

Chemorheology and Thermomechanical Characteristics of Benzoxazine-Urethane Copolymers

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ABSTRACT: In this research, processability and some important thermomechanical properties of polybenzoxazine (BA-a) modified with a highly flexible urethane elastomer (PU) are discussed. This copolymer has been reported to show synergy in its glass transition temperature and some mechanical properties thus provides a fascinating group of high temperature polymers with enhanced flexibility. The results reveal that a processing window of the BA-a/PU mixtures is widened with the increasing urethane prepolymer fraction, that is, the liquefying temperature is lowered and the gel point shifted to higher temperature with the amount of the PU. Synergism in glass transition temperature (T_g) of this copolymer was

clearly confirmed, i.e., T_g 's of the BA-a/PU alloys were significantly greater than those of the parent resins, i.e., BA-a ($T_g = 166^\circ\text{C}$) and PU ($T_g = -70^\circ\text{C}$). In addition, flexural modulus was found to systemically decrease from 5.4 GPa of the neat polybenzoxazine to 2.1 GPa at 40% by weight of the PU. Flexural strength of the alloys also shows a synergistic behavior at the BA-a/PU ratio of 90/10. Coefficient of thermal expansion of the polymer alloys were also found to show a minimum value at BA-a/PU = 90/10. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3669–3678, 2011

Key words: copolymers; crosslinking; gelation; thermosets

INTRODUCTION

Polybenzoxazine, a novel kind of phenolic resin, is one of new thermosetting plastics. The curing of this resin involves ring-opening polymerization without a catalyst or a curing agent and does not produce any by-products during cure which might cause void in the products. Polybenzoxazine possesses various useful properties such as high ability to synthesize from inexpensive raw materials, low melt viscosity before cure resulting in its high processability, no by-product during cure, near zero volumetric shrinkage after processing, low water absorption, high thermal stability, and excellent mechanical properties.^{1–3} However, the application of this polymer is limited to certain areas due to its rather high rigidity. In principle, toughness of polybenzoxazine can be enhanced by

two major strategies. The first strategy is by utilizing a novel molecular design of benzoxazine resins such as a synthesis of linear aliphatic diamine-based benzoxazine and a utilization of high molecular weight benzoxazine precursors.⁴ Second method is by alloy formation or copolymerization with flexible resins or polymers such as urethane elastomer,^{5–7} flexible epoxy,^{6,8} poly(ϵ -caprolactone),⁹ poly(imide-siloxane),¹⁰ and polydimethylsiloxane.¹¹ The latter strategy is a relatively versatile and simple method to improve mechanical property or thermal stability of polybenzoxazine.

Recently, benzoxazine resin (BA-a) alloyed with urethane prepolymer (PU) had been developed by Takeichi et al. The resulting hybrid films were prepared by blending BA-a monomer and PU which was synthesized from 2,4-toluene diisocyanate and adipate polyol (Mw 1000). The obtained films showed a single glass transition temperature suggesting no phase separation in the resulting alloys. The properties of the films ranged from elastomers to plastics depending on the amount of benzoxazine fraction in the alloys.⁴ Other BA-a/PU alloy systems were investigated by Yeganeh group. The PU structure used in this system had glycidol as a blocking agent of urethane prepolymers. The T_g of this system was found to increase with increasing BA-a content.¹² Furthermore, a series of phenol end-functionalized urethane prepolymers was prepared by Yeganeh et al. These telechelic oligomers were used as a

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macro initiator for ring opening polymerization of benzoxazine monomers. Thermal stability of the resulting networks was improved by increasing PU molecular weight as well as BA-a content.¹³ Interesting characteristics of some, benzoxazine-urethane alloy systems were also observed by Rimdusit et al. According to this report, benzoxazine resin (BA-a) was alloyed with isophorone diisocyanate/polyether polyol (Mw 2000) based PU. The obtained alloys not only provided expected enhancement on their flexibility but also exhibited synergism in glass transition temperature (T_g). The T_g value as high as 220°C of this alloy system was observed when 30 wt % of PU was added.^{6,7} Synergism in glass transition of polybenzoxazine from an addition of other resins or polymers has been observed and reported previously in various systems such as benzoxazine-epoxy,^{8,14} benzoxazine-urethane,^{6,7} benzoxazine-polycaprolactone,⁹ or benzoxazine-polydimethylsiloxane¹¹ etc.

From the substantial enhancement on flexibility and the observed synergistic behaviors in T_g of benzoxazine-urethane alloys discussed above, other essential properties of the alloys including their processability or chemorheological characteristics and some thermomechanical properties as a function of alloy compositions will be examined in this work. The chemorheological characteristic is one of the crucial phenomena for material processability. The sol-gel transition and time for gelation obtained from rheological property measurement are important factors to control desirable products with appropriate processing conditions and methods.

EXPERIMENTAL

Materials

Materials used in this research are benzoxazine resin and urethane prepolymer. Benzoxazine resin is based on bisphenol-A, aniline, and formaldehyde. The bisphenol-A (polycarbonate grade) was supported by Thai Polycarbonate Co., Ltd. (TPCC). Para-formaldehyde (AR grade) was purchased from Merck Company and aniline (AR grade) was contributed by Panreac Quimica S.A. Company. Urethane prepolymer was prepared using polypropylene glycol polyol at a molecular weight of 2000 with toluene diisocyanate (TDI). The toluene diisocyanate was obtained from the South City Group whereas the polypropylene glycol polyol at a molecular weight of 2000 was kindly supplied by TPI Polyol Co., Ltd.

Matrix resin preparation

Benzoxazine monomer (BA-a) was synthesized from bisphenol A, aniline, and paraformaldehyde at

a 1 : 2 : 4 molar ratio. This resin was prepared based on a patented solventless method.¹¹ The resulting benzoxazine monomer is solid at room temperature with transparent yellow color. The as-synthesized monomer was ground into fine powder and was taken for material characterization.

