

## Effects of polycaprolactone molecular weights on thermal and mechanical properties of polybenzoxazine

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**ABSTRACT:** Polymer blends of polybenzoxazine (PBA-a) and polycaprolactone (PCL) of different molecular weights ( $M_n = 10,000, 45,000, \text{ and } 80,000 \text{ Da}$ ) were prepared at various PBA-a/PCL mass ratios and their properties were characterized. The results from dynamic mechanical analyzer (DMA) revealed two glass transition temperatures implying phase separation of the two polymers in the studied range of the PCL contents. Moreover, a synergistic behavior in glass transition temperature ( $T_g$ ) was evidently observed in these blends with a maximum  $T_g$  value of  $281^\circ\text{C}$  compared with the  $T_g$  value of  $169^\circ\text{C}$  of the PBA-a and about  $-50^\circ\text{C}$  of the PCL used. The blends with higher  $M_n$  of PCL tended to provide greater  $T_g$  value than those with lower  $M_n$  of PCL. The modulus and hardness values of PBA-a were decreased while the elongation at break and area under the stress-strain curve were increased with an increase of the content and  $M_n$  of PCL, suggesting an enhancement of toughness of the PBA-a. Scanning electron micrographs (SEM) of the sample fracture surface are also used to confirm the improvement in toughness of the blends. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41915.

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### INTRODUCTION

Benzoxazine resins, a novel type of high-performance phenolic resin, can be obtained from the reaction of aldehyde (such as formaldehyde), phenol (or substituted phenols), and amine groups. To synthesize this kind of resin, there is no need of any used catalyst, curing agent, or solvent. In addition, there is no by-product generated when curing that leads to no void in the final products. The polybenzoxazine have gained great attention because of many excellent mechanical and physical properties. Moreover, it has been reported that the polymer possesses high thermal stability, high glass transition temperature ( $T_g$ ) with low water absorption and near zero shrinkage or expansion.<sup>1–7</sup> Furthermore, polybenzoxazines have good electrical insulating properties with ease of processing due to low melt viscosity of the polymers.<sup>8</sup> From these mentioned benefits, in the recent times the polymers have been produced and utilized in some industrial fields. For example, BA-a type benzoxazine monomer has been commercialized by Shikoku Chemical Corporation, Japan. In addition, polybenzoxazines with different backbones has been produced for aerospace purposes by Henkel Corpora-

tion, USA, etc.<sup>5</sup> However, one characteristic that could limit the polymers for some particular usages is their rather brittle nature. Alloying the brittle polybenzoxazine with other flexible monomers or polymers have been reported to enhance its cross-link density and mechanical properties in many blending systems such as benzoxazine/epoxy copolymer,<sup>7,9,10</sup> benzoxazine/epoxy/phenolic ternary systems,<sup>11–13</sup> poly(benzoxazine-urethane) alloys,<sup>8,14–16</sup> polybenzoxazine/dianhydride copolymer,<sup>17</sup> polybenzoxazine/ polycaprolactone blends.<sup>6</sup> Furthermore, there have been reports related to the enhancement of thermal and mechanical properties of polybenzoxazine blended with nature polymers.<sup>18,19</sup> In recent reports<sup>7,9,10</sup>, the alloys between benzoxazine resin and epoxy resin was proved to provide significant improvement on thermal and mechanical properties, flammability and processability of the polymers. Rimdusit *et al.*<sup>8</sup> reported the synergistic behaviors of glass transition temperature for the systems of benzoxazine and epoxy hybrids.

From our past work,<sup>9</sup> we have investigated thermal and mechanical properties of polybenzoxazine/urethane polymer alloys with different molecular weights of polyol. From this

investigation, we observed a significant enhancement in cross-link density of the polybenzoxazine with the presence of urethane resin. This leads to substantial enhancement in glass transition temperature of the resulting alloys although the urethane resin used is elastomeric in nature. In addition, when increasing molecular weight of the urethane polyol, there was no significant difference of degradation temperature ( $T_d$ ) at 5% weight loss, but the char yield of the alloys was increased.

In the blending system of bisphenol-A/methylamine-based benzoxazine resin (BA-m) and poly ( $\epsilon$ -caprolactone) (PCL), at fixed number average molecular weight ( $M_n$ ) of PCL at 10,000 Da, Huang and Yang reported that two glass transition temperatures ( $T_g$ s) were observed, indicating partial miscibility of the two polymers.<sup>6</sup> Furthermore, the presence of PCL provides synergistic behavior in glass transition temperature of the PBA-a i.e., maximum  $T_g$  of ca. 223°C in 40 wt % filled in PBA-a compared with the  $T_g$  value of ca. 185°C in PBA-a and  $T_g$  value of ca. -50°C in PCL. Despite of the observed synergy in  $T_g$  and other interesting features of this PBA-a/PCL system, the effects of molecular weights of the PCL components blended with PBA-a have not yet been studied. Therefore, in this study, the blends of polybenzoxazine/ polycaprolactone with different molecular weights and contents will be prepared and studied. Important thermal properties and mechanical properties of the polymer mixtures will be determined as well. It is expected that the toughness of the polybenzoxazine will be improved when different molecular weights of PCL were used.

## EXPERIMENTAL

### Raw Materials

Bisphenol-A (AR grade), para-formaldehyde (AR grade), and aniline (AR grade) were purchased from Sigma-Aldrich. Polycaprolactone of three different number average molecular weight ( $M_n$ ) of 10,000, 45,000, and 80,000 Da (denoted as 10 K, 45 K, and 80 K, respectively) were obtained from Sigma-Aldrich. All raw materials were used without further purification.

### Synthesis of Benzoxazine Monomer

Benzoxazine monomer (BA-a) was synthesized from bisphenol-A, paraformaldehyde, and aniline at a molar ratio of 1 : 4 : 2. The mixture was heated at 110°C for about 45 min to yield a light yellow solid monomer product according to the patented solventless method.<sup>20</sup> The product was then ground into fine powder and kept in a refrigerator for future use.

### Preparation of Benzoxazine-Polycaprolactone Blends

BA-a monomer and PCL were blended at various mass ratios i.e., BA-a/PCL = 100/0, 90/10, 80/20, 70/30, 60/40, and 0/100. The mixtures were blended thoroughly in an internal mixer and heated at 110°C with a rotation speed of 40 rpm for 10 min. After homogeneous mixture was obtained, a step heating program used for sample curing was 140°C (1 h), 160°C (1 h), 180°C (1 h), 200°C (2 h), 220°C (2 h), and 240°C (1 h). All the specimens were finally left to cool down to room temperature before characterizations.

### Sample Characterizations

**Optical Microscopy.** The solution of polycaprolactone and its blends in tetrahydrofuran (THF) was heated at 60°C and left

to cool down to room temperature before obtaining its micrographs using an optical microscope (Nikon, model ECLIPSE E600POL). The micrographs of the crystal of PCL at different molecular weights were obtained with 200 $\times$  magnification.

