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Enhanced Film Forming Ability of Benzoxazine-Urethane Hybrid Polymer Network by Sequential Cure Method

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ABSTRACT: Uniform copolymer films of benzoxazine resin (BA-a) and urethane prepolymer (PU) were prepared at various BA-a/PU mass ratios (100/0, 80/20, 60/40, 40/60, 20/80, and 0/100) via sequential cure method comprising of moisture cure and thermal cure steps. In the moisture cure step, Fourier Transform Infrared (FT-IR) spectra revealed the network formation between NCO-terminated group and moisture to firstly produce PU solid film. Then in the thermal cure step, the change of tri-substituted benzene ring to tetra-substituted benzene ring was observed suggesting polybenzoxazine network formation in this step. Moreover, the spectra reveal that isocyanate groups in polyurethane structure could react with phenolic hydroxyl groups of BA-a to form biuret and allophanate groups. Dynamic mechanical analysis (DMA) confirms a synergistic behavior in glass transition temperature (T_g) of the alloys with the highest T_g value of 275°C which is uniquely observed in these alloys obtained from traditionally thermal cure method. The proposed sequential cure method above is found to be highly useful for uniform coating or film casting process which lacks in traditional, low A-stage viscosity, benzoxazine resin. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40502.

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INTRODUCTION

Polybenzoxazines are a newly developed class of phenolic resins possessing many unique advantages such as excellent thermal properties, flame retardance, high char yield, molecular design flexibility, very low moisture absorption, near zero shrinkage upon polymerization, low dielectric constant, and low melt viscosities.[1–4] These novel polymers can be synthesized using the patented solventless technology to yield a clean precursor without the need for solvent elimination or monomer purification, which does not create serious threats to environment and human health.[1] From these advantages, recently the polymers have been produced and commercially utilized in some industries; for example, BA-a is scaled up and commercialized by Shikoku Chemical Corporation, Japan. Henkel Corporation, USA, has produced polybenzoxazines with different backbones for aerospace applications etc. The novel polymers were employed as composites for laminating and structural purposes and as encapsulants in electronic packaging applications.[5–7] Although there are a large number of reported outstanding properties of the polymers, some shortcomings still exist and are related to brittleness and film forming ability at room temperature of the polymers.

There have been numerous studies on a combination of BA-a and PU for improving flexibility of polybenzoxazine as well as thermal stability of polyurethane.[8–13] Takeichi et al. reported that the combination of PU and BA-a showed only one glass transition temperature (T_g) that increasing with an increase of BA-a content.[8,9] In addition, thermal stability of PU was greatly enhanced even with the incorporation of a small amount of BA-a. Rimdusit et al.[10] investigated benzoxazine resins alloying with isophorone diisocyanate (IPDI)-based PU, and reported that the obtained alloys provided remarkable improvement in flexibility of the rigid polybenzoxazine (PBA-a). They also reported a positive deviation on T_g of the benzoxazine–urethane alloys. That is T_g of the benzoxazine–urethane alloys with the value beyond 250°C was obtained. The value was significantly greater than those of the parent polymers (ca. 165°C for the polybenzoxazine and −70°C for the polyurethane).

From the past reports up to present, polymer alloys of benzoxazine-urethane systems have been prepared mainly by thermal cure method. However, due to the relatively low A-stage viscosity of benzoxazine resin, the film forming property of this resin and its alloy mixtures is rather limited. Additionally they require relatively high temperature (typically 150–200°C) to solidify the film. In this work, enhanced film forming property of these alloy systems is demonstrated by a sequential cure method. Sequential cure method is a well-known technique for interpenetrating polymer network preparation utilizing different curing mechanisms of the two alloy networks.[14,15] Pandit and Nadkarni[14] synthesized sequential semi-interconnected IPNs of poly(ester-urethane) and polystyrene by completing the PU network formation at room temperature, and then post-curing at 90°C to complete the polymerization of styrene. Yang et al.[15] prepared urethane-acrylate IPNs, two sequential types and one simultaneous type. The sequential IPN prepared by heat cure of PU followed by photo-polymerization of acrylate provided a very fine domain size of <20 nm with single T_g while that formed by photo-polymerization before heat cure rendered domains of much larger size.

