Thermal and Viscoelastic Properties of Sequentially Polymerized Networks Composed of Benzoxazine, Epoxy, and Phenalkamine Curing Agents

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ABSTRACT: By using different ratios of phenalkamine/epoxy (EP) and benzoxazine/epoxy (EB), copolymer networks have been prepared sequentially by partially curing at low temperature followed by a final cure at high temperature. A single exothermic peak was observed in the differential scanning calorimetry (DSC) for the high-temperature curing. Dynamic mechanical thermal analysis showed a single tan δ peak, indicating no phase separation. The copolymer networks showed T_g values lower than the parent EB polymer network. Incorporation of EP in small percentage in the copolymer networks has improved the storage modulus and crosslink densities and the maximum value was observed for a sample containing 80% EB with respect to EP content. The thermal stability of the copolymer networks is better than that of the individual networks. The char yield value at 600°C increased with increasing EB percentage in the networks. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3956–3965, 2006

Key words: phenalkamine; benzoxazine; epoxy; copolymer networks; thermal properties

INTRODUCTION

The increasing demand of new materials for aircraft industry has pushed resin suppliers to work on new systems to meet requirements for high-performance composite applications. Polybenzoxazines are a new addition to thermosetting resins that combines the thermal properties and flame retardance of phenolic resin with excellent process ability and wide design flexibility of advanced epoxy resins.[1–6] Benzoxazine-based thermosets exhibit high glass-transition temperature and high modulus even though they have relatively low crosslink densities. Benzoxazine has been used as a hardener of epoxy resin to improve crosslink density and glass transition as well as to impart greater heat resistance, water resistance, electrical insulation, and mechanical properties.[7,8]

Polymer blending has been attempted to improve or alter the toughness of poly benzoxazine. This polymer has been reported to be able to undergo hybrid network formation with several other polymers.[9–13] Most of the thermosetting polymer blends are immiscible unless there is a favorable intermolecular interaction like hydrogen bonding. Epoxy and urethane resins show highly promising alloying capabilities with benzoxazine resins.[14,15]

The composite industry prefers prepegs for fabrication of composite structures as they eliminate cumbersome resin mixing and excessive resin flow during heat curing. The low-temperature curability of phenalkamines may be an added advantage for making epoxy-benzoxazine (EB) prepegs as partial crosslinking can be affected to get tack-free prepegs before final high-temperature cure.

Phenalkamine is a unique kind of Mannich base, composed of aromatic backbone, which is responsible for high chemical resistance; the side aliphatic chain is hydrophobic and can make this resin water resistant.[16,17] The phenolic groups make phenalkamine very active even at very low temperatures. The amine site is responsible for the high crosslink density. The use of phenalkamine in benzoxazine copolymers has not been reported in literature.

In the present study, we attempt to develop copolymer networks from phenalkamine/epoxy (EP) and EB. These resins were chosen in such a way that two-step curing could be achieved to establish a new and easy method of processing, particularly, fiber-reinforced plastics, without sacrificing its thermal properties. It is of interest to study these copolymer networks containing different ratios of two networks on thermal and viscoelastic properties. The present
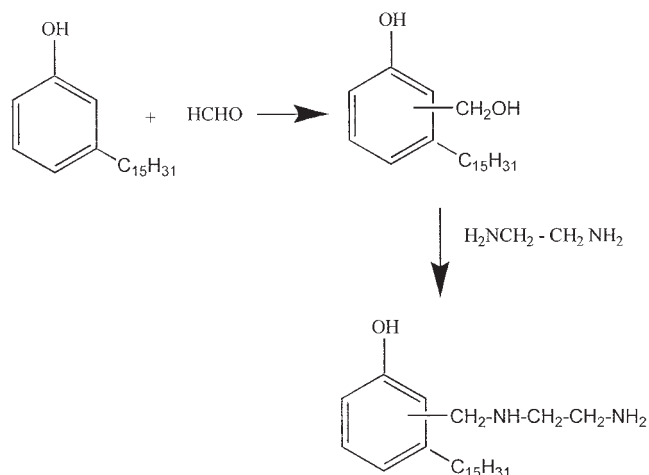
Figure 1 Synthesis of phenalkamine from cardanol, formaldehyde, and ethylene diamine.

article deals with the preparation of copolymer networks, study of their cure behavior, and evaluation of viscoelastic and thermal properties.

EXPERIMENTAL

Materials

Ethylene diamine and para formaldehyde from S.D. Fine Chemicals Ltd., India and aniline from Ranbaxy Fine Chemicals Ltd., India were used as-received. Diglycidyl ether of bisphenol A (Lapox, B-11, EEW = 187) was obtained from Atul Products India Ltd. Cardanol was procured from M/s Rishab Resins and Chemicals Ltd., Hyderabad, India.

Preparation of phenalkamine curing agent

A three-necked flask fitted with a water segregator and a thermometer was charged with 100 g (0.33 mol) cardanol and 30 g (0.5 mol) ethylene diamine. The contents were mixed with magnetic stirrer and heated up to 80°C. Then 16 g (0.53 mol) para formaldehyde was added in five to six portions to the above reaction mixture. After the addition of above contents, the temperature of the mixture was raised to 100–120°C and the reaction was carried out for about 1 h. From the above reaction product, water was distilled off, by applying vacuum (Fig. 1).

