

# Interpenetrating Polymer Networks of Bismaleimide and Polyurethane-Crosslinked Epoxy

J. L. HAN,<sup>1</sup> Y. C. CHERN,<sup>2</sup> K. Y. LI,<sup>2</sup> K. H. HSIEH<sup>2</sup>

<sup>1</sup> Department of Chemical Engineering, National I-Lan Institute of Agriculture and Technology, I-Lan, Taiwan

<sup>2</sup> Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 106

Received 15 September 1997; accepted 24 February 1998

**ABSTRACT:** This study prepared an interpenetrating polymer network of bismaleimide and polybutylene adipate-based polyurethane-crosslinked epoxy (BMI/PU-EP IPN) using the simultaneous bulk polymerization technique. Infrared spectra analysis was also performed to identify the polyurethane-crosslinked epoxy (PU-EP). Also investigated herein were the mechanical properties including tensile strength, fracture energy, and Izod impact strength of various bismaleimide content in PU-EP matrix. In addition, differential scanning calorimetry and thermogravimetric analyses of the BMI/PU-EP IPN were conducted as well. Analyses results demonstrate that the bismaleimide was dissolved primarily in the polyurethane domains of the epoxy matrix to form a compatible system, thereby increasing the mechanical strength of the BMI/PU-EP IPNs. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 529–536, 1998

**Key words:** bismaleimide; polyurethane-crosslinked epoxy; interpenetrating polymer networks (IPNs); mechanical properties; thermogravimetric analysis (TGA); differential scanning calorimetry (DSC)

## INTRODUCTION

The cured 4,4'-bis(maleimidodiphenylmethane) (BMI) shows excellent thermal stability,<sup>1–3</sup> an extremely low elongation at breaking, and no evolution of small molecules during its polymerization.<sup>4–7</sup> However, most BMIs are restricted by solvent retention, high cost, poor processibility (i.e., high curing temperature), and brittleness due to its high crosslinking density. Previous investigations have modified BMI resin to improve their physical properties and processi-

bility.<sup>9–14</sup> Our previous works<sup>15,16</sup> have attempted to enhance the mechanical properties by synthesizing a series of polyurethane-crosslinked epoxy (PU-EP) resins. The cured PU-EP by tertiary amine contains a desirable processibility, excellent mechanical properties, high Izod impact strength, and high fracture energy,  $G_{IC}$ .

The BMIs polymerize through the additional reaction of the double bonds in maleimide group. In our previous studies,<sup>20–22</sup> the PU-EP cured by tertiary amine is a ring-opening reaction. In this study, we mix the BMI resin with the PU-EP resin and then simultaneously polymerize them to form an interpenetrating polymer network (IPN). In addition, the stress-strain property, Izod impact strength, and  $G_{IC}$  of the BMI/PU-EP IPNs are investigated.

---

Correspondence to: K. H. Hsieh.

Contract grant sponsor: National Science Council; contract grant numbers: NSC 83-0405-E002-018 and NSC 84-2216-E002-004.

*Journal of Applied Polymer Science*, Vol. 70, 529–536 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/030529-08

**Table I** Materials

Designation	Description	Source
PBA700	Poly(butylene adipate) glycol, MW = 700	Tai Gin Co., Taiwan
PBA1000	Poly(butylene adipate) glycol, MW = 1000	Tai Gin Co., Taiwan
PBA2000	Poly(butylene adipate) glycol, MW = 2000	Tai Gin Co., Taiwan
MDI	4,4'-Diphenyl methane diisocyanate, Eq. wt. = 125	BASF Wyandotte Co., Switzerland
DGEBA	Diglycidyl ether of bisphenol A, EEW = 186, $n = 0.11267$	Dow-Chemical Co., USA
TDMP	2,4,6-Tri(dimethyl aminomethyl)phenol	Ciba-Geigy Co., Switzerland
DCPO	Dicumyl peroxide	Merk Co., Germany
BMI	4,4'-Bis(maleimide-diphenylmethane)	Merk Co., Germany

## EXPERIMENTAL

Table I lists the materials used for the experiments. Polyols [poly(butylene adipate) (PBA): PBA700, PBA1000, and PBA2000] and the epoxy resin [diglycidyl ether of bisphenol A (DGEBA)] were heated at 60°C and then degassed by vacuum overnight before use.

### Preparation of PU Prepolymers

PU prepolymer were prepared by the reaction of 4,4'-diphenyl methane diisocyanate (MDI) with polyols. MDI was initially placed in a reaction kettle and heated to melting state. Polyols of an exact amount were then poured into the reaction kettle. The mixture was vigorously agitated by a mechanical stirrer.