In our case, urethane resin is known to be cured by moisture[16–18] while benzoxazine resin is cured thermally. It is expected that BA-a/PU alloy samples processed via sequential cure, firstly by moisture prior to heat treatment, could provide restricted mobility of benzoxazine portion at elevated temperature as a result of PU network formation. This should lead to improve uniformity of the resulting film thickness and broaden the applications of the polymer alloys. Since the curing process significantly affects the network formation thus the obtained properties of the alloys, the objectives of this research are to investigate the effects of sequential cure method on the network formation behaviors of the BA-a/PU alloys at varied compositions. Chemorheological and thermomechanical properties of the alloys prepared via this method will be studied.

EXPERIMENTAL

Raw Materials

Benzoxazine monomer was based on bisphenol-A, aniline, and formaldehyde. The bisphenol-A (polycarbonate grade) was provided by Thai Polycarbonate (Thailand). Para-formaldehyde (AR grade) and aniline (AR grade) were purchased from Merck (Thailand) and Panreac Quimica S.A. (Thailand), respectively. 2,4-Toluene diisocyanate (TDI) was obtained from South City Group (Thailand) whereas poly(propylene glycol) with number average molecular weight (M_n) of 2000 g mol^{-1} was obtained from IRPC (Thailand). Dibutyltin dilaurate (DBTL) was used as a catalyst for the PU synthesis.

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 30 min to yield a light yellow solid monomer product according to the patented solventless method.[19] The product was then ground into fine powder and kept in a refrigerator for future use.

Synthesis of Urethane Prepolymer

Urethane prepolymer was prepared by reacting polypropylene glycol with 2,4-toluene diisocyanate (TDI) at molar ratio of 1 : 2 in a four-necked round-bottomed flask. Dibutyltin dilaurate (0.075 wt %) was added as catalyst. The mixture was then stirred at 70°C under nitrogen flow for 2 h. The obtained transparent viscous PU was cooled to room temperature and kept in a nitrogen-purged and closed container.

Preparation of Benzoxazine–Urethane Alloys via Sequential Cure Method

BA-a monomer and PU were blended at various mass ratios i.e., BA-a/PU = 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100. The mixtures were heated at 110°C and mixed thoroughly until the clear homogeneous mixtures were obtained. The molten resin mixture was casted onto aluminum substrate with doctor blade. The polymer mixtures were processed via sequential cure method by first exposed to moisture at room temperature and 90% relative humidity for 24 h in order to achieve urethane network formation, and followed by thermal cure in an air-circulated oven to polymerize the BA-a portion. The step heating program was 130°C (1 h), 150°C (1 h), 180°C (1 h), 190°C (1 h), and 200°C (4 h). All the specimens were finally left to cool down to room temperature before characterizations.

Sample Characterizations

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 with ATR accessories. All spectra were taken as a function of time with 64 scans at a resolution of 4 cm^{-1} and a spectral range of 4000–650 cm^{-1}. For PU, a small amount of a viscous liquid sample was casted as thin film on a potassium bromide (KBr) window.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC model 2910, TA Instruments, USA) was performed in order to study curing behaviors of BA-a/PU resin mixtures. A sample of ~5 mg was put in an aluminum pan with lid. The thermogram was obtained using a heating rate of 10°C min^{-1} from 30 to 300°C under a constant flow of nitrogen of 50 mL min^{-1}.

Dynamic Mechanical Analysis. Dynamic mechanical analyzer (DMA model DMA242, NETZSCH, Germany) was used to investigate dynamic mechanical properties and relaxation behaviors of BA-a/PU polymer alloys. The test in tension mode was performed at a fixed frequency of 1 Hz with the temperature scanned from −130°C to the temperature beyond glass transition temperature (T_g) of each specimen using a heating rate of 2°C min^{-1} under nitrogen atmosphere.

Density Measurement. The density of the polymer blends were measured by water displacement method according to ASTM D792-08 (Method A). All specimens were prepared in a rectangular shape of 50 mm × 25 mm × 2 mm and weighed both in air and in water. The density was calculated using the following equation:

$$\rho = [A/(A-L)]\rho_o \tag{1}$$

where ρ, ρ_o are density of the specimen and liquid at the given temperature, respectively (g cm^{-3}). A, L are weight of the specimen in air and in liquid, respectively.

