Infrared and Thermal Analyses of Polybenzoxazine and Polycarbonate Blends

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ABSTRACT: The thermal properties of physical blends containing benzoxazine monomer and polycarbonate (PC) were studied by nonisothermal differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR). The ring-opening reaction and subsequent polymerization reaction of the benzoxazine were inhibited significantly by the presence of polycarbonate. The glass-transition temperature of the resulting blends decreased as the concentration of polycarbonate increased and deviated markedly from the Fox equation. An earlier degradation event appeared in the blend with 11 and 33 wt % of PC. In addition, FTIR was used to study the extent of the polymerization reaction as well as the hydrogen-bonding behavior. Intermolecular hydrogen bonding between PC and cured polybenzoxazine appeared after 1 h of isothermal curing at 180°C and continued throughout the entire curing process. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1021–1034, 2001

Key words: benzoxazine; blend; Fox equation; hydrogen bonding; polycarbonate; polymerization; reaction; ring-opening

INTRODUCTION

The study of miscibility of polymer blends, in which one component is crystallizable and another is highly crosslinked, has received attention in recent years.[1] From a thermodynamic point of view, an increase in molecular weight of either component of a miscible blend would depress the critical temperature and accelerate the phase separation. Therefore, the occurrence of even partial miscibility in such polymer blends containing one component with an infinite molecular weight (i.e., highly crosslinked) is surprising and requires further comments.[1] Moreover, a crystallizable thermoplastic polymer is cured *in situ* with a thermosetting monomer; thus, how the crystallization and the polymerization are affected by the other component is of great interest and needs to be clarified.

A class of ring-opening phenolic resins, the polybenzoxazines, has shown an excellent balance of mechanical and physical properties along with unusual thermal and physical properties.[2,3] A rich molecular design flexibility has been fully demonstrated in our laboratory by modifying functionalities of the initial raw materials, especially phenolic and primary amine derivatives.[4–7] Earlier studies focused on various polybenzoxazine composite systems, to which inorganic fillers, such as glass fiber,[8] carbon fiber,[9] boron nitride,[10] or $CaCO_3$,[11] were added. As a result, high-performance materials were prepared. Although a few pioneering works reported on the organic mixed system of a benzoxazine resin and an epoxy resin,[12] no investigation has reported on polybenzoxazine/thermoplastic polymer blends.

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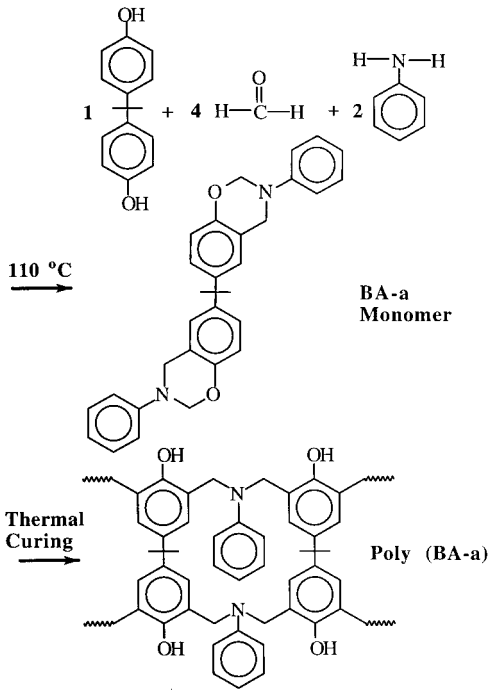
In addition, crosslinked systems tend to be brittle as is the case with polybenzoxazine. Thus, any chemical modification or additive to enhance toughness, with a minimum sacrifice of the original mechanical and physical properties of the polybenzoxazine, is attractive. Toughening may be achieved by mixing the resin with elastomers or even with ductile thermoplastics before curing. Although the fracture energy of resins can be increased by an order of magnitude through rubber cavitation and shear yielding in the matrix phase, tensile modulus and yield strength are sacrificed as a result of the addition of soft inclusions into a stiff matrix. Polycarbonate (PC) was chosen for this purpose because of its relatively high toughness and because this material has carbonyl groups that have the potential to intermolecularly hydrogen-bond with the polybenzoxazine main chain.

This work describes the results of a study on polybenzoxazine resin/PC blend and, in particular, how the degree of ring-opening polymerization is influenced by the second component and thermal properties of the resulting blends.



Scheme 1 Benzoxazine monomer (BA-a) and polymer [poly (BA-a)] nomenclature and structure used in this study.

EXPERIMENTAL

Materials

Bisphenol-A polycarbonate (PC), Lexan, was supplied by General Electric Company (Pittsfield, MA) with a weight-average molecular weight of 43,900 g/mol. Other chemicals for the synthesis of polybenzoxazine precursors, including bisphenol-A, paraformaldehyde, and aniline, were purchased from Aldrich Chemicals (Milwaukee, WI). All materials had purities greater than 99% and were used without further purification.

Synthesis of Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) Isopropane Monomer

The benzoxazine based on bisphenol-A and aniline, bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (abbreviated as BA-a), was synthesized through a Mannich reaction. A detailed procedure of the synthesis and purification is presented elsewhere.[1] The synthesis route and structure of BA-a prior to and after curing are displayed in **Scheme 1**.

Fourier Transform Infrared Spectroscopy (FTIR)

A Bomem Michelson MB 110 Fourier transform infrared spectrometer was used to study hydrogen bonding and curing kinetics. The infrared spectrometer was equipped with a narrow band pass mercury–cadmium–telluride (MCT) detector with a specific detectivity W^* of 1×10^{10} cm $Hz^{1/2}$ W^{-1}. Solution blending was used for the preparation of all the blend samples including unmodified benzoxazine monomers. First, the purified benzoxazine precursor and PC were dissolved separately and solution-blended to form a homogeneous mixture with the aid of chloroform. A thin film of the blend was cast onto a potassium bromide (KBr) plate from a 7–10 wt % solution and kept in a vacuum oven at 40°C for 72 h to remove the residual solvent. A transparent film was obtained at the end of this step. To prepare samples for FTIR study, the cast thin film was cured isothermally at 180°C, without any initiators or catalysts. All of the films used in this study were sufficiently thin to obey Beer–Lambert's law.[13] Spectra were a result of 100 coadded scans and a resolution of 4 cm^{-1} was used. To obtain more accurate quantitative results, a curve analysis program was used. This program was performed on a baseline-corrected spectrum to resolve heavily overlapped bands, using either a pure Gaussian or a mixed Lorentzian–Gaussian function. Calculations were continued until least-squares curve-fitting converged.

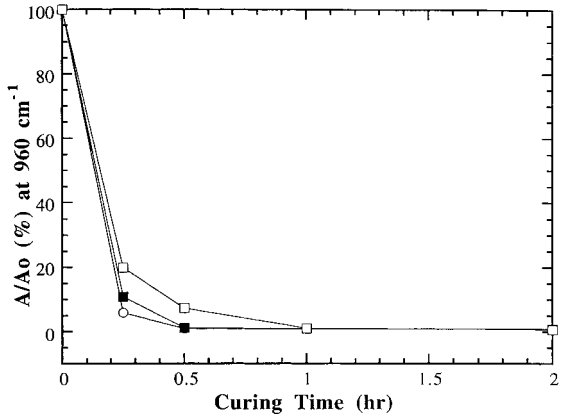


Figure 1 Normalized integrated intensity of oxazine ring mode at 960 cm^{-1}. Samples were cured isothermally at 180°C in air: (○) BA-a, (■) 11 wt % of the PC blend, and (□) 33 wt % of the PC blend.

