Thermomechanical Properties and Morphology of Interpenetrating Polymer Networks of Polyurethane–Poly(methyl methacrylate)

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ABSTRACT: Interpenetrating networks (IPNs) of polybutadiene-based polyurethane (PU) and poly(methyl methacrylate) (PMMA) were synthesized. The effect of the incorporation of 2% glycidyl methacrylate (GMA) and 2-hydroxyethyl methacrylate (2-HEMA) on the thermal, mechanical, and morphological properties of IPNs was investigated. Both 2-HEMA and GMA led to improvements in these properties. However, 2-HEMA-containing IPNs showed somewhat better tensile strength, elongation, and damping characteristics. The morphology of IPNs containing 2-HEMA showed better mixing of the components. The improvement in the properties was observed for up to 40% PMMA in the IPNs. Differential scanning calorimetry thermograms showed the presence of three glass transitions. The third glass-transition temperature was explained by possible grafting of methyl methacrylate onto PU. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1576–1585, 2002

Key words: polyurethanes; IPNs; morphology; viscoelastic properties; mechanical properties

INTRODUCTION

Interpenetrating networks (IPNs), which are specialty blends, have attracted attention in recent years[1–7] because of their versatility and wide spectrum of properties. Differences in the thermodynamic and viscoelastic properties of polymers lead to unfavorable interactions between their molecular segments, causing poor dispersion and incompatibility during mixing. Therefore, like many other polymer–polymer systems, IPNs also have a tendency to show phase separation due to the low entropy of mixing.[8] However, the extent of phase separation is restricted because of the phase-interlocking configuration. Interpenetrating polymerization is a mode of blending two polymers to produce a mixture in which phase separation is not as extensive as it would be otherwise.[9] To optimize interpenetration, it is desirable that the phases be as small as possible. The compatibility between components can also be improved with cocrosslinkers, which encourage further interaction. Crosslinking contributes toward toughness and fatigue, sound and vibration damping, and swelling in solvents.[4,7,10] IPNs synthesized so far exhibit various degrees of phase separation depending mainly on the miscibility of the polymers.[10–17] Because permanent

Table I Chemicals Used for the Synthesis of IPNs

Material	Description	Source
1. HTPB	Hydroxyl value = 45.8 mg of KOH/g Molecular weight = 2600 Yellowish viscous liquid	Vikram Sarabhai Space Centre (Thiruvananthapuram, India)
2. MDI	Mixture of di- and triisocyanates	Vikram Sarabhai Space Centre
3. TMP	PU crosslinker	Fluka AG (Buchs, Switzerland)
4. DBTDL	—	Fluka AG
5. AIBN	—	Spectrochem (Bombay, India)
6. MMA	—	Sisco Chemicals (Bombay, India)
7. GMA	—	Fluka AG
8. DVB	Acrylate crosslinker	Fluka AG
9. 2-HEMA	—	Sisco Chemicals

entanglements can effectively minimize phase separation, increasing phase stability, complete miscibility is not necessary to achieve desirable properties.

Hourston and coworkers[10–12] carried out a detailed investigation of the synthesis and properties of various polyurethane (PU)/polyacrylate IPNs. They used PU derived from the NCO-terminated commercial prepolymer Adiprene L-100 and various acrylates such as poly(ethyl methacrylate),[10] poly(methyl acrylate-co-methyl acrylate),[11] and poly(methyl acrylate).[12] Substantial phase separation was observed in transmission electron microscopy, but dynamic mechanical analysis (DMA) results indicated a certain degree of mixing of components in these IPNs. High damping characteristics were exhibited by some compositions of these IPNs.[10] Suthar and coworkers[13–15] did considerable work in the area of IPNs developed from castor oil-based PUs and polyacrylates such as poly(methyl acrylate),[13] poly(2-hydroxyethyl methacrylate),[14] poly(methyl methacrylate) (PMMA),[15] and poly(n-butyl methacrylate).[15] In a study of the mechanical and morphological properties of PU/poly(n-butyl acrylate)-based IPNs, Fox et al.[16] reported very high phase separation indicating incompatibility.

The IPNs of PU/PMMA have already been reported by many authors.[15,17] However, some of them are based on various other PUs, and in some of them, it is not very easy to establish a structure–property relationship, as they are rather complex. We have undertaken a study of the compatibilization of hydroxy-terminated polybutadiene (HTPB)-based PU/PMMA IPNs with comonomers. Scarito and Sperling[17] examined the effect of glycidyl methacrylate (GMA) in an epoxy/acrylate system. They reported that the incorporation of only 3% GMA in both components

during simultaneous network formation led to sufficient mixing, yielding materials with only one glass-transition temperature (T_g). GMA has a polar epoxy group, whereas another acrylate monomer, 2-hydroxyethyl methacrylate (2-HEMA), has a free OH group that can interact with the free NCO groups of PU. Therefore, 2-HEMA is expected to enhance compatibility and molecular mixing in PU/PMMA IPNs. We developed PU–PMMA IPNs containing either GMA or 2-HEMA. They were characterized for various thermomechanical and morphological properties, and a comparative study was made.

