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Mechanical characterization of copolymers based on benzoxazine and epoxy

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A new class of phenolic-like thermosetting resins has been developed that is based on the ring opening polymerization of a benzoxazine precursor. These new materials overcome many of the traditional shortcomings associated with conventional novolac and resole-type phenolic resins, while demonstrating excellent physical and mechanical characteristics. The benzoxazines are copolymerized with an epoxy resin in order to modify their performance. The addition of epoxy to the polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and strongly influences its mechanical properties. Copolymerization leads to significant increases in the glass transition temperature, flexural stress, and flexural strain at break over those of the polybenzoxazine homopolymer, with only a minimal loss of stiffness. By understanding the structural changes induced by variations of epoxy content and their effect on material properties, the network can be tailored to specific performance requirements. Copyright © 1996 Elsevier Science Ltd.

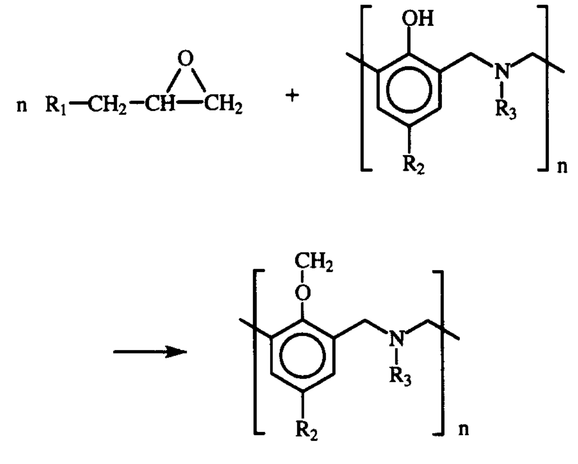
(Keywords: polybenzoxazine; copolymer; dynamic mechanical analysis)

INTRODUCTION

The polybenzoxazines are a newly developed class of thermosetting resins that are based on the ring opening polymerization of benzoxazine precursors[1]. This family of resins seeks to combine the thermal properties and flame retardance of phenolics with the mechanical performance and design flexibility of advanced epoxy resins. A number of polybenzoxazine properties are superior to those of epoxy resins and conventional phenolics. Physical and mechanical characterization has revealed that these new materials possess excellent glass transition temperatures (T_gs), high moduli, low water absorption values, and good dielectric properties, in addition to zero shrinkage or a slight expansion upon cure[2].

Despite their high moduli and T_gs, the polybenzoxazines have been shown to display surprisingly low crosslink densities in comparison to ordinary thermosetting resins with similar properties[2]. It has been proposed that the hydrogen bonding prevalent in the benzoxazines[3] is sufficiently strong to constrain segmental mobility and contribute to the rigidity that has been observed in the glassy state[2]. These intermolecular and intramolecular forces may also impede network formation and limit polymerization to the low crosslink densities that have been observed. As a result, polybenzoxazine materials may possess further untapped potential as high performance thermosetting resins, that can be achieved by tightening their network structure.

It appears that copolymerization of the polybenzoxazine precursor with an epoxy may allow the network structure to achieve a higher crosslink density. Phenols have been shown to react with epoxy resins at elevated temperatures[4]. Because the ring opening polymerization of a benzoxazine produces phenolic groups, copolymerization of the benzoxazine with an epoxy should be possible.



Although epoxy homopolymerization catalysed by the tertiary amine of the benzoxazine ring or bridge structure is possible, it does not appear to be likely. Phenol reactions with epoxy resins in the presence of tertiary amines have been shown to proceed almost exclusively through the phenolic hydroxyls, with the

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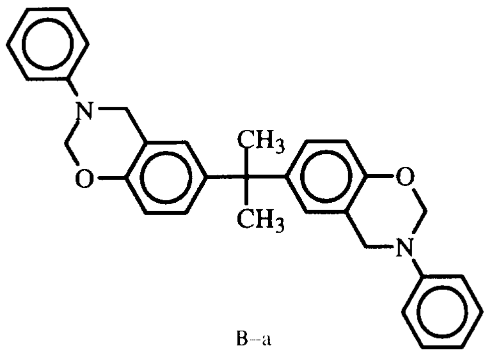
alcohol–epoxy reactions of homopolymerization being suppressed[4]. As was previously shown, the epoxy groups react at a functionality on the benzoxazine structure that is not normally reactive in the homopolymerization of the benzoxazine material. Therefore, additional crosslink points are being introduced into the thermosetting matrix and a higher crosslink density is theoretically possible.

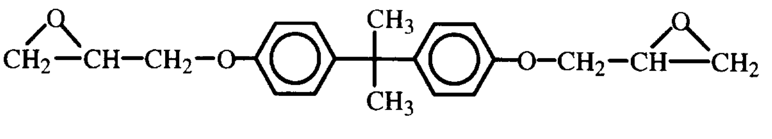
The following work investigates the possibilities of a benzoxazine–epoxy copolymerization from a practical perspective. It will be shown that the copolymerization can in fact produce thermosetting materials with quite favourable characteristics. The T_g, crosslink density, and a variety of mechanical properties will be studied for a series of benzoxazine–epoxy compositions and will be compared to the polybenzoxazine homopolymer in order to determine the effects of epoxy concentration on the copolymer properties.