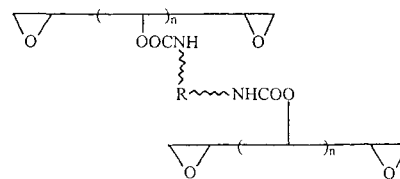
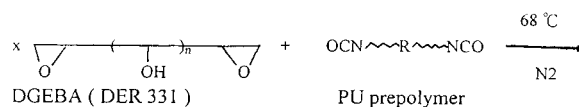
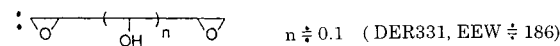
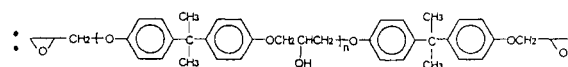
The reaction occurred under a dry nitrogen atmosphere at a temperature of ~ 68°C. The isocyanate content of the reaction mixture was determined by using di-*n*-butyl amine titration methods.<sup>17</sup> The reaction was curtailed when the isocyanate content reached the theoretical value.

### Preparation of PU-EP<sup>15,16</sup>

DGEBA epoxy was placed into a reaction kettle. Dried nitrogen gas was blown into the reaction kettle to remove both air and moisture present. An adequate amount of PU prepolymer was then poured into the kettle to mix with the DGEBA. The temperature was maintained at ~ 68°C. During the reaction, a sample was periodically taken to detect the —NCO group at 2270 cm<sup>-1</sup> in the infrared (IR) spectra. The

reaction was curtailed until the —NCO adsorption peak disappeared. The preparation of PU-EP resin was according to the following reaction:

Diglycidyl ethers of Bisphenol A (DGEBA)

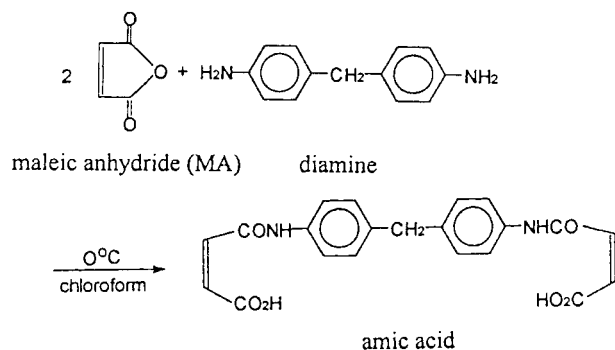


PU-crosslinked epoxy(DGEBA) resin

Where *R* denotes the urethane-terminated polyester diols (PBA). During this period, the epoxide group (916 cm<sup>-1</sup>) absorption peak did not fluctuate.

### Preparation of BMI Monomers

The BMI monomer was prepared according to the procedure described elsewhere.<sup>18</sup> The preparation of the BMI monomer was according to the following scheme:



### Preparation of BMI/PU-EP IPNs

An adequate amount of the previously described PU-EP and various contents of BMI were placed in a cup, into which 3 phr (based on epoxy weight) of curing agent [2,4,6-tri(dimethyl aminomethyl)-phenol] and 0.5 wt % (based on BMI weight) of initiator (dicumyl peroxide) were added. Next, the mixture was vigorously stirred and drafted for several minutes to eliminate all the bubbles produced during agitation. After the bubbles were removed, the reaction mixture was poured into a aluminum mold and pressed at 120°C for 1 h. The sample was then postcured at 180°C for 2 h. Finally, the sample was removed from the mold and placed in a desiccator, where relative humidity was maintained at 50%, for 3 days before testing.

### Testing Method

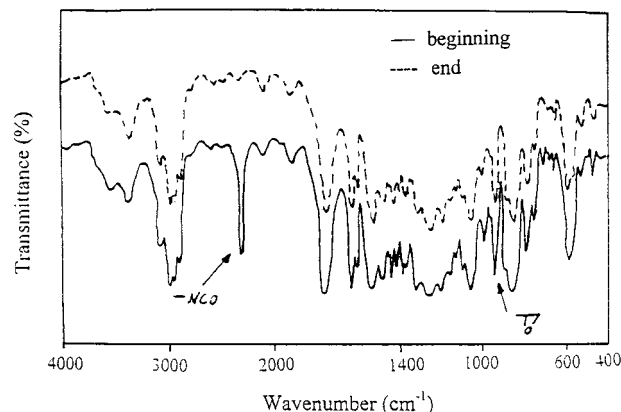
IR spectroscopy was performed using a Hitachi 270-30 IR spectrophotometer. The sample was directly applied by dabbing onto a KBr pellet to detect the —NCO group content in the reaction mixture.

The stress-strain properties were determined by using a Tensilon (Mode: TCF-RC, Yashima Works Ltd., Japan) test unit. The test procedure followed ASTM-D638, at a crosshead speed of 1 cm min<sup>-1</sup>.

The Izod impact strength of BMI/PU-EP IPNs was measured according to the procedure described in ASTM-256.

