

Thermal Analysis and Mechanical Characterization of Maleimide-Functionalized Benzoxazine/Epoxy Copolymers

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ABSTRACT: Maleimide-functionalized benzoxazine is copolymerized with epoxy to improve toughness and processibility without compromising the thermal properties. The incorporation of maleimide functionality into the benzoxazine monomer results in a high performance polymer. All three possible polymerization reactions are confirmed using Fourier transform infrared (FT-IR) spectroscopy. While maleimide-functionalized benzoxazine has a glass transition temperature, T_g , of 252°C, a further 25°C increase of T_g is

observed when copolymerized with epoxy. The flexural properties are also measured, and the copolymers exhibit a flexural modulus of 4.2–5.0 GPa. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1670–1677, 2006

Key words: benzoxazine-epoxy copolymer; dynamic mechanical analysis; FT-IR; high performance polymer; polybenzoxazine

INTRODUCTION

In the past few decades, various high performance polymers have been developed to withstand severe thermal and/or chemical environments for applications in aerospace and electronic industries. However, high performance polymers face processing difficulties due to their high melting points, high viscosity, and low solubility in organic solvents.¹ There are a few approaches to improve their processibility, for example, by incorporating softer molecular segments into the polymer chain, using a two-step curing system, or creating copolymers or blends.

Among polyimides, bismaleimides are one of the most important classes of materials for advanced material applications, due to their good processibility, excellent thermal properties, and relative low cost. As other addition polyimides do, unmodified bismaleimides suffer from brittleness and microcracking due to their high crosslink density and rigid aromatic backbone structure. To improve the toughness of bismaleimides, copolymers and rubber toughened blends have been synthesized.^{2–4} In addition, maleimide modified epoxy compounds have been shown to have good thermal properties, flexural properties, and flame retardance.^{5–7}

Polybenzoxazine has been recently shown to have excellent thermal and mechanical properties, although

the chemistry of the small molecule was first discovered in the 1940s by Holly and Cope.⁸ Further study of benzoxazine and its oligomers was conducted by Burke and others^{9–18} from 1950 to 1960. Polybenzoxazines exhibit excellent mechanical strength and thermal stability, near-zero shrinkage, no release of volatiles during polymerization, low viscosity, no need of harsh catalysts, and rich molecular design flexibility.^{19–24} By taking advantage of its design flexibility, several high performance benzoxazines, such as acetylene-functional benzoxazines, naphthoxazines, and phthalonitrile and phenylnitrile functional polybenzoxazines, have been developed.^{25–29} These polymers showed glass transition temperatures above 200°C with char yields of 50–70%. In addition, maleimide and norbornene-functional benzoxazines have been synthesized, and have char yields above 55% and glass transition temperatures above 250°C.³⁰ Other groups have shown improved thermal properties with benzoxazine-maleimide copolymers, where they copolymerized bisphenol-A based benzoxazine with rubber and/or phenols with maleimide functionality.^{31,32}

To improve the crosslink density and modify the mechanical properties of benzoxazine, copolymers of epoxy and bisphenol-A based benzoxazines were studied by Ishida and Allen.³³ They were able to optimize the copolymer system and observed increases in glass transition temperature, crosslink density, and flexural properties. The focus of the work presented in this article is to improve the toughness and glass transition temperature by incorporating epoxy into maleimide-functionalized benzoxazine. This system

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has three functional groups that can undergo polymerization—the epoxy ring, benzoxazine ring, and maleimide vinylene group—which results in a crosslinked polymer with good thermal and mechanical properties. Furthermore, this system does not require any catalyst for epoxy polymerization since the phenolic group of the polybenzoxazine can act as an initiator and catalyst.

EXPERIMENTAL

Materials

All chemicals were used as received. 4-Aminophenol (98%), maleic anhydride (96%), phosphorous pentoxide (98%), paraformaldehyde (95%), and aniline (99%) were obtained from Aldrich Chemical Company. Epon 825 epoxy resin, which is a diglycidyl ether of bisphenol-A (DGEBA), was obtained from Miller-Stephenson Chemical Company. Sulfuric acid, *N,N*-dimethylformamide (DMF), chloroform, isopropanol, and dichloromethane were obtained from Fisher Scientific Company. All solvents were A.C.S. grade and used as received.

Synthesis

Synthesis of 1-(4-hydroxy-phenyl)-pyrrole-2,5-dione (HPMI)

The HPMI was synthesized according to Choi et al.³⁴ The product was yellow needles with a yield of 57%. The melting point was 176°C. ¹H NMR (200MHz, DMSO-*d*⁶, 298K) δ : 6.80 (d, OH), 7.06 (d, 2H), 7.13 (d, 2H), and 9.70 (s, 2H).

