Synthesis and Characterization of a Vinyl-Terminated Benzoxazine Monomer and Its Blends with Poly(ethylene oxide)

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ABSTRACT: A vinyl-terminated benzoxazine (VB-a), which could be polymerized through ring-opening polymerization, was synthesized through the Mannich condensation of bisphenol A, formaldehyde, and allylamine. This VB-a monomer was then subjected to blending with poly(ethylene oxide) (PEO), followed by thermal curing, to form poly(VB-a)/PEO blends. The specific interactions, miscibility, morphology, and thermal properties of these blends were investigated with Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry, dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM). Before curing, we found that PEO was miscible with VB-a, as evidenced by the existence of a single composition-dependent glass transition temperature (T_g) for each composition. The FTIR spectra revealed the presence of hydrogen-bonding interactions between the hydroxyl groups of poly(VB-a) and the ether groups of PEO. Indeed, the ring-opening reaction and subsequent polymerization of the benzoxazine were facilitated significantly by the presence of PEO. After curing, DMA results indicated that the 50/50 poly(VB-a)/PEO blend exhibited two values of T_g: one broad peak appeared in the lower temperature region, whereas the other (at ca. 327 °C, in the higher temperature region) was higher than that of pristine poly(VB-a) (301 °C). The presence of two glass transitions in the blend suggested that this blend system was only partially miscible. Moreover, SEM micrographs indicated that the poly(VB-a)/PEO blends were heterogeneous. The volume fraction of PEO in the blends had a strong effect on the morphology. © 2007 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 45: 644–653, 2007

Keywords: hydrogen bonding; polybenzoxazine; poly(ethylene oxide); polymer blends

INTRODUCTION

Polymeric materials play vital roles in the electronics industry because of such factors as their ease of processing, low cost, low dielectric constants, and strong adhesive properties. Moreover,

many of the properties of polymers can be altered quite readily when they are processed into polymer blends and composites. Polybenzoxazines are novel thermosetting polymers that possess many physical properties that are superior to those of traditional polymers, such as epoxy and phenolic resins. Polybenzoxazines can be prepared by the Mannich condensation of phenol, formaldehyde, and primary amines.[1] In addition, polybenzoxazines can be cured without the need of a strong

acid or base as a catalyst under conditions that do not produce toxic gases and other byproducts. Poly-benzoxazines have many outstanding performance features, such as low flammability, high thermal stability, low surface free energy, and low dielectric properties.[2,3] The glass transition temperature (T_g) of a typical polybenzoxazine—one prepared from a monomer having a difunctional oxazine ring (B-a), is 180 °C, with a degradation temperature of about 310 °C.[4] In an effort to further improve the thermal stability of polybenzoxazines, polymerizable acetylene side groups have been introduced into the benzoxazine monomer.[5,6] The acetylene-functionalized benzoxazines can be polymerized into three-dimensional network products having high thermooxidative stability and resistance to both solvents and moisture. The acetylene-functionalized benzoxazines can be polymerized at temperatures within the range of 190–220 °C, and the products have a char yield above 50% at 800 °C under nitrogen. Another approach toward improving the properties of polybenzoxazines is to blend them with other polymers, such as poly(imide siloxane), polyurethane, and poly(caprolactone) (PCL), or to incorporate clay into the polybenzoxazine matrix.[7–9] Recently, Agag and Takeichi[10] reported that the incorporation of allyl groups into benzoxazine monomers resulted in polybenzoxazines having high crosslinking densities and high T_g values. Encouraged by this result, for this study, we used allylamine as a raw material for the preparation of vinyl-terminated benzoxazines. We expected that the vinyl unit would serve as another polymerizable group and result in high-performance polybenzoxazines. Furthermore, we blended the vinyl-based benzoxazine with poly(ethylene oxide) (PEO) to prepare polybenzoxazine/PEO blends. It is interesting that the resulting blends exhibited higher T_g values than the virgin polybenzoxazine. PEO is miscible with many polymers, such as poly(4-vinylphenol),[11] phenoxy,[12] and epoxy,[13–15] because the ether groups of PEO form intermolecular hydrogen bonds with their hydroxyl groups. Because polybenzoxazine contains many hydroxyl groups on its main chain after thermal curing, we anticipated that polybenzoxazine might be miscible with PEO as a result of such intermolecular hydrogen bonding. Because the physical properties of polymer blends are influenced strongly by the blending conditions and processes that, in turn, affect the level of mixing of the blends, there is growing interest in studying the miscibility and phase behavior of polymer blends. Various techniques have been employed to investigate the miscibility of polymer blends, including microscopy, thermal analysis, dynamic mechanical analysis (DMA), dielectric measurements, and spectroscopy.[16–19] Although there is growing interest in synthesizing and studying the properties of polybenzoxazines, little attention has been paid so far to the preparation of polybenzoxazine/thermoplastic polymer blends. Ishida and Lee[9,20,21] studied polymer blends of polybenzoxazine (B-a type) and poly(ε-caprolactone) and found evidence from Fourier transform infrared (FTIR) spectra for hydrogen-bond formation between the hydroxyl groups of polybenzoxazine and the carbonyl groups of poly(ε-caprolactone). In addition, Lu and Zheng[22] studied polymer blends of polybenzoxazine (B-a type) and PEO. Therefore, in this investigation, we synthesized a benzoxazine monomer presenting a vinyl group, blended it with PEO, and then thermally cured the benzoxazine monomer to produce polybenzoxazine/PEO blends. Because of its incorporated polymerizable vinyl groups, the vinyl-based polybenzoxazine possessed a T_g (300 °C) higher than those of traditional polybenzoxazines. We used differential scanning calorimetry (DSC), DMA, and FTIR spectroscopy to explore the miscibility, specific interactions, and thermal behaviors of the blends, and scanning electron microscopy (SEM) to determine the morphology of the blends.