Swelling Degree and Gel Content Determination. Volumetric swelling degree and gel content of BA-a/PU alloys were

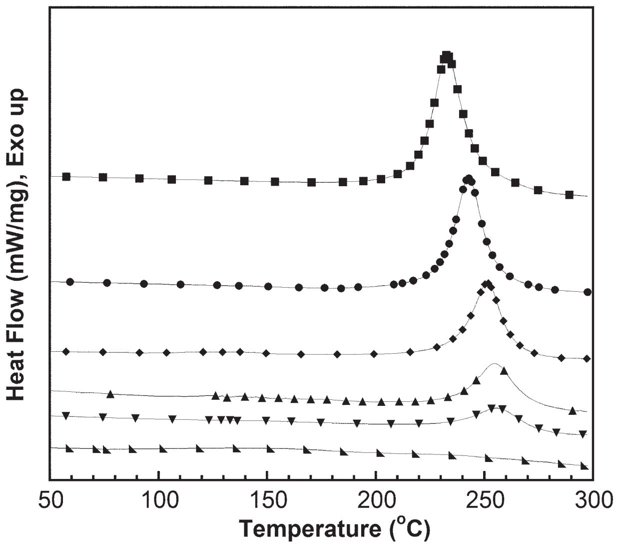

Figure 1. DSC thermograms of BA-a/PU resin mixtures at various BA-a/PU mass ratios: (■) 100/0, (●) 80/20, (◆) 60/40, (▲) 40/60 (▼) 20/80, and (◣) 0/100.

investigated by immersion in chloroform at room temperature for 1 week. The values were calculated using the following formulae[20]:

$$\text{Volumetric swelling degree}: Q=1+\frac{\rho_2}{\rho_1}\times\left(\frac{m_s}{m_t}-1\right) \qquad (2)$$

$$\text{Gel content}\,(\%)=\frac{m_g}{m_t}\times 100 \qquad (3)$$

where ρ_1 is the density of chloroform (ρ_1 =1.489 g cm^{-3}), ρ_2 the density of BA-a/PU alloys (g cm^{-3}), m_s the weight of swollen specimen (g), m_g the dried weight after swelling (g), m_t the initial weight of specimen (g).

The measurement of three specimens was carried out at each composition and the average value was obtained.

Thermogravimetric Analysis. The thermogravimetric analyses were determined using a Perkin Elmer Instrument Technology SII Diamond TG/DTA thermogravimetric analyzer (TGA). The testing temperature program was ramped at a heating rate of 20°C min^{-1} from room temperature to 800°C under nitrogen purging at 100 mL min^{-1}. Weight loss of the samples was measured as a function of temperature.

RESULTS AND DISCUSSION

Thermal Curing Behaviors of BA-a/PU Resin Mixtures

Figure 1 exhibits DSC thermograms of BA-a/PU resin mixtures ranging from 0 to 100% of PU. When the PU was mixed into BA-a, the exothermic peak temperature was found to shift to higher temperature, i.e., the exothermic peaks of the alloys at BA-a/PU ratios of 100/0, 80/20, 60/40, 40/60, 20/80 were located at 232, 242, 250, 253, and 255°C, respectively. This can be explained by the dilution effect on BA-a curing due to the presence of PU. In addition, only a single dominant exothermic peak of the curing reaction was observed in each resin composition. The phenomenon suggested that the BA-a/BA-a and BA-a/PU reactions to form a network structure of these binary mixtures took place simultaneously without the need of any catalyst or curing agent at about the same temperature.[12] The thermograms also revealed a decrease of area under the exothermic peak with increasing mass fraction of PU, attributed to the decrease in the number of mole of the reacted functional groups with the amount of PU. This is because the PU fraction cannot form a network by heat, and requires BA-a monomers as its crosslinker. When the amount of BA-a was decreased, the curing exotherm therefore decreased.

Network Formation of BA-a/PU Alloys Prepared via Sequential Cure Method

When the BA-a/PU mixtures were firstly left in moist air at room temperature prior to thermal cure, the reaction between isocyanate group of urethane resin and moisture could take place. Figure 2 illustrates FT-IR spectra of BA-a/PU mixture at a mass ratio of 20/80 at different exposure time in moist air. The spectra revealed that the moisture cure reaction at room temperature proceeded as a function of time. A decrease of the characteristic absorption band at 2264 cm^{-1} indicated that NCO-terminated group reacted with atmospheric moisture and produced crosslinked networks. The observed urea bonds were revealed by an appearance of absorption bands at 1639 (C═O) and 3291 cm^{-1} (NH stretching vibrations) of the obtained networks. The time to complete PU network formation was determined from the disappearance of isocyanate peak in the FT-IR spectra, which was found to be about 24 h. The moisture cure step merely completed the urethane network formation, but clearly did not influence network formation of BA-a fraction, a thermally curable resin. Consequently, the characteristic absorption bands of BA-a, i.e. 1240 cm^{-1} (symmetric stretching of C─O─C) and 1497 cm^{-1} (tri-substituted of benzene ring), were not changed in this moisture cure step.