Synthesis of 1-(3-phenyl-2h, 4h, benzo[3,4-*e*] 1, 3-oxazaperhydroin-6-yl)azoline-2,3-dione (MIB)

A mixture of HPMI, *p*-formaldehyde, and aniline with a mole ratio of 1 : 2 : 1 was added to a flask and stirred at 110°C for 20 min.³⁵ The product was then dissolved in dichloromethane, filtered, and washed with deionized water. The solvent was evaporated using a rotary evaporator and the product was vacuum dried. The product was a yellow powder with a yield of 80%. The melting point was 147°C. ¹H NMR (200MHz, (CD₃)₂CO, 298K) δ : 4.73 (s, 2H), 5.49 (s, 2H), and 6.80–7.28 (Ar, 10H). ¹³C NMR (200MHz, CDCl₃, 298K) δ : 49.19(O-C-N), 80.50 (Ar-C-N), 121.29–133.86 (Ar), 138.99 (C=C), 138.99–160.42 (Ar), and 177.23 (C=O).

Anal. Calcd. for C₁₈H₁₄N₂O₃: C, 70.58%; H, 4.61%; N, 9.15. Found: C, 70.60%; H, 4.81%; N, 9.00.

Sample preparation

A series of copolymers with different ratios of MIB and DGEBA were prepared. The structures of the two

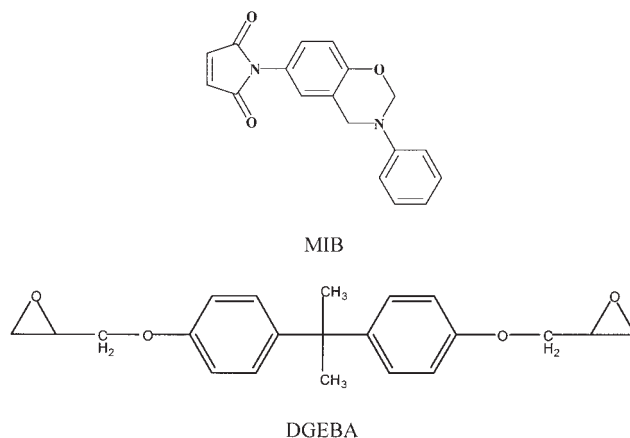


Figure 1 Structures of MIB and DGEBA.

monomers are shown in Figure 1. The two materials were weighed and mechanically mixed at 110°C and placed into a mold. The mold consisted of two glass plates with a 3.2mm thick U-shaped silicone rubber in between. All components of the mold were treated with a silicone based mold release. The filled mold was placed into a vacuum oven at 110°C for 1–3 h to remove residual solvent and trapped air in the silicone rubber. Then the material was placed into an air vented oven where it was subjected to a step cure procedure as follows: 150°C (1 h), 170°C (2 h), 190°C (2 h), and 210°C (30 min–12 h). The samples were then slowly cooled to room temperature over several hours.

Measurements

Fourier transform infrared spectra were obtained using a Bomem Michelson MB100 FT-IR spectrometer, which was equipped with a liquid nitrogen cooled, mercury cadmium-telluride (MCT) detector with a specific detectivity, *D*^{*}, of 1×10^{10} cmHz^{0.5}W⁻¹. Co-addition of 128 scans was recorded at a resolution of 4 cm⁻¹ after 20 min purge with dry nitrogen. FT-IR spectra were taken by casting a thin film of the sample on a KBr plate and heating it in an electronically controlled hot cell.

Nuclear magnetic resonance (NMR) spectra were recorded using a Varian XL 200 nuclear magnetic resonance spectrometer at proton frequency of 200 MHz and the corresponding carbon frequency. Deuterated chloroform, acetone, and dimethyl sulfoxide were used as NMR solvents, with 0.05% tetramethylsilane as the internal standard. Coaddition of 128 transients yielded a good signal-to-noise ratio spectrum for ¹H NMR, while 2000 transients were used for the ¹³C NMR spectrum. Relaxation time (D1) of 10 s was used to obtain the integration results for the proton spectrum.

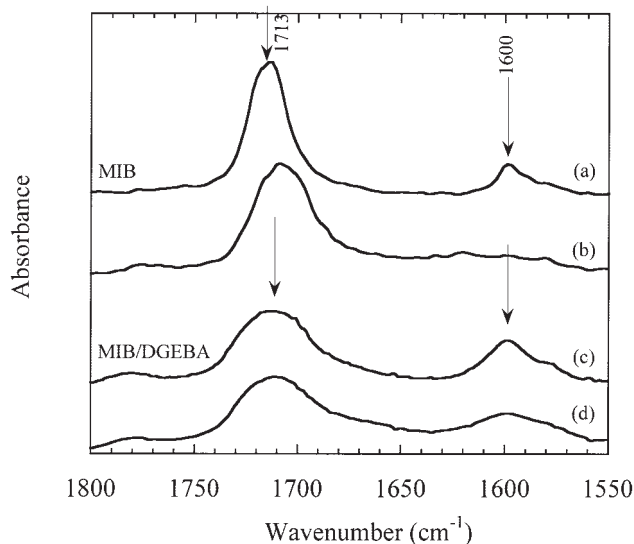


Figure 2 FT-IR spectra of MIB at (a) 160°C and (b) 240°C and 1 : 1 mol ratio of MIB and DGEBA at (c) 160°C and (d) 240°C between 1550 cm^{-1} and 1800 cm^{-1} .