Differential Scanning Calorimetry (DSC)

A 2920 Differential Scanning Calorimeter from TA Instruments was used to study the curing of the benzoxazine monomer/PC blends with nitrogen as the purge gas. Standard hermetic aluminum DSC pans were used and all sample weights were between 5 and 10 mg. Nonisothermal experiments were conducted at 10°C/min from room temperature to 300°C for the first scan to obtain a complete exothermic reaction peak. Samples were removed from the DSC cell immediately after the completion of the first run and quenched in liquid nitrogen to ensure the same thermal history. A second heating was conducted at the same heating rate to analyze the thermal properties of the cured polybenzoxazine and PC blends.

Thermogravimetric Analysis (TGA)

Thermal degradation was studied on a thermogravimetric analyzer (TGA 2950) from TA Instruments. Experiments were conducted at a heating rate of 20°C/min under a nitrogen environment with a flow rate of 90 mL/min.

RESULTS AND DISCUSSION

Quantitative Analysis of Ring-Opening Reaction

It is well known that the benzoxazine monomer will undergo a ring-opening polymerization upon heating,[4,5,14] with gelation taking place in a matter of minutes, depending on the curing temperature, which is usually between 160 and 200°C in the absence of initiators and catalysts. All the samples were cured in an air-circulated oven and FTIR was utilized to investigate the curing process. The ring-opening reaction can be monitored by the disappearance of the oxazine ring, which absorbs at 960 cm^{-1}.[7] The thickness of the sample in the IR beam will change as a result of the low viscosity of the monomer. Therefore, an internal thickness band is necessary for quantitative analysis. The carbon–hydrogen symmetric deformation at 1383 cm^{-1}, which is assigned to the methyl group of bisphenol-A, was chosen as the internal standard.[16]

The relative integrated intensity of the band at 960 cm^{-1} to the internal thickness band is a suitable index for the ring-opening reaction and is shown in Figure 1. The relative intensities are normalized in this figure. The oxazine ring of both neat benzoxazine monomer and PC blends decreased quickly at the beginning of heating. Almost 100% of the oxazine ring of pure BA-a opened after 0.5 h at 180°C, although this high degree of ring-opening does not necessarily mean a high degree of polymerization. No significant change was detected beyond 1 h, implying that the ring-opening reaction has saturated at this particular temperature (180°C). The extent of ring-opening reaction as a function of the PC modifier and curing time is summarized in Table I. The addition of the PC modifier has quite a different effect and its magnitude depends on the amount of the modifier. Three samples, that is, pure BA-a, the blend with 11 wt % of PC, and the blend with 33 wt % of PC, exhibited varying degrees of ring opening at 94.1, 89.1, and 80.1%, respectively, for the first 15 min of heating. However, over 99% of the oxazine rings had opened

Table I Normalized Integrated Intensity (A/A_0) (%) of Oxazine Ring Mode at 960 cm^{-1} Obtained from Curve-Resolved FTIR Spectra

Curing Time (h)	BA-a	11 wt % of PC	33 wt % of PC
0	100.0	100.0	100.0
0.25	5.9	10.9	19.9
0.5	0.9	1.2	7.3
1	0.8	0.9	1.0
2	0.7	0.8	0.5
3	0.7	0.6	0.2
4	0.7	0.6	0.2
5	0.7	0.6	0.2

Samples were cured isothermally at 180°C in air.

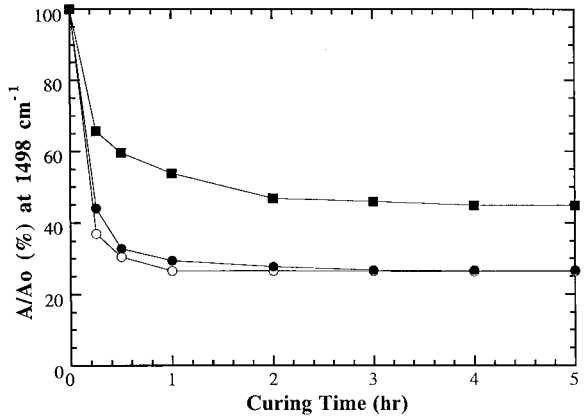


Figure 2 Normalized integrated intensity of trisubstituted benzene ring mode at 1498 cm^{-1}. Samples were cured isothermally at 180°C in air: (○) BA-a, (●) 11 wt % of the PC blend, and (■) 33 wt % of the PC blend.

after 5 h of heating in all samples. These results suggest that the presence of PC tends to postpone the ring-opening of the oxazine groups at the early stage of reaction, but reach similar extents of reaction after prolonged heating.

Quantitative Analysis of Polymerization

Prior to polymerization, both the benzoxazine ring and the opened Mannich base have trisubstituted benzene rings. Thus, the ring-opening reaction alone merely shifts the frequency of this mode and does not diminish the trisubstituted mode. As seen in **Scheme 1**, the trisubstituted benzene ring becomes a tetrasubstituted benzene ring upon polymerization, which could be a suitable index for the extent of polymerization. The integrated intensity of the band at 1498 cm^{-1}, which is assigned to the in-plane carbon–carbon stretching of the trisubstituted benzene ring,[16] is ratioed with the internal thickness band at 1383 cm^{-1} and plotted as a function of curing time, as shown in Figure 2. Again, the relative intensities are shown in this figure as normalized values. The polymerization proceeds quickly at an early stage of curing for all three samples and slows significantly after 1 h. The extent of polymerization at 180°C, as a function of PC modifier and curing time, is summarized in Table II. During the first 15 min of curing, a conversion of 63% is observed for pure BA-a but only 56 and 34% are observed for the blends with 11 and 33 wt % of PC, respectively. The trisubstituted benzene ring band of pure BA-a decreased to 26% at the end of the heating, thus indicating an extent of polymerization reaction of 74% after 5 h at 180°C; the blend with 11 wt % of PC has nearly the same value (73%). However, the blend with 33 wt % of PC shows less conversion (55%).

It is important to clarify at this point that the degree of polymerization determined by the above-described method underestimates the true degree of polymerization. The current method characterizes the reduction of the trisubstituted benzene rings, which assumes that all of the trisubstituted benzene rings will become tetrasubstituted benzene rings during the polymerization reaction. However, it is known that the crosslinking reaction of benzoxazine not only takes place at tetrasubstituted rings such as the one on the bisphenol-A moiety (phenolic Mannich base network) as seen in **Scheme 2(a)** but also occurs at aromatic amine sites (amine Mannich base network), as shown in **Scheme 2(b)**.[17]. In this case, extra trisubstituted benzene rings will be generated after the crosslinking reaction.