EXPERIMENTAL

The series of copolymers utilized for this study was prepared by curing mixtures of a benzoxazine precursor with the diglycidyl ether of bisphenol-A (DGEBA). The chemical structures of these two monomeric compounds are shown below:



B–a



DGEBA

The B-a benzoxazine was prepared in 1-mol batches from bisphenol-A, formaldehyde, and aniline in the molar ratio of 1/4/2 in two litres of dioxane. A detailed description of the synthesis procedure and molecular characterization has previously been described[1]. The formaldehyde (37% in water) and aniline (99.5%) were purchased from Aldrich Chemical Company and were used without further purification. Polycarbonate grade bisphenol-A and Epon 825 epoxy resin were obtained from Shell Chemical Company.

A Bomem Michelson MB single beam Fourier transform infra-red (*FT*i.r.) spectrometer was employed to follow changes in the chemical composition of the benzoxazine/epoxy mixture during cure. This *FT*i.r. spectrometer is equipped with a liquid nitrogen cooled, mercury–cadmium–telluride (MCT) detector that allows data acquisition over the frequency range from 5000 to 500 cm^{-1} and is purged with dry nitrogen gas. The specific detectivity, D^*, of the MCT detector is 1.0×10^{10} cm Hz$^{1/2}$ W^{-1}.

A 60% benzoxazine/40% epoxy mixture was chosen for this spectroscopic analysis and was cast as a thin film onto a KBr plate from a 10% solution in tetrahydrofuran. After the solvent was sufficiently evaporated, the film was covered by a second KBr plate in order to minimize flow of the resin during cure. The sample was then mounted into a heated cell at 25°C and placed inside the spectrometer. After a 30 min nitrogen purge, 300 coadded scans were taken of the initial mixture at a resolution of 2 cm^{-1}. The hot cell was then heated to 100°C and the resin was polymerized in accordance with the cure schedule in *Table 1*. Sixteen coadded scans at a resolution of 2 cm^{-1} were taken at the end of each isothermal stage of cure. To minimize emissive effects, reference spectra were obtained in an identical manner at each of the cure temperatures.

To study the effects of composition on the mechanical properties, sheets of copolymer were moulded throughout the range from 0 to 100% benzoxazine in 5 mol% increments. The molar compositions were based upon a molecular weight of 463 g mol^{-1} for the benzoxazine and 358 g mol^{-1} for the epoxy resin. For each composition, the appropriate amounts of benzoxazine and epoxy resin were weighed into a glass dish and mechanically stirred at 85°C until well mixed. The fluid resin mixture was then poured into a preheated vertical mould consisting of a U-shaped silicon rubber spacer between two glass plates treated with a silicon based mould release agent. The resin filled mould was initially heated under reduced pressure at 100°C for 1 h in order to remove any air entrapped in the mould filling process. The material was then subjected to the curing schedule found in *Table 1*. Upon completion of the curing process, the moulded materials were slowly cooled to room temperature over a time period of 2 h. Because the benzoxazine materials will thermally homopolymerize in the presence of dimers and other higher oligomers found in the as-synthesized materials[1], no external catalyst was used in these experiments. In order to eliminate variability due to monomer purity or cure history, all samples were prepared from

Table 1 Curing profile utilized during the moulding of specimens for dynamic mechanical and flexural analyses

Temperature (°C)	Time (h)	Pressure (+/−)
100	2.0	−
140	0.5	+
160	0.5	+
180	0.5	+
200	0.5	+
205	0.5	+

single batches of both benzoxazine and epoxy, and were cured simultaneously. Samples for mechanical testing were machined to proper test dimensions from these 3.2 mm thick sheets.

Dynamic mechanical analysis (d.m.a.) of the different copolymer compositions was performed on a Rheometrics dynamic mechanical spectrometer (RMS-800) equipped with a 2000 g-cm force rebalance transducer. Specimens with dimensions of approximately 50 × 13 × 3.2 mm were tested in a rectangular torsion fixture. A maximum strain of 0.1% was applied sinusoidally during each temperature sweep at a frequency of 1 Hz. Measurements were collected at intervals of 2°C as the samples were heated at a rate of approximately 2°C min^{-1} to a temperature well above the glass transition of each material.

At 50°C above T_g, as determined by the maximum of the loss modulus, G'', the temperature sweeps were interrupted to perform a stress relaxation experiment on each composition in its rubbery region. For these experiments, a 0.2% strain was applied to each sample immediately prior to the collection of the relaxation spectrum. After monitoring the relaxation of the shear modulus for approximately 4 min, the temperature sweep measurements were continued until well into the plateau region of the storage modulus.

The flexural properties of the copolymers were determined in accordance with ASTM D790 using an Instron model 1125 fitted with a 25 kN load cell and automated control and analysis software. Three specimens with dimensions of 76 × 13 × 3.2 mm were tested for each composition. Samples were flexed until breakage at a rate of 1 mm min^{-1} in three-point loading with a 50 mm support span. Flexural strain was calculated based upon crosshead movement.

RESULTS AND DISCUSSION

Prior to studying the bulk properties of the copolymers, a qualitative infra-red analysis was undertaken in order to verify that both monomeric species were participating in the reaction. The infra-red spectrum of a 60% benzoxazine/40% epoxy sample was obtained after each stage of the cure cycle employed for the preparation of bulk samples. The consumption of epoxy can be monitored by the 913 cm^{-1} and 864 cm^{-1} epoxide ring modes that disappear as the ring is opened. As can be seen in *Figure 1*, the epoxide peaks appear to have almost completely disappeared by the end of the 160°C stage of cure.

