

Modification of Aqueous Polyurethane Dispersions by Polybutadiene

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ABSTRACT: Aqueous polyurethane (PU) adhesives are nontoxic and nonflammable and do not pollute the air. However, they have low adhesive strengths compared to solvent-based PU adhesives because of a low affinity with rubber substrates. In this study, PU adhesives were synthesized from isophorone diisocyanate with dimethylol propionic acid as the ionic center in the main chain, triethylamine as the neutralization agent, and hydrazine as the chain extender. The polyol was modified with hydroxyl-terminated polybutadiene (HTPB) and hydroxyl-terminated acrylonitrile-butadiene copolymer (HTBN). The effect of the HTPB

and HTBN content on the adhesive strength was investigated. The effect of the prepolymer molecular weight was also investigated. Increases in the HTPB and HTBN contents led to an increase in the adhesive strength because of the increase of chemical affinity between the adhesive and the substrate. The adhesive strength increased as the prepolymer molecular weight increased. This was due to an increase in the tensile strength and modulus. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1062–1068, 2005

Key words: polyurethanes; adhesives; polybutadiene

INTRODUCTION

As a consequence of increasing regulations and restrictions worldwide due to environmental issues such as air pollution, ozone depletion, and acid rain, aqueous polyurethane (PU) dispersions have been developed since the 1960s. Because of the use of little or no organic solvent in aqueous PU dispersions, they are nontoxic and nonflammable and do not pollute the air compared to solvent-based PUs.^{1–7} Aqueous PU dispersions have been used for a wide range of commercial applications, including adhesives, coatings for textiles, leather, rubber, and many polymeric substrates, because of their good strength and flexibility characteristics.^{3,8–11}

To make water-dispersed PUs, aqueous PU dispersions can be prepared from NCO-terminated prepolymers containing hydrophilic anionomers. Because of the hydrophilicity of the PU anionomer, the water resistance of aqueous PU dispersions is lower than that of solvent-based PUs. Aqueous PU dispersions have a low adhesive strength because of their low chemical affinity with the substrates. To overcome these disadvantages, various methods, including grafting of other polymers, crosslinking, and blending, have been investigated.^{1,2,5,12–15} One of these approaches has been to modify polyols with butadiene-

based polyols, such as hydroxyl-terminated polybutadiene (HTPB) and hydroxyl-terminated acrylonitrile-butadiene copolymer (HTBN), to improve their water resistance and adhesive strength.^{7,16–18}

We synthesized aqueous PU dispersions from isophorone diisocyanate (IPDI) and poly(tetramethylene glycol) (PTMG) and modified the polyol with HTPB, HTBN, and dimethylolpropionic acid (DMPA) as the ionic center by a prepolymer dispersion process. In our study, the concentration of DMPA was fixed at 5 wt %. The effects of the prepolymer molecular weight (NCO/OH ratio) and the HTPB and HTBN contents on the adhesive strength, particle size, and mechanical properties were investigated.

EXPERIMENTAL

Materials

PTMG [number-average molecular weight (M_n) = 2000, BASF, Inc., Germany], HTPB (M_n = 2800, Idemitsu Chemical Co., Tokyo, Japan), and carboxyl-terminated acrylonitrile-butadiene copolymer (CTBN; M_n = 3400, BF Goodrich Co., Charlotte, NC) were degassed at 65°C for 12 h *in vacuo* to remove moisture before use.

IPDI (Shuls Chemical Co., Germany) and triethylamine (TEA; Showa Chemical Co., Tokyo, Japan) were dried over a 4-Å molecular sieve. DMPA (Aldrich Chemical Co., St. Louis, MO) was dried at 80°C for 6 h before use. *N*-methyl-2-pyrrolidone (NMP; Aldrich Chemical Co.) and hydrazine (Kangnam Chemical Co., Seoul, Korea) were used as received. Ethylene

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TABLE I
Recipes of the PU Aqueous Dispersion Preparations
(Based on Molar Ratios)

	HTPB or				
	IPDI	PTMG	HTBN	DMPA	Hydrazine
PUT 3000	1	0.309	—	0.35	0.341
PUT 5000	1	0.375	—	0.40	0.225
PUT 7000	1	0.409	—	0.425	0.166
PUT/PB 5000 95/5	1	0.357	0.0134	0.4	0.225
PUT/PB 5000 90/10	1	0.338	0.0269	0.4	0.225
PUT/PB 5000 85/15	1	0.319	0.0402	0.4	0.225
PUT/BN 5000 95/5	1	0.357	0.0105	0.4	0.225
PUT/BN 5000 90/10	1	0.338	0.0210	0.4	0.225
PUT/BN 5000 85/15	1	0.319	0.0315	0.4	0.225

