

Dynamic Mechanical Properties of Epoxy-Rubber Polyblends

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Synopsis

The dynamic mechanical properties of the epoxy resin of the diglycidyl ether of bisphenol A cured with varying amounts of a carboxyl-terminated butadiene-acrylonitrile copolymer were determined. Isochronal measurements were made between -90° to 170°C for eight compositions. Mechanical relaxations indicate the degree of interaction and the state of mixing of the two-phase system. Phase reversal occurs at a volume fraction of 0.5, where an intermediate compound is formed. In the low concentration range of the elastomeric phase, the impact strength improvement correlates well with an increase in the energy absorption of the relaxation. The known morphology of the system at this composition range allowed testing of various phenomenological mechanics models proposed to calculate the tensile properties of composite systems.

INTRODUCTION

Thermosets containing a small amount of a rubbery constituent are becoming increasingly important in the high-impact plastics field. The particular system of interest in this study was the epoxy resin of the diglycidyl ether of bisphenol A (DGEBA) containing varying amounts of a carboxyl-terminated copolymer of butadiene-acrylonitrile (CTBN). This is a low molecular weight liquid prepolymer which, under suitable concentration, catalyst, and curing conditions, polymerizes and precipitates as a separate phase in the epoxy matrix.^{1,2}

Previous structure-property work correlated such parameters of the dispersed phase at its \bar{M}_n , acrylonitrile content, size, and morphology of the rubbery inclusions with the fracture energy of the composite.³⁻⁵ A study of the chemistry of this system in relation to the initial concentration of the epoxy-rubber constituents has also been published.⁶

Our study covers the dynamic mechanical properties of the above system over a wide temperature and composition range. Although the useful toughened thermoset consists of a small amount of rubber in the epoxy matrix, the inverse system consisting of an elastomeric epoxy-reinforced matrix could also prove useful. Several studies covering the dynamic

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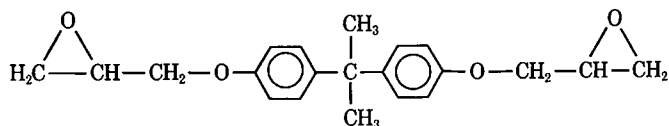
mechanical properties of polymerized epoxy resins appeared in the literature.⁷⁻¹³ However, to the best of our knowledge, no such measurements of the present composite system have been reported.

We aimed at correlating the dynamic mechanical properties with the available morphological and ultimate mechanical behavior. This is possible when the toughened plastics are prepared under similar conditions.¹⁴ The degree of mixing and/or interaction of the two phases as well as the possible formation of new phases as the composition changed was also to be assessed. Finally, the system could be used to test various phenomenological models proposed to predict the properties of a polyblend from those of its pure components.

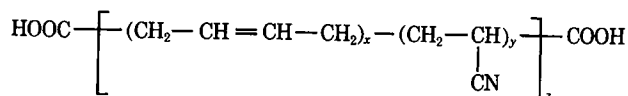
EXPERIMENTAL

Materials and Specimens Preparation

The samples obtained from B. F. Goodrich Chemical Co., Cleveland, Ohio, had been prepared using as resin the DGEBA (Epon 828, Shell Chemical Co.),



and as the rubbery prepolymer, the Hycar CTBN of the structure



where, on the average, $x = 5$, $y = 1$, and $z = 10$. This corresponds to an \bar{M}_n of 3,300 and bound acrylonitrile of 18.8%. Curing was performed by heating the well-mixed, degassed components with piperidine (5 phr based on 100 parts of epoxy) at 120°C for 16 hr.

The following compositions of CTBN/DGEBA were studied: 0/100, 5/100, 10/100, 20/100, 40/100, 80/100, 100/50, 100/25, and 100/12.5. The last three compositions were prepared using the DGEBA from Dow Chemical Co. (Dow ER331) and 1.5 phr of triethylenetetramine as the curing agent. Details on sample preparation have been reported.³

Specimens for the measurements were prepared by cutting thin strips with the microtome (R. Jung A.G., Heidelberg, Germany). Films of uniform thickness down to 0.05 mm could thus be easily obtained. At higher temperatures, thicker specimens were used. For the soft and rubbery materials, uniform strips were cut using a strong blade. During the cutting of the plastic materials, some rolling and surface crazing occurred. This surface deformation was limited to a small fraction, 1/5000 to 1/1000, of the film thickness, and it is assumed that the dynamic mechanical properties were not significantly affected by this. Our data on cured pure resin

