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Model acrylate-terminated urethane blends in toughened epoxies: a morphology and stress relaxation study

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Abstract

Improved toughness of heat-cured epoxies is readily achieved through chemical incorporation of a flexible moiety that phase-separates from the epoxy matrix during thermal cure. Many commercial flexibilizers are inherently polydisperse, which yields dispersions composed of flexibilizer chains of variable length. In this work, we examine the effect of flexibilizer polydispersity on the morphology and stress relaxation behavior of a commercial epoxy. This is achieved by systematically varying the composition of binary and ternary flexibilizer blends of monodisperse acrylate-terminated urethanes differing in molecular weight. Field-emission scanning electron micrographs of fracture surfaces permit quantification of dispersion sizes as a function of blend composition. Tensile stress relaxation data from three-point bend tests performed under isothermal conditions are analyzed in terms of a biexponential model to discern fast and slow characteristic relaxation times. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Rubber-toughening; Stress relaxation; Epoxy

1. Introduction

Chemical incorporation of a flexible moiety into a heat-cured epoxy constitutes an important means of toughening epoxies for specific end-use applications [1–5]. A variety of flexibilizers differing in chemical composition and molecular weight are commercially available for this purpose. Such flexibilizers are generally added at an application-dictated concentration to the epoxy resin prior to cure, and subsequently phase-separate as the molecular weight and branching of the epoxy network, as well as the thermodynamic incompatibility between the flexibilizer and epoxy, increase during cure [6,7]. If the epoxy and flexibilizer are sufficiently incompatible and if the flexibilizer concentration is relatively low, discrete spherical dispersions of flexibilizer, typically measuring on the order of a few microns in diameter, form by nucleation and growth throughout the epoxy matrix and impart toughness to an otherwise brittle system [8–11] (phase separation via spinodal decomposition has also been observed in blends at the critical composition [11–13]). Stress dissipation is widely accepted [14–19] to proceed by a two-step mechanism initiated by flexibilizer cavitation and followed by shear yielding.

Several important criteria must be considered when designing toughened epoxies: (i) the thermodynamic incompatibility between the flexibilizer and cured epoxy at the gelation point (when the liquid → solid transition occurs and phase separation kinetics decrease abruptly) [20,21]; (ii) the chemical composition of the epoxy network (as dictated by the curing agent employed) [22]; (iii) the molecular weight [23] and polydispersity of the flexibilizer; and (iv) the concentration of flexibilizer in the formulation [11]. Incompatibility is strongly dependent on χ (the temperature-dependent Flory–Huggins interaction parameter between the flexibilizer and epoxy) and M (the molecular weight of the flexibilizer), and dictates whether all, part or none of the flexibilizer phase-separates from the curing epoxy [6,7,20,21,23]. In the event that incomplete phase separation occurs, flexibilizer molecules remain homogeneously mixed within the epoxy matrix, and may adversely affect the desirable properties of the epoxy (e.g. the glass transition temperature) [4,23]. As in conventional polymer blends [24], the morphology of a biphasic flexibilized epoxy governs ultimate property development and is likewise expected to be sensitive to flexibilizer molecular weight polydispersity.

A previous study [25] of epoxy resins flexibilized with

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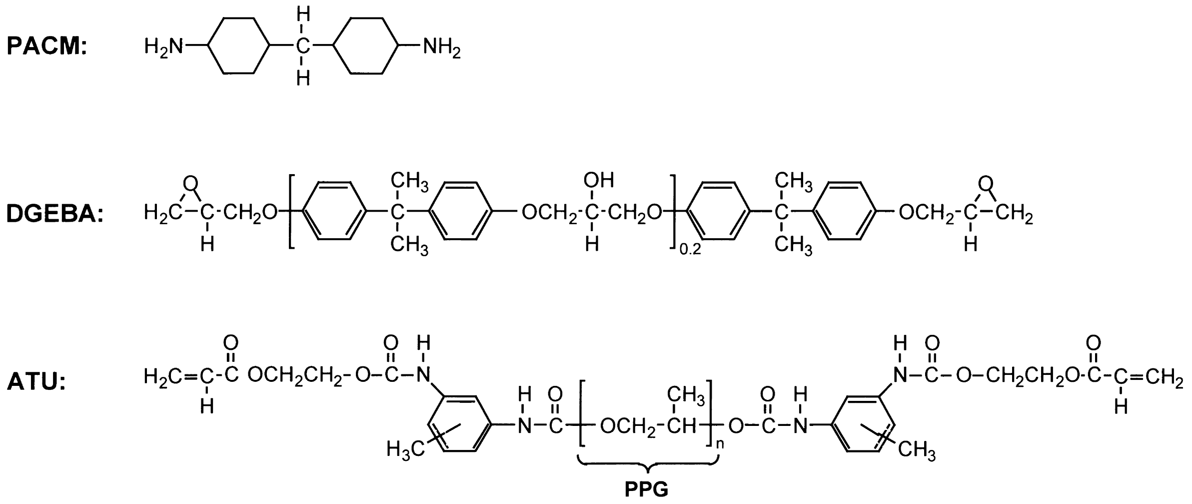

Fig. 1. Chemical structures of the compounds used to produce the flexibilized epoxies examined here. The crosslinking agent is bis(4-aminocyclohexyl) methane (PACM), and the epoxy resin is a diglycidyl ether of bisphenol-A (DGEBA). Acrylate-terminated urethane (ATU) flexibilizers consist of polypropylene glycol coupled via toluene diisocyanate to 2-hydroxyethylacrylate.

