Synthesis and Characterization of a Cured Epoxy Resin with a Benzoxazine Monomer Containing Allyl Groups

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Received 21 August 2009; accepted 5 January 2010
DOI 10.1002/app.32093

ABSTRACT: Vinyl-terminated benzoxazine (VB-a), which can be polymerized through ring-opening polymerization, was synthesized through the Mannich condensation of bisphenol A, formaldehyde, and allylamine. This VB-a monomer was then blended with epoxy resin and then concurrently thermally cured to form an epoxy/VB-a copolymer network. To understand the curing kinetics of this epoxy/VB-a copolymer, dynamic differential scanning calorimetry measurements were performed by the Kissinger and Flynn–Wall–Ozawa methods. Fourier transform infrared (FTIR) analyses revealed the presence of thermal curing reactions and hydrogen-bonding interactions of the epoxy/VB-a copolymers. Meanwhile, a significant enhancement of the ring-opening and allyl polymerizations of the epoxy was observed. For these interpenetrating polymer networks, dynamic mechanical analysis and thermogravimetric analysis results indicate that the thermal properties increased with increasing VB-a content in the epoxy/VB-a copolymers. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3121–3127, 2010

Key words: blends; resins; thermal properties

INTRODUCTION

In recent years, a lot of progress has been made in the development of multicomponent and reactive epoxy–amine systems to achieve heterogeneous structures with tailor-made properties.[1,2] Epoxy resins have excellent chemical resistances to moisture and solvents and good adhesion to many substrates. The versatility in their formulation also makes epoxy resins widely applicable in industry, such as in surface coatings, adhesives, painting materials, pottings, composites, laminates, encapsulants for semiconductors, and insulating materials for electric devices.[3,4] However, conventional epoxy systems cannot satisfy field applications because of the higher requirements in thermal and flame resistance. To prevent the deterioration of other mechanical properties, such as the elastic modulus and yield stress, high-glass-transition-temperature (T_g) engineering thermoplastics such as poly(ether sulfone) and poly(ether imide) have been reported.[5,6] Several approaches have been reported for the modification of the epoxy backbone to enhance the thermal properties of epoxy resins by nanofillers, such as clay and polyhedral oligomeric silsesquioxane.[7–12]

In addition to epoxy resin, polybenzoxazine, an alternative high-performance thermosetting resin, has been developed for electric applications.[13–15] Benzoxazines are heterocyclic compounds synthesized from the Mannich condensation of phenol, formaldehyde, and a primary amine.[16,17] They can be polymerized via a thermally induced ring-opening polymerization without the use of a strong acid or base as a catalyst, and thus, no toxic gases or other byproducts are generated during polymerization. Polybenzoxazines have many outstanding properties, such as a low flammability, high thermal stability, and low dielectric properties.[18,19] More interestingly, Wang and coworkers reported that polybenzoxazines are a new class of nonfluorine, nonsilicon, low-surface, free-energy polymeric materials because of their strong intramolecular hydrogen bonding,[20] which have wide applications in superhydrophobic surfaces,[21–23] lithography patterns,[24] and mold-release materials in nanoimprinting technology.[25] The T_g of the polybenzoxazine synthesized from a typical benzoxazine monomer containing one oxazine ring (3,4-dihydro-3-phenyl-2H-benzooxazine (P-a)) is about 130°C, and its degradation temperature is around 300°C.[26] To further improve the thermal stability of polybenzoxazines, the polymerizable allyl side group has been introduced]into the benzoxazine monomer.[27–31] These benzoxazines with allyl groups [vinyl-terminated benzoxazine (VB-a)] exhibit higher T_g's (ca. 300°C),