EXPERIMENTAL

Materials

The sources of the chemicals used for the synthesis of the IPNs are given in Table I. The diisocyanate was used without any purification. Trimethylol propane (TMP) was dried to a moisture content of less than 0.1%. The monomers were distilled before use.

Synthesis of the IPNs

The IPNs were prepared from PU based on HTPB and methylenediphenyl diisocyanate (MDI). Methyl methacrylate (MMA) was used as the monomer for the second network, and divinyl benzene (DVB) was used as an acrylate crosslinker. The concentration of GMA and 2-HEMA was kept constant at 2% (w/w) of the total acrylate concentration.

In a five-necked reaction kettle fitted with a mechanical stirrer and a nitrogen inlet, 1.0 mol of HTPB dried *in vacuo* for about an hour was

taken. A calculated quantity of diisocyanate (3.25 mol) was then added dropwise under a nitrogen atmosphere at room temperature. The prepolymerization was continued for an hour. To this, TMP (1.5 mol), MMA, DVB (4% w/w), and 2-HEMA/GMA (2% w/w) were added successively. 2,2′-Azobisisobutyronitrile (AIBN) was added as its solution in the monomer. Stirring was continued for 30 min, followed by the addition of the catalyst dibutyl tin dilaurate (DBTDL) and triethylamine. The temperature was increased to 60°C to initiate the polymerization of the PMMA network, and stirring was continued for 15 min. Degassing was carried out to remove the entrapped air. The mixture was poured into glass molds and placed in a closed chamber to prevent monomer loss due to evaporation. Curing was carried out at room temperature for about 15 h and then in an electric oven at 80 ± 1°C for 3 h.

Characterization

The synthesized IPNs were tested as follows.

Tensile Properties

Stress–strain properties were measured with an Instron testing machine (no. 4204) with dumbbell-shaped test specimens and ASTM standard D 638. The gauge length was 50 mm. The crosshead speed was 10 mm/min at 25°C and 50% humidity. The data given are the averages of five measurements.

Thermal Analysis

The thermal transitions of selected IPNs were examined with modulated differential scanning calorimetry (DSC; DSC 2910 TA Instruments, United States). The samples were quench-cooled with liquid nitrogen to the required temperature and heated at a uniform rate of 10°C/min under a 45 mL/min nitrogen flow. T_g was defined as the temperature at the point of intersection between tangents drawn at the point of the inflection of the transition and at the flat part of the curve before the transition.

The thermogravimetric analysis of some selected IPNs was carried out on a Shimadzu DT 30 thermal analyzer at a heating rate of 10°C/min under an air atmosphere with about 5-mg samples.

Scanning Electron Microscopy (SEM)

The surface morphology of the IPNs was examined with a Leica (Cambridge, England) Ste-reoscan 440 scanning electron microscope. Polymer specimens were coated with gold (50 μm thick) in an automatic sputter coater (Polaron Equipment, Ltd., United States). An accelerating potential of 10 kV was used for the analysis of these samples.

DMA

DMA measurements of the selected samples were carried out on a Seiko DMS 200 SDM 5600 analyzer. The 30-mm-long samples had a cross-section area of about 1.8 mm^2. The rate of scanning was 2°C/min. The analysis was carried out between -100 and 150°C at 1, 2, 5, and 10 Hz. The nitrogen flow rate was maintained at 200 mL/min.

Swelling Behavior

The diffusion of organic solvents through the IPN films was investigated with the conventional sorption method[19] with circular samples 1.5 cm in diameter. Various parameters, such as the molecular weight between crosslinks,[19] degree of crosslinking,[19] and crosslink density,[20] were calculated.

RESULTS AND DISCUSSION

The effect of GMA and 2-HEMA on the properties of PU/PMMA IPNs was examined by the preparation of three sets of IPNs. The first set contained various ratios of PU/PMMA (90/10, 80/20, 70/30, and 60/40, respectively) and was designated P/M. The second set contained in addition to the aforementioned compositions, 2% (w/w) GMA, and was designated P/M/G. In the third set designated P/M/H, GMA was replaced with 2-HEMA. Some authors[21,22] have reported glycol-based PU/PMMA IPNs to be nontransparent because of the incompatibility of PMMA and glycols. The P/M films in this system were comparatively less transparent than the P/M/G and P/M/H films. This could be an indication of better component mixing in the systems containing 2-HEMA and GMA.