acrylate-terminated urethanes (ATUs) varying in composition, molecular weight and molecular weight polydispersity has provided evidence that bulk properties, such as the upper (epoxy) glass transition temperature (T_g) and the tensile stress relaxation behavior, of such toughened epoxies are strongly dependent on each of the flexibilizer characteristics examined. Of particular interest in the present work is the influence of molecular weight and polydispersity at fixed flexibilizer concentration. Most commercially available flexibilizers are inherently polydisperse due to the routes by which they are synthesized. Multimodal polydispersity may lead to a flexibilizer phase possessing a multimodal size distribution, which has been found [14,26] to impart greater fracture resistance to an epoxy relative to a comparable unimodal size distribution. Flexibilizer polydispersity also raises questions regarding the packing of end-grafted chains differing in length within a confined geometry, and is fundamentally related to homogeneously ordered block copolymer mixtures [27–31], as well as to bicomponent polymer mixtures chemically grafted to an impenetrable (inorganic) surface [32–36].

In the present work, we investigate the role of flexibilizer polydispersity in ATU-flexibilized epoxy formulations similar to those studied earlier [25] by first synthesizing a series of monodisperse flexibilizers and then incorporating binary and ternary blends of these flexibilizers into uncured epoxy resin. Morphological characteristics of the resulting heat-cured systems are discerned from field-emission scanning electron microscopy (FESEM), and the degree to which flexibilizer partitioning occurs in these systems is ascertained as a function of composition from stress relaxation analysis.

2. Experimental

2.1. Materials

The precursor epoxy resin used in this study was DGEBA, a diglycidyl ether of bisphenol-A (Ancarez 728), and the curing agent was bis(4-aminocyclohexyl) methane (Amicure PACM), both of which were provided by Air Products and Chemicals, Inc. The chemical structures of these moieties are depicted in Fig. 1. Included in Fig. 1 is the chemical structure of the ATU flexibilizer, composed of a polypropylene glycol (PPG) segment end-capped first with 80/20 2,4-/2,6-toluene diisocyanate and then with 2-hydroxyethylacrylate. The steps involved in the synthesis of polydisperse ATU flexibilizers differing in polyol molecular weight have been described elsewhere [25] and are not reproduced here. To synthesize monodisperse flexibilizers for use in systematically varied model blends, a PPG of desired molecular weight was reacted with a 4:1 molar ratio of 60/40 2,4-/2,6-toluene diisocyanate by incrementally adding the glycol to the diisocyanate over a 1-h period at a temperature within the range 50–100°C. Excess 2,4-/2,6-toluene diisocyanate was removed (<0.1 wt% in the product) by reduced pressure distillation. The resultant "perfect" diisocyanate prepolymer was then reacted with 2-hydroxyethylacrylate between 25 and 50°C over a dibutyltindilaurate catalyst to produce the corresponding monodisperse ATU flexibilizer [37–39].

Four such flexibilizers designated as ATU*M*, where *M* denotes the molecular weight (in $\mathrm{kg\,mol^{-1}}$) of the PPG segment (1, 2, 4 and 8 $\mathrm{kg\,mol^{-1}}$), were synthesized and employed throughout this work. Blends of the flexibilizers were prepared by mixing the ATU liquids in predetermined quantities. Five series of flexibilized epoxies with either

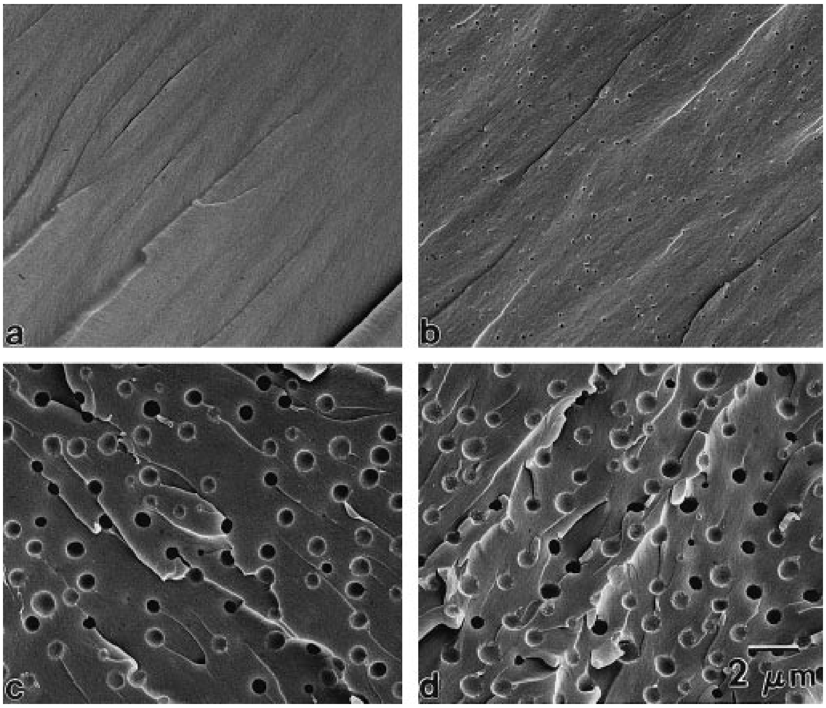

Fig. 2. Scanning electron micrographs of fracture surfaces from epoxies flexibilized with binary blends of ATU1 and ATU4 in which the blend composition (expressed in wt% ATU1) is varied: (a) 100, (b) 80, (c) 40 and (d) 20.

