

# Mechanical Properties of Blocked Polyurethane/Epoxy Interpenetrating Polymer Networks

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Received 17 August 2005; accepted 31 October 2005

DOI 10.1002/app.23612

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The mechanical properties of blocked polyurethane(PU)/epoxy interpenetrating polymer networks (IPNs) were studied by means of their static and damping properties. The studies of static mechanical properties of IPNs are based on tensile properties, flexural properties, hardness, and impact method. Results show that the tensile strength, flexural strength, tensile modulus, flexural modulus, and hardness of IPNs decreased with increase in blocked PU content. The impact strength of IPNs increased with increase in blocked PU content. It shows that the tensile strength, flexural strength, tensile modulus, and flexural modulus of IPNs increased with filler (CaCO<sub>3</sub>) content to a maximum value at 5, 10, 20, and 25 phr, respectively, and then decreased. The higher the filler content, the greater the hardness of IPNs and the lower the notched Izod impact

strength of IPNs. The glass transition temperatures ( $T_g$ ) of IPNs were shifted inwardly compared with those of blocked PU and epoxy, which indicated that the blocked PU/epoxy IPNs showed excellent compatibility. Meanwhile, the  $T_g$  was shifted to a higher temperature with increasing filler (CaCO<sub>3</sub>) content. The dynamic storage modulus ( $E'$ ) of IPNs increased with increase in epoxy and filler content. The higher the blocked PU content, the greater the swelling ratio of IPNs and the lower the density of IPNs. The higher the filler (CaCO<sub>3</sub>) content, the greater the density of IPNs, and the lower the swelling ratio of IPNs. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1826–1832, 2006

**Key words:** interpenetrating polymer networks (IPNs); mechanical properties; polyurethanes; epoxy

## INTRODUCTION

Polyurethane (PU) resins show some unique properties, including excellent elasticity, excellent abrasion resistance, high impact strength, and elongation, which have been widely used in adhesives, coatings, synthetic leather, construction, automatic applications, and shoe soles.<sup>1–3</sup> However, PU could not be utilized in some applications for lack of mechanical modulus and thermal resistance.<sup>4</sup> Epoxy resins are the desired materials for many important applications such as adhesives, semiconductor encapsulants, and structural matrices, because of their high thermal resistance, high tensile strength and modulus, and good chemical resistance. However, epoxys' widespread use is limited in many high-performance applications because of their inherent brittleness.<sup>5</sup> Hence, a blending technique is applied utilizing interpenetrating polymer networks (IPNs) of two polymer components that can improve the deficiencies of each individual

resin. IPNs are a special class of polymer blends in which the polymers are crosslinked.<sup>6,7</sup> These materials are characterized by the presence of two networks strongly entangled ideally only by topological constraints.<sup>8,9</sup>

The objective of using IPNs is to improve the properties of individual polymers. Like most blends, IPNs phase separate at some point during the polymerization of their monomers or prepolymers. Since crosslinking generally limits the phase domain size, domains are small compared with the blends of the corresponding linear polymers. Crosslinking, generally, forms the basis for the interesting properties of IPNs, e.g., improved mechanical properties like toughness and fatigue, sound and vibration damping capabilities, and reduced swelling in solvents. The IPNs are usually heterogeneous systems in which one polymer exists above its glass transition temperature ( $T_g$ ), which has a glassy microstructure at room temperature, while the other polymer exists below its  $T_g$ , which shows a rubbery microstructure at room temperature. By altering the relative amounts of each polymer in the IPNs, the individual polymer properties may be changed, in which the lower  $T_g$  component is shifted to a higher temperature, while the higher  $T_g$  component is shifted to a lower temperature.<sup>10–13</sup> The goal is an understanding of the important factors determining the properties exhibited by the resulting

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Contract grant sponsor: National Science Council, Taiwan, Republic of China; contract grant number: NSC 94–2216-E-034–006.

