

# Effect of Polyisocyanate Hardener on Adhesive Force of Waterborne Polyurethane Adhesives

Mohammad Mizanur Rahman, Han-Do Kim

Department of Organic Material Science and Engineering, Pusan National University, Busan 609-735, Korea

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**ABSTRACT:** A series of waterborne polyurethane (WBPU)/hardener adhesives were obtained from mixing of WBPU containing different types of polyol as a soft segment with aliphatic and aromatic polyisocyanates hardeners. By characterization of allophanate and biuret bonds formed from the reaction of hardener NCO with urethane/urea groups of WBPU using  $^1\text{H}$ NMR spectroscopy. It was found that the optimum number ratio (molar ratio) of NCO group of hardener to urethane/urea group of WBPU that shows the highest adhesion force was depended on the type of hardener (aliphatic/aromatic polyisocyanate) and dimethylol propionic acid (DMPA) content (total content of urethane/urea groups); however independent of the type of soft segment (polyol) of WBPU. The optimum number ratio

(molar ratio) of NCO group of aromatic polyisocyanate hardener to urethane/urea was higher than that of aliphatic hardener to achieve the highest adhesion force of WBPU. The adhesive force increased with increasing hardener content up to the optimum point and then decreased. Poly(tetramethylene adipate glycol) (PTAd) based WBPUs with aliphatic hardener show higher adhesive force than Poly(tetramethylene oxide glycol) (PTMG) and aliphatic hardener-based WBPUs at the optimum number ratio (molar ratio) of NCO group of hardener to urethane/urea group of WBPU. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3663–3669, 2007

**Key words:** polyurethane; adhesion

## INTRODUCTION

Waterborne polyurethane (WBPU) dispersions belong to an important class of polymer dispersions used in many industrial applications such as coatings for wood finishing, glass fiber sizing, textiles, adhesives, automotive topcoats and primers, films for packaging, gloves, and other applications. Pure polyurethane polymers with desirable properties for a number of applications can also be recovered from these dispersions, making them versatile and widely applicable.<sup>1–7</sup>

Very few studies are available on WBPU adhesive in open scientific literature.<sup>8–11</sup> Kwak et al.<sup>8</sup> studied the effect of dimethylol propionic acid (DMPA) on adhesive strength of polyester-based WBPU. They showed that the adhesive strength increased with increasing DMPA content. Yang et al.<sup>9</sup> studied the effect of different types of neutralizing agents on adhesive strength of polycaprolactone-based WBPU. Kim and Kim<sup>10</sup> studied adhesive strength of different types of polyester polyol-based WBPUs. Kwon and Kim<sup>11</sup> used crosslinker to increase the adhesive force of WBPU. Most of the research has been made in industrial laboratories which were not published.

Moreover, the emission of organic solvent restricted the solvent based polyurethane adhesive which is also a driven force to improve the WBPU adhesive.

Generally, a little amount of polyisocyanate hardener is used to improve the adhesive force of WBPU. Both aliphatic and aromatic polyisocyanates are being widely used in industry as a hardener to improve the adhesive force. However, the effect of the type of hardener, more precisely aliphatic and aromatic polyisocyanate hardener and its content with respect of different types of soft segments (polyol) and DMPA content (urethane/urea group) of WBPU was hardly be found. To the best of our knowledge, study on the optimum number ratio (molar ratio) of NCO group of hardener to urethane/urea group for obtaining the high adhesive force of WBPU adhesives was not considered yet. Therefore, in this study, we mixed a little amount of aliphatic and aromatic polyisocyanate hardener with prepared WBPU dispersions, which contain different types of polyol (PTMG and PTAd) as a soft segment, and various DMPA content (urethane/urea group), to obtain the optimum number ratio (molar ratio) of NCO group of polyisocyanate hardener to urethane/urea group of WBPU with regard of adhesive strength. This study also compare the increase of adhesive force using aliphatic and aromatic polyisocyanate hardener after mixed with PTMG and PTAd polyol-based WBPUs.