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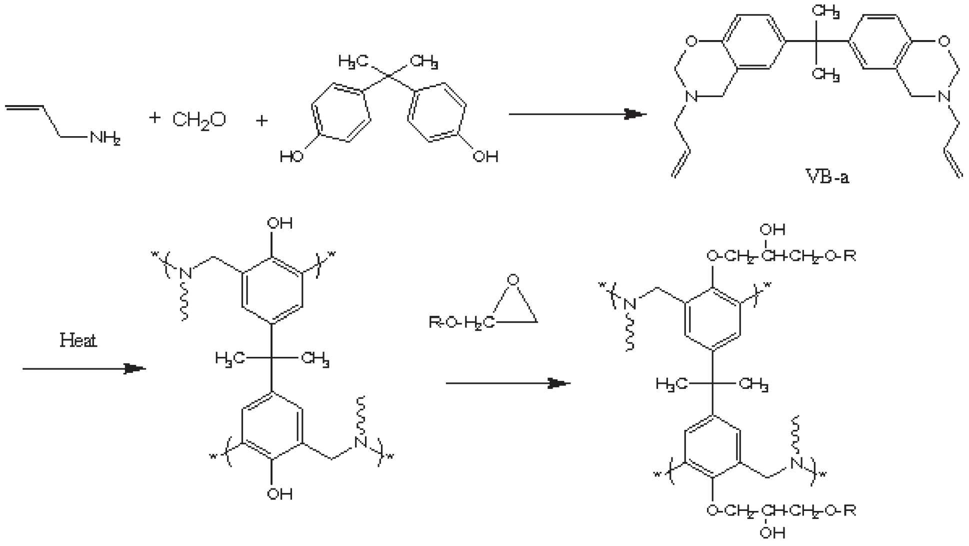
Contract grant sponsor: National Science Council of Taiwan; contract grant numbers: NSC 97-2221-E-110-013-MY3 and NSC 97-2120-M-009-003.

Journal of Applied Polymer Science, Vol. 117, 3121–3127 (2010)



Scheme 1 Preparation of VB-a and reaction scheme for the epoxy/VB-a copolymers.

maintain their storage modulus at higher temperatures, and have better thermal stability than the corresponding polybenzoxazines without allyl groups.

The aim of this study was to obtain high-performance materials with good thermal and mechanical properties. We attempted to design a copolymer network with three reactive groups, including an epoxy ring, benzoxazine ring, and allyl double bond. The phenolic groups resulting from the ring-opening polymerization of benzoxazine could react with epoxy resins at elevated temperatures; meanwhile, homogeneous networks and additional crosslinking points were expected in the matrix, as shown in Scheme 1.[32] In addition, this system did not require any catalyst for epoxy curing because the phenolic group of the polybenzoxazines could act as an initiator and a catalyst. Hence, the copolymerization of epoxy resin with VB-a may have allowed the network structure needed to achieve our aim of a high-performance material.

EXPERIMENTAL

Materials

Aqueous formaldehyde solution (37%), allylamine, and bisphenol A were purchased from Aldrich. Diglycidyl ether of bisphenol A (DGEBA; DER 331; Epoxy equivalent weight (EEW) = 190 g/equiv) was purchased from Nan-Ya Chemical of Taiwan. To prepare the epoxy/polybenzoxazines copolymers, we synthesized a VB-a monomer. The presence of the vinyl group allowed the ring-opening polymerization to be conducted under moderate conditions. The VB-a was prepared according to the procedure outlined in Scheme 1. An aqueous formaldehyde solution (16.5 g) and bisphenol A (11.4 g) were mixed with methyl ethyl ketone (50 mL) in a 250-mL, three-necked flask. With a dropping funnel, allylamine (11.4 g) was added dropwise into the mixture, which was cooled in an ice bath. After stirring for an additional 30 min, the temperature of the mixture was raised gradually to 80°C, and then, the mixture was heated under reflux for 3 h. The solvent and water were evaporated *in vacuo,* and the residue was dissolved in ethyl ether (100 mL). The solution was washed several times with water and 2*N* aqueous NaOH to remove byproducts and unreacted reagents. The ether solution was then dried by sodium sulfate, and the solvent was evaporated at room temperature. The product was obtained as a light yellow solid with a yield of 23.5 g.

Preparation of the epoxy/VB-a copolymers

Stoichiometric amounts of DGEBA with VB-a monomer were mixed in a high-speed stirrer for 10 min at 55°C. After it was degassed *in vacuo,* the cast film was polymerized in a stepwise manner, with heating at 120, 140, 160, and 200°C, each for 2 h. The product was postcured at 220 and 240°C for 30 min each.

Characterization

The dynamic curing kinetics was studied with a TA Q-20 differential scanning calorimeter operating under a nitrogen atmosphere. The sample (ca. 7 mg) was placed in a sealed aluminum sample pan. Dynamic curing scans were conducted from 30 to 350°C at heating rates of 1, 5, 10, and 20°C/min. Fourier transform infrared (FTIR) spectra of the polymer blend films were recorded with the conventional KBr disk method. The film used in this study was sufficiently thin to obey the Beer–Lambert law.

