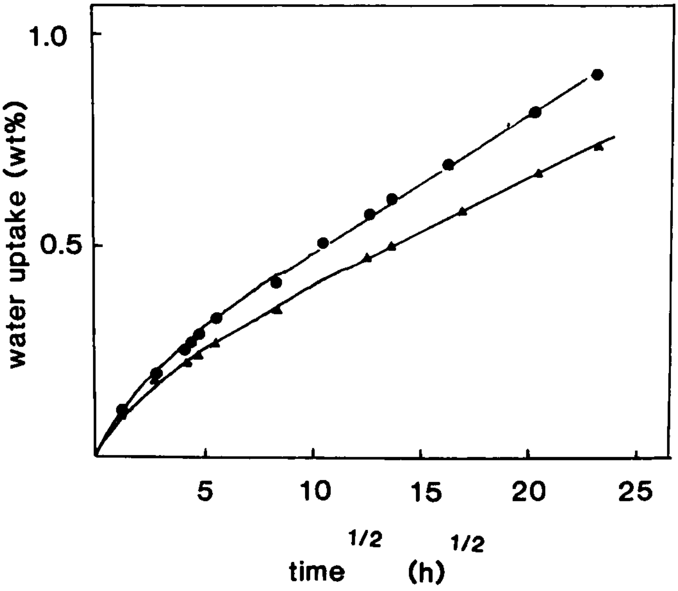

FIGURE 6 Gravimetric determination of water uptake on exposure to 95% humidity air at 25°C. (●) control, (▲▲) 20 phr VCDHAA.

temperatures (<−100°C) the moduli converge. The high temperature moduli are affected to varying degrees, depending on the additive, by the reduction in Tg. The low temperature relaxations, as indicated by peaks on tangent delta and the loss modulus (*G*″), are suppressed by the additives, consistent with a marked decrease in the mobility of the more flexible portions of the polymer backbone.[11,18]

B. Properties of Adhesive Joints

This portion of the work is still in its early stages, but some promising results are shown in Table I and Figure 7. The incorporation of 20 phr EPPHAA causes a consistent increase of about 20% in joint strength (Table I). While such an increase might appear modest, it should be recalled that loads of this magnitude are comparable to the shear strength of the resin, and so an order of magnitude improvement cannot be expected. Also, unlike many adhesive joint tests, the scatter of the data is relatively low (see error bars on Figure 7 which define the limits of scatter), and a 20% increase in joint strength can be considered as a significant improvement. There appears to be an optimum additive concentration for adhesive bonding, since 30 phr of EPPHAA produced a slight decrease in bond strength compared to 20 phr EPPHAA. The addition of 20 phr VCDHAA gave the highest bond strength, and research is continuing to optimize adhesive formulations. Large relative improvements are obtained if low-temperature-cured systems are considered. The beneficial effect of these additives on the low-temperature cure of Epon 828/MDA[15] translate into excellent adhesive bond properties for 80°C cured specimens (Table I).

The performance of these joints after immersion in 57°C water (Figure 7), illustrates the requirement for adequate interfacial bonding if the improved polymer properties are to translate into improved adhesive joint properties. For the first 50h of immersion, the improved polymer mechanical properties, together

TABLE I

Properties of torsional joints

High temp cured (1 h at 120°C + 2 h at 150°C)	Load at break (normalized)
control	100
+20phr EPPHAA	120
+30phr EPPHAA	117
+20phr VCDHAA	128
Low temp cured	
(8h at 80°C)	
+30 phr EPPHAA	>104
Epon 828/Versamid 140/Resorcinol	74
Epon 828/diethylene triamine	43

* These data represent the average of at least 6 specimens. For magnitude of scatter see Figure 7. (scatter of EPPHAA and VCDHAA specimens similar).