The benzene rings that form the backbone of a monomeric benzoxazine molecule are trisubstituted. During polymerization, the oxazine rings open and propagate, at which point the backbone benzene rings become tetrasubstituted. Thus the benzoxazine polymerization may be monitored in the infra-red region by the decrease in the trisubstituted benzene contribution at 1498 cm^{-1} and the corresponding increase in the tetrasubstituted mode at 1477 cm^{-1}. *Figure 2* demonstrates that the ring opening polymerization of the benzoxazine appears to occur without interference by the presence of epoxy. It can be observed that the polymerization of the benzoxazine continues up to the final 205°C stage of cure. The epoxy appears to be reacting with the phenolic hydroxyl groups as soon as the ring opening polymerization makes them available. Thus, the epoxy appears to be completely consumed before the latter stages of cure, as would be expected for this less than stoichiometric concentration of epoxy.

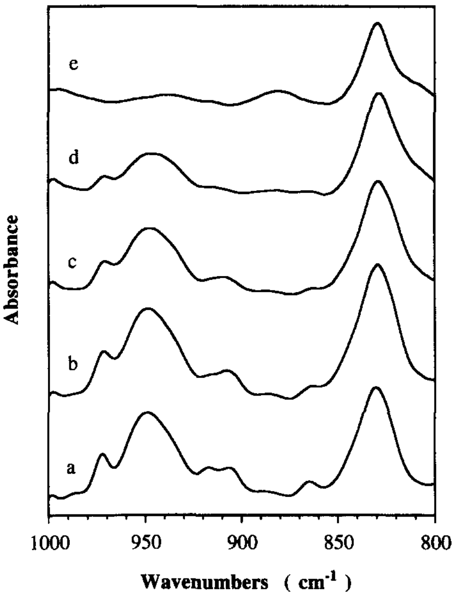


Figure 1 Infra-red spectrum over the region from 1000–800 cm^{-1} of the 40% epoxy copolymer after the (a) 25°C, (b) 100°C, (c) 140°C, (d) 160°C, and (e) 205°C stage of cure

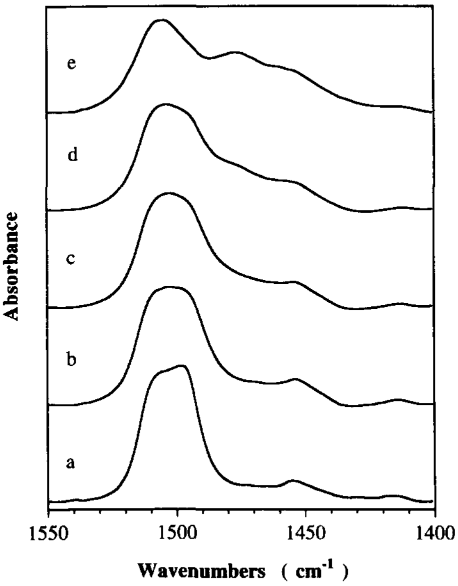


Figure 2 Infra-red spectrum over the region from 1550–1400 cm^{-1} of the 40% epoxy copolymer after the (a) 25°C, (b) 100°C, (c) 140°C, (d) 160°C, and (e) 205°C stage of cure

Benzoxazine–epoxy mixtures throughout the range from 0 to 100% benzoxazine were cured in an effort to produce copolymer specimens with sufficient physical integrity for mechanical analysis. Samples containing at least 50 mol% benzoxazine cured to what appeared to be highly crosslinked, mechanically sound materials. These specimens were optically transparent and free of voids with no visual evidence of phase separation. The series of materials was gradually tinted from a reddish-yellow hue for the samples containing nearly equal amounts of each component to a deep maroon coloration for the benzoxazine homopolymer. Samples containing less than 50 mol% benzoxazine, however, did not appear to have adequately cured to form crosslinked structures. These materials were either still in the liquid state after curing, or had solidified to only an extremely brittle form that fractured upon removal from the mould and thus were excluded from the mechanical analysis. This incomplete cure was due to the fact that no external catalyst for curing the epoxy resin was added to any of the compositions.

The dynamic mechanical properties of the copolymers were obtained as a function of temperature beginning in the glassy state of each composition, through the T_g, and well into the rubbery plateau of each material. These spectra are shown in *Figures 3–5*. There are a number of important material parameters that can be derived from the dynamic mechanical data. The storage modulus, G', of a solid sample at room temperature provides a measure of material stiffness under shear deformation, and is plotted for the copolymers as a function of composition in *Figure 6*. As can be seen from the figure, the storage moduli of the copolymers decrease almost linearly with the addition of epoxy. This decrease in

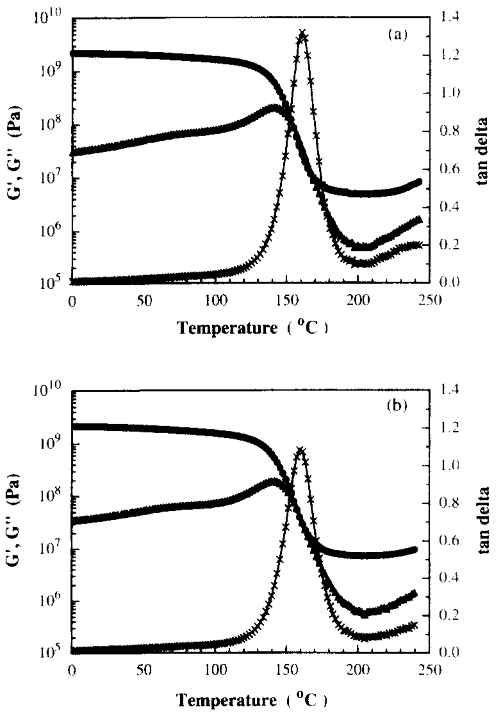


Figure 3 Dynamic mechanical spectra of (a) polybenzoxazine homopolymer (top) and (b) 10% epoxy copolymer (bottom). Each spectrum includes the storage modulus, G' (●), loss modulus, G'' (▲), and dissipation factor, $\tan\delta$ (x)

