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Phase-separation studies of heat-cured ATU-flexibilized epoxies

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Chemical incorporation of a flexible molecule into a heat-cured epoxy offers an important route by which to toughen the epoxy and tailor its ultimate material properties. Acrylate-terminated urethane (ATU) flexibilizers containing polypropylene glycol have been employed in the present work to modify epoxies composed of a diglycidyl ether of bisphenol-A and bis(4-aminocyclohexyl) methane. Differential scanning calorimetry, dynamic mechanical analysis and electron microscopy reveal that the flexibilizer and epoxy undergo phase separation during cure when the flexibilizer loading or molecular weight is sufficiently high. Partial phase miscibility, deduced from both glass transition temperature shifts and stress–relaxation behaviour, is interpreted here in light of thermodynamic and free-volume considerations.

(Keywords: rubber-toughened epoxies; phase separation; acrylate-terminated urethanes; dynamic mechanical analysis; differential scanning calorimetry; electron microscopy)

INTRODUCTION

One of the most important means by which thermoset epoxies can be toughened for specialized end-use applications (e.g. adhesive coatings) is through chemical incorporation of a flexible moiety[1–3]. Numerous experimental studies have been devoted to elucidating the mechanism by which an added flexibilizer improves epoxy toughness, and various conceptual theories have been proposed. Several researchers[4–7], for example, have proposed that a flexibilizer helps to promote crazing of the epoxy matrix in close vicinity to flexibilizer dispersions, whereas Kunz-Douglass and co-workers[8,9] attribute rubber toughening to the elasticity of the flexibilizer. A mechanism that combines shear yielding and enhanced epoxy crazing has been suggested by Bucknall and Yoshii[10]. Flexibilizer cavitation, followed by shear yielding, is presently the most widely accepted explanation for epoxy toughening[11–17], although the precise mechanism of stress dissipation remains the subject of continued investigation.

An issue that must be addressed when the ultimate mechanical properties are to be tailored for a specific application is the extent of phase miscibility between the epoxy and added flexibilizer, since all or part of the flexibilizer may phase-separate from the epoxy. Partridge[3] points out that the extent of phase separation should be sufficiently high to avoid adversely altering desirable epoxy properties (e.g. the glass transition temperature, T_g). In the case of a biphasic material, as in conventional polymer blends and alloys, the morphology of the flexibilizer phase is also expected to play a significant role in property development. Bascom *et al.*[11] as well as Chen and Jan[18], have found, for instance, that a dispersed flexibilizer phase possessing a multimodal size distribution is superior to one with a unimodal size distribution.

The design of new materials requires a complete understanding of the kinetics governing cure[19–24], the diffusion of reactive moieties[25–29] and the dynamics of phase separation[30–35]. In flexibilized epoxies, these phenomena are inherently coupled. For example, as cure proceeds, the molecular weight and branching of the epoxy both increase, and the diffusion rate of reactive species decreases while the driving force favouring phase separation increases. If phase separation is rapid relative to gelation, then the resulting morphology and corresponding properties are dictated by thermodynamic considerations. In the present work, we examine the morphological, mechanical and thermal properties of flexibilized heat-cured epoxies and present a means of predicting the phase behaviour of such systems.

EXPERIMENTAL

Materials

The epoxy resin employed in this work was Epon 828, a diglycidyl ether of bisphenol-A (DGEBA) manufactured by Shell Development Co., and the curing agent was bis(4-aminocyclohexyl) methane (PACM),

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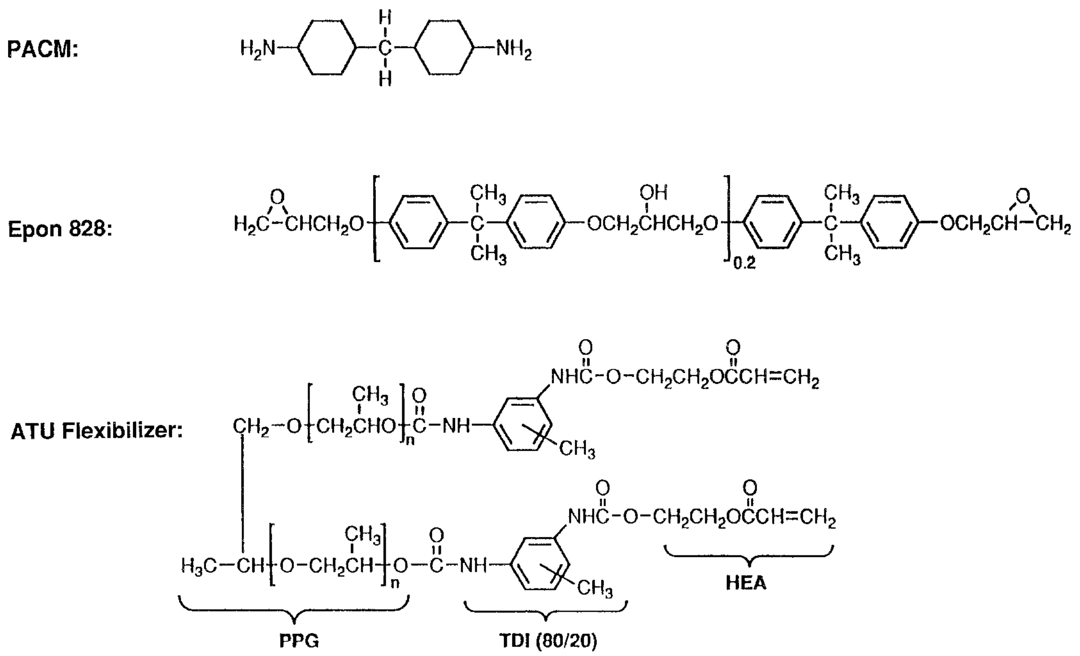

Figure 1 Chemical representation of the moieties employed to produce the flexibilized epoxies examined in this work. The crosslinking agent, bis(4-aminocyclohexyl) methane (PACM), is shown at the top, while the Epon 828 epoxy resin, a diglycidyl ether of bisphenol-A (DGEBA), is displayed below. The acrylate-terminated urethane (ATU) flexibilizers consist of polypropylene glycol (PPG) and hydroxyethylacrylate (HEA), which are coupled via toluene diisocyanate (TDI)

produced by Air Products and Chemicals, Inc. (Note that DGEBA is used hereafter to denote the neat Epon 828/PACM epoxy.) These moieties are depicted schematically in *Figure 1*. Also illustrated in *Figure 1* is the acrylate-terminated urethane (ATU) flexibilizer, which consists of polypropylene glycol (PPG) end-capped with hydroxyethylacrylate (HEA). The weight ratio of flexibilizer to epoxy (Φ) and the molecular weight of the PPG portion of the flexibilizer (M) were both varied in this study to ascertain their respective effects on morphology and bulk properties.