**Differential Scanning Calorimetry.** The crystallinity percentage of PCL with different molecular weights was determined using differential scanning calorimeter (DSC) (Mettler Toledo, model DSC822<sup>c</sup>). The PCL samples of  $\sim$ 10 mg were placed on the 40 mL of aluminum pan and heated from the temperature of -40 to -100°C at heating rate of 20°C/min. After that, the samples were left to room temperature with cooling rate of 20°C/min. The second heating was conducted from -40 to 100°C with the same heating rate. The nitrogen flow rate was kept at 100 mL/min.

**Fourier Transform Infrared Spectroscopy.** Chemical structure and network formation behavior of samples were investigated by Fourier transform infrared spectroscopy (FTIR). The infrared spectra of all samples were obtained using a Spectrum GX FT-IR spectrometer from Perkin Elmer Instrument with an ATR accessory. All spectra were taken with 64 scans at a resolution of 4 cm<sup>-1</sup> and a spectral range of 4000–600 cm<sup>-1</sup>.

**Dynamic Mechanical Analysis.** Dynamic mechanical analyzer (DMA model DMA242, NETZSCH, Germany) was used to investigate dynamic mechanical properties of PBA-a/PCL blends. The test in flexural mode was performed at a fixed frequency of 1 Hz with temperature range of -100°C to 300°C and a heating rate of 2°C/min under nitrogen atmosphere.

**Mechanical Property Investigation.** Flexural modulus, elongation at break, and area under the stress-strain curves or toughness of the specimens were determined according ASTM D790 applying a Universal Testing Machine, Instron, Model 5567 equipped with a 1 kN load cell. The measurement was performed in a 3-point bending mode with a support span of 48 mm and at a crosshead speed of 1.2 mm/min. The average values from a minimum of five samples with a dimension of 25  $\times$  60  $\times$  3 mm<sup>3</sup> were determined.

**Microhardness Measurement.** The microhardness of samples was analyzed using Vickers hardness tester (Future-Tech Corp FM-700, Tokyo, Japan) at a load of 4.9 N (500 gf) and dwell time of 15 s. Diagonal length measurement of the indentation was performed through a micrometric eyepiece with objective lens (50 $\times$  magnification). The average values from ten readings were then reported.

**Thermogravimetric Analysis.** Thermogravimetric analysis (TGA) of PBA-a/PCL polymer blends was carried out using a Perkin Elmer's TG/DTA thermogravimetric analyzer, model SII Diamond. The specimen ( $\sim$ 10 mg) was heated from 30 to 850 C at a dynamic heating rate of 20°C/min under nitrogen purge using a flow rate of 50 mL/min.

**Microstructure Characterization.** Scanning electron microscope (SEM, JEOL, model JSM-5410LV, Japan) was used to investigate morphology of the sample fracture surface with an accelerating voltage of 15 kV and emission current of 10 mA. The fracture surface of a specimen was sputter-coated with gold at the

thickness in the range of 10 to 20 nm with an electric current of 15 mA at 6 Pa for 180 s with a sputter coater (Balzers model SCD 040).

## RESULTS AND DISCUSSION

### Spherulite Appearance and Crystallinity Percentage of PCL

Figure 1(a'–c') present the optical microscope images of pure PCL (10 K, 45 K, and 80 K, respectively) dissolved in THF solvent and placed on a glass substrate. After heating above their melting temperatures and leaving to cool down to room temperature, the micro-images were taken. It could be noticed that PCL with lower molecular weight tended to provide larger spherulite size, i.e., the 10 K PCL provided the largest spherulites, while the 80 K PCL provided the smallest ones. Moreover, the spherulites showed less open and finer texture with an increase of molecular weight of PCL. Figure 1(a–c) exhibit the texture of the spherulite after blending PBA-a with 40 wt % of PCL (10 K, 45 K, and 80 K, respectively) and partial curing at 200°C for 15 min. It was found that the texture of the PCL spherulites became finer and more irregular when the PBA-a was incorporated. The behavior is attributed that the incorporation of the amorphous PBA-a could substantially disturb crystallization of PCL. This phenomenon was also observed in the blends of PCL and Novolac.<sup>21</sup> Moreover, it was also found that sizes of the spherulites at higher  $M_n$  of PCL were smaller than those at lower  $M_n$ . When further heated as seen in Figure 1(d), the spherulites of the fully cured blends for all PCL contents and molecular weights were disappeared, i.e., the complete polymerization of thermoset made it difficult for the optical microscope to observe the spherulites. In addition, PCL with low molecular weight tended to easily form crystal structure, which leads to easiness for phase separation. The percentage of crystallinity for different molecular weights of PCL was determined using DSC technique. The melting temperature ( $T_m$ ) and crystalline temperature ( $T_c$ ) of each PCL type were reported as presented in Table I.

The percentage of crystallinity were calculated as shown in the following eq. (1)<sup>21</sup>

$$X_C = \left( \frac{\Delta H_M - \Delta H_C}{\Delta H_M^0} \right) \times 100 \quad (1)$$

where  $X_C$  is percentage of crystallinity,  $\Delta H_M$  and  $\Delta H_C$  are the enthalpy of melting and crystallization, respectively, and  $\Delta H_M^0 = 136$  J/g (melting enthalpy for 100% of crystalline PCL).<sup>22</sup> From Table I, it could be indicated that the percentage of crystallinity for low molecular weight PCL was higher than that for high molecular weight PCL, i.e., the  $X_C$  values of 10 K, 45 K, and 80 K were 78.4, 67.9, and 59.9, respectively. This is correspondence to the appearance of PCL spherulites observed via optical microscope.

### Intermolecular Interaction Between PBA-a and PCL

In general, FTIR spectrum could provide the information of hydrogen bonds between polybenzoxazine (PBA-a) and polycaprolactone (PCL).<sup>21,23</sup> There are two regions of interest to be observed. i.e., 1760–1690  $\text{cm}^{-1}$  (carbonyl groups) and 3710–2790  $\text{cm}^{-1}$  (hydroxyl groups) as presented in Figures 2 and 3, respectively. All spectra of these two figures were normal-

ized based on the 1384  $\text{cm}^{-1}$ , assigned to the methyl group of bisphenol A.<sup>24</sup>

As seen in Figure 2, two bands have been noticed in this region. The first one is centered at 1728  $\text{cm}^{-1}$ , indicating the non-hydrogen bond carbonyl groups.<sup>23,25</sup> The second one is rather weak band centered at  $\sim 1703$   $\text{cm}^{-1}$  which attributed to the hydrogen bond carbonyl groups of PCL.<sup>23</sup> As calculated from the following equation, the percentages of hydrogen bond carbonyl groups were obtained.

