

# Modification of Aqueous Polyurethanes via Latex AB Crosslinked Polymers

JEONG SAM LEE,\* BYUNG KYU KIM

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

Received 10 March 2000; accepted 10 January 2001

**ABSTRACT:** A series of Latex AB crosslinked polymers have been synthesized from polyurethane (PU) (polymer A) and polystyrene (PS) (polymer B). The effect of PU/PS composition, crosslinking density in the PS domain, as well as in PU has been studied in terms of dispersion size, TEM morphology, mechanical, dynamic mechanical properties, in addition to swellability in water and toluene of the dispersion cast film. An inverted core (PS)-shell (PU) morphology with very fine (tens of nanometers) dispersion was obtained, and the film properties were well controlled by the Latex composition and crosslinking density of both phases. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1315–1322, 2001

**Key words:** Latex AB crosslinked polymers; polyurethane; polystyrene

## INTRODUCTION

As compared with solvent-borne polyurethanes (PU), waterborne PUs are environmentally friendly materials that contain significantly reduced volatile organic compounds (VOC) and find broad applications in coatings, adhesives, and finishings.<sup>1–3</sup> However, the hydrophilic nature of ionic groups or water-soluble segments of waterborne type inevitably poses some problems associated with solvent and water resistance, slow drying rate, and so forth. These problems can more or less be reduced by crosslinkings,<sup>4</sup> grafting with acrylates,<sup>5</sup> or incorporating minimum ionic monomers. Recently, multiblock copolymerization using macroiniferter<sup>6,7</sup> and Latex interpenetrating polymer network (IPN)<sup>8–10</sup> have also

been studied. These hybridization techniques should provide the waterborne PU with versatile properties. In addition to these methods, Latex AB crosslinked polymer (often called ABCP) has also been considered. ABCP is a network in which polymer A is crosslinked by polymer B (and not by polymer A).<sup>11–13</sup> Both in IPN and in ABCP, two different kinds of polymers are combined in a network structure. The difference between the two is that in an ABCP, the two kinds of chains form single network and in an IPN they form two separate networks. However, because of the crosslinking, the processability of the material prepared by bulk polymerization is poor; consequently, its commercial importance has been limited. If ABCP could be prepared as Latex, it could become employed in melt processing and find wider application.

Bamford and Eastmond<sup>14,15</sup> described a general preparation method for ABCP of known structure: react a preformed polymer (the A component) that has reactive halogen in side-chains with a metal carbonyl in the presence of a monomer. The metal carbonyl specifically removes

Contract grant sponsor: Korea Research Foundation; Contract grant number: KRF-97-001-E00496.

Correspondence to: B. K. Kim.

\*Present address: Nanopolymer Inc., Masan, 630-490, Korea.

*Journal of Applied Polymer Science*, Vol. 82, 1315–1322 (2001)  
© 2001 John Wiley & Sons, Inc.

**Table I** Recipe of Polyurethane Acrylate Anionomer

	PPG (2000 g/mole)	DMPA	1,4-BG	IPDI	TEA	HEA	Mn of HVTP
PU-1	65.2	4	0	20.5	3	7.3	3000
PU-2	65.2	4	0.95	21.27	3	5.58	4000
PU-3	65.2	4	1.54	21.75	3	4.51	5000

PU, total solid = 100 g.

PPG, polypropylene glycol; DMPA, dimethyl propionic acid; 1,4-BG, 1,4-butane glycol; IPDI, isophorone diisocyanate; TEA, triethylamine; HEA, 2-hydroxyethylacrylate; HVTP, hydrophilic vinyl terminated prepolymer; PU, polyurethane.

halogen atoms from the preformed polymer to produce radical sites on the side groups of the A chains. These macroradicals initiate polymerization of the chains. Termination by combination of the propagating grafts produces B crosslinks, whereas termination by disproportionation generates B branches on A chains.

We consider a continuation of our efforts to augment the properties of waterborne PU, Latex ABCP of PU with polystyrene (PS) in a broad range of Latex composition; the dispersion size, transmission electron microscopy (TEM) morphology, mechanical, dynamic mechanical properties, and water and toluene swell of the cast films are reported.

