

Moisture Absorption Behavior of Rubber-Modified Epoxy Resins

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ABSTRACT: The moisture absorption behavior of diglycidyl ether of bisphenol A/ethylene diamine resins incorporating a carboxy-terminated butadiene-acrylonitrile rubber was investigated and associated with their morphology of phase separation. Although the diffusion coefficient of moisture was increased with the rubber content, its activation energy and free volume for moisture diffusion were barely changed until phase inversion occurred. After phase inversion, the free volume was significantly increased, and the

activation energy decreased. In addition, the moisture absorption also reduced the β -transition temperature of the resins and slightly increased the glass-transition temperature before phase inversion. However, the reverse was found after phase inversion. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3718–3724, 2002

Key words: resins; rubber; phase separation

INTRODUCTION

Epoxy resins are used in many important industries, such as the aerospace, electronic, and automobile industries. However, because of their brittle nature, they are often toughened by liquid rubbers.^{1–5} One of the most commonly used liquid rubbers is carboxy-terminated butadiene-acrylonitrile (CTBN) rubber because it is soluble in uncured epoxy formulations.⁶ It has been reported that during curing with a small amount of rubber, phase separation occurs, with the rubber-rich phase dispersing in the rubber-poor matrix.⁵ The toughening effect of rubber is increased with the rubber content. However, a phase inversion, in which the rubber-poor phase becomes a dispersed phase, also occurs when the rubber content is increased to a certain extent. After phase inversion, the toughening effect of CTBN decreases with the content.⁷

The moisture absorption behavior of epoxy resins has been widely investigated, but it is still not fully understood. For tetrafunctional epoxy resins such as tetraglycidyl-4,4'-diamino diphenylmethane cured with 4,4'-diamino diphenyl sulfone, moisture absorption can reach 6–7 wt %.^{8,9} The absorbed water acts as an efficient plasticizer, strongly reducing the glass-transition temperature (T_g) of the resin.^{8–10} As for difunctional epoxy resins such as diglycidyl ether of

bisphenol A (DGEBA), moisture absorption ranges from 2.5 to 4.5 wt %, depending on the type and amount of the curing agent used for curing.^{6,11} Their efficiency in plasticizing DGEBA resins is controversial. Ivanova et al.⁶ reported a significant decrease in T_g for the moisture absorption of a dicyandiamide-cured, silica-filled, rubber-modified DGEBA epoxy resin system. However, no plasticization effect was reported for the moisture absorption of DGEBA cured with diethyltriamine.¹¹ In this study, an antiplasticization effect,¹² in which T_g was increased with moisture absorption, was found for DGEBA cured with ethylene diamine (EDA) with and without a CTBN rubber-rich dispersed phase. Once the phase inversion occurred with an increasing content of CTBN rubber, the resin systems became plasticized by the absorbed moisture.

Two forms of absorbed water in an epoxy matrix have been observed with dielectric relaxation methods:^{6,13} free water and bound water. The free water might reduce the free volume of the networks because it behaves like a filler. Conversely, the bound water might increase the free volume because it swells the structure. However, it is still not clear how they disperse in the two-phase networks of rubber-toughened epoxy resins. In this study, we employed dynamic mechanical analysis to investigate their distribution in resin networks.

EXPERIMENTAL

Sample preparation

The DGEBA used in this study was Shell's Epon 826 (Houston, TX) with an epoxy equivalent weight of 187