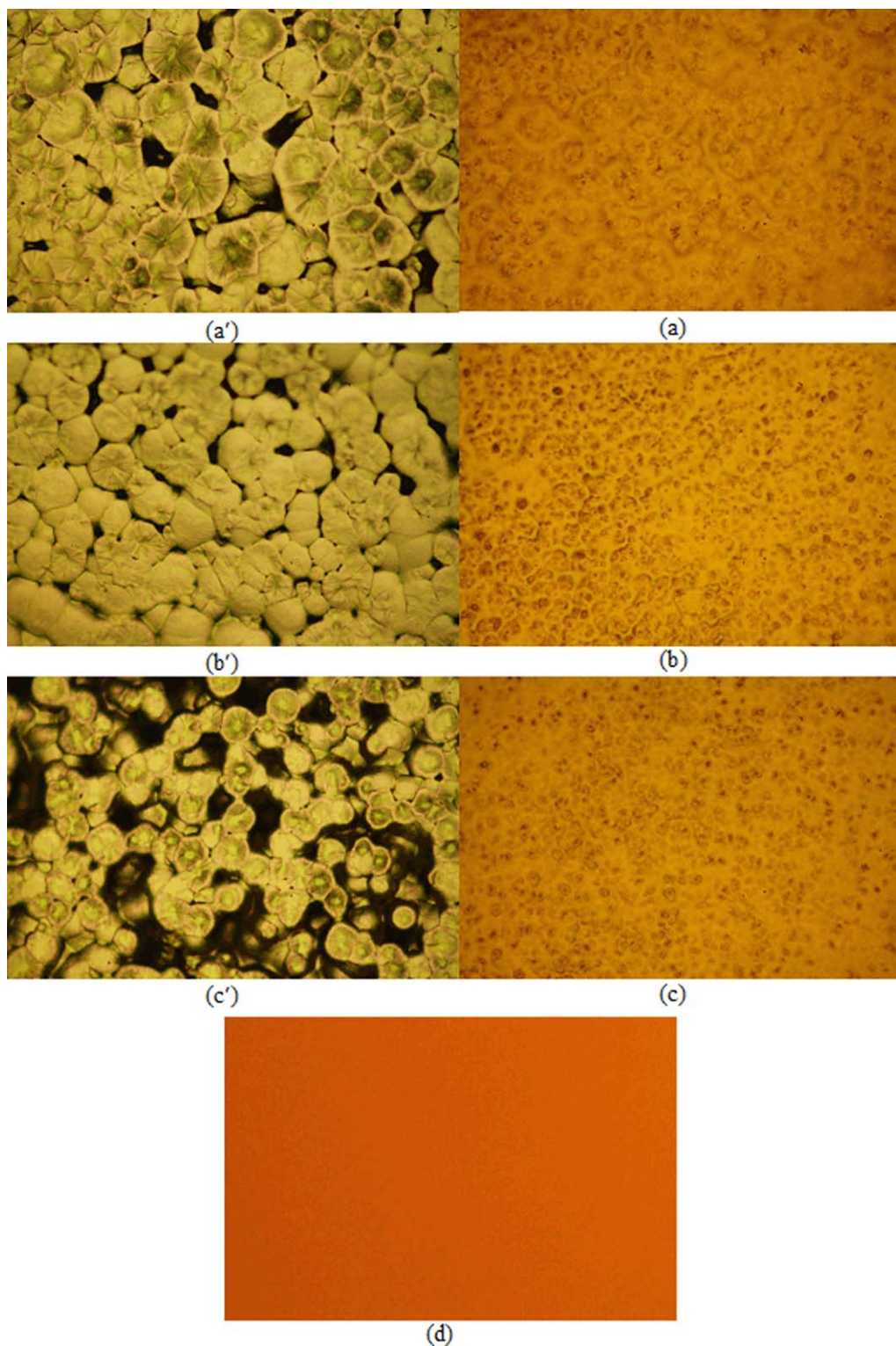
$$\text{Hydrogen Bond Carbonyl Group (\%)} = \frac{A_b}{(A_b + A_a)} \times 100 \quad (2)$$

where  $A_a$  and  $A_b$  are the absorbance intensity of the non-hydrogen bond carbonyl groups and of the hydrogen bond carbonyl groups, respectively. The percentages of hydrogen bond carbonyl group of the blends for 45K PCL with 10, 20, 30, 40 wt % are  $\sim 34$ , 29, 27, and 25%, respectively. It could be seen that the addition of PCL could lead to the decrease of percentage of hydrogen bond. This phenomenon is attributed to the fact that higher PCL content leads to higher phase segregation between two domains. That could decrease the possibility of molecular interaction.<sup>23</sup> In addition, the hydrogen bond carbonyl groups of the blends at 20 wt % with 10 K, 45 K, and 80 K reveal the values of 36, 29, and 21%, respectively. This could be because the higher molecular weight provides greater phase separation as following the modified Flory-Huggins solution theory as following.<sup>26</sup>

$$\Delta G_m = RT \left[ \frac{\phi_A}{M_A} \ln \phi_A + \frac{\phi_B}{M_B} \ln \phi_B + \phi_A \phi_B \chi_{AB} \right] + \Delta G_H \quad (3)$$

where  $\phi_A$ , and  $\phi_B$  are the volume fractions of polymers A and B, respectively.  $M_A$ , and  $M_B$  are molecular weight of polymers A and B, respectively.  $\Delta G_m$  is a change of Gibbs free energy of mixing between polymers A and B.  $R$  is a gas constant, and  $T$  is an absolute temperature.  $\chi_{AB}$  is a Flory-Huggins interaction parameter, related to the nonhydrogen-bonded solubility parameters based on the Scatchard-Hildebrand relation. The last term is relevant to the hydrogen-bonding interactions to mixing. In case that PCL possesses high molecular weight, the  $M_A$  in the eq. (3) is great, which makes the first term in the blanket on the right hand side is close to zero. The last term denoted as  $\Delta G_H$  is important to the miscibility of polymer blends.<sup>26</sup> That means the great opportunity for phase separation. Additionally, from the literatures,<sup>27,28</sup> the difference of hydrogen bonding plays an crucial role on the physical and mechanical properties.

Figure 3 presents the FTIR spectra of the PBA-a/PCL mixtures in the high wavenumber range (3700–2800  $\text{cm}^{-1}$ ) which is the stretching region of hydroxyl groups. The spectrum in this region of pure benzoxazine was found to compose of two components: a broad band centered at 3371  $\text{cm}^{-1}$  assigned to the self-associated hydroxyl group with hydrogen bonding<sup>29</sup> and a comparatively narrow band at 3463  $\text{cm}^{-1}$  attributed to free hydroxyl groups. In the presence of PCL, there was no significant shift of the wavenumber assigned to nonassociated hydroxyl band at low PCL content. The slight shift of wavenumber (from 3372 to 3379  $\text{cm}^{-1}$ ) contributed to nonassociated



**Figure 1.** Optical Micrographs of PBA-a/PCL blends in THF solvent ( $\times 200$  magnification): (a') Pure 10 K PCL, (b') Pure 45 K PCL, (c') Pure 80 K PCL, (a) 10 K 40 wt %, (b) 45 K 40 wt %, (c) 80 K 40 wt %, and (d) fully cured PBA-a/PCL blend (45 K 40 wt %). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

hydroxyl band was found in the high PCL content. However, the shift of wavenumber assigned to free hydroxyl groups was significantly increased with PCL content. This phenomenon identifies the hydrogen bonding between the hydroxyl group of

benzoxazine and carbonyl groups of PCL. In comparison on the mixture modified with PCL at the same content, it is worthy to note that the decreasing shift of wavenumber (assigned to free hydroxyl group) was found to increase with PCL molecular

