# Thermomechanical Characteristics of Benzoxazine–Urethane Copolymers and Their Carbon Fiber-Reinforced Composites

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**ABSTRACT:** Copolymers of polybenzoxazine (BA-a) and urethane elastomer (PU) with three different structures of isocyanates [i.e., toluene diisocyanate (TDI), diphenylmethane diisocyanate, and isophorone diisocyanate ], were examined. The experimental results reveal that the enhancement in glass transition temperature ($T_g$) of BA-a/PU copolymers was clearly observed [i.e., $T_g$ of the BA-a/PU copolymers in 60 : 40 BA-a : PU system for all isocyanate types ($T_g$ beyond 230°C) was higher than those of the parent resins (165°C for BA-a and $-70$°C for PU)]. It was reported that the degradation temperature increased from 321°C to about 330°C with increasing urethane content. Furthermore, the flexural strength synergism was found at the BA-a : PU ratio of 90 : 10 for all types of isocyanates. The effect of urethane prepolymer based on TDI rendered the highest $T_g$, flexural modulus, and flexural strength of the copolymers among the three isocyanates used. The preferable isocyanate of the binary systems for making high processable carbon fiber composites was based on TDI. The flexural strength of the carbon fiber-reinforced BA-a : PU based on TDI at 80 wt % of the fiber in cross-ply orientation provided relatively high values of about 490 MPa. The flexural modulus slightly decreased from 51 GPa for polybenzoxazine to 48 GPa in the 60 : 40 BA-a : PU system. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3823–3830, 2009

**Key words:** composites; curing of polymers; thermosets; reinforcement

## INTRODUCTION

Polybenzoxazine is a newly developed class of thermosetting polymers derived from ring-opening polymerization of their precursors. The polymer possesses various good properties such as near-zero shrinkage upon polymerization as well as high thermal stability and excellent mechanical properties,[1–6] thus showing high potential in many applications.[7–14] Although the high rigidity of polybenzoxazines is a unique strength in polybenzoxazines, reduced rigidity may also be desired for certain applications. Copolymerizing is considered to be a potentially effective measure to toughen polybenzoxazine because the polybenzoxazine has been reported to be able to undergo hybrid network formation with several other polymers or resins.[13–19] For example, epoxy and urethane elastomer were used to blend with benzoxazine monomer to improve thermal stability and mechanical properties of the polymer. The reaction of epoxide and isocyanate functional groups with benzoxazine monomer can yield potentially useful copolymers such as these reported in the works of Takeichi et al. and Rimdusit et al.[15,16] The poly(urethane-benzoxazine) copolymers showed single glass transition temperature ($T_g$), implying no phase separation in the resulting products. The properties of the films ranged from elastomers to plastics, depending on the content of the benzoxazine fraction in the copolymers.[15]

This research aims to develop an alternative approach to improve toughness of polybenzoxazine by copolymerizing with urethane elastomer and to examine the characteristics of the obtained copolymers based on different types of isocyanates in the urethane precursor. In general, elastomeric urethane can be produced by a reaction of a polyfunctional isocyanate, most often, with hydroxyl compounds. The polyfunctional isocyanates can be aromatics, aliphatic, cycloaliphatic, or polycyclic in structure and can be used directly to produce or modify urethane resins. This research was carried out to study the effects of different isocyanate types such as toluene diisocyanate (TDI) and diphenylmethane

diisocyanate (MDI) to substitute the presently used isophorone diisocyanate (IPDI) system because IPDI is less available in Thailand and much more expensive in comparison with the other two systems. Additionally, this copolymer will be utilized as a matrix of carbon fiber. The resulting carbon fiber-reinforced polybenzoxazine (BA-a)/urethane elastomer (PU) copolymers was characterized as a potential use as light weight composites with high performance.

## MATERIALS AND METHODS

### Raw materials

Benzoxazine monomer was based on bisphenol-A, aniline, and formaldehyde and was designated as BA-a. The bisphenol-A (PC grade) was supported by Thai Polycarbonate (Rayong, Thailand). Para-formaldehyde (AR grade) was purchased from Merck Ltd. (Bangkok, Thailand) and aniline (AR grade) was purchased from Panreac Quimica S.A. (Bangkok, Thailand). IPDI was obtained from Degussa-Huls AG (Bangkok, Thailand). Both MDI and TDI were obtained from South City Group (Bangkok, Thailand), whereas the polyether polyol at a molecular weight of 2000 was kindly supplied by TPI Polyol Co., Ltd. (Rayong, Thailand). Carbon fiber filament, Besfight HTA-7-6000, is from Toho Beslon (Japan). The fiber diameter is 7 μm with a tensile strength of 3.0 GPa and a tensile modulus of 240 GPa.