binary or ternary ATU blends (as well as the pure parent ATUs) were produced by adding ATU liquids (blends) to DGEBA resin at a 1:9 mass ratio of ATU (blend) to epoxy. (Throughout this work, the term *blend* refers only to a designated flexibilizer mixture exclusive of the epoxy matrix.) After mixing, the resultant solutions were heated to 60°C and degassed under vacuum for about 30 min. A stoichiometric quantity of PACM, based on the number of active hydrogen sites available in PACM and the equivalent weight of an epoxy/ATU solution, was subsequently added to every solution. Each epoxy/ATU mixture was then cured for 3 h at 120°C in a stainless steel mold measuring $15.2 \times 15.2 \times 0.3\ \mathrm{cm}^3$ and lightly coated with a release agent.

2.2. Methods

Small pieces of the plaques produced above were fractured at ambient temperature and the fresh fracture surfaces were coated with about 20 nm of Au/Pd for FESEM analysis. Images of each formulation examined here were acquired on a JEOL JSM-6400F electron microscope operated at 5 kV. Tensile stress relaxation tests were performed with a three-point bending fixture on a Rheometrics Solids Analyzer (RSA II) at 100°C. Each specimen was subjected to a strain of 0.1%, and the stress (σ) decay at this strain was recorded as a function of time (t) over the course of 250 s.

3. Results and discussion

3.1. Morphological characteristics

Fig. 2 displays a series of FESEM micrographs of epoxy/ATU formulations composed of ATU1/ATU4 blends. In these and subsequent FESEM images, phase separation between a dispersed ATU flexibilizer or flexibilizer blend and the epoxy matrix is evidenced by the presence of holes that arise during cavitation of the ATU phase upon fracture at ambient temperature. On the basis of this criterion, only the ATU4-containing blends in Fig. 2b–d are considered to be phase-separated, whereas the epoxy containing pure ATU1 (Fig. 2a) is homogeneous. This resulting miscibility window (due to the relatively low-molecular-weight PPG content in the ATU1 flexibilizer) is consistent with earlier observations [25] of epoxy/ATU formulations containing polydisperse flexibilizers. Caution must be exercised, however, in such phase discrimination, since the characteristic length scale of the flexibilizer phase may be sufficiently small to preclude formation of holes visible in fracture surfaces either coated with a conductive metal for SEM or visualized uncoated with low-voltage SEM [25]. This potential complication could, in principle, be alleviated through the complementary use of transmission electron microscopy [12,25] or a surface probe microscopy [40], but is beyond the focus of the present study.

Micrographs obtained from epoxy/ATU systems consisting of blends of ATU2 and ATU4 appear qualitatively similar to those presented in Fig. 2 and are not included here for

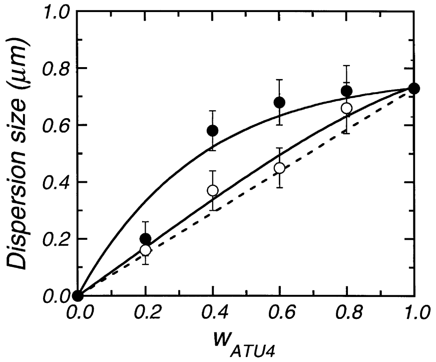

Fig. 3. Dependence of ATU dispersion size on the mass fraction of ATU4 (w_{ATU4}) in epoxies flexibilized with binary blends containing ATU1 (●) and ATU2 (○). The solid lines serve as guides for the eye, and the dashed line denotes a linear rule of mixtures interpolated between the homogeneous epoxy/ATU(1 or 2) and heterogeneous epoxy/ATU4 formulations. The error bars included here denote one standard deviation in the data.

that reason. As with the epoxy/ATU1 analogue (Fig. 2a), the epoxy/ATU2 formulation is macroscopically homogeneous. Careful examination of FESEM micrographs collected from both blend series reveals that the dispersions in the ATU2/ATU4 blends appear, on average, slightly smaller than those in the corresponding ATU1/ATU4 materials. This trend is more clearly seen in Fig. 3, in which the mean ATU dispersion diameter, measured from FESEM micrographs such as those provided in Fig. 2, is displayed as a function of blend composition (expressed in terms of the ATU4 mass fraction, w_{ATU4}) in formulations containing either ATU1 or ATU2. Only the large holes evident in fracture surfaces are included in the size measurements, which are performed so that the major axis of holes appearing slightly elliptical (due to specimen tilt) is used. The population of small holes, most likely arising from dispersions fractured along a non-equatorial plane, is small. No evidence of a bimodal size distribution of dispersions exists in any of the materials examined.) At relatively low w_{ATU4} (<0.4), the flexibilizer dispersions in both blend series are of comparable size and are in good agreement with the linear rule of mixtures interpolated between the epoxy/ATU formulations containing either pure flexibilizer.