Correspondence to: H.-D. Kim (kimhd@pusan.ac.kr).

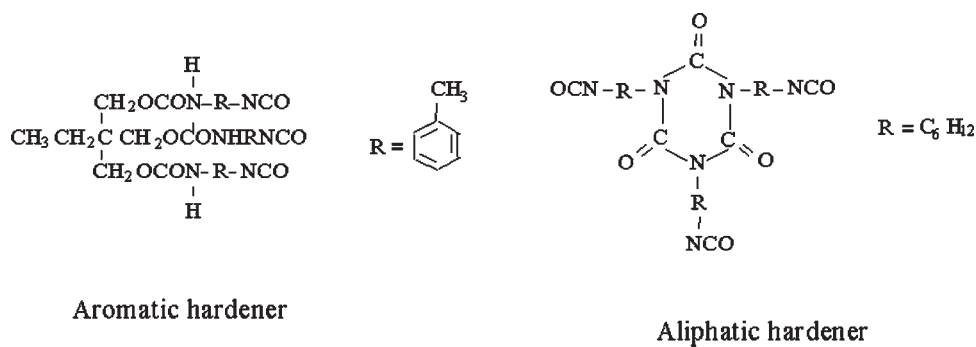


Figure 1 Structure of hardeners.

## EXPERIMENTAL

### Materials

Poly(tetramethylene oxide glycol) (PTMG, number-average molecular weight = 2000 g/mol; Aldrich Chemical), and Poly(tetramethylene adipate glycol) (PTAd, number-average molecular weight = 2000 g/mol; Aldrich Chemical) were dried at 90°C and 1–2 mmHg for 3 h before use. Dimethylol propionic acid (DMPA, Aldrich Chemical, Milwaukee, WI), Triethylamine (TEA; Junsei Chemical, Tokyo, Japan), *N*-methyl-2-pyrrolidone (NMP; Junsei Chemical), 4,4-dicyclohexylmethane diisocyanate ( $\text{H}_{12}$ MDI, Aldrich Chemical), and ethylene diamine (EDA, Junsei Chemical) were used after dehydration with 4-Å molecular sieves for 1 week. Dibutyltin dilaurate (Aldrich Chemical), thickener (L75N, Bayer, Leverkusen, Germany), and hardener (Nippon Polyurethane Industry, Korea) were used without further purification. The structure of the hardeners is shown in Figure 1.

### Synthesis of the waterborne polyurethanes

The WBPU were synthesized with the prepolymer mixing process (Scheme 1). Polyol was placed in a four-necked separable flask equipped with a thermometer, a stirrer, a condenser with a drying tube, an inlet of dry nitrogen, and a heat jacket and was degassed in vacuum at 90°C for 30 min. DMPA/NMP (1/1 w/w) was added to the flask, and the mixture was allowed to cool to 45°C under moderate stirring (175–200 rpm). Then,  $\text{H}_{12}$ MDI was added to the flask, and the mixture was heated to 85°C under moderate stirring (175–200 rpm). The reaction mixture was allowed to react at 85°C until the theoretical NCO content was reached. The change in the NCO value during the reaction was determined with the standard dibutylamine back-titration method (ASTM D 1638). Then, methyl ethyl ketone (MEK; 20 wt %) was added to the NCO-terminated prepolymer mixture to adjust the viscosity of the solution. TEA was added to the reaction mixture to neutralize