### Resin preparation

The benzoxazine monomer (BA-a) was prepared according to the reported method[20] and used as synthesized. The urethane prepolymer was prepared by using polyether polyol mixed with different diisocyanates (i.e., IPDI, MDI, and TDI) at a 1 : 2 molar ratio by using 0.4 g dibutyltin dilaurate as a catalyst. The two reactants for urethane resin preparation were blended and stirred under a nitrogen stream at 90°C for 2 h for IPDI, at 70°C for 1 h for TDI, and at 45°C for 1 h for MDI.

### Benzoxazine/urethane copolymer preparation

The as-synthesized benzoxazine monomer (BA-a) was blended with different types of the urethane prepolymers (PU) to provide BA-a : PU mixtures at various weight ratios (i.e., 100 : 0, 90 : 10, 80 : 20, 70 : 30, and 60 : 40). The mixture was typically heated to about 80°C and mixed until a homogeneous mixture was obtained. The molten mixture was poured into an aluminum mold and step-cured in an air-circulated oven at 150, 170, and 190°C for 1 h each and 200°C for 2 h. The specimen was finally left to cool down to room temperature for further characterizations.

### Composite manufacturing

Carbon fiber and BA-a : PU prepregs were prepared by brush application of the resin mixture solutions (50% by weight in THF) onto a drum-wound unidirectional carbon fiber. Twenty plies of the prepregs were laminated in an (0°/90°) arrangement and were cured at 150, 170, and 190°C for 1 h at each temperature in a hydraulic hot press machine at 14 MPa and 200°C for 2 h in an air-circulating oven. The carbon fiber content in the composite was ∼ 75% by weight.

### Sample characterization

The curing behavior of the benzoxazine monomer with urethane prepolymer at various weight ratios was examined by using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. The thermograms were obtained by using a heating rate of 10°C/min from 30 to 300°C under the purge nitrogen gas flow rate of 50 mL/min.

The degradation temperature ($T_d$) and char yield were studied by using a thermogravimetric analyzer (Perkin-Elmer model Diamond TG/DTA). A heating rate of 20°C/min from 40 to 900°C was used to acquire the thermograms. The purge nitrogen gas flow rate was 100 mL/min. The sample was ∼ 10 mg.

According to ASTM D 790M-93, the flexural properties of the copolymer specimens and the composites were determined by using a universal testing machine (model 5567) from Instron. The five specimens of 25 mm × 60 mm × 3 mm were tested to determine the average values.

The dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH was used to investigate the viscoelastic properties of the specimens in the dimension of $10 \times 50 \times 2$ mm$^3$ (bending mode). The tests were performed under flexural stress in a temperature sweep mode with a fixed frequency of 1 Hz and a strain amplitude of 30 μm. Each specimen was tested by using a heating rate of 2°C/min from 30 to 300°C under nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Network formation of benzoxazine/urethane copolymers

The curing exotherms of the neat benzoxazine monomer and the urethane prepolymer using TDI are exhibited in Figure 1. The investigated compositions of the BA-a : PU mixtures using TDI were 60 : 40, 70 : 30, 80 : 20, 90 : 10, and 100 : 0 mass ratios. It could be observed that the exothermic peak of the as-synthesized benzoxazine monomer was located at 227°C, which is a characteristic of the thermal curability of this resin.[21–23] The exothermic peak of the curing
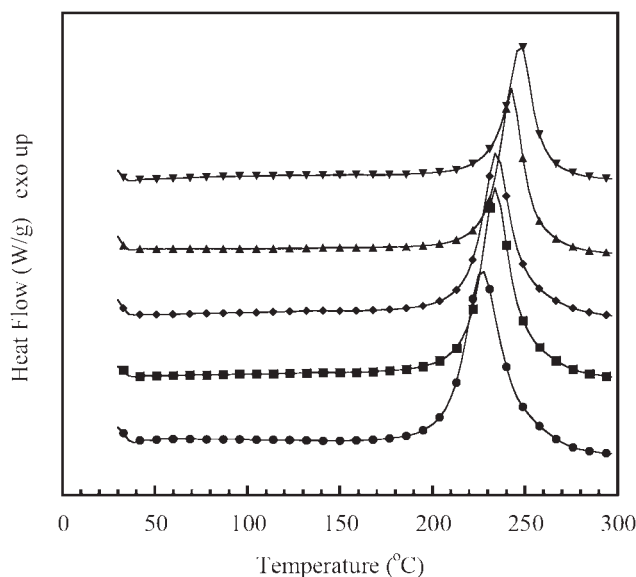
**Figure 1** DSC thermograms of BA-a : PU using toluene diisocyanate (TDI) at various compositions: (●) BA-a, (■) 90 : 10, (◆) 80 : 20, (▲) 70 : 30, (▼) 60 : 40.