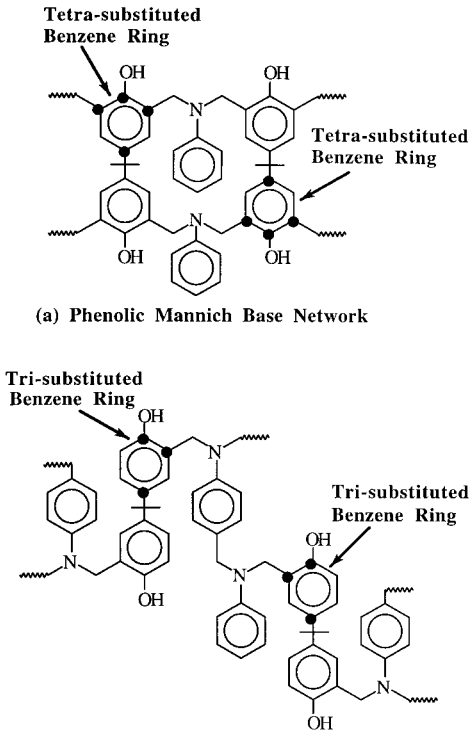
Difference Between Ring-Opening Reaction and Polymerization

It is important to keep in mind that for the pure benzoxazine, curing is autocatalyzed by phenols formed in the ring-opening reaction. Theoretically, the ring-opening reaction and Mannich bridge formation are consecutive reactions, whereby trisubstituted benzene rings are consumed immediately after opening the oxazine rings, a process that continues throughout the entire curing.[18] However, it was previously reported that the opened oxazine rings that cannot

Table II Normalized Integrated Intensity (A/A_0) (%) of Trisubstituted Benzene Ring Mode at 1498 cm^{-1} Obtained from Curve-Resolved FTIR Spectra

Curing Time (h)	BA-a	11 wt % of PC	33 wt % of PC
0	100.0	100.0	100.0
0.25	37.0	44.0	65.7
0.5	30.4	32.8	59.6
1	26.5	29.4	53.9
2	26.5	27.6	46.8
3	26.4	26.7	46.0
4	26.4	26.7	44.9
5	26.4	26.7	44.9

Samples were cured isothermally at 180°C in air.



Scheme 2 Two possible network structures of BA-a monomer after thermal curing: (a) phenolic Mannich base network; (b) amine Mannich base network.

be fully polymerized result in termination rather than propagation, which is most evident in the absence of any catalysts.[18] Therefore, the difference in the conversion monitored by the bands at 1498 and 960 cm^{-1} is significant and of great interest because the difference represents the amount of ring-opened benzoxazine monomers that do not become part of the polymer network.

The difference between the normalized intensities $[(A/A_0)_{960} - (A/A_0)_{1498}]$ of the benzoxazine/PC blends was calculated and plotted in Figure 3. A maximum was observed in all of the blend compositions. This phenomenon was first found in the catalyzed monofunctional benzoxazine system and was systematically studied by Dunkers and Ishida.[18] However, none of the difunctional benzoxazine system was investigated. The sudden increase in the difference between the ring-opening and polymerization reactions can be ascribed to the consequence of these two processes. The activation energy for the thermally induced ring-opening reaction is believed to be lower than that for the polymerization reaction, which is associated with covalent bond formation. Hence, the amount of ring-opened species is greater than the amount of polymerized species at the very early curing stage as a result of the more rapid ring-opening reaction. As the curing proceeds further, when the ring-opening reaction is saturated, polymerization takes place simultaneously at multiple opened oxazine rings. Thus, the difference between the number of opened rings and polymerized species is reduced. The maximum of the difference between two bands increased with increasing PC concentration and appeared at longer curing times in the blend with 33 wt % of PC. It is concluded that the amount of ring-opened oxazine rings that lead to termination is greater, and the rate of polymerization is hindered upon the addition of the PC modifier.

Hydrogen Bonding of Carbonyl Groups

It was previously reported that intermolecular hydrogen bonding plays a dominant role in the miscibility of polar polymers containing carbonyl or carbonate groups.[19] FTIR is a useful technique to investigate the miscibility of polymer blends because changes in the molecular environment of the polymer will generally result in perturbations in the spectra. The fraction of the PC carbonate groups that are hydrogen-bonded to the benzoxazine resin is, therefore, a direct measure of how well the polymers are mixed on a molecular level.[19] There are two areas of interest in the infrared spectra of the blends: one is in the hydroxyl-stretching region from 3600 to 3000 cm^{-1} and the other is in the carbonyl-stretching region from 1800 to 1650 cm^{-1}.

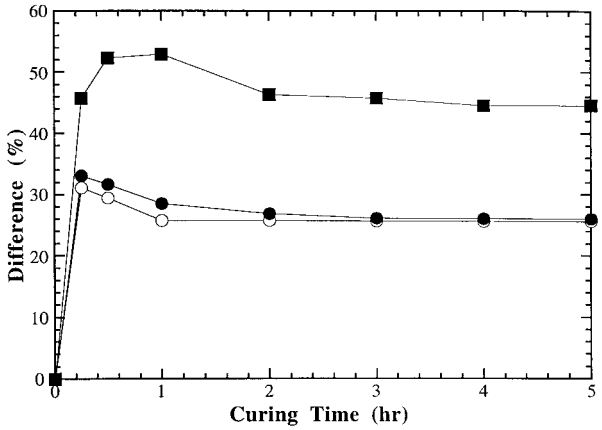


Figure 3 The difference between normalized intensities (A/A_0) of degree of ring-opening reaction (960 cm^{-1}) and extent of polymerization (1498 cm^{-1}) of benzoxazine/PC blend. Samples were cured isothermally at 180°C in air: (○) BA-a, (●) 11 wt % of PC, and (■) 33 wt % of PC in the benzoxazine blend.

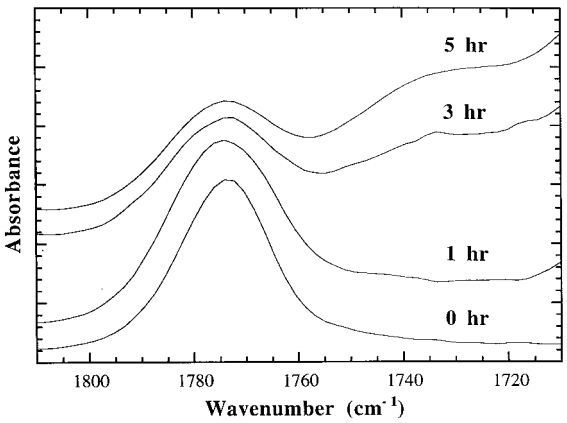


Figure 4 FTIR spectra of the benzoxazine blend with 11 wt % of PC at the carbonyl-stretching region. Samples were cured isothermally at 180°C in air. All the curves shown are displaced so as to discern various curing times.

