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Synthesis and Thermal Properties of Polyurethane, Poly(butyl methacrylate), and Poly(methyl methacrylate) Multi-Component IPN's

Jae Heung LEE and Sung Chul KIM

Department of Chemical Engineering,
Korea Advanced Institute of Science and Technology,
P.O. Box 150, Chongryang, Seoul, Korea

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ABSTRACT: Three component interpenetrating polymer networks (IPN's) of polyurethane (PU)–poly(*n*-butyl methacrylate) (PBMA)–poly(methyl methacrylate) (PMMA) were prepared by the combined synthesis of simultaneous polymerization and sequential polymerization. Two types of IPN's, (PU–PMMA)–PBMA and (PU–PBMA)–PMMA, were obtained by forming PU–PMMA (or PU–PBMA) simultaneous IPN's first and then swelling the network in BMA (or MMA) and ethylene dimethacrylate (EDMA) monomer mixtures followed by sequential polymerization of the imbibed monomers. The glass transition behavior studied by DSC and DMA showed three separate but broad T_g's for (PU–PMMA)–PBMA IPN's, while two T_g's (one broad T_g for PU transition and the other broad T_g at intermediate temperature of PMMA and PBMA transition) were observed for (PU–PBMA)–PMMA IPN's. Both three component IPN's showed high damping characteristics ($\tan\delta = 0.2$—0.4) in the temperature range of −30—90°C. The TGA analysis revealed enhanced thermal stability in all of the two-component and three-component IPN's of polyurethane and polymethacrylate.

KEY WORDS Multicomponent IPN's / DSC / DMA / TGA / Damping Characteristics / Thermal Stability / Interlocking /

Interpenetrating polymer networks can be defined as a mixture of two or more crosslinked polymer networks which can have partial or total physical interlocking between them.[1,2] They have been prepared in three different modes of synthesis; latex blending,[3] sequential polymerization[4,5] and simultaneous polymerization.[6,7] The degree of physical interlocking (or interpenetration) is dependent on the degree of phase separation at the time of interlocking (crosslinking in the presence of already crosslinked networks). Thus, by considering the mixure composition of the three different synthetic methods, polymer–polymer mixing in latex blending, polymer–monomer mixing in sequential polymerization and monomer–monomer (or oligomer–oligomer) mixing in simultaneous polymerization, simultaneous polymerization method would yield higher degree of interpenetration. The modifications on these traditional IPN's are grafted IPN's[8,9] with chemical bonding between the networks and thermoplastic IPN's,[10,11] utilizing physical crosslinks instead of chemical crosslinks, *e.g.*, hard domain in triblock copolymer, crystallite in semicrystalline polymer.

The application of IPN composites as noise and vibration damping materials has been explored,[12,13] particularly semicompatible IPN's of low and high T_g polymers showed high noise and vibration damping characteristics over a broad temperature range.

This study explores the combination of three different polymers; PU ($T_g = -46°C$), PBMA ($T_g = 20°C$), and PMMA ($T_g = 105°C$) by employing both simultaneous polymerization and sequential polymerization, so that the resulting IPN composites could give a high damping characteristics over a very broad temperature range ($-20 \sim 105^\circ$C). The three component IPN's were prepared by first forming two component IPN's of PU–PMMA and PU–PBMA through simultaneous polymerization method.[6,7] The two component IPN's were swollen in BMA monomer (or MMA monomer) containing dissolved benzoin as initiator and EDMA as the crosslinking agent and subsequently polymerized by UV radiation. This study compares the glass transition behavior, dynamic mechanical properties and thermal stability characteristics (by TGA) of the three component IPN's with two component IPN's.

EXPERIMENTAL

Materials

The raw materials used and their descriptions are listed in Table I. Poly(oxytetramethylene) glycol (PTMG), 1,4-butanediol (BD), and trimethylolpropane (TMP) were dried at 60°C for five hours under a vacuum of 2 mmHg. MMA and BMA monomer were washed with 10% aqueous potassium hydroxide solution, followed by distilled water, dried over Linde 4A molecular sieves and distilled at 40°C under vacuum. Other materials were used without further purification.

