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Synergism observed in polybenzoxazine and poly(ε-caprolactone) blends by dynamic mechanical and thermogravimetric analysis

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Abstract

Benzoxazine resins and poly(ε-caprolactone) (PCL) are melt blended and the properties of the blends in the range of 0–15 wt.% of PCL are studied by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). The T_gs of the benzoxazine blends in the presence of PCL are found to be slightly lower than that of neat polybenzoxazine resin. The blends show improved mechanical properties, including higher crosslink densities, rubbery plateau moduli, and flexural strengths compared to pure polybenzoxazine. Moreover, the thermal stabilities at middle temperature range in the presence of PCL modifiers are also enhanced, which is evident from the delayed onset decomposition temperature and the disappearance of the first degradation event. © 2001 Published by Elsevier Science Ltd.

Keywords: Blends; Polybenzoxazine resin; Poly(ε-caprolactone)

1. Introduction

Polybenzoxazine is an attractive class of phenolic resins and it can be used as the matrix component of high-performance materials because of its stiffness, high-temperature stability and a very wide range of molecular design flexibility [1–4]. The mechanical properties of crosslinked benzoxazine resins [5] suggest that, for some applications, improvement of toughness will be useful. By the incorporation of low T_g components, flexural and impact properties of resins are expected to be improved. It is a common practice to add rubber to a brittle resin to enhance the toughness of the matrix phase. Rubber with reactive functionality is generally used to improve the adhesion at the interface or reduce the interfacial tension [6]. However, the majority of polymer–polymer blends are immiscible, i.e. the polymers do not mix on the molecular level. There are serious disadvantages associated with immiscible polymer blends.

However, poly(ε-caprolactone) (PCL) has been reported to be miscible with a number of polymers [7–9], particularly when an opportunity exists for hydrogen bonding [10–13] or other polar interactions with the second polymer. PCL is one of the biodegradable polyesters with a very low T_g (−55°C) and a thermal degradation temperature that is much higher than most of the other low T_g modifiers. The benefits of blending PCL with a broad range of polymers have been described in Ref. [9]. Recently, a study was initiated in our laboratory to evaluate the potential of blending PCL with polybenzoxazine resin [14]. In such a system, the polymerization of polybenzoxazine resin was found to proceed further and it is likely that an even higher network conversion may have formed with PCL modification [14].

The purpose of the present work is to examine PCL blends by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

The thermoplastic polymer used in this blend study is PCL supplied by Polysciences Company and has a number average molecular weight in the range of 35,000–45,000. Difunctional benzoxazine monomers were synthesized from bisphenol-A, paraformaldehyde, and aniline. All chemicals were purchased from Aldrich Chemical Company, which have purities higher than 99%. All these materials were used as received.

2.2. Synthesis of bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane

Bis (3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazinyl) isopropane (abbreviated as BA-a), was synthesized through

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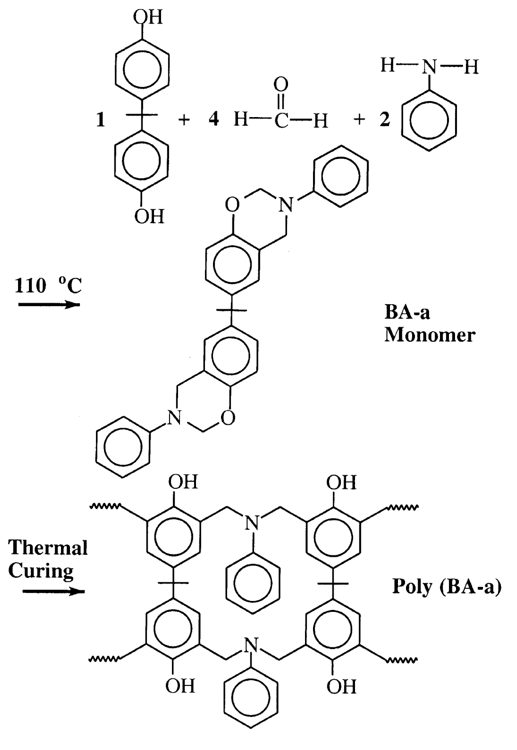

Scheme 1.

Mannich reaction via a solventless method. Stoichiometric amounts (1:2:4) of bisphenol-A, aniline, and paraformaldehyde were mixed for 30 min at 110°C. A detailed description of the synthesis and purification procedures is presented elsewhere [1]. The structures of BA-a prior to and after curing are displayed in Scheme 1 (Benzoxazine monomer, BA-a and polymer, poly(BA-a) nomenclature and structure used in this study).

2.3. Preparation of PCL-modified benzoxazine resins

The PCL polymer and purified BA-a monomer were dried separately at room temperature in a vacuum oven for at least 24 h prior to the blend preparation. Different concentrations of the PCL modifier were added to BA-a at 120°C and a clear homogeneous solution was obtained after thorough mixing. The clear mixture was first degassed in a preheated mold in a vacuum oven at 120°C then step cured in a compression molder. All the samples were polymerized without adding any catalyst or initiator and care was taken to ensure that all cured samples were free of bubbles. The polymerization profile is shown in Table 1. After curing for 5.75 h, the heater of compression molder was turned off and all samples were allowed to cool slowly overnight. Blend compositions, sample abbreviations, and the appearances of the cured specimens are all summarized in Table 2.

