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ORIGINAL CONTRIBUTION

Byung Kyu Kim
Jung Hwan Shin

Modification of waterborne polyurethane by forming latex interpenetrating polymer networks with acrylate rubber

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B.K. Kim (✉)
Department of Polymer Science and Engineering, Pusan National University, Busan 609–735, South Korea
E-mail: bkkim@pnu.edu
Fax: +82-51-5141726

J.H. Shin
R&D Division, SK Evertech, Ulsan, South Korea

Abstract Polyurethane (PU)/poly (acrylic rubber) (PAR) latex interpenetrating polymer networks based on waterborne PUs were prepared by sequential polymerization with methyl acrylate, ethyl acrylate, or butyl acrylate. The effect of PU/PAR composition and the crosslinking density in the PAR domain as well as in the PU domain has been studied in terms of density, mechanical, and dynamic mechanical properties in addition to the drying rate and the contact angle of the dispersion cast film with water. A high degree of interpenetrations was verified by mechanical properties showing positive deviation with a maximum from the additivity. In addition, incorporation with acrylate polymers having low glass-transition temperatures effectively augmented the hydrophobicity without sacrificing the elasticity of the original PUs. In addition, the acrylate monomers were polymerized by UV irradiation to significantly reduce the reaction time.

Keywords Waterborne polyurethane · Latex interpenetrating polymer network · Modification

Introduction

Waterborne polyurethanes (PUs) can be formulated with little or no solvent, and hence they are nontoxic, nonflammable, and do not pollute the air. Such environmental advantages coupled with increasing solvent price have steadily expanded their usages in a number of applications in textile coatings, fiber sizings, and adhesives of many polymeric and glassy surfaces [1, 2, 3].

However, owing mainly to the dispersive nature of the ionic centers of waterborne PUs, certain properties, including water resistance, solvent resistance, etc., are generally inferior to those of solvent-borne PUs, and these problems should be overcome. A number of methods to modify the waterborne PUs have been suggested and some of them have been put into practice [4, 5, 6, 7].

In this study, modification of waterborne PUs by forming latex interpenetrating polymer networks (LIPN) with vinyl monomers was considered. Methyl acrylate (MA), ethyl acrylate (EA), or butyl acrylate (BA) monomers were incorporated with PUs in dispersions via IPN structure, and the PU/poly(acrylic rubber) (PAR) hybrids were studied in terms of the particle size of the dispersion, mechanical and dynamic mechanical properties of the cast films. In addition, the density was measured to understand the specific synergy effect induced by restricted phase separation [8, 9], and the contact angle and the drying rate for the increased hydrophobicity. A high degree of interpenetration was verified by mechanical properties showing positive deviation with a maximum from the additivity. This suggested that an optimum degree of interpenetration might exist for optimum mechanical reinforcement [9, 10]. In addition, hybridization with acrylate polymers having low glass-transition temperatures effectively augmented the hydrophobicity without sacrificing the elasticity of the original PUs. In addition, the acrylate monomers were polymerized by UV irradiation to significantly reduce the reaction time.

Experimental

Materials

Extra pure grade isophorone diisocyanate (IPDI) and dibutyltin dilaurate (DBTDL) were used as received. Dimethylol propionic acid (DMPA, Aldrich) and 1-hydroxy cyclohexylphenylketone (HCPK, Aldrich) were purified by recrystallization and dried at room temperature for 48 h in a vacuum oven. Poly(tetramethylene adiphate) glycol (PTAd, $M_n = 2{,}000$, Aldrich) and 1,4-butane diol (1,4-BD, Aldrich) were dried for 5 h at 80 °C under vacuum before use. Extra pure grades of triethylamine (TEA), triethylene tetramine (TETA), and dimethylformamide were dried over 3-Å molecular sieves before use. Acrylate monomers (MA, EA, BA) and cross-linking agent (ethylene glycol dimethacrylate, EGDMA, Aldrich) were purified and dried by fractional distillation and stored under an inert atmosphere.

Synthesis

The formulations of PU/PAR LIPNs based on waterborne PUs are given in Tables 1 and 2 and the overall reaction scheme is shown in Scheme 1. A 500-ml four-neck, round-bottom separable flask equipped with mechanical stirrer, thermometer, and condenser with a drying tube and N_2 inlet was used as a reactor. First, waterborne PUs having prepolymer molecular weights, M_p, of 3,000, 4,000, and 5,000 were synthesized by prepolymer mixing process (Table 1). IPDI, 1,4-BD, DMPA (3.5 wt% based on base PUs), PTAd and DBTDL (0.03 wt% based on base PUs) were mixed and reacted at 80 °C to obtain NCO-terminated prepolymer. The change in the NCO value during the reaction was determined using a standard dibutylamine back-titration method [11]. Then, the NCO-terminated prepolymer was cooled to 60 °C, and TEA was added to neutralize the ionic centers. PU seed latex was obtained by adding water to the neutralized NCO-terminated prepolymer, followed by chain extension with TETA.