$G_{IC}$  was measured with the sample in the shape of the compact-tension specimen.<sup>19</sup> The  $G_{IC}$  value can be calculated by the following equation:

$$G_{IC} = \frac{Y^2 \left(\frac{a}{w}\right) P^2 a}{EW^2 b^2}$$



**Figure 1** IR spectra during reaction of PU(PBA700) prepolymer with DGEBA resin: (—) beginning of the reaction; (---) end of the reaction.

where

$$Y\left(\frac{a}{w}\right) = 29.6 - 186\left(\frac{a}{w}\right) + 656\left(\frac{a}{w}\right)^2 - 1017\left(\frac{a}{w}\right)^3 + 639\left(\frac{a}{w}\right)^4$$

In addition,  $a$ ,  $b$ , and  $E$  denote the crack length, thickness, and modulus, respectively, of the specimen. Moreover,  $P$  represents the load on the specimen. A sharp precrack was made with a razor blade before the test. The specimens were tested on a screw-driven Tensilon machine at a crosshead speed of 0.1 cm min<sup>-1</sup>.

Differential scanning calorimetry (DSC) analysis was performed at a temperature range of 50°C–300°C on a DuPont 2200 at a heating rate of 20°C min<sup>-1</sup>.

Thermogravimetric analysis (TGA) was performed on a DuPont 9900-951 TGA instrument under a nitrogen atmosphere. Measurement was taken at a heating rate of 20°C min<sup>-1</sup>. The sample weight tested was about 8 mg.

## RESULTS AND DISCUSSION

### IR Spectra

According to the results presented herein, the PU prepolymer can react with the pendant secondary hydroxyl group of DGEBA. Figure 1 indicates that introducing the PU prepolymer into the DGEBA caused the absorption peak of the —NCO

**Table II** Mechanical Properties of BMI/PU(PBA)-EP IPN

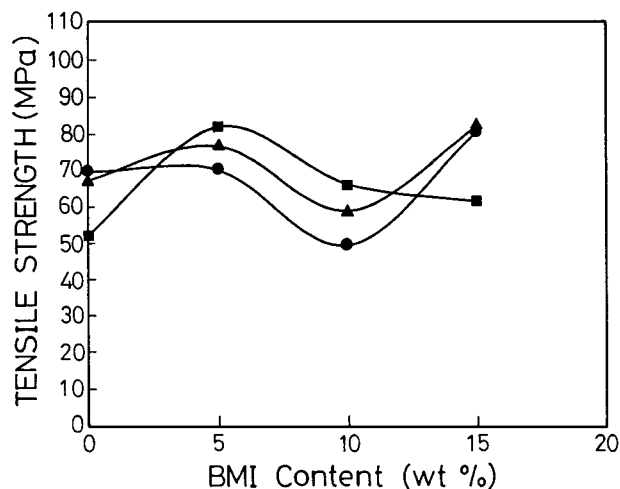
Mechanical Properties				
	BMI Content (%)	Tensile Strength (MPa)	Izod Impact (J m <sup>-1</sup> )	G <sub>IC</sub> (kJ m <sup>-2</sup> )
BMI/PU(PBA700, 5%)-EP	5	70.1	36.4	16.2
BMI/PU(PBA700, 5%)-EP	10	49.5	16.3	3.7
BMI/PU(PBA700, 5%)-EP	15	80.6	20.2	4.2
BMI/PU(PBA700, 10%)-EP	5	79.6	28.9	21.1
BMI/PU(PBA700, 10%)-EP	10	55.9	8.0	2.9
BMI/PU(PBA700, 10%)-EP	15	84.9	10.6	1.9
BMI/PU(PBA700, 15%)-EP	5	70.5	31.3	3.6
BMI/PU(PBA700, 15%)-EP	10	74.2	20.4	5.3
BMI/PU(PBA700, 15%)-EP	15	80.4	12.2	2.5
BMI/PU(PBA1000, 5%)-EP	5	82.1	34.2	14.5
BMI/PU(PBA1000, 5%)-EP	10	66.1	23.0	14.1
BMI/PU(PBA1000, 5%)-EP	15	61.8	17.3	11.0
BMI/PU(PBA1000, 10%)-EP	5	79.1	35.8	24.8
BMI/PU(PBA1000, 10%)-EP	10	85.9	26.7	13.0
BMI/PU(PBA1000, 10%)-EP	15	63.7	18.5	11.8
BMI/PU(PBA1000, 15%)-EP	5	83.9	38.7	16.0
BMI/PU(PBA1000, 15%)-EP	10	77.4	26.6	14.1
BMI/PU(PBA1000, 15%)-EP	15	83.4	16.3	7.5
BMI/PU(PBA2000, 5%)-EP	5	76.9	35.6	11.6
BMI/PU(PBA2000, 5%)-EP	10	58.9	17.2	5.5
BMI/PU(PBA2000, 5%)-EP	15	82.1	14.0	15.6
BMI/PU(PBA2000, 10%)-EP	5	106.4	31.7	10.6
BMI/PU(PBA2000, 10%)-EP	10	63.8	19.6	1.2
BMI/PU(PBA2000, 10%)-EP	15	66.8	9.3	49
BMI/PU(PBA2000, 15%)-EP	5	76.5	31.4	3.9
BMI/PU(PBA2000, 15%)-EP	10	76.0	13.3	0.7
BMI/PU(PBA2000, 15%)-EP	15	35.1	8.5	5.1

group at 2270 cm<sup>-1</sup> to gradually reduce in intensity with reaction time. Finally, the peak disappeared after several hours. This finding suggests that the crosslinking reaction between the —NCO group of the PU prepolymer, and the pendant secondary hydroxyl group of DGEBA was completed.

