Graft-Interpenetrating Polymer Networks of Polyurethane and Bismaleimide

K. H. HSIEH,[1,*] W. Y. HUNG,[1] D. C. LIAO,[1] and S. C. KAO[2]

[1]Department of Chemical Engineering and [2]Taipei Regional Analytical Instrument Center, National Science Council, National Taiwan University, Taipei, Taiwan 106, Republic of China

SYNOPSIS

Graft-interpenetrating polymer networks (graft-IPNs) of polyurethane (PU) and bismaleimide (BMI) were prepared by using a simultaneous polymerization technique. The effects of the PU molecular weight and the amounts of the PU on the mechanical properties, thermal stability, dynamic mechanical properties, density, and morphology of the IPNs are discussed. The graft-IPNs exhibited superior ultimate tensile strength and large improvement in flexural strength when the short soft segments of the PU were introduced. Better thermal stability of the IPNs was shown by increasing the BMI content. The heterogeneous and phase-separated characteristics were found from the results of dynamic mechanical analysis. The maximum density was achieved by the graft-IPNs structure when 33.3 wt % of PU with short soft chain length was added. The graft-IPNs also showed heterogeneous morphology in the micrographs when a large amount of PU was incorporated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polybismaleimides, which are well known as addition-type polyimides, afford crosslinked resins with excellent thermal stability. Their thermal stability is higher than that of the commercial epoxies but lower than that of conventional polyimides.[1-3] They also exhibit similar mechanical strength to that of epoxies. However, the cured bismaleimides (BMI) are high modulus materials with very low elongation at break due to their highly crosslinked structure. Efforts to toughen BMI have been made for many years.[4-11]

In the present study, the concept of interpenetrating polymer networks[12] (IPNs) was adopted to improve the disadvantages of a BMI. Because it showed very serious macrophase separation during the simultaneous polymerization of BMI and polyurethane (PU),[13] grafting reactions between the two components were introduced to enhance the compatibility of the polymeric components. In a previous article,[14] we reported synthesis and characterization

of a series of maleimide terminated PU prepolymers capable of being cured at a lower temperature. In this work, novel graft-IPNs of BMI and PUs were prepared. The grafting reaction between BMI and PU was performed by the introduction of the PU prepolymer with one end terminated by maleimide. The mechanical properties, thermal stability, density, dynamic mechanical analysis, and morphology of the graft-IPNs were investigated and are discussed.

EXPERIMENTAL

Materials

The materials required and their designations are listed in Table I. Poly(tetramethylene oxide) diols (PTMO) with molecular weight 650 (PTMO650) and 1000 (PTMO1000) and poly(butylene adipate) diols (PBA) with molecular weight 700 (PBA700), 1000 (PBA1000), and 2000 (PBA2000) were used as polyols, with trimethylol propane (TMP) as the crosslinking agent. 4,4'-Diphenylmethane diisocyanate (MDI) was used for the PU preparation. 1,4'-Methylene dianiline and maleic anhydride (MAH) were used to synthesize the bismaleimido-

---

Table I Materials

Designation	Description	Source
MDI	4,4-Diphenylmethane diisocyanate	Bayer Chemical Co.
PTM0650	Poly(oxytetramethylene) glycol, MW = 650	Union Carbide
PTMO1000	Poly(oxytetramethylene) glycol, MW = 1000	Union Carbide
PBA700	Poly(butylene adipate) glycol, MW = 700	Tai Chin Chem. Industry Co. Ltd.
PBA1000	Poly(butylene adipate) glycol, MW = 1000	Tai Chin Chem. Industry Co. Ltd.
PBA2000	Poly(butylene adipate) glycol, MW = 2000	Tai Chin Chem. Industry Co. Ltd.
TMP	Trimethylolpropane	Hayashi Pure Chem.
DCPO	Dicumyl peroxide	Merck Chemical Co.
DMF	N,N-Dimethylformamide	Merck Chemical Co.
MDA	1,4-Methylene dianiline	Merck Chemical Co.
TEA	Triethylamine	Merck Chemical Co.
MAH	Maleic anhydride	Merck Chemical Co.
Acetone		Merck Chemical Co.
Chloroform		Merck Chemical Co.

diphenyl methane (BDM) monomer. Chloroform then acetone were chosen as solvents for the BMI reaction stages. Acetic anhydride, triethyl amine, and nickel (II) acetate tetrahydride were used to remove the produced water and accelerate the reaction of imidization. Dicumyl peroxide was the initiator for the polymerization of the unsaturated maleimide groups. Polyols and TMP were continuously stirred and degased overnight at 70°C in the flask before they were used. MDI, 1,4-methylene dianiline, and MAH were employed as received. N,N'-Dimethylformamide (DMF) was dried for at least 48 h using molecular sieves (type 4 Å) before use.