TABLE I  
Raw Materials

Material	Specification	Supplier
Epoxy-prepolymer	DGEBA Reaction of Bisphenol A and Epichlorohydrin Viscosity = 12,000 mPa s at 25°C	Chang Chun Co., Taiwan, ROC
PU-prepolymer	Blocked NCO-terminated PU prepolymer Viscosity = 31,000 mPa s at 25°C $M_w = 4230$	Bayer, Germany
Chain extender (curing agent)	Equivalent weight = 1410 4,4-methylene diamine (C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> ) Molecular weight = 266 Viscosity = 20,000 mPa s at 25°C	Anchor Co., UK
Filler	Specific gravity = 1.11 at 25°C CaCO <sub>3</sub> Specific gravity = 2.7 Particle size = 2.02 μm	Yin Chin Co., Taiwan, ROC

IPNs, so that materials with properties tuned to the required application may be produced.<sup>14</sup>

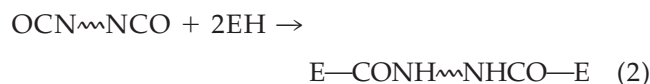
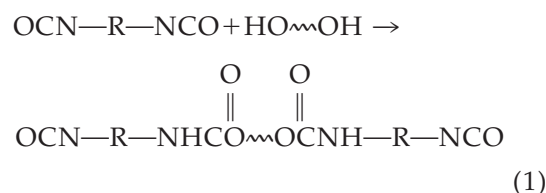
In this study, the simultaneous polymerization (SINs) method<sup>15,16</sup> was used to synthesize blocked PU/epoxy IPNs. The blocked NCO-terminated PU prepolymer with chain extender and epoxy prepolymer with curing agent were mixed simultaneously at room temperature, and interpenetration reaction was carried out at elevated temperature. The paper is focused on the static and damping properties of blocked PU/epoxy IPNs. The effect of blocked PU content and filler content on static mechanical properties was studied. The damping technique was used to determine the dynamic behavior across a temperature range.

## EXPERIMENTAL

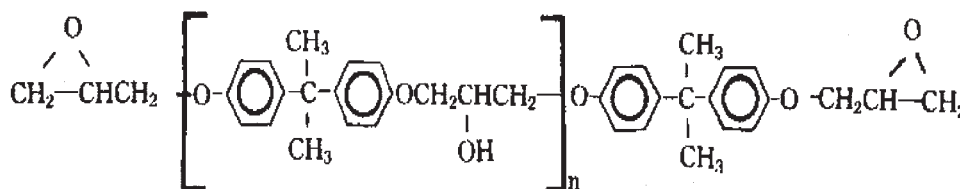
### Materials

The materials used in this study are listed in Table I, including blocked NCO-terminated PU prepolymer, which was prepared from toluene diisocyanate (TDI-80, 80/20 blend of 2,4 and 2,6 isomers) and from polyester at

the NCO-to-OH equivalent ratio of 2 : 1, and then was blocked by blocking agent ( $\epsilon$ -caprolactam) [the reaction proceeds following schemes (1) and (2)], epoxy prepolymer [the chemical structure is described in scheme (3)], curing agent (chain extender) for epoxy and blocked PU polymerization, and filler. Since the blocked NCO-terminated PU prepolymer might contain moisture, and it reacts with isocyanate at high temperature to generate CO<sub>2</sub> gas bubbles, the blocked PU prepolymer was stored under vacuum at 60°C for 4 h.



where EH is blocking agent.

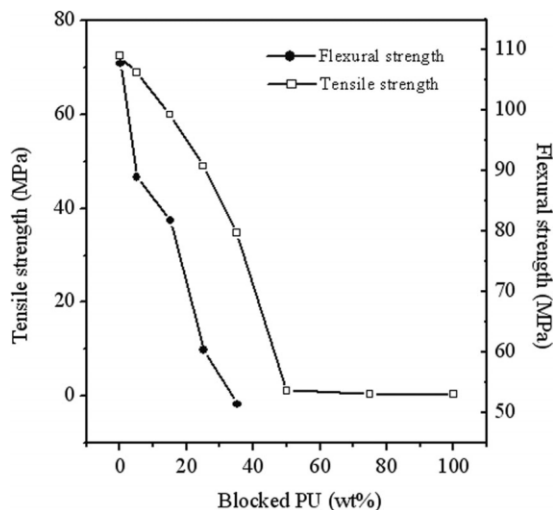


### Preparation of blocked PU/epoxy IPN samples

The blocked PU/epoxy IPN samples were prepared as follows:

1. One equivalent of blocked NCO-terminated PU prepolymer was heated to 70°C and then mixed

with one equivalent of 4,4-methylene diamine homogeneously. The epoxy prepolymer was heated to 70°C and then mixed with one equivalent of 4,4-methylene diamine homogeneously. Then, the two mixtures were blended in various weight ratios at 50°C, and mixed completely using a high-torque stirrer.