reaction was shifted to a higher temperature when the urethane prepolymer fraction in the copolymers increased. Moreover, it can be noted that the positions of the exothermic peaks of BA-a : PU mixtures using TDI at 90 : 10, 80 : 20, 70 : 30, and 60 : 40 mass ratios are 234, 238, 243, and 244°C, respectively. In principle, the reactions between BA-a : PU were expected to comprise at least two reactions: the first reaction is the exothermic curing peak among the benzoxazine monomers, while the second one should be the reaction between the isocyanate group of the urethane prepolymer and phenolic hydroxyl group of the polybenzoxazine.[15,16,24] The second reaction was expected to proceed after the phenolic hydroxyl group from ring opening of the benzoxazine monomer was produced. The thermograms also suggested that the decrease of the area under the curing reaction peaks the binary mixtures when the amount of all urethane prepolymers based on TDI increased. The phenomenon is attributed to the change from the BA-a : BA-a interaction to the BA-a : PU interaction with increasing the PU fraction in the copolymers. The exothermic heat reaction of BA-a : PU mixtures using TDI at 100 : 0, 90 : 10, 80 : 20, 70 : 30, and 60 : 40 mass ratios are 286.4, 232.0, 216.2, 157.7, and 155.5 J/g, respectively. The systematic decrease of the exotherms with the PU implied the BA-a : PU interaction possessed a lower heat of reaction per mole of the reactants. Excessive amount of the PU in the binary mixtures might also lead to the presence of the unreacted PU in the fully cured copolymers, and then the reduction of the heat of reaction.

An effect of the types of isocyanates in PU on the curing behaviors of the BA-a : PU copolymers is

shown in Figure 2. The figure illustrates the curing behaviors of the neat benzoxazine monomer (BA-a) compared with those three binary mixtures (BA-a : PU) at a fixed mass ratio of 60 : 40. From this graph, the addition of the urethane prepolymer based on different types of isocyanates in benzoxazine monomer resulted in a similar shift of the exothermic curing peak of the neat benzoxazine monomer at 227°C to a higher temperature. The exothermic curing peak of BA-a : PU based on IPDI and TDI were found to be about 248 and 244°C, respectively, whereas that of BA-a : PU based on MDI was about 240°C.

Figure 3 indicates the DSC thermograms of the BA-a : PU mixtures based on TDI at a mass ratio of 60 : 40 at various curing conditions. The heat of reaction determined from the area under the exothermic peak was 155.5 J/g for the uncured mixture (i.e., 0% conversion). The values reduced to 111.0 J/g (29% conversion) after curing at 150°C for 1 h and decreased to 65.9 J/g (58% conversion) after further curing at 170°C for 1 h and decreased to 4.5 J/g (97% conversion) for further curing at 190°C for 1 h. After post curing at 200°C for another 1 h, the exothermic heat of reaction disappeared, corresponding to the fully cured stage of the copolymer. The degree of conversion was determined according to the following relationship:

$$\% \text{ Conversion} = \left[1 - \frac{H_{rxn}}{H_0}\right] \times 100 \qquad (1)$$

where $H_{rxn}$ is the heat of reaction of the partially cured specimens; and $H_0$ is the heat of reaction of the uncured resin.
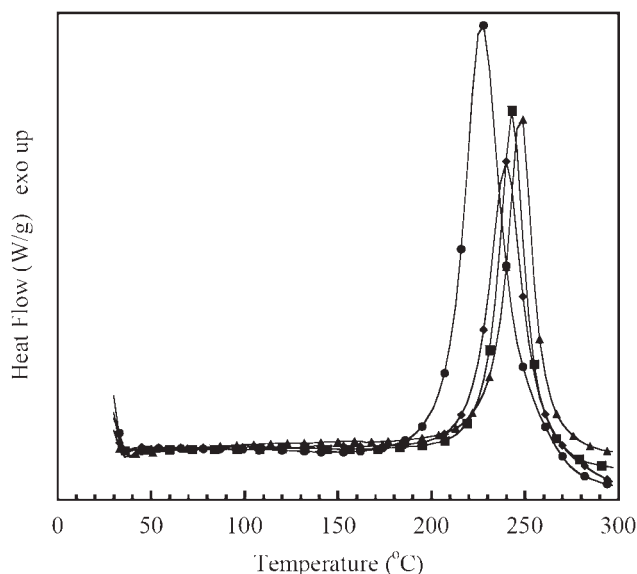