Mechanical Properties

The effect of the weight percentage of PMMA on the tensile strength and elongation at break of the IPNs is illustrated in Figures 1 and 2. All the
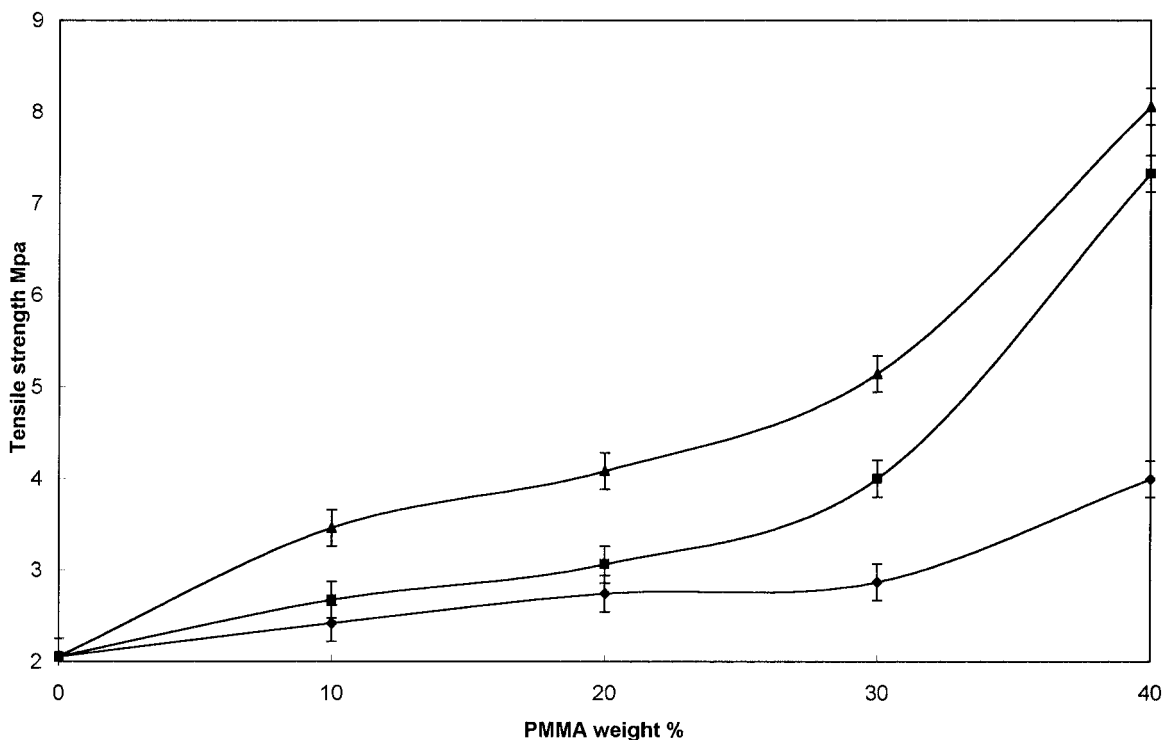
Figure 1 Effect of the weight percentage of PMMA in the IPNs on the tensile strength of PU–PMMA IPNs: (◆) P/M, (■) P/M/G, and (▲) P/M/H.

IPNs show higher tensile strength than pure PU. Among the IPNs, the set containing 2-HEMA, that is, P/M/H, shows the highest tensile strength of all the IPN compositions. The P/M IPN, however, showed the lowest tensile strength. Thus, in the presence of 2-HEMA, there exists satisfactory rubber–matrix adhesion in the IPNs under study. This may be due to the physical entanglements of the two phases, which prevent interfacial decohesion, as seen from SEM and discussed later. The P/M/G IPNs exhibit tensile strengths higher than those of P/M but lower than those of P/M/H, indicating improved phase mixing compared with that of P/M IPNs. There is an approximately 25–35% increase in the tensile strength and an approximately 10% increase in the elongation of the P/M/H IPNs with respect to P/M/G. Thus, although both 2-HEMA and GMA lead to an increase in the tensile strength, 2-HEMA appears to bring better miscibility.

Furthermore, the tensile strength increases with an increasing PMMA weight percentage in all the IPNs. However, with an increase in the PMMA content from 30 to 40%, a sudden increase in the tensile strength can be observed in all three sets. This can be attributed to an increase in the

crosslink density arising from enhanced physical crosslinks caused by interpenetration and improved homogeneity of the 60/40 IPNs, as observed with SEM.

The elongation percentage increases with the weight percentage of PMMA (Fig. 2) up to 20%. A further increase in the PMMA content shows a considerable decrease in elongation. Surprisingly, the elongation of all the 90/10 and 80/20 IPNs is even higher than that of the parent PU. A similar observation was made by Varghese and Krishnamurthy[23] for castor oil-based PU/PMMA and PU/poly(butyl acrylate) IPNs. They attributed an increase in elongation to topological interpenetration,[24] which led to interwoven or interlocked structures without chemical bonding.