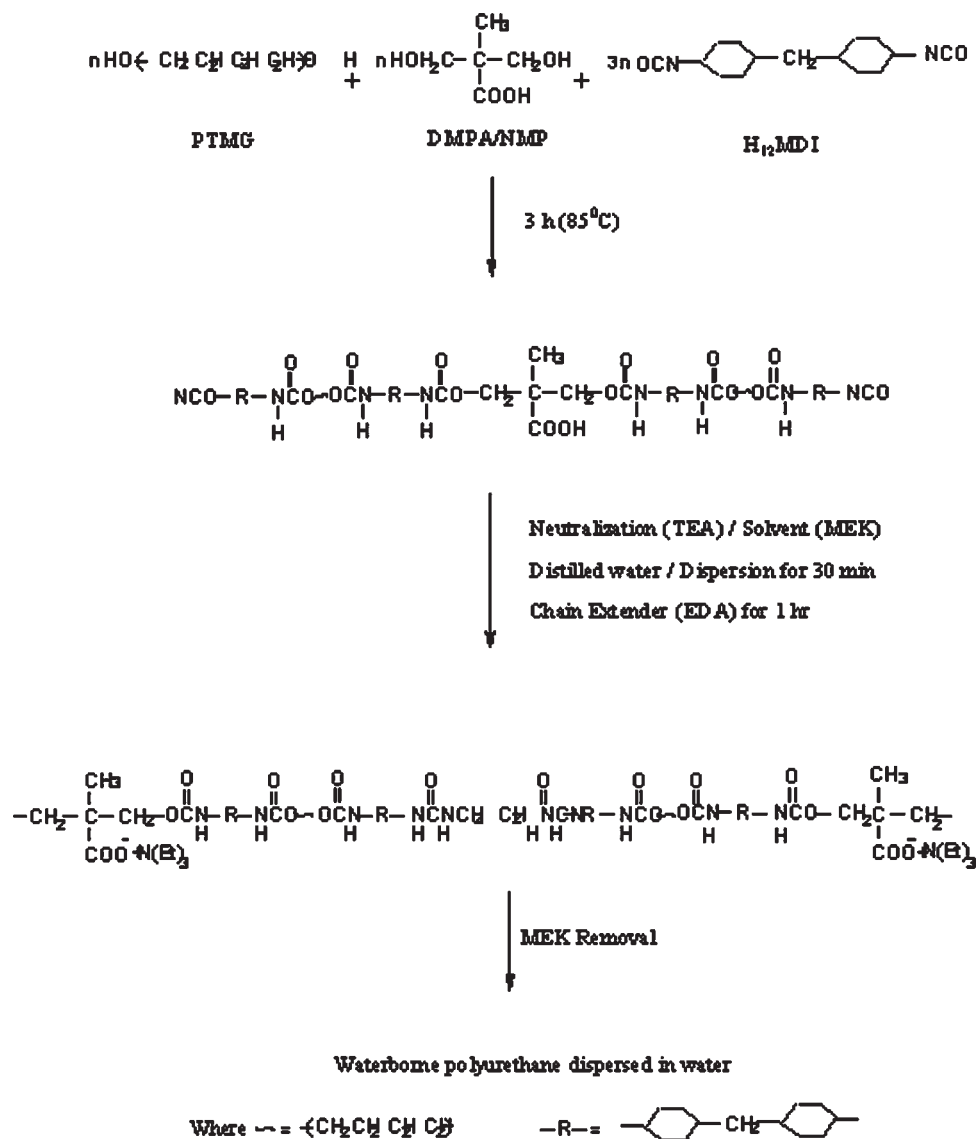
the carboxyl group of the NCO-terminated prepolymer. After 30 min of neutralization, distilled water (60 wt %) was added to the reaction mixture with vigorous stirring (1300–1500 rpm). The neutralized prepolymer was chain-extended by dropping EDA at 40°C for 1 h, and the reaction continued until the NCO peak ( $2270 \text{ cm}^{-1}$ ) in the IR spectra had completely disappeared. All the WBPU (40 wt % solid content) were obtained by the evaporation of MEK and the subsequent addition of an adequate amount of distilled water.