The urethane prepolymer was prepared by using propylene glycol at a molecular weight of 2000 with 2,4-toluene diisocyanate (TDI) at a 1 : 2 molar ratio. Small amount of dibutyltin dilaurate (DBDT) was used as a catalyst for the synthesis. The two reactants for urethane resin preparation were stirred under a nitrogen stream at 70°C for 2 h. 0.075% by weight of dibutyltin dilaurate was used as a catalyst. After the completion of the reaction, the obtained clear and viscous urethane prepolymers were cooled to room temperature and kept in a nitrogen-purged, closed container.

Benzoxazine/urethane polymer alloys preparation

The benzoxazine monomer (BA-a) was blended with the urethane prepolymers (PU) to provide BA-a/PU mixtures. Each resin was measured at the desirable mass fraction. The mixture was then heated to about 100°C in aluminum pan and mixed until a homogeneous mixture was obtained. The molten resin mixture was poured into an aluminum mold and step-cured in an air-circulated oven at 150, 170, 180, 190°C for 1 h each and 200°C for 2 h. Part of the mixture was taken for differential scanning analysis. The specimen was finally left to cool down to room temperature and was then ready for material characterizations.

Characterization methods

Chemorheological properties measurement

Chemorheological properties of each alloy were examined using a Rheometer (Haake Rheo Stress 600, Thermo Electron Cooperation) equipped with 20 mm in diameter parallel plate geometry. The measuring gap was set at 0.5 mm. The experiment was performed under an oscillatory shear mode at 1 rad/s. The testing temperature program was ramped from room temperature at a heating rate of 2°C/min to a temperature beyond the gel point of each resin and the dynamic viscosity was recorded.

Differential scanning calorimetry

The curing behavior and glass transition temperature of benzoxazine resins alloyed with urethane elastomer were examined using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. The thermogram was obtained using a heating rate of 10°C/min from room temperature to

300°C under nitrogen atmosphere maintained to be constant at 50 mL/min. The sample with a mass in a range of 3–5 mg was sealed in an aluminum pan with lid.

Density measurement

The densities of benzoxazine resins alloyed with urethane prepolymer were determined by water displacement method according to the ASTM D 792-91 (Method A). The dimension of specimens was in rectangular shape 25 mm × 50 mm × 2 mm.

Dynamic mechanical analysis

The dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH was used to investigate the dynamic mechanical properties and relaxation behaviors of BA-a/PU polymer alloys. The dimension of specimens was 10 mm × 50 mm × 2 mm. The test was performed in a three-point bending mode. In a temperature sweep experiment, a frequency of 1 Hz and a strain value of 0.1% were applied. The temperature was scanned from –150°C to the temperature beyond the glass transition temperatures (T_g) of each specimen with a heating rate of 2°C/min under nitrogen atmosphere. The storage modulus at glassy state was correlated to molecular rigidity of the polymer network whereas the storage modulus at rubbery plateau was dependent on crosslink density of the network.

Thermogravimetric analysis

The degradation temperature (T_d) and char yield of the BA-a/PU polymer alloys were studied using a DSC-TGA Q600 SDT from TA Instruments. The testing temperature program was ramped at a heating rate of 20°C/min from room temperature to 900°C under nitrogen atmosphere. The purge nitrogen gas flow rate was maintained to be constant at 100 mL/min. The sample mass used was measured to be ~10–20 mg. Degradation temperature of each specimen was determined from the temperature at 5% weight loss whereas char yield was obtained the weight residue at 800°C.

Thermomechanical analysis

The coefficient of thermal expansion (CTE) was measured with a Perkin-Elmer Instrument Technology SII Diamond thermal mechanical analyzer (TMA). The dimension of specimens was 2 mm × 2 mm × 2 mm and had flat surfaces. The specimen was heated from room temperature to the temperature beyond the glass transition temperature at a heating rate of 10°C/min.

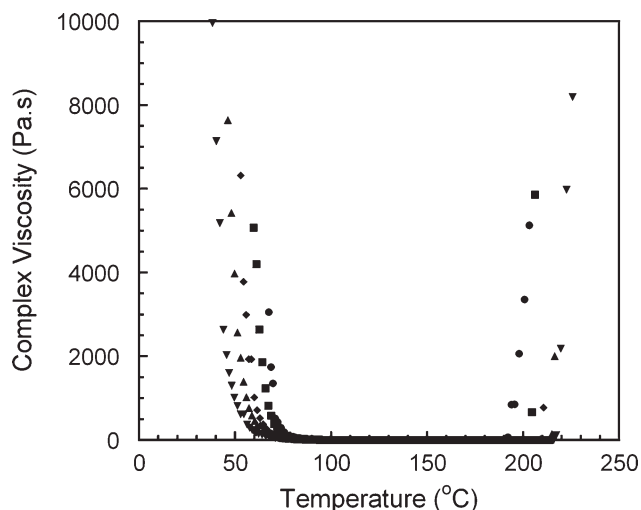


Figure 1 Viscosity of BA-a/PU resin at various compositions: (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, and (▼) 60/40.

Universal testing machine (Flexural Mode)

The flexural properties of the BA-a/PU polymer alloys were determined using a universal testing machine (model 5567) from Instron Co., Ltd. The test method was a three-point bending mode with a supporting span of 32 mm and tested at a crosshead speed of 0.85 mm/min. The dimension of the specimens is 25 mm × 50 mm × 2 mm according to ASTM D790M-93. The measured properties are averaged from eight specimens.

Hardness measurement (Shore D)

The hardness of polymer alloys samples was also measured using a shore D hardness tester (model ES-720G) from Micro Photonics. The specimens were 25 mm × 50 mm × 2 mm, and had flat surfaces following ASTM D2240.