Preparation of PU Prepolymer

To prepare PU prepolymer, two equivalents of MDI were charged into a reaction kettle and heated until molten at about 55°C. Then, one equivalent of polyol was added and mixed with the molten MDI. The mixture was vigorously agitated by a mechanical stirrer. The reaction took place under a dry nitrogen atmosphere at a temperature of approximately 68°C. When the —NCO content reached the theoretical value,[15] the reaction was stopped.
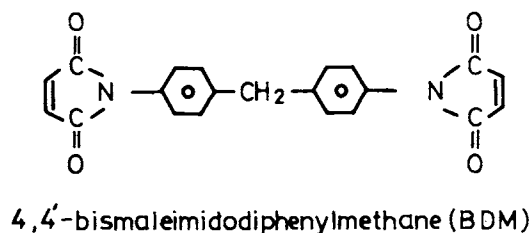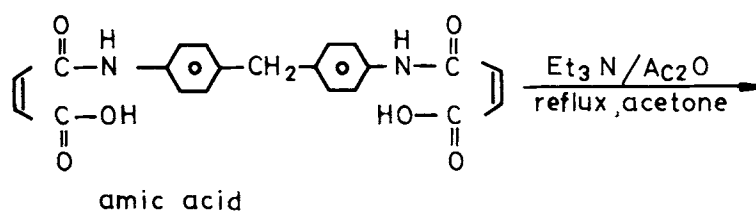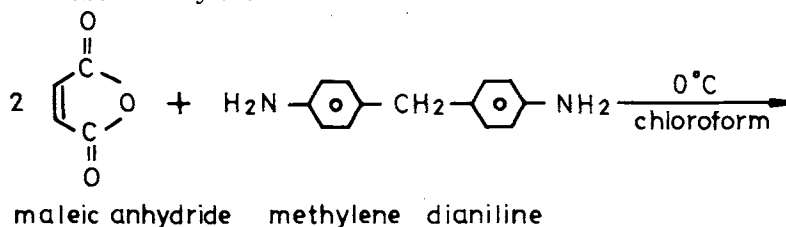
Synthesis of PU Prepolymer with One End Terminated by Maleimide

The maleimide-terminated PU prepolymer (UMI) was synthesized by the condensation reaction of MAH and NCO-terminated PU prepolymer, with 1 : 1 molar ratio, by the following reaction[14]:

maleic anhydride   PU   prepolymer

UMI
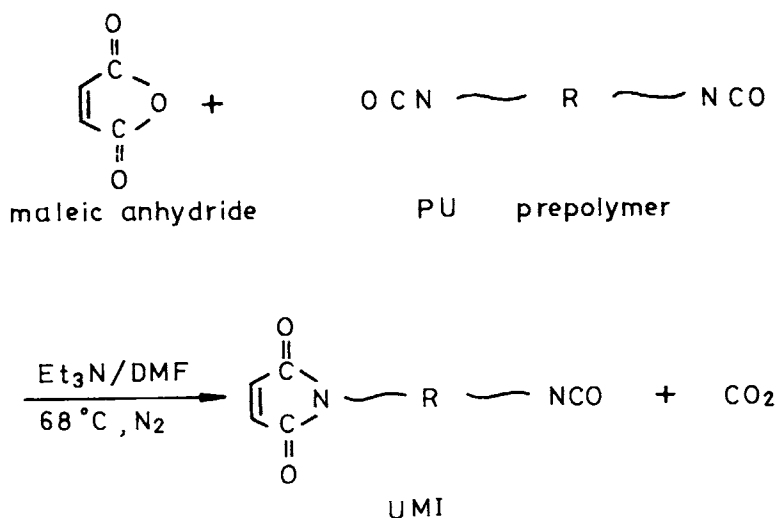
where R is the urethane-terminated polyether or polyester diols.

The reactions were carried out in a three-necked flask equipped with a stirring device, a reflux condenser, thermometer, heating mantle, and constant flow of dry nitrogen. The NCO-terminated PU prepolymer, dissolved in DMF, was added to the solution of MAH and triethyl amine catalyst (TEA) at 68°C. The amount of solvent used was about 1.5 times the weight of the reactants. The TEA catalyst was employed at about 3 mol % of the MAH. The start of the reaction was observed by the evolution of CO_2 gas. During this period, samples were drawn for infrared (IR) analysis. The reaction was stopped when the NCO absorption peak at 2270 cm^{-1} decreased and the C=O (of acid anhydride) absorption peak at 1848 cm^{-1} disappeared. The products dissolved in DMF produced a brown solution.

