# Stress Relaxation Activation in Rubber-Modified Polymer Systems Exhibiting Controlled Miscibility through Blending

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Biphasic polymer systems possessing rigid matrices are generally produced by melt[1,2] or solid[3,4] thermoplastic mixing. An alternate route by which to produce such systems composed of some thermoplastic polymers and all thermosetting polymers is in situ polymerization,[5] in which the matrix component (A) is polymerized in the presence of an existing polymer (B). In this case, polymer B is normally the minor component and is miscible in monomer A. An increase in the molecular weight ($M$) of A promotes an increase in the incompatibility, and the eventual phase separation, of A and B. The result is the formation of a dispersed B phase usually by nucleation and growth,[6,7] but sometimes by spinodal decomposition.[8] Continued polymerization of A further increases the incompatibility between the polymers, as well as the viscosity of the matrix, thereby slowing the kinetics of phase separation. Gelation, followed by vitrification, of polymer A can sufficiently hinder the diffusion of B so that a nontrivial fraction of B remains kinetically trapped within the A matrix. Another consideration in this vein is the molecular weight of B ($M_B$). While an increase in $M_B$ reportedly[9] increases the degree of phase separation between A and B, a low-$M$ fraction of B may *not* be incompatible with polymer A and remain dissolved within the A matrix at equilibrium.[6,7,10−12]

In either case, residual mixing of B within the A matrix often has deleterious effects on the properties of polymer A and may compromise the utility of the biphasic polymer system.[9,11,13] The glass transition temperature ($T_g$) of polymer A, for instance, is highly sensitive to mixing. Since polymer B is typically rubbery in nature (yielding a rubber-modified material), residual mixing of B in A can promote a dramatic reduction in the matrix $T_g$, depending on the degree of mixing. Another property of A that can be adversely influenced by residual mixing is the characteristic stress relaxation time ($\tau$), which can change by more than an order of magnitude, depending on $M_B$.[12] Stress−relaxation analysis has been the subject of considerable theoretical and experimental interest in biphasic polymer systems. Doi and Ohta,[14] Lee and Park,[15] and Vinckier et al.[16] have proposed theoretical models that relate $\tau$ to physical parameters such as dispersed droplet size and aspect ratio, dispersion and matrix viscosities, and interfacial tension. In the present work, stress−relaxation analysis is performed on rubber-modified epoxies composed of *blends* of low-$M$ polymers to ascertain the effect of residual matrix mixing on $\tau$ and stress relaxation activation.

The epoxy used here was a diglycidyl ether of bisphenol A (DGEBA), and the curing agent was bis(4-aminocyclohexyl) methane, which were both provided by Air Products and Chemicals, Inc. Monodisperse acrylate-terminated urethane (ATU) flexibilizers, composed of polypropylene glycol (PPG) endcapped with 80/20 2,4-/2,6-toluene diisocyanate and 2-hydroxyethyl acrylate, were synthesized according to the protocol detailed elsewhere.[12] They are designated as ATU$m$, where $m$ denotes the molar mass (in kg/mol) of the PPG segment (1, 2, 4, and 8), and their chemical structure has been provided earlier.[11,12] Blends of ATU1 and ATU8 were prepared by mixing the liquids in 20 wt % increments, and modified epoxies were produced by adding the pure ATU liquids or ATU1/ATU8 blends to DGEBA resin at a 1:9 mass ratio of ATU (blend) to resin. These solutions were heated to 60 °C and degassed for 30 min under vacuum. After a stoichiometric quantity of curing agent was added, each mixture was heated at 120 °C for 3 h. Tensile stress relaxation tests were performed on the resulting plaques with a three-point bending fixture on a Rheometrics Solids Analyzer (RSA II) at 26.5, 50.0 and 100 °C. Each specimen was strained by 0.1%, and the stress ($\sigma$) decay was recorded as a function of time ($t$) over the course of 250 s.

Prior efforts[12] have demonstrated that ATU1 and ATU2 remain homogeneously mixed with the cured DGEBA epoxy, whereas ATU4 and ATU8 are almost completely phase-separated from the epoxy matrix. Epoxy/ATU formulations with binary ATU1/ATU8 blends varying in composition are therefore anticipated to exhibit differing degrees of residual matrix mixing upon epoxy cure. Figure 1 shows representative stress−relaxation curves obtained from the epoxy/ATU1/ATU8 blend series. In these figures, the stress measured at three different temperatures is normalized with respect to the initial stress to obtain $\sigma_n(t)$. In Figure 1a, an increase in temperature from 26.5 to 50.0 °C yields a slight reduction (about 6%) in $\sigma_n$ at 250 s. Similar behavior is also observed for epoxy/ATU systems consisting of pure ATU2 and ATU4 (data not shown). As the concentration of ATU1 in the ATU1/ATU8 blends is decreased from 100 wt % (Figure 1a) to 0 wt % (Figure 1f), the difference in $\sigma_n(t = 250\ \text{s})$ evaluated at 26.5 and 50.0 °C lessens. According to Figure 1, however, the $\sigma_n(t)$ data acquired at 100 °C appear to be very sensitive to blend composition.