Synthesis of benzoxazine

Bisphenol A and aniline-based benzoxazine was synthesized by a solvent less process according to the method of Ishida.[2] Bisphenol A (2.28 g; 0.01 mol) was weighed into a round-bottom flask and para formaldehyde (1.20 g; 0.04 mol), and aniline (1.869 g; 0.02 mol) were added to the flask and it is placed over a

magnetic stirrer. The temperature was raised to 80–90°C and the heating continued for about 30 min. The mixture became homogeneous and turned into light yellow color. Then the temperature was increased to 130–135°C and the heating continued for another 20–30 min. The whole mixture became transparent yellow in color. It was then cooled and the product was dissolved in ether solvent. The solids were filtered out and the solution was washed three times with 1% NaOH followed by distilled water. The ether phase was dried over Na_2SO_4 and the solvent evaporated (Fig. 2).

### Composition of EP network for room-temperature cure

Phenalkamine was used to establish room-temperature curing of epoxy resin. The equivalent weight of the phenalkamine was decided by its amine value. Phenalkamines are known to react with epoxy nonstoichiometrically. To arrive at a best composition of the network, we have mixed epoxy and phenalkamine curatives in the equivalent ratios of 1 : 1, 1 : 2, and 1 : 3, respectively, at room temperature for 24 h. The higher the primary amine concentration in the mixture the faster it cures. Accordingly, it was observed that 1 : 3 compositions with high primary amine concentration were found to be brittle, whereas 1 : 1 composition with low primary amine concentration took a long time and also the curing was incomplete. We have selected the composition (1 : 2) on the basis of its curing time and properties. The sample is denoted as EP. The cure schedule for this sample is 24 h at room temperature followed by 1 h at 150°C.

Composition of EB network for high-temperature cure

Ishida and Allen[7] have found that samples containing less than 50 mol % of benzoxazine did not cure properly. Therefore, we had chosen a fixed composition of (60 : 40) EB copolymer composition through out this work. Accordingly, 40% molar weight of epoxy was mixed with 60% molar weight of benzoxazine precursor at 85°C. Acetone was used as diluent to facilitate mixing. After 30 min, the mixture is poured into a required mold. The resin-filled mold was initially heated at 150°C for 30 min to remove air trapped in the mold-filling process. Then, the material was subjected to a curing schedule of 1 h each at 160, 180, and 200°C. No catalyst was used in this experiment. The cured samples are denoted as EB.

Preparation of copolymer network system composed of EP/EB

Different % of EP and EB were used to make copolymer networks with varying properties. The % of EB in
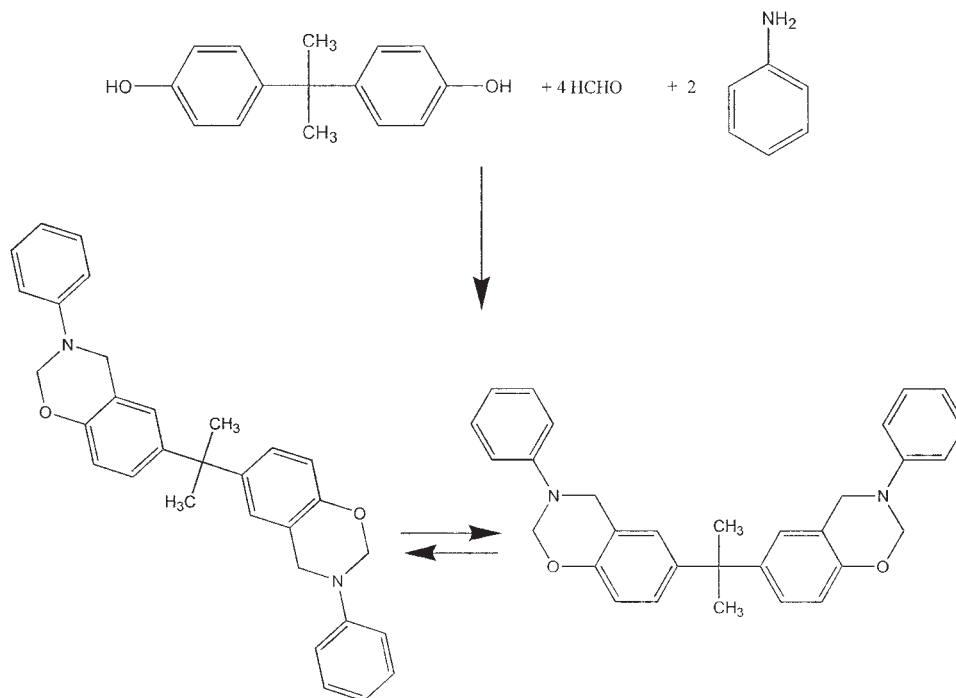
Figure 2 Synthesis of benzoxazine from bisphenol A, formaldehyde, and aniline.

copolymer networks used was 20, 40, 60, and 80 with respect to EP and was labeled as EP/EB-20, EP/EB-40, EP/EB-60, and EP/EB-80. The calculated amount of total epoxy content and benzoxazine were melt mixed at around 80°C and allowed to cool down to room temp. The procedure is followed by the addition and mixing of calculated amount of phenalkamine. According to required dimension it is then casted in standard mold. The first stage curing was done at room temperature. The cure schedule for the second stage was 100°C for 30 min, 140°C for 1 h, 180°C for 1 h, and 200°C for 4 h.