Synthesis of the ATU flexibilizer prepolymers was conducted via a two-stage single-reactor process. In the first stage, an uncapped flexibilizer was prepared by adding 1 mol of a PPG to 2.1 mol of 80 wt% 2,4- and 20 wt% 2,6-toluene diisocyanate (TDI). The mixture was subsequently heated to 70–80°C under continuous agitation for 8 h. In the second stage of the process, the mixture was cooled to 50°C and then combined with 500 ppm of methyl-hydroquinone and 1 molar HEA equivalent (relative to the initial TDI charge). Once the reaction components were thoroughly mixed, 0.5 wt% dibutyltin dilaurate catalyst (DABCO T-12) was added, and the condensation reaction to form urethane was permitted to proceed for at least 1 h. Molecular weight distributions of the resultant prepolymers were ascertained by gel permeation chromatography (g.p.c.).

Flexibilized epoxy plaques were prepared by first mixing Epon 828 resin with an ATU flexibilizer of a specific M at a loading level Φ. Values of Φ explored here were 0.11, 0.43 and 1.0. Each mixture was subsequently heated to 60°C and degassed in a vacuum oven for approximately 30 min. A stoichiometric quantity of PACM, based upon the equivalent weight of the epoxy/ATU solution and the number of active hydrogen sites available in PACM, was then added. The resulting mixture was poured into a stainless steel mould measuring 15.2 cm × 15.2 cm × 0.3 cm. The cure time and temperature were held constant at 3 h and 120°C, respectively.

Methods

The thermal properties of the cured formulations were assessed by differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (d.m.a.). The d.s.c. data were collected from −100 to 200°C with a DuPont 912 calorimeter operated at a heating rate of $10°\mathrm{C\,min}^{-1}$. D.m.a. experiments were conducted on a Rheometrics Dynamic Analyzer (RDA II) operated in a shear mode with a torsion fixture. Shear storage (G') and loss (G'') moduli were obtained at an oscillatory frequency of $6.28\,\mathrm{rad\,s}^{-1}$ between −150 and 250°C in intervals of 6°C. Data were acquired after 1 min at each temperature to ensure isothermal conditions, and the experiments were performed under dry nitrogen to reduce thermooxidative degradation. Tensile stress relaxation experiments were performed on a Rheometrics Solids Analyzer (RSA II) using a three-point bending fixture. Relaxation data were collected for each formulation at 24°C by imposing a 0.1% strain and monitoring the stress (σ) decay over the course of approximately 200 s.

Specimens from plaques with $\Phi = 0.11$ were examined with scanning and transmission electron microscopies (SEM and TEM, respectively). For SEM, some plaques were fractured in liquid nitrogen and imaged without a conductive coating at 1 kV on a Jeol JSM-6400F field-emission microscope. Specimens were also fractured at ambient temperature, sputter-coated with 20 nm of Au, and imaged on the same microscope at 5 kV. Ultrathin specimens for TEM were produced by sectioning cryofractured plaques with a 35° cryodiamond knife on a Reichert-Jung Ultracut-S microtome maintained at −100°C. To facilitate selective staining, 1,4-octadiene was applied to sections for 1 min, after which time

Table 1 Molecular weights and glass transition temperatures of ATU flexibilizer prepolymers

Flexibilizer designation	Polyol M ($\mathrm{g\,mol^{-1}}$)	2:1 Oligomer[a] ($\mathrm{g\,mol^{-1}}$)	3:2 Oligomer[a] ($\mathrm{g\,mol^{-1}}$)	4:3 Oligomer[a] ($\mathrm{g\,mol^{-1}}$)	$\bar{M}_w$ ($\mathrm{g\,mol^{-1}}$)	T_g[b] (°C)
1000 ATU	1 000	1 580	2 760	3 930	2 170	−18
2000 ATU	2 000	2 580	4 760	6 930	3 670	−39
3000 ATU	3 000	3 580	6 760	9 930	5 170	−50
4000 ATU	4 000	4 580	8 760	12 930	6 670	−52

[a] Calculated from stoichiometry
[b] Obtained from d.s.c. ($10°\mathrm{C\,min^{-1}}$)

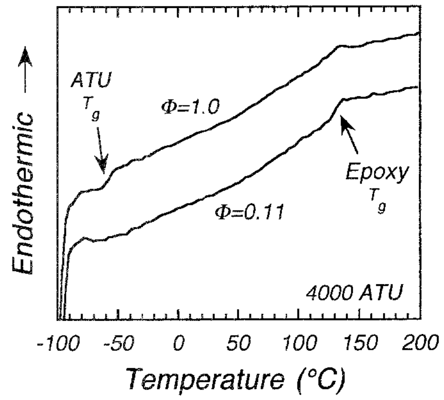

Figure 2 D.s.c. thermograms obtained from two different DGEBA epoxies toughened with the 4000 ATU flexibilizer. Both traces clearly display the epoxy T_g at ~132°C, whereas only the $\Phi = 1.0$ formulation exhibits a discernible second T_g in the vicinity of −57°C

surface excess 1,4-octadiene was removed under vacuum. Residual 1,4-octadiene remaining within elastomer-rich regions was permitted to react with the vapour of 2% OsO_4(aq) for 90 min. Images were obtained with a Topcon 002B electron microscope operated at 100 kV.

RESULTS AND DISCUSSION

Flexibilizer prepolymers

The ATU flexibilizers are known, from g.p.c., to possess a trimodal molecular weight distribution. This characteristic, indicative of oligomerization during prepolymer synthesis, reveals that the relative abundance of the TDI/PPG condensation products, in TDI:PPG ratios of 2:1 (A), 3:2 (B) and 4:3 (C), is 6:3:1 A:B:C. Molecular weights corresponding to the three g.p.c. peaks have been derived from polystyrene standards (since no appropriate standard for these materials is available) and are summarized in *Table 1*. Although the polydispersities of these materials could, in practice, be reduced, the ATU flexibilizers produced here are satisfactory for anticipated end-use applications. For brevity, the flexibilized epoxies presented in this work will be hereafter referenced by the molecular weight of the polyol used to form the flexible segment. These designations, as well as the $\bar{M}_w$ of each molecular weight distribution, are also included in *Table 1*.

Property analysis

Glass transition behaviour. Cured epoxy formulations prepared with the low-molecular-weight flexibilizer (i.e. 1000 ATU) appear optically transparent to the unaided eye at each of the three Φ investigated, while those containing the 2000 ATU flexibilizer are transparent but cloudy. These observations are consistent with phase homogeneity on a size scale greater than ~0.2 μm. Formulations produced with the 3000 and 4000 ATU flexibilizers, however, yield opaque plaques at every Φ investigated. Such behaviour is strongly suggestive of large-scale phase separation. Thus, the molecular weight of the PPG segment (M) appears largely responsible for promoting phase separation in these systems.