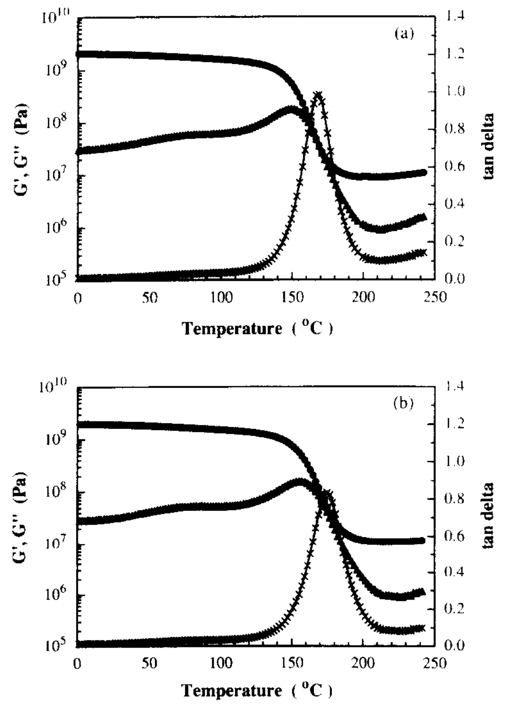


Figure 4 Dynamic mechanical spectra of the (a) 20% epoxy copolymer (top) and (b) 30% epoxy copolymer (bottom). Each spectrum includes the storage modulus, G' (●), loss modulus, G'' (▲), and dissipation factor, $\tan\delta$ (x)

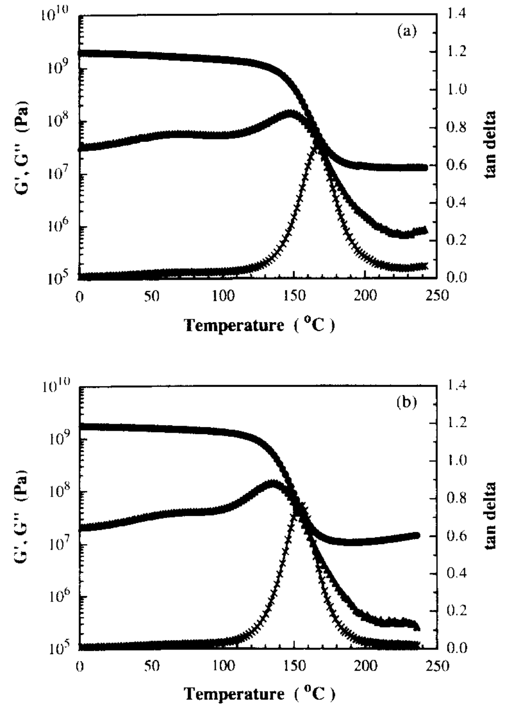


Figure 5 Dynamic mechanical spectra of (a) 40% epoxy copolymer (top) and (b) 50% epoxy copolymer (bottom). Each spectrum includes the storage modulus, G' (●), loss modulus, G'' (▲), and dissipation factor, $\tan\delta$ (x)

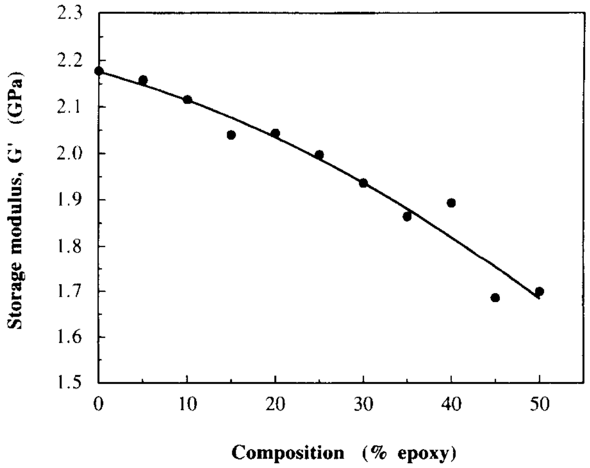


Figure 6 Variation of the dynamic storage modulus, G', as a function of composition for the benzoxazine–epoxy copolymer series

copolymer modulus with increasing epoxy concentration may be explainable by a simple rule-of-mixtures approach. The storage modulus of the benzoxazine homopolymer is approximately 2.2 GPa, while that of a typical amine-cured DGEBA epoxy system[5–7] averages about 1 GPa at room temperature. The modulus of the material produced with equal amounts of benzoxazine and epoxy, 1.7 GPa, is nearly half-way between the two homopolymers. In the glassy state, stiffness is related to changes in the stored elastic energy upon small deformation as the molecular segments resist motion. The epoxy-rich copolymers appear less able to resist segmental motion and thus are not as capable of storing elastic energy, resulting in a lower glassy modulus. The molecular and structural basis for these changes in glassy-state stiffness will be further discussed in a later section.

D.m.a. also allows determination of T_g of each copolymer composition and is detected in the mechanical spectrum as the maximum of the loss modulus, G''. *Figure 7* presents the T_gs of the copolymers as a function of composition. Initially, the incorporation of epoxy in the benzoxazine matrix has the effect of increasing the glass transition temperature of the material over the pure polybenzoxazine. The highest T_g, 156°C, is demonstrated by the material containing 30% epoxy and is approximately 15° higher than the benzoxazine homopolymer. Beyond 45% epoxy, however, the copolymers experience a sharp decrease in T_g, with the material containing equal amounts of benzoxazine and epoxy exhibiting a T_g lower than that of the pure polybenzoxazine. The epoxy rich samples, those with greater than about 45% epoxy, show poor mechanical properties due to the fact that the phenolic groups generated by the oxazine ring opening reaction not only serve to catalyse the copolymerization, but also participate as reactants and therefore are consumed by the reaction. Thus, as the stoichiometric ratio of components is approached, unreacted or small molecular weight epoxy molecules may remain and interfere with network formation or act as a plasticizer.