T = PTMG; PB = HTPB; BN = HTBN. The numbers 5000 denotes the prepolymer molecular weight.

glycol (EG; Aldrich Chemical Co.), methylene chloride (MC; Aldrich Chemical Co.), 1,3-dicyclohexylcarbodiimide (DCC; Aldrich Chemical Co.), and 4-(dimethylamino) pyridine (DMAP; Aldrich Chemical Co.) were used to synthesize HTBN.

Synthesis of aqueous PU dispersions

The content of DMPA was fixed at 5 wt % on the basis of the solid content of the PU aqueous dispersions.

The content of IPDI, polyols, and chain extender were varied to control the prepolymer molecular weight. The recipes for the PU aqueous dispersion preparations are presented in Table I.

Polyol, DMPA, and NMP (10 wt % on solid content) were introduced into a 500-mL, four-necked, round-bottom flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and thermometer. The mixture was stirred at 60°C for 30 min to make a homogeneous solution. After IPDI was added, the reaction proceeded until the desired extent of the reaction was reached; the extent of the reaction was determined by the *n*-butylamine back-titration method.⁹ The prepolymers were cooled to 60°C, and TEA was added to neutralize the carboxyl group of the prepolymer, and the mixture was then stirred for 30 min. Next, PU ionomers were dropped into the distilled water with high-speed stirring, where the chain extender was dissolved; then, chain extension was carried out during the dispersion in water. During the synthesis of the PU prepolymer, a little NMP was used to reduce the viscosity of prepolymer. However, HTPB was not soluble in NMP; therefore, an NMP/cyclohexanone cosolvent was used at a ratio of 7:3 in the PU prepolymer with HTPB. The schematic diagram of the aqueous PU dispersion synthesis is shown in Figure 1.

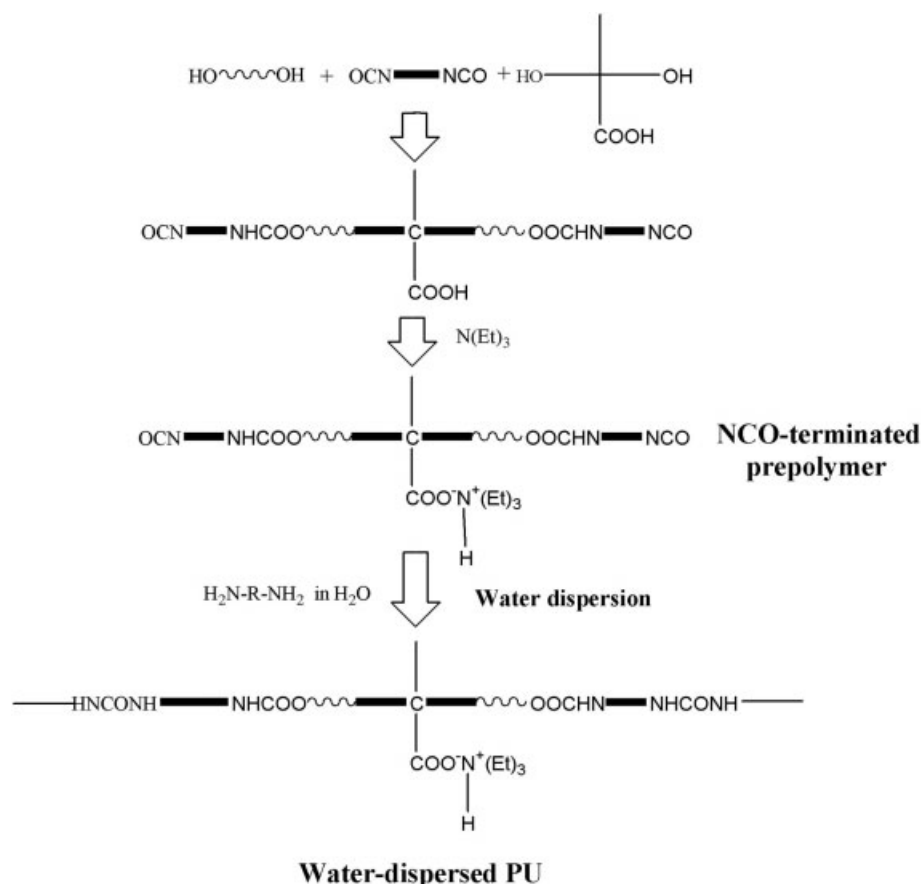


Figure 1 Schematic representation of aqueous PU dispersion synthesis.