Table I. Materials

Designation	Description
MDI	4,4′-Diphenylmethane diisocyanate
PTMG	Poly(oxytetramethylene) glycol (M.W. = 986)
TMP	Trimethylolpropane
BD	1,4-Butanediol
MMA	Methyl methacrylate
BMA	*n*-Butyl methacrylate
EDMA	Ethylene dimethacrylate
BPO	Benzoyl peroxide
LPO	Lauroyl peroxide

Preparation

PU Network: The isocyanate-terminated polyurethane prepolymer was prepared by reacting two equivalents of 4,4′-diphenylmethane di-isocyanate (MDI) with one equivalent of PTMG at 60°C in a resin kettle under dry nitrogen. The reaction was continued until the theoretical isocyanate content (as determined by the di-*n*-butylamine method[14]) was reached. One equivalent of the PU prepolymer was heated to 80°C and then homogeneously mixed with one equivalent of BD–TMP mixture (6 : 1 equivalent ratio) for 3 min using a high torque stirrer. The air bubbles entrapped during mixing were removed by applying vacuum for $5 \sim 10$ min. The mixture was cast on the aluminum mold at 80°C for 20 h and at 120°C for 2 h.

PMMA Network. 98.763 g of MMA monomer, 1.237 g of EDMA and 0.1 g BPO were mixed until all the BPO was dissolved. The monomer mixture was then polymerized in a resin kettle under nitrogen at 80°C. The reaction was continued until $10 \sim 20\%$ conversion was attained and then stopped by rapid cooling. The PMMA syrup thus prepared was poured into a mold made with two glass plates, and polymerized at 45°C for 24 h and at 120°C for 2 h in a forced convection oven.

PBMA Network. Mixture of 98.763 g BMA monomer, 1.237 g EDMA and 0.3 g benzoin was charged into a mold made of two Pyrex glass plates. They were polymerized by ultraviolet radiation using Rayonet Photo-Chemical Reactor (model RPR 100) at room temperature for 24 h.

PU–PMMA SIN. The PU prepolymer–BD–TMP mixture was added to the MMA–EDMA–BPO mixture in varying ratios and homogeneously mixed for 6 min. The air bubbles were removed by applying vacuum for 1 min. The mixture was simultaneously polymerized in a closed glass mold at 60°C for 36 h and at 120°C for 4 h in a forced convection oven.

PU–PBMA SIN. 98.763 g of BMA monomer, 1.237 g of EDMA and 1 g of lauroyl peroxide (LPO) were mixed with PU prepolymer–BD–TMP mixture in varying ratios. The air bubbles were removed and the mixture was polymerized in a closed glass mold at 45°C for 48 h and at 70°C for 12 h and at 120°C for 4 h.

(PU–PMMA)–PBMA IPN. The residual MMA monomer was removed from the PU–PMMA SIN by vacuum drying at 60°C for 24 h. The PU–PMMA SIN was swollen in a mixture of 98.763 g BMA, 1.237 g EDMA, and 0.3 g benzoin and transferred into a Pyrex glass mold. The mixture was polymerized by UV radiation at room temperature for 36 h, then further polymerized thermally at 110°C for 24 h in a forced onvection oven. The unreacted BMA monomer was removed by vacuum drying at 60°C for 24 h (conversion was greater than 99%).

(PU–PBMA)–PMMA IPN. PU–PBMA SIN was swollen in MMA–EDMA–benzoin mixture. Pretreatment and polymerization conditions were the same as (PU–PMMA)–PBMA IPN.

Measurement

DSC. The glass transition temperature was measured by du Pont model 910 DSC with heating rates of 10°C min^{-1} in the temperature range of $-100\sim130$°C. The onset temperature of the transition was noted as T_g. Samples were dried at 50°C for 24 h under vacuum.