Table 1
The reaction condition prior to curing and the stepwise thermal curing profile

Curing temperature (°C)	Reaction time	Experimental condition
130	15 min	Vacuum oven
145	15 min	Vacuum oven
160	15 min	Vacuum oven
175	1.5 h	Compression molder
195	2.0 h	Compression molder
205	1.5 h	Compression molder

Table 2
Sample code and the blend composition by weight percentage in the PCL/benzoxazine system

Sample code	PCL concentration in the benzoxazine blend (wt.%)	Sample appearance after thermal curing
00PCL	0	Transparent
03PCL	2.92	Transparent
06PCL	5.66	Transparent
08PCL	8.26	Transparent
11PCL	10.72	Translucent
13PCL	13.05	Translucent
15PCL	15.25	Opaque

2.4. Characterization

The mechanical characterization was carried out in a Rheometrics Dynamic Mechanical Spectrometer RMS-800 from −120°C to 280°C with a thermal soak time of 45 s. The strain chosen was 0.1%, which was within the range of linear viscoelasticity for the materials while affording reasonable torque responses throughout the temperature range [15]. A typical frequency of 6.28 rad/s (1 Hz) was used in this study. A dual range force rebalance transducer set for the 2000 g cm torque range was used with a rectangular sample torsion fixture. Compression molded samples with an average size of 48 mm × 3 mm × 12 mm were tested and were protected from moisture both during and between experiments through storage under N_2.

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.

The flexural properties of polybenzoxazine resins were measured by a three-point bending test using Instron 5567. Five sets of flexural specimens with a dimension of 60 mm × 25 mm × 3 mm were cut with a water-cooled diamond-cutting wheel. A span of 48 mm giving a span/depth ratio of 16 according to ASTM standard D-790 was used in the flexural test. The rate of crosshead motion is 1.2 mm/min.

3. Results and discussion

3.1. Morphology aspect

The morphology of the blended system plays an essential role in determining the final properties. From the sample appearance shown in Table 2, translucent samples were found in the blend with 11 and 13 wt.% of PCL, yet, the blend with 15 wt.% of PCL appeared to be completely opaque. Hence, microphase separation may have taken place in the blend with 11 and 13 wt.% of PCL. Based on the observation of the melting behavior from the thermal analysis [14], the occurrence of macro-phase separation is possible in the blend with 15 wt.% of PCL.

3.2. Dynamic mechanical analysis

3.2.1. Polybenzoxazine

Dynamic mechanical analysis (DMA) is one of the few techniques that enables one to selectively examine the different components of a multiphase system and their interactions. This is illustrated in Fig. 1 where the spectrum of a typical polybenzoxazine is correlated with specific regions. The features of interest from low temperature to high temperature include: (1) a low-temperature γ-relaxation transition between −120 and 0°C; (2) a relatively broad β-relaxation process of polybenzoxazine resins positioned at 80°C; (3) a relatively intense peak around 170°C in this region can be attributed to the glass transition temperature (T_g) or the α-relaxation process of this material and finally (4) the rubbery plateau region.

3.2.2. Polycaprolactone

The DMA spectrum of pure polycaprolactone is also presented in Fig. 1. We are primarily concerned with the following three aspects: (1) a low temperature or β-relaxation, generally ascribed to in-chain motions in the amorphous region of polycaprolactone [7,16], appearing at −95°C both in loss modulus (G'') and molecular damping (tan δ) curves; (2) the T_g or the α-relaxation process of PCL modifier, which is the major peak of G'' at approximately −60°C and is not only consistent with the data obtained from our previous DSC study [14] but also in agreement with other literature values [9,12]; and (3) the melting behavior also agrees well with the melting point (65°C) obtained from DSC [14]. There have been many investigations conducted on polycaprolactone to correlate the β-relaxation to crystallinity and it was found that the intensity of β-relaxation decreases as the degree of crystallinity increases [16]. Both the intensity and the position of the α-relaxation are also considerably affected by the degree of crystallinity of PCL, which is similar to other polyesters [16]. In general, it has been found that the T_g of PCL increases as the level of crystallinity increases, whereas the magnitude of the α-relaxation decreases [7,16]. Because of the very rapid crystallization rate of PCL, it is difficult to quench it from the melt without obtaining an appreciable amount of crystallinity. Evidence has been presented elsewhere [17] suggesting that the T_g for completely amorphous PCL is −71°C at 1 Hz. According to the DSC analysis in our previous article [14], the relative crystallinity of this test specimen was found to be 52%. Undoubtedly, the significant difference (11°C) in terms of T_g can be attributed to the much higher degree of crystallinity of PCL in our system.