Figure 3 illustrates FT-IR spectra of BA-a/PU mixture at a mass ratio of 20/80 undergoing moisture cure followed by thermal cure steps. From this figure, it was found that after heating the

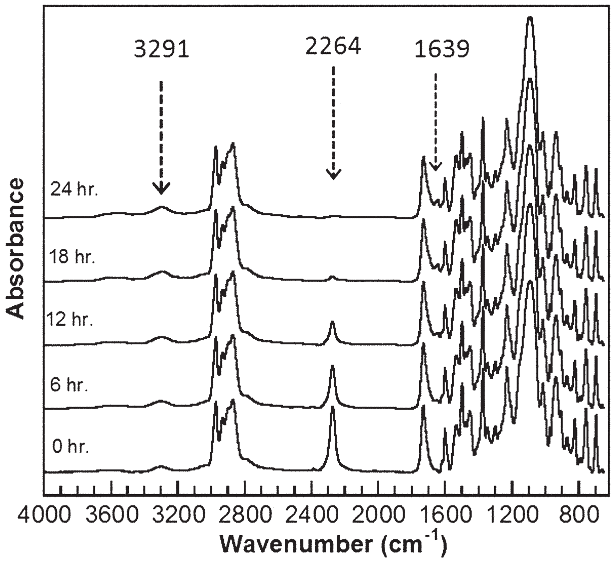

Figure 2. FT-IR spectra of BA-a/PU alloys (20/80) obtained by moisture cure method at various times.

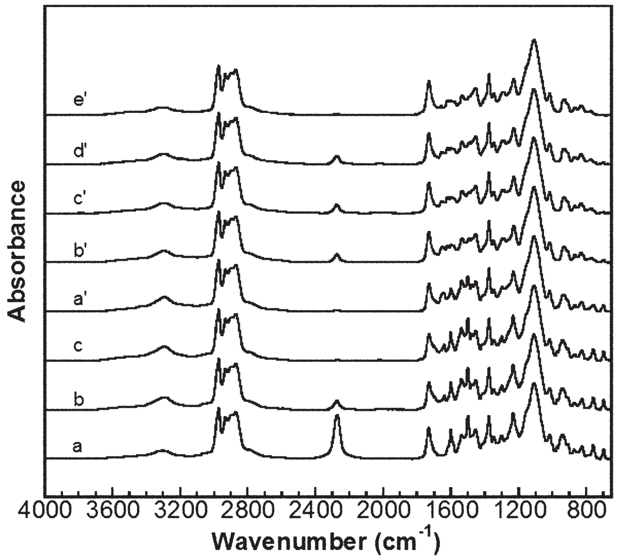

Figure 3. FT-IR spectra of BA-a/PU alloys (20/80) by moisture exposure: (a) 0 h; (b) 8 h; and (c) 12 h; and thermal treated after moisture exposure: (a′) 150°C/1 h; (b′) 180°C/1 hr; (c′) 190°C/1 h, (d′) 200°C/1 h, and (e′) 200°C/4 h.

resin mixture the characteristic absorption bands at 1497 cm^{-1}, both assigned to tri-substituted of benzoxazine ring, almost disappeared as a result of the opening of oxazine rings. However, the absorption bands did not entirely disappear because the absorbance of benzoxazine was superimposed by that of polyurethane. This result corresponds to the research of Takeichi et al.[9] Moreover, it could be seen that isocyanate group in both reversible forms of biuret and allophanate might be reacted with phenolic hydroxyl groups from the ring-opened structure of BA-a.