Characterization techniques

IR spectra were recorded on a Nicolet 740 IR spectrophotometer. ^{1}H-NMR spectra were recorded with Bruker MSL-300 (300 Hz) NMR spectrometer with CDCl$_3$ or DMSO-d$_6$ as solvent. Amine contents were obtained based on ASTM D 2073–92 titration method. Differential scanning calorimetry (DSC) was performed with Perkin–Elmer DSC module (TA instruments, USA) at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analyzer (851 Mettler Toledo TGA instrument) was used to study the thermal decomposition of the copolymer networks. Cured samples were weighed in a sample pan and then heated in TGA furnace at a heating rate of 10°C/min. Viscoelastic properties and transition temperature of cured samples were studied using Dynamic Mechanical Thermal Analyzer (DMTA IV

Model, Rheometric Scientific, UK). Viscoelastic studies of cured samples were done on rectangular bar with specimen dimension $45 \times 10 \times 1.2$ mm^3 in dual cantilever bend mode at 1 Hz frequency with heating rate of 5°C/min. Evolution of storage modulus (E') and energy dissipation (tan δ) with temperature were measured.

RESULTS AND DISCUSSION

Characterization of phenalkamine

The flexibility of the cured epoxies is enhanced by the introduction of cardanol moiety. The amine alkylation of cardanol was done by Mannich reaction, using formaldehyde and ethylene diamine. The IR spectra of adduct indicates characteristic absorption at 3200–3400 cm^{-1} (N—H stretch), 2850–3000 cm^{-1} (alkyl group), 1620–1500 (aromatic C=C stretch), and 1274 cm^{-1} (aliphatic C—N stretch). In the ^{1}H-NMR spectra of cardanol phenalkamine, the peak at 6.5–6.9 δ is due to aryl protons of benzene nuclei, the peak around the region 6.45 δ is owing to the phenolic hydroxyl, and the peak at 5–5.4 δ is due to unsaturated (C=CH) protons of a long alkyl side chain originally present in the cardanol. The small peak at 0.9 δ is due to the terminal methyl group of the side chain. The peak at 1.2–2.5 δ is due to the long aliphatic side chain.[18] The observed peak at 3.5–4.0 δ is the characteristic chemical shift for the methylene linkages (ph—CH$_2$N) in the Mannich structures.[19–21] All these peaks in the
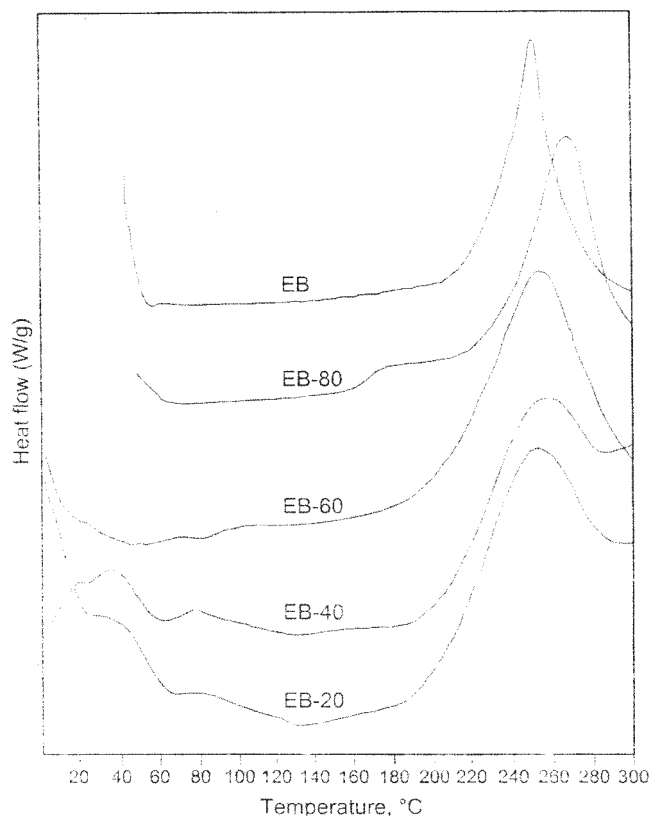
Figure 3 DSC thermograms showing the exothermic curing peak for different copolymer samples.

spectra indicate that the Mannich reaction has taken place.