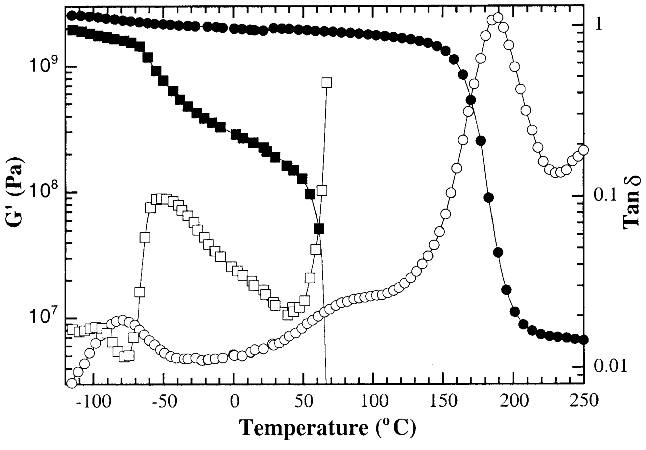

Fig. 1. DMA spectra of unmodified polybenzoxazine resin, poly(BA-a) and neat polycaprolactone, PCL: (●) G' of BA-a; (○) tan δ of BA-a; (■) G' of PCL; and (□) tan δ of PCL.

3.2.3. Comparison between polybenzoxazine and PCL

The storage modulus (G') of PCL at room temperature (30°C) with a value of 0.2 GPa is much lower than that of pure polybenzoxazine which is around 2 GPa. Small amount of lower-modulus component may act as stress concentration site, which is expected to absorb more energy than the brittle matrix phase. Hence, an improved impact-resistant polybenzoxazine material may be obtained in the presence of the PCL.

It is worth pointing out that the full width at half height (FWHH) of the tan δ peak at α-relaxation of the poly(caprolactone) (60°C) is slightly broader than that of the polybenzoxazine resin (50°C). These observations are somewhat different from what was expected. It is thought that the α-relaxation of the thermoplastic material will undergo a sharper damping behavior than thermosetting material owing to the more flexible structure and less restricted molecular motion. The opposite trend found in this particular system can be attributed to the following two factors. First, the degree of crystallinity has a profound influence on the thermal properties. In turn, the T_g from the completely amorphous region (α_1) may overlap with that from the crystalline–amorphous interface region (α_2). It was reported by other researchers that tan δ of polycarbonate (PC) in the α-relaxation exhibited a width of 15°C [18]. The degree of crystallinity of PCL [14] is much higher than that of PC [19]. Hence, the 'broadening effect' on the tan δ peak of PCL would be more obvious. Secondly, the width of the tan δ peak at α-relaxation in the thermosetting resin is correlated to the degree of the network homogeneity. It has been reported [5] that polybenzoxazines have high T_gs but low crosslink densities, which in turn, will lead to a sharper glass transition.

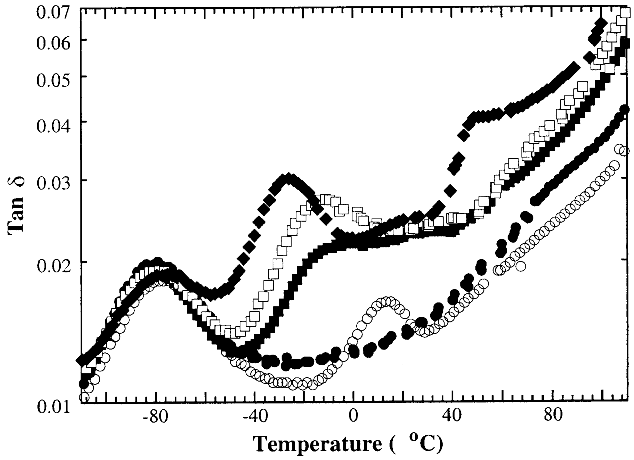

Fig. 2. Tan δ of PCL/polybenzoxazine blends at low and middle temperature region: (●) poly(BA-a); (○) 3 wt.% of PCL; (■) 11 wt.% of PCL; (□) 13 wt.% of PCL; and (◆) 15 wt.% of PCL in the blend.

3.2.3.1. Tan δ at low temperature region: γ-relaxation of poly(BA-a) and α, β*-relaxation of PCL.* The tan δ curves in the low-temperature range of polybenzoxazine/PCL blends are shown in Fig. 2. The position of tan δ peaks in the temperature range between −120 and −50°C did not vary much over the composition range. The temperature of the relaxation peak is generally related to the ease of rotational vibration of the groups [20] or how much thermal energy is needed to activate the transition. Consistent temperature positions suggest that the activation energy for the γ-relaxation remains almost unchanged. It was proposed by Ning and Ishida [15] that the γ-relaxation of polybenzoxazine was associated with the sub-motion of the side group on the Mannich bridge, which is a benzene ring in the poly(BA-a) structure. Since an interaction between PCL and this pendent group from polybenzoxazine is not likely, it is not surprising to see the temperature of γ-relaxation peak remaining constant regardless of the PCL content.

The magnitude of the γ-relaxation is determined by the number of groups per unit length [20] or the amount of the species which are involved in the transition process. Since it was evident that γ-relaxation of poly(BA-a) did not seem to be disturbed upon the addition of PCL, all other changes in loss factor peaks in this temperature regime will be mostly correlated to the β-relaxation of PCL, which is located in the same temperature range. We found that the intensity of the β-relaxation of PCL is approximately of the same order as that of the γ-relaxation of polybenzoxazine. Accordingly, if the dissipation factor can be predicted from the simple rule of mixtures, the damping ability in the low-temperature range will be expected to remain nearly unchanged as seen in Table 3.