The spectra of the blends with 11 and 33 wt % of PC in the carbonyl-stretching region are shown in Figures 4 and 5, respectively. There are two bands in this region: one band centered at 1774 cm^{-1}, attributed to the characteristic peak of the nonassociated carbonate (i.e., nonhydrogen-bonded carbonyl), and another relatively weak band at 1733 cm^{-1}, assigned to the hydrogen-bonded carbonyl groups. The hydrogen-bonded carbonate band of PC was reported at 1755 cm^{-1} for the PC/epoxy blend,[20] which has less frequency difference from the free carbonyl band than that from the PC/benzoxazine blend. This

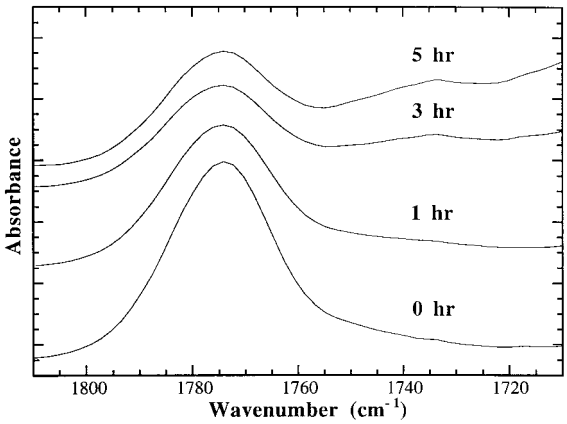
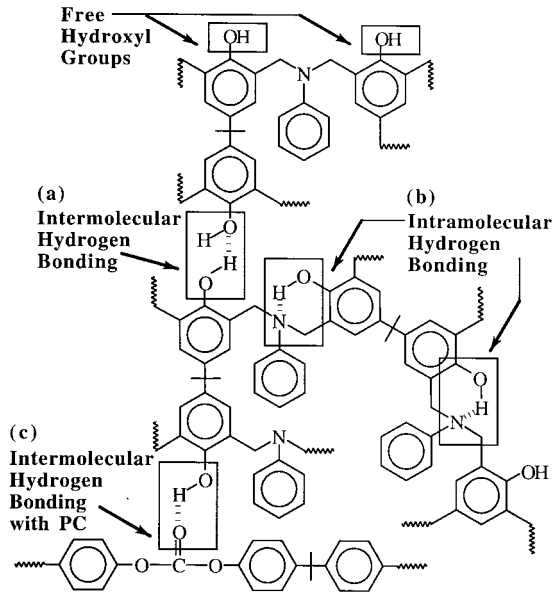


Figure 5 FTIR spectra of benzoxazine blend with 33 wt % PC at the carbonyl-stretching region. Samples were cured isothermally at 180°C in air. All the curves shown are displaced so as to discern various curing times.



Scheme 3 Three types of hydrogen bonding that could possibly occur in PC/polybenzoxazine blend. (a) Intermolecular hydrogen bonding between two hydroxyl groups of polybenzoxazine, (b) intramolecular hydrogen bonding between hydroxyl groups and nitrogen atoms on the Mannich bridge, and (c) intermolecular hydrogen bonding between carbonyl groups of PC and hydroxyl groups of polybenzoxazine.

implies that the hydrogen-bonding strength ($\Delta\nu$) between the PC and the benzoxazine resin is stronger than that in the PC and epoxy resin. Upon curing, these two bands maintain their band positions, although the intensity changes gradually with time, reflecting the changes in population of these carbonyl groups. In both of these compositions, no evidence of hydrogen bonding in uncured blends was found because of the lack of hydroxyl groups in the purified benzoxazine monomer. After curing isothermally at 180°C, hydroxyl groups were produced through ring-opening reactions, leading to the formation of the intermolecular hydrogen bonding with PC. Interestingly, despite the fact that the majority of the benzoxazine rings opened within 15 min at 180°C, as discussed in the previous section, the hydrogen-bonded carbonyl groups of benzoxazine blends with 11 and 33 wt % of PC did not appear until 1 h curing. Three types of hydrogen bonding that could possibly occur in the PC/polybenzoxazine blend are presented in **Scheme 3**. We propose the above-mentioned phenomenon to be the competition between the hydrogen bonding within the polybenzoxazine [Scheme 3(a), (b)] and the intermolecular hydrogen bonding with the PC

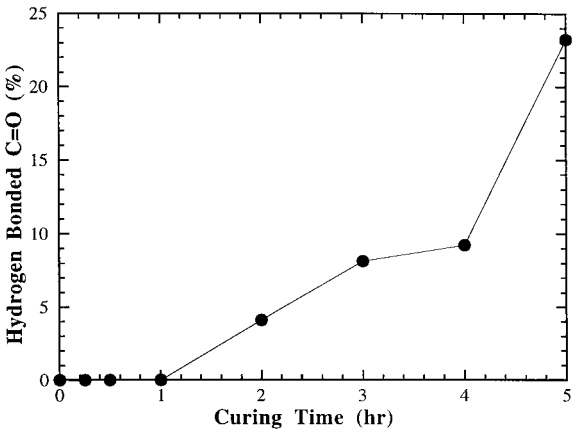


Figure 6 Carbonyl hydrogen–bonding fraction of the benzoxazine blend with 11 wt % of PC as a function of curing time. Samples were cured isothermally at 180°C in air. Results were obtained from the curve-resolved FTIR spectra.

modifier [Scheme 3(c)]. At the early stage of curing, the step in which most of the ring-opening reactions occur, benzoxazine would form intramolecular six-membered hydrogen bonds as a result of the high chain flexibility.[21–23] However, at a higher conversion, the newly formed hydroxyl groups cannot form such conformationally demanding structures as a result of reduced molecular mobility. However, these hydroxyl groups may be accessible to the still mobile PC chains, which are in a rubbery state at the curing temperature.

Figures 6 and 7 show the quantitative analysis of the hydrogen bonding from the carbonyl groups of PC. The amount of hydrogen-bonded carbonyl groups appears to be greater upon curing and the percentage of the hydrogen-bonded carbonyl in the benzoxazine blend with 33 wt % of PC is much lower than that of the blend with 11 wt % of PC. This result is reasonable, considering the concentration of polycarbonate in the blend and the extent of polymerization. The higher the concentration of the PC, the more the carbonyl groups, but there are not enough free hydroxyl groups available for interaction in cured benzoxazine resins. Furthermore, as discussed previously, the blend with 33 wt % of PC appeared to reach a lesser extent of polymerization compared to that of the blend with 11 wt % PC. This would result in fewer free hydroxyl groups available for polycarbonate to hydrogen-bond intermolecularly. Only 10% of the hydrogen-bonded carbonyl groups are found in the blend of 33 wt % of PC after 5 h of curing, although more than 23% of the carbonyl hydrogen–bonding content is observed in the blend with 11 wt % of PC. Similar trends have been observed in other blend systems,[19,24–26] in which the percentage of hydrogen bonding from the ester groups of polycaprolactone (PCL) in different matrix phases is depressed with the increase of the PCL content. This phenomenon may imply that the phase separation may have occurred at a higher content of modifiers,[19] and thus the percentage of hydrogen bonding diminishes because of fewer opportunities for interaction. Based on the absence of PC melting behavior in the entire composition range of the cured polybenzoxazine blend (shown in the DSC thermograms in the next section), it is evident that phase separation did not occur. Consequently, a lesser amount of available hydroxyl groups of ring-opened benzoxazine is the only factor responsible for the lower percentage of hydrogen bonding in the blends with higher PC concentration.