Preparation of BMI Monomers

The 4,4'-bismaleimidodiphenyl methane (BDM) monomer was prepared according to the following structure:

$$2 \quad \text{maleic anhydride} \quad + \quad H_2N\text{—}\langle o \rangle\text{—}CH_2\text{—}\langle o \rangle\text{—}NH_2 \xrightarrow[\text{chloroform}]{0°C}$$

maleic anhydride   methylene dianiline

amic acid $\xrightarrow[\text{reflux, acetone}]{Et_3N/Ac_2O}$

4,4'-bismaleimidodiphenylmethane (BDM)

The crude BDM precipitate was washed with sodium bicarbonate solution to exclude acetic acid in the product. It was then recrystallized from a mixed solvent of $CHCl_3$/MeOH to obtain a yellow solid (mp = 157°C) at 58% yield. The IR spectrum showed absorptions at 3100 cm^{-1} for =CH, 1780 cm^{-1} for C=O out of phase, 1720 cm^{-1} for C=O in phase, 1400 and 1380 cm^{-1} for C—N—C, and 832 cm^{-1} for aromatic maleimide.[16]

Preparation of PU/BMI Graft-IPNs

A solution of BMI monomer and UMI at a 10/1 weight ratio in DMF was placed in a three-necked flask equipped with a stirring device, a reflux condenser, thermometer, heating mantle, and constant flow of dry nitrogen. A solution of a suitable amount of PU prepolymer in DMF was poured into the reaction kettle under nitrogen atmosphere. Then a solution of dicumyl peroxide (0.5 wt % based on the weight of BMI) and a stoichiometric amount of crosslinking agent TMP were added to the reaction kettle and stirred for simultaneous polymerization of the PU, BMI, and UMI. The total solute content was 45 wt % and the temperature was maintained at 120°C. After 1 h the viscous mixture was cast into an aluminum mold and placed in the oven at the same temperature. After the solvent evaporated for 10 h, the resultant polymers were postcured at 150°C for 3 h, 180°C for 1 h under vacuum to remove the solvent residue spontaneously, and 230°C for 15 min to obtain completely crosslinked networks. The samples were then conditioned in a desiccator
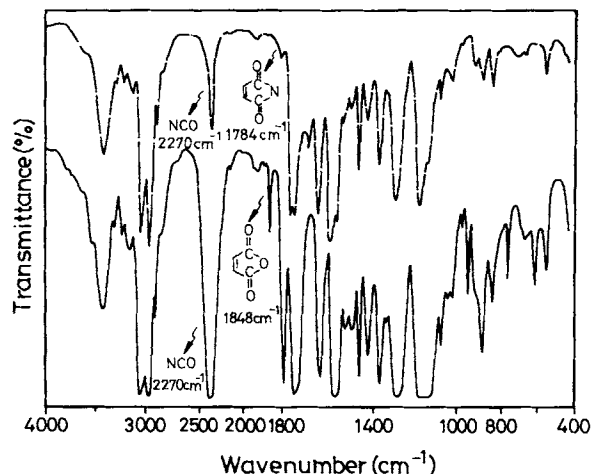
Figure 1 Infrared spectra during reaction of PU (PTMO650) prepolymer with maleic anhydride: (—) beginning of the reaction, (- -) end of the reaction.

at 50% relative humidity for at least 3 days before testing.

Testing Methods

IR analysis was performed on a Hitachi 270-30 IR spectrophotometer. The UMI solution in DMF was cast on a KBr pellet; then the solvent was removed by vacuum.

The stress–strain property was measured using a Tensilon (Mode: TCF-RC, Yashima Works Ltd., Japan). The stress–strain test procedure was followed as described in ASTM D-412 with a crosshead speed of 10 mm/min. At least five specimens were used for the test. Flexural strength was measured by following ASTM D-790 with a crosshead speed of 1 mm/min.

Thermogravimetric analysis (TGA) of the cross-linked polymer samples was carried out on a Perkin–Elmer TGA-7 instrument in nitrogen atmosphere. The measurement was performed at a heating rate of 20°C/min. The weight of samples tested was about 8 mg.

Dynamic mechanical analysis (DMA) was performed on a Dupont 983 DMA unit with an operating temperature range from −120–250°C. The DMA was performed in a resonance frequency mode and the heating rate was set at 5°C/min. The sample size was approximately 60 × 10 × 2 mm.

The density of the graft-IPNs was measured on a Micromeritics Accupyc-1330 densitometer.

Morphological studies were performed by using scanning electron microscopy (SEM, Hitachi S-800). Microphotographs were taken of the surface made
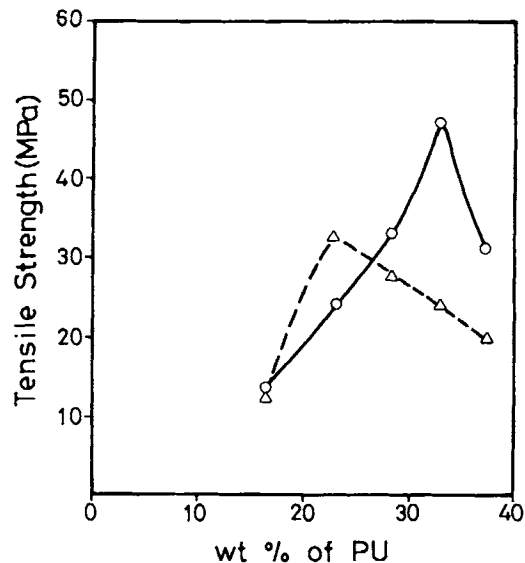

Figure 2 Tensile strength of PU/BMI graft-IPNs with various PU contents for the (- O -) PU (PTMO650) and (- △ -) PU (PTMO1000).

by fracturing the specimen in liquid nitrogen and then coating it with gold (Au) powder.