The width of the damping behavior can be correlated to the temperature distribution at which the transition is activated and the area of peaks can provide some information about the overall number of molecular segments involved in the relaxation process. Thus, both values of the tan δ peak need to be analyzed for each blend in order to observe trends in this particular transition as the composition of the material is varied. The width and integrated intensity appear to be decreasing with the proportion of PCL modifier as summarized in Table 3 and are indicative of a reduction of chain segment mobility. As mentioned earlier, the in-chain motion of the amorphous phase is responsible for the β-relaxation of PCL. Hence, the less intense loss peaks with a narrower temperature distribution can be explained as the restricted molecular segments deriving from the strong interaction between amorphous PCL and poly(BA-a). Such a statement can be confirmed by our current study [14], which has demonstrated the intermolecular hydrogen bonding between the carbonyl groups of PCL and hydroxyl groups of polybenzoxazine even after the gelation.

The temperature range between −50 and 30°C is the location where the α-relaxation process of PCL modifier takes place. As seen in Fig. 2, considerably rich and complex activities were detected for tan δ in this region. Increased peak intensities accompanying with downshift of temperature positions upon the addition of PCL are clearly seen. Peak-shift in the dynamic properties is primarily derived from a strong interaction between components. Since the carbonyl groups from PCL are involved in intermolecular hydrogen bonding [14], the α-relaxation process

Table 3
Analysis of the tan δ curves of the DMA spectra at low- and high-temperature region by the peak height, integrated intensity, and the FWHH for each blend composition. The loss factor curve at the low-temperature range represents both the γ-relaxation of poly(BA-a) and the β-relaxation of PCL. The loss factor curve at the high temperature regime represents the α-relaxation of poly(BA-a)

Sample code	Peak height (low temp.)	Peak height (high temp.)	Integrated intensity (°C) (low temp.)	Integrated intensity (°C) (high temp.)	FWHH (°C) (low temp.)	FWHH (°C) (high temp.)
00PCL	0.02	1.1	1.4	39	47	50
03PCL	0.018	1	1.3	43	47	55
06PCL	0.019	0.8	1.2	45	40	70
08PCL	0.019	0.7	1.2	46	40	77
11PCL	0.019	0.7	1.1	46	38	77
13PCL	0.019	0.6	1.1	46	37	80
15PCL	0.019	0.7	1	29	35	60

of the PCL modifiers are expected to be hindered to some extent and requires a higher temperature to activate this relaxation process. Furthermore, it was also found that the fraction of hydrogen bonding diminished with increasing PCL content [14]. Therefore, higher transition temperature in the blends with lower PCL content is a result of greater amount of intermolecular hydrogen bonding formation in the amorphous state of PCL.

3.2.3.2. Tan δ at middle temperature region: β-relaxation of poly(BA-a) and melting behavior of PCL. The tan δ curves at middle temperature range of the blends are also illustrated in Fig. 2. As described before, the dynamic mechanical behavior in this regime can be correlated to the β-relaxation of polybenzoxazine. If we adopt the hypotheses from the literature [15], the weak relaxation process in this region can be attributed to two factors: one is unreacted molecular segments and the other is heterogeneity in the sample arising from dissimilar crosslink sites [5,10,15]. The curing process of PCL/polybenzoxazine blends have been investigated in situ by FTIR and quantitative analysis revealed that the addition of up to 33 wt.% of PCL could actually increase the degree of benzoxazine polymerization [14]. According to these results, it is reasonable to rule out the possibility that PCL would increase the amount of unreacted segments. It is suspected that the peak centered at 50°C is due to melting of PCL. This assignment could be further confirmed by our previous work [14] in which an endothermic melting peak was detected in a DSC scan at 48.5°C for this particular composition, and is also very close to the peak position obtained from the loss factor curve of PCL.

3.2.3.3. Tan δ and loss modulus at high-temperature region: α-relaxation of poly(BA-a). The tan δ curves of PCL blends at high-temperature region, which contain the α-relaxation of poly(BA-a) are shown in Fig. 3. Slight depression of the peak intensity upon the addition of PCL can be seen in Table 3. Since the damping property is the ratio of viscous to elastic components, it can be surmised that the reduced peak height is associated with a lower segmental mobility and fewer relaxation species, and thus is indicative of a higher degree of crosslinking for the blend sample [21]. Our FTIR analysis [14] has demonstrated that the extent of the benzoxazine polymerization was enhanced upon the incorporation of the PCL. Thus, we can attribute the decreased magnitude of the poly(BA-a) α-relaxation peak to a more extensive crosslinking as PCL is added into the resin.

The peak width at half-height increases with PCL concentration as seen in Table 3, which is the result of decreasing network homogeneity [21]. As PCL modifier is added into the benzoxazine, the temperature distribution at which different mobile network segments become activated has increased. While the peak height decreases and half width increases upon the addition of PCL, the overall peak area as shown in Table 3, which is the combination of these two effects, appears to increase. It is suggested that the total number of chain segments gaining mobility has increased. In other words, the active PCL species have a more pronounced effect over the tighter crosslinked network structure.