Water absorption measurement

Water absorption measurement was conducted in accordance with ASTM D570 using a specimen dimension of 25 mm × 50 mm × 2 mm. Three samples of each composition were submerged in deionized water. The specimens were periodically removed and dried by wiping for weight measurements after which they were immediately returned to the water bath.

RESULTS AND DISCUSSION

Chemorheological behaviors

The effect of BA-a/PU resin mass ratios on chemorheology of the resin mixtures, which are miscible giving homogenous and transparent liquid, is shown in Figure 1. In the rheograms, all resin mixtures

showed a relatively high viscosity at room temperatures due to the solid state nature of these resin mixtures. They were transformed into liquid when the temperature was raised to their liquefying point (i.e., left side of the rheograms). At this point, the complex viscosity of all resin mixtures rapidly decreased. For consistency, the temperature at the viscosity value of 1000 Pa.s was investigated as a liquefying temperature of each resin.^{15,16} From the figure, it can be seen that the increasing urethane polymer fraction in the resin mixtures led to the lowering of their liquefying temperatures. This is due to the fact that the urethane prepolymer used is liquid while the BA-a resin is solid at room temperature. Therefore, the addition of the liquid urethane prepolymer in the solid BA-a resin caused the shifting of the transition from solid state to liquid state to lower temperature. From the above convention, the liquefying temperature of BA-a/PU resins 100/0, 90/10, 80/20, 70/30, and 60/40 were determined to be 71°C, 67°C, 60°C, 57°C, and 51°C, respectively. All resin mixtures became liquid after liquefying point that was the lowest viscosity of each resin system and is normally termed the A-stage viscosity. Lowering the resin liquefying temperature obviously enables the use of lower processing temperature of a compounding process, which is desirable in various composite applications.

Furthermore, at the end of the A-stage viscosity or at higher temperature, the resin mixtures underwent crosslinking reactions past their gel points, which was defined as a transition of liquid (sol) to solid (gel), (i.e., the right side of the rheograms), resulting in a sharp increase in their viscosities. In this case, the maximum temperature at which the viscosity was rapidly raised above 1000 Pa.s was used as gel temperature of each resin.^{15,16} From the figure, the gel point of the BA-a/PU resin mixture increased with increasing mass fraction of the urethane prepolymer. The gel temperature of BA-a/PU resins 100/0, 90/10, 80/20, 70/30, and 60/40 were determined to be 196, 205, 210, 216, and 219°C, respectively. These results suggested that the urethane prepolymer had effect on the curing reaction of the benzoxazine monomer. In other words, the processing window of the BA-a/PU resin mixtures was widened with an addition of the urethane prepolymer. Therefore, one advantage of adding urethane into BA-a/PU resin mixtures was to modify chemorheological behaviors of the benzoxazine resin. The widest processing window was ~ 70 to 215°C for BA-a/PU of 60/40 compared with the range of 90 to 195°C of the neat BA-a. This behavior provides BA-a/PU resins with sufficiently broad processing window for a typical compounding process in a composite manufacturing.

Figure 2 exhibits the effect of urethane prepolymer content on complex viscosity of BA-a/PU resin mix-

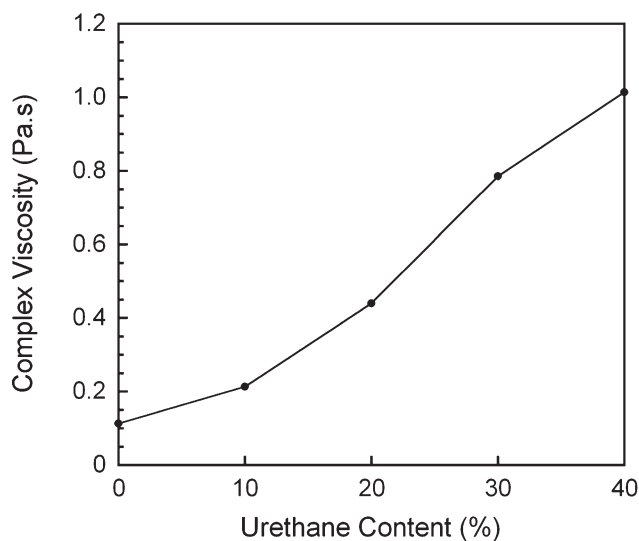


Figure 2 Effect of urethane content on viscosity of BA-a/PU resins determined at 120°C.

tures determined at 120°C. From the experiment, the complex viscosity of the benzoxazine-urethane resin mixtures significantly increased with increasing the amount of the urethane prepolymer as the urethane resin had much higher melt viscosity than that of the neat benzoxazine resin. This might be due to the higher molecular weight of the urethane prepolymer compared with that of the benzoxazine resin. The complex viscosity of BA-a/PU resin mixture at 0, 10, 20, 30, and 40% mass fractions of the PU were determined to be 0.11, 0.21, 0.44, 0.78, and 1.01 Pa.s, respectively. In practice, the lower viscosity of the resin can enhance the ability of the resin to accommodate greater amount of filler and increase filler wettability of the resin during the compounding process in a composite material preparation.^{15,16}

Density measurement of BA-a/PU polymer alloys

In this work, density measurement of all fully cured BA-a/PU specimens was performed to investigate the presence of void in the specimens. Figure 3 shows the density of specimens with various urethane contents comparing with their theoretical density. The calculated one was based on the basis that the densities of the polybenzoxazine and urethane prepolymer were 1.19 g/cm³ and 1.06 g/cm³.^{17,18} Furthermore, the theoretical densities of the BA-a/PU polymer alloys were determined to be 1.190, 1.177, 1.164, 1.151, and 1.138 g/cm³ in BA-a/PU 100/0, 90/10, 80/20, 70/30, and 60/40, respectively. Whereas the measured densities at 100/0, 90/10, 80/20, 70/30, and 60/40 mass ratios of the BA-a/PU alloys were found to be 1.188, 1.177, 1.160, 1.148, and 1.133 g/cm³, respectively. In the result, the densities of the polymer alloys were observed to