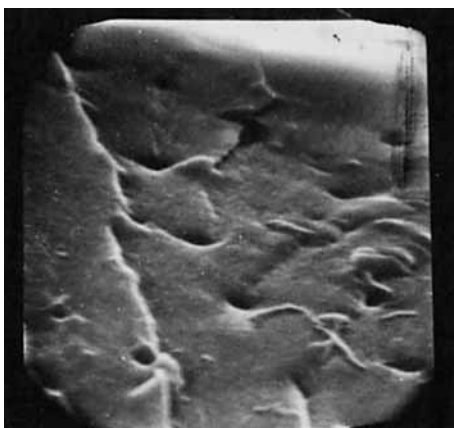


Fig. 1. Scanning electron micrograph of film strip CTBN/DGEB (10/100); $\times 10,000$.

are in agreement with those reported by Nielsen and co-workers.¹¹ The morphology and the extent of surface deformation of a specimen at one composition is indicated in Figure 1. The small holes are due to the rubbery inclusions, some of which have been pulled out by the shearing action of the microtome. Their dimensions are of the order of 3000–4000 Å. This is smaller than the particle dimensions reported previously^{4,5} and is due to the different mode of specimen preparation. In our case, only part of the spherical inclusion has been removed. Film distortion (rolling) was corrected by keeping the specimens extended for a few days between glass plates under light pressure.

Apparatus

Dynamic mechanical data, loss tangent, $\tan \delta$, and complex modulus $|E^*|$ were obtained between -90° and 170°C at 110 Hz. Use was made of the direct-reading viscoelastometer (Rheovibron, Model DDV-II, Toyo Measuring Instruments Co. Ltd., Tokyo, Japan). In calculating the quantity $|E^*|$, the small deformation of the instrument clamps was taken into account. A slow stream of precooled nitrogen kept the measuring chamber free of moisture. Measurements were taken at approximately 3°C intervals, except near the relaxation maxima where the interval was sufficiently small to locate the peak accurately.

RESULTS AND DISCUSSION

The experimental results are summarized in Figure 2 for the loss tangent, in Figure 3 for the storage modulus, and in Figure 4 for the loss modulus. The $\tan \delta$ variation with temperature as a function of composition provides a qualitative picture of the degree of mixing of the two phases. In Figure 2a, we note that inclusion of 5 phr of CTBN does not alter the magnitude and location of the low-temperature relaxation. A small decrease of the

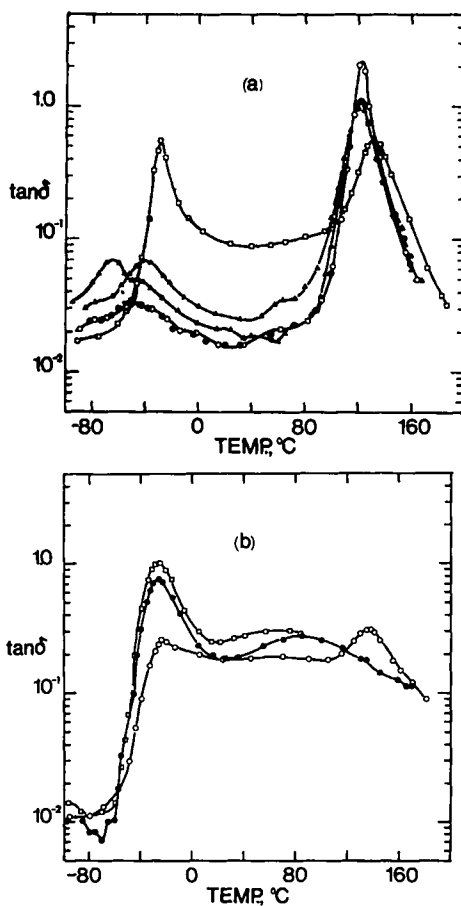
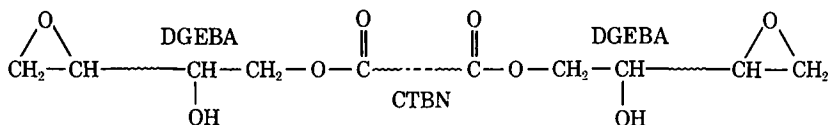