Generally, T_g is defined by the maximum of a G'' curve, which can be seen in Fig. 4 although it is somewhat easier to follow the trend in the tan δ curve than the G'' curve, particularly at higher blend concentrations [7]. Two factors need to be taken into consideration. First, the mechanical damping increases very rapidly and continuously with temperature as a result of the β-relaxation of polybenzoxazine, which ends near 130°C and, therefore, partially overlaps with the α-relaxation of poly(BA-a) in some blends. The other is correlated to the possible micro-phase or macrophase separation, which may broaden the temperature

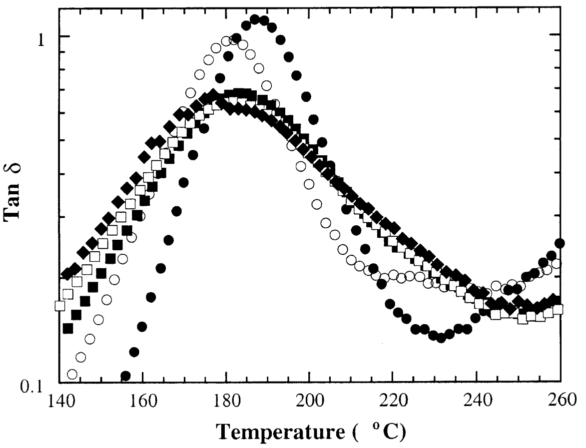

Fig. 3. Tan δ of PCL/polybenzoxazine blends at high temperature region: (●) Poly(BA-a); (○) 3 wt.% of PCL; (■) 11 wt.% of PCL; (□) 13 wt.% of PCL; and (◆) 15 wt.% of PCL. The DMA spectra at this temperature regime represent the α-relaxation of poly(BA-a).

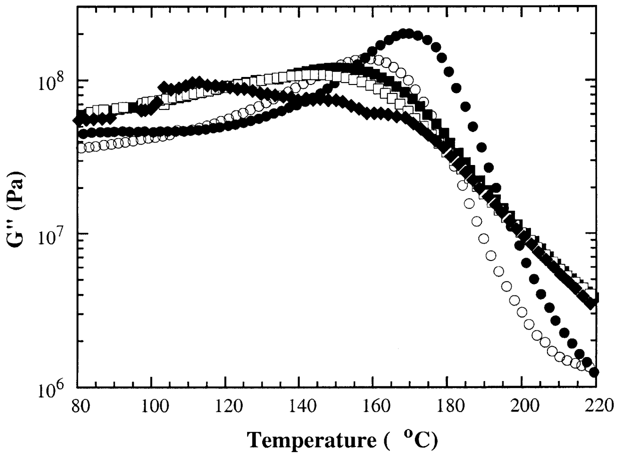

Fig. 4. G'' of PCL/polybenzoxazine blends at high-temperature region: (●) Poly(BA-a); (○) 3 wt.% of PCL; (■) 11 wt.% of PCL; (□) 13 wt.% of PCL; and (◆) 15 wt.% of PCL in the blend. DMA spectra at this temperature regime represent the α-relaxation of poly(BA-a).

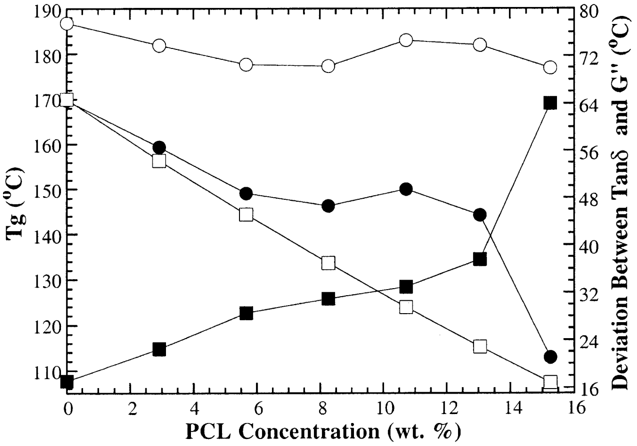

Fig. 5. T_gs of PCL/polybenzoxazine blends determined from maximum of the G'' curve: (●), tan δ curve (○), and Fox equation (□). The T_g discrepancy between the maximum of tan δ and G'' at α-relaxation (■) is also included in this plot.

distribution, derived from the individual dissipation mechanism of each component. The sample containing 15 wt.% PCL showed a broad maximum, which in part, is probably the result of the overlapped α-relaxation and melting transition as well as a more vigorous benzoxazine β-relaxation.

In a phase-separated system, a less symmetric band shape of the relaxation peak would be observed owing to the overlapping peaks from individual components. Apparently, the symmetry of the tan δ peak in the α-relaxation of polybenzoxazine was not altered much upon the addition of the PCL modifiers as seen in Fig. 3. Thus, it is easier to determine the peak position by tan δ. On the contrary, the G'' curves showed multiple peaks in the blend with highest PCL concentration (15 wt.%). Based on the literature, it is believed that the value of T_g from G'' will be several degrees less than that from tan δ [22]. However, it has been reported that the difference between these two values will vary significantly in blended systems [9]. The deviation is least in the pure material and increases dramatically with the proportion of the other component. This increased difference in the blend is in part due to the phase separation. The difference between tan δ and G'' in α-relaxation is plotted in Fig. 5 and shows an increased deviation in this blend system. Particularly, a much higher value of 64°C was observed in the blend with 15 wt.% of PCL where macrophase separation has occurred.