RESULTS AND DISCUSSION

IR Spectroscopy

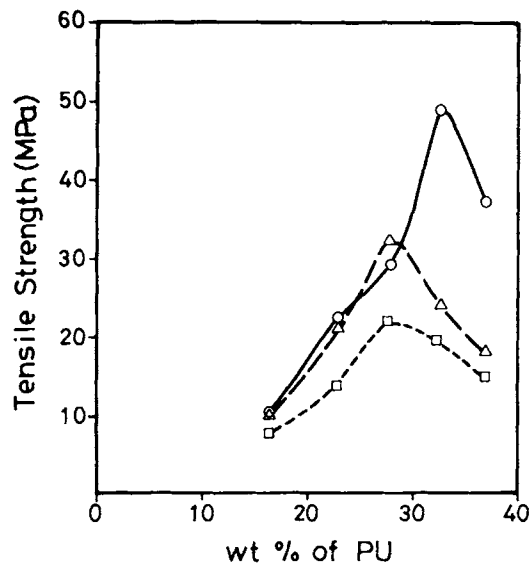The reaction between NCO-terminated prepolymer and MAH was monitored by the change of the char-

Figure 3 Tensile strength of PU/BMI graft-IPNs with various PU contents for (- O -) PU (PBA700), (- △ -) PU (PBA1000), and (- -□- -) PU (PBA2000).

Table II   Properties of PU/BMI Graft-IPNs

Polyurethane Content (wt %)	Tensile Strength (MPa)	Thermal Stability			Density	
		5% wt Loss (°C)	10% wt Loss (°C)	Char Yield	d_{exp}	Δd
0	—	469	481	51%	1.290	
PTMO650	11.2	306	322	6%	1.174	
16.7	13	408	430	36%	1.259	−0.79%
23.1	24	391	413	33%	1.248	−1.04%
28.6	33	387	407	32%	1.265	+0.80%
33.3	47	380	400	30%	1.269	+1.61%
37.8	31	378	399	28%	1.259	+1.27%
PTMO1000	9.8	333	350	4%	1.129	
16.7	12	413	433	32%	1.236	−1.90%
23.1	33	407	424	30%	1.253	0.30%
28.6	28	391	419	28%	1.245	0.41%
33.3	24	390	418	27%	1.235	0.33%
37.8	20	389	411	26%	1.227	0.24%
PBA700	12.5	333	349	6%	1.227	
16.7	10	392	432	40%	1.277	−0.20%
23.1	22	390	417	37%	1.273	−0.14%
28.6	29	389	415	35%	1.279	0.62%
33.3	49	387	410	34%	1.280	0.96%
37.8	37	383	404	31%	1.267	0.11%
PBA1000	9.4	337	354	11%	1.179	
16.7	10	414	436	37%	1.259	−0.84%
23.1	21	410	432	34%	1.267	0.33%
28.6	32	399	422	31%	1.262	0.45%
33.3	24	397	419	29%	1.261	0.81%
37.8	18	393	418	28%	1.252	0.49%

(—)Too brittle to cut for testing. d_{exp}, density measured by experiment; d_{cal}, density calculated by volume addition; $\Delta d = (d_{exp} - d_{cal})/d_{cal}$.

acteristic peaks of the isocyanate group (2270 cm^{-1}) and acid anhydride (1848 cm^{-1}) in IR spectra as shown in Figure 1. The decrease of the strong and broad NCO absorption peak at 2270 cm^{-1} and the disappearance of the C＝O stretching vibration peak of acid anhydride at 1848 cm^{-1} in the IR spectra, is evidence that the reaction took place between the PU prepolymer and MAH. Further, a characteristic carbonyl absorption peak of imides was observed at 1784 cm^{-1}. Reaction conversion was determined from the ratio change of the normalized absorbance of the isocyanate peak at 2270 cm^{-1} to that of the CH peak at 2940 cm^{-1}. When the ratio decreased to about 0.5 and the C＝O stretching vibration peak of acid anhydride at 1848 cm^{-1} disappeared simultaneously, the reaction was accomplished and stopped. Similar results were also observed in the other types of PU prepolymer employed. The detailed identification of urethane modified BMIs was described in the previous study.[14]