### Preparation of the WBPU adhesives using hardener

WBPU films were prepared by pouring the aqueous dispersion on a Teflon disk that was cured at 100°C. The films (typically about 0.5 mm thick) were dried in vacuum at 60°C for 1 day and stored in a desiccator at room temperature. WBPU adhesive materials were formulated from WBPU dispersions, thickener (0.5 wt %), and hardener. An appropriate amount of WBPU dispersion was mixed with the thickener (0.5 wt %) and the hardener to obtain a homogeneous mixture at room temperature. The prepared adhesive material was then coated onto nylon fabric and another nylon fabric was placed on the coated surface and then dried at 100°C under fixed pressure ( $15 \text{ kgf/cm}^2$ ) for 10 min.

### Characterization

The mean particle size of the WBPU dispersions was measured using a laser-scattering equipment (Autosizer, Melvern IIC, Malvern, Worcester, UK). A small amount of aqueous dispersion was added in a deionized water tank and this was followed by the pinhole being set at 200  $\mu\text{m}$ . The average particle diameters were measured at 25°C.  $^1\text{H-NMR}$  spectra were recorded on Varian Unity Plus 300 spectrometer operating at 300 MHz. Thirty microgram of the film was dissolved in 4 mL of deuterated chloroform. TMS was used as an internal reference. The thermal behavior of the WBPU film was analyzed by



Scheme 1 The preparation process of WBPU.

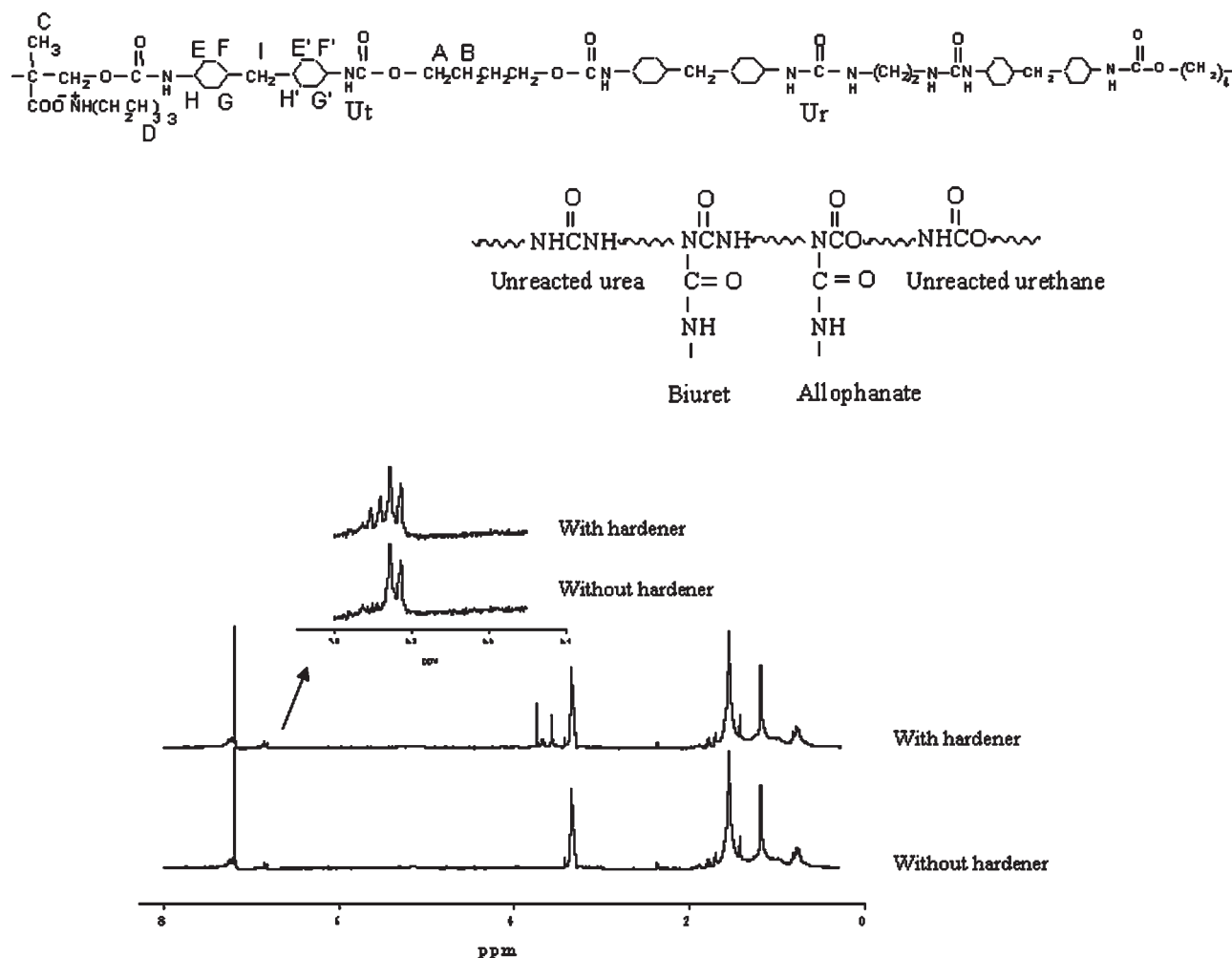
differential scanning calorimetry (DSC; model 220C, Seiko, Chibas, Japan). WBPU (3–4 mg) film was placed in an aluminum pan and the experiment was carried out under dry nitrogen gas atmosphere at a heating rate of 10°C/min. The wide angle X-ray dif-