## EXPERIMENTAL

### Materials

The 1,4-butane glycol (1,4-BG) and polypropylene glycol (PPG, Mn = 2000 g/mol) were dried for 5 h at room temperature and for 2 h at 100°C under vacuum before use. Dimethylol propionic acid (DMPA, Aldrich) was purified and dried at 100°C for 2 h in a vacuum oven. Extra-pure grades of dimethylformamide (DMF) and triethylamine (TEA) were dried over a 3-Å molecular sieve before use. 2-Hydroxyethylacrylate (HEA), styrene, and divinylbenzene were purified and dried by fractional distillation under vacuum and stored under inert atmosphere. Extra-pure grade of isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), and potassium persulfate (KPS) were used as received.

### Synthesis

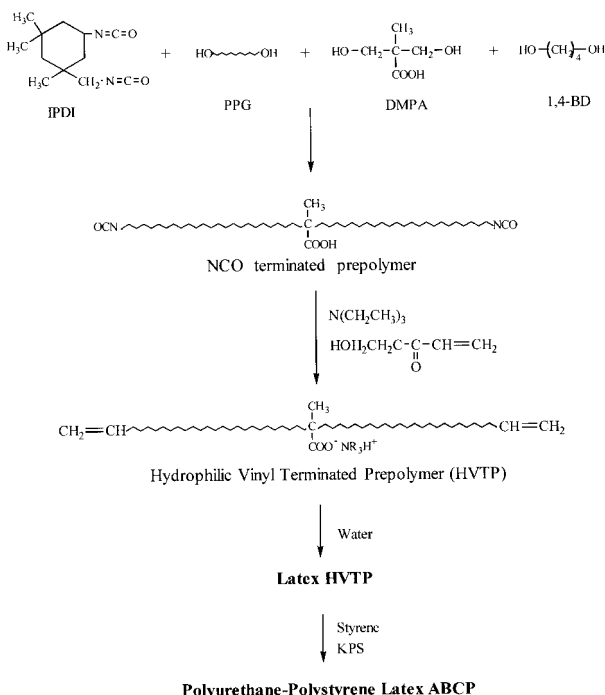
The basic formulations of PU and Latex IPN are given in Tables I and II. The procedure designed

to obtain PU dispersions are available in our earlier works<sup>6,7</sup> and summarized in scheme 1. A 500-mL four-necked round bottom, separable flask equipped with a mechanical stirrer, thermometer, condenser with a drying tube, and N<sub>2</sub> inlet was used as reactor. Reaction was carried out in a constant temperature oil bath. IPDI, 1,4-BG, DMPA, PPG, and DBTDL (0.03 wt % based on base PU) were first mixed and reacted at 80°C to obtain NCO-terminated prepolymer. The change of NCO value during the reaction was determined using a standard dibutylamine back titration method. Then NCO-terminated prepolymer was cooled to 60°C, and TEA and HEA dissolved in DMF (5 wt %-based PU) were added and reacted for 1 h to obtain hydrophilic vinyl terminated prepolymer (HVTP). Since the water addition rate is a critical parameter to obtain stable dispersion, a tubing pump was used and water

**Table II** Recipe of PU/PS Latex ABCP (by Weight Ratio)

Variable	PU-1	PU-2	PU-3	PS/DVB
Latex composition	100			0/0
	80			20/0
	70			30/0
	60			40/0
DVB content	70			30/0
	70			27/3
	70			24/6
Mn of HVTP	70			30/0
		70		30/0
			70	30/0

PU, polypropylene; PS, polystyrene; DVB, HVTP, hydrophilic vinyl terminated prepolymer.



**Scheme 1** The synthesis process of polyurethane-polystyrene latex ABCP.

was added for 10 min at a constant flow rate. Latex ABCP is obtained via radical polymerization of styrene monomers onto the termini of Latex HVTP in the presence of KPS (0.5 wt % based on styrene) for 3 h at 90°C. The resulting product was a stable dispersion with a solid content of about 25%.