3.2.3.4. Storage modulus (G') at various temperatures. The modification by the second component would be expected to alter the dynamic mechanical properties of polybenzoxazine. Since the PCL modifier has a relatively low T_g, the effect of this softer inclusion on mechanical properties at various temperatures is of great interest. These results are summarized in Fig. 6. The modified samples with PCL content greater than 10 wt.% appeared to be very sensitive to temperature. At −100°C, which is the temperature higher than the T_g of PCL ($T < T_{g_{PCL}}$), much greater moduli were found in these samples over neat poly(BA-a). At room temperature ($T_{g_{PCL}} < T < T_{m_{PCL}}$), moduli of these three samples decrease dramatically. Yet, higher values are still observed in comparison with unmodified resin. As temperature increased to 100 and 150°C ($T < T_{m_{PCL}}$), a gradual reduction of modulus in magnitude upon the addition of PCL was finally seen.

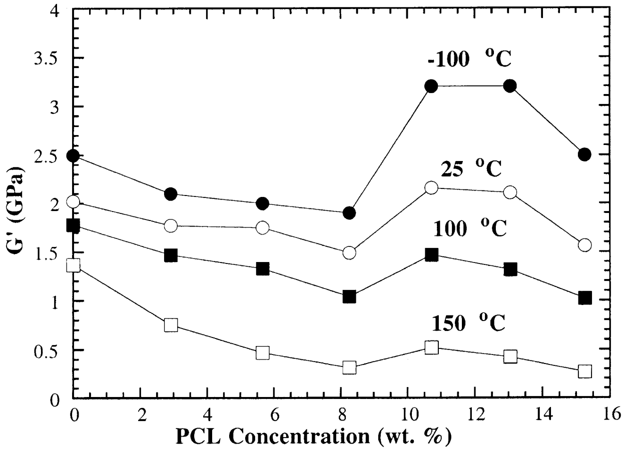

Fig. 6. Storage modulus (G') of PCL/polybenzoxazine blends as a function of PCL composition at various temperatures.

As shown in Fig. 7, all of the compositions except 15 wt.% PCL showed a visible rubbery plateau over a temperature range of 30°C for the blends with lower PCL content and 20°C for higher PCL content. It was reported that a short period of temperature of rubbery plateau is primarily derived from the thermal degradation. Influence from such possibility becomes more apparent during prolonged heating and can prevent accurate stable plateau modulus experiments from being performed [23]. In our blended system, the thermal stability of polybenzoxazine was demonstrated to improve upon the addition of PCL

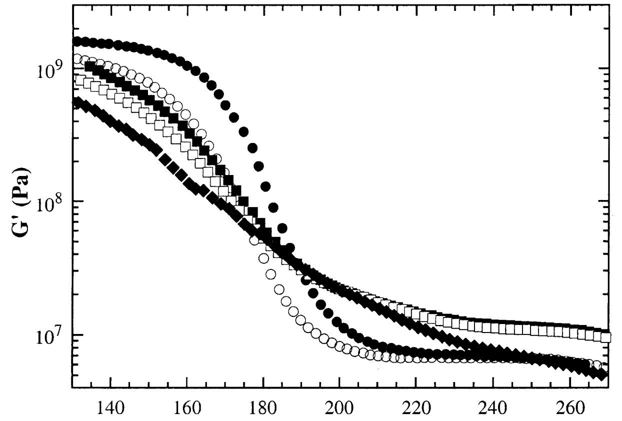

Fig. 7. G' of PCL/polybenzoxazine blends at high temperature region: (●) Poly(BA-a); (○) 3 wt.% of PCL; (■) 11 wt.% of PCL; (□) 13 wt.% of PCL; and (◆) 15 wt.% of PCL in the blend.

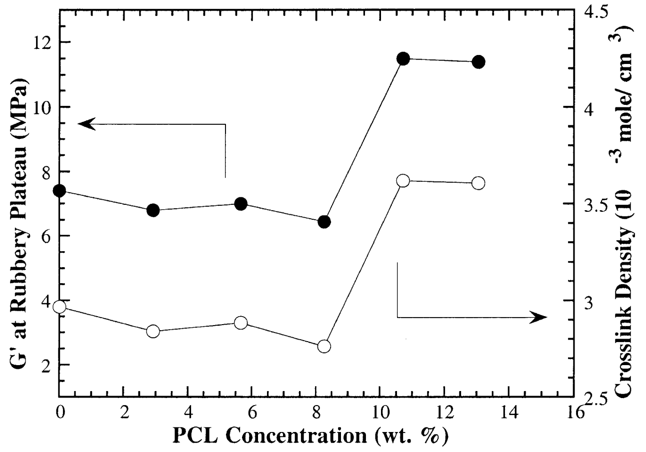

Fig. 8. Storage modulus (G') at rubbery plateau and crosslink density calculate from Nielson's equation.