**Figure 1** Tensile strength and flexural strength versus blocked PU content of blocked PU/epoxy IPNs.

- The mixture was molded in an ASTM standard stainless steel mold, the surfaces of which had been treated by chrome plating.
- The mixture of mold was cured in an oven for 2 h and the temperature was maintained at 145°C.
- Finally, the samples were removed from the mold and kept in a desiccator, where the relative humidity was maintained at 50% for at least 2 days before they were tested.

### Apparatus

A universal material testing machine was used for mechanical property (tensile and flexural) tests, namely Instron 1123 (Instron Co., Norwood, MA). The impact strength testing machine utilized was TMI-43-1 (Testing Machine). The surface hardness testing machine utilized was a Type-D Shore Durometer (Model No. 41-50, TMI Co.). The DMA (dynamic mechanical analyzer) utilized was a Model 9900 analyzer (DuPont Co., Newtown, CT).

### Property measurements

The tensile strength and modulus were measured following the specification of ASTM D-638. The sample was dumbbell shaped, with dimensions of  $165 \times 19 \times 3.0 \text{ mm}^3$  (length  $\times$  width  $\times$  thickness) and a cross-head speed of 10 mm/min. The flexural strength and modulus were measured following the specification of ASTM D-790. The sample dimensions were  $127 \times 12.7 \times 3.0 \text{ mm}^3$  (length  $\times$  width  $\times$  thickness), the span was 90 mm, and the crosshead speed was 2 mm/min. The notched Izod impact strength was measured according to ASTM D-256. The sample dimensions were 63.5

$\times 12.7 \times 3.0 \text{ mm}^3$  (length  $\times$  width  $\times$  thickness), and the notched depth was 2.5 mm. The surface hardness was measured following ASTM D-2240. The DMA was a resonance-frequency type, and the sample dimensions were  $50 \times 12.7 \times 2.0 \text{ mm}^3$  (length  $\times$  width  $\times$  thickness). The rate of heating was 5°C/min, and the temperature range was  $-150$  to  $250^\circ\text{C}$ . The amplitude of oscillation was 1 Hz. The swelling ratio ( $q$ ) was determined using the following equation

$$q = \frac{V}{V_0} = 1 + \frac{(W - W_0) \times \rho_0}{W_0 \times \rho_s}$$

where  $V_0$  is the sample volume before swelling,  $V$  is the sample volume after swelling by immersing in acetone for 72 h,  $W_0$  is the sample weight before swelling,  $W$  is the sample weight after swelling by immersing in acetone for 72 h,  $\rho_0$  is the sample density before swelling, and  $\rho$  is the density of acetone. The density was determined using the following equation according to ASTM D792

$$D = \frac{a \times D_L}{(a - b)}$$

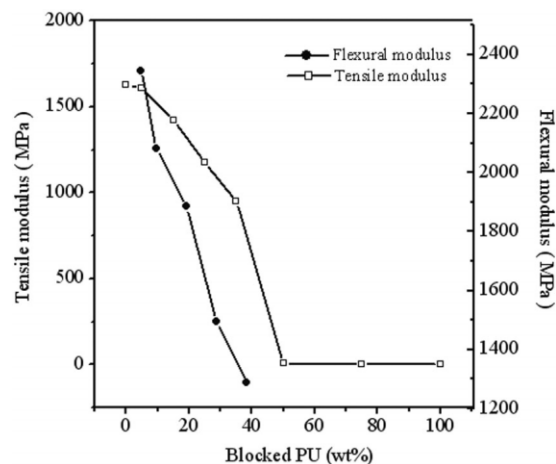
where  $D$  is the sample density,  $D_L$  is the density of used liquid,  $a$  is the sample weight in air, and  $b$  is the sample weight in liquid.