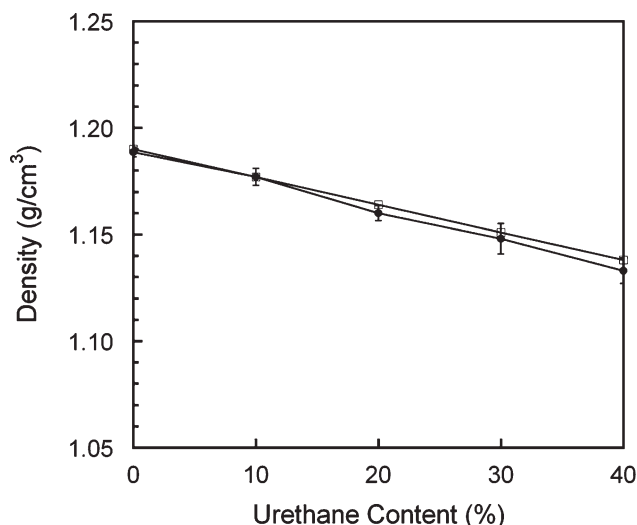


Figure 3 Density of BA-a/PU alloys at various compositions: (□) Theory density and (●) Actual density.

systematically decrease with increasing PU fraction suggesting that the theoretical and actual density of the BA-a/PU alloys followed the rule of mixture. Moreover, it can be observed that the actual densities were about the same with the values slightly lower than those of the theoretical densities. Because of the rather high melt viscosity of the urethane prepolymer, adding more urethane prepolymer directly affected on the mixing behavior and the obtained densities were normally slightly lower than the theoretical values. The phenomenon is likely to be caused by the presence of voids in the specimens as a result of mixing difficulty from an addition of the more viscous PU fraction into the benzoxazine resin.

DMA of the BA-a/PU polymer alloys

Transition temperatures of all BA-a/PU polymer alloys were also determined using DMA since the technique is highly sensitive to even minor transitions or relaxations. DMA senses any change in molecular mobility in the sample when temperature is raised or lowered. The dynamic modulus is one of the most important properties of materials for structural applications. Typically, mechanical damping is often the most sensitive indicator in determining all kinds of molecular motions, which are taking place in polymeric materials particularly in solid state. Figure 4 plots the loss modulus (E'') curves of the benzoxazine-urethane alloys at various compositions which had been fully cured to yield the crosslink structures of the infinite network as a function of temperature. The T_g of the alloys can be roughly estimated from the maximum peak temperature in the loss modulus curve of each specimen. From the figure, we can see that the T_g of the neat polybenzoxazine was determined to be 165°C whereas those

of the polymer alloys were about 177, 192, 220, and 245°C in BA-a/PU 90/10, 80/20, 70/30, and 60/40. Therefore, adding PU into the polybenzoxazine can substantially increase the T_g of the polymer alloys. Synergistic behavior of the T_g of the alloys was evidently observed, i.e., T_g 's of all alloys were greater than those of the BA-a and the PU, i.e., 165°C^{15,16} and -70°C,^{5,19} respectively. This is the unique characteristic of these polymer alloys as it exhibited synergistic behaviors in their glass transition which makes the systems highly attractive for high temperature application. The synergistic behavior of these polymer alloys has been discussed more elaborately in our previous work^{6,7} as to be due to the substantial enhancement in crosslink density of the alloys by the presence of urethane portion in the network. Both the rigidity of the polybenzoxazine and the enhancement on crosslink density from the urethane provided the synergism in glass transition temperature of the resulting polymer alloys. The possible network formation scheme or illustration between the ring-opening reaction of benzoxazine resin and urethane resin has been suggested in the work by Takeichi et al.⁵

Figure 5 shows the storage modulus (E') of BA-a/PU alloys at various compositions. From the figure, three areas including the glassy state, the transition region, and the rubbery plateau were obtained for each sample. Ordinarily, the storage modulus of the materials decreased with increasing temperature. At room temperature, the storage modulus in a glassy state of the BA-a/PU binary systems was expectedly found to systematically decrease with increasing PU mass fraction. We can see that the storage moduli of the BA-a/PU alloys were reduced from 5.2 GPa to 1.8 GPa with the addition of the PU from 0 to 40% by weight. As a consequence, the presence of the

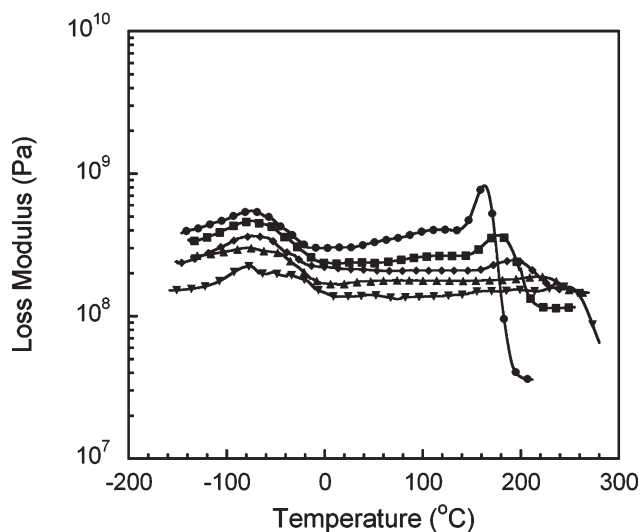


Figure 4 Loss modulus of BA-a/PU alloys at various compositions: (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, and (▼) 60/40.