Determination of the lower and upper glass transition temperatures can provide insight into the degree of phase separation (or mixing) in multicomponent polymer systems. In the present case, the upper T_g corresponds to DGEBA, while the lower T_g is attributed to the ATU flexibilizer. A higher degree of phase mixing is expected *a priori* to increase the lower T_g and suppress the upper T_g, although deviations from this general trend have been observed in rubber-toughened plastics such as acrylonitrile–butadiene–styrene (ABS)[36] and aramid–butadiene multiblock copolymers[37]. Results obtained with d.s.c. from two 4000 ATU flexibilized epoxies with Φ equal to 0.11 and 1.0 are displayed in *Figure 2*. The epoxy T_g at ~132°C is visible in each thermogram, while a lower ATU T_g at −57°C is only evident in the $\Phi = 1.0$ formulation, even though the $\Phi = 0.11$ formulation also appears opaque. Similar behaviour has been observed with the 3000 ATU system, suggesting that d.s.c. analysis is not sufficiently sensitive to detect the ATU T_g at low flexibilizer loadings.

Thermograms collected from the neat flexibilizers clearly indicate that the ATU T_g decreases with increasing M (see *Table 1*). This observation is in marked contrast to the dependence of T_g on M typically observed[38,39] in high polymers. Since the T_g provides a measure of the free volume present in a material[40], the usual increase in T_g with increasing M can be attributed to a reduction in the influence of chain ends, which tend to increase the local free volume via enhanced segmental motion. The decrease in T_g with increasing M, plotted in *Figure 3*, implies that the ATU free volume increases with M. This trend may reflect the fact that these oligomeric materials consist of two different moieties, namely the PPG backbone and the TDI/HEA terminal functionality. *Figure 3* also demonstrates that the ATU T_g can be accurately described by $T_g^{\infty} + B/\bar{M}_w$, where $T_g^{\infty} = 203\,\mathrm{K}$ and $B = 1.13 \times 10^5\,\mathrm{g\,K\,mol^{-1}}$. (The literature value[41] for the T_g^{∞} of PPG is 198 K.)

Representative d.m.a. temperature scans of the neat epoxy and two flexibilized formulations (1000 and 3000 ATU with $\Phi = 0.43$) are presented in *Figure 4*. While the shear moduli (G', G'') of the three specimens displayed in *Figure 4a* are qualitatively similar, each of

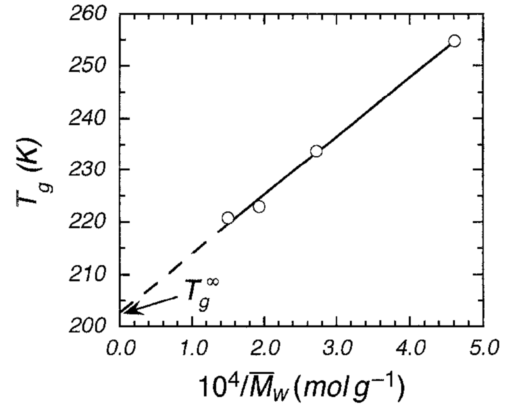

Figure 3 Variation of the neat flexibilizer T_g with inverse $\bar{M}_w$. The solid line corresponds to a linear regression and, upon extrapolation (dashed line), yields $T_g^\infty \approx 203$ K, which is in excellent agreement with the T_g^∞ of pure PPG (198 K)[41]

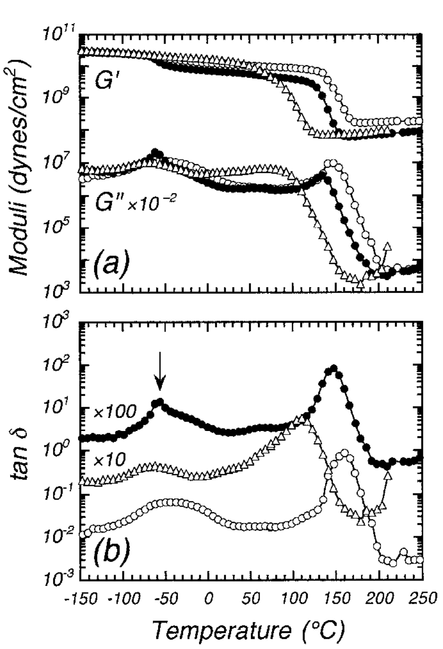

Figure 4 Storage (G') and loss (G'') moduli (a) as functions of temperature for the neat epoxy (○) and two ATU formulations with $\Phi = 0.43$: 1000 ATU (△) and 3000 ATU (●). Corresponding tan δ curves are displayed in (b). These results establish the existence of α (T_g) and β transitions in DGEBA. While the 1000 and 3000 ATU systems also exhibit these transitions, the tan $\delta(T)$ data of the 3000 ATU-based formulations indicate the presence of a second α peak superimposed on the epoxy β transition (arrow). This transition corresponds to the T_g of the flexibilizer

the tan δ curves shown in *Figure 4b* clearly reveals the presence of at least one mechanical transition. The tan δ curve for the neat epoxy, for instance, exhibits an α (T_g) transition at 142°C and a broad β transition centred around −50°C. No other distinguishable transitions are evident. These two transitions are also present in the flexibilized 1000 and 3000 ATU formulations. The tan δ spectrum obtained from the 1000 ATU flexibilized epoxy appears similar to spectra from both the neat epoxy and the 2000 ATU formulation (not shown here), whereas the 3000 ATU formulation possesses an additional tan δ peak (at about −60°C) which is superimposed on the epoxy β transition.

Since the additional tan δ peak from the 3000 ATU system is relatively sharp and occurs in close proximity to the neat flexibilizer T_g (see *Table 1*), it presumably corresponds to the T_g of the chemically incorporated flexibilizer and is therefore indicative of phase separation between the dispersed flexibilizer and the epoxy matrix (in agreement with optical assessment). While this second T_g is observed in all of the phase-separated 3000 and 4000 ATU formulations, the dependence of the ATU T_g on Φ and M is not presented here due to complications arising from the superposition of this lower T_g on the epoxy β transition. The influence of Φ and M on the upper (epoxy) T_g is, on the other hand, clearly discernible from d.m.a. temperature sweeps and is shown in *Figure 5*. In the case of the 1000 ATU formulation, the upper T_g decreases dramatically with Φ, signifying considerable phase mixing between the flexibilizer and the epoxy. Epoxy T_g suppression is also observed, though to a lesser extent, in the case of the 2000 ATU modified formulation. According to *Table 1*, the neat 1000 ATU flexibilizer has the highest T_g, and the lowest free volume, of the entire flexibilizer series and should therefore have the least impact on the epoxy T_g. However, as seen in *Figure 5*, the 1000 ATU flexibilizer has a more marked effect on the upper T_g than does the 2000 ATU. This behaviour indicates that not all of the 2000 ATU flexibilizer serves to depress the epoxy T_g and suggests that the 2000 ATU formulation is phase-separated. This issue is addressed again later.