## RESULTS AND DISCUSSION

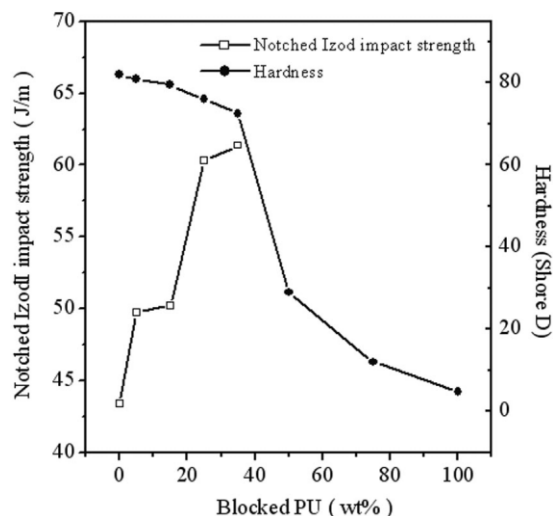
### Static mechanical properties

#### Effect of blocked PU content

Figures 1 and 2 illustrate the tensile strength, flexural strength, tensile modulus, and flexural modulus versus blocked PU content of blocked PU/epoxy IPNs.



**Figure 2** Tensile modulus and flexural modulus versus blocked PU content of blocked PU/epoxy IPNs.

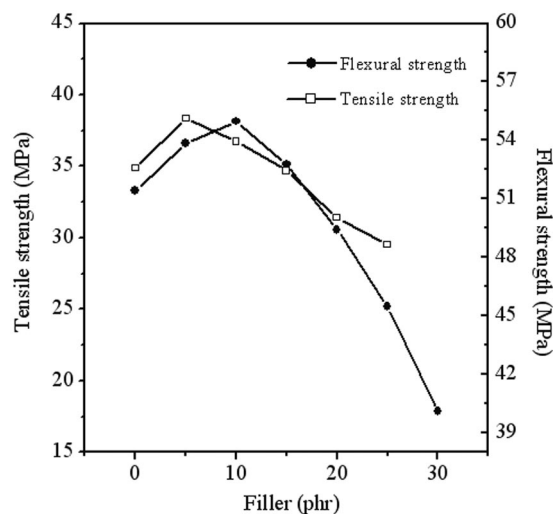


**Figure 3** Shore D hardness and notched Izod impact strength versus blocked PU content of blocked PU/epoxy IPNs.

From these figures, it can be seen that the tensile strength, flexural strength, tensile modulus, and flexural modulus all decreased with increase in blocked PU content. This can be explained because the hard segments of epoxy appeared to have higher strength and modulus properties, and the soft segments of blocked PU appeared to have lower strength and modulus properties; hence, the higher the blocked PU content, the lower the tensile and flexural properties of IPNs. Figure 3 illustrates the shore D hardness and notched Izod impact strength versus blocked PU content of blocked PU/epoxy IPNs. From this figure, one can observe that the shore D hardness of IPNs decreased with increase in blocked PU content, and that the notched Izod impact strength increased with increase in blocked PU content. The shore D hardness decreased, due to the soft segment content of the blocked PU, which is apparent in the blocked PU/epoxy IPNs. The notched Izod impact strength increased as the blocked PU was dissolved in the epoxy matrix and the soft segments of blocked PU toughened the matrix of the blocked PU/epoxy IPNs. The ductility of the matrix plays a very important role in toughening at high shear rate fracturing (that is, notched Izod impact strength).

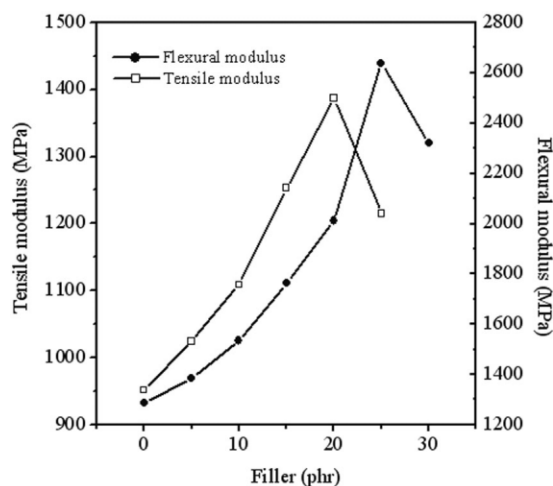
#### Effect of filler ( $\text{CaCO}_3$ ) content