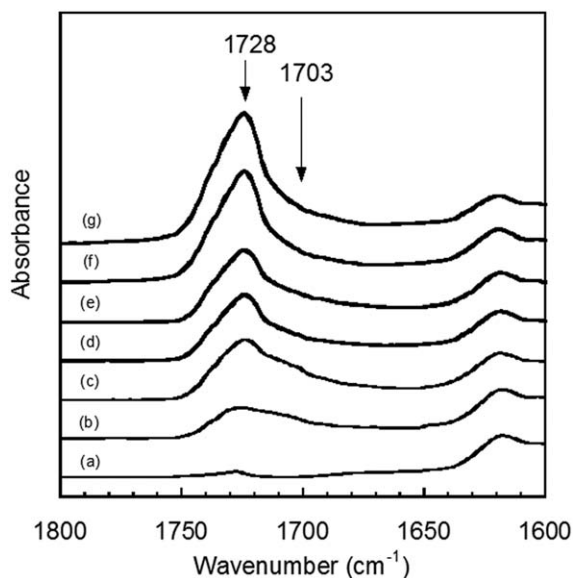
**Table I.** Melting Temperatures, Crystallization Temperature, Enthalpy of Melting, Enthalpy of Crystallization, and Crystallinity Percentage of PCL with Different Molecular Weights

$M_n$ of PCL (Da)	$T_m$ (°C)	$\Delta H_M$ (J/g)	$T_c$ (°C)	$\Delta H_C$ (J/g)	$X_c$ (%)
10,000	56.0	76.0	20.3	-30.6	78.4
45,000	57.3	65.1	18.3	-27.3	67.9
80,000	62.7	58.9	14.3	-22.4	59.9

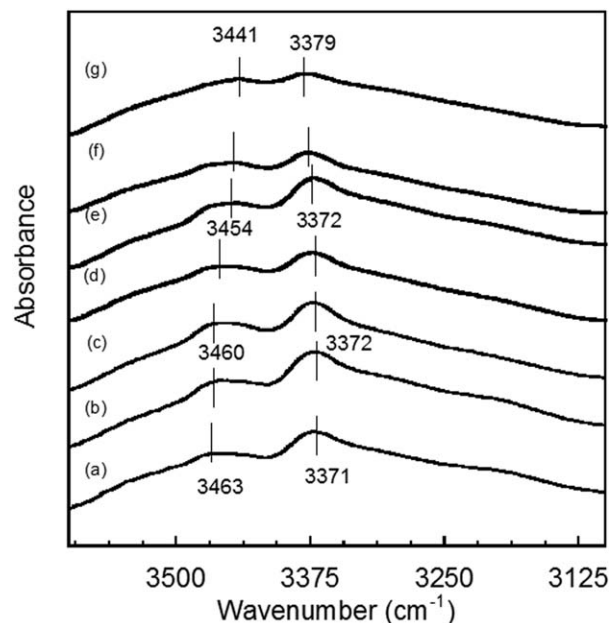
weight, i.e.,  $3460\text{ cm}^{-1}$  (for 10,000 Da) to  $3454\text{ cm}^{-1}$  (for 80,000 Da). That means the hydrogen bonding between the hydroxyl groups and the carbonyl group tended to decrease with the increase of the  $M_n$  of PCL. This result is similar to that was found in the system of Novolac and PCL.<sup>21</sup>

### Effects of PCL Molecular Weights on Dynamic Mechanical Properties

Dynamic mechanical analysis (DMA) of PBA-a/PCL at various PCL contents and molecular weights (10 K, 45 K, and 80 K) were conducted as a function of temperature. The storage modulus for the blends (with fixed  $M_n$  of 45 K) at various PCL contents were illustrated in Figure 4(a). It could be found that at  $-100^\circ\text{C}$  the addition of PCL leads to the decrease of storage modulus. When increasing the temperature, the storage modulus varies within the first glassy state of the curve. However, a drastic decrease was observed when the change in the segmental moving relevant to the glass transition. At the room temperature ( $25^\circ\text{C}$ ), the storage modulus of neat PBA-a was exhibited at 5.3 GPa. The values was decreased to 4.4, 3.5, 2.6, 2.4 GPa at 10, 20, 30, and 40 wt % of PCL, respectively. This could be attributed to the plasticizing nature of PCL incorporated in the system.<sup>30</sup> After further heating to  $\sim 60^\circ\text{C}$ , the value of storage



**Figure 2.** FTIR spectra over the region from  $1800$  to  $1600\text{ cm}^{-1}$  for the BA-a/PCL mixtures at various PBA-a/PCL weight ratios: (a) pure PBA-a, (b) 45 K 10 wt %, (c) 10 K 20 wt %, (d) 45 K 20 wt %, (e) 80 K 20 wt %, (f) 45 K 30 wt %, and (g) 45 K 40 wt %.