Table 1. Formulation of polyurethanes (*PUs*)

M_p	Isophorone diisocyanate	Poly(tetramethylene adiphate) glycol	Dimethylol propionic acid	1,4-Butane diol	Triethylamine	Triethylene tetramine	H_2O
3,000	21.57	70	3.5	0	2.64	2.29	300
4,000	21.47	70	3.5	0.66	2.64	1.73	300
5,000	21.42	70	3.5	1.05	2.64	1.39	300

Numbers designate weight in grams

Table 2. Formulation of PU/poly(acrylic rubber) (*PAR*) latex interpenetrating polymer networks (*LIPNs*)

Compositional variation ($M_p = 3{,}000$, 1 mol% ethylene glycol dimethacrylate)				
Composition (by weight)	PU	MA	Ethylene glycol dimethacrylate	H_2O
100/0	10	–	–	30
90/10	9	0.977	0.023	30
80/20	8	1.955	0.045	30
70/30	7	2.932	0.068	30
60/40	6	3.910	0.090	30
50/50	5	4.887	0.113	30
40/60	4	5.865	0.135	30
30/70	3	6.842	0.158	30
0/100	–	9.775	0.225	30
Cross-linking density of PU [1 mol% ethylene glycol dimethacrylate, PU/poly(methyl acrylate) 50/50]				
M_p of PU	PU	Methyl acrylate	Ethylene glycol dimethacrylate	H_2O
3,000	5	0.4887	0.113	30
4,000	5	0.4887	0.113	30
5,000	5	0.4887	0.113	30
Cross-linking density of poly(methyl acrylate) ($M_p = 3{,}000$, PU/poly(methyl acrylate) 50/50)				
Ethylene glycol dimethacrylate (mol%)	PU	Methyl acrylate	Ethylene glycol dimethacrylate	H_2O
0	5	5.000		30
0.5	5	4.943	0.057	30
1	5	4.887	0.113	30
1.5	5	4.833	0.167	30
2	5	4.780	0.220	30
Type of acrylate rubber ($M_p = 3{,}000$, 1 mol% ethylene glycol dimethacrylate, PU/PAR 50/50)				
Type	PU	Acrylate	Ethylene glycol dimethacrylate	H_2O
Poly(methyl acrylate)	5	4.887	0.113	30
Poly(ethyl acrylate)	5	4.887	0.113	30
Poly(butyl acrylate)	5	4.887	0.113	30

Numbers designate weight in grams

LIPNs were prepared by a sequential and two-stage polymerization method [9, 12]. A mixture of monomer, cross-linking agent (when applied), and HCPK (0.5 wt% of base monomers) was added to the seed latex with the formulation shown in Table 2. Then, polymerization was carried out by UV irradiation at room temperature until over 90% conversion was achieved (Scheme 2). The resulting product was a stable emulsion with a solid content of about 20%.

Characterizations

The particle size of the LIPNs was measured by a light scattering method (Brookhaven BI-2000SM) at room temperature.

LIPN films were prepared by casting the emulsion on a Teflon plate, followed by drying at 60 °C for 24 h and at 80 °C for 48 h. To measure the rate of drying, the original weight of water, W_0, in the LIPN emulsion was measured as a function of the drying time during the film casting according to