modifier, which will be shown in the next section. Thus, rather stable plateau is a result of higher thermal stability. The storage moduli of the blends and neat polybenzoxazine resin in the rubbery region are determined by taking the value at the inflection point of the plateau and are presented in Fig. 8. An empirical formula to describe the molecular weight between crosslinks has been applied to higher crosslink density materials by Nielson [24,25]:

$$\log G' = 7.0 + 293(\rho/M_C) \tag{1}$$

where G' (dyne/cm^2) is elastic modulus in the rubbery plateau region, ρ (g/cm^3) the density of the material at room temperature, and M_C (g/mole) the molecular weight between crosslink points. While the rubber elasticity theory is strictly applicable only to lightly crosslinked materials, this empirical equation will provide means of comparison among blends with the same components. The crosslink densities as calculated by Nielsen's equation are also shown in Fig. 8. Clearly, the blend with 11 and 13 wt.% of PCL exhibited higher crosslink densities than neat poly(BA-a). As discussed earlier, a much higher extent of polymerization was obtained by the addition of PCL [14], which therefore, allows the formation of a tighter network structure.

3.3. Thermogravimetric analysis study

3.3.1. Polybenzoxazine

The thermal degradation behavior of polybenzoxazine (poly(BA-a)) can be monitored by the first derivative weight loss curve as a function of temperature using thermogravimetric analysis (TGA). As seen in Fig. 9, it is apparent that the unmodified polybenzoxazine resins based on bisphenol-A and aniline are dominated by three mechanisms during the thermal degradation. The rather intense primary degradation event is centered at 400°C, while secondary events are noticeable in the peak at 340°C and a broad shoulder from 450 to 550°C. The proposed mechanism as well as an analysis of the evolved gases from degrading polybenzoxazine have been fully discussed elsewhere [26,27].

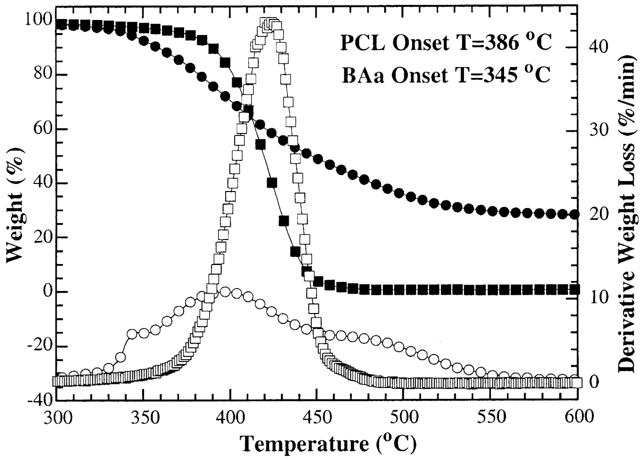

Fig. 9. TGA thermograms of unmodified polybenzoxazine resin, poly(BA-a): (●) weight loss and (○) first derivative of weight loss. TGA thermograms of neat polycaprolactone, PCL: (■) weight loss and (□) first derivative of weight loss.

3.3.2. Polycaprolactone

One of the primary advantages of poly(BA-a) is its high thermal stability. It was suspected that outstanding properties of the thermosetting resins would be sacrificed to some extent upon the addition of another softer and low-T_g component such as PCL. Thus, it is necessary to examine the thermal properties of the resulting blends using TGA. The TGA thermogram of neat PCL is also presented in Fig. 9. Inevitably, without the support of any rigid structure such as a benzene ring in the main chain, PCL underwent severe weight loss upon heating. A rate of weight loss of 43%/min and a residual weight of 0.4% were found in the PCL modifier. However, the onset and peak degradation temperatures appeared to be 40 and 24°C higher than neat polybenzoxazine resin, respectively.

3.3.3. Thermal stability of benzoxazine/PCL blends

From Fig. 10, it is clear that the modified system was still dominated by the three degradation mechanisms of polybenzoxazine, yet the peak positions have shifted. By the incorporation of PCL, which has higher onset and peak temperature than pure poly(BA-a), we might expect the thermal degradation of the modified system to be improved as seen in Fig. 11. The onset degradation temperature, determined by the tangent point of weight loss curves, and temperature at 1% weight loss shifted monotonically toward higher temperatures as the proportion of PCL modifier increased. Additionally, we also found that the rates of weight loss from the first and the second event still surprisingly remains the same. Thus, the modified system has a higher thermal stability in the medium temperature range from 250 to 450°C.

Char yield is typically defined as the total residual weight

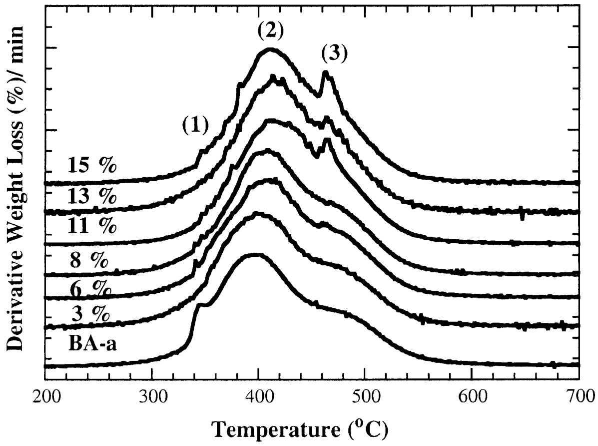

Fig. 10. First derivative of weight loss from TGA thermograms of the PCL/benzoxazine cured blends. Three thermal degradation events can be found at: (1) 340, (2) 400 and (3) 460°C. All the curves are displaced to be able to discern various compositions.