### Tests

The swell of film in water and solvent was measured by emerging a film into water and solvent bath at room temperature until the film is in equilibrium with water and solvent. The percentage swell was calculated by

$$\% \text{swell} = \frac{W - W_0}{W_0} \times 100$$

where  $W_0$  and  $W$  are the original and equilibrium weight of the films, respectively. To determine the amount of linear polystyrene, films were extracted in toluene, and percentage extraction was calculated according to the equation

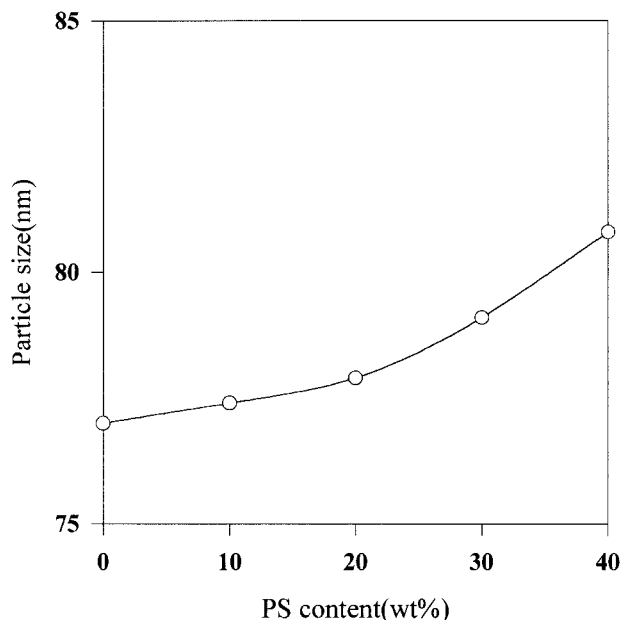
$$\% \text{extraction} = \frac{W_0 - W}{W_0} \times 100$$

where  $W_0$  and  $W$  are the weight of dried film before and after extraction.

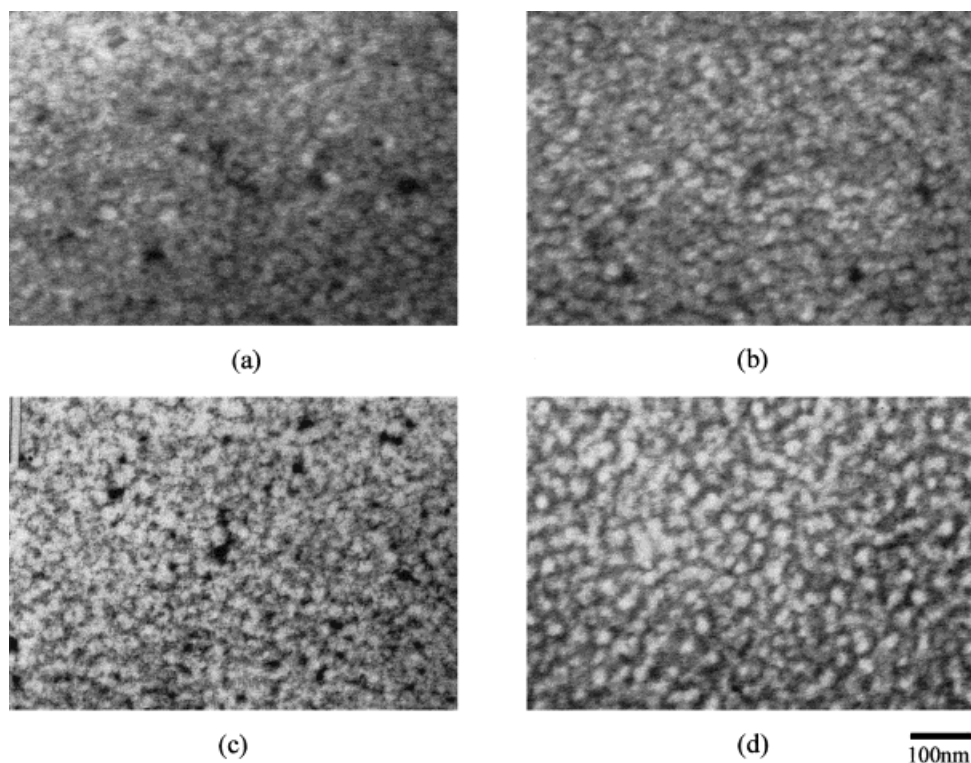
Particle size of dispersion was measured using an Autosizer (Malvern IIC). Approximately 0.15 mL of emulsion was taken and diluted with deionized water to an appropriate concentration for measurements, followed by setting the pin hole 200  $\mu\text{m}$ . The  $z$ -average diameters were measured at 25°C.