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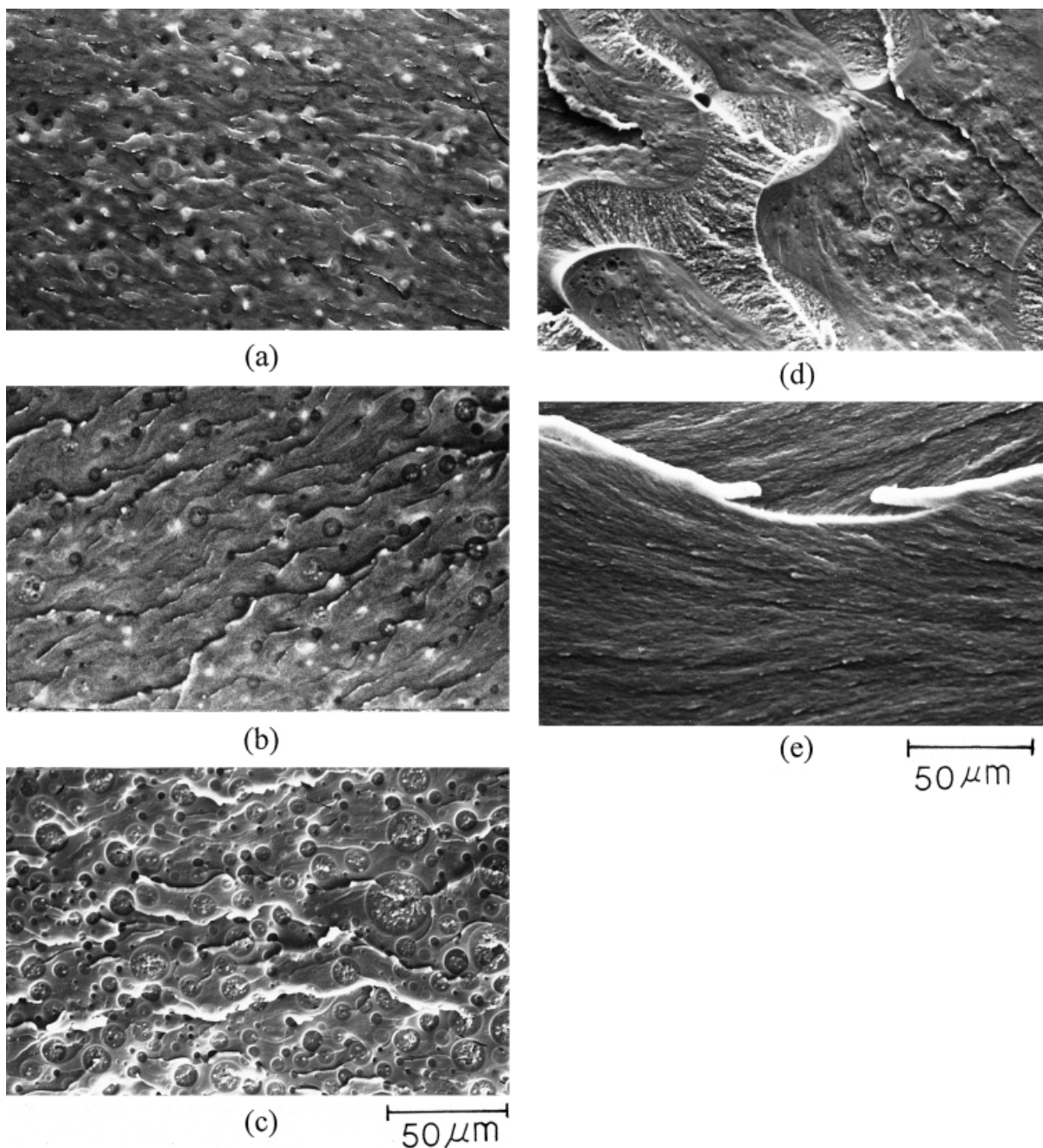


Figure 1 SEM micrographs of the fracture surfaces of DGEBA/EDA epoxy resins incorporating the following amounts of CTBN rubber: (a) 5, (b) 10, (c) 20, (d) 30, and (e) 50 phr.

$\pm 4 \text{ g equiv}^{-1}$, as measured by the hydrochloric acid/methyl ethyl ketone method.¹⁴ The CTBN was obtained from B.F. Goodrich (Cleveland, OH) and contained 17 wt % bound acrylonitrile with a number-average molecular weight of 3500 g mol^{-1} . DGEBA and CTBN were preheated to 90°C , mixed in various concentrations by mechanical stirring until the mixtures became transparent, and cooled to room temperature. The mixtures were added with the EDA curing agent (reagent-grade; Osaka Chemical Industry,

Osaka, Japan) in stoichiometric quantities with the epoxy groups and then were degassed in vacuum before casting. All the specimens were cured at 30°C for 24 h plus 10 h at 128°C for the postcure.

The cured specimens for the moisture absorption tests were cut to $30 \text{ mm} \times 14 \text{ mm} \times 2 \text{ mm}$. The sample edges were polished with $0.03\text{-}\mu\text{m}$ aluminum oxide (Al_2O_3) for the removal of occasional surface irregularities. All samples were stored in a desiccator at 60°C for at least 2 weeks before the initiation of the experiments.