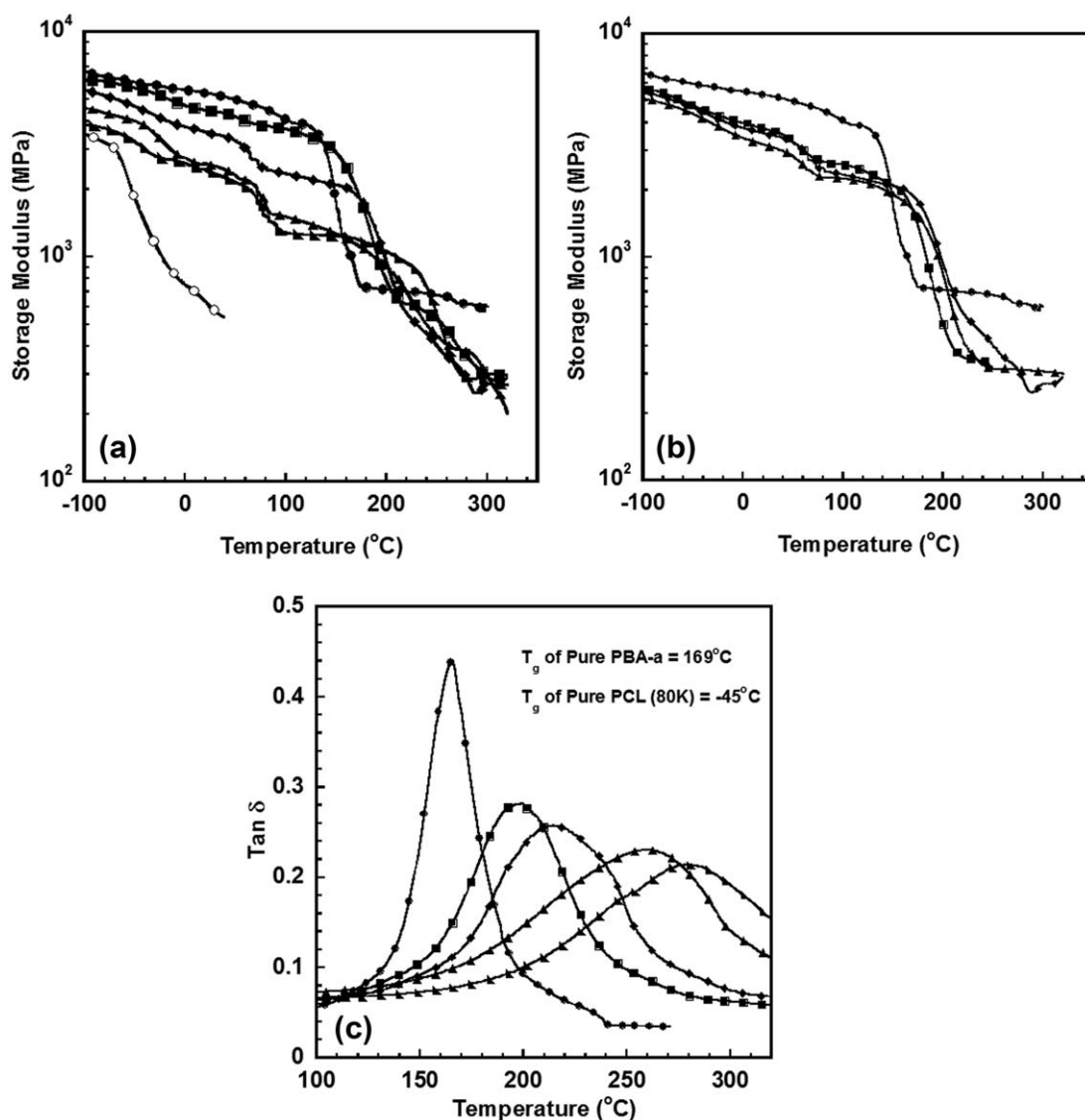
**Figure 3.** FTIR spectra over the region from  $3600$  to  $3100\text{ cm}^{-1}$  for the BA-a/PCL mixtures at various PBA-a/PCL weight ratios: (a) pure PBA-a, (b) 45 K 10 wt %, (c) 10 K 20 wt %, (d) 45 K 20 wt %, (e) 80 K 20 wt %, (f) 45 K 30 wt %, and (g) 45 K 40 wt %.

modulus obviously decreased due to the melting temperature of PCL. Beyond the melting temperature, the storage modulus was again found to be drastically decreased at the glass transition in high temperature region. This phenomenon corresponds to the work of Huang and Yang<sup>6</sup> studying the system of benzoxazine (B-m type) and PCL with  $M_n$  of 10 K.

Figure 4(b) presents the storage modulus of the blends at 20 wt % of PCL at the room temperature were slightly decreased with increasing molecular weight, i.e., the value of pure PBA-a (5.3 GPa) decreased to be 3.7, 3.5, and 3.1 GPa for the blend of 10 K, 45 K, and 80 K, respectively. It was attributed to the basic principle that the addition of the rubbery PCL into the rigid PBA-a can decrease the stiffness of the obtained blends. Furthermore, the storage modulus of pure PCL (10 K, 45 K, and 80 K) from our experiment, are 0.7, 0.6, and 0.5 GPa, respectively.

Figure 4(c) presents the loss tangent ( $\tan \delta$ ) of the blends at  $M_n$  of 80 K. The glass transition temperatures obtained from the peak of loss tangent for different  $M_n$  of PCL were summarized in Table II. It could be seen that the synergistic behaviors of  $T_g$  were observed with different degrees of  $T_g$  shifting. At the same PCL content, the higher PCL molecular weight provided greater degree of  $T_g$  shifting. For instance, the  $T_g$  value of pure PBA-a was exhibited at  $168.8^\circ\text{C}$ , while those of the blends at 40 wt % for 10 K, 45 K, and 80 K were shifted to be  $245.4$ ,  $274.5$ , and  $281.3^\circ\text{C}$ , respectively. This could be because the segmental mobility of the blends with higher molecular weight could be hindered by greater intramolecular force.<sup>23</sup>

Figures 5(a,b) exhibit the glass transition temperatures of the blends with different molecular weights in the high and low temperature regions, respectively. It could be noticed that the PBA-a/PCL mixtures at all compositions revealed two glass

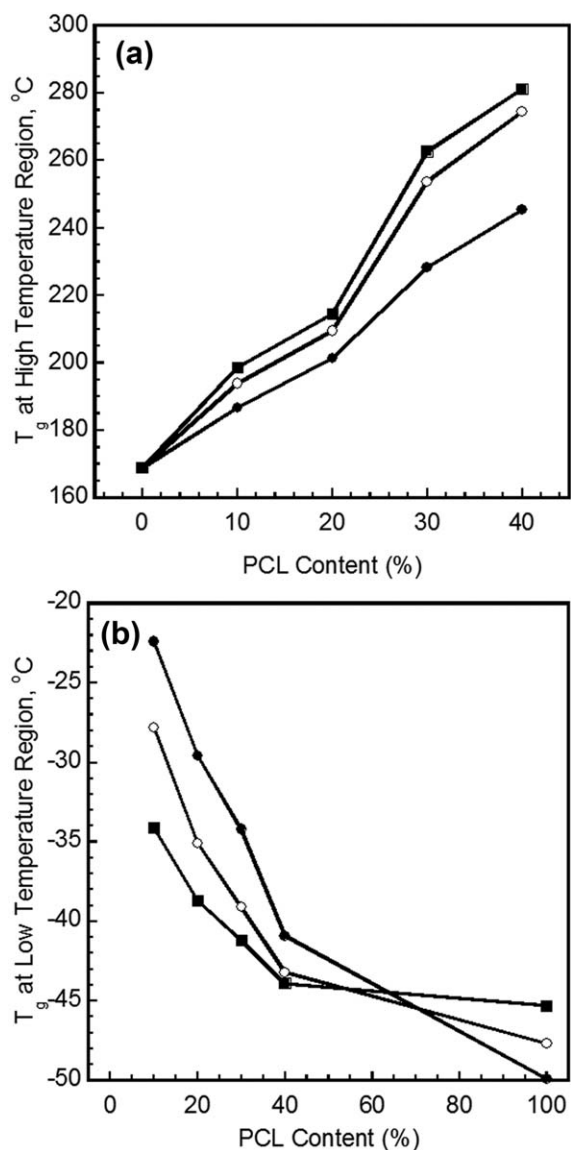


**Figure 4.** (a) Storage modulus of PBA-a alloys modified with PCL ( $M_n = 45,000$  Da): (•) pure PBA-a, (■) 10 wt %, (◆) 20 wt %, (▲) 30 wt %, (▼) 40 wt %, and (○) pure PCL. (b) Storage modulus of PBA-a alloys modified with 20 wt % of PCL: (•) pure PBA-a, (■) 10 K, (◆) 45 K, and (▲) 80 K. (c) Loss tangent of PBA-a alloys modified with PCL ( $M_n = 80,000$  Da): (•) 0 wt %, (■) 10 wt %, (◆) 20 wt %, (▲) 30 wt %, and (▼) 40 wt %.