FTIR spectra were recorded with a Bruker Tensor 27 FTIR spectrophotometer; 32 scans were collected at a spectral resolution of 1 cm^{-1}. Because polymers containing OH groups are hygroscopic, pure nitrogen gas was used to purge the spectrometer's optical box to maintain the sample film's dryness. The dynamic mechanical behavior of the cured sample was studied with a DuPont 2980 dynamic mechanical analyzer. The cured sample was polished to about 3.0 × 13.0 × 30.0 mm^3 and mounted on a single cantilever clamp. The mechanical properties were measured under nitrogen in step mode every 5°C from 25 to 350°C at a frequency of $r = 1$ Hz. The thermal stability of the samples was characterized with a TA Q-50 thermogravimetric analyzer operating under a nitrogen atmosphere. The cured sample (ca. 7 mg) was placed in a Pt cell and heated at a rate of 20°C/min from 30 to 800°C at a nitrogen flow rate of 60 mL/min.

RESULTS AND DISCUSSION

Curing behavior of the epoxy/VB-a copolymers

The curing behavior of the epoxy/VB-a copolymers was examined by differential scanning calorimetry (DSC) analysis. Figure 1 shows the DSC thermogram of the epoxy/VB-a copolymers with different ratios for different heating rates at 1, 5, 10, and 20°C/min. A faster heating rate resulted in a higher maximum temperature (T_p) because the sample had a shorter time to react and release the heat of the reaction. For pure VB-a, shown in Figure 1(d), two exotherms were observed. The onset temperature of the first exotherm was at about 145°C with the exotherm peak at 206°C, and the apparent onset of the second exotherm was at 225°C with the exotherm maximum at 266°C at a heating rate of 10°C/min.[27] The first exotherm was considered to be due to the thermal curing of the allyl group, and the second exotherm was from the ring opening of the oxazine ring; this was discussed in a previous article.[27] As the epoxy concentration increased, the two exotherms became a single peak. The first peak shifted to a higher temperature between 206 and 266°C. This phenomenon was due to the dilute effect of epoxy resin into VB-a monomer, which resulted in a decrease of epoxy curing behavior. The ring-opening polymerization of higher temperature (266°C) of pure VB-a was due to the restricted mobility of VB-a because of the polymerization of the allyl group.[27]

An optimal curing process depends on the understanding of the curing kinetics, the curing mechanism, and an accurate modeling of the curing process. This modeling process includes the determination of the mechanism and an appropriate kinetic equation in terms of the reaction order and activation energy. An accurate model not only helps to