Figure 4 shows the tensile strength and flexural strength versus filler ( $\text{CaCO}_3$ ) content for blocked PU (35 wt %)/epoxy (65 wt %) IPNs. It is observed that the tensile strength of IPNs increased with filler content to a maximum value at 5 phr, and then decreased. The flexural strength of IPNs increased with filler content to a maximum value at 10 phr, and then

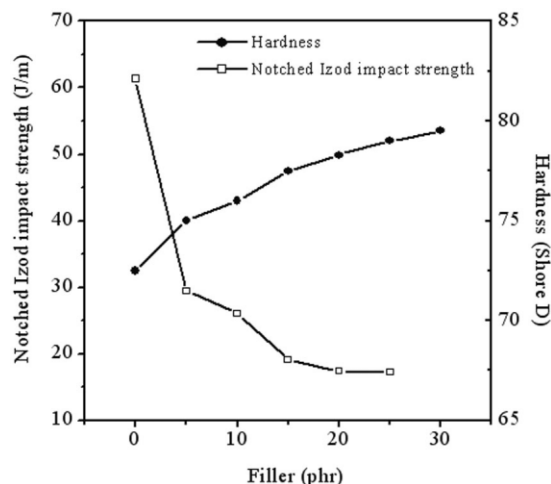


**Figure 4** Tensile strength and flexural strength versus filler ( $\text{CaCO}_3$ ) content for blocked PU (35 wt %)/epoxy (65 wt %) IPNs.

decreased. The tensile modulus and flexural modulus versus filler ( $\text{CaCO}_3$ ) content for blocked PU (35 wt %)/epoxy (65 wt %) IPNs is shown in Figure 5. It is found that the tensile modulus and flexural modulus of IPNs increased with filler content to a maximum and then decreased. The maximum tensile modulus and flexural modulus occurred at 20 and 25 phr filler content, respectively. The resulting maxima of the mechanical properties (tensile strength, flexural strength, tensile modulus, and flexural modulus) for filled IPN systems is due to the addition of the inorganic filler to the IPN systems, which made the IPN become more rigid, hence improving the mechanical properties of IPN with filler content. However, if an excess of filler existed in IPN resin, the IPN systems became more



**Figure 5** Tensile modulus and flexural modulus versus filler ( $\text{CaCO}_3$ ) content for blocked PU (35 wt %)/epoxy (65 wt %) IPNs.



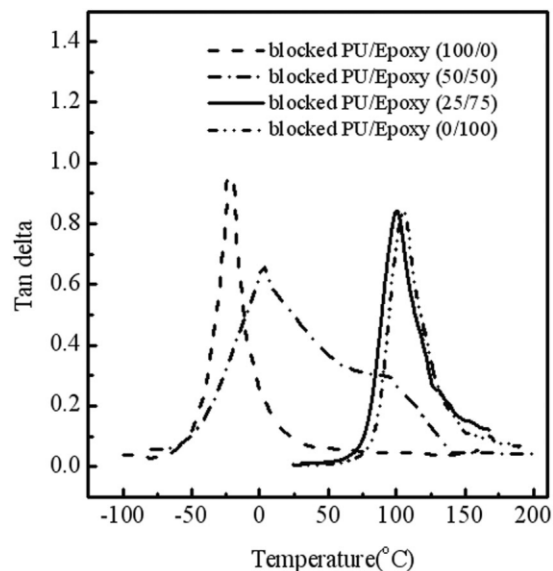
**Figure 6** Shore D hardness and notched Izod impact strength versus filler ( $\text{CaCO}_3$ ) content for blocked PU (35 wt %)/epoxy (65 wt %) IPNs.

brittle; so, the mechanical properties of IPN decreased with filler content. Figure 6 shows the shore D hardness and notched Izod impact strength versus filler ( $\text{CaCO}_3$ ) content for blocked PU (35 wt %)/epoxy (65 wt %) IPNs. It can be seen that the hardness of IPNs increased when the filler content increased. The notched Izod impact strength of IPNs decreased with increasing filler content.