The formulation with 100 wt % ATU1 (Figure 1a) exhibits a substantial initial reduction in $\sigma_n(t)$ at 100 °C, but this reduction becomes less pronounced with decreasing ATU1 content. While the $\sigma_n(t)$ data acquired for ATU1/ATU8 formulations with 40−80 wt % ATU1 appear similar to those measured for the epoxy/ATU2 system (which remains homogeneous upon cure), these epoxy/ATU blend formulations are phase-separated. As the concentration of ATU1 is further decreased (20/80 and 0/100 ATU1/ATU8), the $\sigma_n(t)$ curves evaluated at 100 °C are shifted to lie between (Figure 1e) or above (Figure 1f) the respective curves corresponding to 26.5 and 50.0 °C. Behavior similar to that in Figure 1e is

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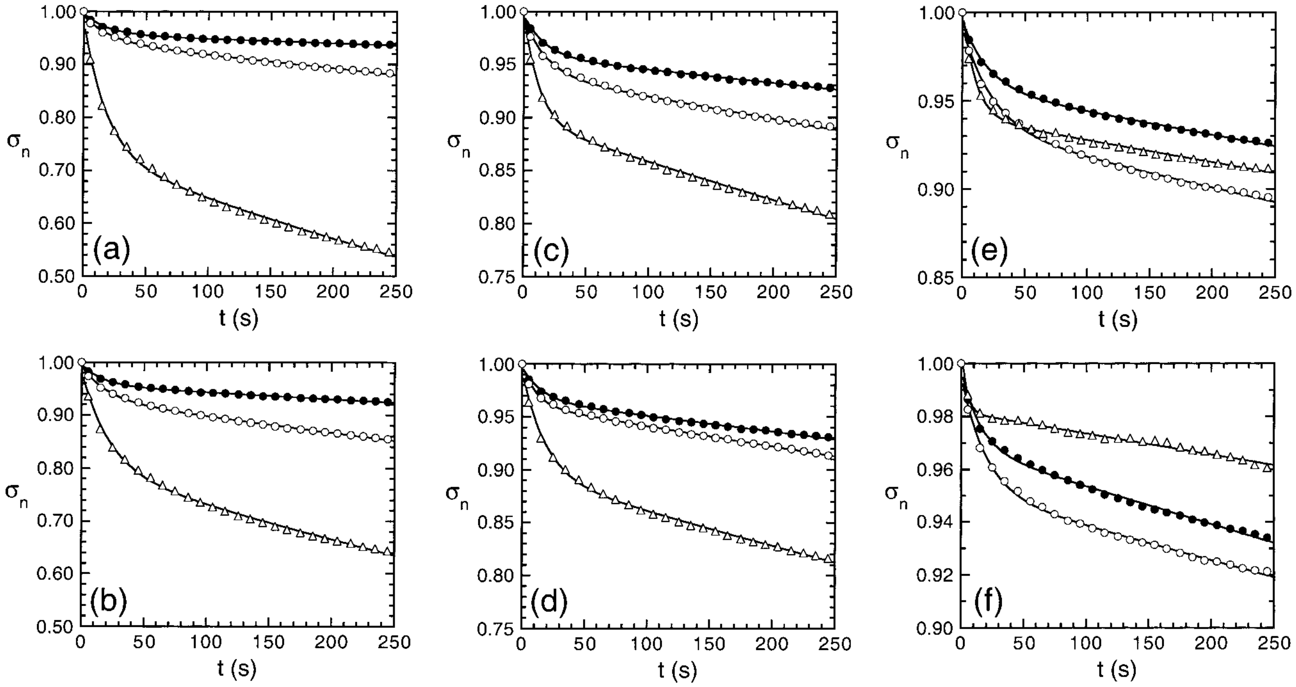

**Figure 1.** Normalized stress–relaxation curves, $\sigma_n(t)$, for epoxy/ATU formulations composed of ATU1/ATU8 blends—(a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80 and (f) 0/100—and evaluated at three different temperatures (in °C): 26.5 (●), 50.0 (○), and 100 (△). The solid lines denote regressed fits of eq 1 to the data (of which only 20% is displayed for the sake of clarity).

observed in the stress–relaxation data acquired from the epoxy/ATU4 formulation. Thus, as the extent of phase separation increases in the present modified epoxy systems, the $\sigma_n(t)$ data become increasingly insensitive to temperatures up to 100 °C. In all cases, though, these stress–relaxation data are well-described by a biexponential Maxwell model,[12,17] which yields two characteristic relaxation times (one fast, $\tau_f$, and one slow, $\tau_s$):

$$\sigma_n = \phi_f \exp(-t/\tau_f) + \phi_s \exp(-t/\tau_s) \qquad (1)$$

Here, $\phi_f$ and $\phi_s$ are adjustable weighting factors that sum to nearly unity (with a mean deviation of ±0.5%).