The curing behavior was investigated by differential scanning calorimetry (DSC) (TA Instruments DSC model 2920), with a heating rate of 10°C/min with a nitrogen flow rate of 65 mL/min for all tests. All samples were crimped in hermetic aluminum pans with lids.

Dynamic mechanical analysis (DMA) of the samples was performed to determine the glass transition temperature, T_g , storage modulus, G' , and loss modulus, G'' . Tests were performed on a Rheometrics dynamic mechanical spectrometer (RMS-800) equipped with a 2kg-cm force rebalance transducer. The maximum strain of 0.1% was applied sinusoidally to samples with dimensions of approximately 50 × 13 × 3.2 mm in a rectangular torsion fixture at each temperature at a frequency of 1Hz. This strain was verified to be within the linear viscoelastic limit by first obtaining strain sweep data. The samples were heated at approximately 2°C/min, and measurement was taken at intervals of 2°C until the temperature reached to about 50°C above the material's T_g . A thermal soak time of 30 s was used to stabilize the sample temperature.

Three point bending tests were conducted to determine the flexural properties in accordance with ASTM D790m. An Instron Universal Testing Machine (model 1125) fitted with a 25kN load cell, an automated control system, and the Merlin analysis software were used. Three specimens with dimensions of 70 × 10 × 3 mm were tested for each composition. Samples with a support span of 48mm were held in ASTM specified boundary conditions until breakage occurred at a crosshead speed of 1mm min^{-1} . Flexural strain was calculated based upon crosshead displacement.

RESULTS AND DISCUSSION

The MIB/DGEBA copolymer system has three possible polymerization reactions: benzoxazine polymerization, epoxy polymerization, and vinyl polymerization. To determine that all reactions took place, Fourier transform infrared spectra (FT-IR) were taken at different temperatures for a monomer sample with 1 : 1 ratio of MIB and DGEBA (Figs. 2 and 3). The epoxy polymerization can be monitored by the disappearance of the epoxide ring modes at 915 cm^{-1} and 861 cm^{-1} . Epoxy polymerization will take place concurrently with the benzoxazine polymerization, since the phenolic groups of the polybenzoxazine act as an epoxy polymerization initiator and catalyst. The epoxide ring bands disappear almost completely after 20 min at about 160°C.

Benzoxazine polymerization can be monitored by the disappearance of the absorption bands at 1500 cm^{-1} and 935 cm^{-1} , which corresponds to the trisubstituted benzene ring mode. Also, the antisymmetric C-N-C stretching mode of the oxazine ring observed at 1117 cm^{-1} decreases as a function of temperature during the benzoxazine polymerization. At the same time, the bands at 1240 cm^{-1} and 1032 cm^{-1} , which correspond to the C-O-C antisymmetric and symmetric stretching modes, respectively, of the benzoxazine ring decrease.³⁶

The maleimide polymerization can be monitored by the bands at 1600 cm^{-1} and 825 cm^{-1} that correspond to the C=C stretching vibration and CH wag of the vinylene group, respectively.³⁷ The C=C stretching band overlaps with the mono-substituted benzene ring mode at 1585 cm^{-1} , which does not disappear

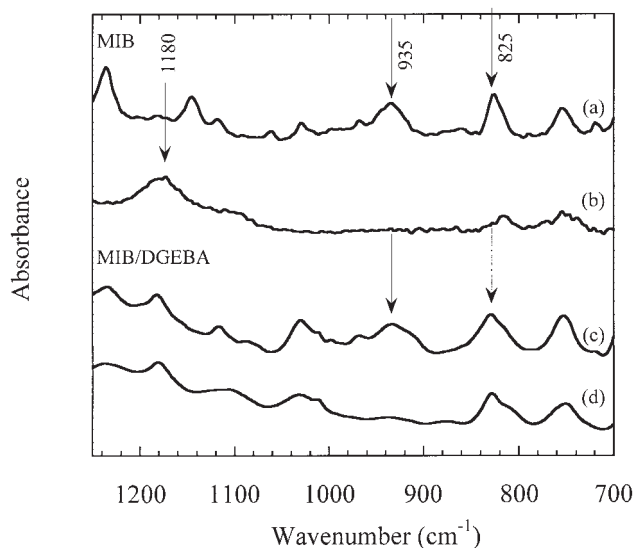


Figure 3 FT-IR spectra of MIB at (a) 160°C and (b) 240°C and 1 : 1 mol ratio of MIB and DGEBA at (c) 160°C and (d) 240°C between 700 cm^{-1} and 1250 cm^{-1} .