### Dynamic mechanical properties

#### Effect of blocked PU content

The glass transition temperature ( $T_g$ ) was measured from the peak temperature of  $\tan \delta$  by DMA. The literature<sup>17</sup> indicated that when the two polymers were mixed, the dynamic mechanical behavior showed two distinct transitions, indicating the incompatibility between the two polymers. As the compatibility increased, the two  $T_g$ 's shifted toward each other and the damping curve ( $\tan \delta$ ) becomes broader. The behavior of the dynamic damping curve ( $\tan \delta$ ) over a range of temperatures for blocked PU/epoxy IPNs at various blocked PU contents is shown in Figure 7. From this figure, one can observe that the peak temperatures of  $\tan \delta$  of pure component epoxy and blocked PU were 105.1 and  $-24.9^\circ\text{C}$ , respectively. When the blocked PU/epoxy system is at the weight ratio of 50/50, it is found that the two  $T_g$ 's ( $97.6^\circ\text{C}$ ,  $10.2^\circ\text{C}$ ) shifted inward by  $35.1^\circ\text{C}$  for blocked PU domain and by  $7.5^\circ\text{C}$  for epoxy domain starting from the  $T_g$ 's of the pure components. In addition, when the blocked PU/epoxy IPNs system is at the weight ratio of 25/75, it is found that there is only one peak temperature of  $\tan \delta$ . The inward shifting of the two  $T_g$ 's in the blocked PU/epoxy IPNs system may imply that



**Figure 7** Dynamic damping curve ( $\tan \delta$ ) versus temperature for blocked PU/epoxy IPNs at various blocked PU contents.

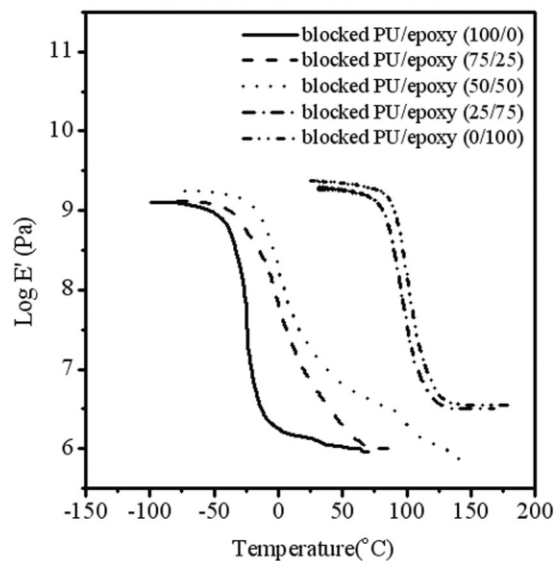
the compatibility between the blocked PU and epoxy would be improved because of the formation of blocked PU/epoxy IPNs. This can be explained by the existence of epoxy hard segments and by the way that the epoxy is dissolved in the blocked PU matrix. Table II lists the glass transition temperatures ( $T_g$ ) determined by DMA of blocked PU/epoxy IPNs of different ratios. From this table, it is found that the shift of  $T_g$  of the epoxy domain is less than that of the blocked PU domain. Figure 8 shows the dynamic storage modulus ( $E'$ ) versus temperature for blocked PU/epoxy IPNs at various blocked PU contents. From this figure, it is evident that the storage modulus ( $E'$ ) increased with increase in epoxy content. This means that the greater the epoxy content, the more rigid the blocked PU/epoxy IPNs.

#### Effect of filler ( $\text{CaCO}_3$ ) content

Figure 9 shows the dynamic damping curve ( $\tan \delta$ ) versus temperature for unfilled and 5-phr filled ( $\text{CaCO}_3$ ) blocked PU (35 wt %)/epoxy (65 wt %) IPNs.