EXPERIMENTAL

Materials

An aqueous formaldehyde solution (37%), allylamine, bisphenol A, and PEO ($M_n = 10,000$) were purchased from Aldrich Chemical Co. The benzoxazine monomer, B-a, was purchased from Shikoku Chemicals Co. (Japan). To prepare the polybenzoxazine/PEO blends, we synthesized a vinyl-terminated version of the benzoxazine monomer (VB-a). The presence of the vinyl group allowed ring-opening polymerization to be conducted under moderate conditions. The benzoxazine monomer 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 to the mixture, which was cooled in an ice bath. After an additional 30 min of stirring, the temperature of the mixture was raised gradually to 80 °C, and then it was heated under reflux for 3 h. The solvent and water were evaporated *in vacuo*, and the residue was
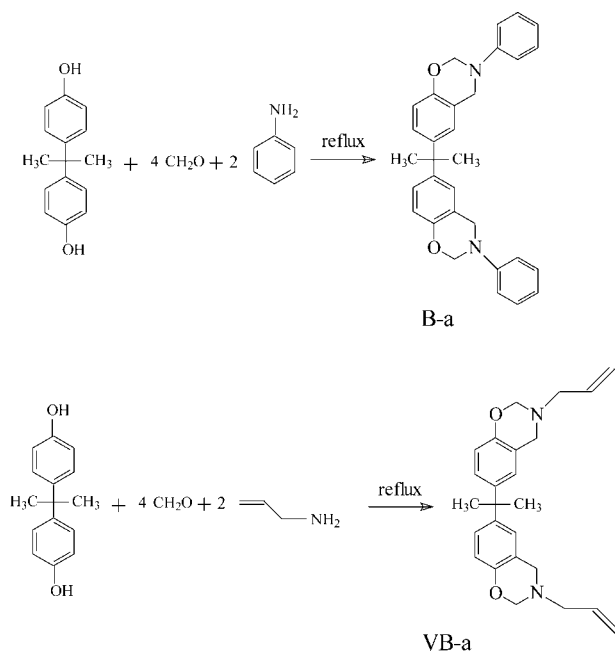
Scheme 1. Preparation of benzoxazine monomers B-a and VB-a.

dissolved in ethyl ether (100 mL). The solution was washed several times with water and 2 N aqueous NaOH to remove any impurities and unreacted monomers. The ether solution was then dried (sodium sulfate), and the solvent was evaporated at room temperature. The product was obtained as a light yellow solid (23.5 g).

Preparation of VB-a-Type Polybenzoxazine and PEO Blends

VB-a/PEO blends of several different compositions were prepared via solution blending in dichloromethane (10 mL). The mixture was stirred for 8 h at room temperature before being poured onto an aluminum plate, dried for 6 h in the open air, placed in an oven, and then heated *in vacuo* at 50 °C for 2 h. The cast film was polymerized in a stepwise manner: 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

Proton Nuclear Magnetic Resonance (¹H NMR) Spectroscopy

¹H NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300 MHz with CDCl₃ as the solvent. The relaxation time used in this study was 2 s. Chemical shifts are reported in parts per million.

FTIR Spectroscopy

Infrared spectroscopy measurements were recorded on a PerkinElmer Spectra One infrared spectrometer; 32 scans were collected with a spectral resolution of 1 cm⁻¹. Infrared spectra of polymer blend films were recorded from samples prepared with conventional NaCl disk methods. Thus, the dichloromethane solution containing the blend was cast onto a NaCl disk, which was dried under conditions similar to those used for the bulk preparation. The films obtained in this way were sufficiently thin to obey the Beer–Lambert law.

DSC

The thermal properties of VB-a, PEO, and their blends were determined with a PerkinElmer DSC-7 differential scanning calorimeter under a nitrogen atmosphere. The samples (ca. 5 mg) were placed in a DSC pan, first heated from 25 to 100 °C at a rate of 10 °C/min (first heating scan), and then maintained at that temperature for 5 min. The samples were then quenched by being placed in a liquid nitrogen bath. The second scan was recorded upon reheating from −90 °C at the same heating rate (10 °C/min). The midpoint of the slope change of the heat capacity of the second heating scan was taken to be T_g. The melting temperature (T_m) was taken to be the maximum of the endothermic peak.