Films were prepared by casting the dispersion on a Teflon plate, followed by drying at 80°C for 5 h. The resulting films were then heated overnight in an oven at 60°C under 2–3 mmHg. Microtensile test specimens were prepared according to ASTM D-1822.

Tensile behavior of the dispersion cast films was measured using a Tinius Olsen tensile tester at a cross head speed of 500 mm/min, and an average of at least five measurements was taken. Dynamic mechanical tests for cast films were performed with a Rheovibron (Orientec, DV-01FP) from  $-100^\circ\text{C}$  to  $100^\circ\text{C}$  at 11 Hz, with a sample size of  $0.03 \times 0.2 \times 3$  cm. Morphologies of the Latex IPN cast film were measured using TEM (Jeol, jsm-1200 EX II). The samples were cut to 100-nm thickness using a microtome (Reichert-Jung SuperNova), and stained with  $\text{OsO}_4$  for over 3 days.



**Figure 1** Particle size vs. PS content of latex ABCP ( $M_n$  of HVTP = 3000, DVB = 0).



**Figure 2** TEM micrographs of PU/PS latex ABCP: (a) PU/PS = 7/3 (Mn of HVTP = 3000, PS/DVB = 10/0), (b) PU/PS = 6/4 (Mn of HVTP = 3000, PS/DVB = 10/0), (c) PU/PS = 7/3 (Mn of HVTP = 3000, PS/DVB = 8/2), (d) PU/PS = 7/3 (Mn of HVTP = 5000, PS/DVB = 10/0).