Fig. 2. Temperature dependence of loss tangent $\tan \delta$ for various compositions of CTBN/DGEBA at 110 Hz: (a) (○) 0/100; (●) 5/100; (Δ) 10/100; (▲) 20/100; (□) 40/100. (b) (○) 80/100; (●) 100/25; (□) 100/12.5.

high-temperature peak is observed. No change in the value of the extensional modulus in Figure 3 is likewise observed. Increasing the amount of CTBN to 10 phr shifts the original peak at -50° to -42°C , and an additional peak appears with a maximum at -65°C . There is also a small decrease of E' around 60°C (see Fig. 3), which indicates a weak transition due to the rubbery inclusion or to an intermediate compound. Further increase of the CTBN content shifts the low-temperature peak to higher temperatures: -34°C at 40 phr of CTBN. The emergence of a new broad relaxation is also evident between the two pure-component peaks. This can be attributed to the formation of an epoxy-rubber compound whose existence is more evident at 80 phr CTBN, Figure 2b. Siebert and Riew⁶ report that a 50-50 mixture of CTBN and DGEBA is compatible and suggest that the precipitated phase is an epoxy-terminated liquid rubber of the structure



Blending of this compound with the resin displaces the high-temperature peak to 135°C, and mixing with the rubber displaces the low-temperature relaxation to -27°C (see Fig. 2b). The occurrence of crystallization of the rubbery phase at the 40 phr CTBN composition is worth noting (see Fig. 3). No such crystallization was observed at higher rubber concentrations as was the case for a completely incompatible system.¹⁵ The low-temperature relaxation peak passes through a maximum between 0–20 phr of CTBN. This maximum at 10 phr is more evident in the loss modulus curves, Figure 4a. In this connection one should note that the maximum in the fracture energy of this composite is at approximately the same composition.⁴ This correlation of low-temperature relaxation height (or area) with impact strength is valid only at low CTBN percentages at which no intermediate peak is observed, and the rubbery phase is precipitated in the form of discrete spherical globules. As the CTBN amount increases, the rubber becomes the matrix where the rubber-epoxy intermediate is dissolved. The high-temperature peak is displaced to 80°C, decreasing in height, while the low-temperature peak is increasing in height and is displaced to lower temperatures (see Figs. 2b and 4b).

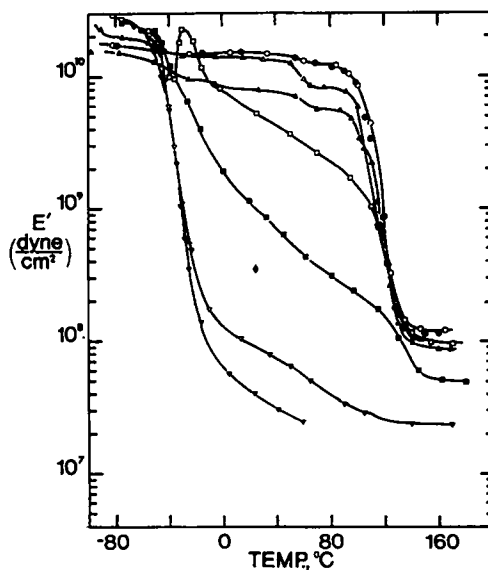


Fig. 3. Temperature dependence of storage modulus E' for various compositions of CTBN/DGEBA: (○) 0/100; (●) 5/100; (△) 10/100; (▲) 20/100; (□) 40/100; (■) 80/100; (◆) 100/50 (at 25°C); (▽) 100/25; (▼) 100/12.5.