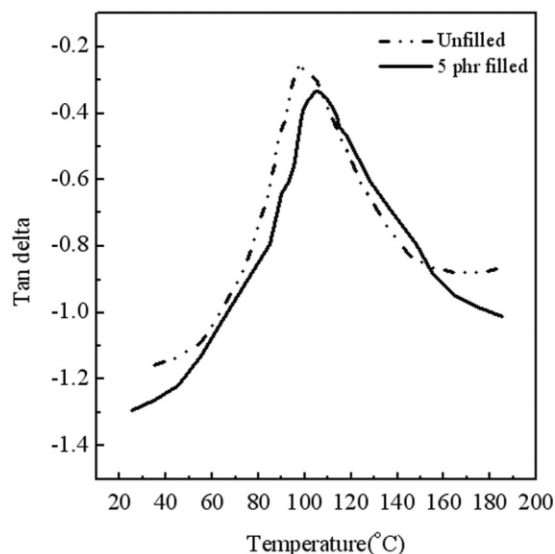
**TABLE II**  
Glass Transition Temperatures ( $T_g$ ) of Different Ratios of Blocked PU/Epoxy IPN System by DMA

Blocked PU/epoxy compositions	$T_{g1}$ ( $^\circ\text{C}$ )	$T_{g2}$ ( $^\circ\text{C}$ )
100/0	-24.9	
50/50	10.2	97.6
25/75	99.2	
0/100	105.1	

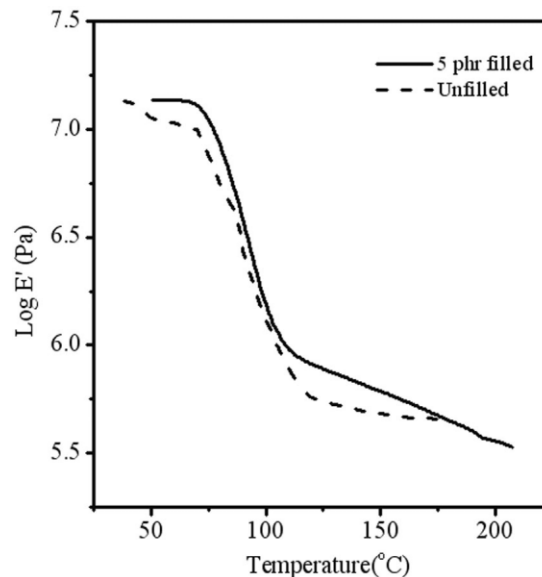


**Figure 8** Dynamic storage modulus ( $E'$ ) versus temperature for blocked PU/epoxy IPNs at various blocked PU contents.

It was found that the glass transition temperature ( $T_g$ ) of IPNs was shifted to a higher temperature in the IPNs with filler content. Figure 10 shows the dynamic storage modulus ( $E'$ ) versus temperature for unfilled and 5-phr filled ( $\text{CaCO}_3$ ) blocked PU (35 wt %)/epoxy (65 wt %) IPNs. From this figure, we can find that the dynamic storage modulus ( $E'$ ) of IPNs with filler was higher than that of unfilled ones. The glass transition temperature ( $T_g$ ) was shifted to a higher temperature, and dynamic storage modulus ( $E'$ ) increased with addition of filler because the IPN



**Figure 9** Dynamic damping curve ( $\tan \delta$ ) versus temperature for unfilled and 5-phr filled ( $\text{CaCO}_3$ ) blocked PU (35 wt %)/epoxy (65 wt %) IPNs.



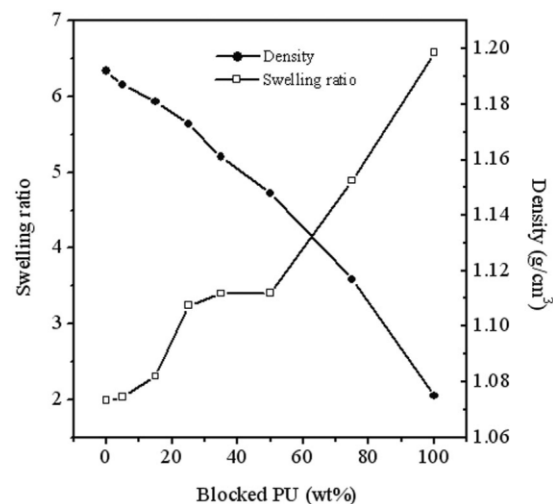
**Figure 10** Dynamic storage modulus ( $E'$ ) versus temperature for unfilled and 5-phr filled ( $\text{CaCO}_3$ ) blocked PU (35 wt %)/epoxy (65 wt %) IPNs.

structures became more tightly constrained when the filler is added.