As w_{ATU4} is increased to 0.4 in Fig. 3, however, the dispersions in the two series diverge in size, with those in the ATU1/ATU4 series consistently appearing larger than those in the ATU2/ATU4 series. The dispersions in the ATU2/ATU4 series gradually increase in size, continuing to closely follow the rule of mixtures between the epoxy/ATU2 and epoxy/ATU4 materials, as w_{ATU4} is increased further. Such behavior in this blend series is not unexpected, due to the similarity in PPG molecular weight of the constituent flexibilizers. In marked contrast, the dispersions in the ATU1/ATU4 blend series exhibit a more abrupt change in size, strongly suggesting that the dispersions in ATU1/ATU4 blends in which $w_{ATU4} > 0.4$ consist principally of ATU4 (since dispersion size in this regime is weakly dependent on composition). Analogous ATU2/ATU4 blends of identical composition are, on the other hand, composed of both ATU2 and ATU4 in closer concentration-dependent proportion. The results seen in Fig. 3 indicate that the flexibilizer molecules can separate from each other, as well as from the DGEBA epoxy, on the basis of PPG molecular weight, and consequently partition to different extents between a flexibilizer-rich dispersed phase and the epoxy-rich matrix phase. This issue is addressed further below.

As anticipated from molecular weight considerations, the ATU-rich dispersions in blends containing ATU8 are, at equal blend composition, larger than those with ATU4. Micrographs of phase-separated materials in the ATU1/ATU8 and ATU2/ATU8 series do not qualitatively differ from those provided in Fig. 2 and are not included for the sake of brevity. To better discern the effect of flexibilizer mixing on morphology and property development in these epoxy/ATU systems, a ternary blend series composed of ATU2, ATU4 and ATU8 has also been prepared and examined; fracture micrographs of the resultant materials are shown in Fig. 4. In this series, the mass fraction of ATU2 is varied from 1.0 to 0.0 in 0.2 increments at equimass fractions of ATU4 and ATU8. Fig. 4 includes blends of intermediate composition, expressed in wt% of ATU2/ATU4/ATU8: 80/10/10 (Fig. 4a), 60/20/20 (Fig. 4b), 40/30/30 (Fig. 4c) and 20/40/40 (Fig. 4d).

Dispersion diameters measured from FESEM micrographs of the three blend series containing ATU2 (two binary, with either ATU4 or ATU8, and one ternary, with both ATU4 and ATU8) are provided as a function of blend composition (w_{ATU2}) in Fig. 5. In the ATU2/ATU8 series, a reduction in w_{ATU2} is accompanied by an abrupt increase in dispersion size. Similar, albeit less pronounced, behavior is observed in the ATU2/ATU4/ATU8 series, in marked contrast to that of the ATU2/ATU4 series, which follows a linear rule of mixtures. Nonlinear dependence of dispersion size on blend composition must therefore be attributed to the presence of the ATU8 flexibilizer. Indeed, this conclusion is confirmed by the composition-dependent dispersion sizes from the ATU1/ATU8 series (data not shown), which exhibit a more dramatic step change than the data in Fig. 3 for the ATU1/ATU4 series. Comparison of the data in Figs. 3 and 5 reveals that the onset of nonlinear size dependence on blend composition is first detected at a flexibilizer molecular weight ratio of about four (ATU1/ATU4 and ATU2/ATU8), implying that (i) the short flexibilizer chains in these blend series do not locate exclusively in the dispersed flexibilizer-rich phase, and (ii) a critical molecular weight ratio exists at which flexibilizer partitioning (between the dispersed and matrix phases) occurs. It is interesting to note at this juncture that molecular-weight-induced component partitioning has been observed in heterogeneous mixtures of block copolymers [27–30].

If a polydisperse flexibilizer or, alternatively, a blend of

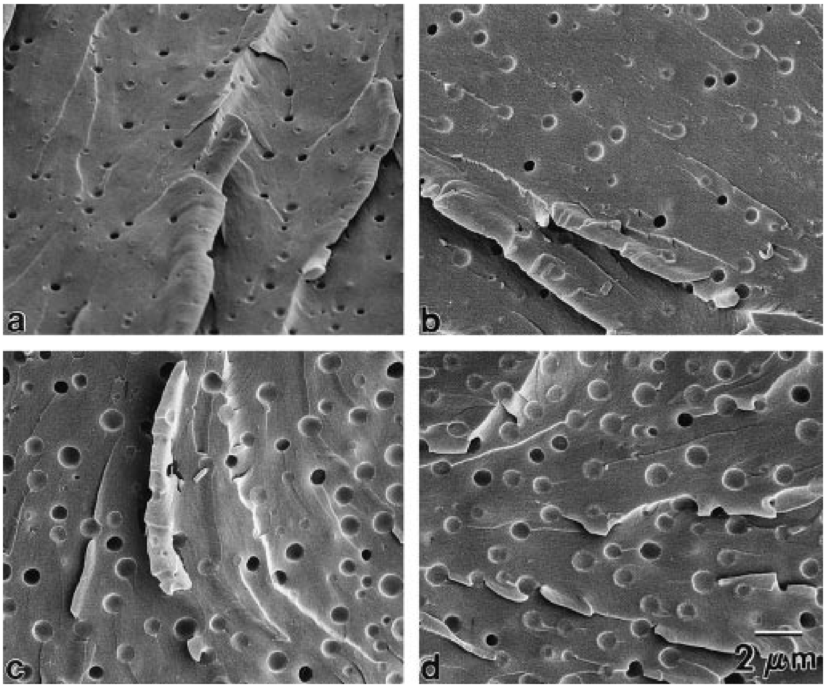

Fig. 4. Scanning electron micrographs of fracture surfaces from epoxies flexibilized with ternary blends of ATU2, ATU4 and ATU8 in which the concentrations (in wt%) of ATU4 and ATU8 are equal and the overall blend composition (expressed in wt% ATU2) is systematically varied: (a) 80, (b) 60, (c) 40 and (d) 20.

monomolecular flexibilizers partitions between one (or more) dispersed flexibilizer-rich phase(s) and the epoxy-rich matrix phase, one can expect substantial variation in the bulk properties of the flexibilized epoxy. In the following section, we address the impact of flexibilizer partitioning on the stress relaxation behavior of the blend series discussed above.