The reasons that not all of the PC carbonyl groups are involved in the hydrogen-bond formation can be described as follows. In any blend composition, the fraction of polar groups from modifiers that are responsible for the hydrogen bonding with the matrix phase will be limited by the physical problem of intimately mixing macromolecules.[25] Also, the mismatch of the repeat unit lengths of the two polymers is an important issue. It appeared that the interdistance between the two carbonyl groups on the PC repeat unit (1.395 nm) is approximately one and a half times longer than the interdistance between the two hydroxyl

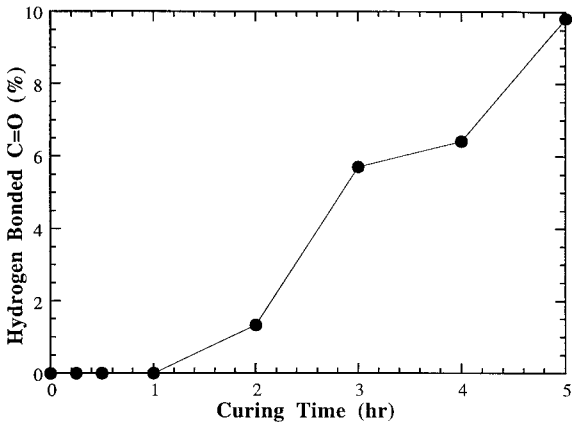


Figure 7 Carbonyl hydrogen–bonding fraction of the benzoxazine blend with 33 wt % of PC as a function of curing time. Samples were cured isothermally at 180°C in air. Results were obtained from the curve-resolved FTIR spectra.

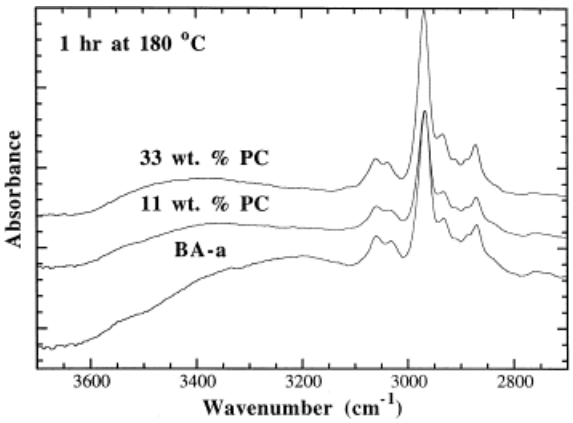


Figure 8 FTIR spectra of unmodified (BA-a) and modified benzoxazine with 11 and 33 wt % of PC, isothermally cured at 180°C for 1 h. Only the hydroxyl-stretching region is shown in this figure. All the curves are displaced so as to discern various blend compositions.

groups on polybenzoxazine (0.872 nm). Consequently, geometric and steric factors will depress the amount of hydrogen bonding, even when molecular mixing occurs.[19,24] Finally, the more favorable intramolecular hydrogen bonding of benzoxazine resin[21–23] also plays a critical role in this process. It is surmised that the PC carbonyl groups cannot overcome the stable intramolecular hydrogen bonding of the polybenzoxazine depicted in **Scheme 3(b)**. Thus, the amount of available hydroxyl groups is limited.

It is important to recognize that the preceding analysis of hydrogen bonding from FTIR is only an approximation. The fraction of hydrogen-bonded carbonyl groups was calculated under the assumption of identical extinction coefficients of the associated and free carbonyl groups.[25] However, a slightly higher extinction coefficient may be expected for the hydrogen-bonded absorptions.[24]

Hydrogen Bonding of Hydroxyl Groups

The representative spectra of pure BA-a and PC blends in the hydroxyl group region are shown in Figure 8. There are at least two components contributing to the spectra in this region: one peak arises in the range of 3540–3520 cm^{-1}, which is assigned to the relatively free hydroxyl groups, and the other bands appear in the range of 3420–3250 cm^{-1}, which can be attributed to the hydrogen-bonded hydroxyl groups. Because of the much more complicated nature in this particular region, it is more difficult to quantitatively determine the percentage of the hydrogen bonding in the same way as that for the carbonyl region. Also, the specific absorptivities of the hydroxyl bands change drastically as a function of the hydrogen-bond strength. However, some theories have been developed, which are widely accepted, to describe the strength of the associated hydroxyl groups, which could be calculated directly from the spectra.

By comparing the frequency difference between the free and bonded hydroxyl groups ($\Delta\nu$), the relative strength of this interaction could be evaluated.[26,27] The results calculated from curve-resolved bands are plotted against curing time in Figure 9. Nonhydrogen-bonding peaks remain almost at the same position upon curing in all compositions, which is expected for the isolated hydroxyl groups. For the associated hydroxyl groups, peak position shifts to lower frequencies as the curing process proceeds. As a result, the strength of hydrogen bonding becomes stronger as the degree of polymerization increases and levels off before the curing process stops. It is clear that $\Delta\nu$ quickly reached 325 cm^{-1} in the unmodified sample (BA-a) once the curing starts, whereas in samples of the PC/benzoxazine blends, $\Delta\nu$ increased gradually with the curing time. We suggest that the interaction between PC modifier and ring-opened polybenzoxazine is a reasonable cause for the shift of the associated hydroxyl peaks. Apparently, $\Delta\nu$ appeared to be greater in the unmodified benzoxazine than that in the system with the addition of PC. Once again, this can

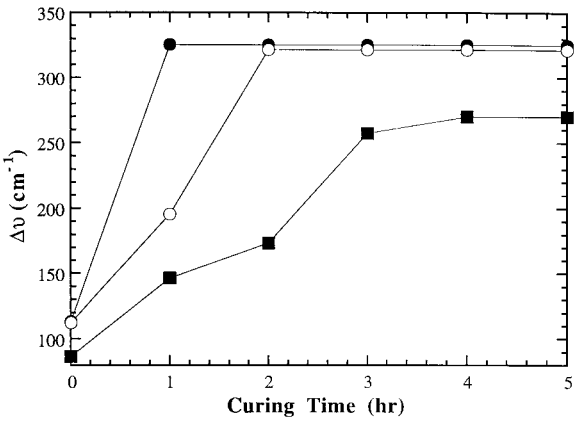


Figure 9 Relative frequency shift ($\Delta\nu$) between the free and the hydrogen-bonded hydroxyl bands as a function of curing time. Samples were cured isothermally at 180°C in air. (●) BA-a, (○) 11 wt % PC, and (■) 33 wt % PC in the benzoxazine blends.