In addition, NCO-terminated group at 2264 cm^{-1} was found to reappear in this heat treatment step but with a much smaller intensity. This phenomenon was possibly due to the breakage R-NHCO— bond of biuret and allophanate, which can transform back to NCO-terminated group. The biuret and allophanate in this system were produced from the excess isocyanate in side reactions.[21,22] An allophanate is formed by the reaction of isocyanate with urethane group, whereas a biuret is generated by the reaction of the —N—H groups of urea and isocyanate. Urethane groups are considered to be hydrogen active compounds due to the hydrogen atom linked with the nitrogen atom. The mechanism of reversible isocyanate at high temperature is reported in the research of Narayan et al.[23]

Properties of the BA-a/PU Polymer Alloys Prepared via Sequential Cure Method

Figure 4 presents the storage modulus of BA-a/PU polymer alloys as a function of temperature. It is evident that the modulus at glassy state of the polymer alloys tends to decrease with increasing PU mass fraction. The storage modulus at room temperature of the neat PBA-a and the PU were determined to be 3.12 GPa and 21.5 MPa, respectively, whereas the polymer alloys at the BA-a/PU ratios of 80/20, 60/40 provided the storage modulus of 1.57 GPa, 0.69 GPa, respectively. This is attributed to the fact that PU is an elastomer possessing higher flexibility than the PBA-a. This result clearly suggests that the addition of PU makes the polymer alloys more flexible and significantly broadens the mechanical properties of the polybenzoxazine. Additionally, when BA-a was a major component, rubbery plateau modulus of the alloy was found to substantially increase with the PU mass fraction. This behavior was also observed in the traditional thermal cure BA-a/PU alloys.

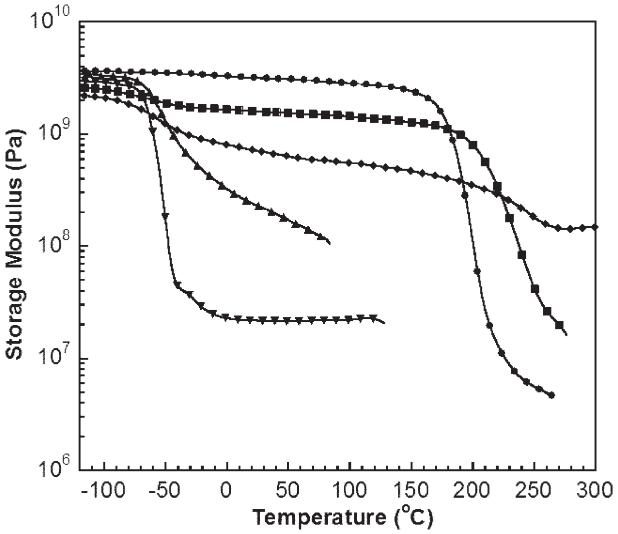

Figure 4. Storage modulus of BA-a/PU alloys at various BA-a/PU mass ratios: (●) 100/0, (■) 80/20, (◆) 60/40, (▲) 40/60, and (▼) 0/100. (Note: BA-a/PU alloy at 0/100 is obtained by moisture cure method).

The visual appearance and flexibility of BA-a/PU alloys films prepared via sequential cure method are presented in Figure 5. The neat PBA-a specimen illustrated in Figure 5(a) exhibits a

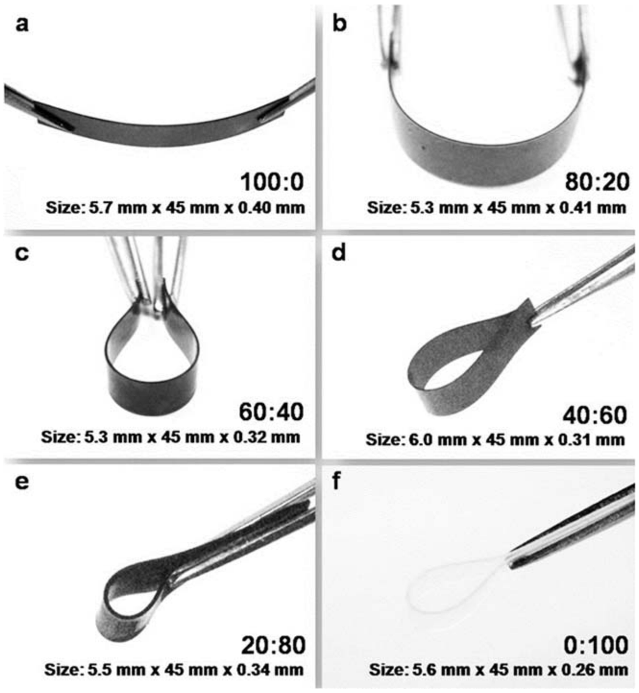

Figure 5. Visual appearance and flexibility of BA-a/PU alloys films.