3.2. Stress relaxation

Previous studies [25,41] of immiscible polymer systems have demonstrated that stress relaxation analysis is sensitive to the microstructure of, and component partitioning between, coexisting phases. In this spirit, tensile stress relaxation, $\sigma_n(t)$, curves obtained from the ATU1/ATU4 and ATU1/ATU8 blend series and normalized relative to the initial stress are presented in Fig. 6a and b, respectively. The epoxy/ATU1 formulation exhibits the greatest stress decay, since the flexibilizer remains in molecular solution with the DGEBA epoxy upon thermal cure. Upon addition of either ATU4 or ATU8, phase separation proceeds and ATU flexibilizer is removed from the continuous epoxy matrix, resulting in a stiffer matrix. The epoxy/ATU4 specimen in Fig. 6a and the epoxy/ATU8 material in Fig. 6b exhibit the greatest extent of epoxy/ATU phase separation, accompanied by the lowest level of stress relaxation, in each blend series. Upon close examination of the $\sigma_n(t)$ data for the epoxy/ATU4 and epoxy/ATU8 systems, the latter exhibits the least relaxation after 250 s, indicating that the ATU8 flexibilizer is more incompatible with, and hence phase-separates more completely from, the DGEBA epoxy than the ATU4 flexibilizer. Similar trends are observed in the $\sigma_n(t)$ data provided in Fig. 7 for the ATU2/ATU4 (Fig. 7a) and ATU2/ATU8 (Fig. 7b) blends. Since the ATU2 flexibilizer possesses a longer polyol segment than the ATU1 flexibilizer but remains homogeneously mixed within the epoxy upon cure, it promotes the greatest reduction in σ_n after 250 s of all the materials investigated in this work. As in the ATU1/ATU4 and ATU1/ATU8 blend series in Fig. 6, an increase in the concentration of either ATU4 or ATU8 in the blend series shown in Fig. 7 generally yields a reduction in the extent of stress relaxation. This trend is also

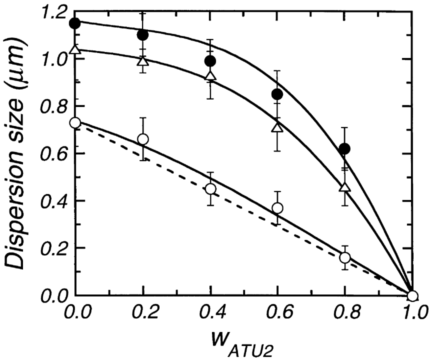

Fig. 5. Dependence of ATU dispersion size on the mass fraction of ATU2 (w_{ATU2}) in epoxies flexibilized with binary blends containing either ATU4 (○) or ATU8 (●) and ternary blends with equal masses of both ATU4 and ATU8 (△). The solid lines serve as guides for the eye, and the dashed line denotes a linear rule of mixtures for the ATU2/ATU4 blends. The error bars included here denote one standard deviation in the data.

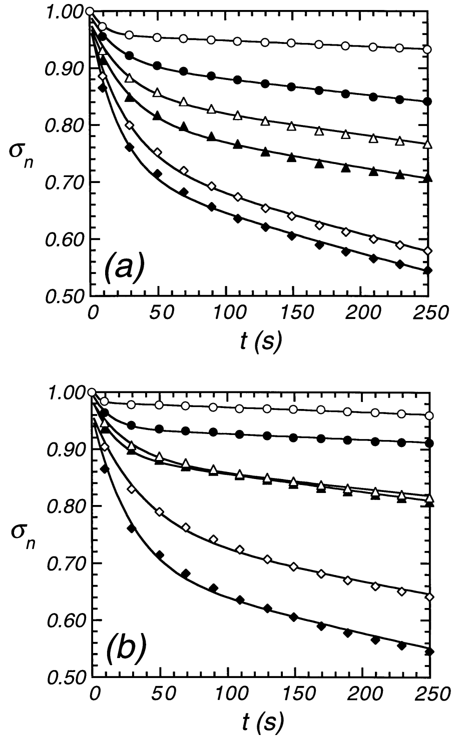

Fig. 6. Normalized stress relaxation curves for epoxies flexibilized with (a) ATU1/ATU4 and (b) ATU1/ATU8 blends in which the blend composition (in wt% ATU1) is varied: 0 (○), 20 (●), 40 (△), 60 (▲), 80 (◇) and 100 (◆). The solid lines are regressions of Eq. (3) to the data.