fraction (WAXD) patterns were recorded using a Philips Xpert XRD System diffractometer at a voltage of 40 kV, and a radiation of wavelength 1.542 Å. Diffraction patterns were obtained in the range of Bragg's angle  $2\theta = 0^\circ\text{--}40^\circ$ . The  $2\theta$  scan rate was 2°C/

TABLE I  
Sample Designation, Composition, and Particle Size of WBPU Adhesive

Sample designation	Composition (mole)					DMPA		Urethane/Urea (mole)	NCO (mole)	Optimum NCO (mole)		Particle size (nm)
	Polyol <sup>a</sup>	DMPA	H <sub>12</sub> MDI	TEA	EDA	Mol %	wt %			Aliphatic hardner	Aromatic hardner	
P1	4.0	3.0	8.9	3.0	1.9	16.85	3.61	8.9	0.05–0.14	0.09	0.10	52
P2	4.0	5.1	11.0	5.1	1.9	23.18	5.53	11.0		0.11	0.12	46
S1	4.0	3.0	8.9	3.0	1.9	16.85	3.61	8.9		0.09	0.10	47
S2	4.0	5.1	11.0	5.1	1.9	23.18	5.53	11.0		0.11	0.12	38

<sup>a</sup> P1, P2 PTMG type; S1, S2 PTAD type.



**Figure 2**  $^1\text{H-NMR}$  spectra of the typical WBPU adhesive sample P2 containing optimum aliphatic hardener and without hardener.

min. The tensile properties were measured at room temperature with a United Data System tension meter (Instron SSTM-1, United Data Systems, Japan) according to the ASTM D 638 specifications. A cross-head speed of 50 mm/min was used throughout these investigations to determine the ultimate tensile strength and modulus and the elongation at break for all the samples. The values quoted are the average of five measurements. The adhesion property was measured with the United Data System tension meter according to the ASTM D 1876-01 (the peel resistance of adhesives, i.e. the T-peel test). The values obtained were the average of five measurements (standard deviation was less than 5%).

## RESULTS AND DISCUSSION

The sample designation, composition and mean particle size of WBPU dispersions are given in Table I. The mean particle size of the dispersions is small in

PTAd-based WBPU (S1, S2) than that of PTMG-based WBPU (P1, P2) because of the presence of high polar ester group. The particle size of the dispersion of sample P2 and S2 is smaller than P1 and S1, respectively, because of more DMPA content.<sup>8,12</sup> It is well known that relatively larger particles are preferred in surface coatings for rapid drying, and smaller ones are desirable when the deep penetration of the dispersion into a substrate is essential. Almost smaller mean particle size of the dispersions prepared in this study indicated that these dispersions are applicable to adhesives with nylon fabrics.