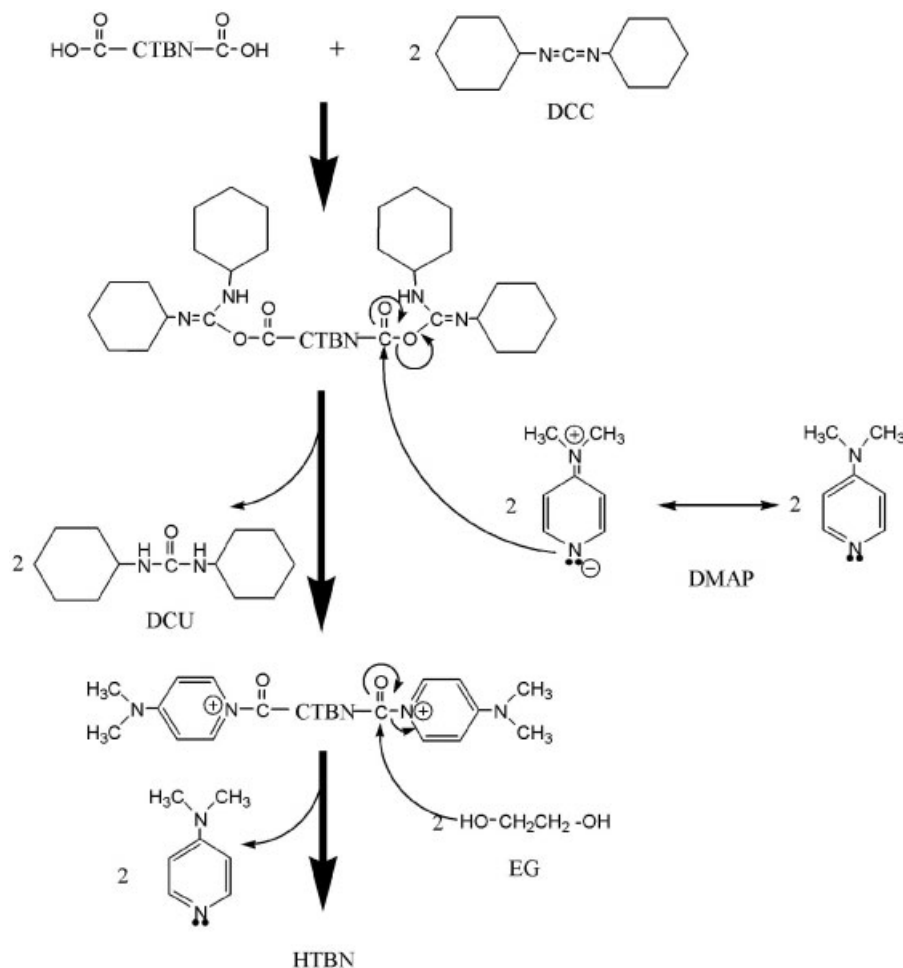


Figure 2 Reaction mechanism of the hydroxylation of CTBN with DCC and DMAP.

PU aqueous dispersions were obtained by the variation of the HTPB and HTBN contents from 0 to 15% (w/w). The NCO/OH ratio was varied (1.52, 1.29, and 1.20) to obtain NCO-terminated prepolymers with molecular weights of 3000, 5000, and 7000, respectively.

Synthesis of HTBN

HTBN was synthesized by the coupling of 1 equiv of CTBN with 2 equiv of EG with DCC and DMAP in the MC solvent at room temperature. The reaction mechanism of the hydroxylation of CTBN with DCC and DMAP is shown in Figure 2.^{19,20} First, CTBN, DCC, and DMAP were dissolved in MC. This solution was added dropwise to PEG in a 1000-mL round-bottom flask through a dropping funnel under vigorous stirring. DCC reacted with the carboxylic acid group of CTBN, and then, DMAP reacted with the activated end group of CTBN. In this step, dicyclohexylcarburea was produced, and it was precipitated during the reaction. After 48 h, the dicyclohexylcarburea was removed by filtration, and the reaction mixture was poured into an excess amount of methanol to