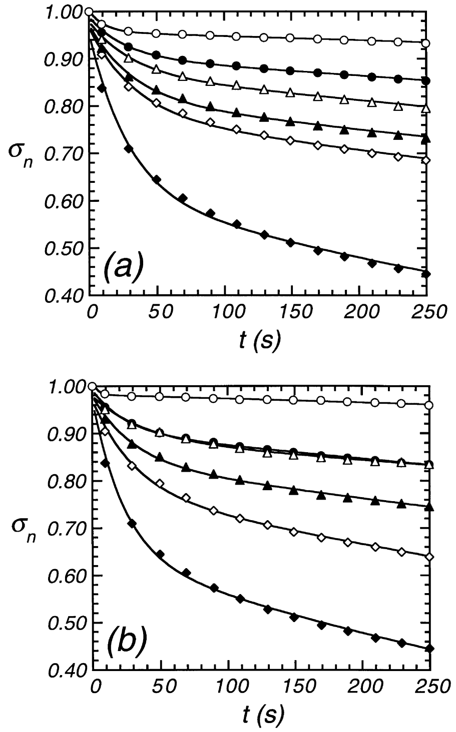

Fig. 7. Normalized stress relaxation curves for epoxies flexibilized with (a) ATU2/ATU4 and (b) ATU2/ATU8 blends in which the blend composition (in wt% ATU2) is varied: 0 (○), 20 (●), 40 (△), 60 (▲), 80 (◇) and 100 (◆). The solid lines are regressions of Eq. (3) to the data.

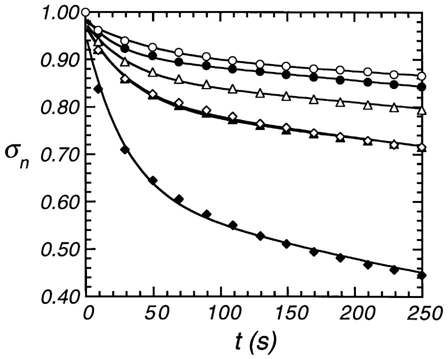

Fig. 8. Normalized stress relaxation curves for epoxies flexibilized with ternary blends of ATU2 and equal mass fractions of ATU4 and ATU8 in which the blend composition (expressed in wt% ATU2) is varied: 0 (○), 20 (●), 40 (△), 60 (▲), 80 (◇) and 100 (◆). The solid lines are regressions of Eq. (3) to the data.

seen in Fig. 8 for epoxies modified with the ternary ATU2/ATU4/ATU8 blend.

Analysis of stress relaxation data typically relies on fitting an exponential function to the data and extracting one or more characteristic relaxation times. For quasi-elastic materials with a single relaxation mode, stress relaxation is adequately described by a Maxwell expression of the form

$$\sigma_n(t) = \exp(-t/\tau) \tag{1}$$

where τ denotes the characteristic relaxation time of the process. Heterogeneous or disordered media possessing coupled decay modes can likewise be analyzed by the Kohlrausch–Williams–Watts (KWW), or stretched exponential, equation [42,43]. The form of this expression is

$$\sigma_n(t) = \exp[-(t/\tau)^b] \tag{2}$$

where b, referred to as the stretching exponent, has values between zero and one. A distribution of coupled relaxation processes is commonly manifested by a reduction in b from unity in the KWW equation, but a single relaxation time is retained. This expression cannot be used to account for a bimodal (or higher order multimodal) relaxation process. Application of the KWW equation (2) to the data shown in Figs. 6–8 yields an overall unsatisfactory fit. Following Barry and Soane [44] in their analysis of second harmonic generation decay in swollen polymer/chromophore systems, we apply here a biexponential, or two-term Maxwell, expression of the form

$$\sigma_n(t) = \phi_{\text{slow}} \exp(-t/\tau_{\text{slow}}) + \phi_{\text{fast}} \exp(-t/\tau_{\text{fast}}) \tag{3}$$

to the data provided in Figs. 6–8. In Eq. (3), ϕ_{slow} and ϕ_{fast} are weighting functions for two hypothesized relaxation processes, one slow and the other fast, with corresponding relaxation times τ_{slow} and τ_{fast}. Interestingly, fitting this equation to the data reported here yields not only reasonably good agreement (demonstrated by the solid lines in Figs. 6–8), but also the relation (not a fit requirement) that $\phi_{\text{slow}} + \phi_{\text{fast}} \approx 1$ (within ±0.5% on average).

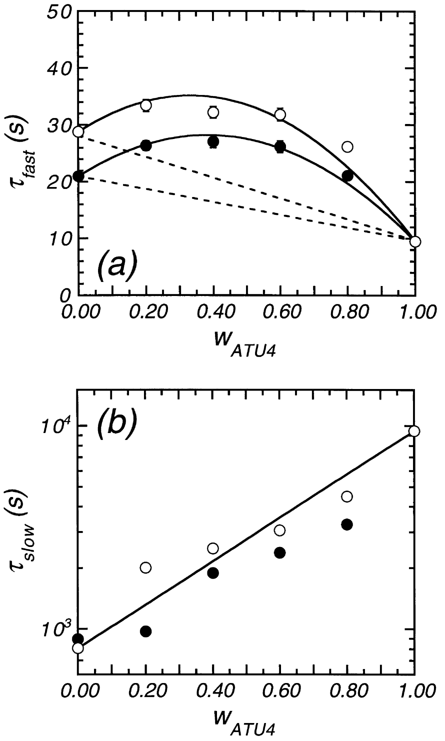

Fig. 9. Dependence of (a) τ_{fast} and (b) τ_{slow} on blend composition (w_{ATU4}) in epoxies flexibilized with binary blends of ATU4 and either ATU1 (●) or ATU2 (○). The solid lines in (a) serve as guides for the eye, and the dashed lines correspond to a linear rule of mixtures. The solid line in (b) denotes an exponential fit to the data. Error bars on the data are included.

