Effects of types of isocyanate and polyol on thermal and mechanical properties of benzoxazine-urethane polymer alloys

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Abstract. Polymer alloys of benzoxazine resin (BA-a) and urethane prepolymer (PU) were prepared at various BA-a : PU mass ratios (100 : 0, 80 : 20, 70 : 30 and 60 : 40) via sequential cure method. Isocyanate end capped urethane prepolymer was synthesized with isocyanates and polyols. Various types of isocyanate groups were used [i.e., TDI, MDI, IPDI and HDI] in this study. Polypropylene glycol and Poly(ethylene, diethylene adipate) glycol represent polyether polyol (E) and polyester polyol (S), respectively. Experimental results revealed that glass transition temperature (T_g), flexural strength and flexural modulus increase with decreasing PU content. Furthermore, the flexural strength and flexural modulus synergism were found in the BA-a:PU based polyester polyol at all mass ratio.

1. Introduction
Polyurethanes (PU) is a synthetic polymeric material used to provide several properties for versatile application, which are the results of two-phase structure separation morphology between hard domain derived from isocyanate and soft domain from long-chain diol or triol [1]. Polyurethane have excellent properties such as solvent resistance, superior toughness, and impact resistance, high tear strength and elongation, etc. However, it is not without drawback which is poor thermal stability at high temperature, limiting their application in many fields [9, 12]. Enhancement of thermal properties can be achieved by several approaches. One convenient method for effective thermal stability enhancement is to blend polyurethane with better thermal stability polymer [2]. Polybenzoxazine (PBA) is a novel class of phenolic resins which exhibits many unique properties such as high thermal stability, excellent mechanical properties, low moisture absorption, low melt viscosity, high char yield, low coefficient of thermal expansion and near-zero shrinkage. Moreover, it can be synthesized via either solvent or solventless technology. The benzoxazine monomer requires no catalyst for the ring opening polymerization [2-7]. Although Polybenzoxazine (PBA) offer many excellent properties as mentioned above, its high rigidity limits their widespread use [2, 4, 6]. Hence, researchers make great effort to enhance its toughness. Another outstanding property of benzoxazine which has attracted many researchers’ attention is its capability to mix with various resins by alloying or blending.

The existing phenolic hydroxyl groups in polybenzoxazine were considered to be a good match for polyurethane by reacting with the NCO groups in PU prepolymer, forming cross-linked copolymers. Therefore, considering the aforementioned statements, alloying urethane/benzoxazine is considered as the most promising approach. Not only does this display improvement of thermal stability in polyurethane but also the toughening of polybenzoxazine led them to be used as high performance polymer alloy in a wide range of applications [2, 3, 5].
2. Experimental

2.1. Material.
Sources of the Materials used for the synthesis of benzoxazine monomer and urethane pre-polymer are listed in Table 1.

Table 1. Materials used for the synthesis of benzoxazine monomer and urethane pre-polymer.

| Chemical                                | Source                                      |
|-----------------------------------------|---------------------------------------------|
| BA-a resin                              | PTT Phenol Co., Ltd (Thailand).             |
| Bisphenol A (polycarbonate grade)       | Merck Company                               |
| Formaldehyde (AR grade)                 | Loba Chemie Pvt. Ltd.                       |
| Aniline                                 |                                             |
| PU prepolymer                           | IRPC Polyl Co., Ltd.                        |
| Polypropylene glycol (Mn 1000 g/mol)    | Foamtec International Co., Ltd.             |
| Poly(ethylene, diethylene adipate) glycol | Foamtec International Co., Ltd.             |
| 2,4-toluene diisocyanate (TDI)          | Foamtec International Co., Ltd.             |
| Methylene diphenyl diisocyanate (MDI)   | Vencorex (Thailand) Co., Ltd.               |
| Isophorone diisocyanate (IPDI)          | Vencorex (Thailand) Co., Ltd.               |
| Hexamethylene diisocyanate (HDI)        |                                             |

2.2. Specimen preparation

2.2.1. Isocyanate end capped urethane prepolymer synthesis. The urethane prepolymer was synthesized via mixing excess isocyanate with polyols at a molar ratio of 1.5 : 1, and varying the type of isocyanate and polyol components used. Components and conditions used in the synthesis of PU prepolymer are given in Table 2.