Characterization of benzoxazine

Bisphenol A and aniline-based benzoxazine was synthesized by a solventless process according to the method of Ishida.[2] IR spectrum of purified benzoxazine showed peak at 945, 1027, and 1230 cm^{-1} due to the formation of benzoxazine ring structure. The spectra also showed a peak at 1490 cm^{-1} because of trisubstituted benzene ring. The structure is confirmed by NMR, which indicated a peak at 1.5 ppm owing to gem dimethyl group of bisphenol A. The methylene proton of benzoxazine ring appeared at 4.5 and 5.3

ppm, respectively, and aromatic protons are observed as a multiplet at 6.5–7.2 ppm. The peak assignments are in conformity with the published work.[22,23]

Curing studies by DSC

Copolymer networks with varying properties were prepared by mixing different percentages of EB and EP. The samples were cured at room temperature for 24 h to give specimens ranging from hard to soft gel depending on the percentage of EP in the network composition. After this first stage of isothermal curing, the samples were studied by DSC to obtain high-temperature curing characteristics. DSC of blend provides valuable data, such as cure initiation, peak cure temperature, and maximum cure temperature, and this allows us to have an idea whether a reasonable cure window exists or not.

The DSC of all the samples was given in Figure 3. In the spectra EB-20, EB-40, and EB-60 indicated an endothermic peak at around 60°C, which might be expected due to T_g of the room temperature-cured EP network in these samples. EB-80 did not show this peak because of reduced EP content in the blend sample. A single well-defined exotherm is observed for pure EB, with the onset of cure at 175°C and peak exotherm at 248°C. This is the region where thermal opening of benzoxazine ring takes place and gives phenolic resin.[4–6] The curing characteristics of the copolymer blend samples are given in Table I.

The curing of copolymer networks is complicated and a variety of reactions take place. Primary amine and secondary amine reactions with epoxy take place at room temperature, resulting in hard to soft gels. Phenolic OH of phenalkamine reacts with epoxy at an intermediate temperature. The homopolymerization of epoxy by secondary hydroxyl-epoxy reaction, benzoxazine homopolymerization, leading to novolac resin and phenolic OH of novolac with epoxy, may take place at high temperature.[21–23] A possible copolymer network is shown in Figure 4. Although DSC could not distinguish these high-temperature reactions, the shape is dependent on the extent to which these reactions take place in the copolymer networks. The copolymer networks are mainly showing a broad

TABLE I
Curing Characteristics of Copolymer Samples from DSC Analysis

Sample	Cure initiation temperature, T_i (°C)	Peak curing point (°C)	Maximum curing temperature, T_{max} (°C)	ΔH (J/g)
EB20	194.2	253.0	285.0	90
E840	200.0	255.0	285.0	70
EB60	200.0	251.0	290.0	179
EB80	210.0	261.7	300.0	212
EB	175.0	247.9	290.0	282
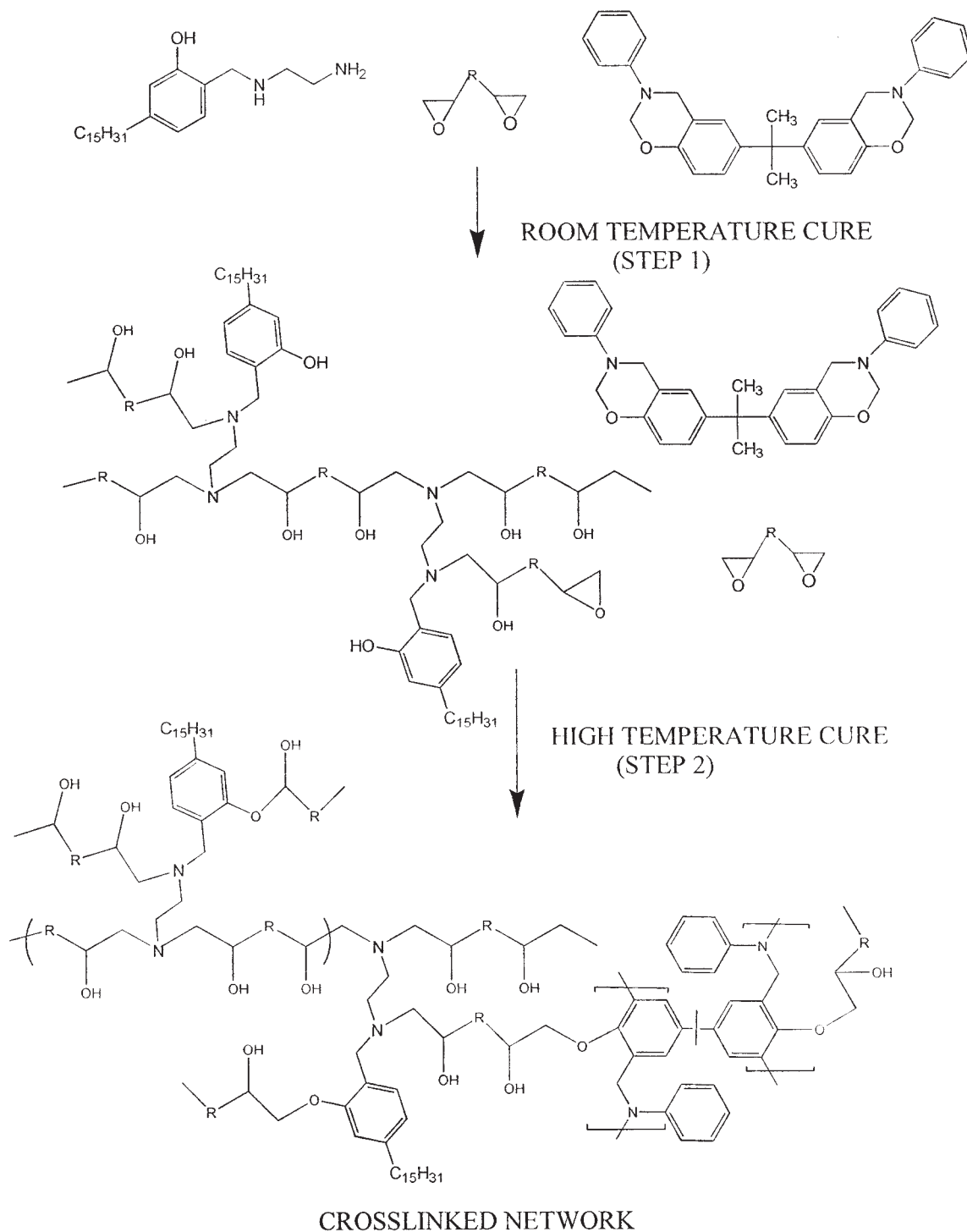
Figure 4 Formation of copolymer network from phenalkamine, epoxy, and benzoxazine.