**Figure 2** DSC thermograms and the curing behaviours of BA-a and BA-a : PU at fixed mass ratios of 60 : 40 for different types of isocyanates: (●) BA-a, (■) BA-a using TDI, (▲) BA-a : PU using MDI, (▼) BA-a : PU using IPDI.
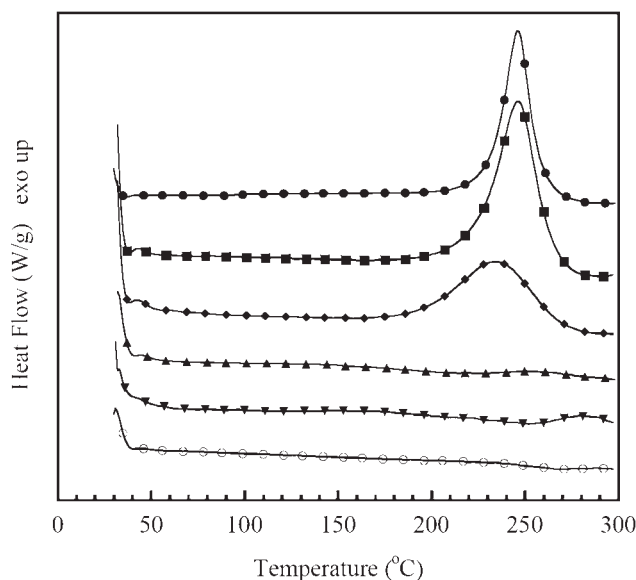
**Figure 3** Curing condition of BA-a : PU using TDI at fixed mass ratios of 60 : 40. (●) Uncured, (■) 150°C/1 h; (◆) 150°C/1 h, 170°C/1 h; (▲) 150°C/1 h, 170°C/1 h, 190°C/1 h; (▼) 150°C/1 h, 170°C/1 h, 190°C/1 h, 200°C/1 h; (○) 150°C/1 h, 170°C/1 h, 190°C/1 h, 200°C/2 h.

Both $H_{rxn}$ and $H_0$ values can be obtained from DSC experiments. The calculated conversion suggested that the curing reaction of BA-a : PU copolymers could rapidly occur at high temperature. As a consequence, the curing temperature at 150°C for 1 h, 170°C for 1 h, 190°C for 1 h, and 200°C for at least 1 h was chosen to affirm that the samples were fully cured.

## Dynamic mechanical properties of BA-a : PU copolymers

Due to the ultimate properties in $T_g$ and flexural properties of TDI systems, these copolymers were further evaluated as a potential use for matrices of carbon fiber composites. Figure 4 shows the dynamic mechanical properties of BA-a : PU copolymers by using TDI at various compositions. The storage modulus in the glassy state of the copolymers was observed to systematically decrease with increasing PU mass fraction as a result of the more flexible characteristics of elastomeric PU as recently reported.[15,16] At room temperature, the storage modulus reduced from 6.0 to 2.2 GPa after an incorporation of PU from 0 to 40 wt % into the binary mixtures. These values showed similar trends as in our previous work.[16] Additionally as the mass fraction of the PU in the copolymers increased, the copolymer modulus-temperature curve showed the increase of the slope. This characteristic implies more thermal stability of polybenzoxazine than that of polyurethane. In addition, the presence of PU in the copolymers was able to enhance the crosslink
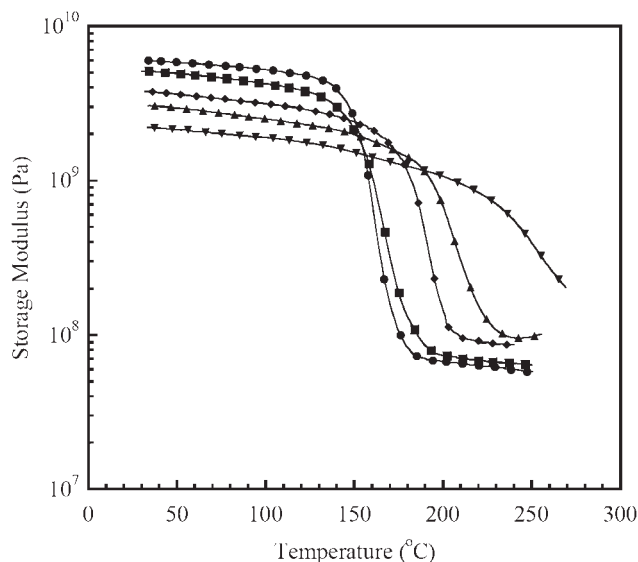


**Figure 4** Storage modulus of BA-a : PU alloys using TDI at various compositions: (●) BA-a, (■) 90 : 10, (◆) 80 : 20, (▲) 70 : 30, (▼) 60 : 40.

density of fully cured specimens as reported by Takeichi et al.[15] and Rimdusit et al.[16] that the rubbery plateau modulus values of BA-a : PU trended to increase with the PU mass fraction.