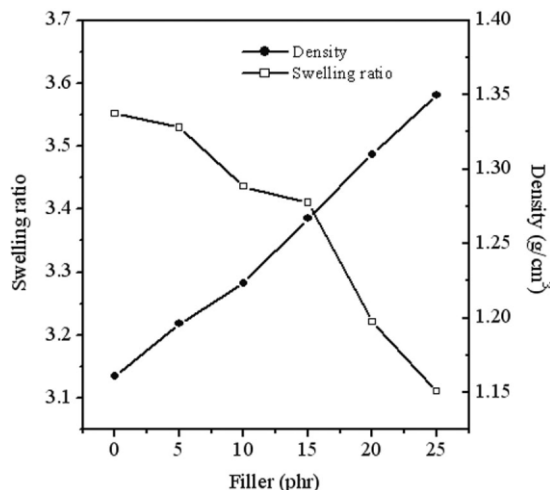
### The swelling ratio and density properties

#### Swelling ratio

To understand that the IPN structures were influenced by component segments, the important swelling properties of IPNs must be discussed. In general, the higher the component soft segments existed in IPNs, the greater the swelling ratio of IPNs. Figure 11 shows the swelling ratio versus blocked PU content of blocked



**Figure 11** Swelling ratio and density versus blocked PU content of blocked PU/epoxy IPNs.



**Figure 12** Swelling ratio and density versus filler ( $\text{CaCO}_3$ ) content for blocked PU (35 wt %)/epoxy (65 wt %) IPNs.

PU/epoxy IPNs. It was found that the swelling ratio of IPNs increased with increase in blocked PU content. Because the structures of blocked PU and epoxy are the soft segments and hard segments, respectively, the higher the blocked PU content, the greater the swelling ratio is. The swelling ratio versus filler ( $\text{CaCO}_3$ ) content for blocked PU (35 wt %)/epoxy (65 wt %) IPNs is shown in Figure 12. It is observed that the swelling ratio decreased with increasing filler content because the higher the filler content, the higher the hard segment contents in IPNs.

### Density

Figure 11 illustrates the density versus blocked PU content of blocked PU/epoxy IPNs. The densities of pure blocked PU and pure epoxy are 1.075 and 1.192  $\text{g}/\text{cm}^3$ , respectively. It is evident that the density of IPNs decreased with increasing blocked PU content. As shown in Figure 12, the greater the filler ( $\text{CaCO}_3$ ) content, the higher the density of IPNs.

## CONCLUSIONS

In this study, blocked PU/epoxy IPNs were synthesized from the blends of blocked PU prepolymer with chain extender and epoxy prepolymer with curing agent using SInS method. The mechanical properties of IPNs were studied by means of static and damping properties. The conclusions of this study include the following subjects:

1. The tensile strength, flexural strength, tensile modulus, flexural modulus, and hardness of

IPNs decreased with increase in blocked PU content. The impact strength of IPNs increased with increase in blocked PU content.

2. The tensile strength, flexural strength, tensile modulus, and flexural modulus of IPNs increased with filler ( $\text{CaCO}_3$ ) content to a maximum value at 5, 10, 20, and 25 phr, respectively, and then decreased. The higher the filler content, the greater the hardness of IPNs and the lower the notched Izod impact strength of IPNs.
3. The damping mechanical properties of IPNs were studied by the DMA method. The glass transition temperatures ( $T_g$ ) of IPNs were shifted inwardly compared with those of pure blocked PU and epoxy, which indicated that the blocked PU/epoxy IPNs showed excellent compatibility. The dynamic storage modulus ( $E'$ ) versus temperatures of IPNs increased with increase in epoxy content.
4. The  $T_g$  was shifted to a higher temperature with increasing filler ( $\text{CaCO}_3$ ) content. The dynamic storage modulus ( $E'$ ) versus temperatures of IPNs increased with increase in filler content.
5. The higher the blocked PU content, the greater the swelling ratio of IPNs and the lower the density of IPNs. The higher the filler ( $\text{CaCO}_3$ ) content, the greater the density of IPNs and the lower the swelling ratio of IPNs.

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