Rubber-Modified Epoxies: Interfacial Tension and Morphology

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Synopsis

The interfacial tension between carbomethoxy-terminated butadiene–acrylonitrile copolymers and an epoxy resin as a function of temperature and copolymer composition is investigated. Using a digital image processing technique, the shape of a pendant drop of the epoxy in the copolymer is determined. Analysis of the drop shape is performed by profile discrimination and subsequent robust shape analysis. The data are used to examine the relationship between interfacial tension and particle size of the dispersed copolymer-rich phase in rubber-modified epoxy resins, that are immiscible in the uncured state.

INTRODUCTION

The fracture properties of glassy polymers can be improved via the addition of reactive butadiene–acrylonitrile copolymers to the glassy matrix.[1-3] These rubber-modified resins have been studied for over a decade, with most of the work focusing on modified epoxy resins.[4-8] Toughness improves on increases in the volume fraction of the dispersed rubber-rich phase,[1,9] the epoxy–rubber compatibility,[3,7] and depends on the particle size distribution of the dispersed phase.[3,10] Most studies have focused on liquid systems where phase separation occurs during the curing process. Typically, the variables studied include rubber composition and concentration, composition and concentration of the curing agent(s), cure time and temperature, and time to gelation.

More recently, a thermodynamic model predicting the particle size distribution in rubber-modified thermosets was developed by Williams et al.[11,12] Although the model considers a number of parameters, these authors found that the morphological character of rubber-modified epoxies depended primarily on the difference in extents of reaction at the onset of phase separation and at gelation. As this difference becomes larger, the particle size is predicted to increase and the tendency for coalescence and subsequent macroscopic demixing is favored.

The validity of the model predictions were examined by experimentation with a rubber-modified resin prepared from bisphenol A diglycidyl ether, 4,4'-diaminodiphenylsulfone, and random copolymers of butadiene and acrylonitrile terminated with carboxyl groups. Reasonable agreement between the

model predictions and experimental size distributions was obtained. In fitting the model, they assumed that coalescence could be neglected for the polymerization conditions employed, and concluded that interfacial tension was not an important parameter to be considered.

There is some question, however, as to the validity of the reported interfacial tensions employed in their work. These values were estimated by determining the pure component surface tensions by the capillary rise technique and subsequently applying Antonoff's rule[13] to estimate the interfacial tension. This procedure is known to be inaccurate for polymeric materials.[14] In addition there is an error in the surface tension units reported by Williams et al.[15] In this manuscript we report surface and interfacial tensions for a series of acrylonitrile–butadiene rubber-modified epoxy systems determined by shape analysis of pendant fluid drop profiles.

We also compare these values to the morphologies of a series of solid rubber-modified epoxy systems investigated by Romanchick et al.[16] These systems differ from those studied by Williams et al. in that the epoxies are extended (to equivalent molecular weights of 800–2000 g eq^{-1}) and are prereacted with the rubber. These materials were developed for powder coating applications, are solids at room temperature, and are already phase-separated in the uncured state. The final particle size in materials of this type may therefore depend on interfacial tension through its role in affecting additional processes such as mixing (i.e., blending) and coalescence. Deliberate adjustment of the rubber/epoxy interfacial tension in systems of this type may therefore comprise a means for the control of the dispersed rubber phase morphology and subsequently the material fracture properties.

EXPERIMENTAL

The rubber/epoxy interfacial tensions and pure component surface tensions were determined by measurement and analysis of pendant drop profiles. The analysis of pendant drop profiles is a well-established method for the determination of interfacial tension between two liquid phases,[17] and its application to polymers has been described by Wu.[14]

Pendant and sessile drop profiles result from the balance of forces owing to gravity and surface or interfacial tension. Bashforth and Adams expressed this balance as[18]

$$2 + B\frac{z}{a} = \frac{1}{R/a} + \frac{\sin \phi}{x/a} \tag{1}$$

where the shape factor B is given by $B = a^2 \Delta\rho g/\gamma$, with a the radius of curvature at the drop apex, R the radius of curvature at coordinate (x, z), ϕ the angle between a tangent to the drop profile and the horizontal axis, $\Delta\rho$ the mass density difference between the fluid and the surrounding medium, g the gravitational constant, which is negative for a pendant drop configuration, and γ the interfacial tension.