DMA. The dynamic mechanical properties were obtained by du Pont model 981 DMA (a resonance frequency type) with heating rates of 10°C min^{-1} in the temperature range of $-100\sim130$°C. The samples were vacuum-dried as in DSC. The specimen dimensions were 15 mmL × 10 mmW × 1 mmT.

TGA. TGA thermograms were obtained by du Pont model 951 TGA with heating rates of 10°C min^{-1} under nitrogen atmosphere.

Equilibrium Swelling. Specimens of 20 mmL × 15 mmW × 2 mmT were swollen in monomer for 48 h and weight percent swelling was calculated after wiping out the monomer on the surface.

RESULTS AND DISCUSSION

Glass Transition Temperature

Table II shows the glass transition temperature (T_g) of the IPN's obtained by DSC. The onset temperature of the transition was noted as T_g since the IPN's showed very broad transition and hence it was difficult to determine the midpoint of the transition. The U50-M50 SIN (50% PU–50% PMMA) showed two separate but inwardly shifted transition temperatures. The PU transition at 235 K was 8°C higher than the pure PU transition and the PMMA transition at 370 K was 8°C lower than the pure PMMA transtion. The inward shift of the T_g was interpreted as due to the effect of the mixed layers around the dispersed domains where the two polymer chains were molecularly mixed and physically interlocked. The U50-B50 SIN, however, showed smaller shift in T_g; 6°C shift in PU transition and no shift in PBMA transition.

Table II. Glass transition temperature by DSC (K)

Composition[a,b]	Low T_g	Medium T_g	High T_g
Homopolymer			
U100	227	—	—
M100	—	—	378
B100	—	293	—
IPN's			
U50–M50	235	—	370
U50–B50	233	293	—
(U39.4–M39.4)–B21.2	235	298	367
(U29.2–B29.2)–M41.6	234	—	310

[a] U, PU; M, PMMA; B, PBMA.

[b] Numbers denote composition in wt%.

Table III. Equilibrium swelling ratio of polymer at 35°C (wt%)

Polymer	Monomer	
	MMA	BMA
U100	162.1	88.4
M100	132.9	1.1
B100	320.0	223.0

The results implied that PU network was more compatible with PMMA network than PBMA network and thus provided higher probability of forming physical interlocking at the domain boundaries. This agreed well with the solubility parameter consideration

$\{(\mathrm{PU})=10,\ (\mathrm{PMMA})=9.5,\ (\mathrm{PBMA})=8.75\ (\mathrm{cal\ cm}^{-3})^{1/2}\}$.[15]

The swelling behavior of PU, PMMA, and PBMA network in MMA and BMA monomers was studied because the three component IPN's were prepared by swelling two component SIN's in BMA or MMA monomer at room temperature and subsequently polymerizing the monomer by UV radiation at room temperature. The maximum temperature reached during UV radiation was 35°C and the equilibrium swelling was determined at that temperature (Table III). The solubility parameters for the monomers are $\delta(\mathrm{MMA})=8.8$ and $\delta(\mathrm{BMA})=8.2$ $(\mathrm{cal\ cm}^{-3})^{1/2}$. Thus PU, PMMA, and PBMA networks are more compatible with MMA monomer. The PMMA network was glassy at 35°C and thus showed very little swelling in BMA monomer. The three component networks of (U39.4–M39.4)–B21.2 showed three separate transitions; PU transition at 235, PBMA 298, and PMMA 367 K. The imbibed BMA monomer did not penetrate into the PMMA network and formed separate domains, although the T_g of the PBMA increased by 5°C possibly due to the effect of the partial mixing of the PMMA networks. The PMMA transition was also lowered additionally by 3°C from the T_g of U50–M50 SIN. Thus, in (U39.4–M39.4)–B21.2 IPN's, there was partial interpenetration between PU–PMMA phase and between PBMA–PMMA phase, but not much interaction between PU–PBMA phase.