When M is increased further and large-scale phase separation is observed to occur, the epoxy T_g is relatively unaffected by the addition of flexibilizer. In fact, as seen in *Figure 5*, the upper T_g in the 3000 and 4000 ATU formulations is about 10°C lower than that of the neat epoxy. All of these measurements of the epoxy T_g are reproducible to ≈1°C (on the first scan). The decrease in epoxy T_g probably reflects a small amount of flexibilizer present in the epoxy phase.

Network formation. The degree of cure in a heat-cured epoxy resin provides valuable insight into the three-dimensional crosslinked epoxy network, and may be assessed in several different ways. One is to compare the crosslink density at any time with the ultimate crosslink density, while another is to measure the diminishing exotherm observed in partially cured epoxies subjected to successive d.s.c. scans. Thermograms obtained from neat epoxies cured at 120°C for 3 h do not exhibit an appreciable residual exotherm, whereas those from plaques cured for one week at room temperature display substantial exotherms upon heating. In addition, the plaques cured at room temperature exhibited T_gs approximately 70°C lower than their heat-cured counterparts. While a successive d.s.c. scan of the heat-cured epoxy typically results in a 5–6°C increase in T_g, a 50°C T_g increase is observed in plaques cured at ambient temperature. This combination of results is interpreted to mean that the heat-cured plaques are fully cured.

The degree of crosslinking is quantified through the effective molecular weight between crosslinks, M_c, which can be estimated by first assuming an idealized network and then implementing the classical theory of rubber elasticity. Upon doing so, M_c is related to the equilibrium shear modulus (G_e) at infinitesimal deformations through

$$G_e = \frac{\gamma \rho R T}{M_c} \tag{1}$$

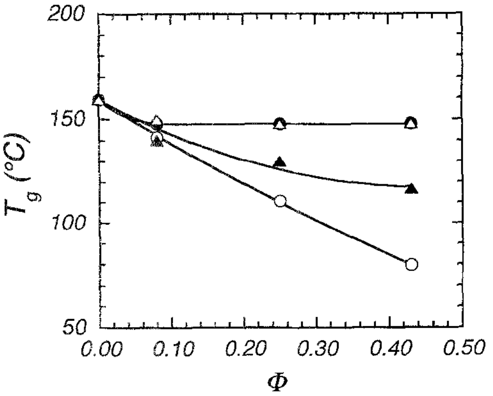

Figure 5 Effect of Φ on the upper (epoxy) T_g for four flexibilized-epoxy formulations: 1000 ATU (○), 2000 ATU (▲), 3000 ATU (●) and 4000 ATU (△). Addition of the 1000 ATU flexibilizer significantly reduces the upper T_g at large Φ due to phase mixing

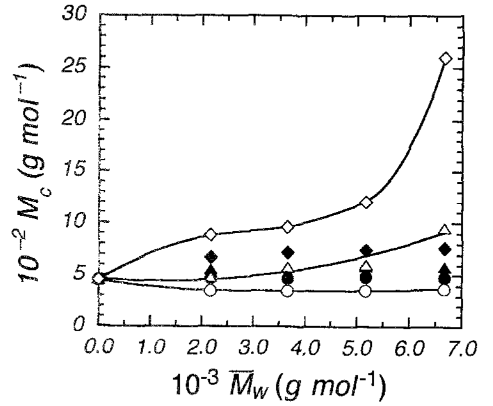

Figure 6 Calculated and predicted values of the effective molecular weight between crosslinks (M_c) as functions of $\bar{M}_w$ and flexibilizer contents (Φ): 0.0 (○), 0.11 (△) and 1.0 (◇). Open symbols correspond to M_c values derived from the rubbery plateau G', whereas filled symbols denote predictions from equation (3). Solid lines are guides to facilitate determination of data trends

where the factor $\gamma \approx 1$, ρ is the mass density, R is the gas constant and T is the absolute temperature. Approximating ρ as 1 g cm^{-3} and considering only small strains, equation (1) becomes

$$M_c = \frac{RT}{G'} \tag{2}$$

where G' is the shear storage modulus measured in the rubbery plateau region above T_g. Values of M_c determined from equation (2) for all the heat-cured epoxies examined in this work are shown as a function of flexibilizer $\bar{M}_w$ in *Figure 6*. It should be noted that classical rubbery plateaus are not observed in formulations possessing large Φ.

Also displayed in *Figure 6* are theoretical predictions for M_c obtained from the expression proposed by Scanlon[42], i.e.

$$M_c \approx 2\rho\left(\sum_{f=3}^{\infty} fC_f\right)^{-1} \tag{3}$$

Here, ρ is again taken as 1 g cm^{-3} and C_f is the concentration of polyfunctional reactants (expressed in mol cm^{-3} of cured epoxy). *Figure 6* reveals that the predicted M_c of the neat cured epoxy (440 g mol^{-1}) agrees very well with the M_c derived from d.m.a. (450 g mol^{-1}). As Φ is increased, however, experimental data and predictions differ significantly, with the predictions overestimating the M_c data at low Φ (= 0.11) and, conversely, underestimating the data at high Φ (= 1.0). These inconsistencies are attributed to the absence of an ideal, homogeneous network [upon which equations (1) and (2) are derived] for each of the flexibilized formulations.

Inhomogeneous networks are expected *a priori* to develop in the formulations wherein phase separation precedes gelation. Network formation relies on chemical-reaction efficiency, which, in turn, depends on the mutual diffusion rates of the reacting molecules. A phase boundary between the epoxy matrix and a flexibilizer dispersion effectively reduces the probability of chemical reaction between epoxy and flexibilizer by acting as an energy barrier to molecular diffusion. Alteration of the crosslinked epoxy network through phase separation must therefore be considered in the flexibilized epoxies examined here, especially considering that PACM should preferentially reside within the epoxy, rather than the flexibilizer phase (discussed later).