The chemical structure of WBPU after mixed with hardener was characterized by  $^1\text{H-NMR}$  spectroscopy. The signals in the range of 0.76–0.85 ppm are complex and have been assigned to the E, F, G, H, I and E', F', G', H' protons (Fig. 2) of  $\text{H}_{12}\text{MDI}$ . The singlet at 1.19 ppm was due to the free methyl group of DMPA and TEA. The peak at 1.55 and 3.35 ppm can be ascribed to the polyol proton of B and A (Fig. 2) respectively. There were two peaks at 6.82

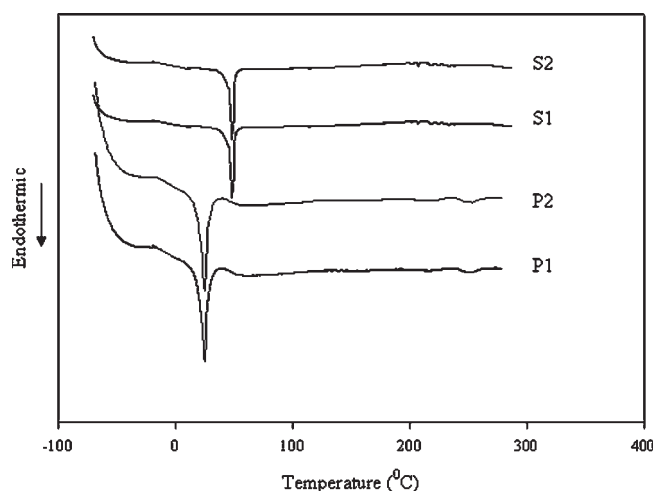


Figure 3 DSC curves of WBPU films.

and 6.86 ppm for urea and urethane respectively. The cured WBPU adhesives show newly formed allophanate and biuret bonds at 6.88 and 6.91 ppm, respectively, (Fig. 2). This implies that hardener NCO group reacts with urethane/urea group and results on crosslinked structure of WBPU. However, the peak for urethane and urea group is still remaining indicates that all of the urethane and urea group could not participate in reaction. Because of stearic hindrance, very small amount of urethane and urea group could form allophanate and biuret bonds.

The thermal properties of WBPU films were studied by differential scanning calorimetry (DSC). It was found that all of the samples showed significant endotherm melting peaks of soft segments (Fig. 3). PTAd based WBPU (S1, S2) show higher melting point (47°C) of soft segments than PTMG based WBPU (P1, P2) (25°C). However, the melting temperature of the soft segments of WBPU was almost

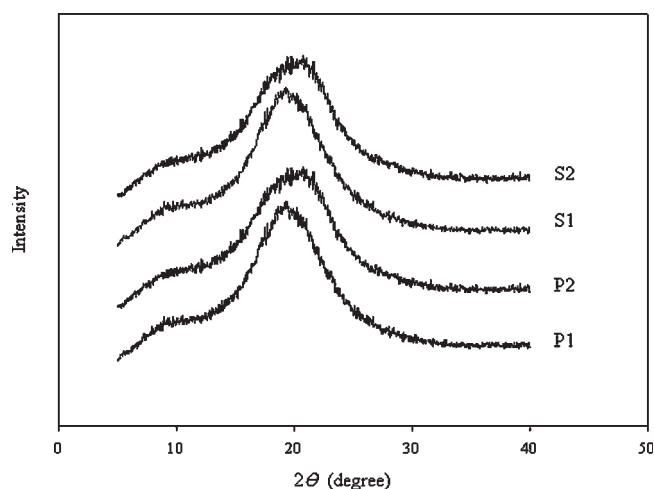


Figure 4 WAXD patterns of WBPU.

fixed with different DMPA content of same type of soft segment (PTMG/PTAd). This indicated that the phase mixing of soft segments with hard segments was almost not occurred. Moreover, the melting temperature of hard segments was not observed indicating the amorphous structure of hard segment region of WBPU prepared in this study.