TABLE I
Summary of DSC Results

MIB %	DGEBA %	Exotherm peak temperatures	ΔH_{rxn} (J/mol of MIB)
100	0	213°C, 244°C	0.87
90	10	214°C, 247°C	1.26
80	20	214°C, 247°C	1.25
70	30	230°C, 257°C	1.19
60	40	244°C	0.98
50	50	246°C	0.68

during polymerization. These bands that correspond to the vinylene group disappear at temperatures above 240°C, which shows that maleimide polymerization occurs at higher temperatures than benzoxazine polymerization. The evidence of vinyl polymerization can also be obtained by the shift of the band at 1180 cm^{-1} due to the symmetric C-N-C bending mode of the succimide group.

From the pure monomer studies with different free radical initiators, it was shown that the order of the polymerization at the different functional groups affects the final network structure and properties.³⁰ The spectra indicate that for the MIB/DGEBA copolymer, although clear evidence of benzoxazine polymerization can be observed at 240°C, there is significantly less maleimide polymerization compared to the spectrum of the MIB polymer. The dilution of monomer results in decreased proximity of the maleimide bonds and less vinyl polymerization takes place, especially at high concentrations of epoxy.

The polymerization behavior was also studied by differential scanning calorimetry (DSC), as summarized in Table I. The MIB monomer has two exotherm peaks at 214°C and 243°C. The first exotherm peak corresponds to the benzoxazine polymerization, and the overlapping exotherm at the higher temperature corresponds to the maleimide polymerization.³⁰ As the epoxy concentration is increased, the exotherm peaks shift to a higher temperature (Fig. 4). This is due to the dilution of benzoxazine monomers, which would also result in the decrease of epoxy polymerization initiators. At high concentrations of MIB, the homopolymerization exothermic peak is more prominent at 213°C; but with addition of epoxy, the copolymerization peak at around 240°C heightens in intensity. Eventually, at 30% or more epoxy content, only the copolymerization exotherm, overlapping with the maleimide polymerization, is observed, due to the dilution of MIB. The heat of reaction, which is proportional to the extent of reaction, was highest at approximately 10–20% DGEBA. It appears that, at this stoichiometry, the polymerization is optimum because of the lowered viscosity by the presence of epoxy, which improves the mobility of the monomers, and because of the minimized dilution of MIB monomer.

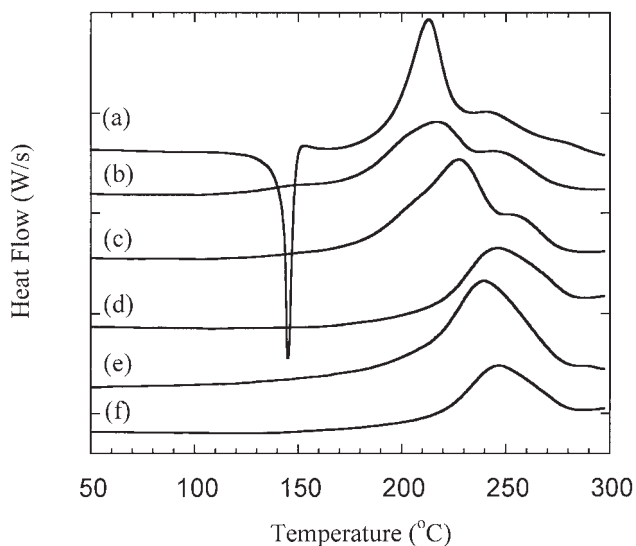


Figure 4 DSC thermogram of (a) MIB, and MIB/DGEBA copolymers with different % of DGEBA: (b) 10%, (c) 20%, (d) 30%, (e) 40%, and (f) 50%.

Dynamic mechanical analysis (DMA) was performed for different compositions of MIB/DGEBA. DMA can provide important thermal and mechanical properties, such as storage modulus, G' , and loss modulus, G'' . The storage modulus at room temperature, which provides the material stiffness under shear stress, was compared at different compositions (Fig. 5). As epoxy content is increased, the modulus decreases, since epoxy segments are more flexible than the MIB segments. An amine initiated epoxy polymer has a modulus of about 1.0 GPa, while the polybenzoxazine homopolymer from MIB has a higher mod-

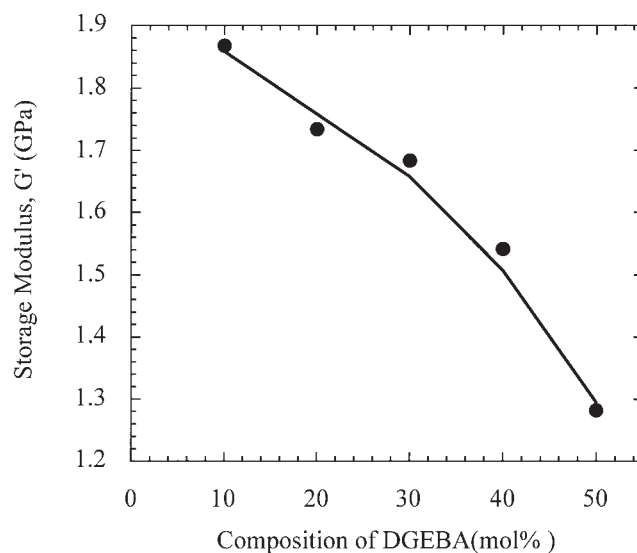


Figure 5 Storage modulus versus different compositions of MIB/DGEBA copolymer.