The high tensile strength and lowest elongation of the 60/40 PU/PMMA IPNs could be due to the onset of phase inversion,[23] in which PU acts as the plasticizer and PMMA acts as the continuous phase.

SEM

SEM images of tensile-fractured specimens of 60/40 PU/PMMA IPNs are shown in Figure 3(A–
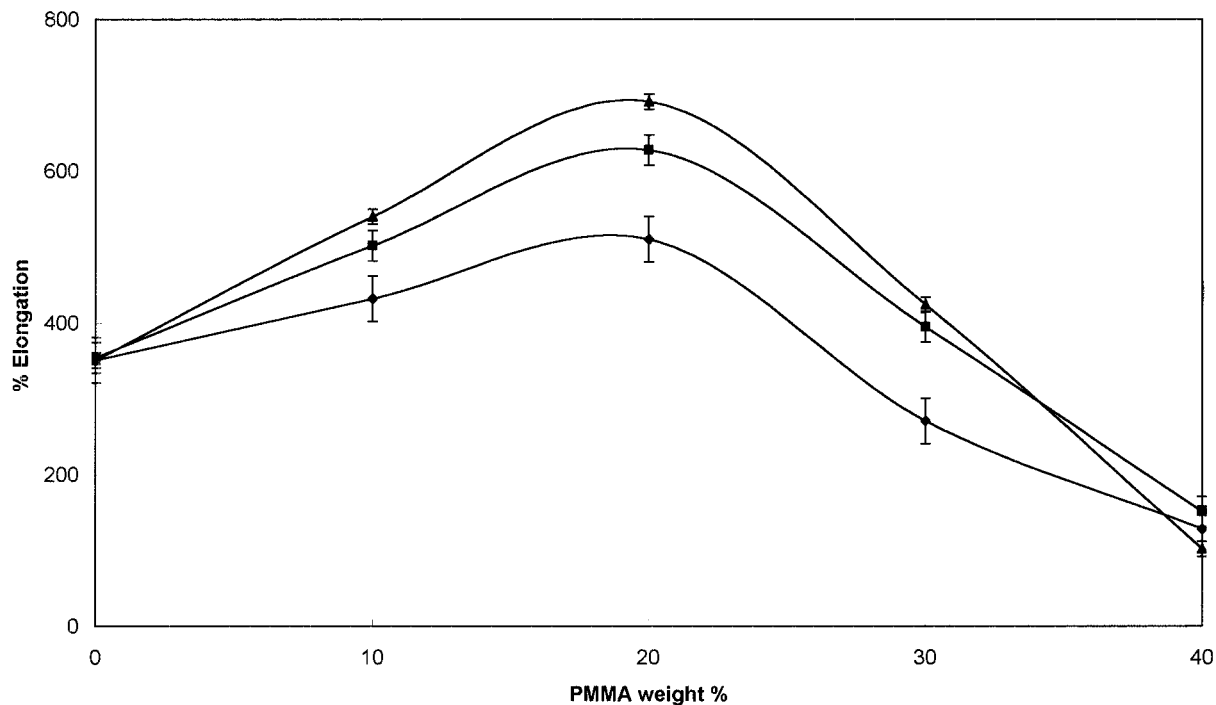
Figure 2 Effect of the weight percentage of PMMA on the elongation of PU–PMMA IPNs: (♦) P/M, (■) P/M/G, and (▲) P/M/H.

C). The SEM of the P/M IPN [Fig. 3(A)] exhibits a large extent of phase separation. With the addition of 2-HEMA and GMA, increased phase mixing is observed [Fig. 3(B,C)]. The better compatibility of the two phases in the case of P/M/H (Fig. 3C) compared with the P/M/G system [Fig. 3(B)] is probably due to more pronounced entanglements of bridged MMA in the PU network in this system. The P/M/G 60/40 composition also shows the presence of cavities created during the fracture process. No such cavities were observed in the electron micrograph of P/M/H IPN. However, a single phase, as reported by Scarito and Sperling[17] for epoxy/*n*-butyl acrylate and GMA-based IPNs, was not observed. This was due to the much higher concentration of GMA used by them.

The significant rise in the tensile strength with an increase in the PMMA content from 30 to 40% can be explained with Figure 3(C,D). As the percentage of PMMA increases, the bicontinuous morphology probably leads to the beginning of phase inversion. Furthermore, the small holes and randomly distributed particles observed in Figure 3(D) are absent in Figure 3(C), indicating improved morphology of the IPN containing 40% PMMA.