DMA

DMA measurements were performed with a TA Instruments DMA Q800 (DuPont) instrument operated in a single cantilever bending mode over a temperature range of −100 to 350 °C. Data acquisition and analysis of the storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were recorded automatically by the system. The heating rate and frequency were fixed at 2 °C/min and 1 Hz, respectively. Samples for DMA experiments were prepared via molding; the sample dimensions were $3 \times 0.8 \times 0.2$ cm.

Morphological Observations

The samples of the poly(VB-a)/PEO blends were fractured cryogenically with liquid nitrogen. The fractured surfaces were immersed in chloroform
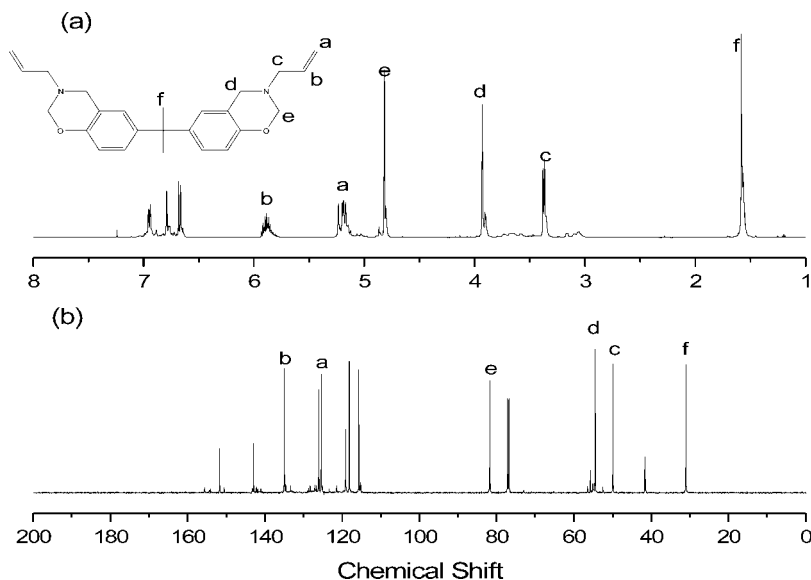
Figure 1. (a) ^{1}H and (b) ^{13}C NMR spectra of VB-a.

at room temperature for 20 min. The morphologies of the cryogenically fractured surfaces of the specimens were examined with a Hitachi (Japan) S-570 scanning electron microscope. The fractured surfaces of the samples were coated with thin layers of gold (ca. 100 Å).

RESULTS AND DISCUSSION

Characterization of VB-a

Figure 1 displays the ^{1}H and ^{13}C NMR spectrum of VB-a. In the ^{1}H NMR spectrum, the vinyl group appears as two resonances, at 5.21 and 5.88 ppm, whose intensities have a 2:1 ratio. We assign the peaks at 3.9 and 4.8 ppm to protons in the methylene bridge of the oxazine. The signal of the protons located between the vinyl group and the nitrogen atom appears at 3.37 ppm. The peaks at 1.57 and 6.66–6.96 ppm are attributed to the C(CH$_3$)$_2$ and aromatic protons, respectively. The ^{13}C NMR spectrum of VB-a is presented in Figure 1(b). The signals of the carbon atoms of the terminal olefin unit appear at 116 and 138 ppm. We assign the characteristic signals at 52 and 82 ppm to the carbon atoms of the oxazine ring. These NMR spectra confirm that we successfully synthesized VB-a. The FTIR spectrum of the difunctional benzoxazine compound VB-a has been reported previously.[10,23] Figure 2 displays infrared spectra of the B-a and VB-a benzoxazine monomers. We can observe the characteristic absorptions of the benzoxazine at 1230

(asymmetric stretching of C—O—C units) and 1498 cm^{-1} (attributable to the 1,2,4-trisubstituted benzene ring). The characteristic absorption bands of the allyl group appear at 3075 (stretching of =C—H bonds) and 1644 cm^{-1} (stretching of C=C bonds). All results are indicative of the presence of vinyl-terminated benzoxazine groups.

Miscibility of the Uncured VB-a/PEO Blends

DSC is used extensively to investigate the miscibility of polymer blends. A single composition-dependent glass transition is an indication of full miscibility at a dimensional scale between 20 and
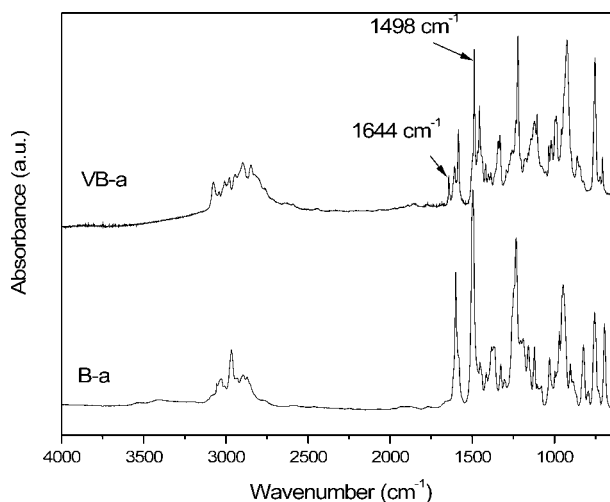