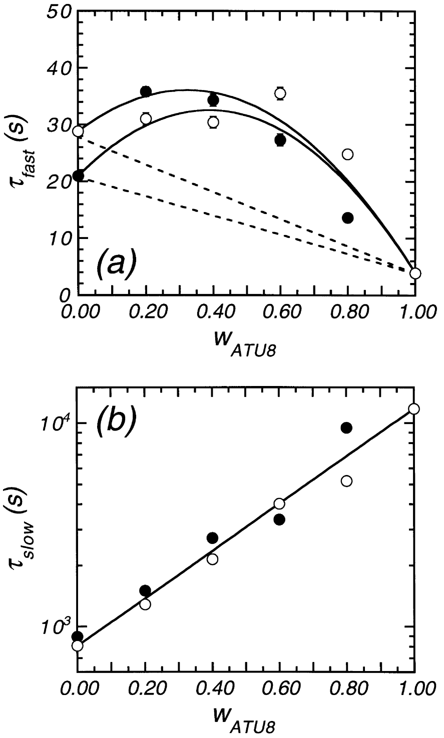

Fig. 10. Dependence of (a) τ_{fast} and (b) τ_{slow} on blend composition (w_{ATU8}) in epoxies flexibilized with binary blends of ATU8 and either ATU1 (●) or ATU2 (○). The solid lines in (a) serve as guides for the eye, and the dashed lines correspond to a linear rule of mixtures. The solid line in (b) denotes an exponential fit to the data. Error bars on the data are included.

Displayed in Figs. 9 and 10 are τ_{slow} and τ_{fast} extracted from the stress relaxation data in Figs. 6 and 7 for the binary ATU blends, and presented as functions of blend composition (w_{ATU4} in Fig. 9 and w_{ATU8} in Fig. 10). Consider first the data for τ_{fast} in Figs. 9a and 10a, in which several features are noteworthy. As the molecular weight of the PPG segment in the neat flexibilizers is increased from 1 to 8 kg mol^{-1}, τ_{fast} increases initially (between ATU1 and ATU2 in the homogeneous formulations) and then decreases slightly (from ATU4 to ATU8 in the heterogeneous systems). The initial increase in τ_{fast} (from 21.0 to 28.8 s) with increasing PPG molecular weight in the single-phase systems reflects a change in segmental dynamics within the glassy epoxy/ATU solutions, and any explanation proposed for the observed increase in τ_{fast} with increasing PPG chain length in these two systems requires detailed information regarding the distribution of flexibilizer within the crosslinked DGEBA matrix. Since such information is not presently available, no conclusive explanation for the observed increase in τ_{fast} can be offered. If, however, a cured homogeneous epoxy/ATU formulation behaves in similar fashion as an entangled homogeneous polymer melt, an increase in PPG molecular weight would be expected to promote an increase in characteristic relaxation time [45].

Upon increasing the PPG molecular weight from 2 to 4 kg mol^{-1}, τ_{fast} is found to decrease abruptly (from 28.8 to 9.5 s), signaling the onset of phase separation between epoxy and ATU flexibilizer. Formation of ATU-rich dispersions expedites stress dissipation in these toughened epoxies and correspondingly reduces the time needed for flexibilizer relaxation. The marginal reduction in τ_{fast} induced by increasing PPG chain length in the two phase-separated systems (ATU4 and ATU8) may be due to dispersion shape recovery (regulated by interfacial tension which, in turn, depends on molecular weight), but is too small in magnitude (9.5 versus 3.9 s) to warrant detailed analysis here. In addition to these results acquired for formulations with a *single* flexibilizer, Figs. 9a and 10a also reveal that τ_{fast} does not vary according to the linear rule of mixtures for any of the flexibilizer blends investigated in this work. Indeed, in some cases, a maximum in the composition dependence of τ_{fast} appears to exist (most clearly seen in Fig. 9a) due most likely to flexibilizer partitioning between the epoxy- and ATU-rich phases.

In Figs. 9b and 10b, τ_{slow} is presented as a function of blend composition on semi-logarithmic coordinates for the same blends shown in Figs. 9a and 10a, respectively. In both data sets, τ_{slow} is seen to increase substantially with either increasing w_{ATU4} (Fig. 9b) or w_{ATU8} (Fig. 10b), reflecting an increase in the extent of phase separation between the DGEBA epoxy and ATU flexibilizer(s). The solid lines

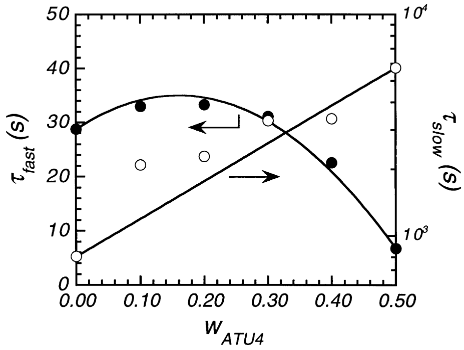

Fig. 11. Dependence of τ_{fast} (●) and τ_{slow} (○) on blend composition (w_{ATU4}) in epoxies flexibilized with ternary blends of ATU2, ATU4 and ATU8 in which the mass fractions of ATU4 and ATU8 are equal. The solid curve connecting the τ_{fast} data serves as a guide for the eye, whereas the solid straight line denotes an exponential fit to the τ_{slow} data. Error bars on the data are included.

included in these figures correspond to the linear rule of mixtures for log τ_{slow}. Values of τ_{slow} in Fig. 9b are in fair agreement with this approximation, whereas those in Fig. 10b are in surprisingly good overall agreement, suggesting that this correlation may be useful in the design of comparable blends wherein the epoxy and at least one flexibilizer are significantly incompatible. For completeness, values of τ_{fast} and τ_{slow} extracted from the ATU2/ATU4/ATU8 ternary blend stress relaxation data (see Fig. 8) are presented as a function of composition (recall that $w_{\text{ATU4}} = w_{\text{ATU8}}$ in this blend series) in Fig. 11. Trends similar to those seen in Figs. 9 and 10 for flexibilized DGEBA epoxy formulations composed of binary ATU blends are likewise evident in this figure, thereby supporting the correlations identified above.