at 800°C under nitrogen. If the rule of mixtures applies, we can obtain the expected char yield from the equation below:

$$\mathrm{CY} = \mathrm{CY}^*_{\mathrm{B}}w + \mathrm{CY}^*_{\mathrm{M}}(1 - w) \tag{2}$$

where CY (%) is the char yield of the resulting blend and CY_B (%), CY_M (%) is the char yield of the pure polybenzoxazine resin and PCL modifier, respectively, and w is the weight fraction of the PCL in poly(BAa) blend. Calculated results are also plotted in Fig. 11 along with the experimental results. The experimental char yield is less than the expected value throughout the composition range studied, and their deviation increased significantly as PCL concentration is increased. Yet, the influence of the added PCL on the char yield is nearly undetectable (<1% reduction) in the blends with a PCL concentration less than 8 wt.%.

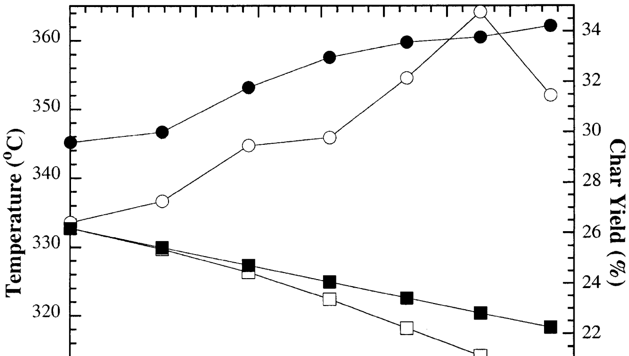

Fig. 11. Summary of thermal stability from TGA analysis: (●) onset degradation temperature and (○) temperature at 1% of weight loss in the cured PCL/benzoxazine blends. Residual weight at 800°C under nitrogen (char yield) of cured PCL/polybenzoxazine blends: (■) expected values were calculated based on a simple rule of mixture and (□) experimental data were obtained from TGA weight loss curves.

Table 4
Flexural properties

Sample	Flexural modulus (GPa)	Flexural strength (MPa)
00PCL	5.5 ± 0.2	93.5 ± 9
11PCL	3.9 ± 0.3	120.4 ± 7
15PCL	3.2 ± 0.1	140.2 ± 5

3.4. Flexural properties

The flexural properties of PCL-modified polybenzoxazine resins were examined and are given in Table 4. The flexural strength of neat polybenzoxazine resin showed a value of 93.5 MPa, which is comparable with commercial grade of epoxy resins (EPON) [28,29]. By the modification of PCL, significant amount of enhancement was observed. An improvement of 29% on the flexural strength was found with the addition of 11 wt.% of PCL. The use of high-performance thermoplastics has been considered as one of the most feasible approaches to improve the fracture toughness of thermosetting resins in comparison with the traditional rubber-toughening methods. For instance, poly(etherimide) (PEI), has been widely investigated as a toughener for epoxy. By curing epoxy precursor in the presence of 15 wt.% PEI polymer, 37% of improvement on the flexural strength was observed [28]. In our study, a dramatic value of 50% was demonstrated in the same amount of PCL modifier. It is once again the strong intermolecular interactions that optimize the toughening effect through the interfacial adhesion between the dispersed PCL phase and the benzoxazine matrix.

4. Conclusions

Poly(ε-caprolactone) (PCL) possesses the unique thermal properties of a low T_g temperature and melting temperature yet exhibits a relatively high thermal stability below 400°C as compared to most other low-T_g thermoplastic polymers. The former feature can facilitate the processing of this mixture simply by blending benzoxazine precursors with polycaprolactone polymer at a low temperature without the use of any additional solvent and the latter has demonstrated the ability to improve the thermal stability of the resulting blends over unmodified polybenzoxazine resin.

Two interesting features have been observed from dynamic mechanical measurement in the temperature range of -120 to 80°C. Less intense loss peaks with a narrower temperature distribution at β-relaxation of PCL and the tan δ peaks at PCL α-relaxation regime which shift toward higher temperature are both derived from the hydrogen bond formation between the hydroxyl groups of poly(BA-a) and the carbonyl groups of PCL. Both γ- and β-relaxation of polybenzoxazine did not seem to be altered much upon the incorporation of PCL. A suppressed damping property in magnitude at α-relaxation of polybenzoxazine is a result of a tighter crosslink structure with increased PCL content in the blend. However, increased peak width and area are both attributed to more mobile molecular segments at this relaxation process upon the addition of PCL.

Morphology of the blend system is demonstrated to play a crucial role in the final properties. The modified resins with 11 and 13 wt.% of PCL exhibited microphase separated structures and the blend with 15 wt.% of PCL appeared to be macrophase separated. A dramatic T_g discrepancy (64°C) determined from the maximum of tan δ and G'' curve in the blend with 15 wt.% of PCL further supported the occurrence of two-phase morphology in this particular composition.

Based on flexural properties of the modified resin along with TGA and DMA results, it is therefore concluded that the toughness improvement of cured polybenzoxazine can be achieved by using PCL as modifier without the reduction of any other thermal and mechanical properties.

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