Thermal Analysis

DSC thermograms of PU and 60/40 PU/PMMA IPNs are shown in Figure 4. The thermogram of PU exhibits only one T_g corresponding to the soft segment at $-69.9°C$. IPNs show the glass transition of PU around $-60°C$ and that of PMMA around $100°C$. An additional T_g around $10–15°C$ was also observed. Furthermore, T_g of PU in the IPNs shifts to the slightly higher side in comparison with the PU network. Although no shift is observed in T_g of PMMA in the IPNs, a shift in the T_g of the PU network was observed by Hourston and Zia[6] in their study of PU/poly(methyl acrylate)-grafted IPNs. They made use of unsaturated PU and suggested that grafting as well as some spontaneous mixing may be responsible for the shift of the PU glass transition. The PU used in this investigation is also derived from unsaturated HTPB. Therefore, it is likely that possible grafting of MMA onto PU is playing some role in the observed shift in T_g. The PMMA segments close to the active sites probably interact with PU segments and give rise to the T_g at about $10°C$. The remaining PMMA segments constitute a pure phase. The relative insensitivity of the PMMA
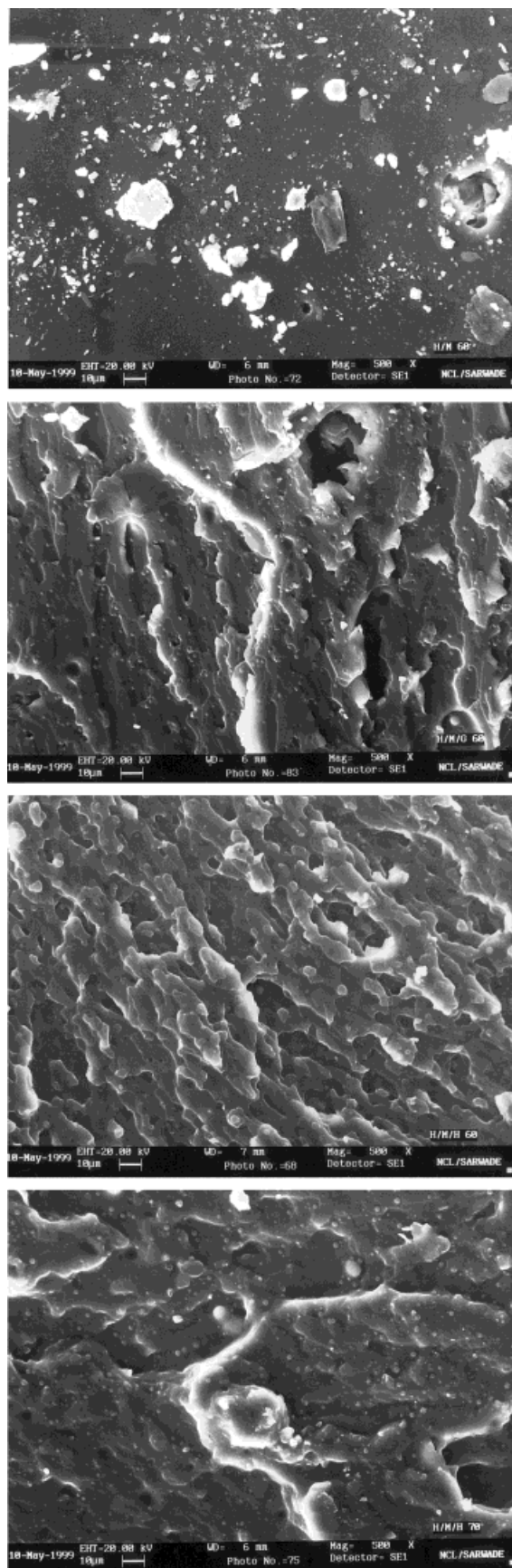
transition to shifting also supports the aforementioned possibility.

For P/M/H or P/M/G IPNs, the shift in the T_g of the PU network was observed to be much higher than in P/M (Fig. 4), indicating increased molecular interactions.[10,14]

Thermogravimetric analysis curves of the IPNs are given in Figure 4(A,B). All the IPNs are thermally stable up to 325°C and decompose completely around 650°C. Figure 5(A) shows improved thermal stability with increasing PMMA content. The major decomposition temperatures given in Table II shift to the higher side with interpenetration of PMMA up to 40%. It is observed from Figure 5(B) that the P/M/H IPN shows higher thermal stability.

The unusual thermal and mechanical behavior of the 60/40 P/M/H composition may be due to the increased crosslinking and homogeneity, which is reflected in the morphology.