A prior study [25] of polydisperse ATU-flexibilized epoxies has demonstrated that the dependence of σ_{n}, evaluated at an arbitrary reference time ($t_{\text{ref}} = 200$ s), on average polyol molecular weight ($\langle M_{\text{PPG}} \rangle$) exhibits a minimum. To discern whether this feature is general, the $\sigma_{\text{n}}(t)$ data from the epoxy/ATU systems composed of monodisperse ATU flexibilizers and binary ATU blends (Figs. 6 and 7) in the present work have been recast into this format according to $\langle M_{\text{PPG}} \rangle = [w_i/M_i + (1 - w_i)/M_j]^{-1}$ for each i–j ATU blend pair with molecular weights M_i and M_j at a composition (mass fraction) w_i. These results are displayed in Fig. 12 and reveal that $\sigma_{\text{n}}(t_{\text{ref}})$ increases with increasing $\langle M_{\text{PPG}} \rangle$ for all the blends investigated in this work. Since $\sigma_{\text{n}}(t_{\text{ref}})$ must increase again as $\langle M_{\text{PPG}} \rangle \to 0$ (the dashed line in Fig. 12 corresponds to $\sigma_{\text{n}}(t_{\text{ref}})$ for the epoxy/ATU8 formulation and constitutes a reasonable approximation of $\sigma_{\text{n}}(t_{\text{ref}})$ for the unmodified DGEBA epoxy due to the extent of phase separation between the ATU8 flexibilizer and the epoxy [23]), a minimum in $\sigma_{\text{n}}(t_{\text{ref}})$ as a function of $\langle M_{\text{PPG}} \rangle$ must exist, confirming the previously reported results. Another important design consideration is evident from the data in Fig. 12: the trends in this figure are not superimposable, but rather appear sensitive to the molecular weight of the low-molecular-weight flexibilizer. These data therefore provide direct evidence that the molecular weight distribution, and not just the average molecular weight, of the flexibilizer must be explicitly considered in the design of toughened epoxies with highly tailored mechanical properties.

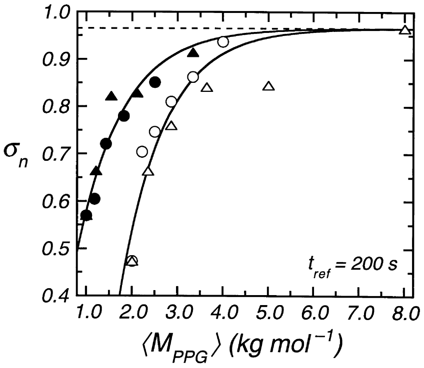

Fig. 12. Normalized stress relaxation (σ_{n}) values evaluated at 200 s for the four series of binary blends containing combinations of ATU4 (circles), ATU8 (triangles), ATU1 (filled symbols) and ATU2 (open symbols). The dashed line denotes σ_{n} for the epoxy/ATU8 formulation (which is the most incompatible, and hence phase-separated, of all the materials examined here), whereas the solid lines serve as guides for the eye.

4. Conclusions

Four monomolecular acrylate-terminated urethane flexibilizers have been synthesized, blended and added to DGEBA epoxy to ascertain the effect of systematically varied bi- and trimodal flexibilizer polydispersity on the morphological characteristics and stress relaxation behavior of toughened epoxies upon thermal cure. Two of the flexibilizers (of relatively low polyol molecular weight) remain homogeneously mixed with the crosslinked epoxy, whereas the remaining two (of higher polyol molecular weight) phase-separate from the epoxy and form spherical dispersions via nucleation and growth. Binary and ternary blends of the high- and low-molecular-weight flexibilizers are consistently found to phase-separate from the epoxy, although morphological evidence suggests that the low-molecular-weight flexibilizer component may partition between flexibilizer- and epoxy-rich phases. Such partitioning becomes increasingly more pronounced as the molecular weight disparity between the flexibilizers in a given blend increases.

Tensile stress relaxation data from these blends are well represented by a biexponential decay expression possessing two characteristic relaxation times for fast and slow relaxation processes. An increase in polyol chain length in formulations composed of a pure flexibilizer yields a marginal reduction in the fast characteristic relaxation time in heterogeneous systems, but an anomalous increase in this relaxation time in homogeneous systems. In contrast, blends of flexibilizers promote a broad maximum in the fast characteristic relaxation time. Pure flexibilizers and flexibilizer blends with longer polyol segments (on average) induce an increase in the slow characteristic relaxation time due presumably to increased phase separation between the epoxy and flexibilizer phases [23,25]. Examination of the dependence of stress relaxation on average flexibilizer molecular weight reveals that this average is not sufficient to characterize an epoxy/flexibilizer formulation. Instead, the molecular weight distribution must be considered explicitly in the design of toughened epoxies with tailored properties.

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