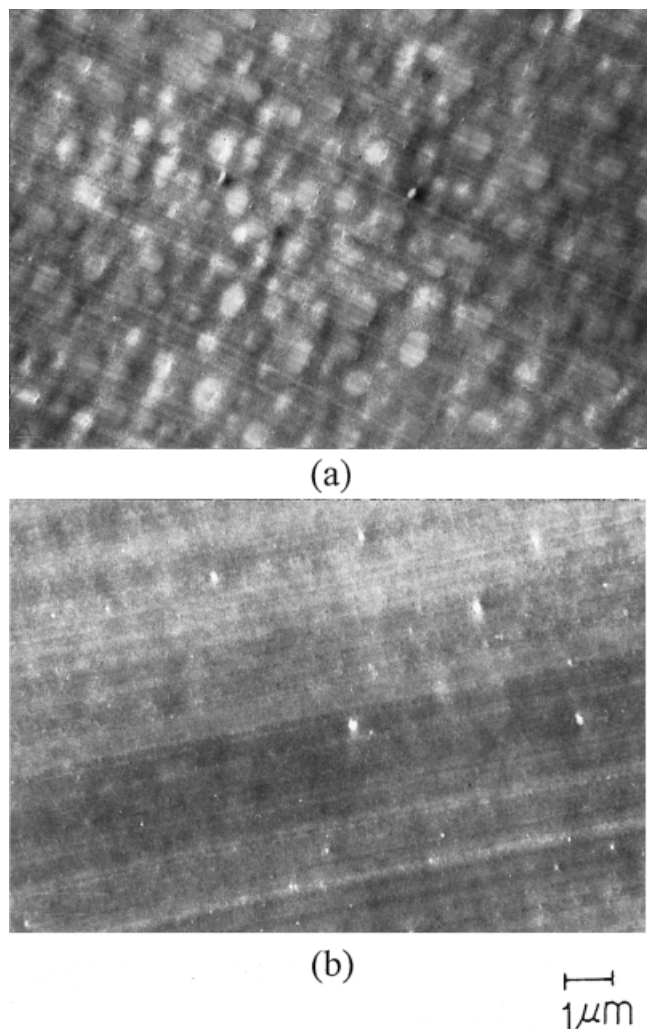


Figure 2 TEM micrographs of OsO_4 -stained DGEBA/EDA epoxy resins incorporating the following amounts of CTBN rubber: (a) 50 and (b) 70 phr.

Testing procedure

For the preparation of the fracture surfaces of cured specimens for scanning electron microscopy (SEM) investigations, the samples were cast and cured in a compact-tension-specimen mold and fractured according to ref. 15. The fracture surfaces obtained were gold-spattered and investigated with a JEOL JWM-5200 scanning electron microscope (Tokyo, Japan). The specimens for transmission electron microscopy (TEM) were cast and cured in capsules and then were stained with osmium tetroxide (OsO_4) before being sectioned with an ultrathin microtome. A JEOL JEM-100U transmission electron microscope was used to investigate the microstructure.

The moisture absorption experiments of the samples were conducted in an environmental chamber controlled at 60°C and 100% relative humidity (RH), at 70°C and 100% RH, and at 80°C and 100% RH. At chosen time intervals, the samples were removed from

the environmental chamber and immediately weighed to 0.00001 g. Dynamic mechanical measurements were performed with a TA 9900-983 dynamic mechanical analyzer (New Castle, DE). Tests were run from -100 to 200°C at a heating rate of 10°C/min and at an oscillation amplitude of 0.2 mm peak to peak. The moisture-saturated samples were wrapped with aluminum foil before testing.

RESULTS AND DISCUSSION

Morphology of the rubber-modified epoxy resins

Figure 1 shows the SEM micrographs of fracture surfaces of DGEBA/EDA epoxy resins incorporating various amounts of CTBN rubber. When the rubber content was lower than 30 phr, the rubber-rich particles, 1–30 μm in diameter, were dispersed in the rubber-poor matrix. The particle size increased with the rubber content [see Fig. 1(a–c)] until the rubber-rich phase intermingled with the rubber-poor phase to form a cocontinuous-phase structure, as shown in Figure 1(d). When the rubber content was increased to 50 phr, phase inversion, in which the rubber-rich phase became a continuous phase, occurred [see Fig. 1(e)]. By using OsO_4 to stain the CTBN molecules in the ultrathin-microtomed specimens, we were able to observe the rubber-poor particles 0.5 μm in diameter dispersed in the rubber-rich matrix by TEM, as shown in Figure 2(a). When the rubber content was increased to 60 phr, two kinds of specimens were obtained: opaque specimens that had a similar two-phase morphology [Fig. 2(a)] and transparent specimens that had a homogeneous single-phase morphology. When the rubber content was increased to 70 phr, only transparent specimens were obtained, a TEM micrograph of which is shown in Figure 2(b).