DMA

The common feature of the linear loss modulus E'' or tan δ–temperature plots for all three types of IPNs is the existence of a glass-transition region between -65 and -75°C, suggesting a rubbery nature of IPNs above room temperature. IPNs of PU/PMMA are probably microseparated, two-phase systems of a nonpolar PU component (due to the nonpolar polyol HTPB) in a polar matrix of PMMA or vice versa. T_g of PMMA was observed as a continuous increase of E'' and tan δ rather than as clear sharp peaks as for pure polymers. Thus, the polybutadiene PU seems to show appreciable phase separation with PMMA. Earlier reports on caprolactone-based PU IPNs with PMMA[25,26] showed the presence of two distinct T_g's with large domains clearly visible under an electron microscope. The use of 2-HEMA and GMA in IPNs leads not only to broadening of the peaks but also toward inward shifts of the loss peaks with respect to those of individual networks. This is also a sign of improved miscibility, although a single T_g could not be observed.

Figure 6 shows a representative plot of tan δ versus temperature for the 60/40 PU/PMMA IPNs at 1 Hz. A small but distinct shoulder occurs on

Figure 3 SEM micrographs of tensile-fractured IPNs: (A) 60/40 P/M, (B) 60/40 P/M/G, (C) 60/40 P/M/H, and (D) 70/30 P/M/H.
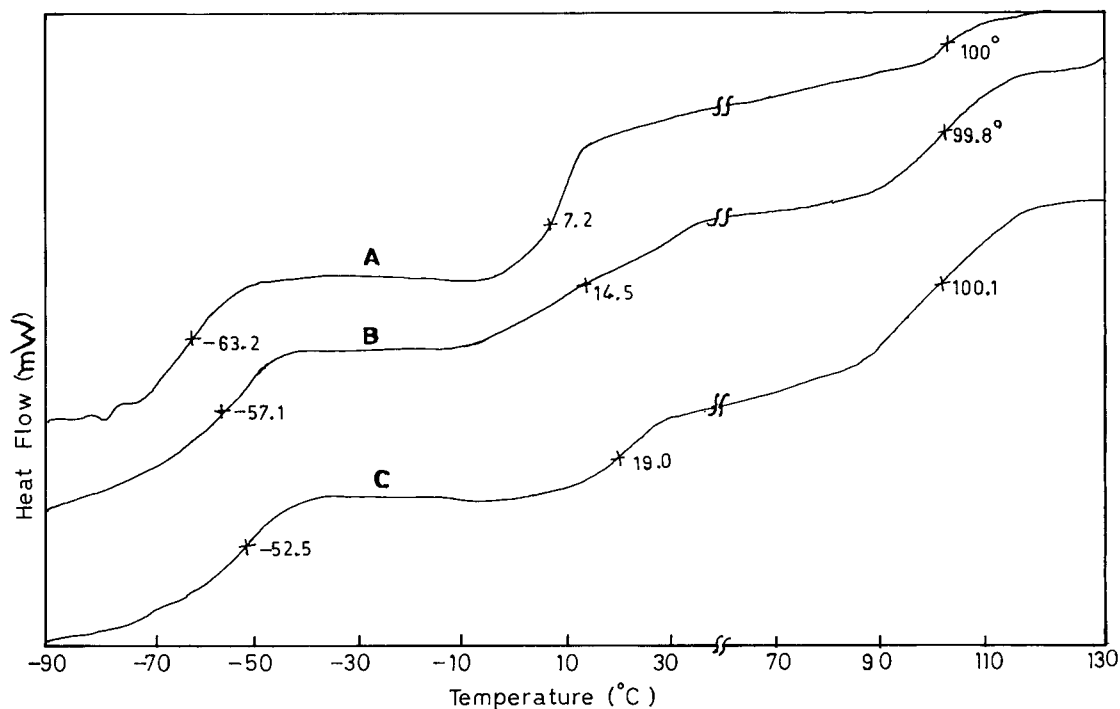
Figure 4   DSC thermograms of 60/40 PU/PMMA IPNs: (A) P/M, (B) P/M/G, and (C) P/M/H.
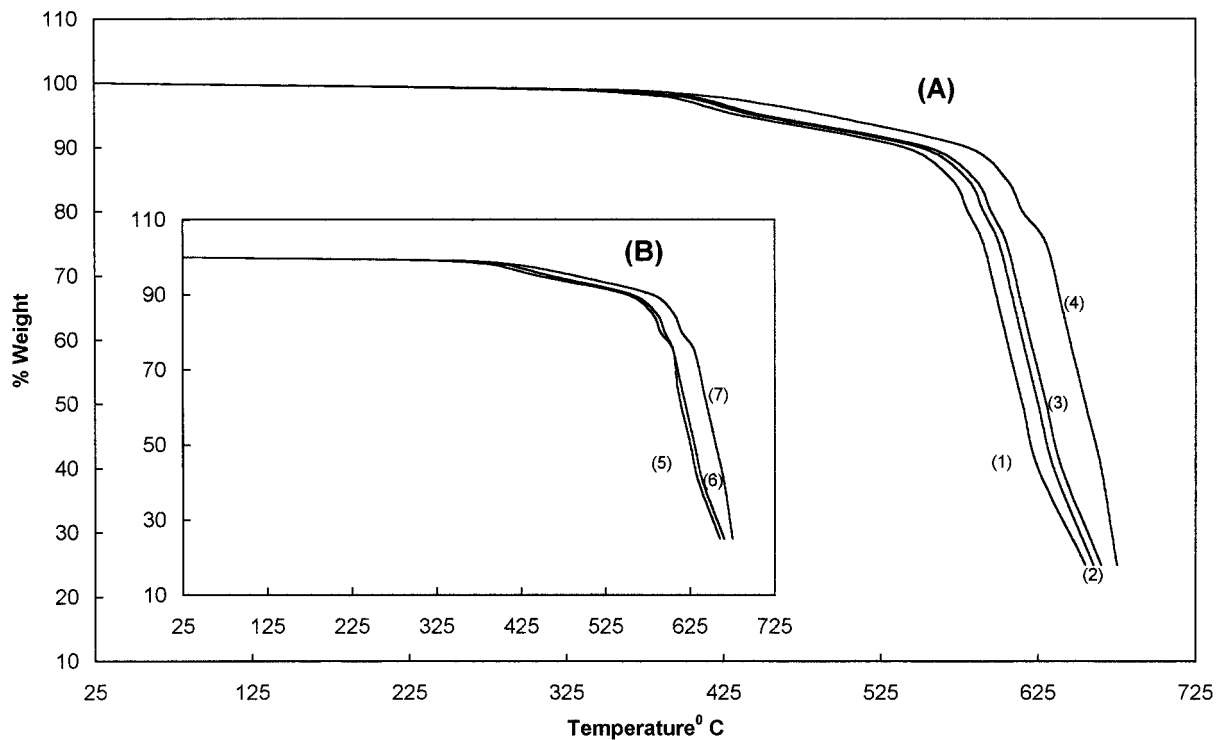