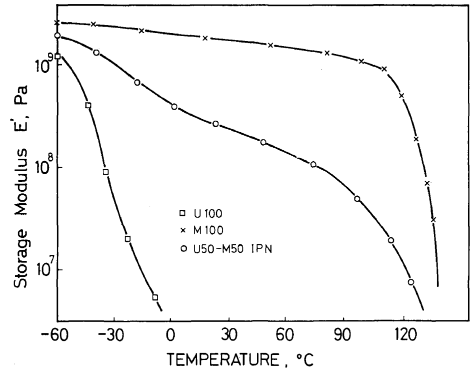

Figure 1. Storage modulus *vs*. temperature for PU–PMMA SIN and homopolymers.

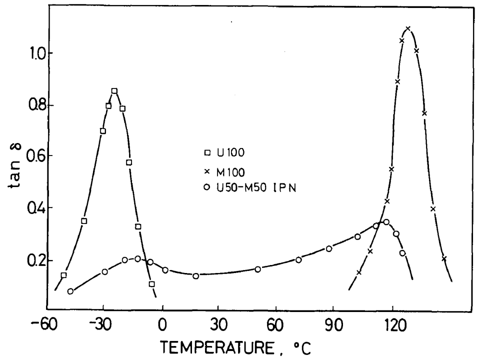

Figure 2. Tan δ *vs*. temperature for PU–PMMA SIN and homopolymers.

The three component networks of (U29.2–B29.2)–M41.6 showed quite different behavior. Since the PBMA network was very compatible with MMA monomer, the MMA penetrated into the PBMA phase and formed a single phase with PBMA network during the UV polymerization step. The resulting IPN showed PU transition at 234 K and a single broad transition at 310 K (onset temperature) which was intermediate between PBMA and PMMA transition.

Dynamic Mechanical Analysis

The DMA results for the U50–M50 SIN are

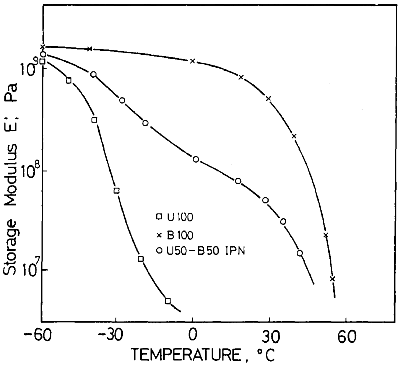

Figure 3. Storage modulus *vs.* temperature for PU–PBMA SIN and homopolymers.

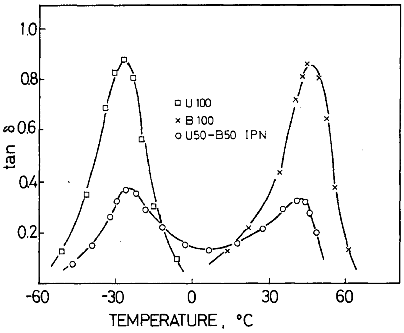

Figure 4. Tan δ *vs.* temperature for PU–PBMA SIN and homopolymers.

shown in Figures 1 and 2. The storage modulus and tan δ curve both showed inward shift of the two T_g's as observed in DSC measurement. The tan δ peaks were relatively broad compared to the homopolymer tan δ peaks. The PU–PBMA SIN (U50–B50) showed that the inward shift of the T_g was small and tan δ peaks were sharper (Figures 3 and 4), which implied relatively lower degree of intermixing at the phase domain boundaries. By comparing the modulus values of U50–M50 SIN' s at room temperature with those of the reported modulus behavior of PU–PMMA SIN's,[16] it is presumed that the SIN's also undergo phase inversion process around this composition and have co-continuous phase morphology.

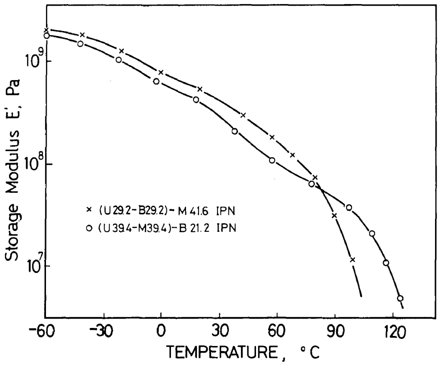

Figure 5. Storage modulus *vs.* temperature for three component IPN's.