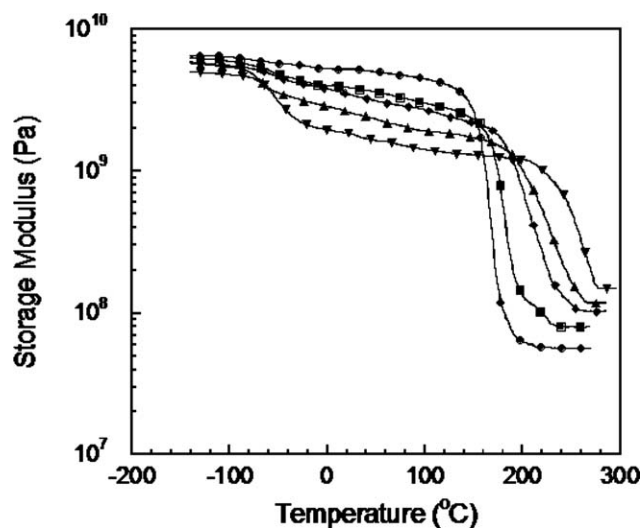


Figure 5 Storage modulus of BA-a/PU alloys at various compositions: (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, and (▼) 60/40.

more flexible PU in the copolymers resulted in the more flexible polymer hybrids as seen from the lower room temperature modulus.

Effects of urethane prepolymer on the storage modulus in the rubbery plateau region of their polymer alloys are illustrated in Figure 6. From the figure, the storage modulus in the rubbery plateau region tended to increase with the mass fraction of the PU which was an opposite trend to the storage modulus in the glassy state. The storage moduli in the rubbery plateau region were systematically increased from 56 MPa to 148 MPa with an addition of the PU fraction from 0 to 40% by weight. This suggested that the increase in the PU content in the polymer alloys possibly resulted in an enhancement of the crosslink density

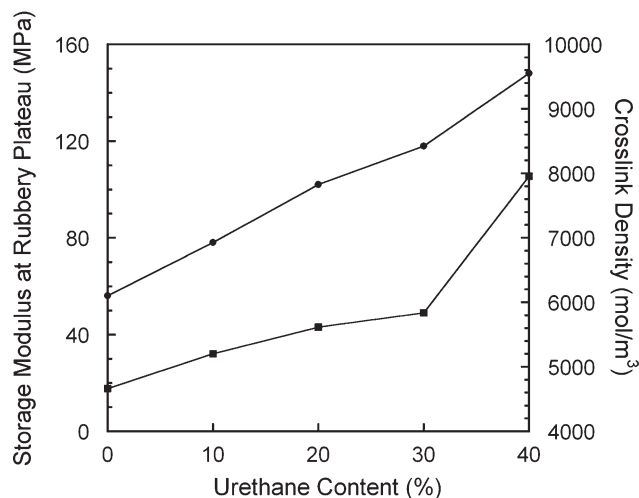


Figure 6 Storage modulus at rubbery plateau and crosslink density of BA-a/PU alloys at various compositions: (●) Storage modulus at rubbery plateau and (■) Crosslink density.

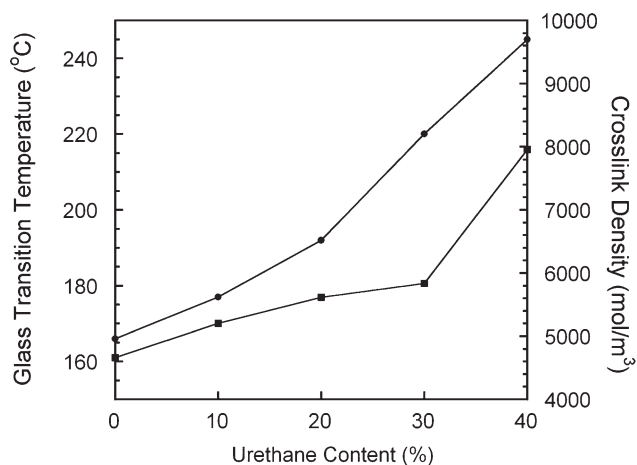


Figure 7 Glass transition temperature and the crosslink density of BA-a/PU alloys at various compositions: (●) Glass transition temperature and (■) Crosslink density.

sity of the fully cured specimens which was closely related to the rubbery plateau modulus. For a tight network structure, i.e., rubbery plateau modulus is greater than 10^7 Pa such as in our case, the non-Gaussian character of the polymer network becomes more and more pronounced and the equation from theory of rubbery elasticity no longer holds. The approximate relation expressed in eq. (1) below proposed by Neilsen^{20,21} is thus preferred and is reported to better describe the elastic properties of dense network, e.g., in epoxy systems.^{3,22,23}

$$\log\left(\frac{E'}{3}\right) = 6.0 + 293(\rho/M_c) \quad (1)$$

where E' (Pa) is the storage modulus in a rubbery plateau region, ρ (g/cm^3) is the density of the material at room temperature, and M_c (g/mol) is the molecular weight between crosslink points. The crosslink density of our polymer alloys was found to increase with the mass fraction of the urethane prepolymer. The crosslink density of the BA-a/PU polymer alloys was estimated to be 4338 mol/m^3 in BA-a/PU 100/0, 4829 mol/m^3 in BA-a/PU 90/10, 5227 mol/m^3 in BA-a/PU 80/20, 5443 mol/m^3 in BA-a/PU 70/30, and 5779 mol/m^3 in BA-a/PU 60/40.