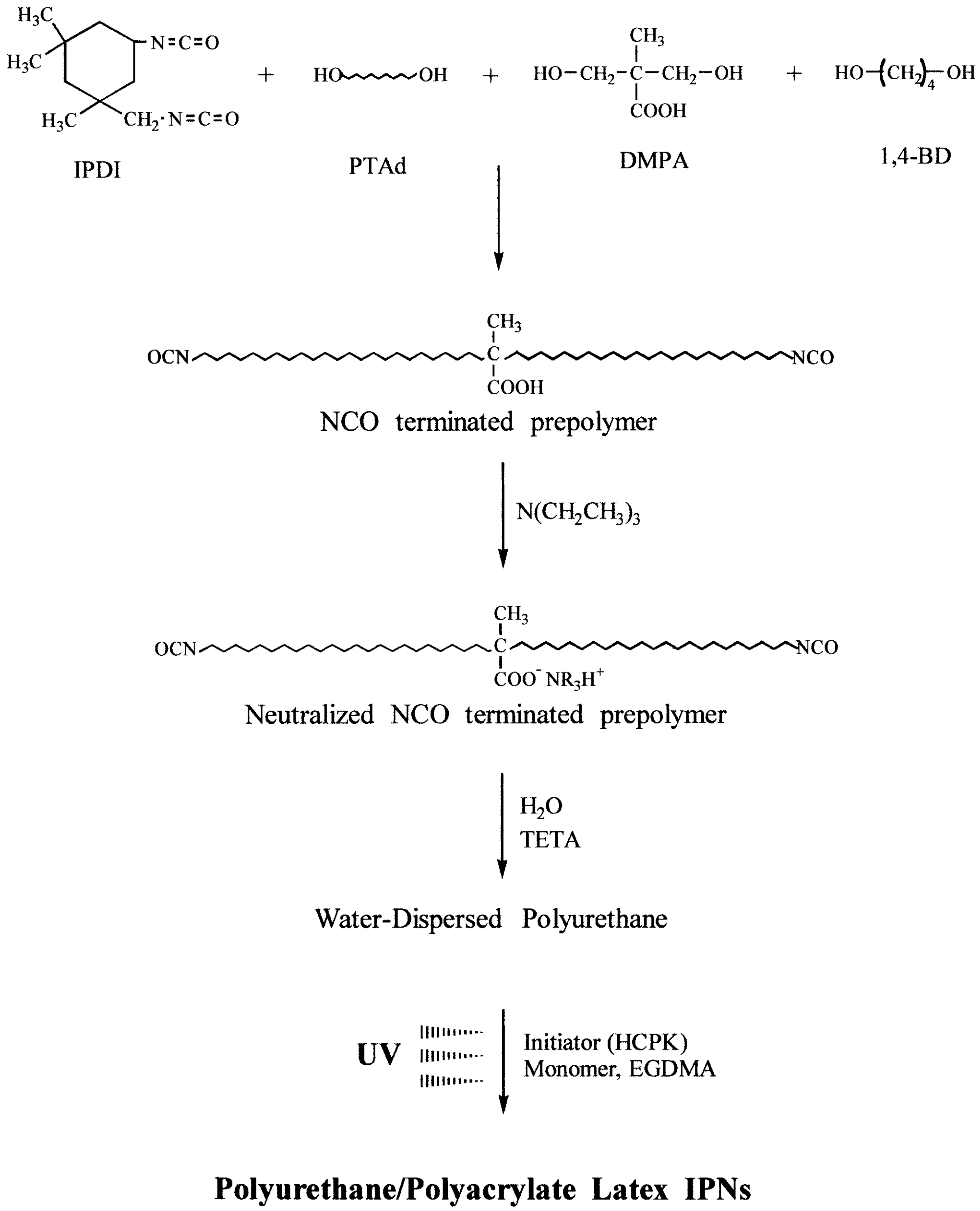
$$\text{Water content (\%)} = \frac{W_0 - W}{W_0},$$

where W is the weight of dried water in LIPN emulsion.

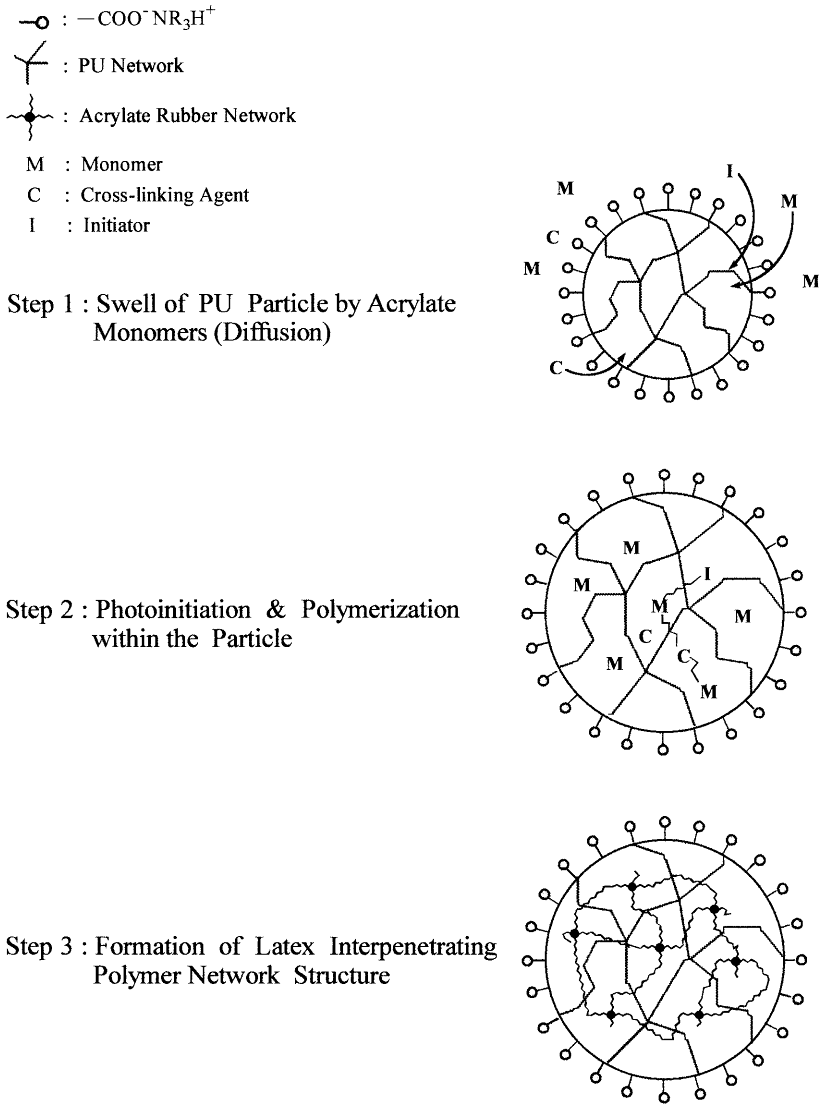
The contact angle of the film with a water drop was measured using an Erma G-1 instrument at room temperature.