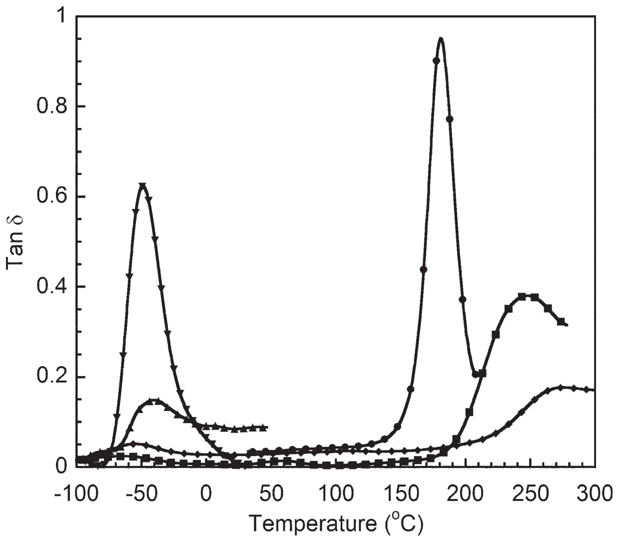

Figure 6. Tan δ of BA-a/PU alloys at various BA-a/PU mass ratios: (●) 100/0, (■) 80/20, (◆) 60/40, (▲) 40/60, and (▼) 0/100.

rather rigid character with minimum flexibility corresponding to its highest value of tensile modulus from DMA thermogram at room temperature i.e. 3.12 GPa. However, in Figure 5(b–e), the alloy samples were observed to be increasingly bendable. That is the flexibility of the alloys was greatly increased with the PU content. In addition, the appearance of transparent and deep red PBA-a sample was turned into lighter orange color in the resulting alloys.

Glass transition temperature (T_g) of BA-a/PU polymer alloys was determined from the peak maximum of loss tangent (tan δ) curves. Figure 6 shows tan δ curves as a function of temperature of the BA-a/PU alloys prepared by a sequential cure method. As T_g depends largely on the amount of thermal energy required to keep the polymer chains moving, there are many factors affecting on the chains rotation and thus T_g values, i.e. (1) chain flexibility, (2) molecular structure (steric effect), (3) molar mass, and (4) branching and crosslinking.[22] From the figure, the 60/40 BA-a/PU alloy films showed two peak maxima or two T_g values. The T_g of -50°C belongs to the polyurethane domain in the alloys, while another peak at higher temperature is the T_g of BA-a/PU alloys. This result suggests that BA-a/PU alloys films was a heterogeneous network which is composed of polyurethane and benzoxazine domains.

From Figure 6, the T_g of the neat PBA-a was determined to be 200°C, whereas those of the polymer alloys at BA-a/PU ratio of 80/20 and 60/40 were $\sim$247 and 275°C, respectively. Therefore, the addition of urethane elastomer into PBA-a can substantially increase the T_g of the polymer alloys even in the alloy films processed sequentially. Moreover, the synergistic behavior of the T_g of the alloys was evidently observed that T_g values of all alloys showed greater values than those of both polybenzoxazine and polyurethane (i.e., 200 and -50°C, respectively). The phenomenon was also observed in the alloy samples processed via traditional thermal cure method. As a consequence, the sequential cure BA-a/PU alloys tend to provide a fully cured sample with similar characteristic to the thermal cure method. This is due to the fact that the urea linkage in PU network obtained from moisture cure tends to disintegrate at elevated temperature in the following thermal cure step and can form chemical bonds with hydroxyl group of the ring-opened benzoxazine monomers.[9,24] It was reported that the formation of urea linkage is thermally reversible.[25] When PU is heated, the urea linkage can dissociate to form a carbamic acid and an amine. The carbamic acid is generally not stable under normal circumstances and undergoes further reaction. Then, the reaction between NCO in PU and phenolic hydroxyl group of PBA-a could occur as confirmed by FTIR spectra.[9] Thus rather than forming interpenetrating polymer network of PU and PBA-a in this sequential cure process, a kind of polymer alloys was formed and produced similar polymer network as that obtained from solely thermal cure process which was reported in our previous works.[10,12,26] This explains the similar mechanical and thermal characteristics of the fully cured samples from both processing techniques. Therefore, by curing the BA-a/PU resin mixture sequentially, the film forming property at room temperature is achieved while all the good properties of the fully cured polymer alloys are maintained as those obtained from thermal curing.