Stress–relaxation behaviour. The mechanical properties of polymeric materials strongly depend on the characteristic time scale required for individual chains (or network, as in the case of a crosslinked epoxy) to respond to an imposed deformation[43]. One approach by which to obtain such time scale information is to perform stress–relaxation experiments. Stress–relaxation curves obtained from the neat DGEBA epoxy and three 1000 ATU formulations (with varying Φ) are presented in *Figure 7a*. Here, σ_n is used to denote stress normalized with respect to initial stress. Within the time frame of the experiment, the neat heat-cured epoxy is incapable of relaxing beyond 6% once it is subjected to a 0.1% strain. As the concentration of flexibilizer is increased, however, stress dissipation is greatly facilitated, as best demonstrated by the Φ = 1.0 formulation. The dependence of σ_n (evaluated at 200 s) on Φ is presented for 1000 ATU materials in *Figure 7b*.

In the same fashion, normalized stress–relaxation curves from formulations with Φ = 0.11 and various polyol molecular weights are shown in *Figure 8a*. As in *Figure 7a*, the neat epoxy relaxes the least in the series. An interesting feature evident in *Figure 8a* is that the relaxation curves decrease when the PPG molecular weight is relatively low and then increase as M is increased further. This apparent trend, suggesting that a particular M imparts maximum flexibility to the epoxy, is more clearly seen in *Figure 8b*, in which σ_n at 200 s is provided as a function of PPG M. In addition to the flexibilizers listed in *Table 1*, a 425 ATU formulation (possessing $\bar{M}_w$ of 1306 g mol^{-1}) and a 50:50 blend of the 1000 and 2000 ATU formulations (referred to as 1500 ATU) are included in *Figure 8b* to help deduce the flexibilizer which imparts greatest stress dissipation. These results clearly demonstrate that the observed minimum σ_n corresponds to the 1000 ATU flexibilizer. Recall from *Figure 5* that epoxy T_g suppression is greatest in the 1000 ATU formulation.

Another characteristic of *Figure 8b* is that the 4000 ATU formulation comes closest to exhibiting the same normalized stress (at 200 s) as the neat epoxy, implying that little of the flexibilizer is phase-mixed

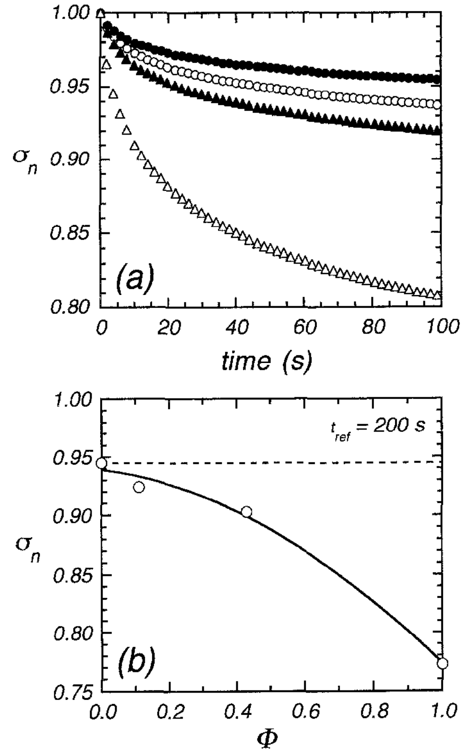

Figure 7 Normalized stress–relaxation curves (a) for four fully-cured 1000 ATU flexibilized epoxies possessing different loadings (Φ): 0.0 (●), 0.11 (○), 0.43 (▲) and 1.0 (△). With little flexibilizer, the formulation upon 0.1% strain does not relax significantly over the course of the experiment. In (b), σ_n at a reference time (t_{ref}) of 200 s is shown as a function of Φ and reveals that, as Φ is increased, stress dissipation is greatly enhanced

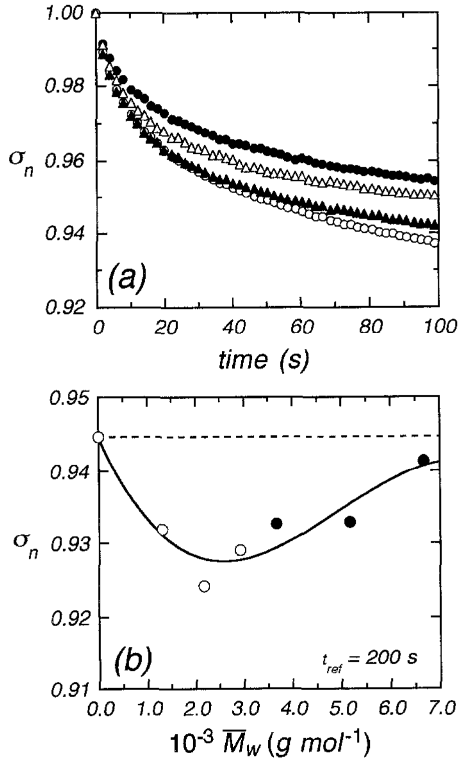

Figure 8 Normalized stress–relaxation curves (a) for four heat-cured materials possessing $\Phi = 0.11$ and different flexibilizers: neat epoxy (●), 1000 ATU (○), 2000 ATU (▲) and 4000 ATU (△). As the PPG chain length is increased, σ_n initially decreases, reaches a minimum, and increases. This trend is evident in (b), in which σ_n at 200 s is presented as a function of flexibilizer $\bar{M}_w$ for seven different formulations. Filled symbols in (b) denote phase-separated materials

within the epoxy matrix (again in agreement with the T_g measurements provided earlier). The response of the 3000 ATU material, on the other hand, differs noticeably from that of the 4000 ATU, suggesting that some of the 3000 ATU flexibilizer is solubilized within the matrix. It appears, then, that stress–relaxation is very sensitive to the extent of phase mixing in flexibilized epoxies. Accordingly, since the 2000 ATU-based formulation exhibits a similar stress–relaxation response as the 3000 ATU system, it is also expected to be partially phase-separated, in qualitative agreement with the results shown in *Figure 5*.

Morphological characteristics

In the previous section, thermal and mechanical property analyses and qualitative optical assessment have provided conclusive evidence that the 3000 and 4000 ATU flexibilizers phase-separate from the epoxy matrix. *Figure 9* consists of a series of SEM micrographs obtained from specimens of the 1000, 2000, 3000 and 4000 ATU-based formulations ($\Phi = 0.11$) fractured at ambient temperature. According to the micrographs of the fracture surfaces shown in this figure, the 2000, 3000 and 4000 ATU materials each exhibit holes or indentations, while the 1000 ATU flexibilized epoxy appears topologically homogeneous. The holes and indentations evident in *Figures 9b–d* are interpreted as domains of phase-separated flexibilizer which, due to the rubbery nature of the ATU flexibilizer at ambient temperature, have undergone cavitation upon fracture. This behaviour is consistent with the low-voltage SEM micrograph presented in *Figure 10*. Dispersed flexibilizer-rich domains in the cryofractured 4000 ATU formulation shown in this micrograph remain intact since PPG undergoes brittle fracture as a glass at liquid nitrogen temperatures.