From DMA thermograms (Fig. 5), the $T_g$s of the BA-a : PU copolymers (applying TDI at various compositions) were exhibited by using the maximum of tan δ curve. As mass fraction of PU increased, the peak height of tan δ trended to decrease, and the peak position shifted to a higher temperature. Because tan δ is defined as the ratio of viscous to elastic components of dynamic modulus of material, it suggested the reduction in the segment mobility of
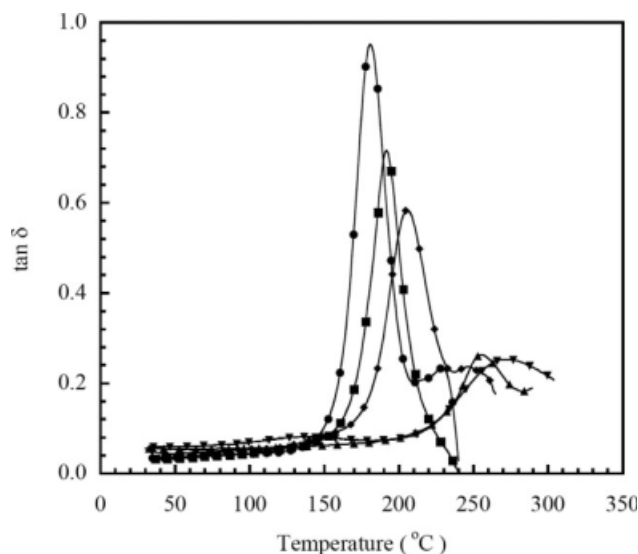


**Figure 5** tan δ of BA-a : PU alloys using TDI at various compositions: (●) BA-a, (■) 90 : 10, (◆) 80 : 20, (▲) 70 : 30, (▼) 60 : 40.
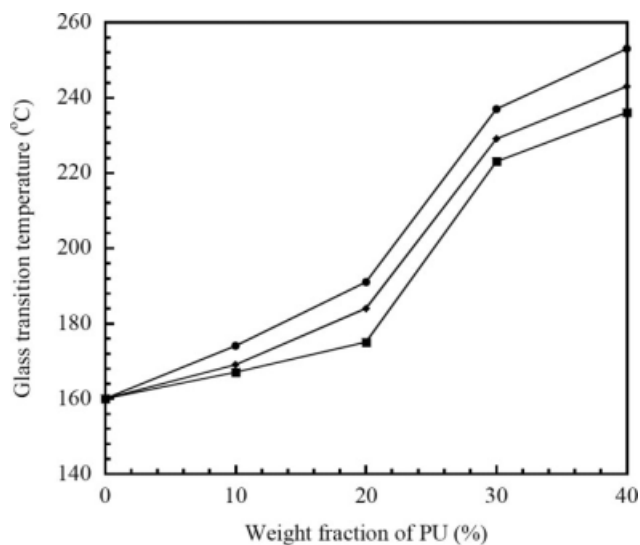
**Figure 6** Glass-transition temperature of BA-a : PU alloys for different types of isocyanates at various compositions: (●) BA-a : PU based on TDI, (■) BA-a : PU based on MDI, (◆) BA-a : PU based on IPDI.

chain due to increasing crosslink density with the increase of PU mass fraction in the copolymers. Moreover, the tan δ curves of BA-a : PU copolymers were broader than the neat polybenzoxazine, which represents the broader distribution of polymer network structure in the BA-a : PU copolymers.