Tensile properties of PU/PAR LIPN cast films were measured using a Tinius Olsen tensile tester at a crosshead speed of 200 mm/min, and an average of at least five measurements was used for the analysis. The density was measured using a density gradient column with sodium bromide aqueous solution at 25 °C [11]. Dynamic mechanical properties of the LIPN cast films were measured with a DMTA (Rheometrics MK3E) from –100 to 150 °C at 11 Hz and a strain of 0.05 with a sample size of 0.5×5×8 mm.

Scheme 1. Overall reaction scheme of polyurethane (*PU*)/poly(acrylic rubber) (*PAR*) latex interpenetrating polymer networks (*LIPNs*)



Scheme 2. Schematic representation of the synthesis of PU/PAR LIPNs



Results and discussion

Effect of LIPN compositions

This series of PU/poly(methyl acrylate) (PMA) LIPNs was prepared with PMA as the second polymer (M_P= 3,000, EGDMA 1 mol%). It is seen that particle size increases with increasing PMA content (Table 3). This implies that acrylate monomers are polymerized in PU particles, augmenting the particle mass. In addition, the decreased hydrophilicity due to the decreased average ionic content per particle (3.5→1.05 wt%) should result in an increase in the particle size. At high PMA content, particle unstability due to insufficient surface ionic content should also contribute to the increased particle size.

Figure 1 shows that the water content of PU/PMA LIPN cast films at a given time decreases remarkably as the PMA content increases. This is mainly due to the hydrophobic nature of PMA compared with PU evidenced from the contact-angle measurements (Table 3) [7].

The tensile strength, the elongation at break and the density (Fig. 2) of PU/PMA LIPN cast films show positive deviations from additivity with a maximum which is a specific behavior of the bulk properties for IPN [8, 9]. This is due to physical interlockings and permanent entanglements introduced by the interpenetrating structure between the PU and PMA networks. The maximum appearing at a PU/PMA composition of around 50/50 implies that the maximum degree of interpenetration is formed at this composition. The well-balanced network structure at this composition should also contribute to the observed synergy. It seems that PU particles are saturated at around this composition beyond which not all of the MA monomers are polymerized in the core of PU shells.

Table 3. Density, contact angle, and particle size of PU/PAR LIPN cast films. The particle size of waterborne PU is given in *parentheses*

Composition	M_p of PU	Ethylene glycol dimethacrylate (mol%)	Type of acrylate	Density (g/cm^3)	Contact angle (degrees)	Particle size (nm)
100/0	3,000	1	Poly(methyl acrylate)	1.1580	67	117.9
90/10				1.1603	70	120.5
80/20				1.1619	71	122.8
70/30				1.1756	73	127.2
60/40				1.1813	74	135.0
50/50				1.1815	76	146.0
40/60				1.1798	79	155.6
30/70				1.1777	80	169.0
0/100				1.1787	82	–
50/50	3,000	1	Poly(methyl acrylate)	1.1815	76	146.0 (117.9)
	4,000			1.1801	76	117.6 (86.8)
	5,000			1.1734	77	112.6 (92.2)
50/50	3,000	0	Poly(methyl acrylate)	1.1707	77	171.5
		0.5		1.1783	76	153.9
		1		1.1815	76	146.0
		1.5		1.1823	75	143.9
		2		1.1856	75	140.7
50/50	3,000	1	Poly(methyl acrylate)	1.1815	76	146.0
			Poly(ethyl acrylate)	1.1291	83	158.0
			Poly(butyl acrylate)	1.0933	88	226.1

Figure 3 shows the tanδ of the LIPN cast films. PU shows one peak around –30 °C corresponding to the glass-transition temperature, T_g of the soft segment. T_g of PMA is seen around 30 °C. PU/PMA LIPNs again show single peak between the two, implying that PU and PMA chains are highly interpenetrated and hence phase separations are suppressed to such an extent that a simple dynamic stimulus cannot isolate their respective responses. However, the broadening of the peak for LIPNs shows that there is a broad distribution of relaxation mechanisms, indicative of a certain degree of microphase separation between PU and PMA.