remove unreacted components. The product was dried *in vacuo* at 60°C for 24 h. The hydroxylation of CTBN was confirmed by ¹H-NMR and acid number determination. The ¹H-NMR spectrum of HTBN showed two peaks at 3.8 and 4.2 ppm due to the ethylene group adjacent to the carboxyl group; these two peaks were not evident before hydroxylation. In Figure 3, the ¹H-NMR spectrum of CTBN and HTBN are shown. From the acid number determination of HTBN, we confirmed that all of the carboxyl end groups of the CTBN reacted with the hydroxyl end groups of EG.

Particle size measurements

The particle sizes of the aqueous PU dispersions were measured with dynamic light scattering (Brookhaven Instruments Co., Holtsville, NY BI-200SM) with a 532-nm laser source at 25°C. The detecting angle was 90°. Samples were prepared with deionized water at a concentration of 0.005 wt %. The sample cell was positioned at the center of a brass thermostat block filled with refractive index matching fluid (decalin).

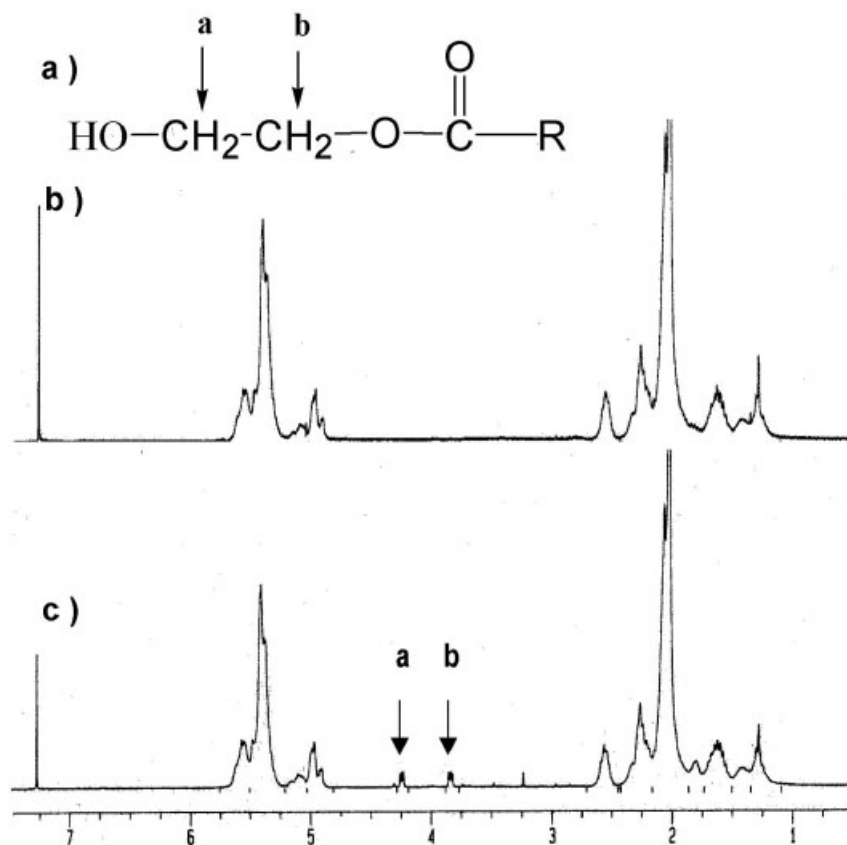


Figure 3 $^1\text{H-NMR}$ spectra of CTBN and HTBN: (a) structure of the end group of HTBN, (b) CTBN, and (c) HTBN.

Gel permeation chromatography measurements

The molecular weight and molecular weight distribution values were measured by gel permeation chromatography (Waters Co., USA, model 410) at 23°C . The eluent was tetrahydrofuran used at a 1 mL/min flow rate. For calibration, monodisperse polystyrene standards were used.

Measurement of mechanical properties

The synthesized aqueous PU dispersions were cast on glass plates covered with polypropylene film and dried at room temperature for 24 h and then at 70°C for 5 h to obtain PU films for tensile testing. Tensile testing was performed at a crosshead speed of 20 mm/min with a microtensile specimen (ASTM D1708-93) in a universal testing machine (Instron, model 4202).