## RESULTS AND DISCUSSION

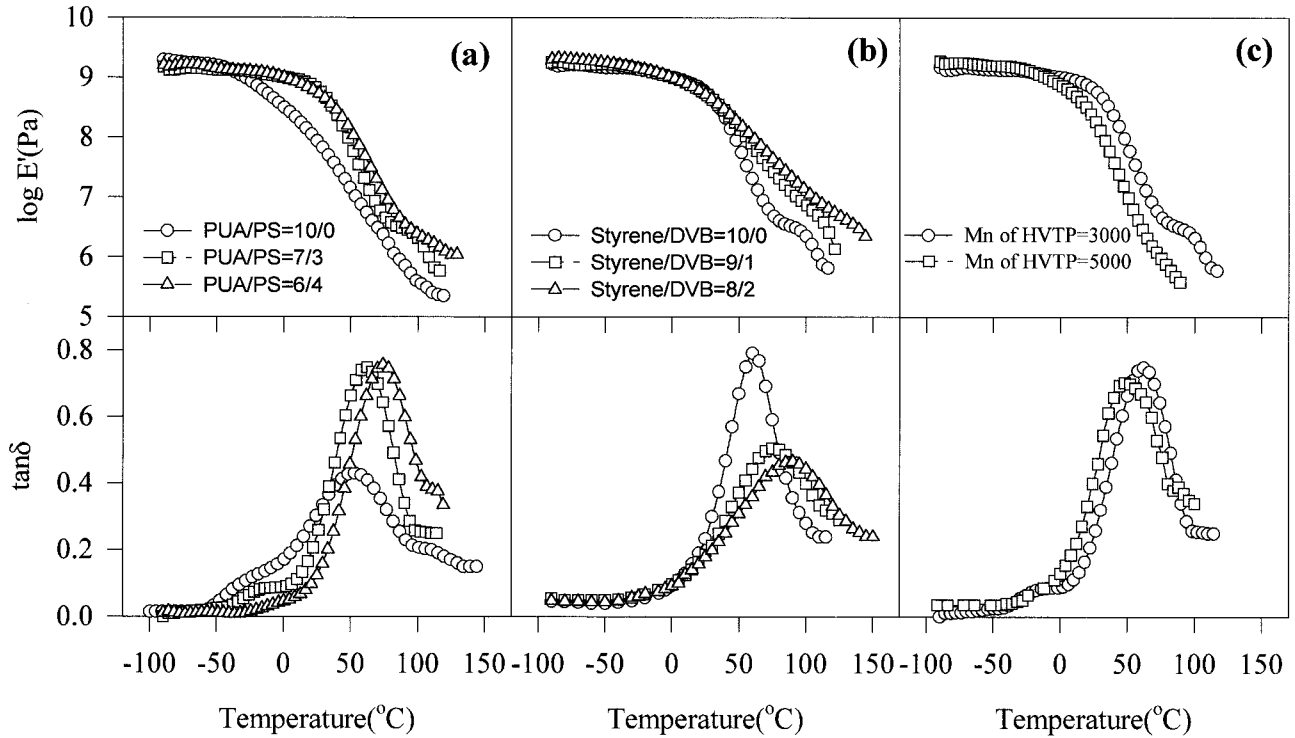
### Latex Particle Size

Figure 1 shows the average particle size of the dispersion as a function of PS content. It is seen that the particle size is virtually insensitive to PS content, although it increases from about 77 nm to about 81 nm as the PS content of the ABCP increases from 0% to 40%. The increase is primary because of the inclusion of PS in PU particles to form inverted core-shell morphology to follow. The hydrophobic nature of PS should reduce the swell of water into the particles, leading to a small increase in particle size.

### Film Morphology

Figure 2 shows the TEM morphologies of the Latex IPN cast films. In these micrographs, the bright isolated domains are PS-rich (hereafter called PS) domains; the dark continuous phase is PU-rich (PU), which is stained with OsO<sub>4</sub>. The inverted core (PS)-shell (PU) morphology is obvi-

ous, confirming that styrene monomers are polymerized in the core of the Latex particles. The average domain size of cast film, on the order of 10 nm, is smaller than the Latex particles (Fig. 1) when compared at the same condition. This is simply because the Latex particles include both PU and PS, whereas the domains in film are only PS. The domain size is shown to increase with an increasing amount of PS [Fig. 2(a) vs. (b)] and with increasing Mn of HVTP [Fig. 2(a) vs. (d)] and to decrease upon introducing crosslinkings in PS domains [Fig. 2(a) vs. (c)]. A HVTP is a tetrafunctional prepolymer, as it contains vinyl group (HEA) on both ends, which are subject to chain extension reaction via a radical mechanism. Thus, Mn of HVTP correspond to the molecular weight between crosslinking (Mc) in PU phases. Therefore, an increase in domain size with increasing the Mn of HVTP is expected due to the decreased number of physical interlockings between PU and PS chains. Decrease in domain size with increased crosslinkings in PS domains implies that PU-PS phase separation is suppressed due to the intensive

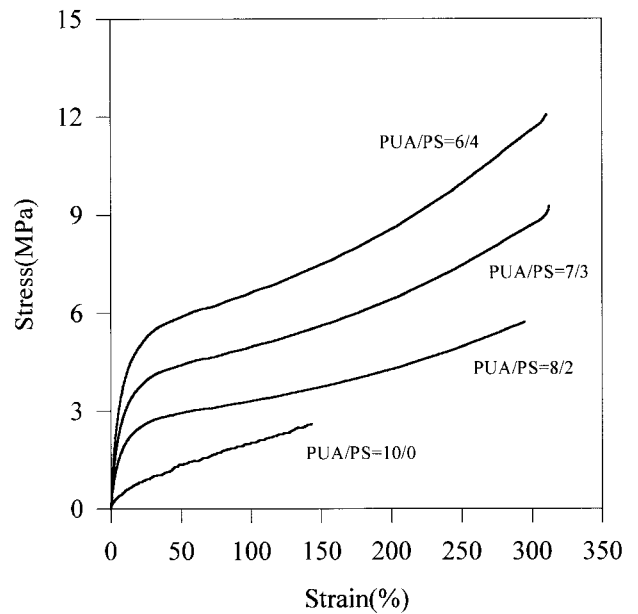


**Figure 3** Storage modulus ( $E'$ ) and  $\tan\delta$  of PU/PS latex ABCP: (a) effect of composition (Mn of HVTP = 3000, DVB = 0), (b) effect of DVB content (PU/PS = 7/3, Mn of HVTP = 3000), (c) effect of Mn of HVTP (PU/PS = 7/3, DVB = 0).