The interfacial tensions were obtained experimentally by regression of this equation on the experimental drop profile. Images of the drop profile were recorded digitally by feeding the output of a video camera to a Tecmar Video

Butadiene-acrylonitrile copolymer

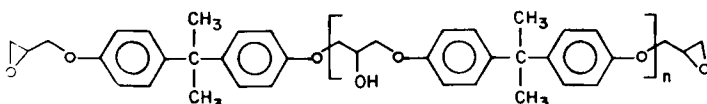ROOC $\left[\left[CH_2CH = CHCH_2 \right]_x \left[CH_2CHCN \right]_y \right]_z$ COOR
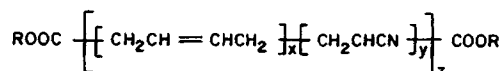
Epoxy

Fig. 1. Chemical structures of the epoxy resin and the butadiene–acrylonitrile copolymers.

Van Gogh frame grabber resident in a microcomputer. Discrimination of the drop profile (i.e., edge detection) was accomplished by global thresholding. A piecewise rotationally resistant smoothing routine was then applied to minimize discretization effects in the profile. The comparison of eq. (1) and the experimental profiles was effected with a robust shape comparison algorithm based on repeated median concepts.[19,20] These analysis procedures have been discussed in detail in previous communications.[21,22]

The carboxy-terminated butadiene–acrylonitrile copolymers (CTBNs) used in the surface and interfacial tension studies, prepared by a process that yields polymers with lower polydispersity compared to the commercially available CTBNs, were provided by the B. F. Goodrich Co. The methyl esters of the carboxy-terminated copolymers were prepared by refluxing the copolymer in methanol, with reaction progress monitored by infrared spectroscopy. The epoxy resins used were derived from the diglycidyl ether of bisphenol A (DGEBA). For interfacial tension measurements, Epon 828 (Shell Chemical) was used ($n \sim 0.1$). The structures of these materials are shown in Figure 1.

The acrylonitrile content of the copolymers and their solubility parameters, both obtained from technical information of the B. F. Goodrich Co., are given in Table I. The material densities, also given in Table I, were determined over the range of 25–95°C with digital density meters, DMA 45/DMA 512, manufactured by Paar Instrument Corp. that are capable of measuring density as a function of temperature to five significant figures. The accuracy of these measurements is critical to the determination of the interfacial tension, since the important quantity is the density difference between the two materials. Since this difference is often small, greater measurement

TABLE I
Properties of CTBNs and Epoxy

Material	Acrylonitrile (%)	Solubility parameter (δ)	$\rho(T)$ (°C)
X162	0	8.04	$0.92792 - 6.2695 \times 10^{-4}T$
X8	18	8.77	$0.96776 - 6.1081 \times 10^{-4}T$
X13	27	9.14	$0.98521 - 5.7453 \times 10^{-4}T$
Epon 828	—	10.2[15]	$1.18773 - 7.2290 \times 10^{-4}T$

TABLE II
Molecular Weights of CTBNs

CTBN	M_w	M_n	$P = M_w/M_n$
X162	9100	5400	1.68
X8	8900	5300	1.68
X13	7300	5900	1.23

TABLE III
Morphology vs. Copolymer Composition

CTBN in epoxy	Acrylonitrile in copolymer (%)	Average diameter (μm) dispersed phase
X162	0	0.35
X8	18	0.30
X13	27	0.29[a]

[a] 200–500 Å domains also present.

accuracy yields more accurate interfacial tension values. The molecular weights of the elastomers were determined from gel permeation chromatographic data, calibrated from polystyrene standards, and are given in Table II.