Since a fracture plane follows a trajectory along the path of least resistance through a composite material, stereological considerations dictate that only the maximum, not mean, diameter of flexibilizer-rich dispersions can be estimated from the holes or indentations visible in fracture surfaces. Dispersion diameters measured from micrographs such as those presented in *Figure 9* are plotted as a function of ATU $\bar{M}_w$ in *Figure 11* and are seen to increase substantially with flexibilizer chain length. The dispersions in the 3000 and 4000 ATU-based formulations clearly exceed the optical limit for transparency (~0.2 μm) and are therefore responsible for the observed opacity in heat-cured plaques.

Transmission electron micrographs of each formulation, preferentially stained with a combination of 1,4-octadiene and OsO_4 as described earlier, are provided in *Figure 12*. If phase separation between the flexibilizer and epoxy occurs, residual 1,4-octadiene remains within the flexibilizer phase, which possesses more free volume than the epoxy phase[44,45]. The 1000 ATU flexibilized epoxy (*Figure 12a*) appears to possess weakly stained (flexibilizer) dispersions measuring less than 50 nm in diameter, whereas the 2000 ATU system (*Figure 12b*) exhibits larger dispersions (about 100 nm in diameter). The existence of dispersions in *Figure 12a* indicates that phase separation occurs in the 1000 ATU material, but not to the same extent as in the other toughened epoxies examined here. *Figure 12b* supports earlier macroscopic-property evidence (e.g. the epoxy T_g depression in *Figure 6*, the stress–relaxation behaviour seen in *Figure 8* and the SEM micrograph in *Figure 9b*), indicating that this

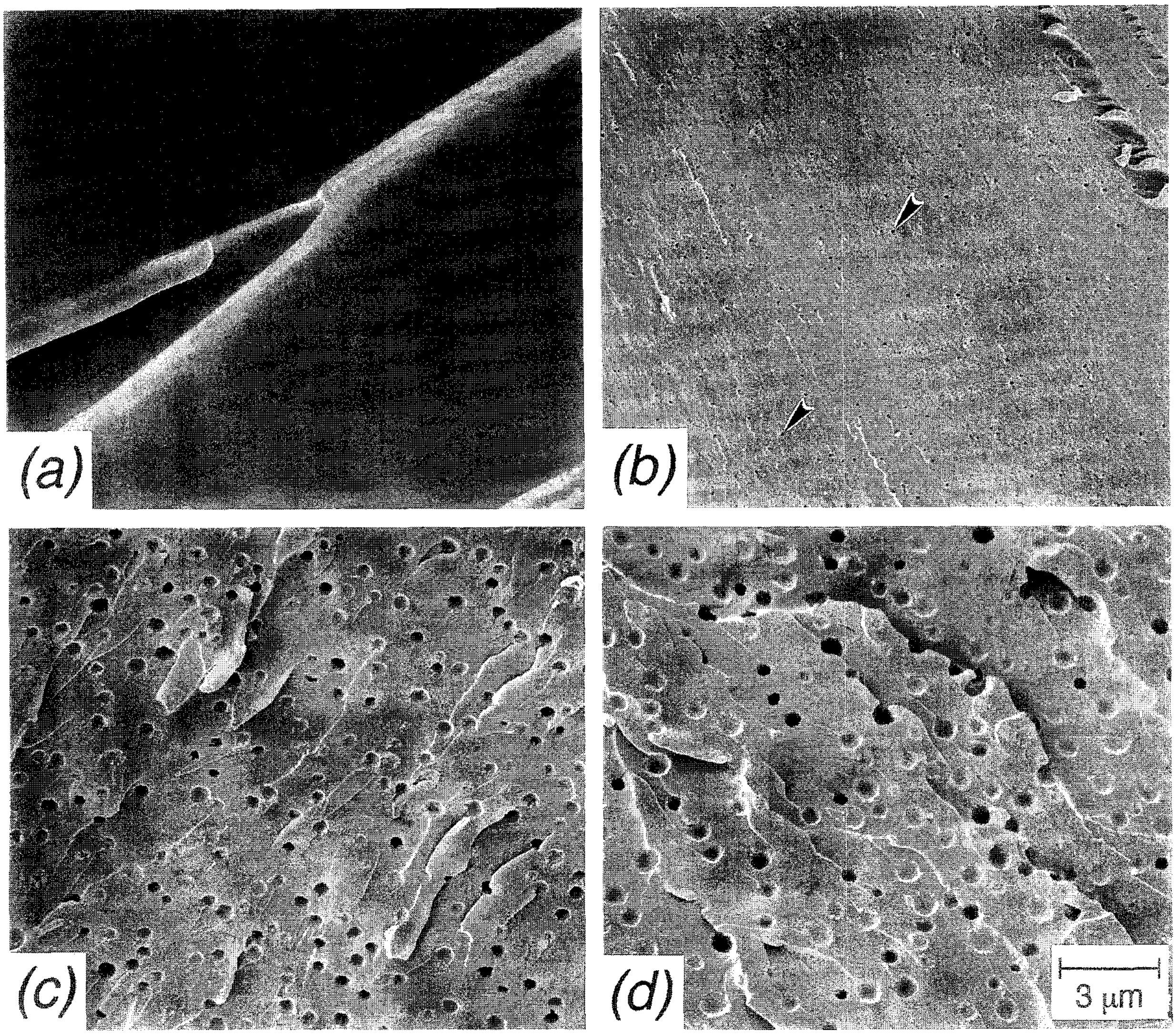

Figure 9 Series of conventional SEM micrographs obtained from flexibilized epoxies with $\Phi = 0.11$: (a) 1000 ATU, (b) 2000 ATU, (c) 3000 ATU and (d) 4000 ATU. Since the ATU flexibilizers are rubbery at ambient temperature and cavitate during fracture, the holes and indentations seen in some of these micrographs, highlighted by arrowheads in (b), correspond to dispersions of flexibilizer