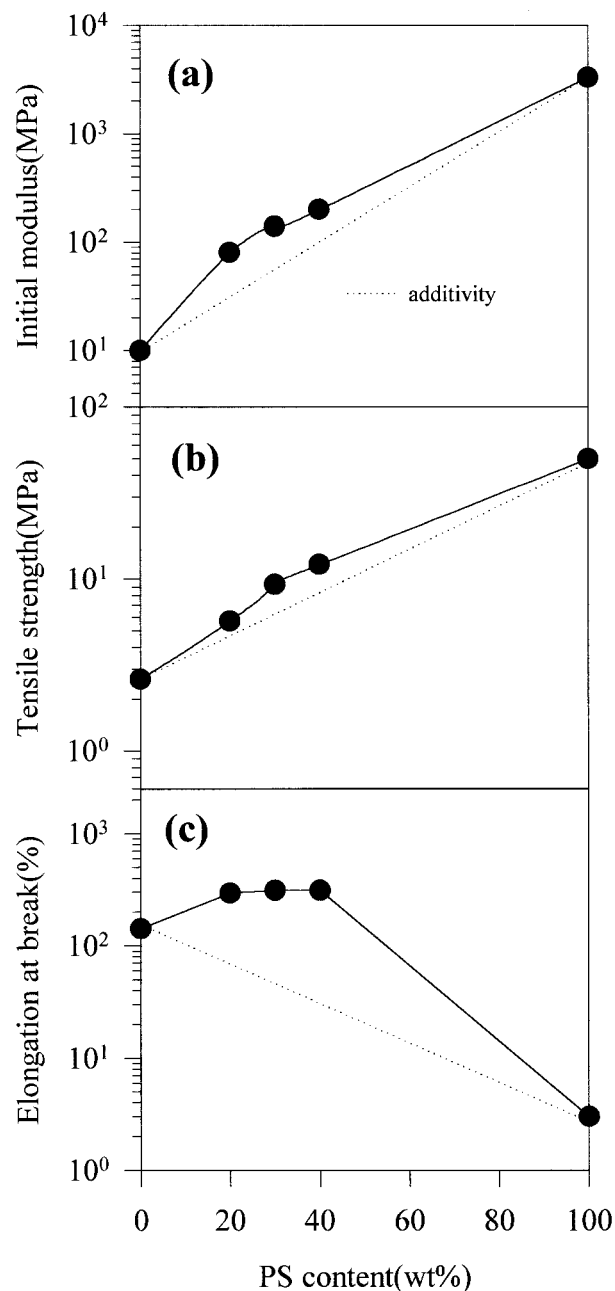
interlockings between PU and PS chains, especially, at the interfaces. It seems that control of crosslinking density in both phases is an effective way to controls the domain size and hence the extent of phase separations.

**Dynamic Mechanical Properties**

Dynamic mechanical properties of PU/PS Latex ABCP cast films are shown in Figure 3. The storage modulus ( $E'$ ) increases with the increase in PS content [Fig. 3(a)], and crosslinking density of PS [Fig. 3(b)] as well as PU [Fig. 3(c)] phases. Notably, rubbery modulus increases and extended up to higher temperature with high DVB content [Fig. 3(b)]. A similar effect is obtained with low Mn of HVTP [Fig. 3(c)]. Regardless of the ABCP formulations, the  $\tan\delta$  shows single peak, implying that the phase separation of PU-PS is very much suppressed. This makes a sharp contradiction with Latex IPN, which generally display two discrete peaks. As expected, peak temperature increases with increasing PS content and DVB content and decreases with Mn of HVTP. It appears that the glass-transition tem-