Moreover, the magnitude of tan δ peak reflects the large scale mobility associated with alpha relaxation. The peak height of the tan δ at high temperature tended to decrease with increasing PU content. This suggested the reduction in segmental mobility of chain with increasing crosslinked density as PU mass fraction in the polymer alloys increased. Furthermore, the width at half height of the tan δ curves, corresponded to the network heterogeneity, of BA-a/PU alloys was broader with increasing PU content suggesting more heterogeneous network in the alloys.

The crosslinking densities of polymer networks of BA-a/PU alloys were characterized in terms of their swelling degree in chloroform. Swelling is the process of dissolution of a polymer in a defined solvent. At first, the solvent molecules slowly diffuse into the polymer to produce a swollen gel. If the polymer–polymer intermolecular forces are higher than polymer–solvent interactions due to crosslinking, crystallinity, or strong hydrogen bonding, the swelling phenomena occurs. However in case that polymer–solvent interactions forces are greater, the dissolution of the polymer take places.[27] The process of swelling results actually from the balance between repulsive and attractive phenomena i.e., (i) the thermodynamic mixing between the net polymer and the solvent, (ii) Interaction between fixed charged groups and free ions as happens in proton-exchange membranes, and (iii) the elastic force of the polymer and also interchain attractive forces. A relationship between the swelling degree of BA-a/PU alloys and PU content is illustrated in Figure 7. The film specimen can swell at a different degree in chloroform. In this figure, it is clearly observed that the volumetric swelling degree of the BA-a/PU alloys increased gradually along with PU content up to 80 wt % i.e. 3.5. The neat PU however exhibits a sharp increase in the swelling degree i.e. 17. The result implies that the presence of benzoxazine fraction can effectively suppress the swelling of the PU fraction likely due to the strong molecular bonding in the obtained polymer network.

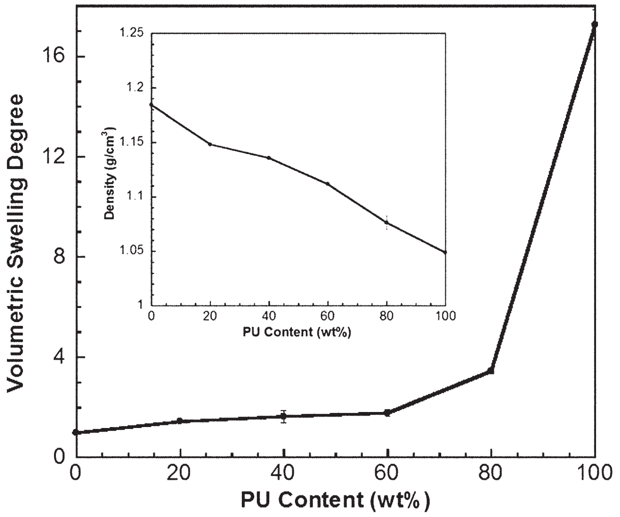

Figure 7. Volumetric swelling degree of BA-a/PU alloys at various PU contents. Actual density of BA-a/PU alloys at various PU compositions.

Gel contents of BA-a/PU alloys in chloroform at various compositions are presented in Figure 8. It is clearly seen that the gel fraction of the alloys decreased with increasing PU content. The gel content of neat polybenzoxazine (1 week of immersion) was determined to be 96%, while that of the polyurethane was observed at ~45%. It could be observed that the gel fraction was drastically decreased at over 20 wt % of PU. Therefore, the incorporation of benzoxazine structure can improve the network deformation of the resulting polymer alloys. From Figure 4, the addition of PU made the rubbery plateau region higher than the neat polybenzoxazine. Theoretically, the crosslink density (ρ_x) of the polymer network can be estimated from the rubbery plateau modulus (E') as presented in eq. (3).[28–30]

$$\rho_x = \frac{E'}{(3RT_r)} \tag{4}$$

where T_r is equal to $T_g + 30°\mathrm{C}$ (in Kelvin unit); E' is the storage modulus at T_r; R is the gas constant ($8.314\ \mathrm{m^3\ Pa^{-1}\ K^{-1}}$).