transition temperatures, which presents phase segregation between two domains. This phenomenon is corresponding to the report of Ishida and Lee studying the system of BA-a and poly( $\epsilon$ -caprolactone) ( $M_n = 35,000$ – $45,000$  Da) at the content of 0–15 wt %. They reported that the phase separation was observed at the poly( $\epsilon$ -caprolactone) content at least ca. 10 wt %.<sup>23</sup> In the system of polybenzoxazine (B-m type) and PCL ( $M_n = 10,000$  Da), it was reported that the blending system revealed partial miscibility.<sup>6</sup> From Figure 5(a) and Table II, all mixtures of PBA-a/PCL presented the synergistic behaviors of  $T_g$  at high temperature region. In other words, the  $T_g$  of the mixture was higher than those of parent polymers, i.e.,  $168.8^\circ\text{C}$  (for pure PBA-a) and  $-49.9$ ,  $-47.7$ , and  $-45.3^\circ\text{C}$  (for 10 K, 45 K and 80 K, respectively). The  $T_g$  of the mixture was increased with PCL content. For example, in the presence of 80 K PCL, the  $T_g$  values at 10, 20, 30, and 40 wt % were found to be

**Table II.** Glass Transition Temperatures of the PBA-a/PCL Blends

PCL content (wt %)	Glass transition temperature ( $^\circ\text{C}$ )					
	10 K	45 K	80 K	10 K	45 K	80 K
0	–	168.8	–	168.8	–	168.8
10	–22.4	186.6	–27.8	193.8	–34.1	198.6
20	–29.6	201.3	–35.1	209.5	–38.7	214.6
30	–34.2	228.3	–39.1	253.8	–41.2	262.7
40	–40.9	245.4	–43.2	274.5	–43.9	281.3
100	–49.9	–	–47.7	–	–45.3	–



**Figure 5.** (a) Glass transition temperature of PBA-a modified with PCL of different molecular weights in high temperature region: (●) 10,000 Da, (○) 45,000 Da, and (■) 80,000 Da. (b) Glass transition temperature of PBA-a modified with PCL of different molecular weights in low temperature region: (●) 10,000 Da, (○) 45,000 Da, and (■) 80,000 Da.

198.6, 214.6, 262.7, and 281.3 °C, respectively. Moreover, at same PCL content, the blends with high PCL molecular weight provided significantly higher  $T_g$  than those with low PCL molecular weight. This phenomenon could be due to low free volume of molecular motion in case of either high PCL content or high molecular weight.<sup>6</sup> In Figure 5(b) and Table II, pure PCL with higher molecular weight provided higher  $T_g$  value due to the lower mobility of long polymer chains. In case of the blends for all PCL molecular weights, the shift of  $T_g$  value in low temperature region was decreased with increasing PCL content. For the blends with 10 K, the  $T_g$  at 10 wt % was –22.4 °C (27.5 °C higher than pure PCL), while that at 40 wt % was –40.9 °C (9.0 °C higher than pure PCL). This could be because the miscibility at high PCL content was lower than that at low content.

**Table III.** Rubbery Plateau Moduli and Crosslink Densities of the PBA-a/PCL Blends

	Rubbery plateau modulus (MPa)	Crosslink density (mol/cm <sup>3</sup> )
pure PBA-a	713	9737
10 K 40 wt %	403	8892
45 K 10 wt %	610	9506
45 K 20 wt %	459	9085
45 K 30 wt %	375	8787
45 K 40 wt %	284	8375
80 K 40 wt %	266	8276

In this partially miscible system, the  $T_g$  in the low temperature region (from the PCL rich domain) shift toward the  $T_g$  of pure polybenzoxazine. The shifting degree of  $T_g$  was related to the degree of miscibility. Furthermore, at the same PCL content, the blends with higher PCL molecular weight tended to provide lower shift of  $T_g$ . At 10 wt %,  $T_g$  of the blend of 10 K was –22.4 °C (27.5 °C higher than pure 10 K PCL), while that of the blend of 80 K was –34.1 °C (11.2 °C higher than pure 80 K PCL). The PCL with higher molecular weight provided lower miscibility to polybenzoxazine due to greater phase segregation.

The effects of PCL content and molecular weight on the crosslink density of the blending network can be calculated from the rubbery plateau storage modulus at  $T_g + 30$  °C as followed to eq. (4) derived from Nielsen's theory.<sup>31</sup>

$$\log(G_r') = 6.0 + 293(\rho_x) \quad (4)$$

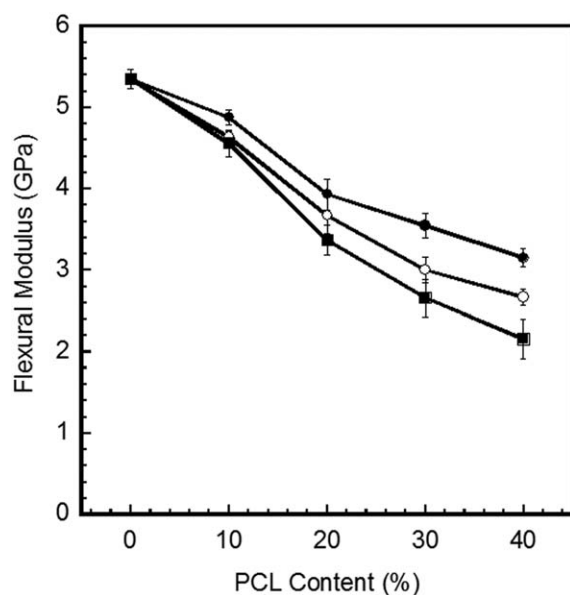
where  $G_r'$  is an equilibrium value of rubbery plateau modulus ( $P_a$ ) and  $\rho_x$  is the crosslink density (mol/cm<sup>3</sup>). As presented in Table III, it could be noticed that at the same PCL content, the rubbery plateau storage modulus and crosslink density were decreased with PCL molecular weight. In addition, these values were decreased with PCL contents. This phenomena could be due to the plasticizing nature of PCL as previously mentioned.<sup>30</sup>

#### Mechanical Property Determination of the PBA-a/PCL blends

In general, elongation at break and area under the stress–strain curve are able to describe the toughness properties of the tested specimen, i.e., the tough polymers typically provide high values. Table IV reveals elongation at break, area under the