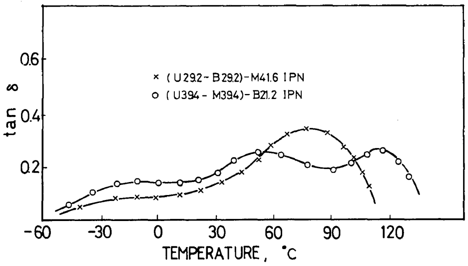

Figure 6. Tan δ *vs.* temperature for three component IPN's.

The modulus curve of (U39.4–M39.4)–B21.2 IPN (Figure 5) showed continuous decline in modulus in the temperature range of −60 to 120°C and showed the not-clearly defined three separate transitions. The tan δ curve (Figure 6) of (U39.4–M39.4)–B21.2 IPN also showed very broad three separate transitions. In the (U29.2–B29.2)–M41.6 IPN, only two transitions were shown in both modulus and tan δ curve. The PBMA and PMMA transitions were merged to form one transition in the temperature range of 50 to 100°C as was observed in DSC studies. It is presumed that the mixed phases of PBMA–PMMA network formed in (PU–PBMA)–PMMA three component IPN are not homogeneous, but have broad concentration distributions. The tan δ values of both three component IPN's were high over a broad temperature range, which was characteristic of a good noise and vibration damping material. The (U39.4–M39.4)–

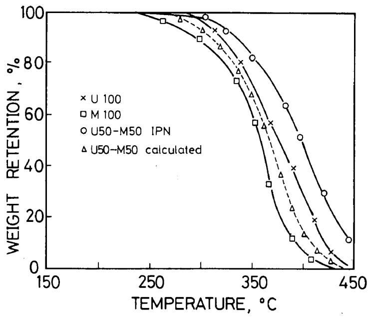

Figure 7. TGA thermograms of PU–PMMA SIN and homopolymers.

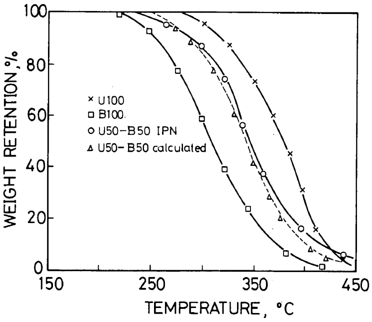

Figure 8. TGA thermograms of PU–PBMA SIN and homopolymers.

B21.2 IPN maintained high tan δ over a broad temperature range ($-20 \sim 120$°C) but the (U29.2–B29.2)–M41.6 IPN has higher damping characteristics in the temperature range of $50 \sim 100$°C.

Thermogravimetric Analysis (TGA)

The enhancement of thermal stability of PU–PMMA and PU–PS IPN's was reported and explained that the unzipped MMA or styrene monomer acts as free radical scavengers for the PU degradation products.[17] The mechanism requires a close juxtaposition of the two polymers, and thus the degree of intermixing of the polyurethane–polymethacrylate network may play an important role in the enhancement of thermal stability. By comparing Figures 7 and 8, U50–M50 SIN showed much higher enhancement in thermal stability compared with U50–B50 SIN.

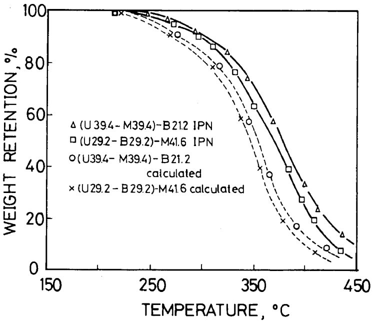

Figure 9. TGA thermograms of three component IPN's.

The three component IPN's both have enhanced thermal stability compared with the theoretically calculated values based on linear additivity rule (Figure 9).

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