### Tensile Strength

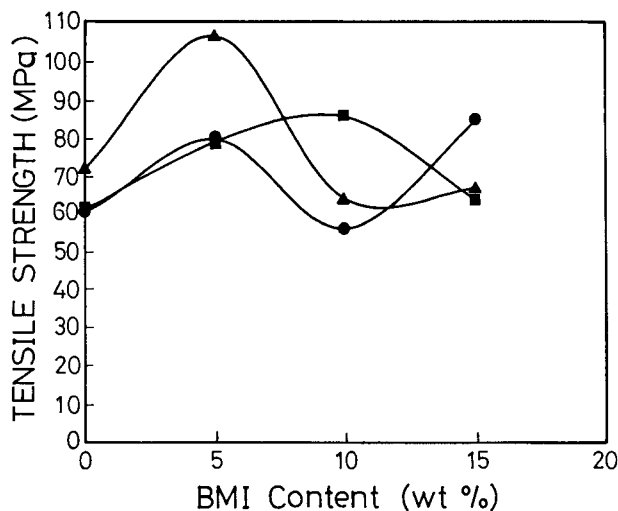
Table II lists the mechanical properties of BMI/PU-EP IPN. Figures 2 to 4 display the tensile strength of the BMI/PU-EP IPN. According to those results, regardless of the molecular weight of the polyester-type PU used, the tensile strength of the BMI/PU-EP IPN increased with an increasing BMI content to a maximum value.

The strength subsequently decreased to a minimum value and then gradually increased again with a further increase in BMI content [i.e., an “N”-shaped curve, the maximum value occurred at 5 wt % of BMI content in the system (Figs. 2 and 3)]. The reason for this occurrence, as investigated in our previous studies,<sup>15,16</sup> is that despite the molecular weight of the polyester PU used, the PU-crosslinked epoxy was formed in a uniform phase. As the BMI was introduced into the PU-EP, its good miscibility with the polar PU domain led to an uniform distribution of the BMI in the matrix. The compatible-cured BMI with epoxy contributed to the characteristics of a rather high crosslinked density and rigidity. Consequently, the interpenetration of the BMI and

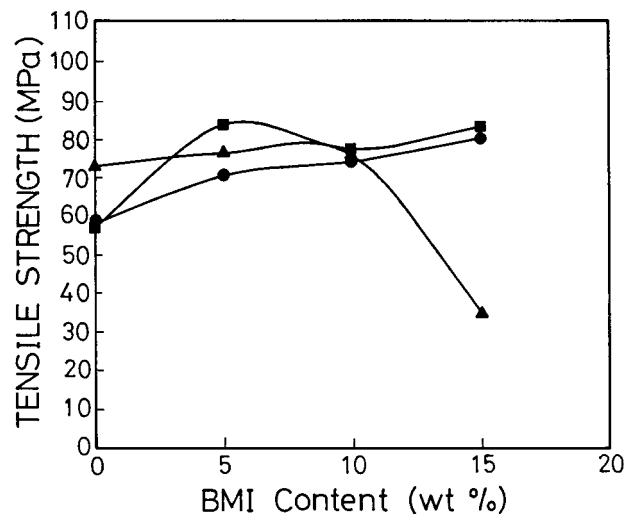


**Figure 2** Dependence of tensile strength of BMI/PU(PBA, 5 wt %)-EP IPN on various BMI content. (●) BMI/PU(PBA700)-EP IPN; (■) BMI/PU(PBA1000)-EP IPN; (▲) BMI/PU(PBA2000)-EP IPN.

the PU-EP in the networks increased with an increasing BMI content and, ultimately, results in an increasing tensile strength of the BMI/PU-EP IPN with an increasing BMI content (i.e., the compatibility effect). When the content of BMI increases  $> 5$  wt %, the BMI obviously controls the rigidity and brittleness in the PU domain. This finding reveals that the tensile strength of BMI/PU-EP IPN decreases with the increasing



**Figure 3** Dependence of tensile strength of BMI/PU(PBA, 10 wt %)-EP IPN on various BMI content. (●) BMI/PU(PBA700)-EP IPN; (■) BMI/PU(PBA1000)-EP IPN; (▲) BMI/PU(PBA2000)-EP IPN.