**Figure 4** Stress-strain curve of PU/PS latex ABCP vs. PS content (Mn of HVTP = 3000, DVB = 0).

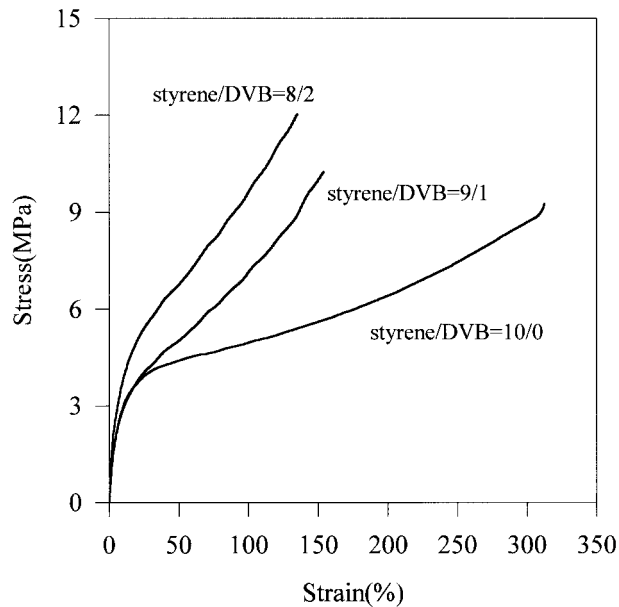


**Figure 5** Additivity of mechanical properties for vs. PS content of PU/PS latex ABCP (Mn of HVTP = 3000, DVB = 0): (a) initial modulus, (b) tensile strength, (c) elongation at break.

perature of the PU/PS ABCP can be easily controlled within a broad temperature range.

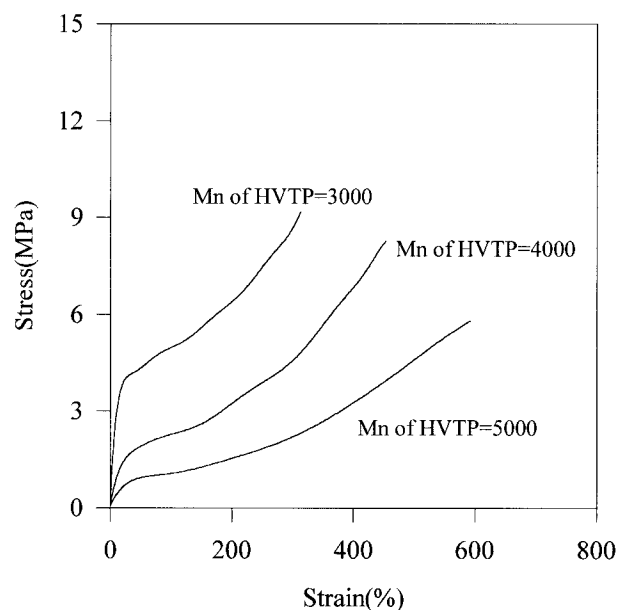
**Mechanical Properties**

Figures 4 and 5 display the mechanical properties of the Latex ABCP cast films. With the addition



**Figure 6** Stress-strain curve of PU/PS (7/3) latex ABCP vs. DVB content (Mn of HVTP = 3000).

and increasing amount of PS, the tensile modulus and strength of the cast films increase monotonically. Elongation at break also increases from about 150 (PU) to about 300% for PU/PS (8/2) ABCP, but remains almost constant with further addition of PS.



**Figure 7** Stress-strain curve of PU/PS (7/3) latex ABCP vs. Mn of HVTP (DVB = 0).

**Table III** Amount of Swell and Extraction of Cast Films

		Swell in Water (%)	Swell in Toluene	Extracted in Toluene (%)	Remarks
Latex composition	10/0	17.2	2.3	3.8	Mn = 3000 DVB = 0
	9/1	22.2	2.2	4.8	
	8/2	21.7	2.6	6.1	
	7/3	16.4	2.8	6.7	
	6/4	12.0	2.9	7.4	
DVB content	0	18.2	2.8	6.7	PU/PS (7/3) Mn = 3000
	10	11.5	2.1	2.4	
	20	10.5	1.7	1.3	
Mn of HVTP	3000	18.2	2.8	6.7	PU/PS (7/3) DVB = 0
	5000	31.8	3.7	10.7	
	7000	33.4	4.3	15.7	

PU, polyurethane; PS, polystyrene; DVB, HVTP, hydrophilic vinyl terminated prepolymer.