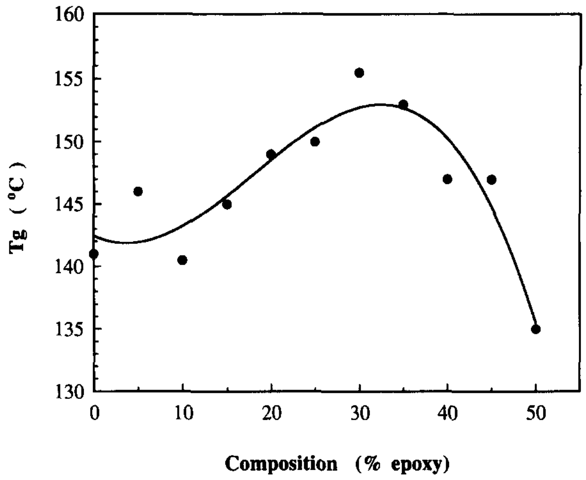


Figure 7 Variation of T_g of the benzoxazine–epoxy copolymers as a function of composition

Table 2 Analysis of the α-relaxation peaks from the tan δ curves of the dynamic mechanical spectra, including the position of the peak, peak height, and the width of the peak at half of the maximum height for each composition

Composition (% epoxy)	Position (°C)	Height (arbitrary units)	Width (half ht.) (°C)
0	161	1.32	23.5
5	166	1.23	23.9
10	159	1.09	25.4
15	163	1.06	25.8
20	169	0.99	26.3
25	168	0.93	26.5
30	175	0.83	28.4
35	171	0.78	29.1
40	168	0.71	31.0
45	168	0.62	34.0
50	154	0.76	34.0

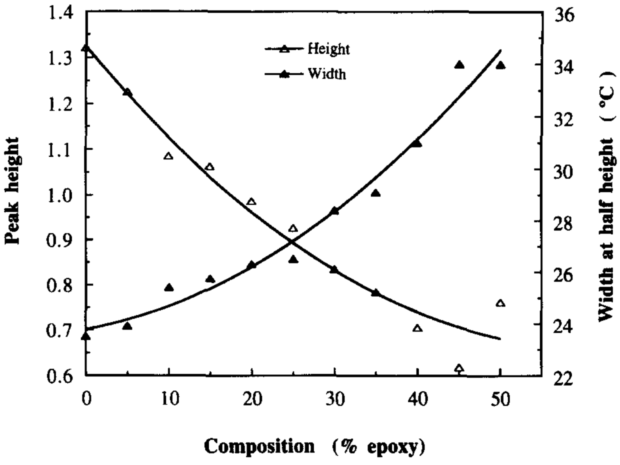


Figure 8 Analysis of the α-relaxation peaks from the tan delta curves of the dynamic mechanical spectra, including the peak height (△) and the peak width at half of the maximum height (▲) as a function of copolymer composition

Further investigation of the d.m.a. spectra may provide an explanation for the behaviour of the T_g data. The α-relaxation peak of the loss factor, tan δ, is associated with the glass transition and may be analysed to provide qualitative insight into the network structure of the copolymers. Inspection of the tan δ curves for each composition reveals only one peak that can be associated with the glass transition. If the two starting materials had phase separated and prevented copolymerization, then two glass transition peaks would be expected, one for each of the homopolymers. Similar behaviour has been observed for immiscible or partially miscible thermoplastic blends. The ability to identify only a single tan δ peak associated with the glass transition supports the previous contention that the monomeric materials had in fact copolymerized without any detectable phase separation. The height and width of the α-relaxation peak may also be analysed for each copolymer in order to observe trends in the crosslink density and network homogeneity[8] as the composition of the materials is varied. The position, height, and width at half height of the tan δ peak for each copolymer composition is summarized in *Table 2*. As can be observed in *Figure 8*, the height of the tan δ peak, which is associated with crosslink density, decreases as the epoxy content in the samples is increased. Because tan δ is the ratio of viscous to elastic components, it can be surmised that the decreasing height is associated with a lower segmental mobility and fewer relaxing species, and thus is indicative of a higher degree of crosslinking for the epoxy rich samples. The peak width at half-height, however, broadens as the

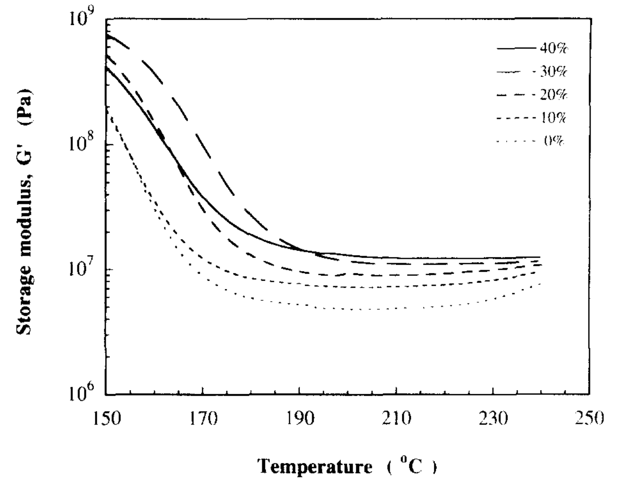


Figure 9 Plateau of the storage moduli, G', from the dynamic mechanical analysis of the benzoxazine–epoxy copolymers in the rubbery region. Spectra shown are the copolymers containing 0, 10, 20, 30, and 40% epoxy