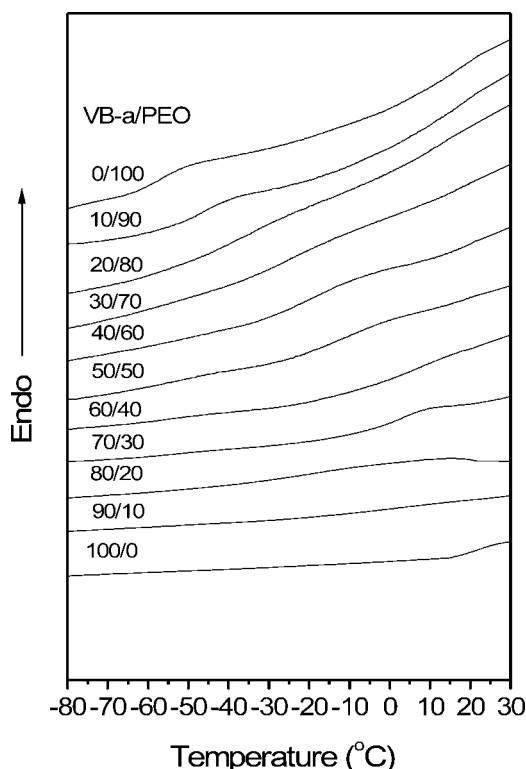**Figure 2.** FTIR spectra, recorded at room temperature, of B-a and VB-a.

Figure 3. DSC thermograms, recorded within the temperature range of −80 to 20 °C, of PEO, VB-a, and their blends.

40 nm.[24,25] Figure 3 displays the DSC thermograms for quenched VB-a, PEO, and VB-a/PEO blends recorded at a heating rate of 10 °C/min; Table 1 summarizes the data. We observed essentially only one value of T_g for each composition, with the value of T_g for PEO being −58.5 °C. The value of T_g rose monotonically with increasing VB-a content in the blends, suggesting full misci-

Table 1. Thermal Properties of the VB-a/PEO Blends

VB-a/PEO	T_g (°C)	T_m (°C)	ΔH_f (J/g)[a]
0/100	−58.5	65.3	199.4
10/90	−48.2	64.0	185.3
20/80	−39.6	62.3	176.5
30/70	−27.4	61.1	168.4
40/60	−21.2	59.7	162.7
50/50	−12.4	58.3	156.2
60/40	−3.1	57.8	123.8
70/30	−0.9	54.7	115.4
80/20	—	52.3	90.5
90/10	—	—	18.2

[a] The heat of fusion is based on the weight fraction of PEO present in the blend.

bility of these blends. Furthermore, T_m of the blend decreased with increasing VB-a content in the blends, as indicated in Figure 4. The 80/20 VB-a/PEO blend exhibited a cold crystallization temperature before T_m (as indicated by the arrow). This result implies that the presence of a higher VB-a content retards PEO crystallization from the glassy state; this phenomenon is normally expected for a miscible polymer pair. We observed no trace of a melting endotherm for the blend containing 90% VB-a. This result is similar to the situation observed in our previous study of poly(butylene-2,6-naphthalate) (PBN) and poly(ether imide) (PEI) blends.[17]

Curing and Polymerization of the VB-a/PEO Blends

Figure 5 displays FTIR spectra of 80/20 VB-a/PEO blends cured at 180 °C for different curing times. The significant decreases in the intensity of the bands at 926 and 1232 cm^{-1}, which is the band indicating the presence of the benzoxazine ring,[23] imply that ring-opening reactions occurred. This result was confirmed by the appearance of new bands within the range of 3100–3600 cm^{-1},
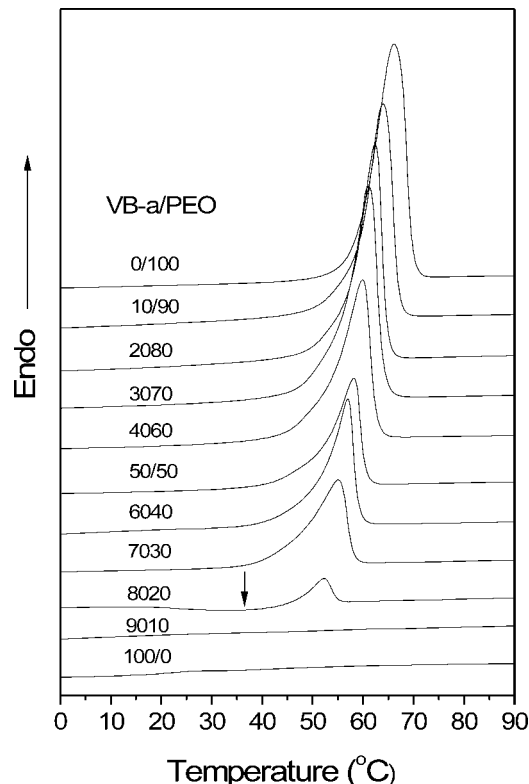