Because the phase separation of rubber-modified epoxy resins took place in many curing stages (i.e., during curing at 30°C, during postcuring at 128°C, and during further cooling to room temperature after postcuring), the rubber-rich domains also experienced many stages of phase separation. Therefore, the small particles in the rubber-rich domains shown in Figure 1(b–c) were formed during the phase separation within the domains. The small particles were rubber-poor domains with structures similar to those found in the dispersed phase of epoxy resins containing 50 phr CTBN, as shown in Figure 2(a).⁷ In brief, the CTBN rubber content for phase separation was as high as 60 phr. At a lower rubber content, the rubber-rich phases (containing ~60 phr CTBN) were dispersed in the rubber-poor matrix (containing <5 phr CTBN) until a 30 phr rubber content was reached. After 30 phr, a phase inversion occurred.

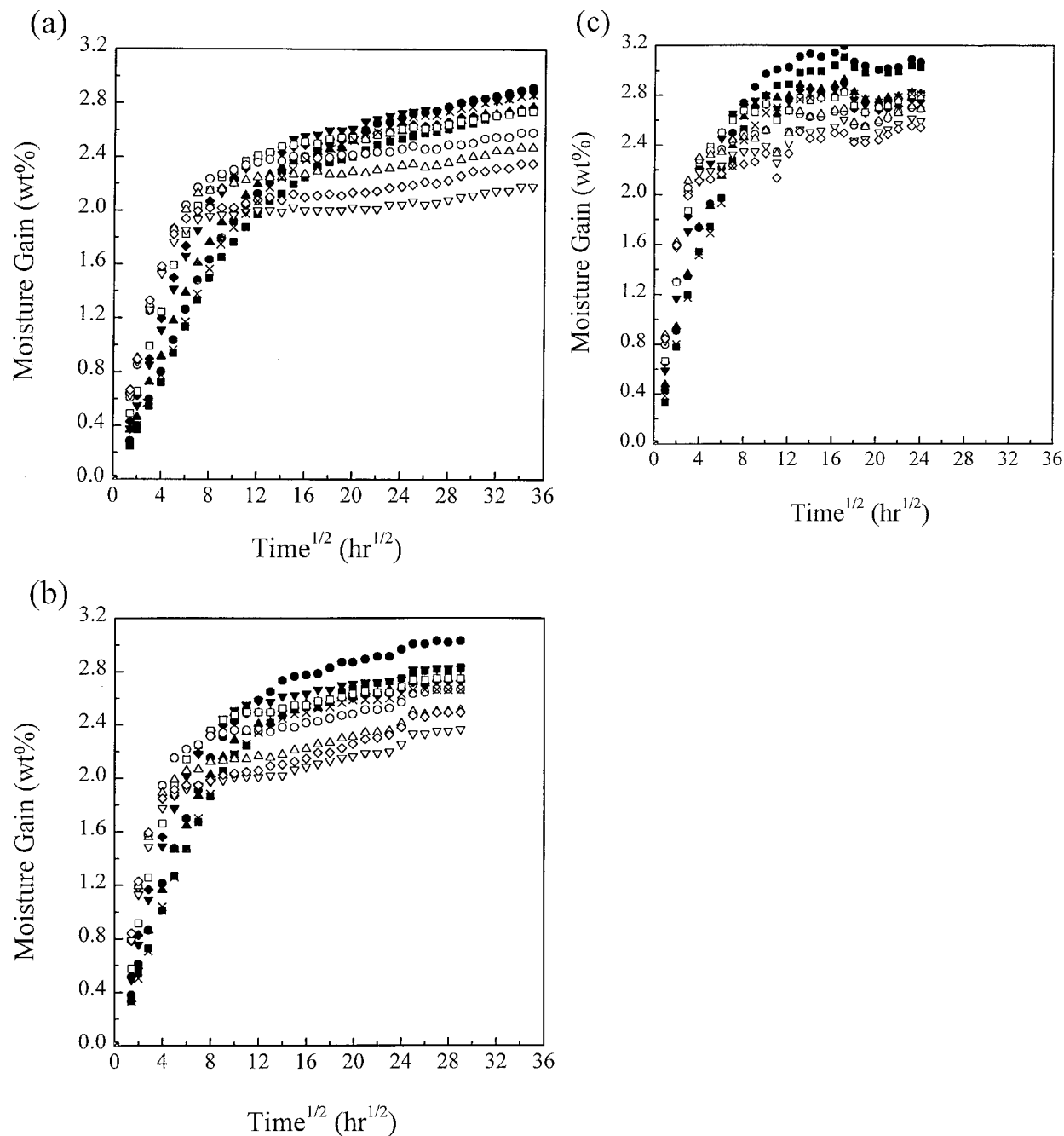


Figure 3 Moisture gains of DGEBA/EDA epoxy resins incorporating the following amounts of CTBN rubber, (\times) 0, (\blacksquare) 0.5, (\bullet) 5, (\blacktriangle) 10, (\blacktriangledown) 20, (\blacklozenge) 25, (\square) 30, (\circ) 50, (\triangle) 60, (\triangledown) 60*, and (\diamond) 70 phr, as a function of the square root of the time for which they were exposed to (a) 60°C and 100% RH, (b) 70°C and 100% RH, and (c) 80°C and 100% RH. The asterisk denotes specimens with a two-phase morphology.