Stress–Strain Properties

The stress–strain properties of both kinds of graft-IPNs with various PU chain lengths and compositions are shown in Figures 2 and 3 and are listed in Table II. The pure BMI sample was too brittle to cut for testing. The tensile strength at break increased with the PU content up to a maximum value, then decreased with a continuous increase of the PU in graft-IPNs. The initial increase in tensile strength results from the interpenetrating effect and the following decrease is due to more softness of the PU introduced.[17] It was also observed that the PU/BMI graft-IPN with shorter soft segments in the PU (i.e., PTMO650 or PBA700) had significantly higher tensile strengths than those with longer soft segments in the PU (i.e., PTMO1000, PBA1000, or PBA2000). The reason for this behavior is the increased crosslinking density in the PU with the shorter chains and because more grafting sites result
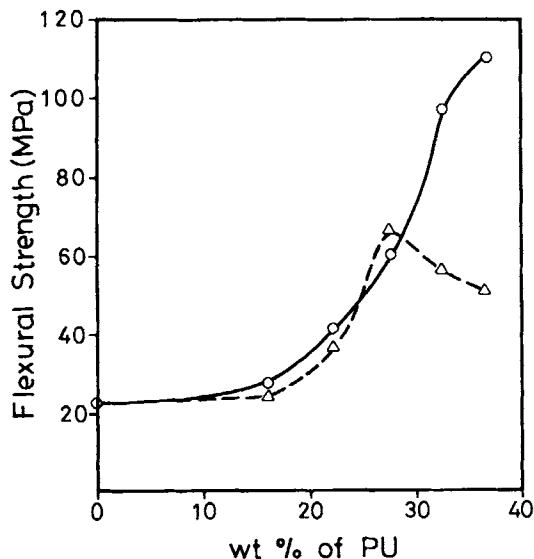
Figure 4 Flexural strength of PU/BMI graft-IPNs with various PU contents for (- O -) PU (PTMO650) and (- △ -) PU (PTMO1000).

from the larger amount of UMI molecules per unit volume.

Flexural Strength

Figures 4 and 5 show the results of flexural tests of the PU/BMI graft-IPNs. The flexural strength of the BMI was about 22 MPa. The flexural strength
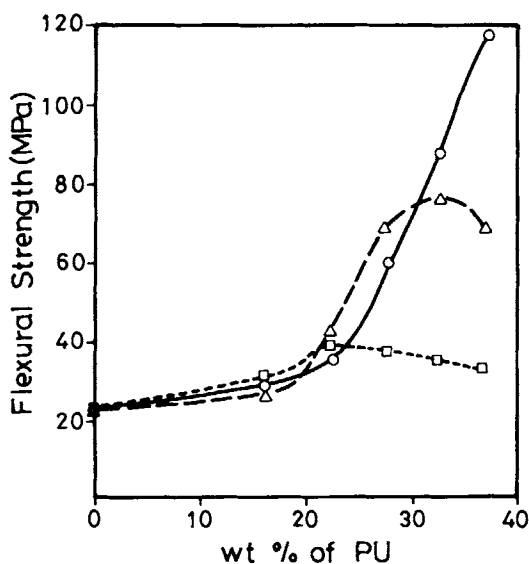

Figure 5 Flexural strength of PU/BMI graft-IPNs with various PU contents for (- O -) PU (PBA700), (- △ -) PU (PBA1000), and (- - - □ - - -) PU (PBA2000).
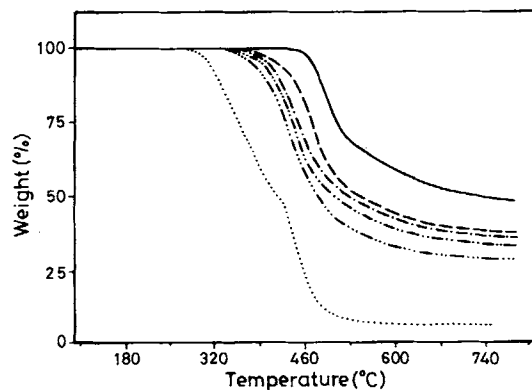
Figure 6 Thermograms of PU (PTMO650)/BMI graft-IPNs at various PU/BMI ratios: (—) 0 : 100, (- - -) 16.7 : 83.3, (- · - · ·) 23.1 : 76.9, (- · · · · ·) 28.6 : 71.4, (- · · · · · · ·) 37.8 : 62.2, and (· · ·) 100 : 0.

of the graft-IPNs was greatly improved for both the PTMO650/BMI and PBA700/BMI graft-IPNs with the increase of PU content in the graft-IPNs. In particular, when 37.8 wt % of PU was employed, the flexural strength of the graft-IPNs was about 5 times greater for the PTMO650/BMI system, and 5.5 times greater for the PBA700/BMI system, than that of the neat BMI resin. When the PU with longer chain length was introduced, the flexural strength increased to a maximum value with increasing PU content up to 28.6 wt % for PTMO1000/BMI, 33.3 wt % for PBA1000/BMI, and 23.1 wt % for PBA 2000/BMI graft-IPNs. This behavior in the flexural strength shows that the initial increase is due to an interpenetrating effect and then the softness of the matrix is considered a dominant effect when large
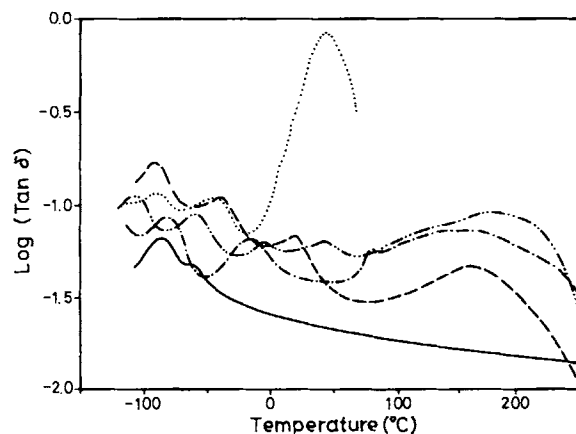