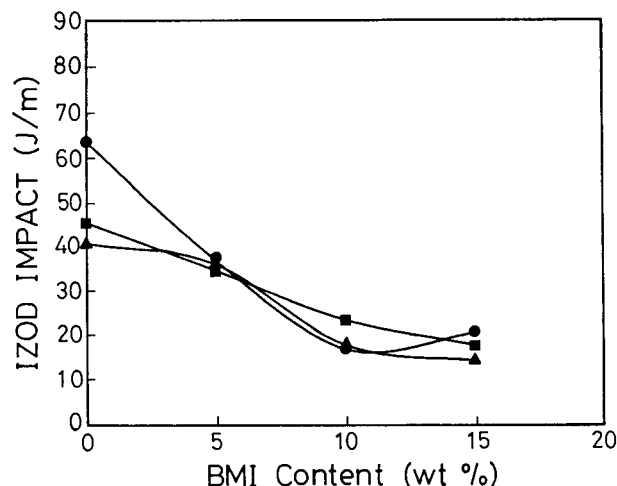


**Figure 4** Dependence of tensile strength of BMI/PU(PBA, 15 wt %)-EP IPN on various BMI content. (●) BMI/PU(PBA700)-EP IPN; (■) BMI/PU(PBA1000)-EP IPN; (▲) BMI/PU(PBA2000)-EP IPN.

content of BMI. As the BMI content is continuously added to the system and exceeds 10 wt %, the tensile strength of BMI/PU-EP IPN again increases with an increasing BMI content. Such an occurrence is attributed to both the networks of BMI and PU-EP, which had formed the highly IPN structure. Therefore, the intermolecular physical entanglement (i.e., IPN effect) is increased and enhanced as well. This event causes the crosslinking density of BMI/PU-EP IPN to again increase with an increasing BMI content; the tensile strength of BMI/PU-EP IPN is thus increased. Interestingly, although the PU content is low, the IPN effect of BMI/PU-EP IPN is significant. Consequently, the tensile strength of BMI/PU-EP IPN has an extremely high value of 106 MPa at 5 wt % BMI content in the PU(PBA2000)-EP matrix of PU(PBA2000) content at 10 wt % (Fig. 3 and Table II). However, when the PU content increases up to 15 wt %, the compatibility between the BMI and PU domain in epoxy matrix profoundly determines the tensile strength of the BMI/PU-EP IPN. Thus, the IPN effect is more significant due to a higher PU content in the PU-EP, which can dissolve more BMI. Therefore, the tensile strength of BMI/PU-EP IPN does not display the "N"-shaped curve with increasing BMI content (Fig. 4).

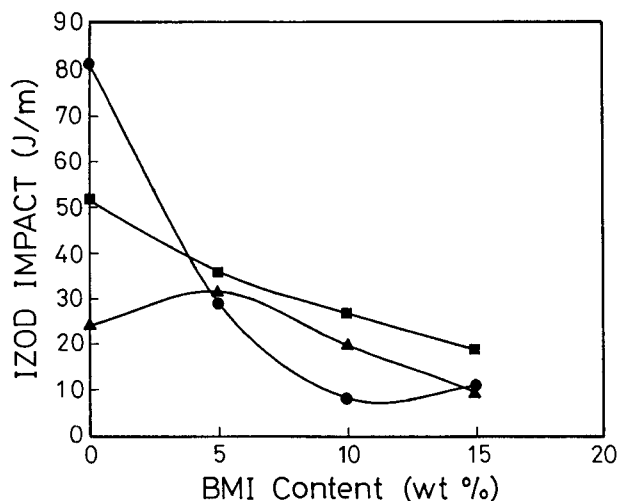
#### Izod Impact Strength

Figures 5–7 and Table II illustrate the Izod impact property of BMI/PU-EP IPN with various

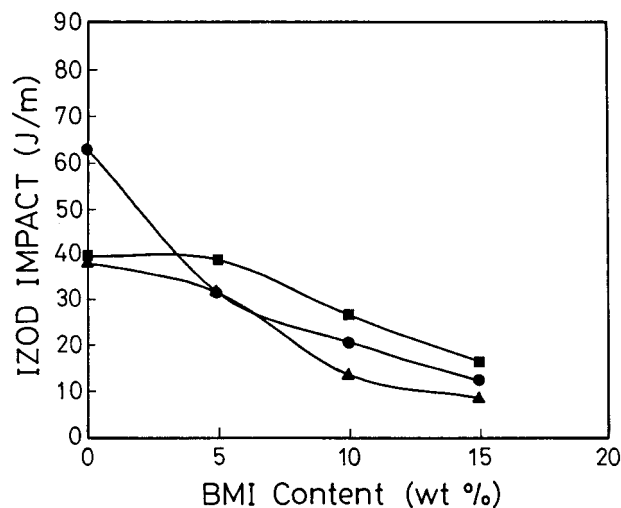


**Figure 5** Dependence of Izod impact strength of BMI/PU(PBA, 5 wt %)-EP IPN on various BMI content. (●) BMI/PU(PBA700)-EP IPN; (■) BMI/PU(PBA1000)-EP IPN; (▲) BMI/PU(PBA2000)-EP IPN.