exothermic peak from 190 to 290°C. The retardation of the curing reaction of the EB system is observed as a shift of the exotherm to high temperature. The peak maximum got sharper with increasing EB content in the copolymer networks. The values of the total heat of reaction (ΔH) are given in Table I. EB copolymer had a ΔH value of 282 J/g, and with increasing EP content in the networks, the value reduced to 90 J/g incase of EB-20 and a further low value of ΔH 70 J/g was observed with EB-40.

Cured resin viscoelastic properties

Rectangular bars of cured specimen were subjected to DMTA for viscoelastic properties. DMTA provides a

TABLE II
Dynamic Mechanical Thermal Analysis Data for the Cured Copolymer Networks

| Sample | E' at room temperature (10^9) (Pa) | Temperature at E' decline (°C) | | | Crosslink density (mol/cm^3) |
		$T_{g,\text{onset}}$	$T_{g,\text{intersect}}$	$T_{g,\text{midpoint}}$	
EP	1.50	73.0	100.0	120.0	1.0×10^3
EB20	1.35	76.0	102.0	115.0	1.8×10^3
EB40	1.19	87.5	114.0	127.0	1.5×10^3
EB60	1.42	112.5	128.0	145.0	1.9×10^3
EB80	6.30	115.5	131.0	150.5	1.3×10^4
EB	1.70	131.5	157.0	178.5	2.1×10^3

direct link between material's chemical make up and its mechanical behavior. The scan was recorded as a function of temperature from 50°C to 250°C covering three areas (the glassy state, the transition state, and the rubbery plateau) of each sample. The storage modulus (E') and dissipation energy (tan δ) are the important parameters that can be extracted from the spectra.

The storage modulus of a solid sample at room temperature provides a measure of material's stiffness under shear deformation; the numerical values are summarized in Table II. The comparative analysis of storage modulus curves has been figured in Figure 5(a). It can be observed that the storage modulus of copolymer network systems at room temperature is increasing with increasing percentage of EB content, except EB-40 with which a slight reduction was observed. In general, this can be ascribed to the increase in stiffness of the network due to incorporation of rigid EB network.

The onset of modulus reduction is related to glass transition, the temperature at which the material transforms from a relatively rigid or glassy state to a more deformable or softened state. Different definitions have been used to facilitate experimental determination of T_g from storage modulus. Temperature corresponding to the onset of drop in storage modulus ($T_{g,\text{onset}}$), temperature at which the extrapolated line of the initial modulus intersects that of the steepest slope ($T_{g,\text{intersect}}$) and temperature corresponding to the midpoint of the T_g region ($T_{g,\text{midpoint}}$) are the practical methods. All these values are given in Table II. These values are increasing with increasing percent of EB.

It must be noted that the values of T_g for the same material may differ slightly or significantly depending on the definition. Frequently, the temperature corresponding to tan δ peak is used as a marker of T_g. Several factors, such as composition, molecular weight, and features of chemical structure (crosslinking, side groups), can alter the T_g. The peak of the tan δ is associated with the glass transition and may be analyzed to provide qualitative insight into the network structure of the system. Inspection of the DMTA (tan δ) curves [Fig. 5(b)] reveals a single T_g with the copolymer networks. If the two starting materials had

phase separated then two peaks would have arisen corresponding to T_g of individual chains. It can be observed that the copolymer networks are showing T_g values in between their parental polymer networks EB and EP (see Table III). EB copolymer had the highest T_g due to the higher molecular rigidity of benzoxazine and high crosslink density imparted by epoxy. With increasing percentage of EB content in the copolymer networks, the T_g showed proportional increase. The observed copolymer networks display single T_g in DMTA, indicating intimate and uniform mixing.

The height and width of α relaxation peak may also be analyzed to get an idea of network structure. It is observed [Fig. 5(b)] that the height of the tan δ peak decreases as the EB content increases. Compared to the parental polymer system, the peak width at half height of the copolymer networks is low and the value is increasing with increasing percentage of EB content. Increasing percentage of EB system increases the number of branched structure and results in a wider distribution of molecules, and consequently, the range of temperature at which the different network segments gain mobility increases.