Peel test

To measure the peel strength of the aqueous PU adhesive, the 180° peel test was used. The specimen used in the 180° peel test is shown in Figure 4. A 1.5 mm thick acrylonitrile-butadiene rubber (NBR) sheet was used as the substrate for the specimen without any additional surface treatment. Wood was used as the

backing material and was adhered to the NBR sheet with a commercial PU adhesive. The aqueous PU dispersions were applied on one substrate and allowed to dry at room temperature for 1 h; then, the other substrate was applied and again allowed to dry for 7 days. The 180° peel test was carried out with the universal testing machine.

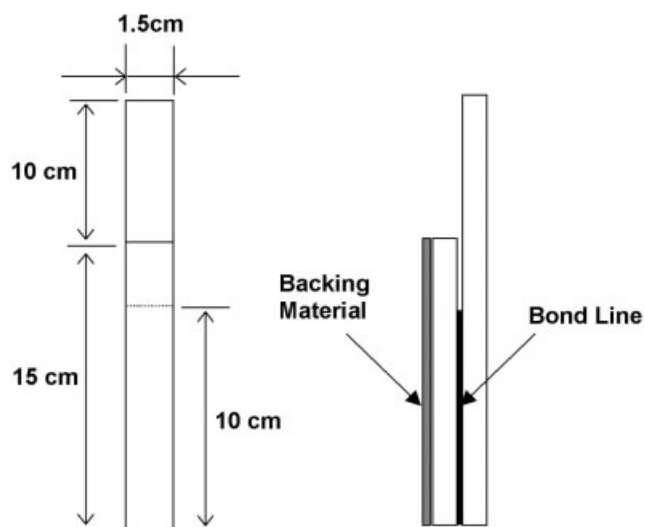


Figure 4 Test specimen used in the 180° peel test.

TABLE II
Molecular Weight 3 of the PU Dispersions

	M_n	M_w	Polydispersity
PUT 3000	45,900	225,800	4.92
PUT 5000	35,100	107,300	3.05
PUT 7000	27,700	85,400	3.08
PUT/PB 5000 95/5	22,700	67,400	2.97
PUT/PB 5000 90/10	20,900	69,600	3.34
PUT/PB 5000 85/15	18,900	67,600	3.57
PUT/BN 5000 95/5	34,000	126,200	3.71
PUT/BN 5000 90/10	39,100	157,900	4.04
PUT/BN 5000 85/15	35,700	153,500	4.30

T = PTMG; PB = HTPB; BN = HTBN. The number 5000 denotes the prepolymer molecular weight.

Measurement of surface energy

The surface energy of the PU film was obtained by contact angle measurement. The static contact angles of the PU film surface–air–water system and the PU film surface–air–EG system were measured by a contact angle goniometer (Erma,1, model G-I type). The surface energy of the PU film and the interfacial energy between the PU film and the substrate were calculated from the harmonic mean equation as follows.^{21–23}

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} \right) - 4 \left(\frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right) \quad (1)$$

where γ is the interfacial tension and γ^d is its dispersion component and γ^p is its polar component.

RESULTS AND DISCUSSION

Molecular weight of the aqueous PU dispersions

The molecular weights of the PU dispersions are shown in Table II. M_n and the weight-average molecular weight (M_w) of the aqueous PU dispersions increased with decreasing prepolymer molecular weight. As the molecular weight of the prepolymer decreased, the NCO/OH ratio increased, and the exposed NCO concentration of the prepolymer increased. As the chain extension of the NCO-terminated prepolymer occurred by the reaction of the exposed NCO end group with amine groups, we concluded that the chain extension occurred much more with the prepolymer with a higher exposed NCO concentration. Therefore, the molecular weights of the aqueous PU dispersions increased with decreasing prepolymer molecular weight, namely, increasing the NCO/OH ratio. In PU dispersions with HTPB and HTBN, M_n of the PU dispersions did not show a clear difference with an increase in the HTPB and HTBN contents. The polydispersity indices in all of the synthesized samples ranged from 3.0 to 4.9.