BMI contents. In our previous work, we demonstrated that the Izod impact property (i.e., a high shear-rate fracturing of the polymeric materials) depends on the overall matrix toughness.<sup>15</sup> Although the compatible BMI/PU-EP IPN system has excellent mechanical properties, the cured BMI still contributes to the rigidity and brittleness in the system. Thus, the Izod impact strength of the BMI/PU-EP IPN was not significantly enhanced. Notably, the Izod impact



**Figure 6** Dependence of Izod impact strength of BMI/PU(PBA, 10 wt %)-EP IPN on various BMI content. (●) BMI/PU(PBA700)-EP IPN; (■) BMI/PU(PBA1000)-EP IPN; (▲) BMI/PU(PBA2000)-EP IPN.



**Figure 7** Dependence of Izod impact strength of BMI/PU(PBA, 15 wt %)-EP IPN on various BMI content. (●) BMI/PU(PBA700)-EP IPN; (■) BMI/PU(PBA1000)-EP IPN; (▲) BMI/PU(PBA2000)-EP IPN.

strength of BMI/PU-EP IPN decreases with an increasing BMI content (Figs. 5–7).

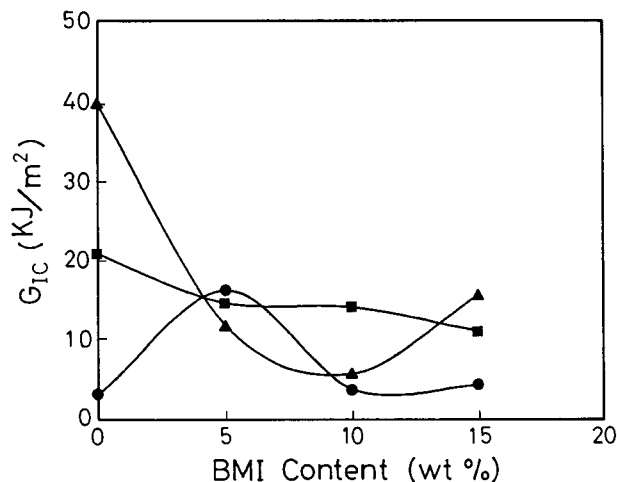
#### $G_{IC}$

As previously described,<sup>15</sup> the toughening mechanism for this low shear-rate fracturing test (i.e.,  $G_{IC}$  measurement) differs from that in the high shear-rate fracturing test (i.e., Izod impact test). The rubber particle dispersed in the matrix in general plays a prominent role in  $G_{IC}$  because it can accumulate the energy from the reinitiating crack of the continuous plastic matrix. Figures 8–10 and Table II present  $G_{IC}$  of BMI/PU-EP IPN with different BMI contents.  $G_{IC}$  of BMI/PU-EP IPN is slightly improved at a low BMI content (i.e., 5 wt %). This slight increase in  $G_{IC}$  is probably attributed to the increase in toughness of the matrix through the high compatibility between the BMI, which is a high crosslinking density material, and the PU-EP. The decrease in  $G_{IC}$  with a further increase of BMI content is likely attributed to the contribution of rigidity and brittleness from the cured BMI in the matrix.

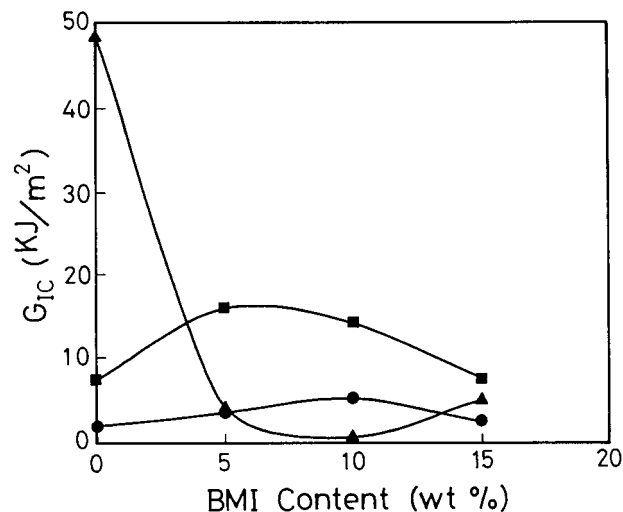
#### Thermal Properties

Figure 11 presents the DSC analysis of the BMI/PU(PBA700)-EP IPN with various BMI contents. According to this figure, the BMI/PU(PBA700)-EP IPN exhibits a single glass transition temperature





**Figure 8** Dependence of fracture energy of BMI/PU(PBA, 5 wt %)-EP IPN on various BMI content. (●) BMI/PU(PBA700)-EP IPN; (■) BMI/PU(PBA1000)-EP IPN; (▲) BMI/PU(PBA2000)-EP IPN.