Figure 5   Thermogravimetric curves for (A) P/M/H IPNs [(1) 90/10, (2) 80/20, (3) 70/30, and (4) 60/40] and (B) 60/40 PU/PMMA IPNs [(5) P/M, (6) P/M/G, and (7) P/M/H].

Table II   Decomposition Temperatures of IPNs

Degradation (%)	Temperature (°C)						
	P/M 60/40	P/M/G 60/40	P/M/H 60/40	P/M/H 70/30	P/M/H 80/20	P/M/H 90/10	PU
1	325	335	355	330	325	320	315
5	445	460	490	450	445	435	430
25	605	605	630	605	600	590	585
50	625	630	655	630	625	615	610
75	660	665	675	665	660	655	670

the high-temperature side of the main transition. This shoulder may correspond to the third T_g (10°C) observed in the DSC thermograms.

The loss factor peak heights are commonly used to obtain information about the continuous phase.[1] The material exhibiting a higher loss factor peak usually represents the continuous phase. The loss factor half-peak width was used as an indication of the miscibility of IPNs by Fox et al.[27] When two components give a single T_g, a narrower peak indicates better miscibility. The half-peak width of the P/M/H IPN is highest (Table III). This is due to the broadening of the tan δ peak because of the large difference in the T_g's of the two networks. The energy of activation for the glass transition calculated from the relation between the frequency and temperature of tan δ_{max}^{28} are the same for the three IPNs within experimental error. Because of the frequency dependence of the transition phenomenon, T_g's obtained from DMA (Table III) differ only to a small extent from those obtained by DSC.[28]
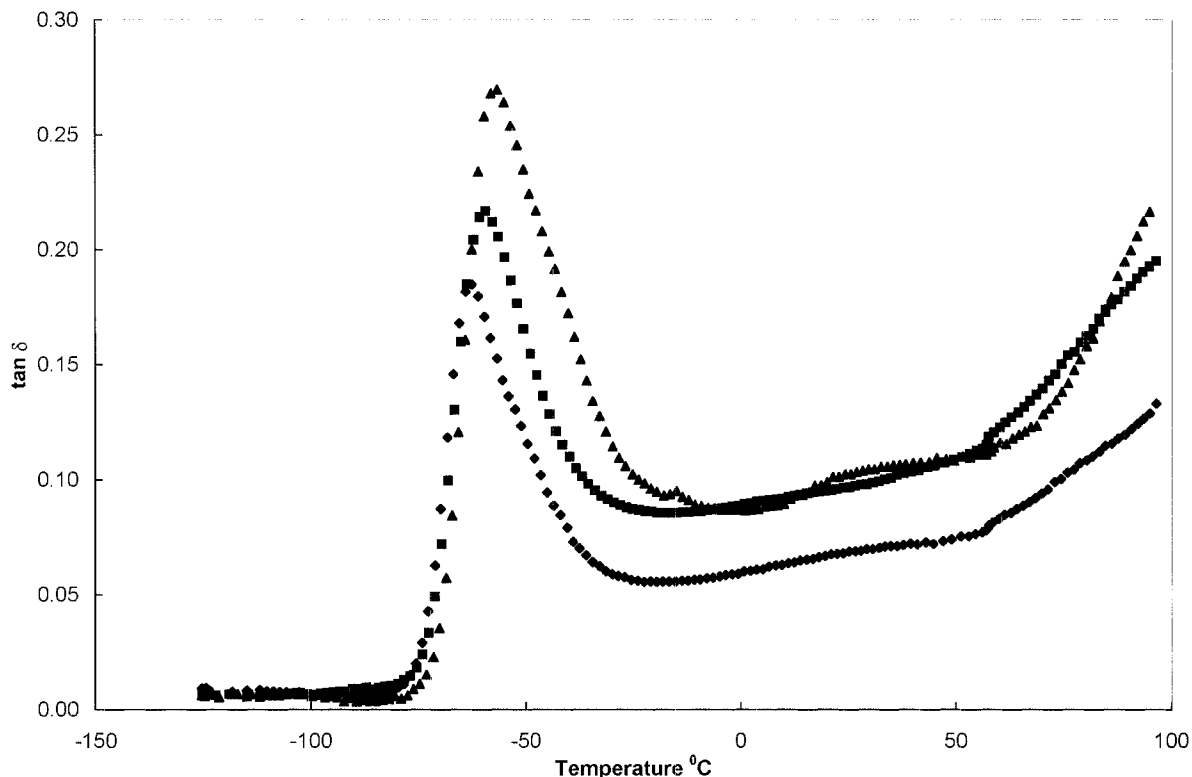

Figure 6   Variation of tan δ with temperature for 60/40 IPNs at 1 Hz: (♦) P/M, (■) P/M/G, and (▲) P/M/H.

Table III   DMA Data for 60/40 PU/PMMA IPNs at 1 Hz

Code	T_g (°C)	Tan δ_{max}	Half Peak Width (°C)	E''_{max} (N/m^2)	E_{act} (kcal/mol)
P/M 60/40	−63	0.19	24	4.1×10^8	41.9
P/M/G 60/40	−59	0.22	27	4.3×10^8	44.3
P/M/H 60/40	−56	0.27	30	4.4×10^8	44.7