Moisture absorption of the rubber-modified epoxy resins

Figure 3 shows the moisture gains of DGEBA/EDA epoxy resins containing various amounts of CTBN rubber versus the square root of the time for which they were exposed to a 100% RH environment at 60, 70, and 80°C. The maximum moisture absorption was slightly decreased with the rubber content be-

fore phase inversion, as shown in Figure 4. After phase inversion, the decrease was more pronounced. In addition, the resin containing 60 phr CTBN with a two-phase morphology had lower moisture gain than that with a one-phase morphology. Apparently, the rubber-rich phase absorbed less moisture than the rubber-poor phase. However, if we assume that the moisture absorption followed

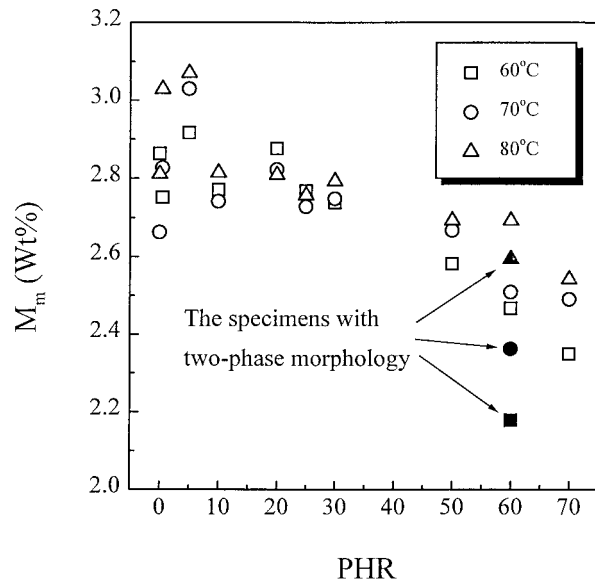


Figure 4 Maximum moisture (M_m) gains of rubber-modified DGEBA/EDA epoxy resins as a function of the CTBN content after exposure to 100% RH at (\square) 60, (\circ) 70, and (\triangle) 80°C.

the Fickian second law, the diffusion coefficient can be calculated as follows:⁹

$$D = \pi \left(\frac{h}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (1)$$

where M_1 and M_2 are the moisture gains at times t_1 and t_2 in the initial linear portion of the cures shown in Figure 3. The results are plotted with the rubber content in Figure 5. Before phase inversion, D almost