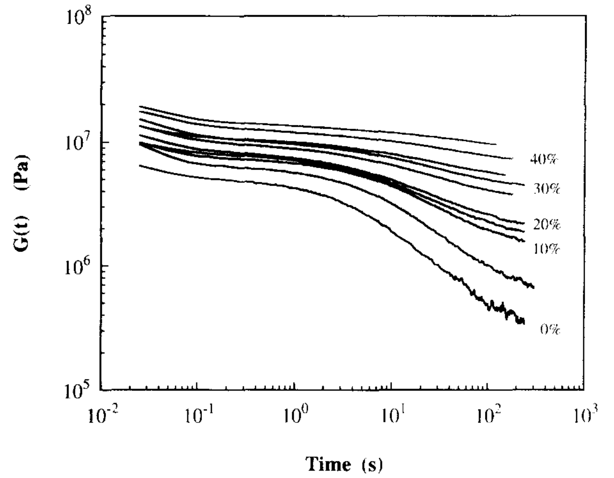


Figure 10 Response of the shear modulus during the stress relaxation experiments performed on each benzoxazine–epoxy copolymer at 50°C above T_g

addition of epoxy increases the number of modes of branching and results in a wider distribution of structures. Consequently, the range of temperatures at which the different network segments gain mobility has increased.

The crosslink density of each copolymer may be estimated from the plateau of the elastic modulus in the rubbery state using an equation from the statistical theory of rubber elasticity[9].

$$G_e = \phi \nu RT = \phi(\rho/M_c)RT$$

where G_e is the equilibrium modulus in the rubbery region, ϕ is a front factor which is unity for ideal rubbers, R is the gas constant, and T is absolute temperature. The crosslink density or concentration of network chains, ν, is the number of moles of network chains per unit volume of the cured polymer. If the density of the polymer, ρ, is known, then the molecular weight between crosslinks, M_c may also be calculated. However, this equation is strictly valid only for lightly crosslinked materials and therefore was used only to qualitatively compare the level of crosslinking among the various copolymer compositions and for comparison to other thermosets, which have reported values for crosslink density that were calculated in a similar manner.

As can be seen in *Figure 9*, the value of the storage modulus in the rubber plateau increases with the epoxy content of the copolymers. Thus, the crosslink density of the copolymers appears to be increasing as epoxy is added to the benzoxazine matrix. While the plateau modulus is acceptable for estimating crosslink density or the molecular weight between crosslinks from rubber elasticity theory, it is more strictly valid to use the equilibrium value of the relaxation modulus of the polymer in its rubbery state. Hence, the relaxation of the shear modulus was measured as a function of time for each copolymer in its rubbery state. To assure that each material was in its rubbery region, each sample was tested at a temperature 50°C above its T_g. It is evident from the relaxation spectra presented in *Figure 10* that the crosslink density of the copolymers increases, and thus the molecular weight between crosslinks decreases, as epoxy is copolymerized with the benzoxazine. The samples containing low concentrations of epoxy appeared to have an initial equilibrium value of the relaxation modulus at times less than about 10 s, but then underwent a secondary relaxation process at longer times. As a result, the crosslink density and molecular

Table 3 Crosslink density and molecular weight between crosslinks calculated from the stress relaxation spectrum of the different copolymers at the arbitrary relaxation times of $t = 1$ and $t = 100$ s

Composition (% epoxy)	Crosslink density ($\mathrm{mol\,m^{-3}}$)		M_w between crosslinks ($\mathrm{g\,mol^{-1}}$)	
	$t = 1$ s	$t = 100$ s	$t = 1$ s	$t = 100$ s
0	1100	122	971	8740
5	1140	262	742	4070
10	1740	511	611	2080
15	1830	589	582	1810
20	1870	668	569	1600
25	2240	1040	475	1030
30	2420	1250	440	854
35	2500	1440	426	738
40	3050	1980	350	537
45	3430	2480	311	429
50	2550	1960	418	544

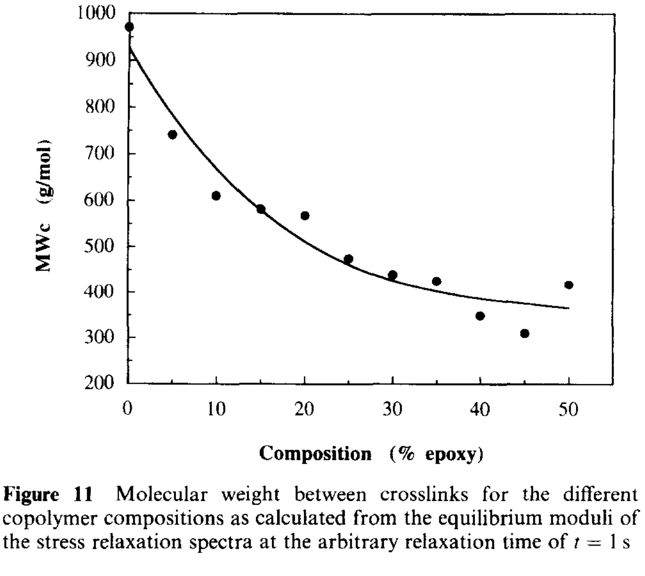


Figure 11 Molecular weight between crosslinks for the different copolymer compositions as calculated from the equilibrium moduli of the stress relaxation spectra at the arbitrary relaxation time of $t = 1$ s