These same materials were used as precursors in the preparation of the solid rubber-modified epoxy resins.[16] The actual epoxies employed were extended by advancement reactions to attain equivalent weights of 800–2000 g eq^{-1} and were prereacted with the rubbers. The morphology of these rubber-modified epoxy resins as a function of composition was described by Romanchick et al.[16] In contrast to the materials studied by Williams et al.,[12] these resins were already phase-separated in the uncured state. The dispersed phase consisted of core–shell particles with an epoxy core and a rubber shell, and showed a strong tendency for coalescence during polymerization. Table III shows the average final particle diameter of the dispersed rubber-rich phase as a function of copolymer composition for 10 wt % copolymer. It was found that as the acrylonitrile content of the copolymer decreases, the size of the domains of the dispersed phase increases. Since the epoxies used by Romanchick et al. were solids at room temperature, they are not suitable for interfacial tension measurements. Instead we report data taken from similar systems based on the epoxy precursor, Epon 828. The relative interfacial tensions between Epon 828 and the various rubber systems are still appropriate to describe the solid epoxy systems since these values scale similarly with molecular weight.

RESULTS

The surface tensions of several rubber copolymers and the epoxy monomer were determined by pendant drop analysis as a function of temperature over the range 25–100°C (Fig. 2). Esterifying the carboxylic acid end groups results in a decrease in the surface tension, which may be explained by the existence of a hydrogen bond network in the carboxylic acid-terminated copolymers
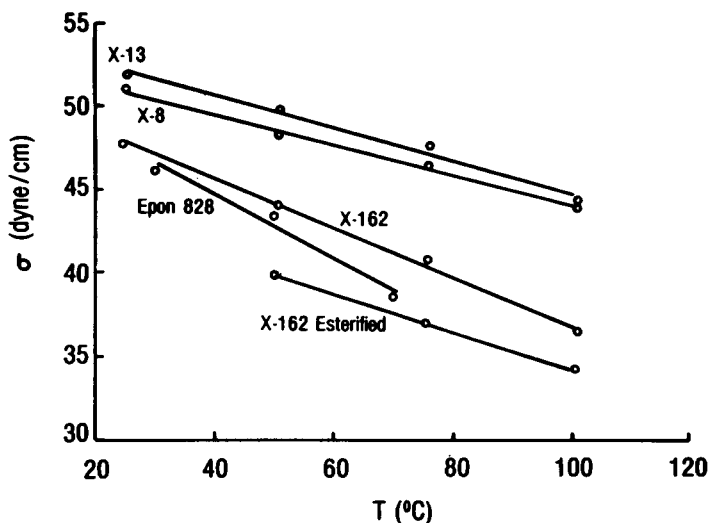
Fig. 2. Temperature dependence of the surface tension.

that causes the copolymer to behave as though it had a much greater molecular weight. Evidence for such a network was provided by the observation of a significantly higher viscosity for the carboxy-terminated material. With the methyl-ester-terminated copolymer, no such network exists, and the polymer behaves as a low molecular weight polymer. These carbomethoxy-terminated copolymers are used as a model system, where end group association can be avoided, and the influence of polymer properties on interfacial tension is explored, not the effect of end groups. The temperature dependence of the surface tension for the four samples is ~ −0.1 dyn/cm °C, consistent with temperature dependencies observed in other polymer systems (most dependencies are ~ −0.06 dyn/cm °C).[14] Weaver determined the surface properties of several epoxy systems and found the temperature dependence of the surface tension to be −0.11 dyn/cm °C.[23]

The interfacial tension of three copolymer-epoxy pairs was determined at 55°C; the results are given in Table IV. At this temperature, all systems are below the cloud point,[12] and no mixing occurs, even though the components are miscible at higher temperatures. As the acrylonitrile content of the copolymer increases, the interfacial tension decreases. This is reasonable based on solubility parameter arguments, in that the copolymer's solubility parame-

TABLE IV
Interfacial Tension vs. Copolymer Composition at 55°C

System	Acrylonitrile in copolymer (%)	γ (dyn/cm)
X162–epoxy	0	1.52
X8–epoxy	18	0.58
X13–epoxy	27	0.55

ter approaches that of the epoxy as the acrylonitrile content increases, and the two materials become more compatible.