**Table IV.** Elongations at Break, Flexural Strengths, and Areas Under the Stress–Strain Curves

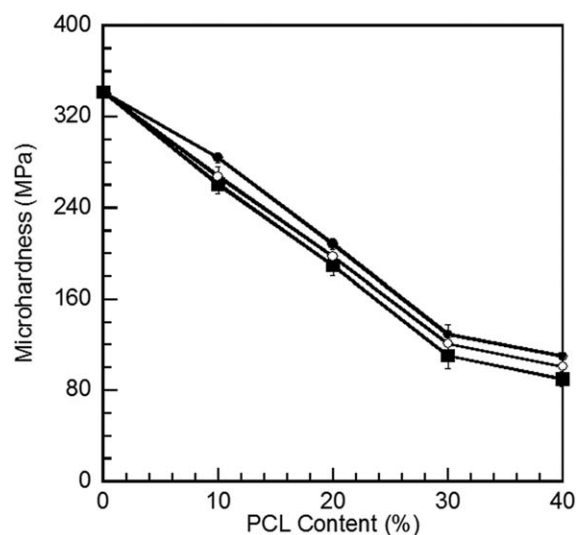
Sample	Elongation at break (%)	Area under the curve (MPa)	Flexural strength (MPa)
Pure BA-a	1.7	42.1	145.6 ± 8.7
10 K 10 wt %	3.2	137.9	125.0 ± 5.4
45 K 10 wt %	2.4	109.7	125.2 ± 5.4
80 K 10 wt %	2.0	59.8	126.3 ± 5.5
80 K 20 wt %	2.2	62.2	114.3 ± 8.3
80 K 40 wt %	3.4	73.1	87.2 ± 7.2



**Figure 6.** Flexural modulus of PBA-a/PCL alloys with different molecular weights of PCL: (•) 10,000 Da, (○) 45,000 Da, and (■) 80,000 Da.

stress–strain curve, and flexural strength of the PBA-a/PCL blends at different molecular weights and contents of PCL. The elongation at break and the area under the stress–stress curve of pure PBA-a present the values of 1.69% and 42.1 MPa, respectively, which revealed the brittleness of the polybenzoxazine. At the same PCL content, the mixtures with lower  $M_n$  of PCL provided significantly higher elongation at break and area under the curve, exhibiting more toughness. It is worthy to note that the elongation at break and the area under the stress–strain curve of pure PBA-a were increased for  $\sim 187\%$  (from 1.69 to 3.16%) and 328% (from 42.1 MPa to 137.9 MPa), respectively, when the 10 K PCL was applied at 10 wt %. Moreover, at the same molecular weight, the elongation was increased with PCL, i.e., when the 80 K PCL was applied at 10, 20, and 40 wt %, the elongation of the PBA-a was increased for 117%, 131%, and 201%, respectively. While the area under the curve of PBA-a was increased for 142%, 148%, and 174%, respectively. Moreover, it could be noticed that the flexural strength of polybenzoxazine was decreased with the increase of PCL because of low flexural strength of PCL in nature. Additionally at the same PCL content, there was no significant difference between the strength of the blends with different PCL molecular weights.

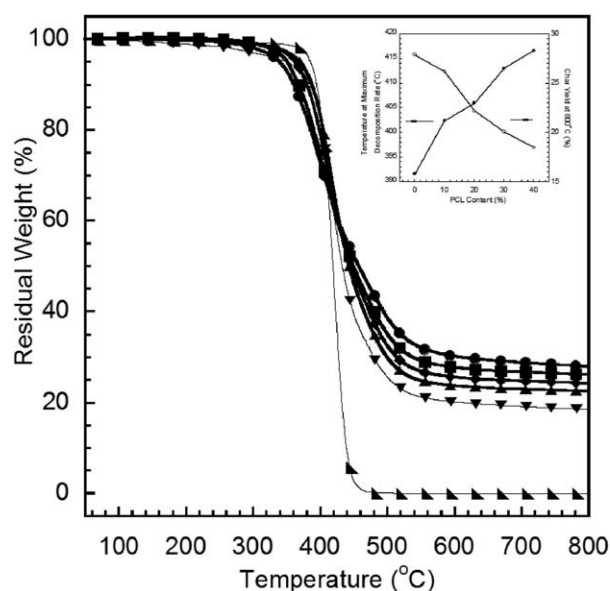
Figure 6 exhibits the flexural modulus of the blends of PBA-a/PCL with different  $M_n$  values. It could be noticed that the modulus of the mixture decreased with the addition of PCL for all molecular weights. The similar results were found in the report of Ishida and Lee studying polybenzoxazine/poly( $\epsilon$ -caprolactone) blends at the  $M_n$  of 35,000–45,000 Da.<sup>23</sup> In addition, the mixtures with higher molecular weights of PCL tended to provide the lower modulus value,<sup>30</sup> i.e., the modulus of pure PBA-a was  $\sim 5.4 \pm 0.1$  GPa, while the values of the blends at 20 wt % for the PCL of 10 K, 45 K, and 80 K were decreased to be  $3.9 \pm 0.2$ ,  $3.7 \pm 0.2$ , and  $3.4 \pm 0.2$ , respectively. That means the toughness of PBA-a could be enhanced because the PCL exhibited the characteristic of low modulus in nature.<sup>30</sup> Moreover, it



**Figure 7.** Hardness of PBA-a/PCL alloys with different molecular weights of PCL: (•) 10,000 Da, (○) 45,000 Da, and (■) 80,000 Da.