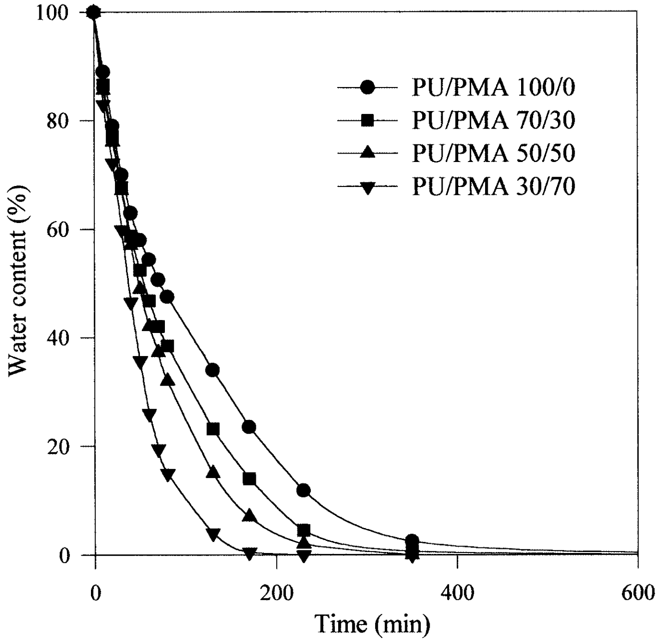


Fig. 1. Drying rate versus poly(methyl acrylate) (*PMA*) content of polyurethane (*PU*)/PMA latex interpenetrating polymer networks (*LIPNs*) (M_p = 3,000, 1 mol% ethylene glycol dimethacrylate, *EGDMA*)

Effect of cross-linking density

This series of PU/PMA LIPNs was prepared at a specific composition, PU/PMA = 50/50 to utilize the maximum synergy. Table 3 shows that the particle size decreases with increasing M_p of PU, due probably to the high chain flexibility of high M_p [13, 14], evidenced from the decreased T_g of PU. The particle size again decreases with increasing EGDMA content (Table 3), due probably to the decreased swelling of water into the particle, since water swelling is decreased with increasing cross-linking density. The hydrophilicity of EGDMA containing two ester groups should also contribute to make the particle small, also giving rise to a smaller contact angle (Table 3).

The stress–strain behavior of PU/PMA LIPNs as a function of cross-linking density of each constituent is shown in Figs. 4 and 5. As expected, the modulus and strength increase and elongation at break decreases as the cross-linking density of each component increases. Density measurements (Table 3) show the increase in the modulus and strength with increasing cross-linking density of each phase. That is, the increase in the cross-linking density in each component gave an

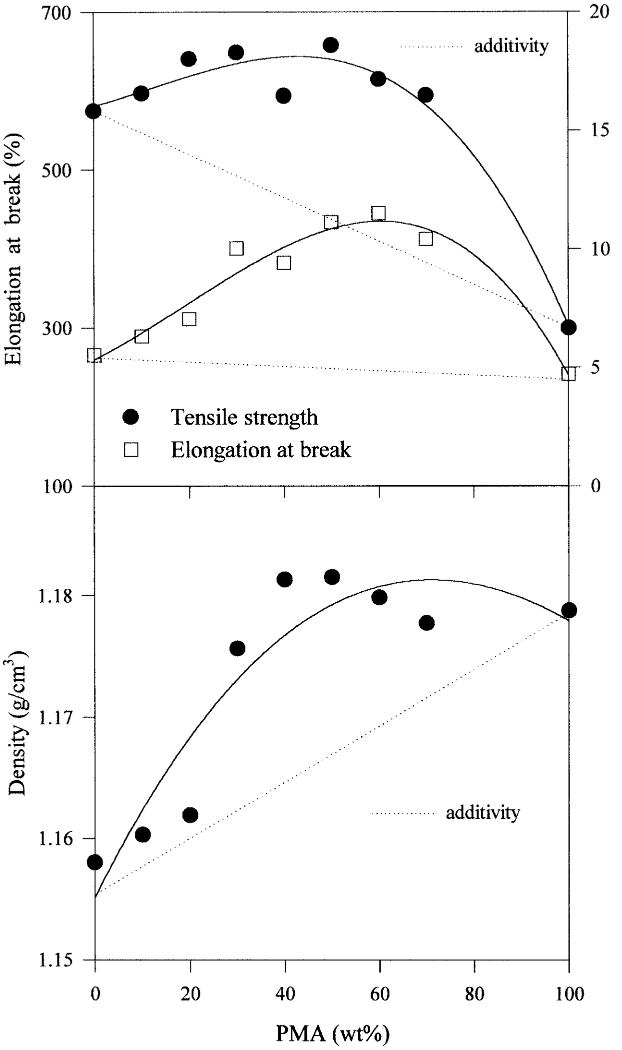


Fig. 2. Tensile strength and elongation at break versus PMA content of PU/PMA LIPNs ($M_p = 3000$, 1 mol% EGDMA)

increased bulk density of the LIPN cast films, and this augmented the modulus and strength.

Figure 6 shows tanδ as a function of M_p of PU. Regardless of the M_p, a single tanδ peak is obtained, also implying that PU and PMA chains are sufficiently interlocked to behave as a single network. In addition the peak temperature slightly increases with decreasing M_p of PU [15, 16] due mainly to the increased chain rigidity which on the other hand is due to the increased cross-linking density since the prepolymer is chain-extended with tetrafunctional amine (TETA). On the other hand, as the EGDMA content increases (Fig. 7), the peak temperature decreases and this can be interpreted as due to the enhanced molecular mixing by the increased cross-linking density of the PMA phase. It seems that the glass-transition temperature of PU/PMA LIPNs can be controlled to some extent by the variation of the cross-linking density of each constituent.