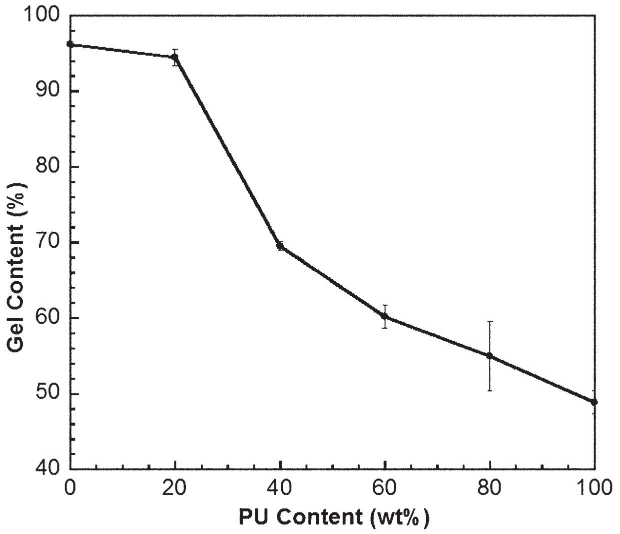

Figure 8. Gel content of BA-a/PU alloys at various PU contents.

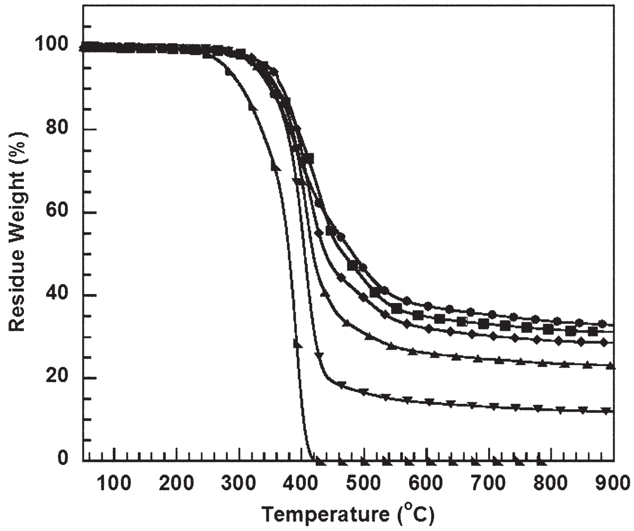

Figure 9. TGA thermograms of BA-a/PU alloys obtained by sequential cure method at various BA-a/PU mass ratios: (●) 100/0, (■) 80/20, (◆) 60/40, (▲) 40/60, (▼) 20/80, and (◣) 0/100. (Note: BA-a/PU alloy at 0/100 is obtained by moisture cure method).

The crosslink density of polybenzoxazine at 0, 20, and 40% of PU were calculated to be 2324, 4294, and 10323 mol $\mathrm{m^{-3}}$, respectively. That means the crosslink density values tended to increase with PU content. In other words, the networks of the alloys were denser than the neat benzoxazine. These results also revealed that the additional crosslink density would clearly increase the T_g of the alloys.[30,31] Moreover, it could be noticed that at the PU content beyond 20 wt % the crosslink density was significantly increased and the gel fraction was drastically decreased. In addition, the calculated crosslink density values of the alloys obtained from the sequential cure method were found to be closed to those obtained from traditional cure method.[32–34]

TGA thermograms of BA-a/PU alloys under sequential cure method at various urethane contents are exhibited in Figure 9. The thermal decomposition in each alloy under sequential cure method was found to show a single stage weight loss. The T_d values (at 5% weight loss) of the neat polybenzoxazine and the polyurethane were determined to be 326 and 274°C, while those of BA-a/PU 80/20, 60/40, 40/60, 20/80 were presented to be 329, 329, 327, and 321°C, respectively. The T_d values of the polymer alloys were found to slightly change with increasing urethane content. However, when mass fraction of urethane prepolymer was more than that of the benzoxazine resin, T_d's of the polymer alloys were found to decrease with the PU mass fraction.

CONCLUSIONS

Polybenzoxazine alloying with urethane elastomer was developed via sequential cure method. This novel curing process provided the BA-a/PU resin mixture with film forming ability at room temperature which is impossible in typical benzoxazine resins or benzoxazine alloys. FT-IR spectra revealed that network formation of BA-a/PU alloys obtained from sequential cure method comprising of first network formation of PU by moisture crosslinking and then network formation of BA-a from thermally induced ring opening polymerization. The synergistic behavior of T_g was observed from the peak of loss tangent in the dynamic mechanical analysis. The storage modulus of a solid polymer at its glassy state tends to decrease with increasing the PU mass fraction in the alloys, enhancing the flexibility of the alloy product. Moreover, the swelling degree of the BA-a/PU alloys was suppressed by the BA-a fraction. The gel content was improved also by the addition of the BA-a.

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