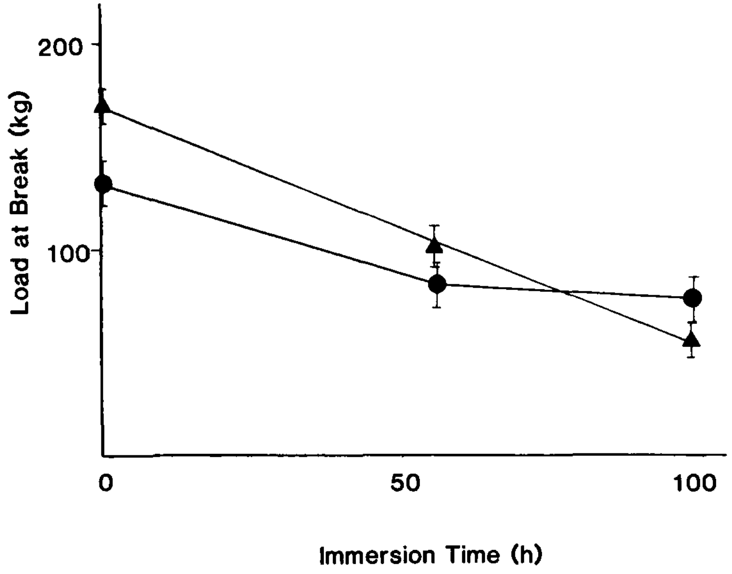

FIGURE 7 Adhesive joint strength as a function of time of exposure to water at 57°C, (●) control, (▲▲) +20 phr VCDHAA.

perhaps with a decrease in water uptake (*cf.* Figure 6), result in improved adhesive bond strength, but once interfacial bonding has degraded below a critical value, the benefits of the additives are lost.

DISCUSSION

The occurrence of an increased stiffness, increased strength, a yield before fracture, a decreased CTE, a decreased water sorption, and a low-cure temperature, makes these materials at least of potential interest as adhesives. We will attempt to explain the basis of these property improvements, and then speculate on the advantages and drawbacks of these materials in adhesive applications.

When a low molecular weight material is added to a polymer, the resultant free volume of the system (f) can be described by the relationship[18]

$$f = V_1 f_1 + V_2 f_2 + K V_1 V_2$$

where V_1 is the volume fraction of polymer and f_1 is the fractional free volume of the polymer, while V_2 and f_2 refer to the additive. K is an interaction parameter. The most common case (plasticization) is that the small additive molecule has a high f_2, while K is negative but small, and so a free volume increase occurs. If, however, the additive is a stiff polar molecule which interacts strongly with the polymer, a combination of a low f_2 and a large negative K can cause the free volume to decrease. Such a phenomenon is referred to as antiplasticization[6–9,11] and has been reported for several glassy thermoplastics.

The antiplasticization of crosslinked polymers has been less widely studied. Hata *et al.*[19] describe the addition of polychlorinated biphenyls (PCBs) and oligomeric species to an amine-cured epoxy resin, as have several Russian authors.[20,21] The relatively small increase in modulus, combined with the environmental unpopularity of PCB's and the marked depression in Tg, led to a decrease of interest in this area.

The decrease in free volume, associated with the anomalous increase in density of at least 2% will clearly lead to a decrease in mobility and hence an increase in modulus.[4,11,18] The more surprising aspect of the tensile curves is the occurrence of yielding before fracture. We attribute this phenomenon to the increase in free volume which occurs when the material is strained, although we again caution the reader that "ductility" in a tensile test does not necessarily equate with "toughness' in an impact fracture test. Figure 2 shows that there is a considerable increase in volume (ΔV_{strain}) as the specimen is subjected to tensile strain. Not all the extra volume produced by strain will be accessible to other segments for self diffusion, because of changes in molecular conformation and orientation, and so a correction factor (γ) is introduced such that the free volume change produced by strain ($\Delta V_{f,\text{strain}}$) is:

$$\Delta V_{f,\text{strain}} = \gamma \Delta V_{\text{strain}}$$

The free volume increase with temperature ($\Delta V_{f,\text{temp}}$) may be visualized in terms of the expansion volume (V_E), *i.e.* the amount by which the volume exceeds that of a crystalline form of that material at zero Kelvin. At temperatures below Tg, V_E increases with temperature with an expansion coefficient α_g while, after Tg, V_E increases more rapidly with an expansion coefficient α_l. (see, for example, Figure 5 to illustrate this process). Typically, values of V_E for polymers are 12–15%. Undoubtedly, this is an overestimate of the true free volume available for segmental diffusion, because not all the extra space generated by thermal motion will be accessible to other segments. Therefore, a correction factor (β) is introduced to allow for the increase in molecular dimensions with temperature. At temperatures less than Tg:

$$\Delta V_{f,\text{temp}} = \beta \Delta V_E \tag{1}$$

The free volume change produced by strain can be equated to the free volume change produced by temperature:

$$(\gamma \Delta V_{\text{strain}})_0^{\varepsilon} = (\beta \Delta V_E)_T^{T^*} \tag{2}$$

where ε is the strain, T is the test temperature and T^* is now a fictive sample temperature,[22] *i.e.* the temperature at which an unstrained sample has an equivalent free volume. Yielding will occur when T^* exceeds Tg.