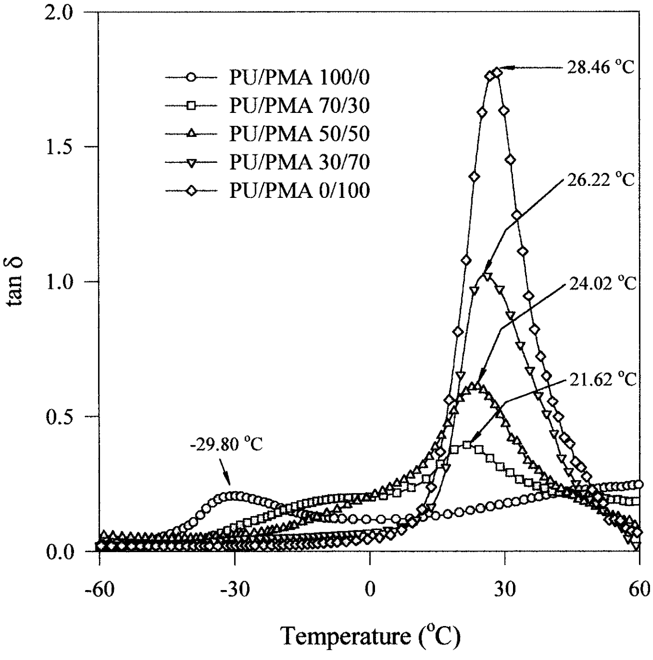


Fig. 3. tanδ versus PMA content of PU/PMA LIPNs ($M_p = 3{,}000$, 1 mol% EGDMA)

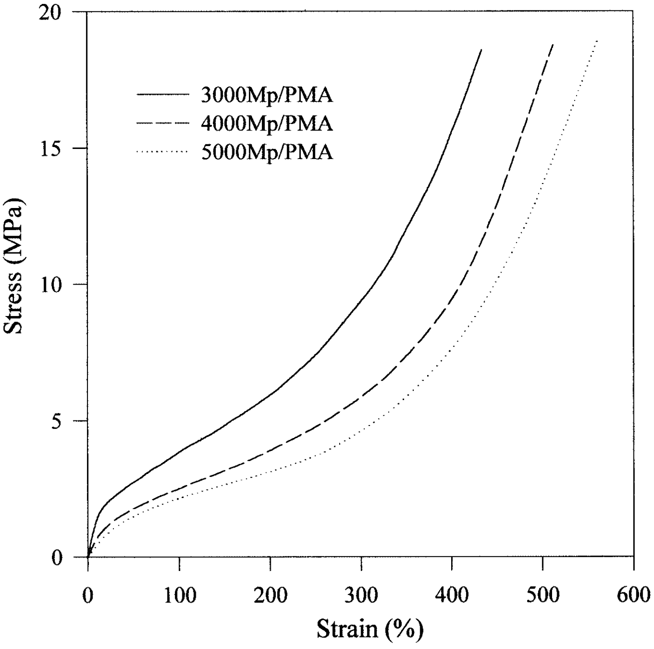


Fig. 4. Tensile behavior versus PU cross-linking density of PU/PMA LIPNs (1 mol% EGDMA, PU/PMA 50/50)

Effect of type of acrylate

This series of PU/PMA LIPNs was prepared at a fixed IPN composition (PU/PAR 50/50) and cross-linking density($M_p = 3000$, EGDMA 1 mol%). Three types of

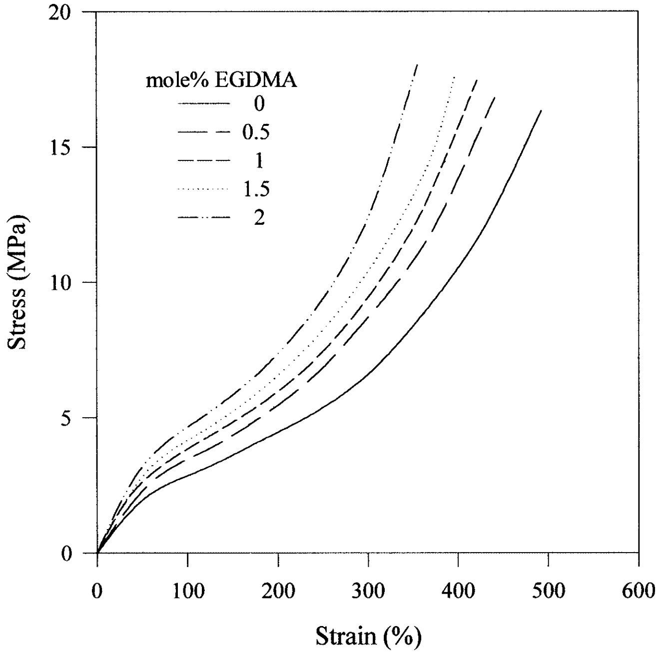


Fig. 5. Tensile behavior versus PMA cross-linking density of PU/PMA LIPNs ($M_P = 3{,}000$, PU/PMA 50/50)