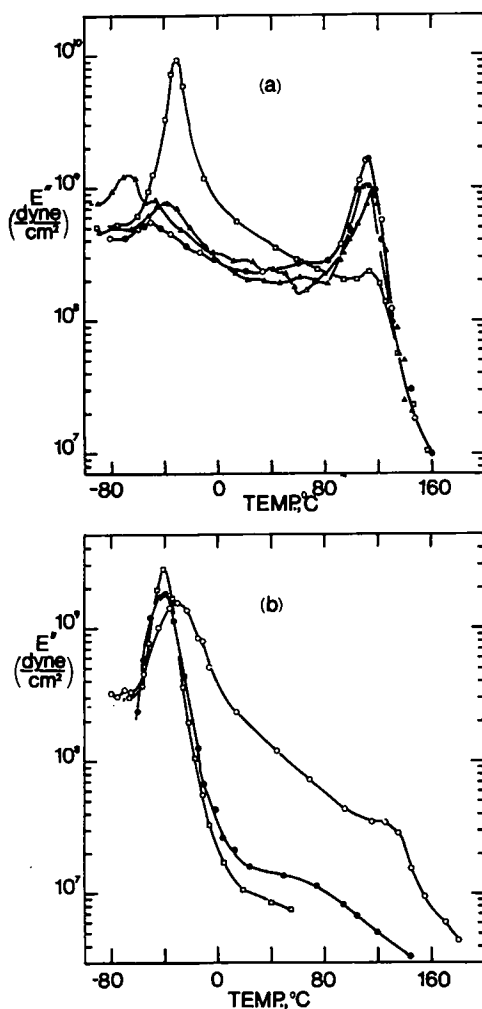
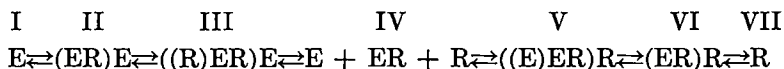


Fig. 4. Temperature dependence of loss modulus E'' for various compositions of CTBN/DGEBA: (a) (O) 0/100; (●) 5/100; (Δ) 10/100; (\blacktriangle) 20/100; (\square) 40/100. (b) (O) 80/100; (●) 100/25; (\square) 100/12.5.

According to Kaelble,¹⁶ these mixing states can be summarized according to the following scheme:



where R denotes the rubbery and E the epoxy component. The parentheses indicate a discontinuous, included phase. The useful toughened thermosets would correspond to state II where the rubbery phase with chemically attached epoxy is precipitated as a distinct phase, in the epoxy matrix. This attachment is important for toughening to occur. Simple

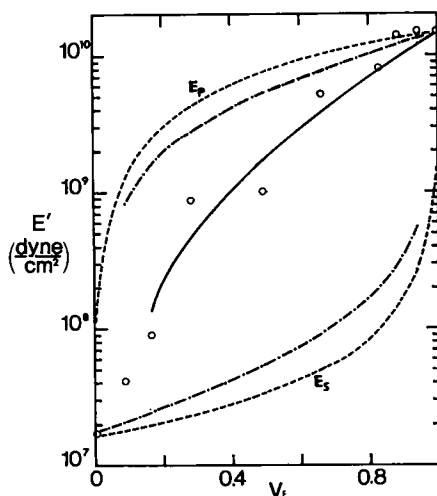


Fig. 5. Comparison of observed and calculated elastic modulus at 25°C: (O) observed; (---) series and parallel models; (-·-·-) Kerner's model; (—) Hashin's model.

elastomeric inclusions of a noncarboxylic elastomer phase do not improve toughness. Also, direct morphological evidence indicates that the precipitated particles are not a homogeneous elastomer.^{5,17}

State IV indicates limited phase separation of the intermediate formed from the other pure components (see Fig. 2b, 80 phr CTBN), and the subsequent states indicate matrix reversal and the increasing rubbery character of the composite. The broadness of the intermediate relaxation in Figure 2b shows the compatibility of ER with both E and R. The existence of a discrete rubbery phase in state III could be supported by the E' -versus-temperature variation in Figure 3, which manifests crystallization reinforcement (40 phr CTBN). There is no experimental evidence for the existence of the corresponding inverse system V.

The known morphology of the dispersed phase^{4,5} and the composition dependence of our mechanical spectroscopy data prompted us to test various mechanics models predicting the effective composite modulus. The results of this comparison are shown in Figure 5. The values for the pure CTBN were calculated by extrapolating to $V_R = 1.0$, data on rubber-rich composites. The Poisson ratio ν of the composites was taken as the arithmetic mean of their components weighted as their volume fraction. For the CTBN, $\nu = 0.48$,¹⁸ for the DGEBA, $\nu = 0.34$.¹⁹ The corresponding elastic moduli at 25°C were 1.70×10^8 and 1.50×10^{10} (dynes/cm²). In Figure 5, the experimental data indicate that small amounts of CTBN do not weaken the matrix; this, combined with the increased toughness of these compositions, has important applications. At $V_R > 0.30$, the weakening of the thermoset is evident. At these compositions, the spherical rubbery domains approach each other, and from geometric considerations (for a cubic lattice) one would expect coalescence at approximately $V_R \approx$

0.50. These changes reflect on the discontinuity of the modulus-versus-composition curve.

The parallel and series models in Figure 5 serve only as an estimate of the upper and lower bounds of the composite modulus.