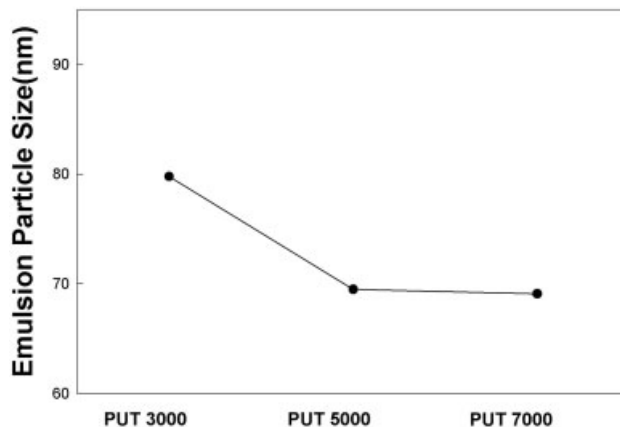


Figure 5 Particle sizes of PU aqueous dispersions with different prepolymer molecular weights (T = PTMG).

Emulsion particle sizes of the aqueous PU dispersions

The particle sizes of the aqueous PU dispersions with different prepolymer molecular weights are shown in Figure 5. The particle size increased from 70 to 80 nm with decreasing prepolymer molecular weight. The increased particle size was attributed to the higher molecular weight of the PU dispersions due to enhanced chain extension. As the molecular weight of the PU dispersions increased, we expected the viscosity of the PU dispersions to also increase. The particle sizes of the PU dispersions with HTPB and HTBN in polyol are shown in Figure 6. There were some factors that affect the particle size; it was mainly affected by the degree of hydrophilicity of main chain. The insertion of HTPB and HTBN led to the hydrophobicity of the main chain of PU relative to PTMG. As expected, the particle size of the PU dispersions with HTPB increased from 70 to 76 nm and that with HTBN increased from 70 to 88 nm.

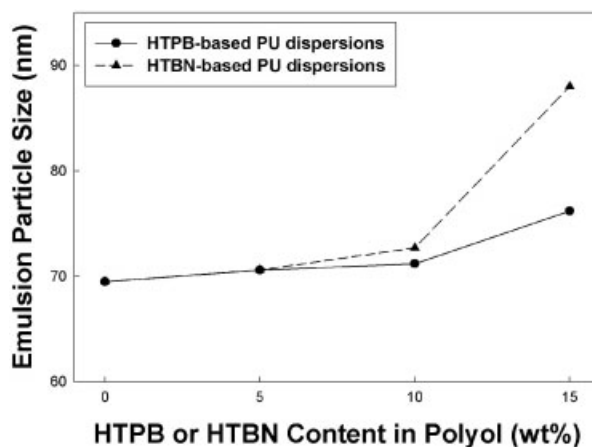


Figure 6 Particle sizes of PU dispersions with HTPB and HTBN.

TABLE III
Tensile Strength and Modulus of PU Films

	Tensile strength (MPa)	Modulus (MPa)
PUT 3000	27.24	3.15
PUT 5000	11.41	2.10
PUT 7000	9.96	1.28
PUT/PB 5000 95/5	4.74	0.70
PUT/PB 5000 90/10	3.72	0.68
PUT/PB 5000 85/15	2.18	0.57
PUT/BN 5000 95/5	4.21	0.61
PUT/BN 5000 90/10	7.32	1.83
PUT/BN 5000 85/15	9.77	1.99

T = PTMG; PB = HTPB; BN = HTBN. The number 5000 denotes the prepolymer molecular weight.

Tensile strengths and moduli of the PU films

The tensile strengths and moduli of the PU films obtained by the casting of the PU dispersions are shown in Table III. The tensile strengths and moduli of the PUs with different prepolymer molecular weights increased with decreasing prepolymer molecular weight because of the increase in the molecular weight of the PUs. With decreasing prepolymer molecular weight and increasing NCO/OH ratio, the content of urethane and urea linkage increased, which meant that a smaller prepolymer molecular weight, because of the increase in the formation of hydrogen bonds, is another factor for improving the tensile strength and modulus. In Table III, the tensile strengths and moduli of PUs with HTPB and HTBN are also presented. The tensile strengths and moduli of PUs with HTPB decreased with increasing HTPB content. That was because the repeating unit of HTPB was more flexible than that of PTMG and was less polar than that of PTMG. Therefore, the reduced polarity due to the reduced hydrogen bonding led to a decreased tensile strength. As shown in Figure 7, the tensile strengths and moduli of PUs with HTBN increased with increasing HTBN content in polyol. In PUs with HTBN, the repeating unit was less flexible than that of PTMG, and the acrylonitrile was a polar segment. In addition, M_w values of PUs with HTBN were higher than those