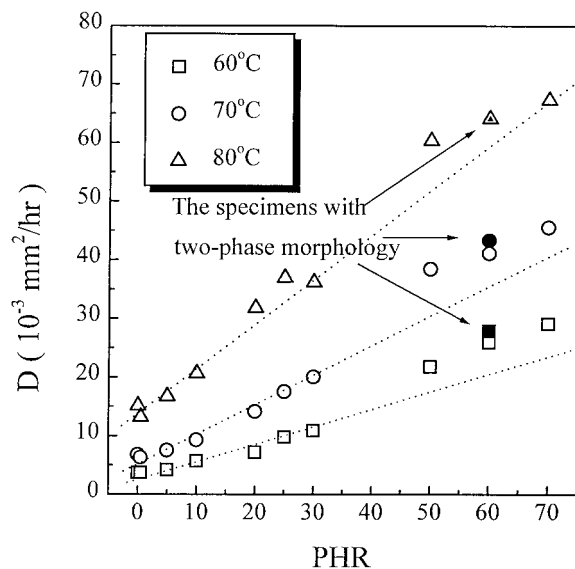


Figure 5 D of rubber-modified DGEBA/EDA epoxy resins as a function of the CTBN content after exposure to 100% RH at (\square) 60, (\circ) 70, and (\triangle) 80°C.

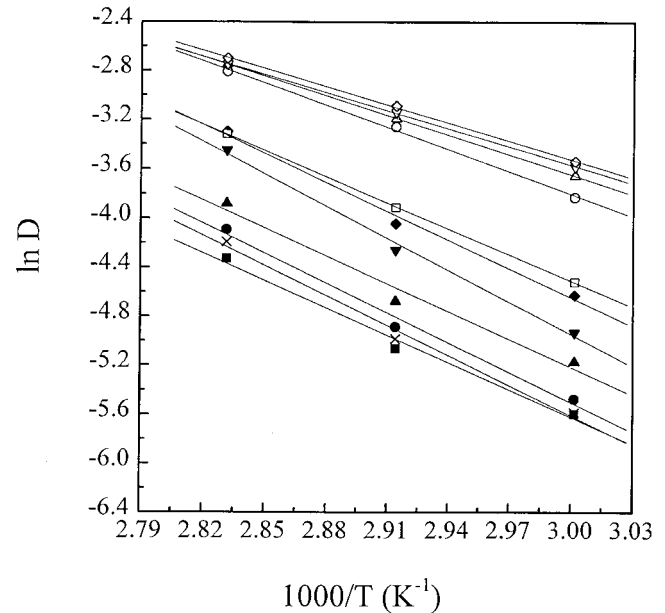


Figure 6 Arrhenius plots of $\ln D$ versus $1000/T$ for DGEBA/EDA epoxy resins incorporating the following amounts of CTBN rubber: (\times) 0, (\blacksquare) 0.5, (\bullet) 5, (\blacktriangle) 10, (\blacktriangledown) 20, (\blacklozenge) 25, (\square) 30, (\circ) 50, (\triangle) 60, (∇) 60*, and (\diamond) 70 phr. The asterisk denotes specimens with a two-phase morphology.

increased linearly with the rubber content. However, after phase inversion, D increased a little higher than the linear relation, as indicated in Figure 5. By using the Arrhenius plots,¹⁶ that is, the logarithmic plots of D versus the reciprocal of temperature, as shown in Figure 6, we were able to estimate the activation energy E_D for moisture diffusion:

$$D = D_0 \exp \left(-\frac{E_D}{RT} \right) \quad (2)$$

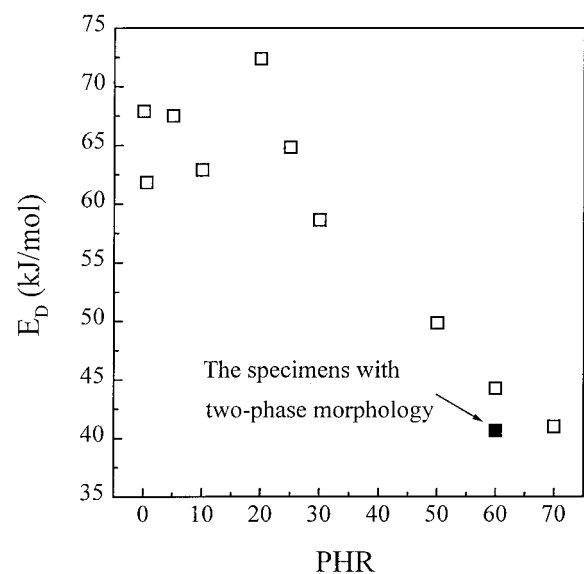


Figure 7 E_D of rubber-modified DGEBA/EDA epoxy resins as a function of the CTBN content.