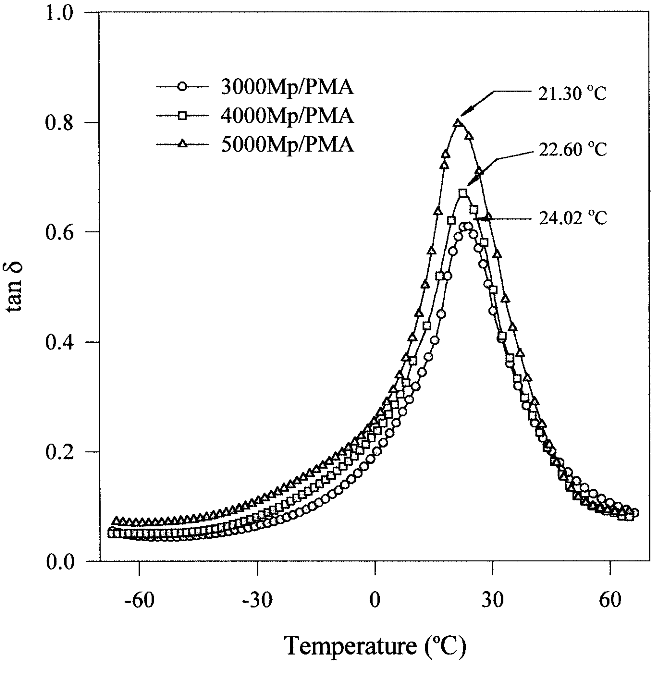


Fig. 6. tanδ versus PU cross-linking density of PU/PMA LIPNs (1 mol% EGDMA, PU/PMA 50/50)

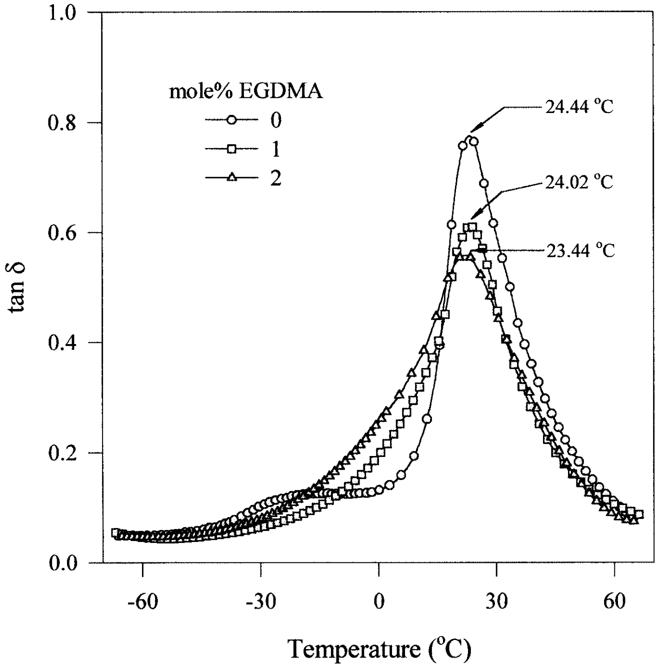


Fig. 7. tanδ versus PMA cross-linking density of PU/PMA LIPNs (Mp = 3,000, PU/PMA 50/50)

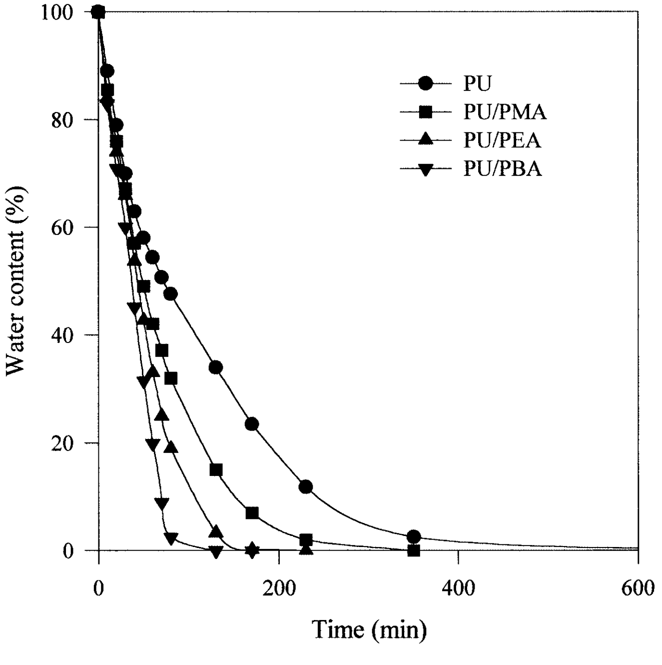


Fig. 8. Drying rate versus type of acrylate of PU/PAR LIPNs (Mp = 3,000, 1 mol%, EGDMA, PU/PAR 50/50)

monofunctional acrylic rubber (PMA, PEA, PBA) were incorporated. Table 3 shows that particle size increases with increasing side-chain length, viz. PMA < PEA < PBA. The drying rate (Fig. 8) and the contact angle (Table 3) also increase with increasing side-chain length. The hydrophobic nature of the alkyl side chain should add hydrophobicity to PU/PAR LIPNs, leading to the results reported.