Table 2. Component and condition synthesis for PU prepolymer.

| Urethane prepolymer | Condition |
|---------------------|-----------|
|                     | Time (h)  | Temperature (°C) |
| PU-TDI/Polyol       | 1.30      | 70               |
| PU-MDI/Polyol       | 1         | 45               |
| PU-IPDI/Polyol      | 2         | 90               |
| PU-HDI/Polyol       | 2         | 90               |

After the reaction completed, the obtained urethane prepolymer was purged with nitrogen gas before closing the lid. It was then left at room temperature to cool down then kept in a refrigerator for future use.

2.2.2. Benzoxazine monomer (BA-a) synthesis. BA-a monomer was synthesized by using bisphenol-A, formaldehyde and aniline at a molar ratio of 1 : 4 : 2 by solventless technology. The resin was a transparent yellow solid at room temperature. It was grounded into powder before alloying with PU prepolymer.

2.2.3. Benzoxazine-urethane polymer alloys preparation. Polymer alloy comprises of a mixture of BA-a and urethane prepolymer at various mass fraction (100 : 0, 80 : 20, 70 : 30 and 60 : 40). Both of
the components were heated at 125 °C in an aluminum pan and stirred to yield a homogeneous mixture. The molten resin mixture was step-cured in an air-circulated oven. After the curing process, the samples were cut into various shapes for each specific characterization.

3. Characterization

3.1. Dynamic mechanical analysis (model DMA242, Netzsch, Germany)
was carried out to determine the thermo-mechanical behavior of the specimen dimension of 10 mm×50 mm×1.5 mm by using three-point bending mode. The testing was evaluated at a heating rate of 2 °C min\(^{-1}\) from 30 °C–250 °C under nitrogen atmosphere.

3.2. Flexural Property Measurement.
The flexural properties of the BA-a:PU alloy specimens were determined using a universal testing machine (model 5567) from Instron Co., Ltd. Following ASTM D 790M-93 (three point bending mode) with a support span of 32 mm using a constant crosshead speed of 1 mm/min. The sample dimension was 10 mm×50 mm×1.5 mm.

4. Results and Discussion

![Figure 1. Loss tangent of BA-a : PU-TDI/S polymer alloys at various mass ratio: 100 : 0 (●), 80 : 20 (■), 70 : 30 (◆) and 60 : 40 (▲).](image-url)

| BA-a:PU-TDI/S mass ratio | \(T_g\) (°C) | \(T_g\) range (°C) | \(\Delta T_g\) (°C) |
|-------------------------|-------------|-------------------|-----------------|
| 100:10                  | 170         | 130 to 190        | 60              |
| 80:20                   | 135         | 70 to 170         | 100             |
| 70:30                   | 120         | 40 to 180         | 140             |
| 60:40                   | 80          | 30 to 140         | 110             |

Table 3. Glass transition temperatures of neat BA-a and BA-a : PU-TDI/S polymer alloys.
Table 3 presents interpreted data of tan $\delta$ curve per Figure 1. The result shows that the range of $T_g$ ($\Delta T_g$) increases as urethane content in polymer alloy increases. Previous researches suggest the appropriate range of $T_g$ should be about 75 °C– 110 °C for shape memory application.

Figure 2. Flexural strength (●) and flexural modulus (■) of BA-a : PU-HDI/E polymer alloy as a function of PU-HDI/E content.

Figure 3. Flexural strength (●) and flexural modulus (■) of BA-a : PU-HDI/S polymer alloy as a function of PU-HDI/S content.

Comparison of flexural properties of the BA-a : PU alloy specimens with HDI base by varying polyol types (Polypropylene glycol; E and Poly(ethylene, diethylene adipate); S) at various urethane mass fractions exhibited in Figure 2 and 3. The results show that the reduction in flexural modulus of both
figures were caused by an increase in urethane content but the relationship between urethane content and flexural strength didn’t exhibit a linear behaviour. The synergistic behaviour was at the maximum with a BA : PU ratio of 80 : 20 for both polyol types. The synergistic behaviour in their flexural strengths as mentioned above was the result of the enhancement of the crosslink density of the polymer alloys with the addition of urethane.

Figure 4 shows the flexural properties of the BA-a : PU alloy specimens with polyester polyol base at a fixed mass ratio of 60 : 40. It is observed that maximum flexural properties were obtained when using MDI to synthesize urethane prepolymer. This statement is based on the assumption that having two benzene rings in monomeric MDI structure

5. Conclusions

In this research, alloying of BA-a : PU not only improves the thermal properties of urethane and benzoxazine but also provides further insight in shape memory research.

6. References

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