Figure 4. DSC thermograms, recorded during the second heating scan, of PEO, VB-a, and their blends.
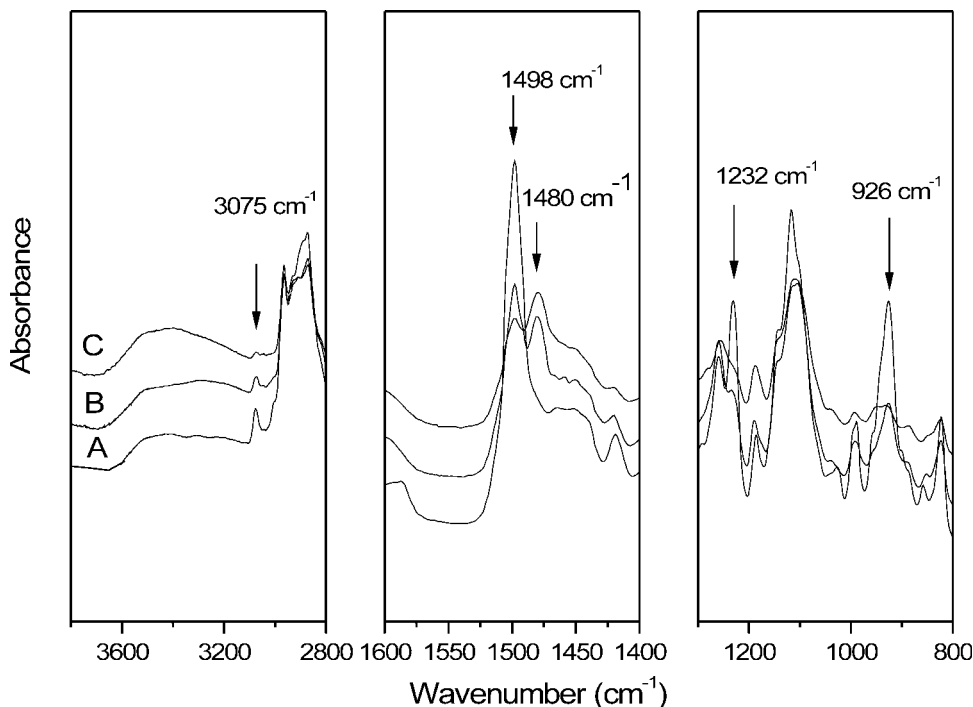
Figure 5. FTIR spectra of 80/20 VB-a/PEO blends that had been cured at 180 °C for different lengths of time: (A) 0, (B) 20, and (C) 120 min.

which we assign to the hydrogen-bonded hydroxyl units of the opened oxazine ring species. The degree of polymerization of the vinyl groups in the VB-a monomer can be followed by the monitoring of the changes in the intensity of the band at 3075 cm^{-1}, which is associated with C—H stretching of the vinyl group. In addition, a new band for the tetrasubstituted aromatic ring of the polymerized VB-a appears 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}).

Hydrogen Bonding between Poly(VB-a) and PEO

FTIR spectroscopy is a powerful tool for investigating specific intermolecular interactions. It is known that intermolecular hydrogen bonding plays a dominant role in determining the miscibility of polymers containing ether and hydroxyl groups.[26] Figure 6 displays infrared spectra of VB-a and VB-a/PEO blends (containing 20, 40, or 60 wt % PEO) that were cured isothermally at 180 °C for 120 min. In the region of 1600–1400 cm^{-1}, the intensity of the band at 1480 cm^{-1}, with respect to that at 1498 cm^{-1}, was higher when a higher PEO content was present in the blend. This phenomenon implies that the ring-opening

and subsequent polymerization reactions were facilitated by the presence of PEO as a modifier. In the region associated with hydroxyl group stretching (4000–2350 cm^{-1}), four different kinds of hydrogen-bonding interaction were involved: the O$^-$—H$^+$N intramolecular hydrogen bonding at about 2750 cm^{-1}, the OH—N intramolecular hydrogen bonding at about 3200 cm^{-1}, the OH—O intermolecular hydrogen bonding at about 3400 cm^{-1}, and the OH—π intramolecular hydrogen bonding at about 3550 cm^{-1}, which have been discussed in
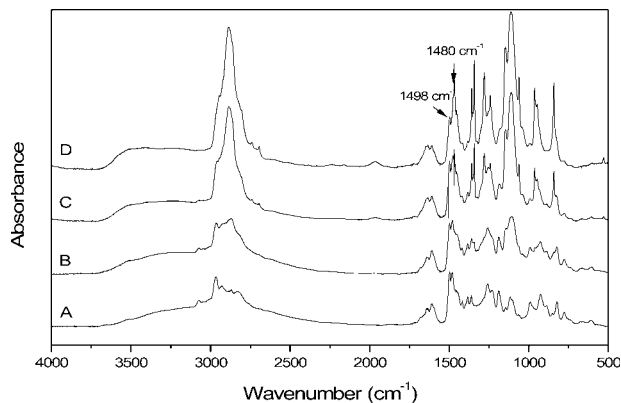