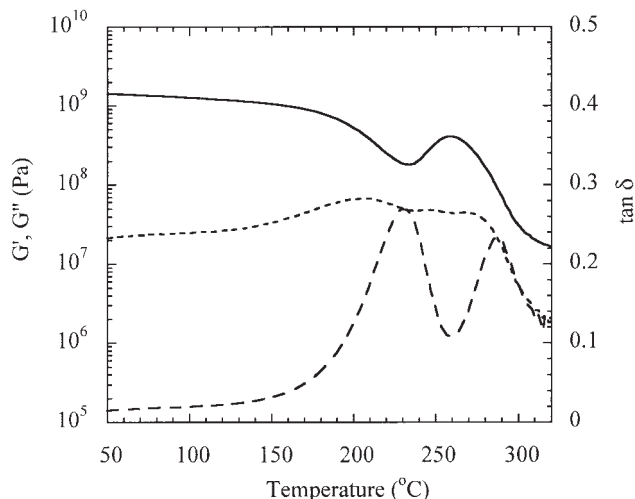


Figure 6 Dynamic mechanical spectra of 30% epoxy copolymer, cured at 150°C (1 h), 170°C (2 h), 190°C (2 h), and 210°C (30 min). G' (solid line), G'' (dotted line), and $\tan \delta$ (dashed line).

ulus, of about 2.0 GPa. According to the rule of mixtures, we can expect the modulus of the copolymer to be between these two values.

In addition, DMA was taken for two samples with different cure profiles for different compositions. The 30% DGEBA sample was greatly affected by the cure profile and exhibited an incomplete cure after 30 min at 210°C (Figs. 6 and 7). This phenomenon was indicated by the increase in G' above 250°C in the DMA scan. On the other hand, the 10% DGEBA sample with different curing profiles hardly showed any change in modulus and transition temperature (Figs. 8 and 9). At higher concentrations, due to the dilution of the ben-

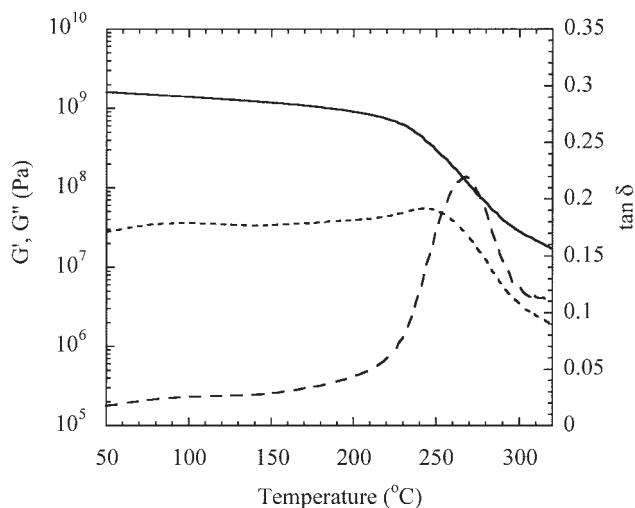


Figure 7 Dynamic mechanical spectra of 30% epoxy copolymer, cured at 150°C (1 h), 170°C (2 h), 190°C (2 h), and 210°C (12 h). G' (solid line), G'' (dotted line), and $\tan \delta$ (dashed line).

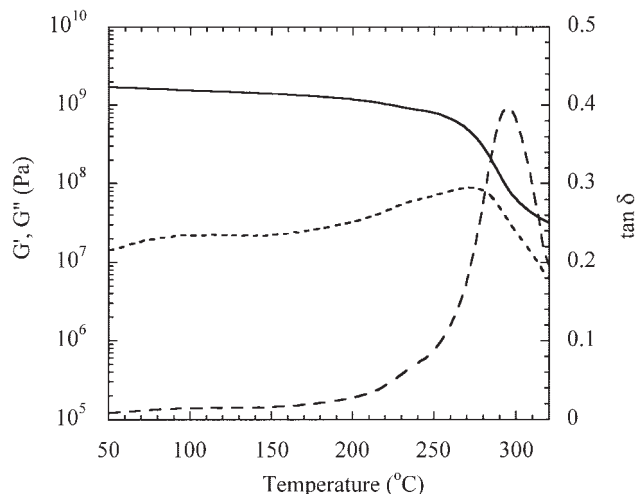


Figure 8 Dynamic mechanical spectra of 10% epoxy copolymer, cured at 150°C (1 h), 170°C (2 h), 190°C (2 h), and 210°C (30 min). G' (solid line), G'' (dotted line), and $\tan \delta$ (dashed line).

zoxazine, the completion of polymerization takes significantly longer, while at low concentrations of epoxy, a shorter curing time is sufficient.