Figure 7 Temperature dependence of tan δ of PU (PTMO650)/BMI graft-IPNs at various PU/BMI ratios: (—) 0 : 100, (- - -) 23.1 : 76.9, (- · · · ·) 33.3 : 66.7, (- · · · · ·) 37.8 : 62.2, and (· · ·) 100 : 0.
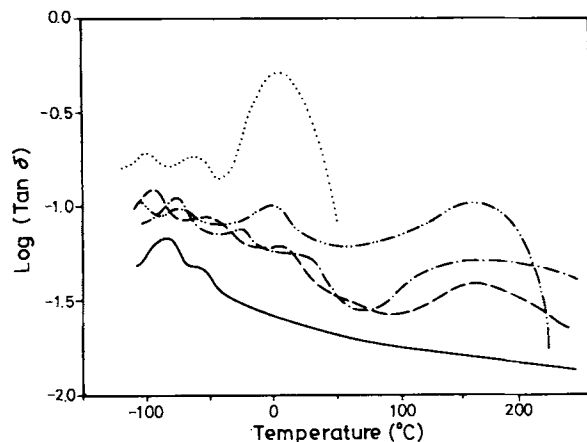
Figure 8 Temperature dependence of tan δ of PU (PTMO1000)/BMI graft-IPNs at various PU/BMI ratios: (—) 0 : 100, (- - -) 16.7 : 83.3, (- - - - -) 23.1 : 76.9, (- - - - - -) 28.6 : 71.1, and (· · ·) 100 : 0.

Thermal Stability

The thermogravimetric behavior of PTMO650/BMI graft-IPNs is shown in Figure 6. The temperatures on the basis of 5 and 10% weight loss were used to indicate the thermal stability of the PU/BMI graft-IPN systems. The corresponding temperatures and values of the char yields after thermal degradation are listed in Table II. Compared with the pure PU crosslinked elastomers, it is evident that the IPNs have greater thermal stability as the BMI content increases. Further, greater thermal stability was
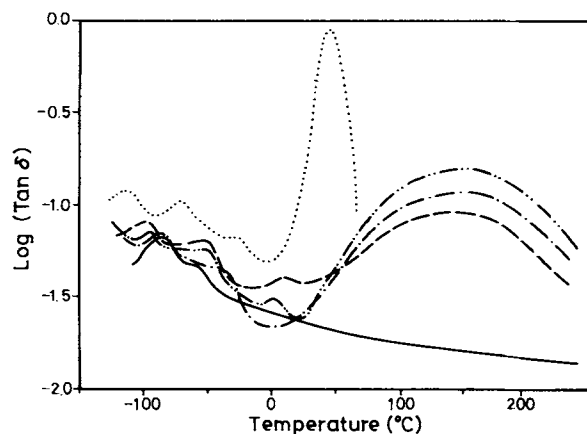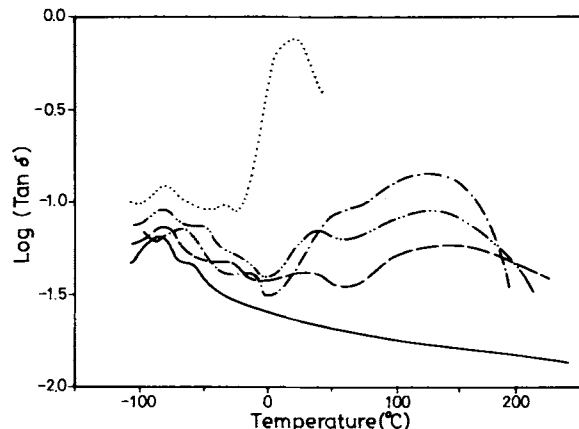

Figure 9 Temperature dependence of tan δ of PU (PBA700)/BMI graft-IPNs at various PU/BMI ratios: (—) 0 : 100, (- - -) 23.1 : 76.9, (- - - - -) 33.3 : 66.7, (- - - - - -) 37.8 : 62.2, and (· · ·) 100 : 0.