Figure 6. FTIR spectra of VB-a and VB-a/PEO blends that had been cured at 180 °C for 120 min. The PEO contents were (A) 0, (B) 20, (C) 40, and (D) 60 wt %.
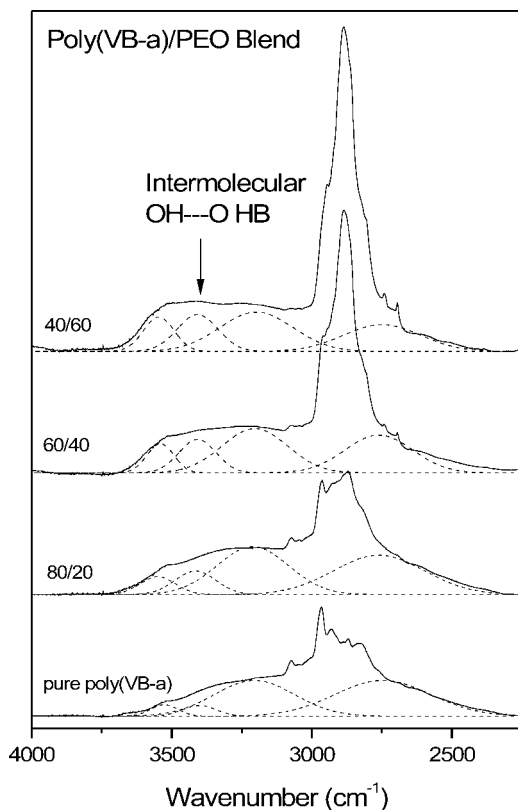
Figure 7. Curve-fitting results in FTIR spectra at the hydroxyl stretching region of poly(VB-a)/PEO blends.

a previous study.[27] Figure 7 shows their corresponding curve-fitting results with various poly(VB-a)/PEO blends, indicating that the fraction of intramolecular hydrogen bonding decreases significantly at about 2750 and 3200 cm^{-1}, whereas the OH—O intermolecular hydrogen bonding at about 3400 cm^{-1} increases with the increase in the PEO content. The increase in the intermolecular hydrogen bonding comes from the interaction between the hydroxyl group of poly(VB-a) and the ether group of PEO. In conclusion, the result indicates that the hydrogen-bonding interaction is from the intramolecular hydrogen bonding (OH—N) to the intermolecular hydrogen bonding (OH—O) between poly(VB-a) and PEO with the increase in the PEO content, which enhances the miscibility behavior in the poly(VB-a)/PEO blend system.

DMA

We examined the viscoelastic properties of the vinyl polybenzoxazine poly(VB-a) along with those of the typical polybenzoxazine poly(B-a). Figure 8
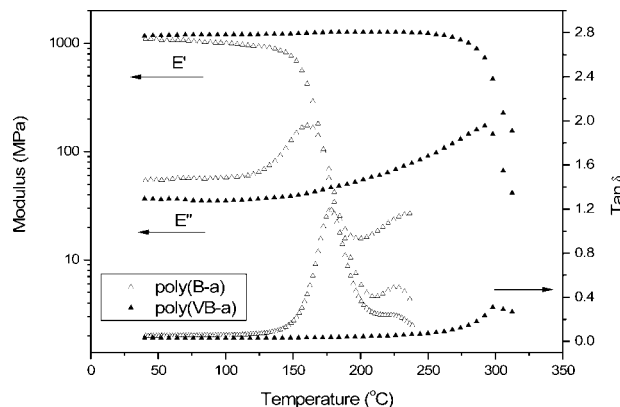

Figure 8. E', E'', and tan δ of poly(B-a) and poly(VB-a).