Kerner's equations²⁰ do not offer any improvement. His theory is based on the assumption that the inclusions are spherical and there is perfect adhesion between the phases. Another model tested in Figure 5 was proposed by Hashin²¹ and is expressed by

$$K_c = K_m + (K_d - K_m) \frac{(4G_m + 3K_m)V_D}{4G_m + 3K_p + 3(K_m - K_p)V_D} \quad (1)$$

wherein subscripts c , m , and d refer respectively to the composite, matrix, and dispersed phase properties; K and G to the bulk and shear modulus; and V_D the volume fraction of the dispersed phase. Bulk and shear moduli were calculated using the standard expression

$$E = 2G(1 + \nu) = 3K(1 - 2\nu) \quad (2)$$

wherein E is Young's modulus.

The inclusions are assumed to be perfectly spherical, uniformly dispersed with no interactions. Thus, the model cannot be expected to hold well

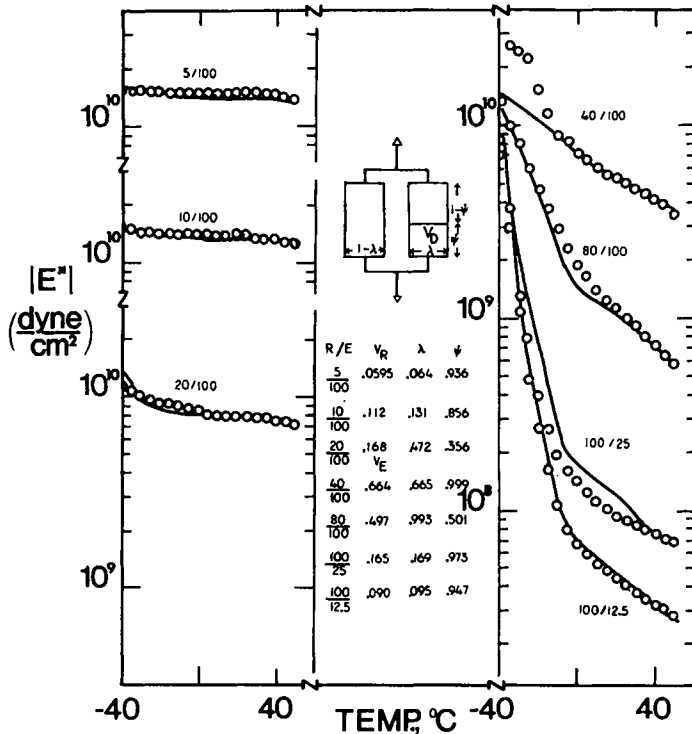


Fig. 6. Testing of Takayanagi's model between -40° to 50°C for various compositions of CTBN/DGEBA (R/E): (O) observed; (—) calculated.

when $V_R > 0.3$. It is seen that the modulus is adequately predicted over a wide composition range.

The results were also analyzed using the models proposed by Takayanagi.²² The experimental results could be best fitted to the following model (see Fig. 6), defined by

$$E_C^* = \lambda \left(\frac{\psi}{E_R^*} + \frac{1 - \psi}{E_E^*} \right)^{-1} + (1 - \lambda)E_E^* \quad (3)$$

$$V_D = \lambda\psi$$

wherein E_C^* , E_R^* , and E_E^* are the complex moduli of the composite, the rubbery, and epoxy phase, respectively; and the λ , ψ parameters define the volume fraction of the dispersed phase. These were determined by solving simultaneously the above equations at 5°C intervals between -40° and 50°C and choosing that pair of λ and ψ which reproduced E_C^* with the smallest deviation. The degree of fit is shown in Figure 6, where the various model parameters are also reported. The poor fit at 40 phr of CTBN is due to crystallization phenomena which affect E_C^* , while the pure CTBN values were obtained from compositions where no crystallization was observed. The results again indicate that at compositions of up to 20 phr CTBN the epoxy serves as the matrix. At higher rubber concentrations the matrix becomes the CTBN.

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