The crosslink density, ρ, can be calculated using the equation of state for rubbery elasticity.[24,25]

$$\rho = E'/3\Phi RT$$

where Φ is the front factor, T is the absolute temperature, R is the gas constant, and E' is the storage modulus of the sample at temperature T. This equation is applicable to polymer networks that have a rubbery plateau region. The rubbery modulus equation is commonly used for thermosets even though the accuracy is limited at high crosslink densities. Therefore, in our study, the ρ values of the samples were calculated at the T_g plus 40°C according to this equation to compare the crosslink density of each sample. The crosslink density values are presented in Table II.

Crosslink densities of copolymer networks are higher than that for EP network. However, EB 80 is showing very high crosslink density compared to the other copolymer networks. The reason for huge increase in crosslink density for EB-80 is due to the
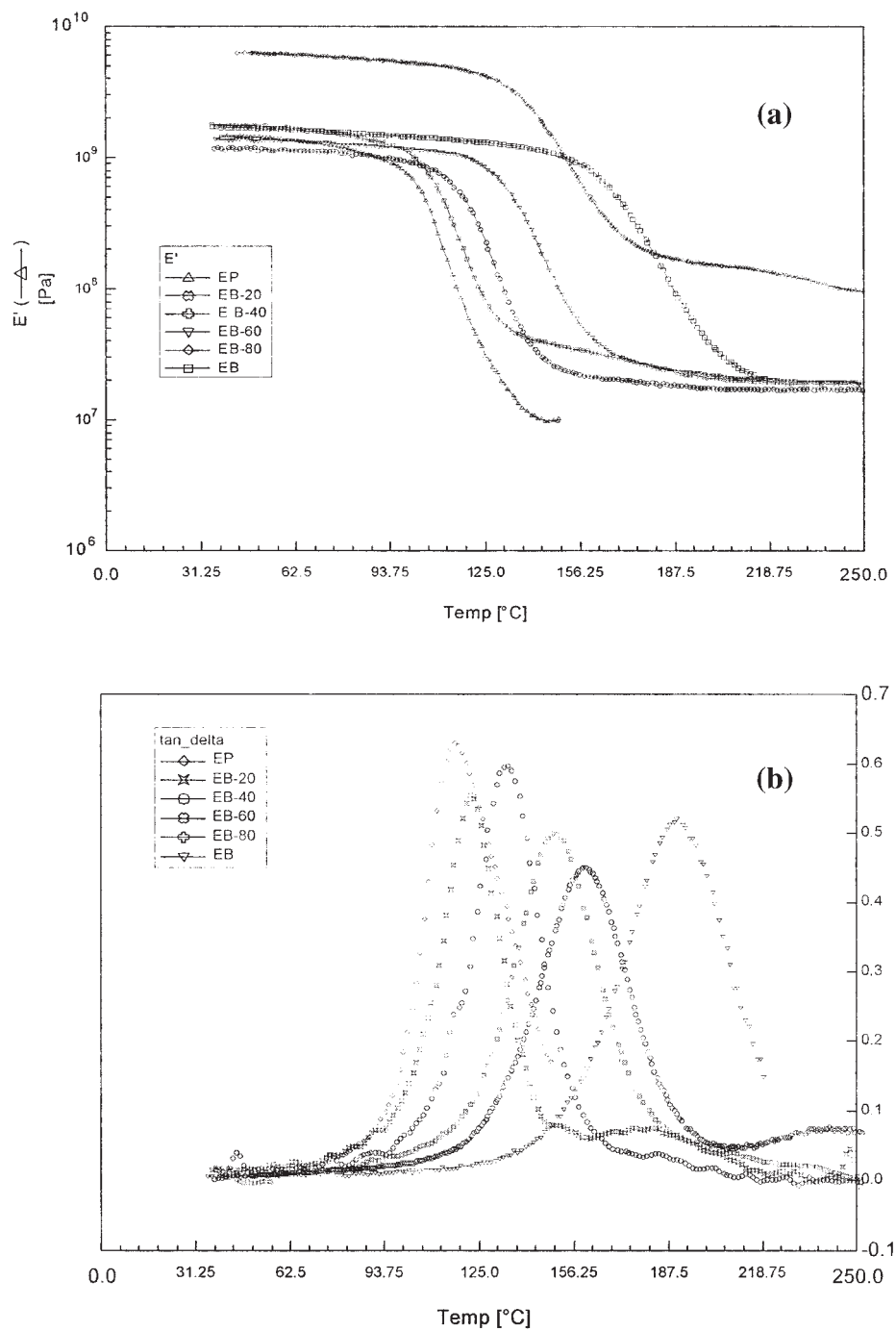
Figure 5 DMTA thermograms obtained for the samples along with EP and LB copolymers. (a) overlay of storage modulus; (b) overlay of tan δ (energy dissipation).