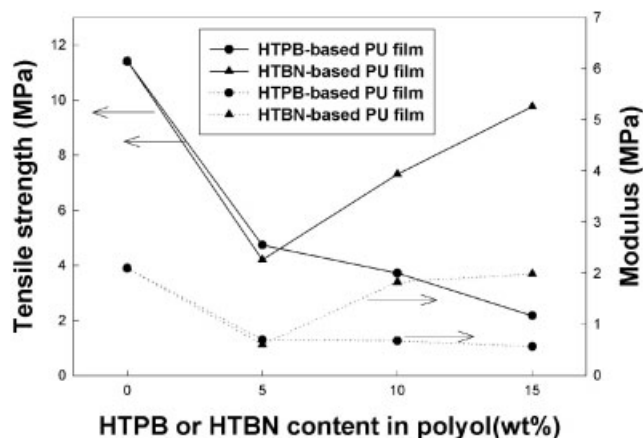


Figure 7 Tensile strengths and moduli of PU films with HTPB and HTBN.

of PU without HTBN, as shown in Table II, whereas M_w of PU with PTMG was 107,300 g/mol and that of PU with 15% HTBN was 153,500 g/mol. Therefore, the tensile strengths and moduli of PUs with HTBN increased with increasing amount of HTBN.

Effect of HTPB and HTBN content on the surface energy and peel strength of the PU adhesives

We expected that the adhesion of aqueous PU adhesives with NBR substrate would increase when the PU adhesive was modified with the butadiene-based polyol. Actually, the use of only the butadiene-based polyol was the best way to increase the adhesive strength of the aqueous PU adhesive with NBR. However, it was difficult to disperse PU in water because of the hydrophobicity of the butadiene-based polyol. Hence, we investigated the effects of the HTPB and HTBN contents on the adhesive strength. The adhesive strength of PU with 15% HTPB in polyol increased by approximately 30% relative to that of PU without HTPB. As shown in Table IV, with increasing HTPB in polyol, the interfacial energy between the PU adhesive and the NBR substrate decreased. This improved the chemical affinity between the PU adhesive, and the NBR substrate led to an increase of the adhe-

TABLE IV
Peel Strength and Surface Energy of PUs with HTPB and HTBN

	Contact angle with water (°)	Contact angle with EG (°)	$\gamma_{\text{PU-Air}}$ (mJ/m ²)	$\gamma_{\text{PU-NBR}}$ (mJ/m ²)	Peel strength (Pa m)
PUT 5000	83.1	65.0	31.80	0.5822	42.60
PUT/PB 5000 95/5	87.4	70.3	28.74	0.2352	47.09
PUT/PB 5000 90/10	89.0	71.7	27.80	0.1569	48.46
PUT/PB 5000 85/15	92.3	73.0	26.53	0.0758	57.08
PUT/BN 5000 95/5	84.6	68.2	28.74	0.4024	72.32
PUT/BN 5000 90/10	84.9	69.3	29.96	0.3575	78.01
PUT/BN 5000 85/15	85.5	69.8	29.59	0.3177	82.06

T = PTMG; PB = HTPB; BN = HTBN. The number 5000 denotes the prepolymer molecular weight.

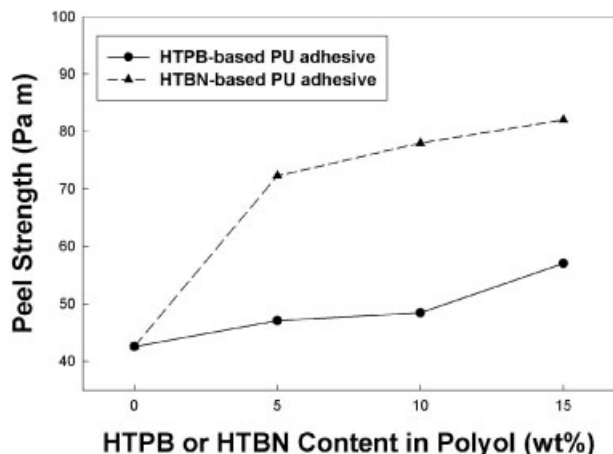


Figure 8 Peel strengths of PU aqueous dispersions applied on NBR substrates with HTPB or HTBN.