In addition, the effect of molecular weight between crosslinks (i.e., inversely proportional to its crosslink density) on a T_g of a copolymer or a non-uniform polymer network can be accounted for using the equation also proposed by Neilsen.^{21,24}

$$T_g - T_{g(0)} = \frac{k}{M_c} \quad (2)$$

The number average molecular weight between crosslinks is M_c . $T_{g(0)}$ is the glass transition temperature of the uncrosslink polymer. Figure 7 illustrates

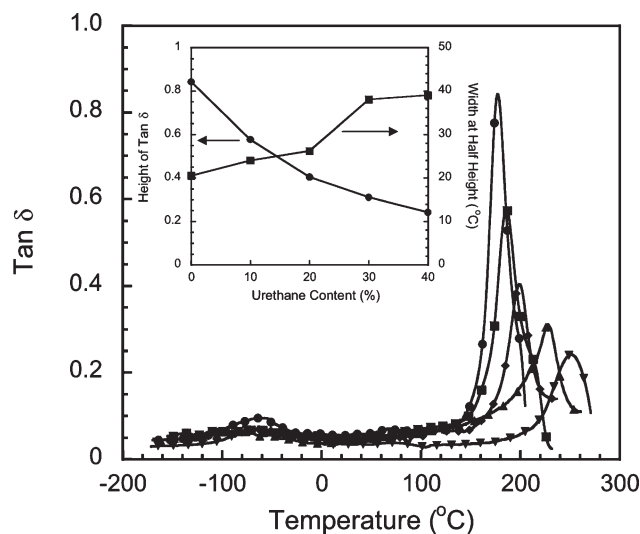


Figure 8 Tan δ of BA-a/PU alloys at various compositions: (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, and (▼) 60/40.

the T_g from loss modulus and crosslink density of BA-a/PU alloys at various compositions. As seen from this figure, the T_g of the polymer network increased when its crosslink density in the alloys increased, which is in good agreement with our DMA results.

Tan δ or loss tangent curves, obtained from the ratio of energy loss or viscous part (E'') to storage energy or elastic part (E') of dynamic modulus of material, are shown in Figure 8. The T_g of the polymer alloys can also be determined from the maximum peak temperature on the tan δ curve of each sample. As shown in the figure, T_g 's of the alloys were observed to shift to higher temperature when the urethane prepolymer content in the alloys increased. Furthermore, an inset of Figure 8 illustrates the magnitude of the tan δ peak maximum reflecting the large scale mobility associated with α relaxation. The peak height of the tan δ was found to decrease with increasing the mass fraction of the PU. This confirmed the reduction in segmental mobility of polymer chains with increasing crosslink density as PU fraction in the alloy increased. The width at half height of the tan δ relates to the network homogeneity. The width at half height of the tan δ curves of our BA-a/PU polymer alloys were broader in the PU rich systems implying network heterogeneity to be more pronounced with an increasing amount of the PU.⁸

Thermal degradation of BA-a/PU polymer alloys (TGA)

Thermal degradation of BA-a/PU polymers was investigated by thermogravimetric analysis (TGA). Figure 9 shows the degradation temperature and

char yield at various urethane contents under nitrogen atmosphere. The T_d 's of the neat polybenzoxazine and the polyurethane were determined to be 325°C and 305°C whereas their alloys showed the T_d values of 326, 327, 334, and 336°C in BA-a/PU 90/10, 80/20, 70/30, and 60/40. As evidently seen in the figure, the T_d 's of the polymer alloys were found to be slightly higher than that of the neat polybenzoxazine. Consequently, synergistic behavior of T_d of these alloys were also observed, i.e., the T_d 's of all alloys were greater than that of the neat BA-a (325°C) and the neat PU (305°C). Therefore, an incorporation of the PU into the polybenzoxazine was found to enhance thermal stability of the polybenzoxazine. These results might be due to the reaction of the isocyanate in urethane prepolymer and the hydroxyl of the polybenzoxazine to increase a crosslink density of the polymer alloys as aforementioned.

Another interesting feature in the TGA thermograms is the percent residual weight of our polybenzoxazine alloys which reported at 800°C under N_2 atmosphere. It can be seen that the residual weight of the BA-a/PU alloys were found to systematically decrease with increasing PU fraction. This is due to the fact that polybenzoxazine possessed higher char yield value of about 29% while no char residue was found for the polyurethane used. The chemical structure of the polyurethane composed of a less thermally stable aliphatic structure of the polypropylene glycol polyol compared with the prevalent benzene rings in the molecular structure of the polybenzoxazine. The char yields of BA-a/PU alloys at 10, 20, 30, and 40% mass fractions of the PU were determined to be 24.1 wt %, 23.4 wt %, 20.7 wt %, and 18.7 wt %, respectively. This result is also

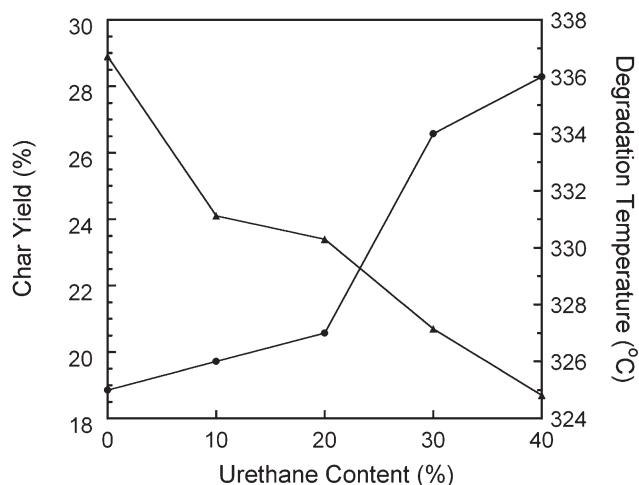


Figure 9 Thermal degradation of BA-a/PU alloys at various compositions: (▲) Char yield and (●) Degradation temperature.