Application of eq 1 to the stress–relaxation data reported here yields the solid curves shown in Figure 1. Values of $\tau_f$ are less than 40 s and do not, within experimental uncertainty, correlate with temperature. The dependence of $\tau_s$ on reciprocal temperature, on the other hand, is presented in Figure 2 for the epoxy/ATU*m* formulations (Figure 2a), as well as for the epoxy/ATU1/ATU8 systems (Figure 2b), and reveals that the long-time component of stress relaxation in some of the formulations examined here exhibits Arrhenius behavior

$$\tau_s = \tau_0 \exp\,(Q_\eta/RT) \qquad (2)$$

where $\tau_0$ is a constant, $Q_\eta$ is the activation energy, $R$ is the gas constant and $T$ denotes absolute temperature. The data in Figure 2a indicate that values of $\tau_s$ for the homogeneous epoxy/ATU1 and epoxy/ATU2 systems obey eq 2 (and yield identical values of $Q_\eta$), whereas those derived from the phase-separated epoxy/ATU4 and epoxy/ATU8 formulations do not. The same trend is evident in Figure 2b, in which $\tau_s(T)$ for the systems composed of either 20/80 or 0/100 ATU1/ATU8 deviates markedly from Arrhenius-type behavior. Evaluation of $Q_\eta$ from the values of $\tau_s$ provided in Figure 2b yields the results shown in Figure 3, which clearly demonstrates that $Q_\eta$ decreases linearly with increasing ATU8 blend fraction ($w_{ATU8}$) for those epoxy/ATU1/ATU8 systems displaying Arrhenius behavior. This intriguing relationship remains open to molecular interpretation, which must address the partitioning of ATU1 and ATU8 molecules between the matrix and dispersed phases upon cure. A curious feature of Figure 3 is that, upon

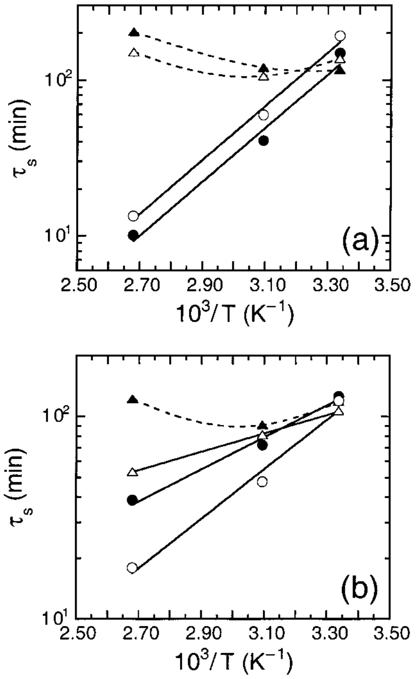

**Figure 2.** Temperature dependence of $\tau_s$ for epoxy/ATU systems consisting of (a) pure ATU*m* additives and (b) ATU1/ATU8 blends. In part a, the values of *m* are 1 (○), 2 (●), 4 (△), and 8 (▲). In part b, the concentrations of ATU1 (in wt %) are 80 (○), 60 (●), 40 (△), and 20 (▲). The solid lines denote regressed fits of eq 2 to the data, and the dashed lines serve as guides for the eye.

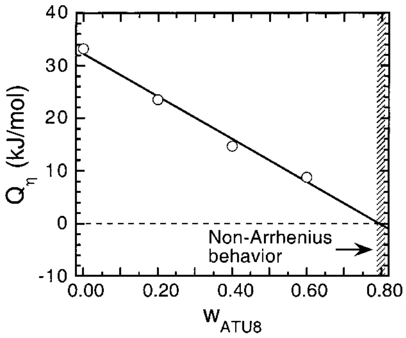

**Figure 3.** Stress relaxation activation energy ($Q_\eta$) as a function of ATU1/ATU8 blend composition ($w_{ATU8}$) for four epoxy/ATU formulations. The solid line is a linear fit to the data, and the crosshatching identifies the composition at which Arrhenius behavior is not observed in Figure 2b.

extrapolation, the linear $Q_\eta(w_{ATU8})$ relationship decreases to zero ($\tau_s$ is temperature independent) for a blend with 80 wt % ATU8, which corresponds to the onset of non-Arrhenius behavior in the ATU1/ATU8 series.

Residual matrix mixing of biphasic polymer systems produced by in situ polymerization can significantly alter the intrinsic properties of the matrix polymer. In this study, the influence of residual matrix mixing on stress relaxation activation energy, the energy required for stress-induced segmental motion, has been probed through the use of model flexibilizer blends. Partially miscible formulations reflect partitioning of the blend components between the dispersed and matrix phases, and possess characteristic relaxation times that display Arrhenius behavior. This is not true for systems that are almost completely phase-separated. Values of $Q_\eta$ are found to depend linearly on composition, indicating that the inclusion of rubbery chains in the matrix has a direct composition-dependent effect on segmental mobility in the epoxy network, for those partially miscible systems in which the relaxation time exhibits Arrhenius behavior.

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## References and Notes

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