Figure 10 Temperature dependence of tan δ of PU (PBA1000)/BMI graft-IPNs at various PU/BMI ratios: (—) 0 : 100, (- - -) 23.1 : 76.9, (- - - - -) 33.3 : 66.7, (- - - - - -) 37.8 : 62.2, and (· · ·) 100 : 0.

achieved when longer soft segments were introduced into the graft-IPNs. Because the urethane (carbamate) linkage has a lower degradation temperature at 270–280°C[18,19] in the PU/BMI graft-IPNs, the longer soft segments introduced into the graft-IPNs resulted in a lower density of the urethane linkage and therefore increased the onset of degradation temperature of the IPNs.[13,14] On the other hand, the PU/BMI graft-IPNs are more thermally resistant when polyester type PU was used, because polyester segments tend to have lower hydrogen-to-carbon and higher oxygen-to-carbon ratios than polyether segments.[11,20]

DMA

The DMA was performed in the resonance frequency mode and the tan δ of the PU/BMI graft-

Figure 11 Scanning electron photomicrographs for PU (PBA700)/BMI graft-IPNs at the PU/BMI ratio of 16.7/83.3.

amounts of PU with long soft segment chains are employed.
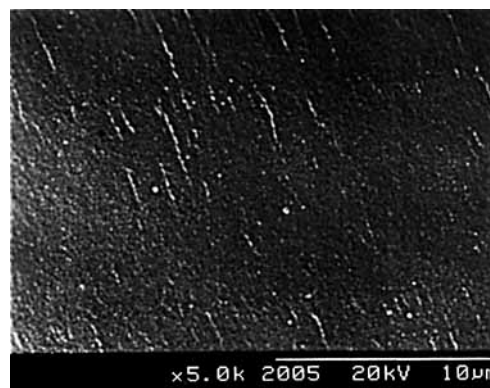
Figure 12   Scanning electron photomicrographs for PU (PBA700)/BMI graft-IPNs at the PU/BMI ratio of 28.6/71.4.
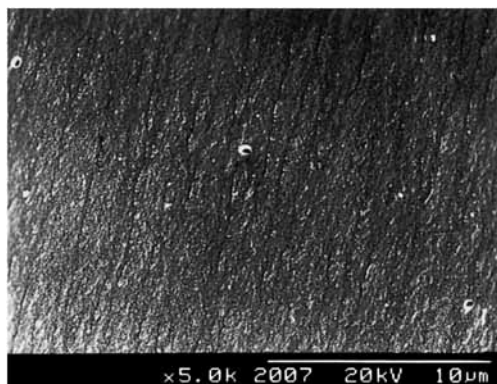

Figure 13   Scanning electron photomicrographs for PU (PBA700)/BMI graft-IPNs at the PU/BMI ratio of 37.8/62.2.

IPNs and those of the component polymers are shown in Figures 7–10. The α-relaxation of the cured neat BMI has been reported[21] to be above 360°C and therefore it was not observed within our temperature range. The effect of the PU (PTMO) content in the PU/BMI graft-IPNs on the tan δ-temperature curves is shown in Figures 7 and 8. When 23.1 wt % of the PU (PTMO650) was introduced into the IPNs, a broad transition peak appeared at about 170°C. It resulted from the α-transition of the PU/BMI graft-IPNs structure. A second transition peak at about 18°C also occurred. Further, multipeaks were also found in the temperature range of 0–200°C for the other compositions. This meant that heterogeneous morphology was present and resulted from the inherent thermodynamic incompatibility of the component polymer networks.[22–24] As for the PTMO1000/BMI graft-IPN (Fig. 8), a slight increase in the compatibility between PU and BMI was found at the PU (PTMO1000) content of 23.1% in the graft-IPNs, because the corresponding transition peaks shifted inward.

As shown in Figure 9, polyester type PU of molecular weight 700 (PBA700) was employed to prepare PU/BMI graft-IPNs. When 33.3 wt % of the PBA700 was added, only a broad transition peak was found and the transition peak ascribed to PU disappeared. This indicated that the probability of permanent entanglement and interlocking was significantly enhanced due to high compatibility at this component composition.[25] As for the PBA1000/BMI graft-IPN (Fig. 10), those two transition peaks shifted inward, especially when 33.3% PU (PBA1000) was introduced. The compatibility was also improved when the PU
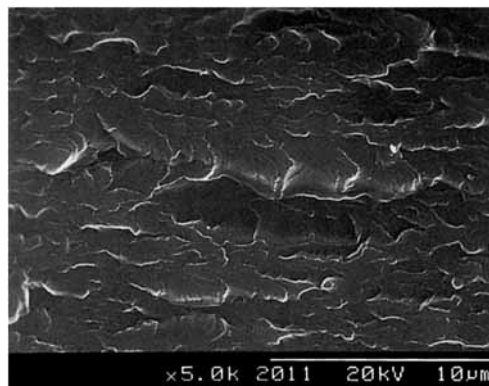
(PBA1000) was introduced into the PU/BMI graft-IPNs structure.