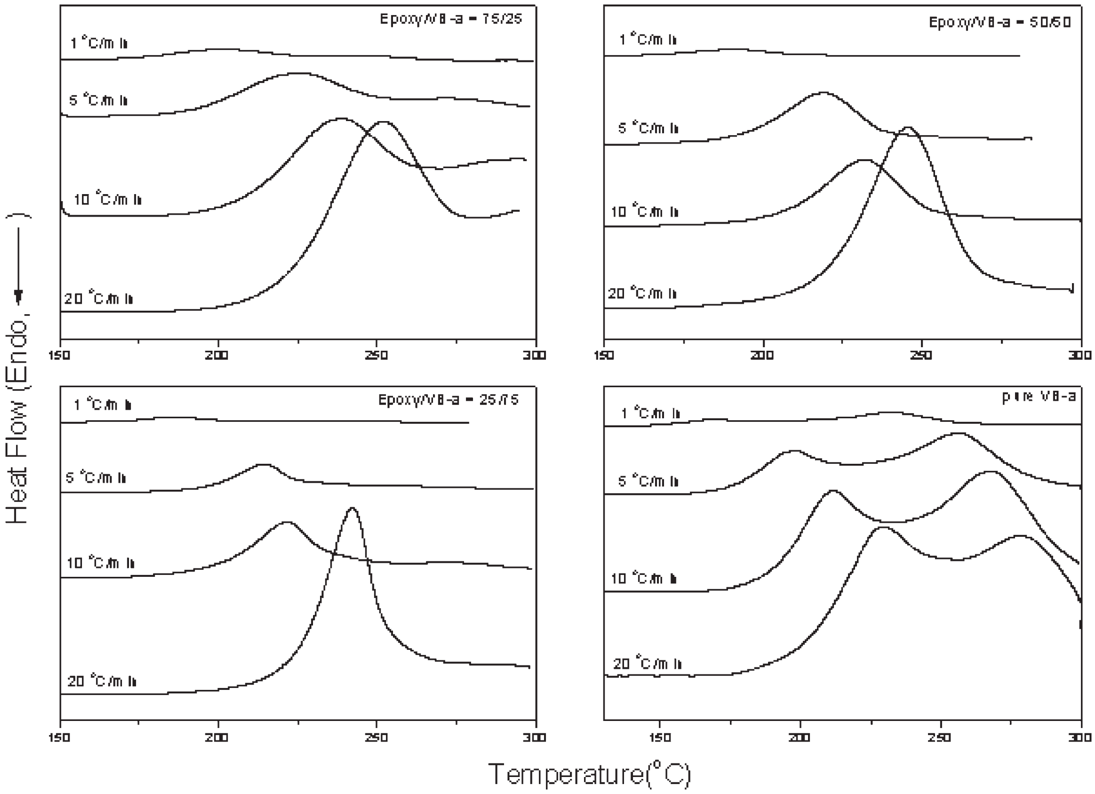


Figure 1 Dynamic DSC exothermic curves at different scan rates for epoxy/VB-a copolymers of various weight ratios.

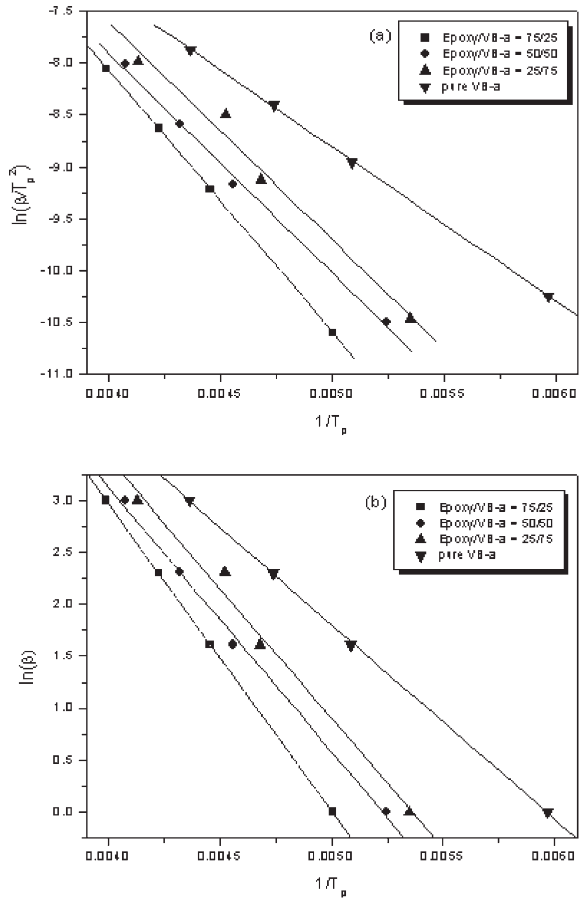


Figure 2 Plots for the determination of the activation energy of the curing reaction by the (a) Kissinger and (b) Flynn–Wall–Ozawa methods.

predict the curing behavior and assist in process design and control but also can be used to predict the aging and degradation of thermosetting polymer systems. The model can further be used to compare the curing behavior of different systems or formulations with different matrices, catalysts, fillers, and additives. Nonisothermal analysis can include the single-heating-rate method and the multiple-heating-rate method. The single-heating method measures the curing process on the basis of only a single constant rate cycle suitable for the *n*th-order reaction. Furthermore, these multiple heating rate methods are applicable for both *n*th-order and autocatalytic reactions. Two such multiple-heating-rate methods were proposed by Kissinger[33] and Flynn–Wall–Ozawa.[34] These two methods were used in this study instead of other nonisothermal methods because they did not require prior knowledge of the reaction mechanism to quantify the kinetic parameters.

According to the Kissinger method, the activation energy is obtained from the maximum reaction rate, where $d(d\alpha/dt)/dt$ is zero under conditions of a constant heating rate (β). The resulting relation can be expressed as

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT} \tag{1}$$

where T_p is the temperature at which the rate is maximized; A is the Arrhenius preexponential factor (or frequency factor); E_a is the energy of activation; R is the universal gas constant and T is the absolute temperature. Therefore, a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ gives the activation energy without the need to make any assumptions about the conversion-dependent function.