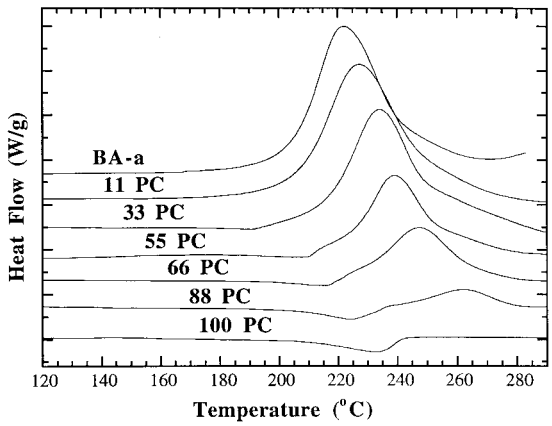


Figure 10 DSC thermograms of the PC/benzoxazine monomer blends (first scan). All the curves are displaced so as to discern various blend compositions.

be attributed to the hydrogen-bonding formation of polybenzoxazine itself, as seen in Scheme 3(a), (b). It is believed that these rich interactions strongly influence the final network structure.[21–23] Because $\Delta\nu$ was calculated from the frequency shift between the free and bonded hydroxyl groups, the value should represent the overall effect from three types of hydrogen bonding in the blend sample or two types of hydrogen bonding in the unmodified polybenzoxazine. Therefore, a smaller $\Delta\nu$ is indicative of a less-stiff hydrogen bond of the hydroxyl groups upon the addition of PC modifier.

It is worth pointing out that network development can be correlated to the hydrogen-bonding formation, especially from a kinetic point of view. From the degree of polymerization shown in Figure 2, the polymerization reaction has saturated within various prolonged heating times in the various blend compositions, which are 1 h for pure BA-a, 3 h for the blend with 11 wt % of PC, and 4 h for the blend with 33 wt % of PC. This saturation time, as defined by the time when there is no intensity change from the trisubstituted benzene ring detected in the spectra, coincides with the time that the hydrogen-bonding strength saturates to the maximum values. The hydrogen-bonding strength of the hydroxyl groups on the polybenzoxazine main chain reaches an asymptotic value because, after the benzoxazine network is formed at a particular temperature or composition, no further hydroxyl groups will be produced. Moreover, the hydrogen-bonding strength of the blend with 11 wt % of PC ($\Delta\nu$ = 322 cm^{-1}) is relatively strong compared to that of the sample with 33 wt % of PC ($\Delta\nu$ = 270 cm^{-1}). This observation is similar to that of the other blending systems from earlier researchers,[26] who showed that the hydrogen-bonding strength in the hydroxyl-stretching region from epoxy decreases significantly upon the modification of polycaprolactone (PCL) in this particular miscible polymer blend. Once again, this phenomenon can be ascribed to the hydrogen-bonding interaction between the hydroxyl groups of the benzoxazine and the carbonate groups of the PC modifier.

DSC Analysis

The DSC thermograms of the benzoxazine/PC blends for various PC concentrations are plotted in Figure 10. The curing exothermic peak shifts toward a higher temperature as the concentration of PC increases. The inhibited polymerization reaction is in agreement with the result shown previously from FTIR. This observation can be attributed to the following two features: (1) polycarbonate dilutes the concentration of the benzoxazine monomer and delays the polymerization reaction, and (2) upon the addition of higher molecular weight PC, the diffusion of the benzoxazine monomer will be reduced as a result of the increased viscosity. Onset and peak polymerization temperatures during nonisothermal curing are plotted against the blend compositions in Figure 11. Both the onset and peak temperatures of the benzoxazine exotherms increase as a function of the PC content, indicating inhibited polymerization upon the addition of PC modifier.

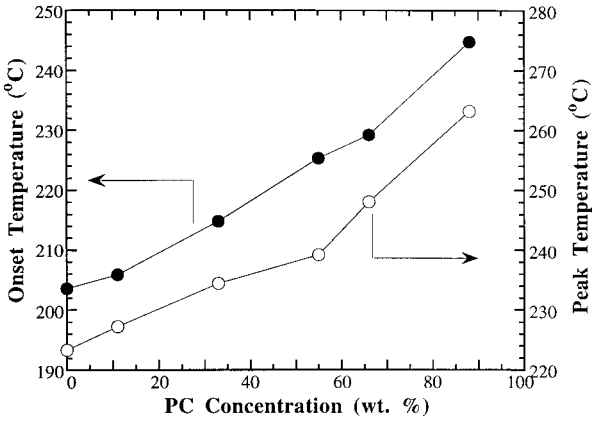


Figure 11 Onset and peak polymerization temperatures of benzoxazine/PC blends as a function of PC concentration obtained from nonisothermal DSC traces (first scan).

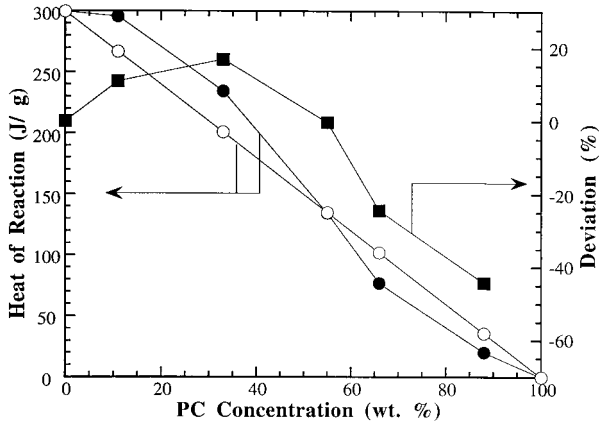


Figure 12 Expected (○) and experimental (●) heat of reaction of the PC/benzoxazine blends as a function of PC concentration obtained from nonisothermal DSC traces (first scan). The percentage of deviation (■) between these two values is also included in this plot.

Because only the fraction of the pure BA-a monomer is capable of polymerizing, we can calculate the expected heat of reaction based on the following equation:

$$\Delta H_p = \Delta H_p^\circ \times (1 - w) \tag{1}$$

where ΔH_p° is the heat of reaction for pure BA-a monomer, ΔH_p is the expected heat of reaction of BA-a in the PC blends, and w is the weight fraction of PC in the blends. The calculated results and the experimental data are plotted in Figure 12 along with the percentage of deviation between these two values. The heat of the reaction appears to have a nonlinear relationship against PC composition. The experimental heat of reaction reduces gradually as the amount of modifier increases but is slightly higher in comparison with the expected value of the blend with 11 and 33 wt % of PC. When the addition of PC modifier is above 55 wt %, the observed heat of reaction is lower than predicted. From the FTIR results obtained in the earlier section, it is apparent that the degree of polymerization is lesser in the presence of PC modifier. Therefore, the additional heat detected in the DSC thermograms may be a result of side reactions.[28] Two general trends, a positive and negative deviation, are found in the blend with lower (<55 wt %) and higher (>55 wt %) amounts of PC, respectively, and a nearly zero deviation is observed in the blend with 55 wt % of PC. This observation may imply that phase inversion occurred at this particular PC/benzoxazine monomer composition.