Williams et al. modeled the segregation of a dispersed phase during a thermoset polymerization.[11,12] The free energy change for the formation of spherical domains is given by

$$\Delta G = (4/3)\pi r^3 \Delta G_N + 4\pi r^2 \sigma \tag{2}$$

where r is the radius of the dispersed domains, ΔG_N the free energy change involved in the separation of a dispersed phase of any composition, and σ the surface tension. ΔG reaches a maximum for the critical radius r_c, and

$$r_c = 2\sigma/|\Delta G_N| \tag{3}$$

Particles of size r_c or larger are thermodynamically stable and grow spontaneously. When nucleation is the controlling factor, the particle size is thus expected to be directly proportional to the interfacial tension. Williams et al.,[12] on the other hand, concluded that growth was the controlling process, and that interfacial tension had practically no effect on the final particle size distribution.[15]

Wu investigated the interfacial and rheological effects on the formation of a dispersed phase in incompatible polymer blends during melt extrusion.[24] The relationship for the master curve obtained is

$$\frac{G\eta_m a}{\gamma} = 4\left(\frac{\eta_d}{\eta_m}\right)^{\pm 0.84} \tag{4}$$

where G is the shear rate, a the particle diameter, η_m the matrix viscosity, and η_d the dispersed-drop viscosity. Thus the dispersed-drop size is predicted to be directly proportional to the interfacial tension, as was found if nucleation was the controlling step.

The prereacted epoxy resins are already immiscible in the uncured state. In this case, it might be expected that either of relations (3) or (4) would apply. The dispersed phase size for the pre-reacted epoxy systems (Table III) does decrease significantly with decrease in the interfacial tension (Table IV). It is interesting to note that the X8–epoxy and X13–epoxy systems have similar interfacial tensions and particle sizes, even though the solubility parameter differences are quite different (Table I) for the two systems. These observations provide qualitative support for the hypothesis that particle size for the prereacted systems is dependent to a certain extent on the interfacial tension.

The relationship between interfacial tension and particle size is much weaker, however, than the direct relationship predicted by eqs. (3) and (4). The failure of these simple relationships is probably related to the complexity of the systems studied. The particles have an internal structure (i.e., core–shell), and, after blending, coalescence is apparent during the reaction. A more sophisticated model, including the effects of coalescence, would be required to quantitatively account for the resultant particle size of these prereacted types of rubber-modified epoxies.
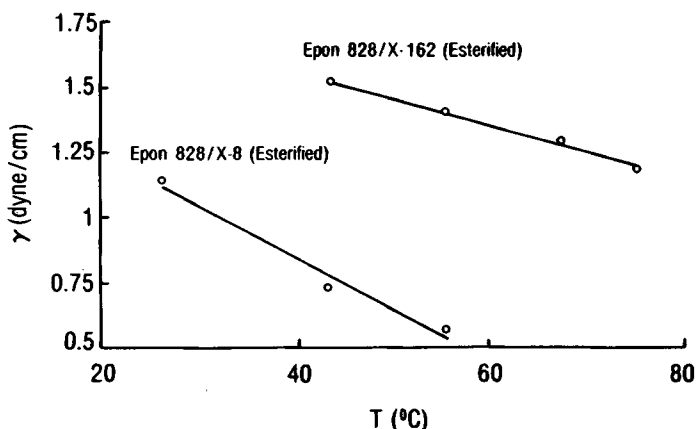
Fig. 3. Temperature dependence of the interfacial tension.

The effect of temperature on interfacial tension was studied using two rubbers, one with no acrylonitrile (carbomethoxy-terminated PBD), the other containing 18 wt % acrylonitrile. Plots of interfacial tension versus temperature are shown in Figure 3. As the temperature increases, the interfacial tension decreases linearly for both pairs, with a value of $\sim$ 0.01 dyn/cm °C for both systems. This value compares favorably with those found in other polymer pairs, such as PDMS/PBD.[22]

If we extrapolate the experimental interfacial tension data for Epon/X8 (esterified) in Figure 3 to $\gamma = 0$, we find a predicted critical point of ca. 87°C. This value compares favorably with the cloud point data of Williams et al.[12] (The composition used in the interfacial tension measurements was approximately 15% rubber by volume.) The interfacial tension data can be used to evaluate the applicability of Antonoff's rule[13] for these systems. This rule states that the interfacial tension is simply related to the difference in surface tensions of the two constituents. The results of application of this rule to the surface tension data for Epon and esterified X162 (Fig. 2) are given in Table V. The estimates by Antonoff's rule do generally produce the correct magnitude of interfacial tension, but clearly are not quantitative.