For bisphenol-A based benzoxazine/DGEBA copolymers, only copolymers with 25% or lower DGEBA content were successfully cured. However, in our system, even samples with a high concentration of 70% DGEBA had mechanical integrity, which shows that maleimide based benzoxazine is more compatible with epoxy than bisphenol-A based benzoxazine.

It should be noted that, in this research, T_g was determined by the peak position of the G'' spectrum. However, due to the insensitivity of $\tan \delta$ to the geo-

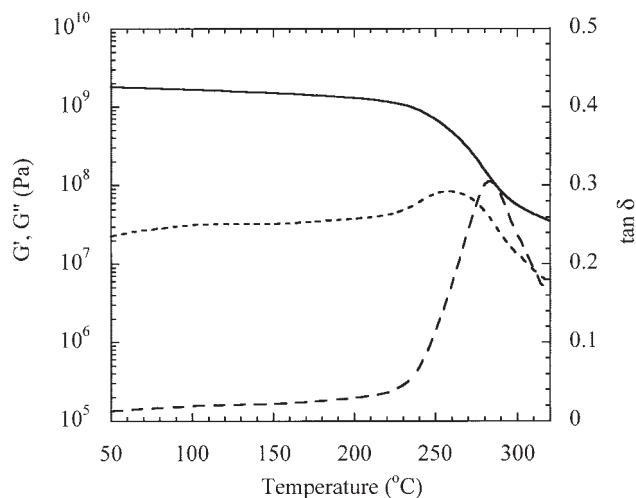


Figure 9 Dynamic mechanical spectra of 10% epoxy copolymer, cured at 150°C (1 h), 170°C (2 h), 190°C (2 h), and 210°C (12 h). G' (solid line), G'' (dotted line), and $\tan \delta$ (dashed line).

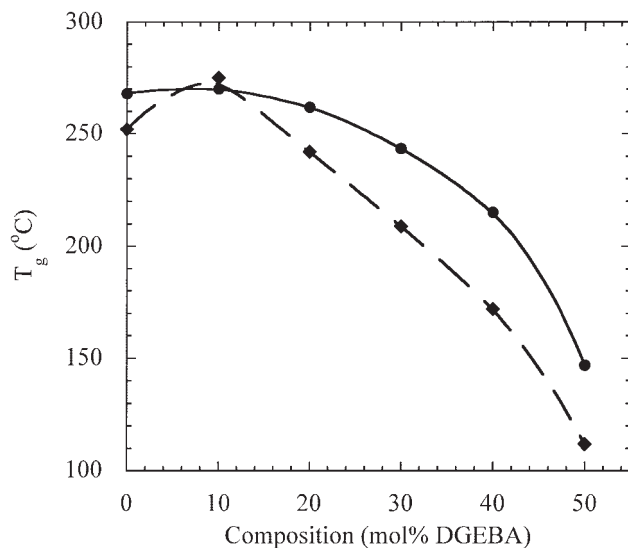


Figure 10 Glass transition temperature versus composition of DGEBA. (●) cured at 150°C (1 h), 170°C (2 h), 190°C (2 h), and 210°C (12 h). (◆) cured at 150°C (1 h), 170°C (2 h), 190°C (2 h), and 210°C (30 min).

metrical variation of samples, $\tan \delta$ was used to compare the transition behavior of the samples with various compositions. The T_g s of copolymers were determined for polymers of the same composition with two different curing profiles. The first sample was cured according to the cure profile described in the previous section, while another sample was postcured for an additional 11 h at 210°C. The T_g of typical benzoxazines was lowered during an extended postcuring, due to the rearrangement of the molecular structure at this temperature.³⁸ However, maleimides usually undergo long postcuring stages for further crosslinking reactions that result in the improvement of thermal stability. For T_g of MIB/DGEBA copolymer, an increase of 15 to 30°C was observed for the postcured material, as shown in Figure 10. This is more evident at higher concentrations of epoxy because the benzoxazine and maleimide polymerization are slowed by the dilution effect of epoxy and further postcuring allowed a more complete polymerization. Furthermore, while the T_g of MIB homopolymer was between 253°C and 268°C, we observed a maximum T_g of 278°C at a mole ratio of 10 mol % DGEBA. This cor-

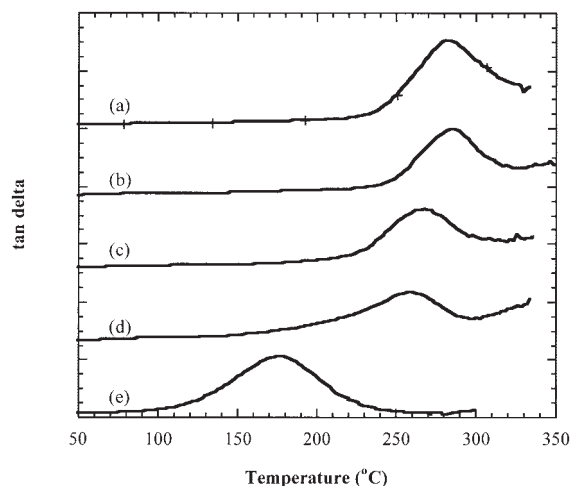


Figure 11 Tan δ curve from dynamic mechanical analysis with (a) 10%, (b) 20%, (c) 30%, (d) 40%, and (e) 50% DGEBA.