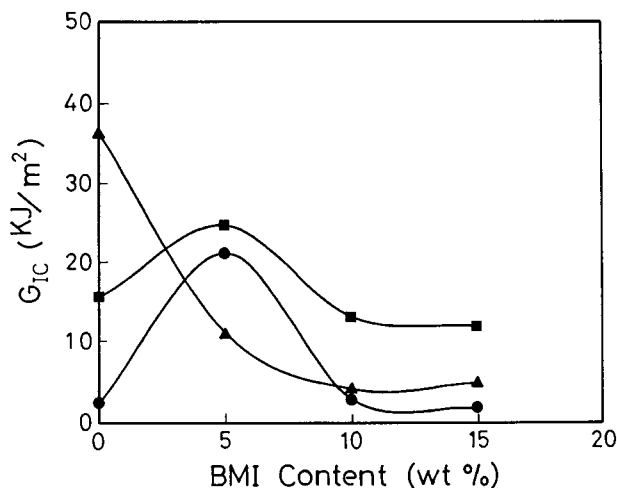


**Figure 10** Dependence of fracture energy of BMI/PU(PBA, 15 wt %)-EP IPN on various BMI content. (●) BMI/PU(PBA700)-EP IPN; (■) BMI/PU(PBA1000)-EP IPN; (▲) BMI/PU(PBA2000)-EP IPN.

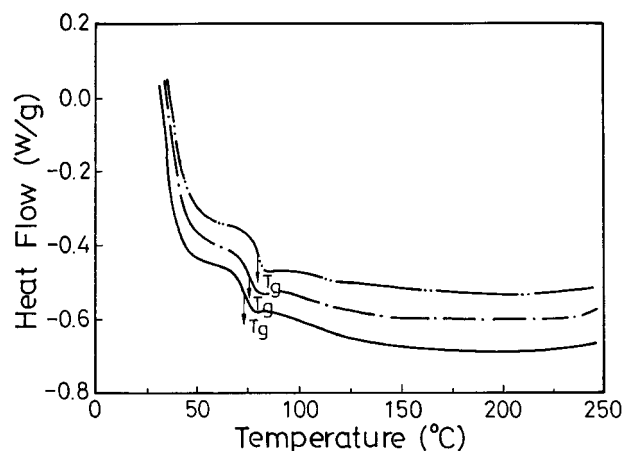
( $T_g$ ). In addition, the  $T_g$  of pure BMI network cannot be found in this study. The fact that its  $T_g$  exceeds above 380°C, and the BMI/PU-EP IPN is initially decomposed at 350°C (see TGA diagram; Fig. 12) accounts for why the BMI/PU-EP IPN cannot identify the  $T_g$  of the BMI network. The  $T_g$  (based on the DSC test) of the BMI/PU(PBA700)-EP IPN increases with an increasing BMI content, as attributed to the good compatibility between the BMI and PU in the epoxy matrix. In addition, the IPN effect

between the BMI and PU(PBA700)-EP networks also facilitates the increase of  $T_g$ . The previously described results are identical to the previous behavior in mechanical properties.

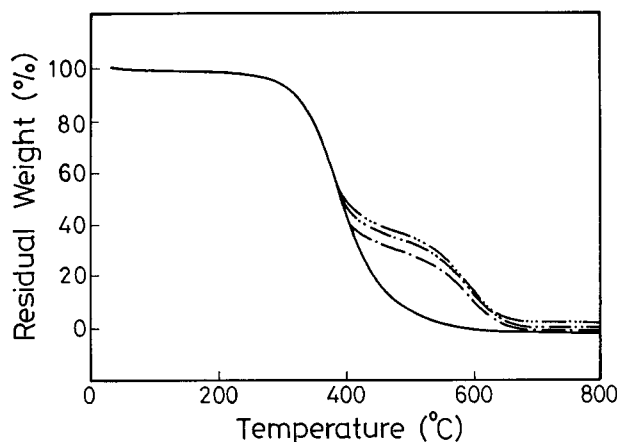
Figure 12 displays the TGA of the BMI/PU(PBA2000)-EP IPNs. According to this figure, the BMI/PU(PBA2000)-EP IPNs have two decomposition temperatures ( $T_d$ ) of one high  $T_d(T_{dh})$  at 600°C and the other low  $T_d(T_{dl})$  at 350°C. The latter is the decomposition temperature of the PU(PBA2000) presented in the epoxy matrix.



**Figure 9** Dependence of fracture energy of BMI/PU(PBA, 10 wt %)-EP IPN on various BMI content. (●) BMI/PU(PBA700)-EP IPN; (■) BMI/PU(PBA1000)-EP IPN; (▲) BMI/PU(PBA2000)-EP IPN.