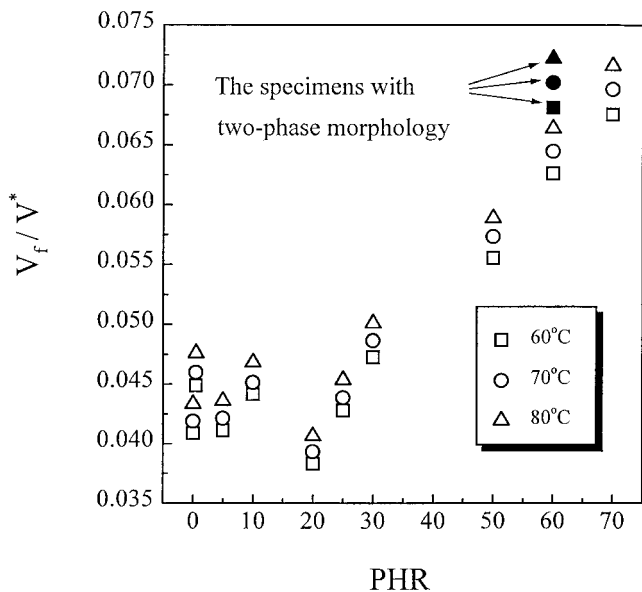


Figure 8 V_f/V^* of rubber-modified DGEBA/EDA epoxy resins for moisture diffusion as a function of the temperature and CTBN content.

where $D_o = [(\phi_o\delta^2)/6]$, which is the diffusion coefficient of moisture at $T = \infty$, is constant; ϕ_o is the jump frequency of water molecules at $T = \infty$; δ is the jump length of water molecules; R is the gas constant; and T is the absolute temperature.

The estimated E_D values of the epoxy resins containing various amounts of CTBN are shown in Figure 7. E_D was almost constant before a 30 phr rubber content and then decreased with the content. The resin containing 60 phr CTBN with a two-phase morphology had an E_D value even lower than that with a one-phase morphology. Apparently, the constant E_D value at a low rubber content was mainly due to the fact that the composition of the rubber-poor matrix did not change until a cocontinuous phase appeared (30 phr rubber content), by which the rubber-poor matrix was intermingled with the rubber-rich phases. At a 50 phr rubber content, the rubber-rich phase became a matrix, so E_D was decreased even further. At 60 phr, the specimens with a two-phase morphology had more rubber content in the matrix than those with a one-phase morphology, so E_D was further lowered.

The moisture diffusion was also dependent on the free volume V_f of the resin networks, as indicated by the Doolittle equation:¹⁷

$$D = D_o \exp\left(-\frac{BV^*}{V_f}\right) \quad (3)$$

where B is usually considered to be unity and V^* is the critical amount of free volume for a water molecule to jump to a new position. Therefore, the calculated V_f/V^* values from eq. (3) as functions of the rubber

content and temperature are plotted in Figure 8. The free volume increased with the temperature but barely changed with the rubber content until 30 phr was reached. Then, the free volume significantly increased after phase inversion. In addition, at a 60 phr rubber content, the specimens with a two-phase morphology had more free volume than those with a one-phase morphology. Obviously, the detected free volume for moisture diffusion was mainly in the resin matrix instead of the dispersed phase because the specimens with a two-phase morphology had more rubber in the matrix than those with a one-phase morphology.

The T_g value of the rubber-modified epoxy resins measured at the loss modulus peak in the dynamic mechanical spectra barely changed with the rubber content before phase inversion, as shown in Figure 9. After phase inversion, T_g decreased with the rubber content. Again, at a 60 phr rubber content, the specimens with a two-phase morphology had lower T_g values than those with a one-phase morphology. Obviously, the glass-transition behavior of the rubber-modified epoxy resins was dominated by the resin matrix instead of the dispersed phase. When the specimens were moisture-saturated at 60°C and 100% RH, the T_g values of the specimens before phase inversion began were almost higher than those of the corresponding dry samples. Water molecules behaved like fillers, reducing the free volume of the resin matrix. After phase inversion, the absorbed moisture significantly reduced T_g of the resin matrix. This indicates that the plasticization effect of water only occurred in the rubber-rich matrix.