Flynn, Wall, and Ozawa developed an alternative method to calculate the activation energy on the basis of the following equation:

$$E_a = \frac{-R\Delta \ln \beta}{1.052\Delta(1/T_p)} \tag{2}$$

With this equation, a more accurate value of the activation energy can be obtained by iteration or least-squares techniques to improve the linear approximation of the temperature integration term. Both the Kissinger and Flynn–Wall–Ozawa methods assume that the DSC peak exotherm is an isoconversion and that its value is independent of the heating rate. By applying the Flynn–Wall–Ozawa and Kissinger methods to the observed maximum reaction rate (i.e., the peak of the DSC thermogram), we determined the activation energy from the slope of the line presented in Figure 2. The calculated activation energies for the curing of the epoxy/VB-a system are summarized in Table I according to the Kissinger and Flynn–Wall–Ozawa methods. Clearly, the

TABLE I
Thermal Properties and Activation Energy of the Epoxy/VB-a Copolymers

Sample	T_g	Thermal degradation temperature (T_d)	Char yield (wt %)	E_a (kJ/g) Flynn–Wall–Ozawa method	E_a (kJ/g) Kissinger method
75/25 epoxy/VB-a	171.9	374.6	16.7	25.94	20.88
50/50 epoxy/VB-a	204.2	367.1	21.0	20.01	17.56
25/75 epoxy/VB-a	279.9	376.1	23.1	19.97	17.39
Pure VB-a	323.5	390.7	26.0	14.64	12.32

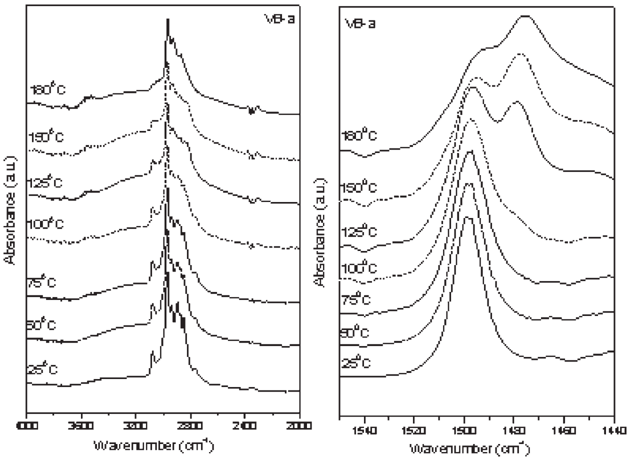


Figure 3 IR spectra of pure VB-a after each curing stage at (a) 4000–2000 and (b) 1600–1440 cm^{-1}.

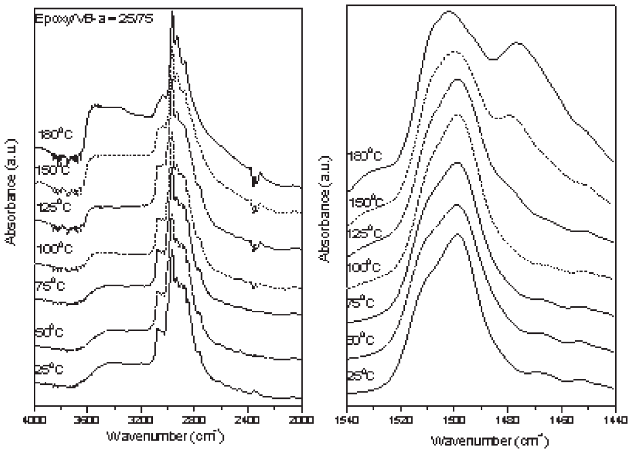


Figure 4 IR spectra of 25/75 (w/w) epoxy/VB-a after each curing stage at (a) 4000–2000 and (b) 1600–1440 cm^{-1}.

activation energy of the epoxy/VB-a copolymer system decreased with increasing VB-a content; this was reasonable because the phenol group resulting from the ring opening of VB-a could act as a curing agent for the epoxy ring, and the value of activation energy was smaller than that of a typical epoxy/phenol system.[35]