indicates the temperature dependence exhibited by E', E'', and tan δ of the polybenzoxazines. In the case of the typical polybenzoxazine [poly(B-a)], the glass transitions appeared to occur at 160 °C, as determined from the maxima of E''; for poly-(VB-a), the corresponding values of T_g shifted to as high as 294 °C as a result of the introduction of the vinyl groups. Thus, these analyses of the viscoelastic properties reveal that a significant increase in T_g (ca. 134 °C) occurred for the vinyl polybenzoxazine, indicating the crosslinking density that was afforded by the introduction of the vinyl groups as additional crosslinkable units. Agag and Takeichi[10] reported a similar finding. Figure 9 displays E' and E'' of pure PEO and 20/80 and 40/60 poly(VB-a)/PEO blends recorded over the temperature range of −80 to 80 °C. From a comparison of the E' values of PEO and its blends, it is clear that those of the latter were higher than that of pure PEO. As indicated in Figure 9, the maximum of E'' of PEO, corresponding to its T_g, was −56 °C. From the E'' curves, we can clearly observe a
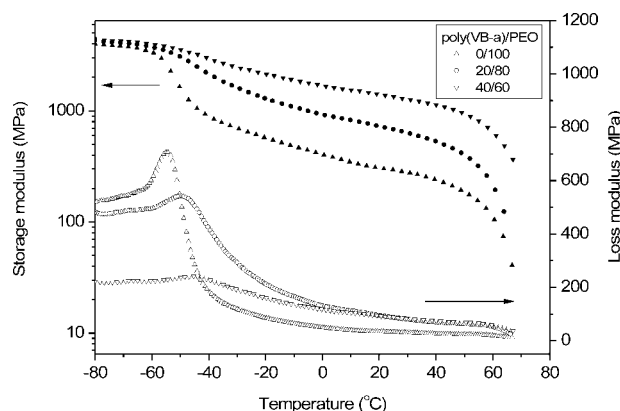

Figure 9. E' and E'' of PEO and 20/80 and 40/60 poly(VB-a)/PEO blends.
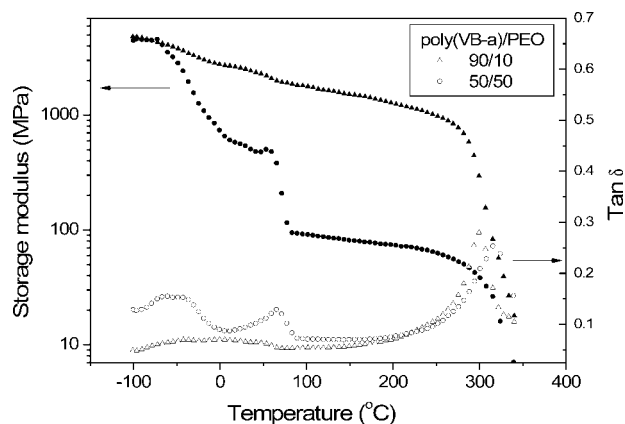
Figure 10. E' and tan δ of 50/50 and 90/10 poly(VB-a)/PEO blends.

decreased peak intensity accompanying an upshift of the temperature positions after the addition of poly(VB-a). A peak shift in the dynamic properties of a blend results primarily from strong interactions between its components. Because the hydroxyl groups of poly(VB-a) are involved in intermolecular hydrogen bonding, the α-relaxation process of the PEO blends will be hindered to

some extent, and thus it will require a higher temperature to become activated. Figure 10 displays E' and tan δ for the 90/10 and 50/50 poly(VB-a)/PEO blends. In the tan δ curve of the 50/50 poly(VB-a)/PEO blend, the peak centered at 60 °C is due to the melting of PEO (see also Fig. 4). Furthermore, the 50/50 poly(VB-a)/PEO blend exhibits two values of tan δ: one broad peak appears in the lower temperature region, which we attribute to the α relaxation of the PEO, and the other, in the higher temperature region (at ca. 327 °C), represents the α relaxation of the poly(VB-a); this latter value is higher than that of pristine poly(VB-a) (301 °C). The result is different with polybenzoxazine blending with PCL: the α relaxation of poly(B-a) is reduced with the increase in the PCL content.[9] The presence of two values of tan δ for this blend suggests that it is immiscible. In addition, in Figure 10, we can observe a slight depression of the peak intensity with increasing PEO content. Because the damping property is provided by the ratio of the viscous and elastic components, we surmise that the reduced peak height is associated with lower segmental mobility and fewer relaxation species, and thus it is indicative of stronger
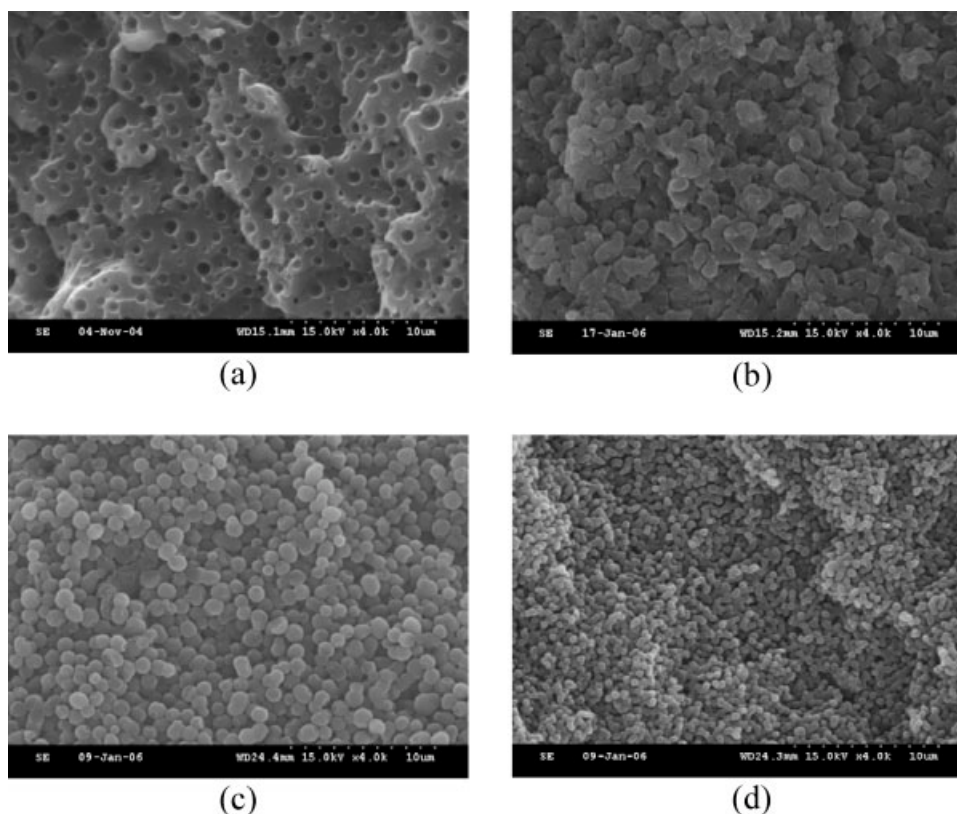