However, the β -transition temperature (T_β) of the moisture-saturated specimens measured at the loss

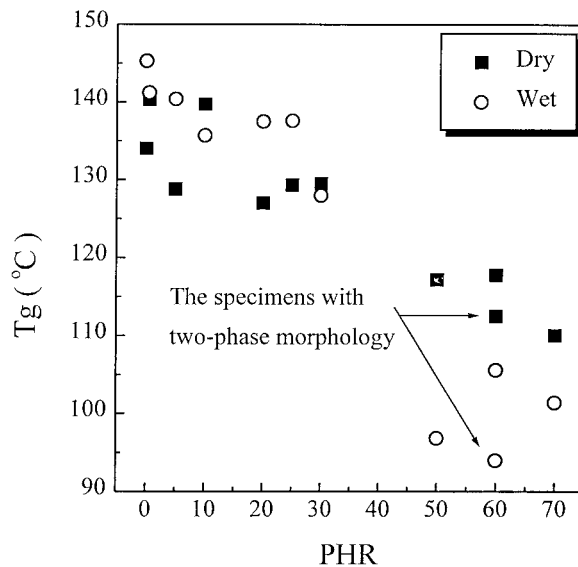


Figure 9 T_g of rubber-modified DGEBA/EDA epoxy resins as a function of the CTBN content: (■) without moisture absorption and (○) after moisture saturation at 60°C and 100% RH.

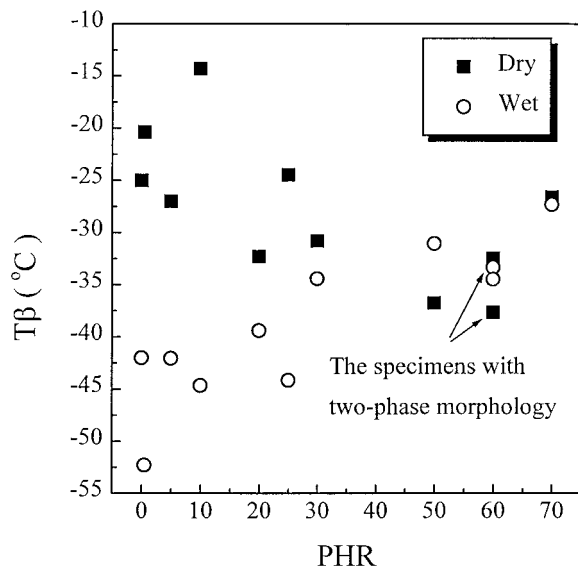


Figure 10 T_{β} of rubber-modified DGEBA/EDA epoxy resins as a function of the CTBN content: (■) without moisture absorption and (○) after moisture saturation at 60°C and 100% RH.

modulus sub- T_g peak in the dynamic mechanical spectra was significantly lower than that of the respective dry specimens before phase inversion (Fig. 10). After phase inversion, T_{β} was either increased (for the specimens with a two-phase morphology) or barely reduced (for the specimens with a single-phase morphology) by moisture absorption. The change in T_{β} with the rubber content was contrary to that of T_g . It was also reported that in the initial moisture absorption of tetrafunctional epoxy resins, the monitored T_{β} decreased rapidly to a lower temperature, but T_g was barely changed.⁹ Once the T_{β} leveled off, T_g decreased rapidly, along with a significant swelling of the specimens. The decrease in T_{β} was explained by the lubricity theory,¹⁸ in which the absorbed moisture was viewed as a lubricant that facilitated movements of the chain segments of the networks, even if other parts of the networks behaved like a gel network. Although some uncertainty over the exact molecular origin of the β transition remains, it is generally accepted that the β -transition peak is contributed by the starting of crankshaft motion of chain segments.^{19–21} Therefore, it is possible that because the absorbed moisture before phase inversion behaved like a filler in the resin matrix, it lubricated the local motion of chain segments.

After phase inversion, it behaved like a plasticizer and decreased T_g by swelling the resin matrix. Because of the strong interaction between the water molecules and the chain segments, the former retarded the local crankshaft motions of the latter. Therefore, T_{β} was increased.

CONCLUSIONS

The moisture absorption behavior of the rubber-modified epoxy resins under study was strongly affected by the phase inversion. Before phase inversion, the activation energy and free volume for moisture diffusion were almost independent of the rubber content. After phase inversion, the free volume was significantly increased, and the activation energy was reduced. In addition, before phase inversion, the absorbed moisture behaved like a filler that filled the free volume of the resin matrix and lubricated the local crankshaft motion of chain segments. After phase inversion, the absorbed moisture reduced T_g but retarded the local motions of chain segments.

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