responds well to our DSC results, where the most complete reaction at 10 mol % DGEBA was observed. A similar trend was observed for bisphenol-A based benzoxazine, where a maximum T_g of 156°C was observed at 15 mol % DGEBA.³³

The glass transition temperatures of the copolymers with free radical initiators were investigated at different DGEBA concentrations, as summarized in Table II. When benzoyl peroxide was added to the homopolymer, a 15°C decrease in T_g was observed, while larger shifts in T_g were observed for higher concentrations of DGEBA. For example, a 70°C decrease of T_g was observed for 40% DGEBA. The formation of the rigid backbone at lower temperatures by the maleimide polymerization decreases the mobility of the molecular segments to hinder benzoxazine and epoxy polymerization. The combination of the lowered mobility and the dilution effect of epoxy results in a larger decrease of T_g at the higher concentration DGEBA copolymers.

Further analysis of the DMA results shows that the height of the $\tan \delta$ peak decreases and the transition peak shifts as epoxy concentration is increased, as shown in Figure 11. The formation of more crosslinks by the epoxy between the linear benzoxazine chains results in the lower mobility of the segmental chain

TABLE II
Summary of Glass Transition Temperatures from DMA Results

Polymerization conditions	T_g of MIB	T_g of 20% DGEBA	T_g of 40% DGEBA
Shorter cure* 210°C (30 min)	252°C	242°C	215°C
Longer cure* 210°C (12 hr)	268°C	262°C	232°C
Shorter cure with BPO	246°C	222°C	159°C

* The complete polymerization procedure is described in the Experimental section.

TABLE III
Summary of Tan δ Peaks from DMA

MIB %	DGEBA %	Tan δ peak temperature	Peak height
50	50	177°C	0.21
60	40	259°C	0.18
70	30	268°C	0.22
80	20	286°C	0.25
90	10	282°C	0.31

and a decrease in tan δ peak height (Table III). In addition, while the shift in the tan δ peak is no larger than 30°C for concentrations between 10 and 40% DGEBA, between 40 and 50%, there is a shift of 100°C due to a possible phase inversion. At 50% DGEBA, the volume fraction of the epoxy becomes larger than that of MIB, resulting in the drastic shift of the peak.

Densities of the copolymers were measured according to ASTM standards, and the densities were between 1.32 g/cm³ and 1.25 g/cm³, as shown in Figure 12. The density increased linearly with the increase in MIB concentration and, by extrapolating from the data, the density of the homopolymer was estimated to be 1.34 g/cm³.

The flexural properties were determined by the three point bending test, and the results are shown in Figures 13–15. Flexural strength of polymers is affected by glass transition, network structure and regularity, free volume, chemical structure, and other factors. In this system, since there is a change in the glass transition temperature and we are also changing the network structure by adding more physical crosslinks, it was expected that the flexural properties would change. The flexural strain at breakage was 1.5% at 10% DGEBA and increased to 3.2% with 50%

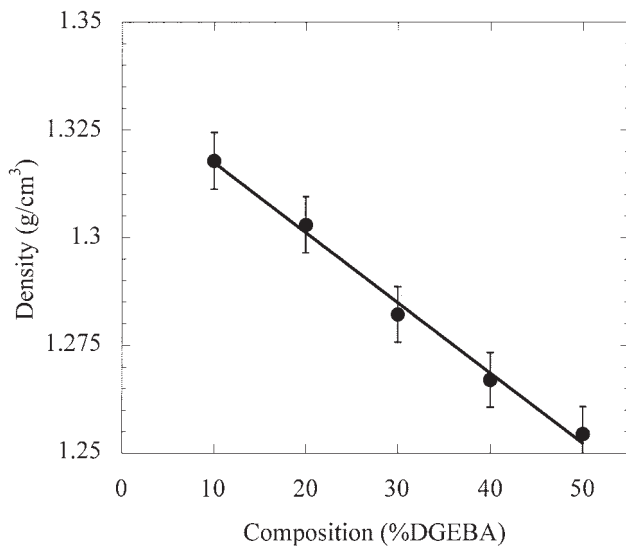


Figure 12 Density versus composition of DGEBA.