As a first approximation the two constants β and γ may be equated because factors which are responsible for an increase in occupied volume with temperature (making $\beta < 1$) will also produce an increase in occupied volume with strain

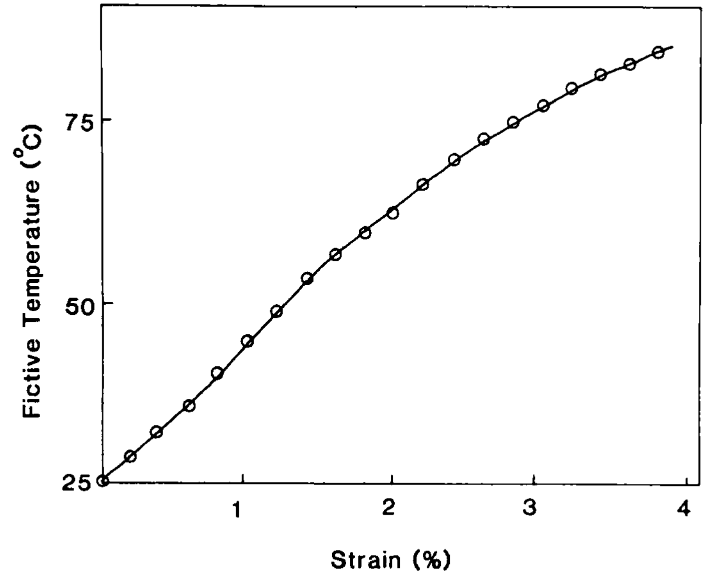

FIGURE 8 Fictive temperature *versus* tensile strain for sample containing 30 phr EPPHAA.

(making $\gamma < 1$). A ductile failure mode, *i.e.* yielding before failure, will occur when

$$(\Delta V_{\text{strain}})_0^{\varepsilon_y} > (\Delta V_E)_T^{T_g} \tag{3}$$

This very simplistic model may be tested with the data we have available in Figure 2 and the results of TMA measurements. A graph of fictive temperature *vs* strain may be constructed using equation 2, and is shown in Figure 8. At strains of about 5%, the fictive temperature of the EPPHAA containing specimen will exceed 100°C, which is approaching the Tg. A similar analysis for VCDHAA-containing specimens predicts yielding at a higher fictive temperature, as expected from the higher Tg of the material. For the control, a combination of a higher thermal expansion coefficient (Figure 5) and a smaller strain-induced increase in volume (Figure 2) mean that the fictive temperature is lower for a constant strain. For example, a strain of 5% yields of fictive temperature of <80°C, which is far below the Tg. In spite of the crudeness of the approximations made here, this semi-quantitative agreement of prediction and experiment can be considered as strong support for the proposed model.

The prediction of ultimate material strength is complicated by its interelationship with the flaw distribution and the mechanism of fracture. As a first approximation, we may apply the Griffith failure criterion, which assumes the largest flaw is a sharp crack of length L. The ultimate tensile strength is given by[23]

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

where W is the work done in generating unit area of fracture surface and E is the Young's modulus. If no change in flaw size is assumed, and given the relatively small effect on K_{Ic}, the additives would be expected to increase the strength to a slightly lesser degree than the increase in the modulus, as is indeed observed (Figure 1).

A decrease in water sorption is entirely consistent with a reduction in free volume, and hence of penetrant mobility. However, it should be cautioned that we have incorporated appreciable amounts of hydrophilic amide and hydroxyl functionality and so at high temperatures, when the free volume reduction is counterbalanced by a lower Tg, the equilibrium water content could be increased. The water uptake of the polymer and the performance of an adhesive joint may, therefore, depend appreciably on the conditions of the test.

Our initial adhesive joint data indicate that these materials may be beneficial in some adhesive bonding situations, particularly when high stiffness and strength are required. The low cure temperature and reduced CTE could be of benefit for relatively large structures. The apparent improvement on hygrothermal resistance indicates that a reduction in free volume may provide a route to reducing water access to an adhesive bond. It should be cautioned, however, that as yet we have no fatigue and long term durability data, which are crucial to successful adhesive performance.

There are several other areas which we are exploring with these additives. Polyimides have many of the drawbacks in mechanical properties which are observed in epoxies, and we observe qualitatively similar beneficial effects to those reported here with both thermoplastic and thermosetting polyimides. Rubber toughening will also provide a route to increasing fracture toughness and we have some evidence that these stiffening additives (which we describe by the generic name of "fortifiers" and are manufactured under license by Polysar Ltd. of Sarnia, Ontario) may operate in a synergistic fashion with rubber tougheners. Finally, we are exploring the use of these materials as primers, so as to produce a gradation of properties from a metal surface into the adhesive, and will be reporting the results elsewhere.

Acknowledgement

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