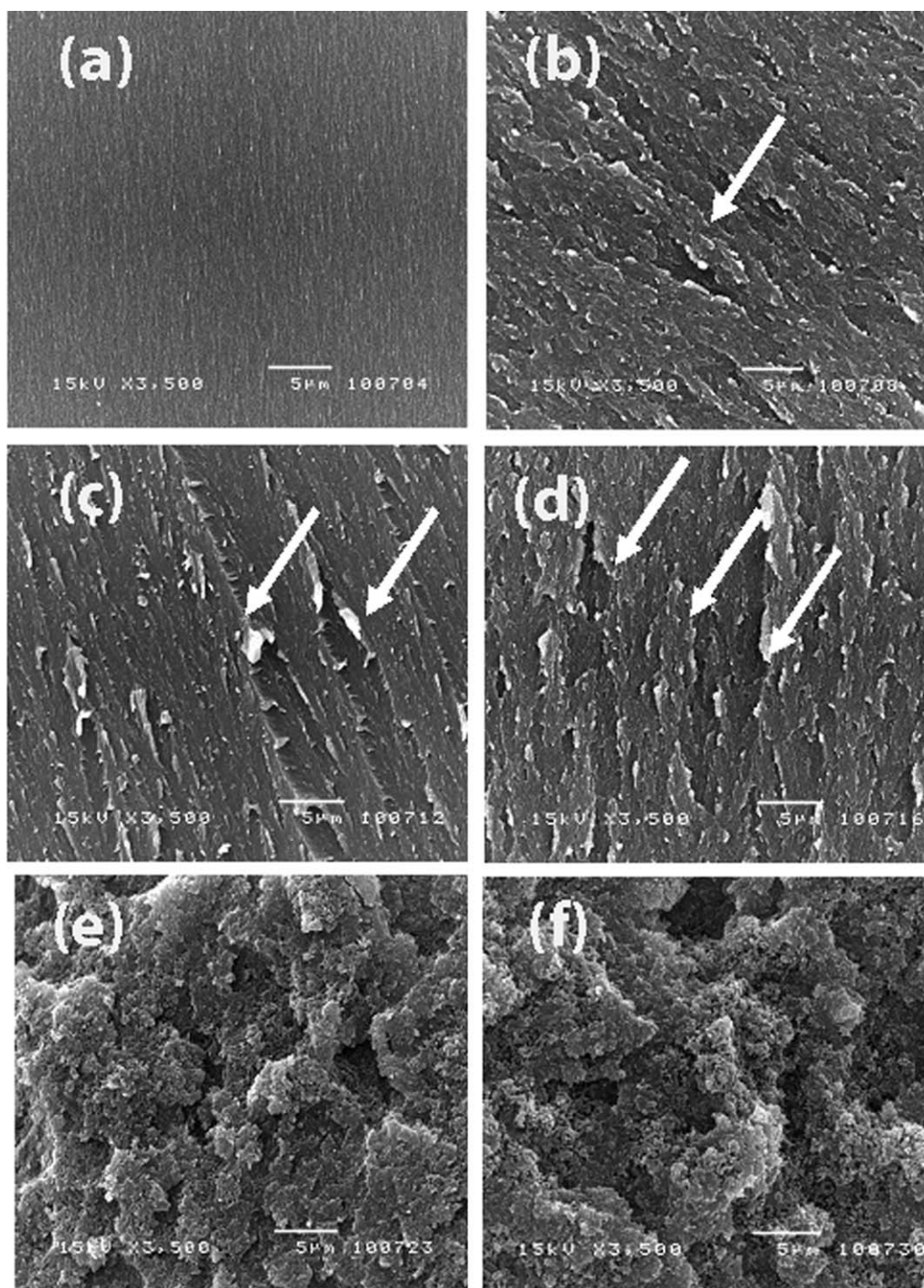
could be noticed that the PCL with lower molecular weight provided higher value of crystallinity. That leads to the greater values of modulus of the blends.

Figure 7 presents the microhardness of the polymeric blends of PBA-a and PCL with different molecular weights. It can be noticed that the microhardness of the blends was decreased with the increase of PCL content. Moreover, the value was slightly decrease with the molecular weight of PCL, i.e., the microhardness of Pure PBA-a was  $342 \pm 4$  MPa. At 10 wt % of PCL with the molecular weight of 10 K, 45 K, and 80 K, the microhardness exhibits the values at  $284 \pm 4$ ,  $268 \pm 0.8$ , and  $261 \pm 8$  MPa, respectively. This phenomenon is attributed to



**Figure 8.** TGA thermograms of the of PBA-a/PCL alloys ( $M_n = 45,000$ ) at different PCL contents: (•) Pure PBA-a, (■) 10 wt %, (◆) 20 wt %, (▲) 30 wt %, (▼) 40 wt %, and (◄) pure PCL. Temperature at maximum decomposition rate and char yield of the alloys.





**Figure 9.** SEM images of the fracture surface of the PBA-a and PCL alloys at different molecular weights and contents of PCL ( $\times 3500$  magnification): (a) Pure PBA-a, (b)  $M_n = 10,000$  Da, 10 wt %, (c)  $M_n = 45,000$  Da, 10 wt %, (d)  $M_n = 80,000$  Da, 10 wt %, (e)  $M_n = 45,000$  Da, 20 wt %, and (f)  $M_n = 45,000$  Da, 30 wt %.

the hardness of pure PCL was as low as  $47 \pm 1$ ,  $40 \pm 1$ ,  $28 \pm 0.5$  MPa, respectively. According to the rule of mixtures, the blend with greater PCL content could provide lower microhardness value. In other words, the rigidity which is the drawback of polybenzoxazine could be decreased when the PCL with high  $M_n$  was applied. The decrease of modulus and hardness with the

increase of molecular weight was also reported in the system of polyethylene with different crystallinity values.<sup>32,33</sup>

#### Thermal Stability Determination of the PBA-a/PCL Blends

The information from a thermogravimetric analyzer of the polymers has played an importance role to describe the thermal

stability of various systems.<sup>34–37</sup> In comparison between the PBA-a/PCL of different molecular weights, it was found that there was no significant difference among the decomposition temperatures and the char yields of each mixture at the same PCL content. That means the molecular weight of the PCL has no effects on the thermal stability of the mixtures. Therefore, only the TGA thermograms of the system with 45 K PCL was presented in Figure 8. The inset of this figure describes the temperature at maximum decomposition rate ( $T_{dmax}$ ) and the char yield at 800°C. It could be noticed that with the increase of PCL contents the  $T_{dmax}$  of the PBA-a/PCL mixtures was increased, while the char yield was decreased. This phenomenon is in agreement with the report of Ishida and Lee<sup>23</sup> studying the system of PBA-a and PCL at the content of 0–15 wt %. They reported that the decomposition temperature of the mixture was enhanced in the region of medium temperature as high as 250 to 450°C. In our study, the thermal decomposition temperature at maximum rate was increased from 391°C (pure PBA-a) to 416°C (40 wt % of PCL), while the char yield was decreased from 27.9% (pure PBA-a) to 18.5% (40 wt % of PCL).

#### Morphological Study of the Fracture Surface

Morphology of blending systems between PBA-a and PCL was characterized using scanning electron microscopy (SEM) technique. Figure 9 exhibited SEM images of fracture surface of the blends. It could be noticed that Figure 9(a) presents the flat surface of rigid PBA-a. In the presence of PCL with different molecular weights [as seen in Figures 9(b–d)], at the same PCL content, the surface fracture trended to be slightly rougher in case of the PBA-a modified with higher molecular weight of PCL. That indicates slightly higher ductility when adding greater molecular weight of PCL. Furthermore, the surface fracture was rougher when PCL content was increased as observed in Figures 9(e,f). These results are corresponding to the results of low hardness when increasing PCL content as previously presented.

#### CONCLUSIONS

Polybenzoxazines (PBA-a) modified with polycaprolactone (PCL) of different weight number average molecular weights ( $M_n$ ) were studied at various PCL contents. The optical microscope revealed the spherulite sizes of pure PLC and the blends with higher  $M_n$  of PCL were greater than those with lower  $M_n$  of PCL. The decrease of the PCL contents led to the decrease of the spherulite size. The FTIR spectra reveal that the increase of the  $M_n$  and content of PCL could decrease the interaction between two domains. The DMA thermograms revealed two glass transition temperature ( $T_g$ ) values indicating the phase segregation of the blending systems. Interestingly, the synergistic behaviors of the  $T_g$  in the high temperature region were found when PCL was incorporated. At the same PCL content, the PCL with higher  $M_n$  provided the greater  $T_g$  values. Moreover, the flexural modulus of the blends was decreased, while the elongation at break and the area under the stress-strain curves were increased with the increase of the  $M_n$  and content of PCL. That indicates the toughness of the PBA-a could be improved. These results were in correspondence with the SEM images at the fracture surfaces.

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