sive strength. Interfacial adhesion failure occurs when the bond strength at the interface is lower than the internal strength of the adhesive. Generally, adhesive failure at the interface and cohesive failure inside the adhesive itself are common and in many cases; adhesive failure and cohesive failure occur simultaneously, which is called *mixed failure*.³ As shown in Table III, the tensile strength and modulus of the PU adhesive with HTPB decreased with increasing HTPB content in polyol. However, the effect of decreased tensile strength and modulus on the peel strength was smaller than the effect of the increased chemical affinity on the peel strength. Therefore, the adhesive strength was improved. The interfacial energy between the PU adhesive with HTBN and substrate is shown in Table IV. The interfacial energy of PU decreased sequentially from the PU with 0% HTBN to the PU with 15% HTBN. These results were in agreement with the peel strength, as shown in Figure 8. The peel strength increased from 43 to 82 Pa m by approximately 90% with increasing HTBN content in polyol up to 15%. The interfacial energy of the PU adhesive with HTPB was lower than that of the PU adhesive with HTBN. Namely, the chemical affinity of the PU with HTPB was higher than that of the PU with HTBN. However, as shown in Table III, the higher cohesive strength of the PU adhesive modified with HTBN led to a higher peel strength.

CONCLUSIONS

The effect of the prepolymer molecular weight on adhesive strength was investigated. With increasing prepoly-

mer molecular weight, the residual NCO groups exposed for the chain extension reaction and the molecular weight of the PU dispersion decreased, which resulted in a decrease in the tensile strengths and moduli of the PU adhesives. The effects of the HTPB and HTBN contents on the adhesive strength were investigated. With increasing HTPB and HTBN content, the hydrophobicity of PU increased, and the particle size also increased. With increasing HTPB and HTBN contents, the interfacial energy between the aqueous PU adhesive and the NBR substrate decreased because of the increase in chemical affinity, which resulted in an increase in the adhesive strength. The adhesive strength of the PU with 15% HTBN increased about 100% relative to that of the PU without HTBN.

References

- Dieterich, D. *Prog Organic Coat* 1981, 9, 281.
- Kim, B. K. *Colloid Polym Sci* 1996, 274, 599.
- Szycher, M. *Szycher's Handbook of Polyurethanes*; CRC: New York, 1999.
- Oertel, G. *Polyurethane Handbook*, 2nd ed.; Hanser: Munich, 1985.
- Kim, B. K.; Lee, J. C. *Polymer* 1996, 37, 469.
- Delpech, M. C.; Coutinho, F. M. B. *Polym Test* 2000, 19, 939.
- Coutinho, F. M. B.; Delpech, M. C.; Alves T. L.; Ferreira, A. A. *Polymer Degrad Stab* 2003, 81, 19.
- Kim, T. K.; Kim, S. J.; Kim, B. K. *Polymer (Korea)* 1992, 16, 604.
- Hepburn, C. *Polyurethane Elastomers*, 2nd ed.; Elsevier: New York, 1955.
- Jhon, Y. K.; Cheong, I. W.; Kim, J. H. *Colloids Surf A* 2001, 179, 71.
- Kim, B. K.; Lee, J. C. *J Polym Sci Part A: Polym Chem* 1996, 34, 1095.
- Wei, X.; Ying, Y.; Yu, X. *J Appl Polym Sci* 1998, 70, 1621.
- Lu, M. G.; Lee, J. Y.; Shim, M. J.; Kim, S. W. *J Appl Polym Sci* 2002, 86, 3461.
- Kim, B. K.; Lee, Y. M. *J Appl Polym Sci* 1994, 54, 1809.
- Tharnikkarasu, K.; Kim, B. K. *J Appl Polym Sci* 1999, 73, 2993.
- Coutinho, F. M. B.; Delpech, M. C.; Alves, L. S. *J Appl Polym Sci* 2001, 80, 566.
- Haska, S. B.; Bayramle, E.; Pekel, F.; Ozkar, S. *J Appl Polym Sci* 1997, 64, 2355.
- Zawadzki, S. F.; Akcelrud, L. *Polym Int* 1997, 42, 422.
- Zalipsky, S.; Gilon, C.; Zilkha, A. *Eur Polym J* 1983, 19, 1177.
- Park, S. Y. Ph.D. Dissertation, Korea Advanced Institute of Science and Technology, 2002.
- Andrade, J. D.; Ma, S. M.; King, R. N.; Gregonis, D. E. *J Colloid Interface Sci* 1979, 72, 488.
- Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: New York, 1990.
- Schrader, M. E.; Loeb, G. I. *Modern Approaches to Wettability*; Plenum: New York, 1992.