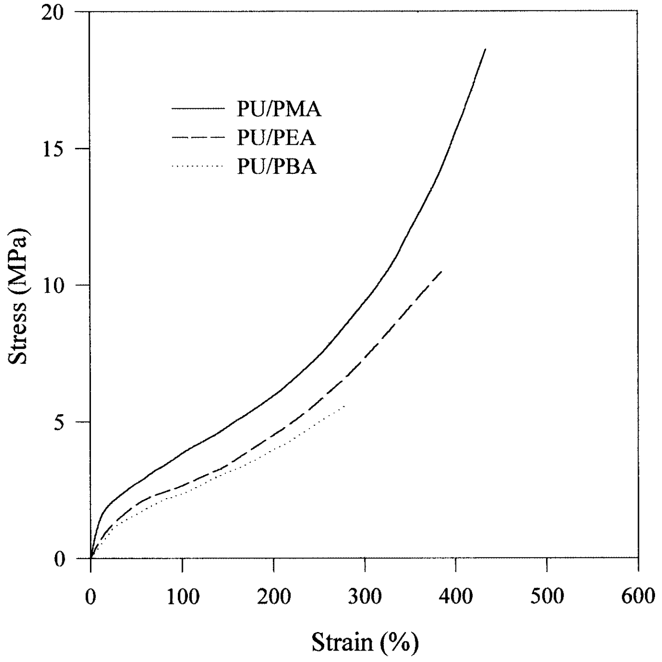


Fig. 9. Tensile behavior versus type of acrylate of PU/PAR LIPNs (Mp = 3,000, 1 mol% EGDMA, PU/PAR 50/50)

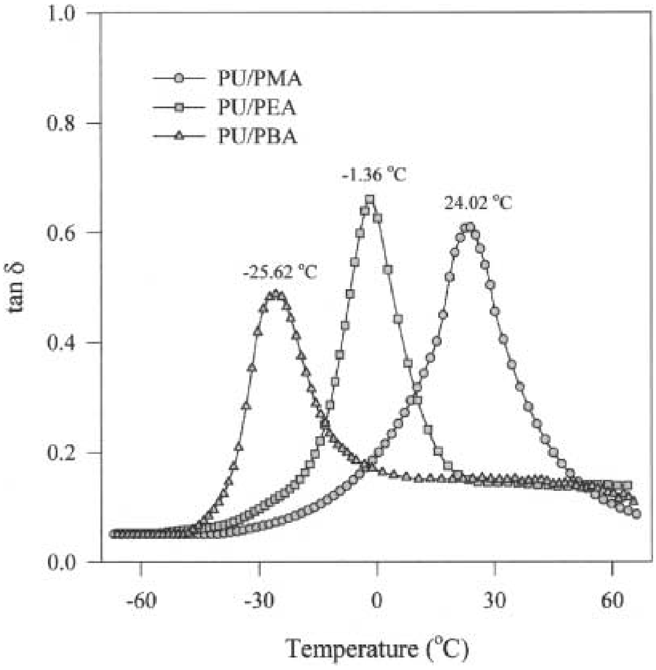


Fig. 10. tanδ versus type of acrylate of PU/PAR LIPNs (M_p = 3,000, 1 mol% EGDMA, PU/PAR 50/50)

Figure 9 and Table 3 show that the tensile modulus, strength, and densities of LIPN cast films decrease with increasing side-chain length, due mainly to the poor main-chain packing with longer pendant groups, together with the plasticizer effect of the alkyl side chain [17, 18, 19].

The effects of the type of acrylate on the dynamic mechanical properties of PU/PAR LIPN cast films are shown in Fig. 10. Regardless of the type of acrylate, LIPNs show single tanδ peak at –25.62, -1.36, and 24.02 °C, each approximately corresponding to the T_g of the acrylate homopolymers [17, 18, 19]. These results imply that the degree of molecular mixing is sufficient for all types of acrylate to restrict phase separation between the constituent polymers.

Conclusions

PU/PMA LIPNs show single T_g regardless of the prepolymer molecular weight of PU and the EGDMA content. This implies that PU and PMA chains are sufficiently interlocked to behave as a single network. However, the effect of the cross-linking density on the dynamic behavior seems to be opposite. That is, an increased cross-linking density of PU (decreased M_p) gave higher T_g, whereas increased cross-linking density of PMA (increased EGDMA content) gave lower T_g. It seems that cross-linkings of PU provide the IPNs with rigidity and those of PMA closely interlock the PU chains with PMA. Maximum synergy effects obtained at around 50/50 (PU/PMA) in terms of density and mechanical property should indicate that the maximum degree of interpenetration is obtained at this composition, which on the other hand is due to the proper saturation of PU with PMA, leading to an ideal network structure to give maximum synergy.

We found that the properties of PUs can be greatly modified by forming LIPNs with various types of acrylate, composition, and cross-linking density of PU as well as polyacrylates.

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