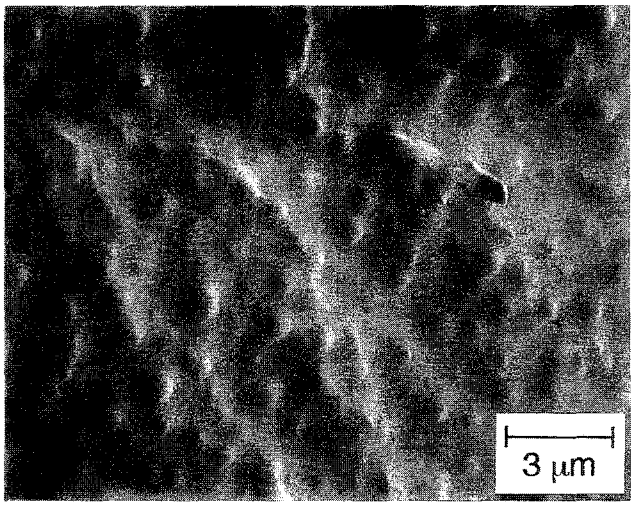

Figure 10 Low-voltage scanning electron micrograph of a 4000 ATU formulation ($\Phi = 0.11$) cryofractured in liquid nitrogen. The spheroidal protrusions ('bumps') correspond to intact phase-separated flexibilizer dispersions

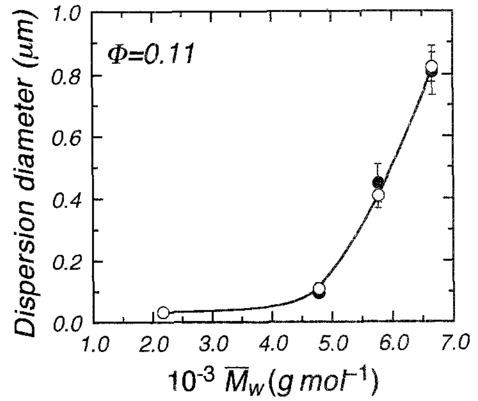

Figure 11 Variation of dispersion size with PPG $\bar{M}_w$ for formulations in which $\Phi = 0.11$. The data shown here are obtained from conventional SEM images of fractured specimens (●) and TEM micrographs of selectively-stained sections (○). The error bars correspond to standard deviations, and the solid line is a guide for the eye

formulation must be at least partially phase-separated. As in *Figures 9* and *10*, the 3000 and 4000 ATU flexibilized epoxies (*Figure 12c* and *12d*, respectively) are composed of relatively large dispersions. Dispersion diameters, as discerned by TEM, are included for

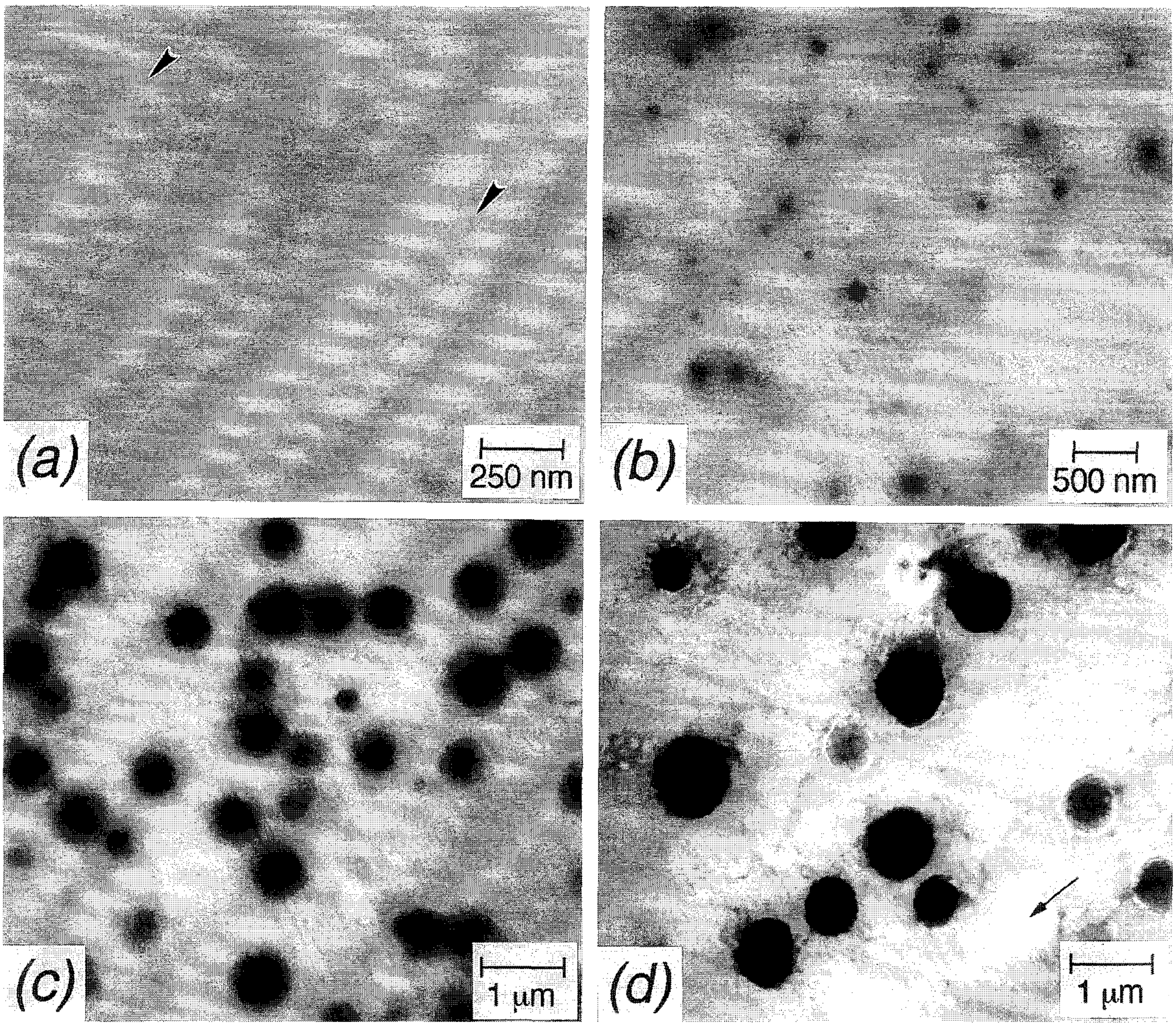

Figure 12 Transmission electron micrographs of the formulations described in the caption of *Figure 9*. Flexibilizer dispersions appear dark due to selective OsO_4 staining of 1,4-octadiene, which was permitted to permeate through sectioned TEM specimens. These micrographs reveal that these ATU formulations exhibit flexibilizer phase-separation to different extents. In (a), 1000 ATU dispersions appear weakly stained (arrowheads), while some dispersions in the phase-separated 4000 ATU material (d) have either partially or completely pulled out from the epoxy matrix (arrow)

comparison in *Figure 11* and are seen to be in excellent agreement with measurements from SEM micrographs.