Figure 6 shows the $T_g$ of the BA-a : PU copolymer with the PU based on TDI, IPDI, and MDI, respectively. The enhancement of the $T_g$ was observed in all three copolymer systems. The effect of the urethane mass fraction on the $T_g$ of the BA-a : PU copolymers was previously reported by Rimdusit et al.[16] using DMA. In their case, $T_g$ of the copolymers at each composition was defined by using the maximum of the loss modulus. They reported that their $T_g$s showed a synergistic behavior with the mass fraction of urethane prepolymer. Similarly, the $T_g$s of the BA-a : PU copolymers in our case also increased with the mass fraction of urethane prepolymer confirming the previous report.[16] However, this kind synergistic behavior in $T_g$ was also observed in some other polybenzoxazine hybrids.[25–30] This mechanism is likely the competition in hydrogen bonding resulting in the crosslinked structure changes. In general, the $T_g$s of urethane elastomer based on IPDI and polybenzoxazine were reported to be about −70°C and 165°C, respectively. In our study, $T_g$s of the copolymers were also found to increase with the mass fraction of urethane prepolymer at least up to 40 wt % of the urethane fraction. The observed increase in the crosslink density of the binary systems with urethane prepolymer in the DMA investigation is one possible reason for the enhancement in the $T_g$ of the resulting copolymers,

although urethane prepolymer is a softer molecular species having much lower $T_g$ and is expected to lower the $T_g$ of the copolymers. The additional cross-linking was proposed to be caused by the reaction between isocyanate group on the urethane monomer and hydroxyl group on polybenzoxazine after the phenolic hydroxyl group from ring opening polymerization of benzoxazine monomer was produced.[15]

In Figure 6, the $T_g$s of these BA-a : PU based on TDI at various compositions rendered the highest values among the three isocyanate systems. Ghosh and Krishnamurti.[31] studied the properties of polyurethane based on polyethylene glycol at a molecular weight of 200 by using different diisocyanates (hexamethylene diisocyanate (HDI), IPDI, and TDI). They reported that the $T_g$ values from the maximum peak of tan δ were 10, 14, and 50°C for polyurethane based on HDI, IPDI, and TDI, respectively. Because HDI, IPDI, and TDI contain a flexible aliphatic chain, alicyclic ring, and rigid aromatic ring, respectively, the above results point toward the effect of structural features of diisocyanates on their $T_g$s that the more rigid isocyanate gives higher $T_g$ value in the polyurethane. Therefore, the TDI-based system tends to possess the highest $T_g$ among the three evaluated copolymers.

## Thermal degradation of BA-a : PU copolymers

The thermogravimetric analysis (TGA) thermograms of polybenzoxazine and the BA-a : PU copolymers based TDI at various compositions are shown in Figure 7. Generally, degradation temperature ($T_d$) at 5% weight loss is one of the key parameters needed to be considered for high temperature applications.
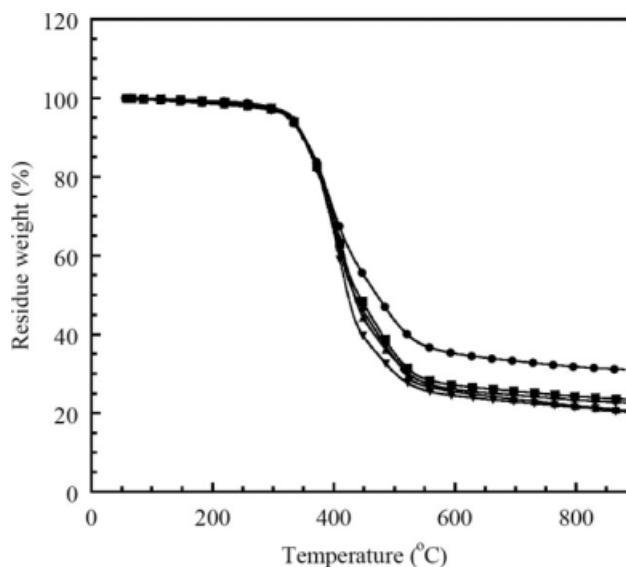


**Figure 7** TGA thermograms of BA-a : PU alloys using TDI at various compositions: (●) BA-a, (■) 90 : 10, (◆) 80 : 20, (▲) 70 : 30, (▼) 60 : 40.

TABLE I
Flexural Properties of BA-a/PU Copolymers at Various PU Contents Using Different Isocyanate Types

| PU content (wt %) | Flexural strength (MPa) | | | Flexural modulus (GPa) | | | Flexural strain (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | TDI | MDI | IPDI | TDI | MDI | IPDI | TDI | MDI | IPDI |
| 0 | 133 | 133 | 133 | 5.8 | 5.8 | 5.8 | 2.44 | 2.44 | 2.44 |
| 10 | 155 | 137 | 146 | 5.2 | 4.8 | 4.9 | 3.15 | 2.51 | 3.19 |
| 20 | 134 | 112 | 130 | 3.8 | 3.7 | 3.7 | 3.56 | 2.84 | 4.04 |
| 30 | 116 | 98 | 104 | 3.3 | 2.8 | 3.0 | 4.39 | 3.56 | 4.59 |
| 40 | 70 | 39 | 57 | 2.0 | 1.7 | 1.8 | 4.68 | – | – |