The effect of the PC content on the glass-transition temperature (T_g) of the blends can also be found in the DSC thermograms shown in Figure 13. Only one T_g is observed in the entire composition range and no melting behavior of PC is detected in the cured benzoxazine blends, suggesting that polybenzoxazine and polycarbonate may be an example of a miscible polymer pair. Several theoretical and empirical equations have been proposed to describe the overall glass-transition temperature and composition dependence of the polymer blends. The Fox equation[29] is the most general one, which derives the T_g from the simple law of additivity. The formula is

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{2}$$

where w_1 and w_2 are the weight fraction of components 1 and 2, respectively, and T_{g1} and T_{g2} are the glass-transition temperatures of the two polymers. The calculated values from the Fox equation along with the actual experimental data are plotted in Figure 14. The experimental data greatly deviate from the theoretical predictions, even at lower PC concentrations, which is in agreement with the FTIR results. The presence of PC modifier would tend to inhibit the ring-opening polymerization and results in the inevitable decrease of the final T_g. Moreover, this unexpectedly large deviation from the empirical equation is indicative of possible copolymer formation that

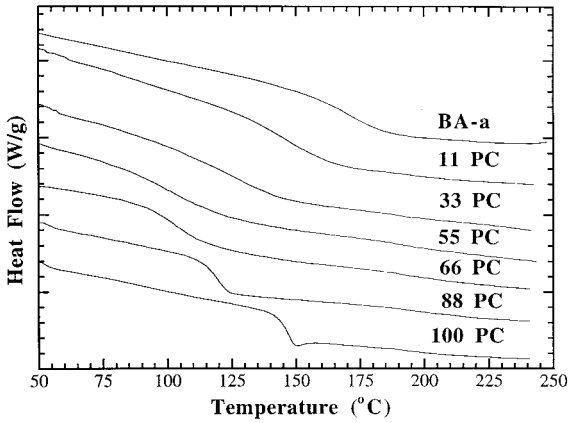


Figure 13 DSC thermograms of PC/benzoxazine blends (second scan). All the curves are displaced so as to discern various blend compositions.

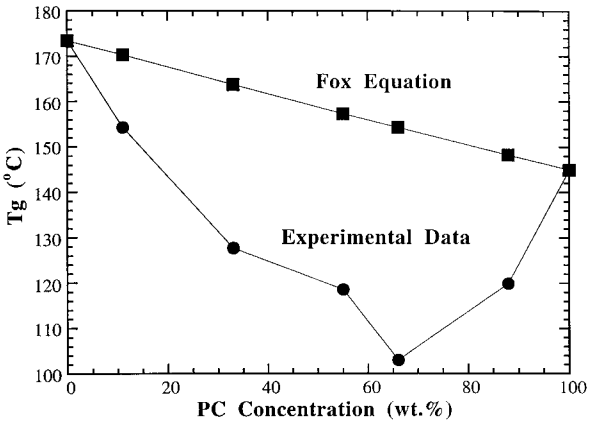


Figure 14 Glass-transition temperature (T_g) from the experimental data and the theoretical predictions (Fox equation) of PC/polybenzoxazine blends as a function of PC concentration.

can disrupt the formation of normal polybenzoxazine networks.[28]

Melting-Point Depression of PC in the Presence of Benzoxazine Monomer (Uncured Blends)

The depression of the PC melting point of the uncured blends is shown in Figure 15. The melting point of pure polycarbonate is 230°C. After blending with benzoxazine monomer, not only does the heat of fusion resulting from the melting of the spherulites decrease but the melting point also decreases. The melting point decreased to 190°C for the blend with 33 wt % of PC. It was previously shown for blends with crystallizable components that both the depression of the crystallinity and crystallization rate are indicative of miscibility phenomena in the amorphous state.[30] The depression of the melting point of the crystallizable component in the miscible blends is well documented,[31,32] in which a negative Flory–Huggins interaction parameter (χ_{12}) between two polymer constituents is evident from the thermodynamic point of view. In other words, the melting-point depression results from the reduction in chemical potential of the PC component in the amorphous phase caused by the diluent benzoxazine monomer.[33] Moreover, similar results have been found in other blending systems including epoxy/PC[30] and epoxy/poly(ethylene oxide) (PEO).[34] The melting-point depression with increased PC content is more substantial than results usually observed for miscible polymer blends having one crystallizable component, which is attributed to the contribution from both enthalpic and entropic effects in the benzoxazine/PC blends as a result of the small molecular weight of the benzoxazine monomer. In the case when the molecular weights of both components are adequately large (e.g., cured epoxy), only the enthalpic contribution to the melting-point depression needs to be considered.[1,30] In the present case, it can be seen from Figure 13 that no melting endotherm was detected for any of the cured blends, implying that either the crystallization of PC did not occur during the quenching shortly after the first DSC scan or that the macrophase separation did not occur in the entire concentration range. It was previously reported that polycarbonate usually takes more than 1 week to crystallize. Accordingly, it would not be surprising to observe the absence of the PC melting behavior in the second run, which was carried out shortly after the liquid nitrogen quenching followed by the first scan. The DSC thermogram in Figure 10 does not show a melting behavior in the benzoxazine monomer blend with 11 wt % of PC, implying that a complete dissolution occurred in this particular blend concentration and below.

The overall percentage crystallinity X_c (blend) of PC/benzoxazine monomer can be calculated from the following equation[25]:

$$X_c \text{ (blend)} = \frac{\Delta H_m}{\Delta H_m^\circ} \tag{3}$$

where ΔH_m° = 109.50 J/g is the heat of fusion for 100% crystalline PC[29] and ΔH_m is the heat of fusion of PC in the blend, obtained directly from the DSC traces. Because only a fraction of the PC

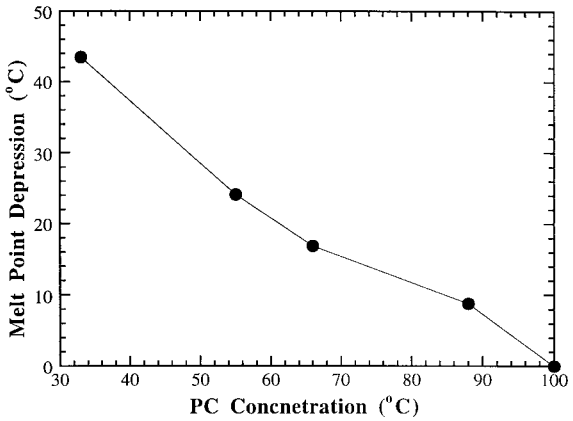


Figure 15 Melting-point depression of PC against various blend compositions in the uncured benzoxazine blends (first DSC scan).