weight between crosslinks was calculated from the relaxation modulus at the arbitrary times of 1 and 100 s. The results of these calculations are summarized in *Table 3*. *Figure 11* shows the decrease in the molecular weight between crosslink points as epoxy is reacted with the benzoxazine material. The polybenzoxazine homopolymer appears to be the least crosslinked of the series and on the average has chain segments with a molecular weight of nearly 1000 g mol^{-1} between network points. The average molecular weight of the chains between crosslinks can be decreased to a minimum of approximately 300 g mol^{-1} by the addition of 45% epoxy. Typically, stoichiometrically balanced amine-cured epoxies have a molecular weight between crosslinks of approximately 300–400 g mol^{-1} [7-10].

It is believed that extensive intermolecular and intramolecular hydrogen bonding disrupts the network formation in the polybenzoxazines and is responsible for their loosely crosslinked nature. Based on the secondary relaxation observed in the stress relaxation spectra of copolymers with low concentrations of epoxy, it appears that these materials have failed to establish a macroscopic network structure. It is hypothesized that these materials may contain clusters of branched chains or very loose networks of chemical crosslinks augmented by a large number of 'physical' crosslinks that are caused by hydrogen bonding. In other words, hyperbranched polymer chains may be physically interacting through strong hydrogen bonds. Thus, on short time scales these copolymer compositions behave as though they are well crosslinked. But as the physical interactions are overcome on larger time scales, they begin to display the flow characteristics and long range relaxation ability of a branched cluster or a very loose network. It may be possible to correlate the molecular weights between crosslinks calculated at long relaxation times ($t = 100$ s) with the length scale of this secondary motion. As can be seen from the relaxation spectra, the magnitude of this secondary relaxation process decreases until it is nearly eliminated by copolymerization with increasing amounts of epoxy. The epoxy molecules have the ability to chemically connect the individual crosslinked domains and eventually produce a macroscopic network structure. Thus, the tightening of the network by the addition of epoxy eliminates the large scale motion associated with the homopolymer that is evident in the shear modulus relaxation spectra.

The flexural properties were also determined for this series of epoxy–benzoxazine copolymers. The flexural modulus as a function of composition shows a behaviour nearly identical to that of the storage modulus determined by d.m.a. From *Figure 12*, it is evident that the modulus again shows a systematic decrease as the copolymer becomes richer in epoxy content. By the point at which there are equal amounts of benzoxazine and epoxy, the copolymer modulus has dropped to approximately 80% of the value for the benzoxazine homopolymer. In the dynamic analysis, this modulus drop was interpreted through a rule-of-mixtures approach. Now that crosslink density information is available, this analysis must be re-evaluated.

It was previously shown that increasing the epoxy content of the copolymer results in a higher crosslink density but a lower glassy modulus. There are a number of important factors that may be responsible for this phenomenon. First, by increasing the epoxy content, a greater percentage of the phenolic hydroxyl groups will have reacted with the epoxy and be unavailable for the intermolecular and intramolecular hydrogen bonding that was believed to increase stiffness in the glassy state. Additionally, the higher crosslinking may also disrupt molecular packing and increase free volume in the copolymer. Empirically, one expects that increasing the crosslink density by shortening the molecular weight between network points would have the effect of increasing the material stiffness in the glass state. However, a number of studies of model epoxy–amine network structures[5,10,11] have indicated that the glassy state modulus cannot be directly correlated with either crosslink density or the position of the glass transition. Instead, low strain glassy properties were demonstrated to be governed by chain interactions, free volume, and intermolecular packing considerations. High concentrations of crosslinks were shown to inhibit the intermolecular packing and enhance network flexibility. Thus increasing the crosslink density may increase the free volume in a material by molecular packing constraints. The increased intermolecular distance between chains would then decrease steric hindrance and other chain interactions, and reduce the resistance to place change

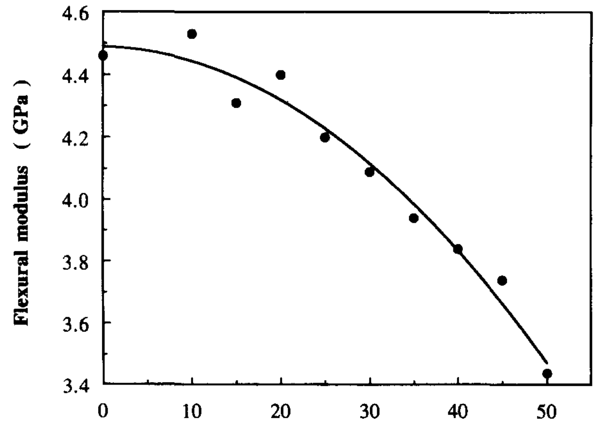


Figure 12 Variation of the flexural modulus as a function of composition for the benzoxazine–epoxy copolymer series