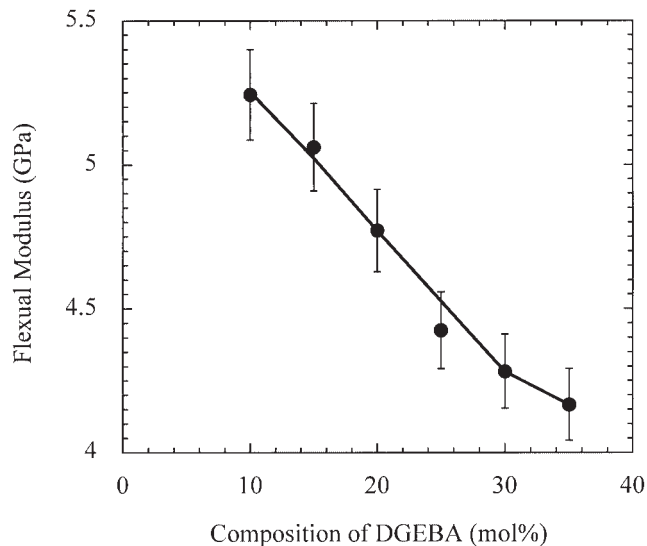


Figure 13 Variations of flexural modulus of different compositions of MIB/DGEBA.

DGEBA. In addition, the stress at break increased about 50 MPa with the addition of 50% epoxy. Previous studies have also shown that increasing the epoxy content in copolymers results in an increase of flexural strain and a decrease in modulus since the segmental mobility of the epoxy chain is greater than the benzoxazine chain. The modulus was between 4.2 MPa and 5.0 MPa, and the greatest modulus was found at the highest concentration of benzoxazine monomer for MIB/DGEBA copolymer as expected.

CONCLUSIONS

The thermal and mechanical properties of maleimide-functionalized benzoxazine and diglycidyl ether bis-

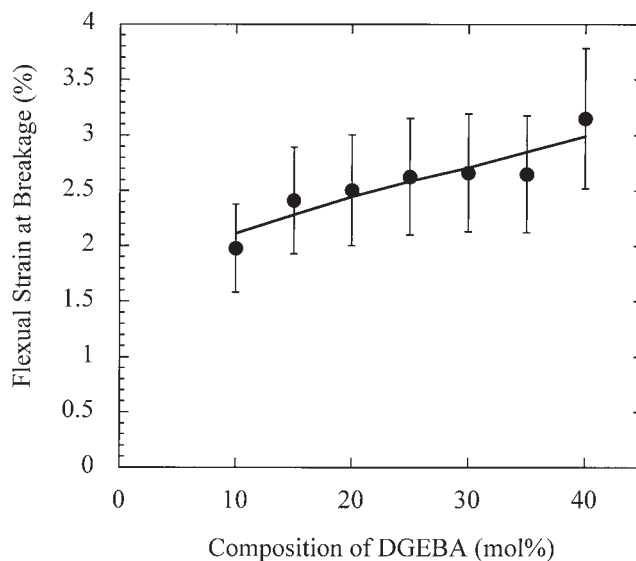


Figure 14 Variations of flexural strain at breakage of different compositions of MIB/DGEBA.

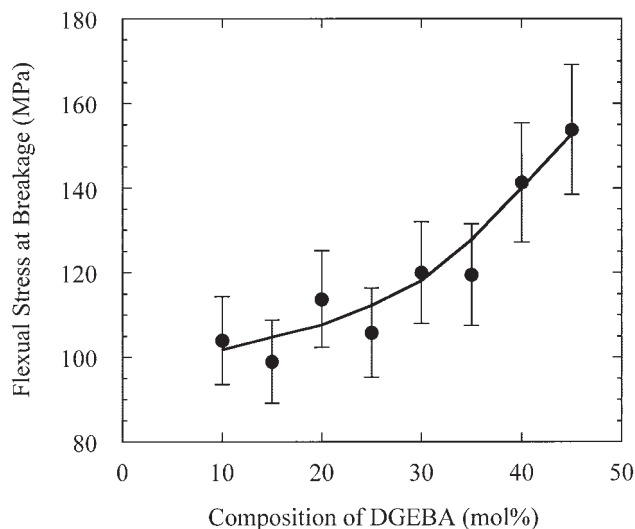


Figure 15 Variations of flexural stress at breakage of different compositions of MIB/DGEBA copolymers.

phenol-A were investigated for different compositions of epoxy. We observed that the two monomers copolymerized without any addition of initiator or catalyst. The three polymerization reactions, which include an epoxy ring, a benzoxazine ring, and a vinyl polymerization, were confirmed to have taken place using DSC and FT-IR. For copolymers with high content of epoxy, we observed less complete polymerization of the maleimide group, while epoxy and benzoxazine polymerizations were less affected. The resulting polymer achieved a high glass transition temperature of 278°C at 10 mol % DGEBA and was higher than the homopolymer that has a T_g of 253°C. Also, the curing time and temperature affected the glass transition temperature about 10 to 30°C due to the further crosslinking of the maleimide bond. While flexural strain at breakage increased with the increase in epoxy content, the flexural modulus was approximately 5.0 GPa for 10 mol % DGEBA and decreased to 4.2 GPa with 50 mol % DGEBA. In conclusion, maleimide-functionalized benzoxazine can be successfully copolymerized with epoxy to tailor for desired flexural properties without decreasing the thermal properties.

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