Thermodynamic considerations

While it is clear from the property and morphological analyses presented herein that ATU flexibilizers are capable of phase-separating from a DGEBA epoxy matrix, several important questions remain unanswered. The first and most important addresses the competition between network formation and phase separation. Although this issue requires additional investigation, phase separation is assumed, for simplicity, to precede crosslinking, in which case the flexibilizer/epoxy mixture can be considered as a polymer–solvent solution. Thermodynamic compatibility in a classical polymer solution can be accurately described in terms of the Gibbs free energy, expressed relative to a reference state which is taken as a homogeneous and random mixture of the chemical species involved.

The free energy of demixing (Δg_{demix}) for an incompressible pseudo-binary mixture* can be written as

$$\frac{\Delta g_{\text{demix}}}{RT} = -\left(\frac{x_{\text{m}}\bar{M}_{\text{m}}}{\bar{\rho}_{\text{m}}} + \frac{x_{\text{f}}M_{\text{f}}}{\rho_{\text{f}}}\right)\frac{(\bar{\delta}_{\text{m}} - \delta_{\text{f}})^2}{RT}\phi_{\text{m}}\phi_{\text{f}} - x_{\text{m}}\ln\phi_{\text{m}} - x_{\text{f}}\ln\phi_{\text{f}} \qquad (4)$$

where ρ denotes mass density, and x and ϕ correspond to mole fraction and volume fraction, respectively. The subscripts refer to the epoxy matrix (m) and flexibilizer (f) constituents, and an overbar indicates a mixture property. Solubility parameters (δ_i, $i = \text{m}$ or f) are employed in equation (4) as a means of estimating the chemical dissimilarity between the flexibilizer and epoxy matrix, and can be calculated from group-contribution methods, such as the one proposed by van Krevelen[46]. The solubility parameters for Epon 828 and PACM are estimated to be 10.9 and 10.1 H, respectively, and the average matrix solubility parameter [$\bar{\delta}_{\text{m}}$ in equation (4)] is obtained by weighting these values by the volume fraction of each species present. Since the molar mass of the PPG flexibilizer is variable in this study, δ_{f} (given in

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*The Epon 828/PACM epoxy matrix is considered here as a single component with averaged properties

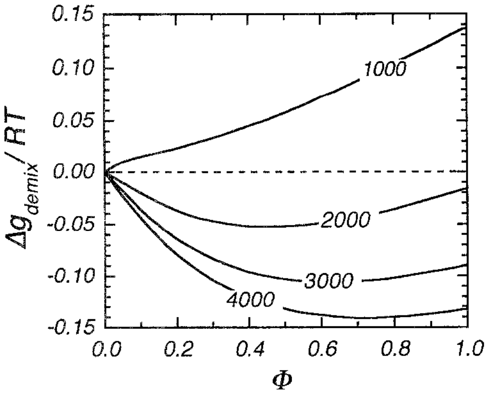

Figure 13 Predicted dependence of Δg_{demix} on Φ for four flexibilized epoxies containing (from top to bottom) 1000 ATU, 2000 ATU, 3000 ATU and 4000 ATU. Phase stability considerations based upon $d^2\Delta g_{\text{demix}}/d\Phi^2$ suggest that the 1000 ATU formulation should remain homogeneous up to $\Phi \approx 0.2$. The dashed line corresponds to $\Delta g_{\text{demix}} = 0$

units of H) is expressed explicitly in terms of the PPG degree of polymerization (n):

$$\delta_{\text{f}} = \left[\frac{5994 + 978.2n}{595.2 + 115.5n}\right] \qquad (5)$$

In the limit of infinite PPG molecular weight (i.e. $n \to \infty$), $\delta_{\text{f}} \to 8.5$ H.

Figure 13 illustrates the dependence of Δg_{demix} on composition (Φ) and n for monodisperse analogues of the systems investigated here. The relationships shown in *Figure 13* reveal that Δg_{demix} decreases (i.e. becomes increasingly more negative), and the driving force favouring phase separation increases, with n (or, equivalently, M). Moreover, the curve corresponding to the 1000 ATU formulation possesses negative curvature ($d^2\Delta g_{\text{demix}}/d\Phi^2 < 0$) up to $\Phi \approx 0.2$, while each remaining $\Delta g_{\text{demix}}(\Phi)$ curve exhibits positive curvature ($d^2\Delta g_{\text{demix}}/d\Phi^2 > 0$) over the entire composition range. According to the stability criterion for phase separation[47], only the 1000 ATU flexibilizer is predicted to be miscible with Epon 828, at low Φ in agreement with experimental results. These predictions suggest that (at $\Phi = 0.11$) a critical n exists which promotes phase separation.

A more detailed thermodynamic analysis of the binodal and spinodal boundaries would be necessary to identify the critical conditions leading to incipient phase separation, but is beyond the scope of the present work. It should be remembered that, as the epoxy forms a three-dimensional network during cure, its molecular weight and degree of branching also increase. Factors addressing cure-increased molecular weight and branching, as well as (i) the rate of phase separation relative to that of network formation and (ii) the polydispersity of the PPG prepolymer (see *Table 1*), must be considered in the development of a more realistic expression for Δg_{demix}.

While the predicted results shown in *Figure 13* provide insight into the effect of M on phase demixing, another factor that must be addressed is the chemical nature of the PPG flexibilizer, as exemplified by δ_{f}. Complementary studies in which a comparable polyol, poly(tetramethylene ether glycol) (PTMEG), was substituted for PPG reveal that cured PTMEG-based plaques consisting of 1000 and 2900 ATU formulations at Φ of 0.11 and 1.0 are optically transparent. Thermal and mechanical analyses of these four PTMEG-based materials, in contrast to those containing PPG, also indicate that phase separation does not occur despite the threefold increase in prepolymer M. In the limit of infinite molecular weight, the solubility parameter of the PTMEG flexibilizer is 9.3 H, which is closer in magnitude to δ_{m} (10.1–10.9 H) than that of the PPG flexibilizer at infinite molecular weight (8.5 H). Thus, phase separation in the present class of flexibilized epoxies can be controlled by judicious choice of both the polyol (δ_{f}) and the molecular weight of the ATU flexibilizer.

CONCLUSIONS

The thermal and mechanical properties of a series of heat-cured epoxies flexibilized with PPG-based acrylate-terminated urethanes have been investigated. Their phase behaviour has been examined in terms of composition and flexibilizer molar mass with d.s.c. and d.m.a. Analysis of the flexibilizer and epoxy glass transition temperatures reveals that phase separation between the two chemical species is principally dominated by the PPG molar mass. Stress–relaxation studies are found to be extremely sensitive to the degree of phase separation, while SEM and TEM provide direct evidence for flexibilizer/epoxy phase separation. By assuming phase separation occurs quickly relative to network formation during cure, the thermodynamic characteristics of these flexibilized epoxies can be semi-quantitatively described as a pseudo-binary solution composed of DGEBA and ATU flexibilizer.

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