Figure 11. SEM micrographs of (a) 90/10, (b) 80/20, (c) 70/30, and (d) 60/40 poly(VB-a)/PEO blends.

hydrogen bonding for the 50/50 poly(VB-a)/PEO blend. Moreover, the peak width at half-height increases with increasing PEO content, and this is a result of decreasing network homogeneity.[28] After PEO is added to poly(VB-a), the temperature distribution at which the different mobile network segments become activated is increased.

Morphology of the Poly(VB-a)/PEO Blends

We investigated the morphology of the poly(VB-a)/PEO blends with SEM. Figure 11 displays SEM micrographs of the chloroform-etched fracture surfaces of the blends. We observed heterogeneous morphologies for each of the blends investigated, which correspond well to the results that we obtained through DMA; that is, the blends were phase-separated. For the 90/10 poly(VB-a)/PEO blend, after the rinsing of the PEO phase, we observed that PEO had been dispersed uniformly in the continuous matrix, with cavity diameters of about 0.5–1.5 μm [Fig. 11(a)]. With increasing PEO content, the blends displayed remarkably different morphologies [Fig. 11(b–d)]. For the 80/20 poly(VB-a)/PEO blend [Fig. 11(b)], we found that the PEO domains began to interconnect and that they exhibited irregular shapes. Because the PEO phase had been dissolved in chloroform, the spherical particles, having a broad size distribution, were composed of the poly(VB-a) component. It is clear that phase inversion had begun to appear; indeed, we observed totally phase-inverted morphologies for blends having PEO contents above 20 wt %. The average size of the spherical particles decreased with increasing PEO content in the blends, as indicated in Figure 11(c,d). These results are similar to those of the poly(B-a)/PCL blend system.[29] The connected-globule structures visible in our SEM images imply the presence of a two-phase morphology of interconnected spherical domains of a poly(VB-a)-rich phase dispersed regularly in a matrix of PEO. When the PEO volume fraction was further increased, the diameters of the poly(VB-a) particles became even smaller (average: 0.4 μm), and their shapes became more regularly spherical. The greater volume fractions of PEO probably cushioned the poly(VB-a) spheres from direct impingement. Similar observations have been described for some thermoplastic-modified epoxy systems,[22,30] for which the sizes of the epoxy particles decreased with an increasing concentration of the thermoplastic; this phenomenon was attributed to the deceleration of phase separation and coarsening that resulted from the inclusion of a high-viscosity thermoplastic.[31]

CONCLUSIONS

We synthesized and characterized a vinyl-terminated benzoxazine monomer (VB-a) featuring terminal vinyl groups. We prepared VB-a/PEO blends by the solution blending of this benzoxazine monomer and PEO, followed by thermal curing of the benzoxazine. DSC analysis indicated that a single T_g existed for the uncured blend and that its value increased with increasing content of VB-a. In addition, both T_m and the degree of crystallinity of the PEO component in the blend decreased with increasing VB-a content. The addition of PEO to the poly(VB-a) network greatly increased the hydrogen bonding and strongly influenced its thermal properties. FTIR spectra indicated that, after curing, hydrogen bonds existed between the ether groups of PEO and the hydroxyl groups of poly(VB-a). At relatively low volume fractions of PEO in the blends, a full-scale phase inversion was observed in the cured poly(VB-a)/PEO networks. With an increasing PEO volume fraction in the blends, the spheres not only became smaller in size but also became more regularly spherical in their geometry as a result of a lower degree of impingement. DMA indicated that T_g increased from 301 °C for the neat poly(VB-a) to 327 °C for the 50/50 poly(VB-a)/PEO blend as a result of the latter system's increased hydrogen bonding.

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