Interfacial tension can be also calculated from the surface tensions of the two phases by harmonic-mean or geometric-mean equations[14]; however, a more rigorous treatment of the interfacial region is possible by using a statistical thermodynamic theory (mean-field theory) as given by Helfand and

TABLE V
Comparison of Experimental Interfacial Tensions for Epon/X162-esterified
with the Predictions of Antonoff's Rule

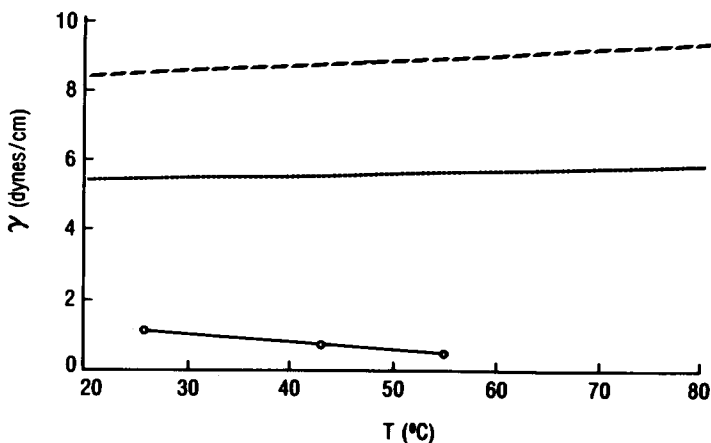| Temperature (°C)	Interfacial tension (dyn/cm)	
	Experimental	Calculated
50	1.47	3.5
70	1.25	1.0

Fig. 4. Comparison of the theoretical and the experimental (○) temperature dependence of the interfacial tension, for Epon 828 against X8: the (---) theoretical prediction generated using interaction parameters reported by Williams et al.[12]; (...) the theoretical prediction which is based upon solubility parameters.

Tagami.[25] For infinite molecular weight, they obtained the expression

$$\gamma = (\chi/6)^{1/2}\rho_0 bkT \tag{5}$$

where χ is the Flory–Huggins interaction parameter, b the effective statistical segment length, and ρ_0 the average monomer density. The theory was extended by Helfand and Sapse to remove the restriction of property symmetry of the polymers.[26]

Figure 4 shows the theoretical and the experimental relationships of the temperature dependence of the interfacial tension for the two polymer pairs. The interaction parameter required was obtained by two procedures: from the solubility parameters according to the regular solution expression

$$\chi = (\delta_A - \delta_B)^2/\rho_0 kT \tag{6}$$

where δ_i is the solubility parameter of component i (Table I); and from the expression obtained from cloud point measurements on a similar system,[12] $\chi = 0.336 + 69.457/T$. The statistical segment length b was estimated using the value of $r_0/M^{1/2}$ for PBD. The theory using either expression for χ overestimates the interfacial tension by a factor of 4, and yields a temperature dependence that is opposite from that found experimentally. The poor agreement may be associated with the fact that the infinite molecular weight assumption invoked by the theory is probably invalid for our systems.

SUMMARY

The interfacial tension between an epoxy resin and butadiene–acrylonitrile copolymers are determined, using digital image processing techniques and a recently developed robust statistical algorithm. The effects of copolymer composition and temperature on the interfacial tension are explored. The

interfacial tension is found to correlate qualitatively with the morphology of prereacted epoxy systems: increasing acrylonitrile content of the copolymer results in a decrease in the interfacial tension and a corresponding decrease in the domain size of the dispersed rubber phase in the epoxy matrix. This correspondence is much weaker, however, than that predicted from either nucleation or rheological arguments. The interfacial tension data are compared to the theoretical predictions of Helfand and Tagami using both the interaction parameters reported by Williams et al. and those estimated from solubility parameters. In both cases, the theory strongly overestimates the magnitude, and fails to reproduce the appropriate temperature dependence of the interfacial tension.

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