Density

The measured densities and calculated densities based on the volume additivity of the components are listed in Table II. The compositions of the maximum density in the PTMO650/BMI, PBA700/BMI, and PBA1000/BMI systems, are all at 33.3 wt %. The large increase in density when 33.3 wt % PU with shorter soft chain length (i.e. PTMO650 or PBA700) was introduced is coincident with the significant increase of the tensile strength in these two systems. These corresponding properties indicated that the interpenetrating effect in the IPNs reaches a maximum value at this composition, which causes a high density of the material with high mechanical strength.
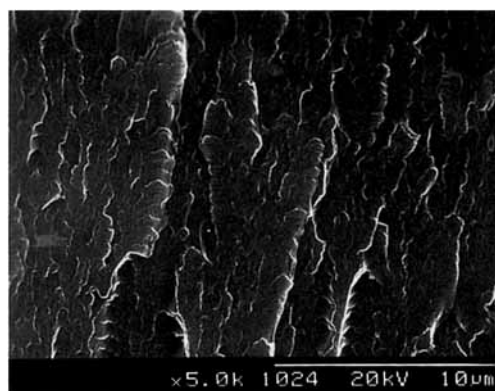

Figure 14   Scanning electron photomicrographs for PU (PTMO1000)/BMI graft-IPNs at the PU/BMI ratio of 37.8/62.2.

Morphology

Figures 11–14 are representative scanning electron micrographs of the PU/BMI graft-IPNs. When more of the PU (PBA) was added, the fractured surface possessed more roughness as shown in the figures. It indicated a heterogeneous morphology. Similar results were also found in the PTMO/BMI graft-IPNs systems.

CONCLUSIONS

The maximum tensile strength of the PU/BMI graft-IPNs occurs at 33.3 wt % PU content as short soft segments were added. The flexural strength also shows a great improvement when the short soft segments of PU were introduced. Thermal stability was enhanced by increasing the BMI content. From the results of DMA it was found that a heterogeneous morphology network structure formed in the PU/BMI graft-IPNs. Rough fractured surfaces were observed in SEM micrographs for the PU/BMI graft-IPNs.

REFERENCES

1. C. E. Sroog, A. L. Endreg, S. V. Abramo, 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, Macromol. Sci., Chem., A19, 209 (1983).
3. A. V. Galanti and D. A. Scola, J. Polym. Sci., Polym. Chem. Ed., 19, 451 (1981).
4. A. D. Gupta, J. Appl. Polym. Sci., 30, 3879 (1985).
5. I. K. Varma and D. S. Varma, J. Polym. Sci., Polym. Chem. Ed., 22, 1419 (1984).
6. J. V. Grivello, J. Polym. Sci., Polym. Chem. Ed., 14, 159 (1976).
7. J. E. White and M. D. Scaia, Polymer, 25, 850 (1984).
8. S. Jakeda and H. Kakiuchi, J. Appl. Polym. Sci., 35, 1351 (1988).
9. N. Suzuki, A. Nagai, M. Suzuki, and A. Takahashi, J. Appl. Polym. Sci., 44, 1807 (1992).
10. T. Pascal, R. Mercier, and B. Sillion, Polymer, 31, 78 (1990).
11. D. C. Liao, K. H. Hsieh, and S. C. Kao, J. Polym. Sci., Polym. Chem. Ed., to appear.
12. L. H. Sperling, Interpenetrating Polymer Networks and Related Materials, Plenum, New York, 1981.
13. D. C. Liao, C. S. Tsai, K. H. Hsieh, and K. C. Frisch, J. Polym. Res., 1, 69 (1994).
14. D. C. Liao and K. H. Hsieh, J. Polym. Sci., Polym. Chem. Ed., 32, 1665 (1994).
15. C. Hepburn, Polyurethane Elastomer, Applied Science Publishers, New York, 1982.
16. S. K. Kim and S. C. Kim, Polym. Bull., 23, 141 (1990).
17. K. H. Hsieh and J. L. Han, J. Polym. Sci., Polym. Phys. Ed., 28, 623 (1990).
18. H. K. Lee and S. W. Ko, J. Appl. Polym. Sci., 50, 1269 (1993).
19. K. Nakamura, T. Hatakeyama, and H. Hatakeyama, Polym. Adv. Technol., 3, 151 (1992).
20. C. T. Hilado, in Polyurethane Technology, P. F. Bruins (Ed.), Interscience Publishers, New York, 1969, p. 118.
21. S. Jakeda, H. Akiyama, and H. Kakiuchi, J. Appl. Polym. Sci., 35, 1341 (1988).
22. K. H. Hsieh, Y. C. Ching, Y. C. Chern, W. Y. Chiu, and C. C. M. Ma, Angew. Makromol. Chem., 194, 15 (1992).
23. S. Krause, in Polymer Blends, Vol. 1, D. R. Paul and S. Newman (Eds.), Academic Press, New York, 1978, p. 16.
24. Y. S. Lipatov, in Advances in Interpenetrating Polymer Networks, Vol. 1, H. L. Frisch, L. H. Sperling, Y. S. Lipatov, and H. X. Xiao (Eds.), Technomic, Lancaster, PA, 1990, p. 261.
25. S. C. Kim, D. Klempner, K. C. Frisch, and H. L. Frisch, Macromolecules, 17, 263 (1975).