From these results, the $T_d$ of the neat BA-a at 5% weight loss was determined to be 321°C. In addition, the $T_d$s of BA-a : PU copolymers were found to be about the same (i.e., ~ 329°C) for all tested copolymer compositions. Therefore, the benefit of mixing the urethane prepolymer into benzoxazine monomer was to improve the thermal stability of the polybenzoxazine. The slight enhancement of the decomposition temperature in this study is in good agreement with the results from our previous work.[16,32] 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 copolymers as previously explained. However, the residual weights at 800°C of all BA-a : PU systems based on TDI were found to decrease with increasing the PU mass fraction in the copolymers. The char yield at 800°C of the polybenzoxazine was determined to be about 32 wt %, which was also consistent with the value reported in our previous works,[16,33] whereas the TDI-polyethyleneadipate polyol-based polyurethane possesses a smaller value of char yield of only 6 wt % at 800°C.[16] In our case, the addition of the PU in the polybenzoxazine expectedly decreased the char yield of the copolymers. Furthermore, the chemical structure of the polyurethane prepolymer composed of aliphatic structure was less thermally stable than the predominant aromatic structure of polybenzoxazine. Therefore, the increase of the PU mass fraction resulted in the lowering of the char yield in the copolymer.

### Flexural properties of BA-a : PU copolymers

Flexural properties of BA-a : PU copolymers are tabulated in Table I, which presents the flexural strength of BA-a : PU copolymers at different types of isocyanates and various mass fractions of PU. The BA-a : PU copolymers with three isocyanates were observed to exhibit a synergistic behavior with the maximum value at the BA-a : PU ratio of 90 : 10 in all three systems. This synergistic phenomenon was consistent with that reported by Rimdusit et al.[16,32] In addition, the further increase of the PU fraction for the three isocyanate types systematically decreased the flexural strength of the copolymers. In

principle, the addition of the softer PU fraction in the copolymers should result in the decrease of their strength as observed in the 20–40 wt % region. The phenomenon of the increase in flexural strength at ~ 10 wt % of PU and the decrease after 10 wt % of PU was consistent and was explained in our recent published work.[29] Furthermore, it was observed that the addition of PU elastomer systematically lowered the modulus of the obtained copolymers. In addition, PU elastomer was observed to significantly improve the flexural strain of the BA-a : PU copolymer as indicated by a greater flexural strain value than that of the neat polybenzoxazine.

### Flexural properties of carbon fiber composites based on BA-a : PU copolymers

Flexural properties of carbon fiber-reinforced BA-a : PU composites based on TDI at various mass fractions of PU were presented in Table II. The fiber content determined from TGA was ~ 80 wt % in all composites. The flexural strengths of carbon fiber-reinforced BA-a : PU composites were found to be at least three times higher than those of the matrix copolymers for all BA-a : PU compositions. From the table, the flexural strength of carbon fiber-reinforced polybenzoxazine was measured to be 397 MPa, which is similar to the value reported by Jang and Yang.[34] The increase of the PU fraction in the matrix increased the flexural strength to 490 MPa for 60 : 40 BA-a : PU. The enhancement in the composite strength with PU was possibly due to the improved interfacial adhesion between the carbon fiber and

TABLE II
Flexural Properties of Carbon Fiber Reinforced–Reinforced BA-a : PU Base on TDI at Various Compositions (20% of Matrix Content)

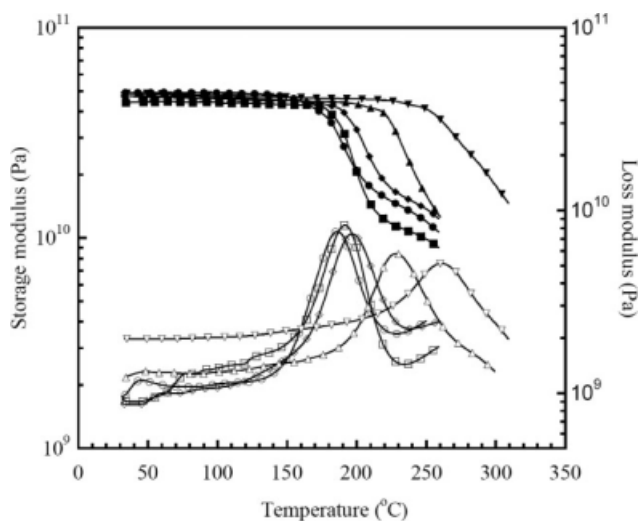| PU content (wt %) | Flexural strength (MPa) | Flexural modulus (GPa) | Flexural strain at maximum stress (%) |
|---|---|---|---|
| 0 | 397 | 50.9 | 1.21 |
| 10 | 329 | 43.5 | 1.71 |
| 20 | 435 | 44.1 | 0.93 |
| 30 | 444 | 47.3 | 0.85 |
| 40 | 490 | 48.2 | 0.73 |