**Figure 11** DSC for BMI/PU(PBA700, 15 wt %)-EP IPN on various BMI content. (—) 5 wt %; (---) 10 wt %; (-.-) 15 wt %.



**Figure 12** TGA of BMI/PU(PBA2000, 10 wt %) EP IPN on various BMI content. (—) 0 wt %; (---) 5 wt %; (- - -) 10 wt %; (- · - ·) 15 wt %.

Thus, the former,  $T_{dh}$ , is the decomposition temperature of the BMI network in the BMI/PU(PBA2000)-EP IPN.

## CONCLUSIONS

As the polyester-type PU of below 10 wt % content was introduced into the BMI/PU-EP IPN, the tensile strength show an “N”-shaped curve, with the increase of BMI content. The maximum value of tensile strength occurred at 5 wt % of the BMI content. When the PU content was increased up to 15 wt % into the BMI/PU-EP IPN system, the interpenetrating effect between the BMI and the PU-EP networks was not obvious. Thus, the tensile strength of the BMI/PU-EP IPN at various BMI content did not show an “N”-shaped curve. The Izod impact strength of the BMI/PU-EP IPN was not significantly improved.  $G_{IC}$  of BMI/PU-EP IPN was slightly improved at low BMI content. The BMI/PU(PBA700)-EP IPN show a single  $T_g$  (based on DSC test), and the  $T_g$  increased with BMI content. TGA data of the BMI/PU(PBA2000)-EP IPNs showed that the BMI/PU-EP IPNs have two decomposition temperatures of one high at 600°C and the other low at 350°C, respectively.

## REFERENCES

1. C. E. Sroog, A. L. Enderg, S. V. Abrams, C. S. Beer, W. M. Edward, and K. L. Oliver, *J. Polym. Sci., Polym. Chem. Ed.*, **3**, 1373 (1965).
2. I. K. Varma, G. M. Fohlen, and J. A. Parker, *J. Macromol. Sci. Chem.*, **19**, 209 (1983).
3. A. V. Galanti and D. A. Scola, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 451 (1981).
4. G. J. Kwiatkowski, L. M. Robeson, G. L. Brode, and A. W. Bedwin, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 961 (1975).
5. J. E. White, M. D. Scaia, and D. A. Snider, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 589 (1984).
6. J. E. White, M. D. Scaia, and D. A. Snider, *J. Appl. Polym. Sci.*, **29**, 891 (1984).
7. H. D. Stenzenberger, M. Herzong, W. Roner, R. Scheiblich, and N. J. Reeves, *Polym. J.*, **15**, 2 (1983).
8. W. J. Gilwee, R. W. Roser, and J. A. Parker, *16th National SAMPE Symposium*, **16**, 284 (1973).
9. M. S. Hsu, T. S. Chen, J. A. Parker, and A. H. Hermbuch, *29th National SAMPE Symposium*, **29** (034/1984); *SAMPE J.*, **July/Aug.**, 11 (1985).
10. H. D. Stenzenberger, M. Herzong, W. Roner, and R. Scheiblich, *29th National SAMPE Symposium*, **29**, 1043 (1984).
11. D. C. Liao, C. S. Tsai, K. H. Hsieh, and K. C. Frisch, *J. Polym. Res.*, **1**, 69 (1994).
12. T. Pascal, R. Mercier, and B. Sillion, *Polymer*, **31**, 78 (1990).
13. D. C. Liao, K. H. Hsieh, and S. C. Kao, *J. Polym. Sci., Polym. Chem. Ed.*, **33**, 481 (1995).
14. D. C. Liao and K. H. Hsieh, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 1665 (1994).
15. J. L. Han, S. M. Tseng, J. H. Mai, and K. H. Hsieh, *Die Angew. Makromol. Chem.*, **182**, 193 (1990).
16. J. L. Han, S. M. Tseng, J. H. Mai, and K. H. Hsieh, *Die Angew. Makromol. Chem.*, **184**, 89 (1990).
17. C. Hepburn, *Polyurethane Elastomers*, Applied Science Publishers, New York, 1982, p. 280.
18. S. K. Kim and S. C. Kim, *Polym. Bull.*, **23**, 141 (1991).
19. R. T. Ting and R. L. Cottingham, *J. Appl. Polym. Sci.*, **25**, 1815 (1980).
20. J. L. Han, K. H. Hsieh, and W. Y. Chiu, *J. Appl. Polym. Sci.*, **50**, 1099 (1993).
21. J. L. Han, K. H. Hsieh, W. Y. Chiu, and L. W. Chen, *J. Polym. Res.*, **2**, 115 (1995).
22. J. L. Han, C. C. M. Ma, Y. C. Chern, K. H. Hsieh, and W. Y. Chiu, *J. Appl. Polym. Sci.*, to appear.