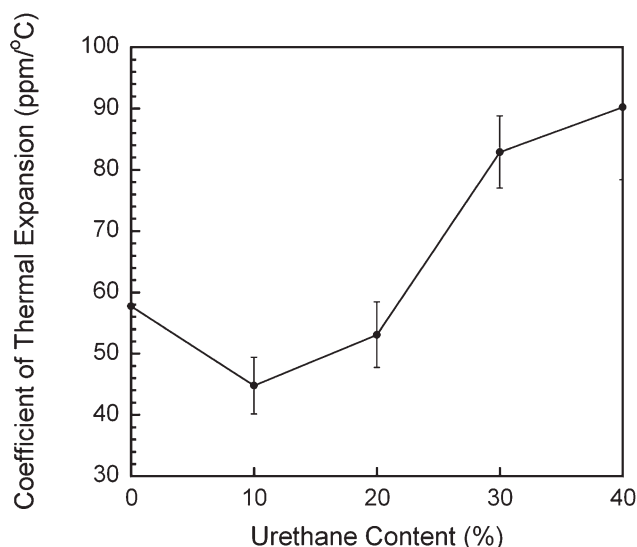


Figure 10 Effect of urethane content on coefficient of thermal expansion of BA-a/PU alloys at various compositions.

consistent with those reported by Takeichi et al. and Takeichi.^{5,19}

Coefficient of thermal expansion of BA-a/PU polymer alloys

During heat transfer, the energy that is stored in the intermolecular bonds between atoms changes. When the stored energy increases, so does the length of the molecular bonds. As a result, solids typically expand in response to heating and contract on cooling. This dimensional response to temperature change is expressed by its CTE. Figure 10 exhibits the CTE characteristics of BA-a/PU alloy specimens at various urethane mass fractions. The CTE values of BA-a/PU 100/0, BA-a/PU 90/10, BA-a/PU 80/20, BA-a/PU 70/30, and BA-a/PU 60/40 were determined to be 57.7, 44.7, 53.0, 82.8, and 90.2 ppm/°C, respectively. It was clearly observed the CTE of our alloys did not show a linear relationship with the composition of the alloys but also exhibited a synergistic behavior with the minimum CTE value at BA-a/PU 90/10 mass fraction. The CTE of BA-a/PU at 90/10 and 80/20 weight ratios were found to be lower than that of the neat polybenzoxazine and increased to higher values when the amount of PU fraction was greater than 20 wt %. In principle, the addition of the PU which is more expansible than BA-a due to its elastomeric nature, the resulting BA-a/PU alloys should result in an increase in their CTE values as observed in the PU content of greater than 20% by weight region. The observed synergistic behavior in CTE of these polymer alloys in the vicinity of 10–20% by weight of implied that the effect of crosslink density enhancement in the alloy's CTE

dominated the effect of the higher expansion of the PU provided that the PU mass fraction was maintained below 20% by weight.

Flexural properties of BA-a/PU polymer alloys

In this investigation, the specimens for flexural analysis were loaded until failure and the stress–strain curves were obtained for each sample. The flexural strength of a thermosetting resin is influenced by a number of interrelated system parameters including T_g , molecular weight between crosslinks, crosslink density, free volume, chemical structure, network irregularity and perfection, and many other contributing factors.²⁵ Flexural properties (flexural strength, flexural modulus, and elongation at break) of BA-a/PU polymer alloys were shown in Table I. The flexural strength of the neat polybenzoxazine was determined to be 130 MPa. Interestingly, the strength values of the BA-a/PU alloys were observed to exhibit also a synergistic behavior with the maximum flexural strength value of 142 MPa observed at the BA-a/PU mass ratio of 90/10. In addition, with an increase of the PU fraction (i.e., 20 wt %, 30 wt %, and 40 wt %), the flexural strength values were found to decrease systematically. Those flexural strengths of the BA-a/PU alloys were determined to be 120, 89, and 60 MPa in BA-a/PU 80/20, 70/30, and 60/40. This finding coincides with the phenomenon found in CTE and T_g as discussed earlier. Our result is also in good agreement with the result previously reported by Rimdusit et al.⁶

The maximum flexural modulus value of 5.5 GPa belonged to neat polybenzoxazine. The flexural modulus was also found to linearly decrease with increasing amount of PU for all BA-a/PU alloy systems. The flexural modulus values of BA-a/PU alloys were 4.1 GPa, 3.4 GPa, 2.5 GPa, and 2.1 GPa for BA-a/PU of 90/10, 80/20, 70/30, and 60/40 mass ratios, respectively. The flexural modulus shows a behavior nearly identical to that of the storage modulus at room temperature determined by DMA. This phenomenon was due to the fact that the addition of the softer urethane resin into the benzoxazine resin was expected to lower the stiffness of the

TABLE I
Flexural Properties of BA-a/PU Copolymers at Various Compositions

| PU content (%) | Flexural strength (MPa) | Flexural modulus (GPa) | Flexural strain at break (%) |
|----------------|-------------------------|------------------------|------------------------------|
| 0 | 130 | 5.5 | 2.5 |
| 10 | 142 | 4.1 | 3.5 |
| 20 | 120 | 3.4 | 3.8 |
| 30 | 89 | 2.5 | 4.1 |
| 40 | 60 | 2.1 | 5.1 |

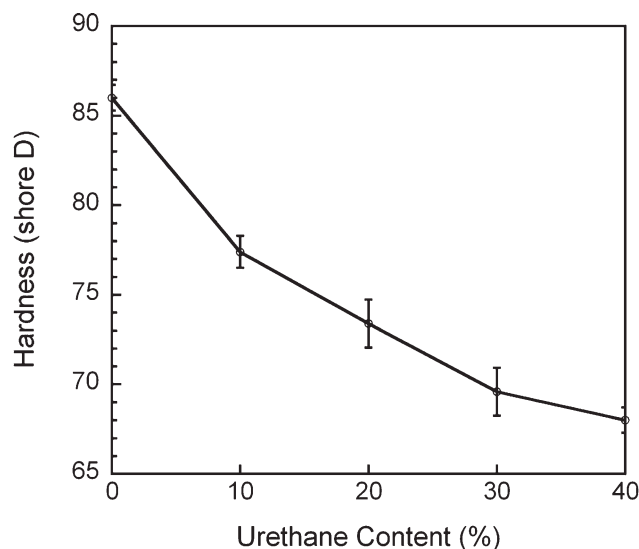


Figure 11 Effect of urethane content on surface hardness of BA-a/PU alloys at various compositions.