incorporation of EP, a low T_g network in small quantity. This allows the system to cure completely before it loses mobility, whereas with higher percentage of EP, the EB network has to cure in vitrified glassy network of EP. The mobility is restricted and curing may not be complete, leading to some graft copolymer formation in the network. The shape of curing exotherm in DSC is also an indication. The curing exotherm after reaching peak temperature displayed high

base line values, particularly in samples EB-20 and EB-40, indicating some retardation in curing. The ΔH values are also very low for these two samples. Also, as depicted in Figure 3, grafting of polybenzoxazine to EP network may also take place when the initially formed networks mobility is restricted at high temperature. The result is dangling side chains in the cured network giving reduced crosslink density. Samples EB-20 and EB-40 may be having higher proportion of
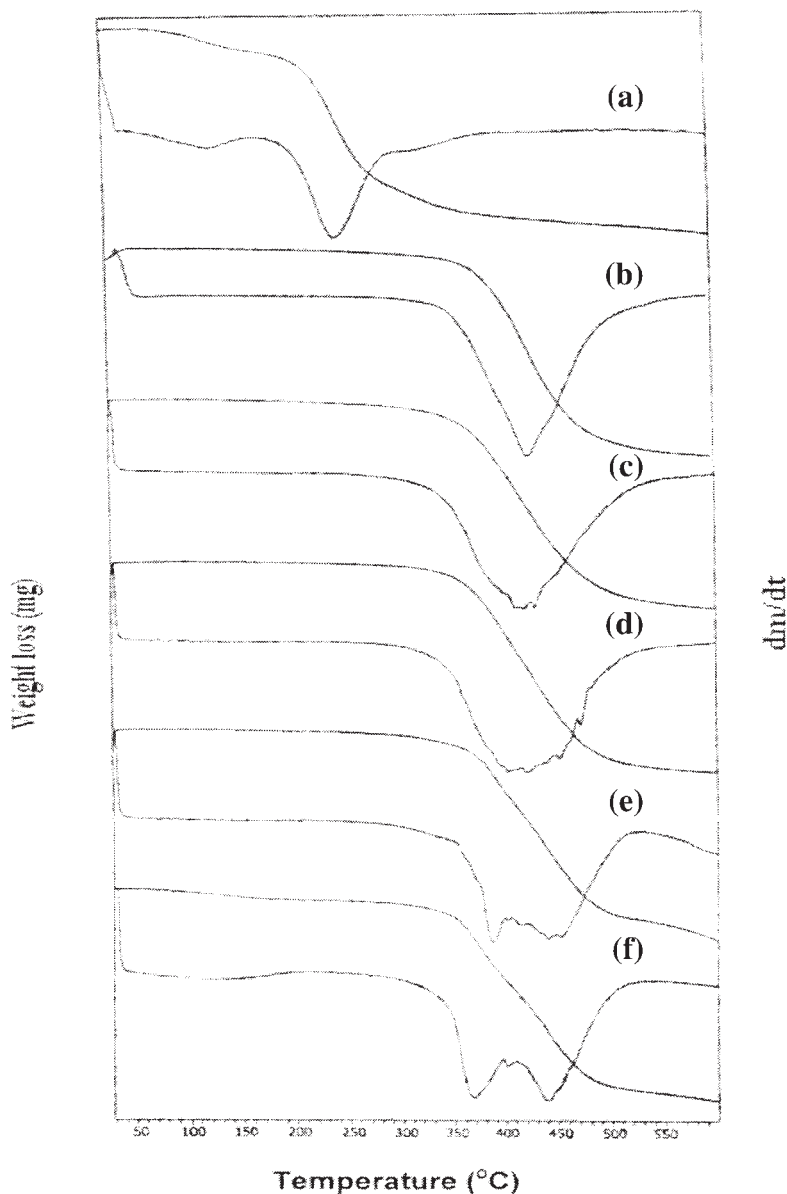
TABLE III
Tan δ Characteristics of Cured Copolymer
Networks Samples by DMTA

Sample	Tan δ (°C)	Tan δ peak height	Tan δ width at half height
EP	116.5	0.63	30
EB20	120.3	0.57	24
EB40	133.0	0.61	26
EB60	148.6	0.54	33
EB80	158.4	0.45	35
EB	187.8	0.51	44

grafting besides crosslinking. In spite of the observed high crosslink densities, the T_g displayed by this copolymer network is lower than that of EB copolymer due to disruption of packing symmetry by high crosslinking.

Thermogravimetric analysis

Thermogravimetric analysis of the samples was conducted under nitrogen atmosphere. TGA traces of the sample are shown in Figure 6 and the results are compiled in Table IV. Initial decomposition temperature (IDT), maximum decomposition temperature (D_{max}), char yield, and integral procedural decomposition temperature (IPDT) were determined. The EB

Figure 6 TGA thermograms of copolymer networks showing weight loss and dm/dt. (a) EB copolymer; (b) EB-80; (c) EB-60; (d) EB-40; (e) EB-20; and (f) EP.