Curing process

To make clear which reaction was occurring at each exotherm in the DSC analyses, we characterized the curing process of the epoxy/VB-a copolymer systems by FTIR spectroscopy at different temperatures. Figure 3 shows the IR spectra after each curing cycle of pure VB-a; clearly, the characteristic absorption band assigned to the unsaturations of the allyl group, that is, 3080 cm^{-1}, was found to disappear at 180°C. In addition, a new band for the tetrasubstituted aromatic ring of the polymerized VB-a appeared at 1480 cm^{-1}, with a corresponding decrease in the intensity of the band representing the trisubstituted aromatic ring of VB-a (1498 cm^{-1}). For 25/75 epoxy/VB-a, the IR spectra (Fig. 4) was similar to pure VB-a, with the disappearance of the absorptions attributed to benzoxazine ring; however, the characteristic absorption band assigned to the unsaturations of the allyl group, that is, 3080 cm^{-1}, was found to disappear at a much earlier state of curing. This confirmed that the allyl group reacted first; this was followed by the ring-opening polymerization. Figure 5 shows the uncured epoxy, uncured VB-a, and epoxy/VB-a copolymers after the curing reaction. Both the absorptions at 1498 and 943 cm^{-1} were assigned to the trisubstituted benzene ring in the benzoxazine structure in Figure 5(a), and the absorption at 914 cm^{-1} was assigned to the epoxy group in Figure 5(f). From Figure 5(c) to Figure 5(e), the epoxy peak at 914 cm^{-1} totally disappeared, and the broad band absorption at about 3350 cm^{-1} was assigned to the secondary hydroxyl by the ring-opening reaction of epoxy groups, amine groups from the curing agent of VB-a, and a very small amount of phenolic groups after the curing reaction. The curing reaction mechanism is also summarized in Scheme 1.

Dynamic mechanical analysis and thermogravimetric analysis (TGA)

We examined the viscoelastic properties of the epoxy/VB-a copolymers. Figures 6 and 7 indicate the temperature dependence exhibited by the storage modulus and loss tangent (tan δ) of the epoxy/VB-a copolymers. The characterizations of these copolymers and a reference epoxy resin (DGEBA/D230, where D230 is Jeffamine with a molecular weight of 230) are summarized in Table I. In the case of the typical epoxy resin (DGEBA/D230), the glass transitions appeared at 84°C, as determined from the

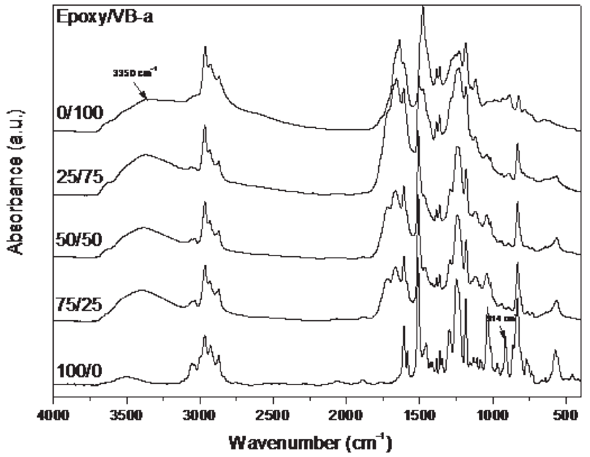


Figure 5 IR spectra of the pure epoxy before curing and epoxy/VB-a copolymers of various weight ratios after curing.

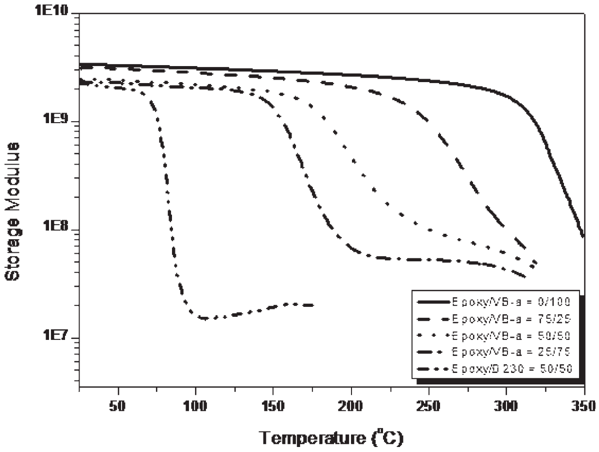


Figure 6 Storage moduli for epoxy/VB-a copolymers of various weight ratios and epoxy/D230.