Swelling Behavior

The swelling behavior of selected IPNs in organic solvents was studied, and the molecular weight between crosslinks (M_C) was determined from the Flory–Rehner equation.[19] With values of M_C, the crosslink density (v_e) was calculated:[20]

$$v_e = \rho/M_C \tag{1}$$

The degree of crosslinking (v) was obtained from the following equation:[20]

$$v = 1/2M_C \tag{2}$$

In Table IV, the swelling data for the series of IPNs containing 2-HEMA and 60/40 P/M and P/M/G IPNs are given. With increasing PMMA content, M_C decreases and v_e increases. It is also seen that v is in the order P/M/H > P/M/G > P/M. These observations are in agreement with the results obtained from the mechanical, thermal, and morphological properties. Furthermore, in the P/M/H system, the values change sharply from composition 60/40 to 70/30. A similar sharp change was also observed in the morphology of the IPNs and was explained by the onset of phase inversion.

CONCLUSIONS

Studies of PU/PMMA IPNs showed that the incorporation of only 2% 2-HEMA/GMA led to an improvement in the thermomechanical properties and morphology. There was about a 25–35% increase in the tensile strength and about a 10% increase in the elongation of the P/M/H IPNs with respect to P/M/G.

In a comparison of IPNs containing 2-HEMA and GMA, we observed that 2-HEMA more effectively improved the molecular mixing of two phases, leading to enhanced thermomechanical properties. The bicontinuous morphology observed with SEM and the broadening of the tan δ peaks in DMA supported this observation.

Table IV   Swelling Data for PU/PMMA IPNs in Carbon Tetrachloride

Code	M_C	$v \times 10^4$	$v_e \times 10^4$
P/M 60/40	2900	1.72	3.79
P/M/G 60/40	1900	2.63	6.05
P/M/H 60/40	1300	3.85	8.30
P/M/H 70/30	3000	1.65	4.05
P/M/H 80/20	4100	1.21	3.90
P/M/H 90/10	5400	0.93	2.54
PU	6700	0.75	1.49

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