polybenzoxazine alloys as a result of an elastomeric nature of the PU used.^{5,19}

The effect of urethane prepolymer on the flexural strain at break of polybenzoxazine as can be seen in Table I. The flexural strain at break of polybenzoxazines alloyed with urethane prepolymer at 0, 10, 20, 30, and 40% were determined to be 2.5, 3.5, 3.8, 4.1, and 5.1, respectively. Normally, the addition of the more flexible urethane prepolymer to the rigid polybenzoxazine matrix should also contribute to the increased strain at breakage for the alloys.^{5,19}

Surface hardness of BA-a/PU polymer alloys

Hardness is defined as the resistance offered by a specimen to the penetration of a hardened steel truncated cone (Shore-A), pointed cone (Shore-D), or a spherical or flat indenter (foam hardness). In this study, Shore-D hardness was measured on a scale that was graduated from 0 to 100 divisions; 0 denoting the lowest and 100 the highest degree of hardness. In Figure 11, the surface hardness (Shore D) values of the BA-a/PU polymer alloys at different PU content were presented. As expected, the surface hardness of the polymer alloys was found to systematically decrease with increasing PU fraction. An addition of PU to BA-a was found to diminish the resistance of the BA-a deformation. The surface hardness values of the fully cured BA-a/PU alloys were observed to be 86, 77, 73, 69, and 68 shore D in BA-a/PU 100/0, 90/10, 80/20, 70/30, and 60/40. The surface hardness of the urethane was reported to be ~ 40 shore D.²⁶ As a consequence, the hardness of the BA-a/PU alloys tended to follow a

simple rule of mixture. This phenomenon was similar to hardness values of polyurethane reinforced with aluminum oxide (Al_2O_3) particles reported by Zhou et al.²⁷

Water absorption of BA-a/PU polymer alloys

Figure 12 shows percent water absorption of BA-a/PU alloys versus time. It can be seen in this figure that the percent water absorption value of BA-a alloyed with the PU tended to increase with an addition of the PU. Moreover, the percent water absorption was observed to increase sharply in the first 24 h of the test, and reach a plateau value of 1.3% in BA-a/PU 100/0, 2.0% in BA-a/PU 90/10, 2.8% in BA-a/PU 80/20, and 4.3% in BA-a/PU 70/30, and 4.7% in BA-a/PU 60/40. To explain the diffusion in the material, the generalized equation can be expressed as

$$\frac{M_t}{M_\infty} = k_n t^n \quad (3)$$

where M_t is the mass of sample at time t and M_∞ the mass of sample at saturation or infinite time.

The diffusion behaviors can be classified as: super case II ($n > 1$), case II ($n = 1$), anomalous ($1/2 < n < 1$), classical/Fickian ($n = 1/2$), or pseudo-Fickian ($n < 1/2$).²⁸ From the plots of $\log M_t/M$ versus $\log t$, the obtained slope of the neat polybenzoxazine was about 0.71 implied that its diffusion behavior was an anomalous type. The slopes of the BA-a/PU polymer alloys were determined to be in a range of 0.23–0.32 suggesting Fickian type diffusion behavior.

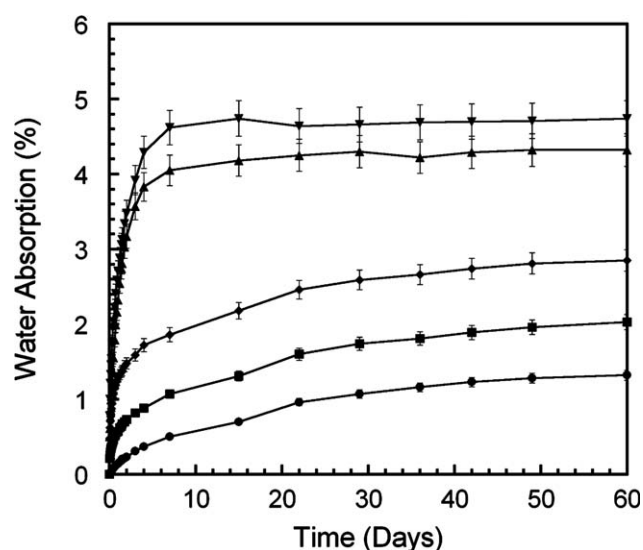


Figure 12 Percentage water absorption of BA-a/PU alloys at various compositions: (●) 100/0, (■) 90/10, (◆) 80/20, (▲) 70/30, and (▼) 60/40.

CONCLUSIONS

An addition of urethane resin in BA-a/PU resin mixtures was found to substantially widen their processing window. Density of the alloys decreased with the urethane contents. Synergism in thermal stability was clearly observed in these polymers. The phenomenon was explained by an ability of the PU fraction to substantially enhanced crosslink density of the resulting polymer alloys. Furthermore, the char yield of the BA-a/PU alloys was found to systematically increase with the increasing amount of the BA-a fraction. Whereas the CTE of the alloys was observed to show a minimum at the BA-a/PU = 90/10 mass ratio. The flexural strength of the BA-a/PU alloys exhibited the ultimate value at BA-a/PU = 90/10 mass ratio whereas the flexural modulus, flexural strain at break and surface hardness showed behaviors following a rule of mixing. Last but not least, BA-a fraction in the alloy was used to effectively lower the water absorption of the resulting polymer.

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