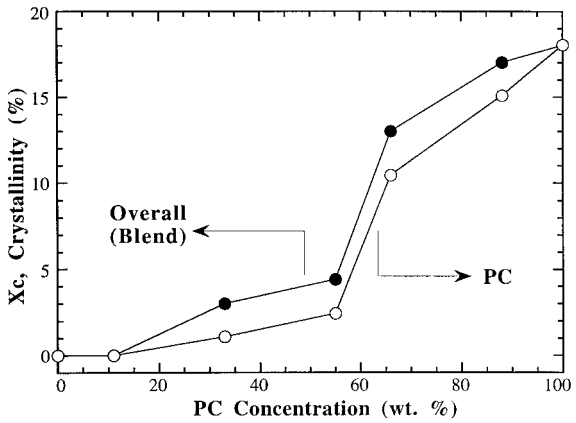


Figure 16 Degree of crystallinity of the blend [X_c (blend)] and degree of crystallinity of PC [lsqb[X_c (PC)] in the uncured monomer blends (first DSC scan) as a function of PC concentration.

is capable of crystallizing, it is necessary to evaluate the percentage crystallinity of PC [X_c (PC)] by the formula

$$X_c\,(\mathrm{PC}) = \frac{\Delta H_m}{\Delta H_m^\circ \times w} \tag{4}$$

where ΔH_m° and ΔH_m are the same as described in eq. (3), and w is the weight fraction of PC in the blend. The results obtained for the uncured PC blend are presented in Figure 16. Both the overall and PC crystallinity are suppressed as more benzoxazine is added into PC, indicating that the crystallization of the PC in the monomer blend becomes progressively more difficult with increased benzoxazine content. It should be noted that the presence of low-viscosity benzoxazine monomer can act as a solvent to dilute the PC polymer, thus inhibiting the crystallization. Because the dilution effect is best seen in the blend with a lesser amount of PC, it may also help to explain the sudden decrease in relative percentage crystallinity from higher to lower PC content, as seen in Figure 16. Additionally, a sudden change in the relative percentage crystallinity coincides with the phase inversion point, which is around 55 wt % of the PC blend. It is suggested that the PC crystallization was hindered dramatically when the PC modifier served as a dispersed phase.

Thermogravimetric Analysis (TGA)

The derivatives of residual weights of the PC blends are shown in Figure 17. The curve on the top of the TGA thermogram, which represents the pure BA-a resin, indicates that there are two dominant thermal decomposition mechanisms. A major weight loss event occurs at approximately 390°C, and a minor weight loss event takes place at 480°C. The curve at the bottom of the thermogram, which represents the pure polycarbonate, shows only a relatively sharp peak around 520°C. The thermal degradation process of polybenzoxazine is relatively slow in the middle temperature range. PC is rather stable at a high temperature but the rate of weight loss is much more rapid than pure polybenzoxazine. Therefore, the expected thermal properties in the blends would be a compromise between those of two pure components. However, it is surprising that a significant thermal decomposition appeared at a much lower temperature around 310°C in the blends with 11 and 33 wt % of PC modifier. A summary of TGA results is presented in Figure 18. Both the onset and peak degradation temperatures exhibited a similar pattern as that of the T_g's, suggesting that the thermal properties of polybenzoxazine upon the addition of PC were significantly disturbed. In blends with 11 and 33 wt % of PC modifier, particularly, the thermal stability was worse than that in the unmodified polybenzoxazine.

Possible Side Reactions

Based on the observation of the positive deviation between the expected and experimental heat of reaction in the blends with 11 and 33 wt % of PC, an exothermic side reaction possibly occurred in the presence of polycarbonate. Several indirect evidences from the FTIR and TGA results also support this claim. We propose that it is the

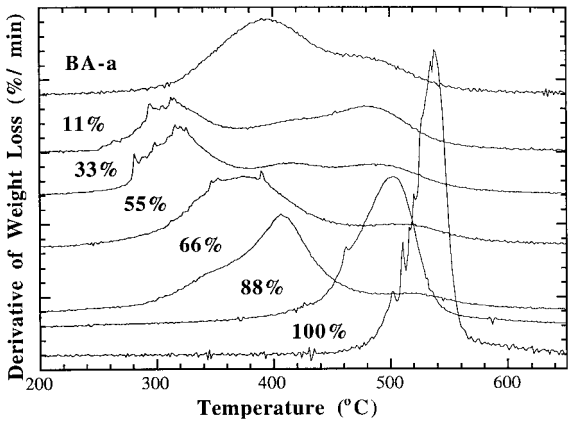


Figure 17 First derivative of residual weight of PC/polybenzoxazine blends from TGA. All the curves are displaced so as to discern the different compositions.

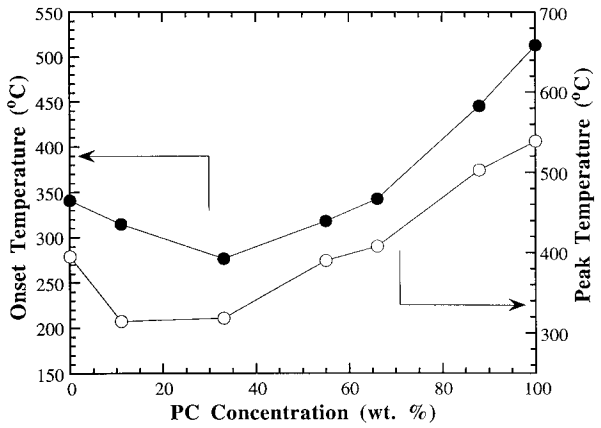


Figure 18 Summary of TGA analysis: onset and peak thermal degradation temperatures of polybenzoxazine/PC blends as a function of PC concentration.

transesterification between the hydroxyl groups of polybenzoxazine and the carbonate groups of the PC that results in the inevitable decrease of the glass-transition temperature. A more systematic investigation is reported elsewhere.[28]

CONCLUSIONS

In summary, PC is completely miscible with the cured polybenzoxazine resin, based on the observation of a single glass-transition temperature and the disappearance of the PC melting behavior in the DSC thermograms. The hydrogen-bonding interaction in the PC blends occurs between the hydroxyl groups of polybenzoxazine and the carbonyl groups of the PC, and we conclude that it is this driving force that results in the miscibility of the PC/benzoxazine blend in the entire composition range along with possible copolymer formation.

The hydrogen-bonded carbonyl groups do not appear until 1 h of curing at 180°C, which is the result of the rather stable intramolecular hydrogen bonding within the flexible polybenzoxazine main chain at an early curing stage. The content of hydrogen-bonded carbonyls starts to increase gradually after prolonged heating because the hydroxyl groups are more accessible to the mobile PC chains after gelation. Moreover, both the fraction of hydrogen-bonded carbonyls of PC and the strength of the hydrogen-bonded hydroxyl groups of polybenzoxazine are greater in the blends with a lower PC concentration.

According to the relative hydrogen-bonding strength ($\Delta\nu$), calculated from the free and associated hydroxyl groups, the stiffness of the interaction increases progressively upon curing and levels off after most of the ring-opening reaction has completed. The saturation time at which the polymerization is almost complete coincides with the time at which the strength of the hydrogen-bonded hydroxyl groups levels off at the maximum values, suggesting that there is a strong correlation between the benzoxazine network development and the hydrogen-bonding formation.

A sudden drop of the PC crystallinity in the benzoxazine monomer blend prior to curing is shown in the blends with a PC content lower than 55 wt %. In addition, the experimental heat of reaction exhibits a negative deviation from the expected value in the blend with a PC concentration higher than 55 wt %. It is suggested that this particular composition is the phase inversion point at which PC changes from the dispersed phase to the continuous phase.

It is found that the addition of PC modifier results in slower ring-opening and polymerization reactions at an early curing stage and a lesser extent of polymerization is observed in the blend with a higher percentage of PC. These phenomena are further confirmed by DSC experiments in which the exothermic peaks of polymerization shift toward a higher temperature and the glass-transition temperatures of PC blends appeared to be lower than the predicted values from the Fox equation.

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