**Figure 8** Storage and loss modulus of carbon fiber reinforced–reinforced BA-a : PU using TDI at various compositions: storage modulus (●) BA-a, (■) 90 : 10, (◆) 80 : 20, (▲) 70 : 30, (▼) 60 : 40, loss modulus (○) BA-a, (□) 90 : 10, (◇) 80 : 20, (△) 70 : 30, (▽) 60 : 40.

matrix resin with increasing mass fraction of the PU. Jang and Yang[35] studied the effect of ATBN rubber on the flexural properties of carbon fiber/polybenzoxazine composites. They reported that ATBN rubber did not decrease the flexural strengths of the composites, even though ATBN rubber was flexible. The possible reason for the observed behavior is that these ATBN modified composites had strong interface. As our case, the interfacial strength between carbon fiber and BA-a : PU matrix could be explained by the mechanisms of mechanical interlocking and fiber wetting. The addition of softer PU into a more rigid polybenzoxazine possibly rendered the increase interaction between the nonpolar polyol of PU and the nonpolar carbon fiber. That led to a 25% increase of the flexural strength of the composites.

Furthermore, flexural modulus of carbon fiber-reinforced BA-a : PU composites at various urethane mass fractions in comparison with BA-a : PU matrix based on TDI was tabulated in Table II. The flexural modulus of carbon fiber-reinforced BA-a : PU composites was found to be significantly higher than that of BA-a : PU copolymers for all BA-a : PU compositions. The flexural moduli were found to be in a range from 43 to 48 GPa when adding PU from 10 to 40 wt %. As the results, the effect of PU fraction on the modulus of the BA-a : PU composite was thus marginal comparing with the effect of the carbon fiber reinforcement.

**Dynamic mechanical properties of carbon fiber composite of BA-a : PU copolymers based on TDI**

Figure 8 shows the dynamic mechanical properties of carbon fiber-reinforced BA-a : PU composites at

various BA-a : PU compositions. Again, the storage modulus in the glassy state showed a systematical increase with an incorporation of PU from 10 to 40 wt % (i.e., about 43–48 GPa). The addition of PU content may improve the interfacial adhesion between the carbon fiber and the BA-a : PU matrix.

The loss modulus from DMA of the carbon fiber-reinforced BA-a : PU composites at various BA-a : PU contents is presented in Figure 8. $T_g$ of carbon fiber-reinforced BA-a : PU composites at each composition was defined by using the maximum of the loss modulus curve. It can be seen that the addition of the PU into carbon fiber-reinforced BA-a : PU composites was found to increase the $T_g$ of carbon fiber-reinforced BA-a : PU composites. The characteristic is consistent with the result observed in DSC and DMA thermograms of the copolymers. The $T_g$ values of the carbon fiber composites tended to be the same as those of the copolymers. The behavior suggested that the strong bonding between the carbon fibers and BA-a : PU matrices to be unlikely as very high stiffness of the carbon fiber cannot effectively restrict the molecular mobility of the matrices; thus, it caused only marginal change of the $T_g$s of the composites.

## CONCLUSIONS

The effects of different types of isocyanates used in the urethane resin preparation on properties of their copolymers were examined. The presence of urethane resin in benzoxazine monomer was observed to retard the curing reaction of the BA-a : PU resin mixture. Curing conditions of all BA-a : PU copolymers were 150°C/1 h, 170°C/1 h, 190°C/1 h, and 200°C/2 h. No significant change in thermal stability of the polybenzoxazine was observed with an addition of the urethane elastomer. On the other hand, a synergistic behavior of flexural strength was observed at the BA-a : PU ratio of 90 : 10 for all three BA-a : PU copolymer systems. Finally, the flexural modulus of the polybenzoxazine was found to systematically decrease with an addition of PU in the copolymers. These copolymers were also proved to be useful as matrices of carbon fiber composites with relatively high mechanical properties while still maintaining high thermal stability of the polymer matrices.

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