Latex ABCP yielded a positive deviation in modulus [Fig. 5(a)], strength [Fig. 5(b)], and elongation at the break [Fig. 5(c)] from the simple additivity (dotted lines in Fig. 5). Positive deviation in mechanical properties is caused by the intimate physical interlockings,<sup>16</sup> and the extent of phase mixing seemingly governs the extent of deviations.<sup>17</sup>

Figure 6 shows the effect of DVB content on the tensile behavior of Latex IPN. As expected, modulus and strength increase but elongation at break significantly decreases with increasing DVB content. As expected, modulus and strength decrease and elongation at break increase with increasing Mn of HVTP (Fig. 7).

### Swell and Extraction

Swell in water, toluene, and extraction in toluene of the Latex ABCP cast films are shown in Table III. As expected, water swell generally decreases with increasing PS and DVB content and increases with increasing the Mn of HVTP. The increase of water swell with initial addition of PS to PU is probably due to the interruption of otherwise homogeneous PU structure with PS. Swells in toluene, a good solvent for PS increases with the PS content and Mn of HVTP, and decreases with DVB content. Weight decrease of the films upon extraction in toluene is proportional to the amount of linear PS formed in the IPNs. Thus, the percentage extraction increases with PS content and Mn of HVTP, and decreases with DVB.

### CONCLUSIONS

Latex AB crosslinked polymer between polyurethane (PU, A) and Polystyrene (PS, B) formed an inverted core (PS)-shell (PU) morphology with fine domains, on the order of tens of nanometers in dried film. This fine domain morphology gave a single  $\tan \delta$  peak from dynamic mechanical measurements. The dispersed domain size, mechanical, dynamic mechanical properties, and swellability of the dispersion cast films were easily controlled by the composition of ABCP and crosslinking densities of the PU and PS phases.

This work was supported by the Korea Research Foundation Grant (KRF-97-001-E00496).

### REFERENCES

- Dieterich, D. *Prog Org Coat* 1981, 9, 281.
- Xiao, H. X.; Frisch, K. C., Eds.; *Advances in Urethane Ionomers*; Technomic: Basel, 1995.
- Satguru, R.; McMahan, J.; Padgett, J. C.; Coogan, R. G. *J Coating Technol* 1994, 66, 47.
- Markusch, P.; Noll, K.; Dieterich, D. 1980, US Patent 4238378.
- Rosthauser, J. W.; Nachtkamp, K. In Frisch, K. C.; Klempner, D., Eds.; *Advances in Urethane Science and Technology*; Technomic: Lancaster, 1987.
- Kim, B. K.; Tharanikkarasu, K.; Lee, J. S. *Colloid Polym Sci* 1999, 277, 285.
- Tharanikkarasu, K.; Kim, B. K. *J Appl Polym Sci* 1999, 73, 2993.

8. Dong, A.; Wan, T.; Sun, D. *J Polym Sci Part B: Polym Phys* 1999, 37, 2462.
9. Hourston, J.; Schafer, F. U.; Bates, J. S. *J Appl Polym Sci* 1996, 60, 2409.
10. El-Aasser, M. S.; Hu, R.; Dimonie, V. L.; Sperling, L. H. *Colloid Surf* 1999, 153, 241.
11. Klemperer, O.; Sperling, L. H.; Utracki, L. A. Eds.; *Interpenetrating Polymer Networks*; American Chemical Society: Washington, D.C., 1994.
12. Sheu, R. H.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Part A: Polym Chem* 1990, 28, 629.
13. Hourston, D. J.; McCluskey, J. A. *J Appl Polym Sci* 1987, 34, 901.
14. Bamford, C. H.; Eastmond, G. C.; Whittle, D. *Polymer* 1969, 10, 771.
15. Bamford, C. H.; Eastmond, G. C.; Whittle, D. *Polymer* 1971, 12, 147.
16. Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum: New York, 1981.
17. Hourston, D. J.; Schafer, F-U. *Polymer* 1996, 37, 3521.