Sample	IDT_1 (°C)	D_{max1} (°C)	IDT_2 (°C)	D_{max2} (°C)	Char yield at 600°C	IPDT (°C)
EP	300	365	420	440	10.2	383.4
EB20	300	385	420	450	15.7	406.2
EB40	300	420	—	—	18.4	394.8
EB60	300	430	—	—	20.0	389.1
EB80	330	425	—	—	23.8	400.5
EB	110	200	270	380	25.3	263.7

copolymer showed high IDT, maximum decomposition temperature (D_{max}), and final decomposition temperature (T_f). According to the literature, the D_{max} is due to the simultaneous degradation of phenolic linkages and Mannich bases in polybenzoxazines.[26] Cleavage of the isopropylidene group also occurs at approximately the same temperature.[27] It has been generalized that the first weight loss event in the TGA thermogram is due to the cleavage of C—C, C—N bonds occurring simultaneously, resulting in the degassing of amines from benzoxazine. The second weight loss is assigned to the phenolic degradation of EB system.[28] The phenalkamine-cured epoxy (EP) also shows two-step degradation: first step at 300–390°C (IDT_1, 300°C and D_{max}, 365°C) and second stage at 410–500°C (IDT_2, 420°C and D_{max}, 440°C). The first and second stage degradation may be assumed due to aliphatic chain of Mannich base and Mannich base-cured epoxy polymer degradation, respectively.

The thermal stability of the copolymer network is enhanced from their parent polymer. The two degradation peaks observed in TGA derivative thermograms of EP copolymer network merged into a single peak for EB-40, EB-60, and EB-80, with increasing percentage of EB polymer content. The percent weight loss *versus* temperature of copolymer network samples were given in Figure 7. Their integral procedural decomposition temperature proposed by Doyle[29] assessed the relative thermal stability of the polymers.

$$IPDT = A^*(T_f - T_i) + T_i$$

where A^* is the ratio of the area under the experimental curve divided by the area under total TGA thermogram. T_i and T_f are the initial and final experimental temperatures, respectively. IPDT value represents the relative thermal stability of the sample investigated. The observed trend is as follows: EB20 > EB80 > EB40 > EB60 > EP > EB.

With increasing percentage of EP polymer, thermal stability of the polymer is increasing except EB80 for reasons not known, but the copolymer networks showed better thermal stability compared to their parental polymers (EB and EP). The relative flammability can be judged from their char residue. EB copoly-

mer degrades with high char residue due to higher aromatic content as compared with its counterpart EP polymer network. Char residue of copolymer networks dropped in between their parental polymer values. Increased percentage of EB in copolymer networks results as a higher char residue. On the basis of char yields, the following order is observed for the copolymer networks: EB > EB80 > EB60 > EB40 > EB20 > EP.

CONCLUSIONS

Copolymer networks have been prepared using different ratios of EP and EB networks. In this system, the EP was used for room-temperature curing as well as to provide soft network. The rigid network EB was used for high temperature cure. These systems can be partially cured at room temperature and final curing can be done at high temperature, giving wide temperature latitude for processing. To know the cure behavior of these networks, DSC analysis was carried out. The copolymer systems mainly showed a broad exothermic peak from 190 to 290°C. But its curing initiation temperature is shifted towards higher temperature. A variety of reactions may take place, such as primary, secondary amine, phenolic, secondary hydroxyl
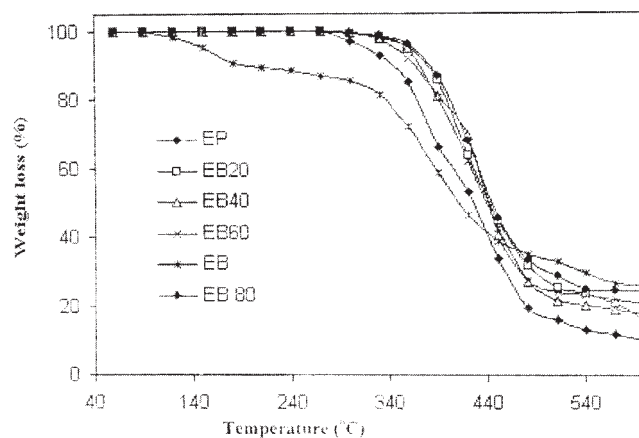

Figure 7 Thermogravimetric analysis of different samples showing percent weight loss versus temperature.

groups with epoxy resin and ring opening of benzoxazine, leading to homopolymer. All these reactions take place at a marginal temperature range barring primary amine epoxy reaction, giving rise to one exothermic peak in DSC.

DMTA was used for the characterization of viscoelastic properties of the networks. A single T_g was observed for the copolymer networks, indicating that no phase separation occurred during curing. The T_g's of the copolymer networks are in between their parent networks, the values being dependent on the composition, and are incremental towards the high T_g EB network. Sample EB-80 displayed higher crosslink density and a low tan δ value than EB copolymer. Incorporation of a low T_g material like EP in EB network allows the system to cure completely before the system loses mobility, leading to a high crosslink density and a high storage modulus. The thermal stability of the copolymer networks is better than their parent networks. The copolymer networks showed two-stage degradation, and with increasing percentage of EB polymer content, the DTG peaks are merged into a single degradation peak. The relative thermal stability was assessed by IPDT, which indicated the following trend for the copolymer networks: EB20 > EB80 > EB40 > EB60 > EP > EB.

The char yields at 600°C read from the thermograms indicated higher values for EB and a progressive decrease in case of copolymer networks, depending on the percent of EB composition.

The sequentially polymerized copolymer networks may be useful for applications such as fabrication of printed circuit boards where prepegs can be made at room temperature and curing can be done at elevated temperature to get composites with good mechanical properties.

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