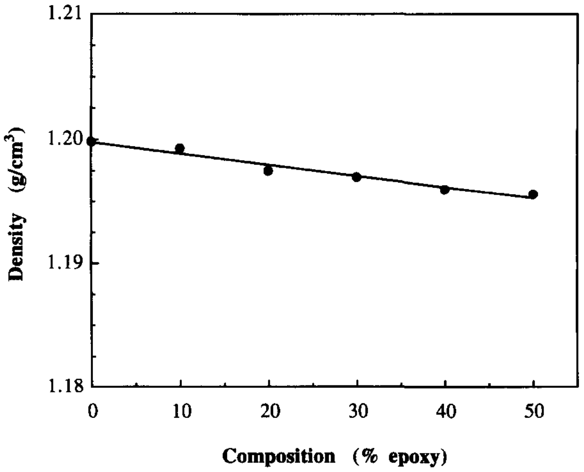


Figure 13 Variation in the bulk density of the benzoxazine–epoxy copolymers as a function of composition

and rotation of molecular segments. The linear molecular shape of the epoxy used in this study may also enhance segmental mobility and network flexibility as it replaces a tetrafunctional molecule that contains a bulky pendant phenyl ring on its bridge structure. It is noteworthy to mention that the bulk density, as determined by ASTM D792, decreases slightly as the copolymer composition becomes richer in epoxy, as is demonstrated in *Figure 13*. Because composition is not constant, bulk density results cannot provide concrete evidence that free volume increases with crosslinking, although it does help lend credibility to this theory.

The specimens for flexural analysis were loaded until failure such that both flexural stress and strain at breakage could be measured for the benzoxazine–epoxy copolymer series. As can be seen in *Figure 14*, flexural strength increases linearly as epoxy is incorporated into the benzoxazine network structure. The flexural strength of a thermosetting resin is influenced by a number of interrelated system parameters, including T_g, molecular weight between crosslinks, free volume, chemical structure, network regularity and perfection, and many other contributing factors[7,10,11]. The increase in crosslink density and initial increase in T_g that is observed by the addition of epoxy to the benzoxazine would be expected to strengthen the copolymer system and appear to dominate over any detrimental effects a higher free volume may have on the system. Also, it was suggested earlier that the benzoxazine homopolymer and copolymers with low concentrations of epoxy may contain clusters of branched chains or at best may be characterized as a loosely crosslinked network. The addition of epoxy molecules allows the clusters to be joined, the network tightened, and the perfection of the network improved with a subsequent increase in flexural strength.

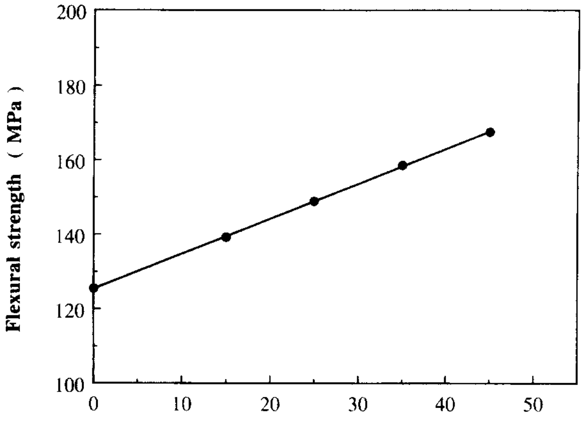


Figure 14 Variation in the flexural strength of the benzoxazine–epoxy copolymers as a function of composition

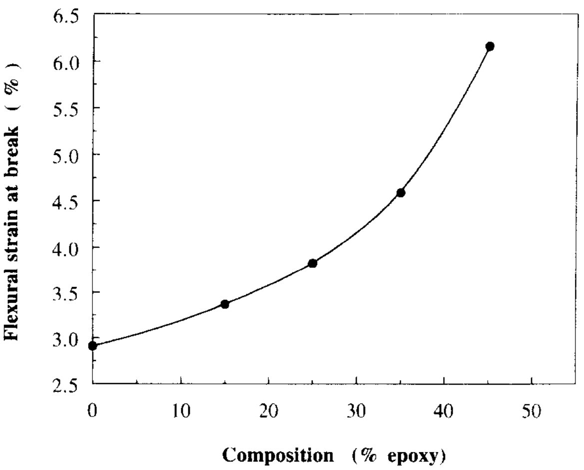


Figure 15 Variation in the strain at break as a function of composition for the benzoxazine–epoxy copolymers during flexural testing

The flexural strain at break for the copolymers was also observed to increase as epoxy was added to the network structure and can be seen in *Figure 15*. The extensibility of a crosslinked polymer in its glassy state is constrained largely by its available free volume. A higher free volume decreases chain interactions and enhances the ability of segments to flow under load by such means as rotational configurational changes. It was postulated earlier that the increased crosslink density achieved by the addition of epoxy to the benzoxazine matrix may cause an increase in the free volume of the copolymers. These effects on free volume may be at least partially responsible for the improved strain behaviour observed in the copolymers. The ability of chain segments to reach their fully extended state is also dependent on the intramolecular flexibility of the segments as well as their intermolecular packing constraints. Thus, the addition of the more flexible epoxy segments to the polybenzoxazine matrix should also contribute to the increased strain at breakage for the copolymer materials.

CONCLUSION

Benzoxazine–epoxy copolymers may be produced without the use of an external curing agent by the coreaction of a polybenzoxazine precursor with the diglycidyl ether of bisphenol-A. It is believed that the copolymerization reaction occurs via the opening of the epoxide ring by the phenolic hydroxyl functionalities present in the polybenzoxazine precursor. The incorporation of epoxy into the polybenzoxazine network structure results in copolymers that have both a higher crosslink density and T_g than the polybenzoxazine homopolymer. Additionally, the copolymers demonstrate improved mechanical properties over the homopolymer. The benzoxazine–epoxy copolymers exhibit strains at breakage that are up to twice the strain for the pure polybenzoxazine and a flexural strength that is significantly improved with only a minimal sacrifice in modulus value. Thus, by varying the epoxy concentration, benzoxazine–epoxy copolymers can be tailored to the thermal and mechanical requirements of a specific application.

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