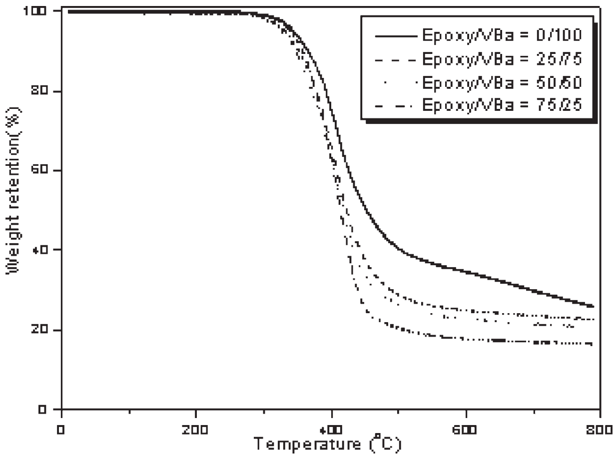


Figure 8 TGA of the epoxy/VB-a copolymer.

maxima of the loss tangent; for pure poly(vinyl-terminated benzoxazine) (poly(VB-a)), the corresponding values of T_g shifted to as high as 323.5°C. The storage modulus and T_g increased with increasing VB-a content in the epoxy/VB-a copolymer system. In a previous copolymer network system [epoxy/2,2-bis(3,4-dihydro-3)-phenyl-1,3-benzoxazine)propane (Ba) = 50/50],[36] the T_g behavior was around 150–160°C. In our study, epoxy/VB-a = 50/50 showed a significantly higher T_g, at about 204.2°C; the introduction of the allyl group as a crosslinking site into polybenzoxazines improved the rigidity of the polymer and increased the crosslinking density (the rubbery plateau modulus increased with increasing VB-a content). The storage modulus significantly improved and remained constant up to temperatures compared to the systems of epoxy/Ba and epoxy/D230. However, the T_g of the epoxy/VB-a copolymer was lower than that of the pure poly(VB-a) system.[27]

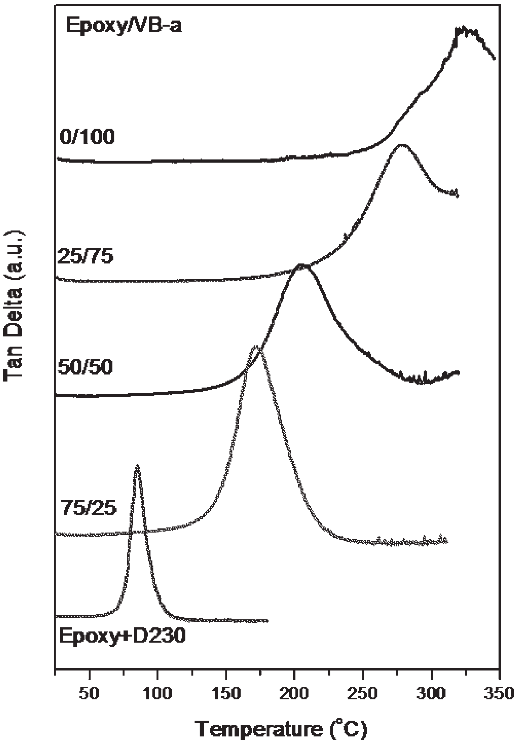


Figure 7 Tan δ for epoxy/VB-a copolymers of various weight ratios and epoxy/D230.

TGAs of the samples were conducted in a nitrogen atmosphere, as shown in Figure 8, and the values of various decomposition temperatures (20 wt % loss) and char yields are summarized in Table I. In general, the decomposition temperature and char yield increased with increasing VB-a content in the epoxy/VB-a copolymers. The introduction of allyl groups increased the crosslinking site of the benzoxazine monomer into the epoxy resin, which increased the thermal stability in this case.

CONCLUSIONS

We synthesized and characterized a novel benzoxazine monomer (VB-a) featuring terminal vinyl groups. We successfully designed a copolymer network system with three reactive groups, including an epoxy ring, benzoxazine ring, and allyl double bond. A series of homogeneous epoxy/VB-a copolymers networks were prepared by thermal curing. DSC analysis showed that the activation energies of epoxy/VB-a decreased with increasing VB-a content, as demonstrated by the Kissinger and Flynn–Wall–Ozawa methods. FTIR spectra indicated that, after curing, hydrogen bonds existed between the epoxy/VB-a copolymers, and the ring-opening and allyl polymerizations occurred. Dynamic mechanical analysis and TGA indicated that the thermal properties improved in the epoxy resin with increasing VB-a content in the epoxy/VB-a copolymers.

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