X-ray diffraction patterns of WBPU containing different soft segments and DMPA contents are shown in Figure 4. Broad scattering halos near  $2\theta = 10^\circ$  and  $20^\circ$  are present in all samples, but the intensity is different with changing of DMPA content. Soft segments form crystalline structure in the segmented polyurethane due to their long order structure.<sup>13</sup> The DMPA content also influences the crystallinity of WBPU.<sup>14</sup> Therefore, in our study we recorded WAXD patterns of WBPU containing different soft segment and DMPA content to understand the influence of soft segment and DMPA content on WBPU structure. Though both of the polyols (PTMG and PTAd) have crystalline character, but here none of WBPU shows a sharp crystalline peak like pure polyol, and all samples shows broad haloes, that may be due to the amorphous structure or presence of small amounts of crystalline structure.<sup>15</sup> This is due to less soft segment content and high DMPA content. Moreover, the sample P2 and S2 is more amorphous than P1 and S1, respectively, which is due to the presence of more DMPA content. DSC results confirmed the endothermic peak of WBPU; therefore, the broad haloes all of the samples are due to the presence of small crystallites, which may be dispersed in the polymer matrix and could hardly be detectable by WAXD.

Figure 5 shows the stress-strain curves of WBPU. The mechanical properties of the films are summarized in Table II. The PTAd polyol based WBPU (S1, S2) show the high tensile strength and initial modu-

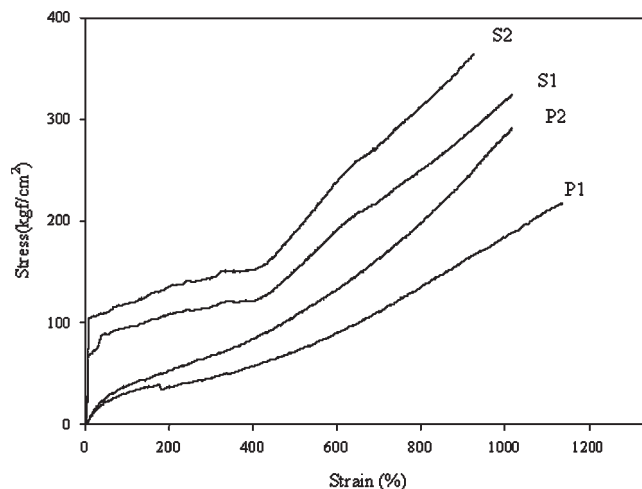


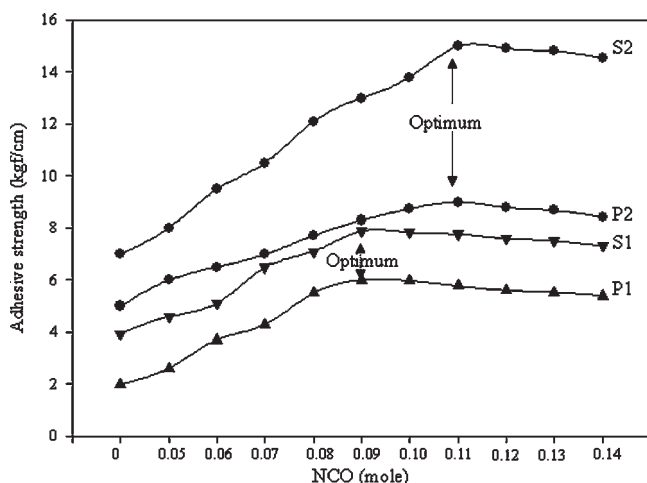
Figure 5 Stress-strain curves of WBPU films.

**TABLE II**  
Mechanical Properties of Waterborne Polyurethane Films

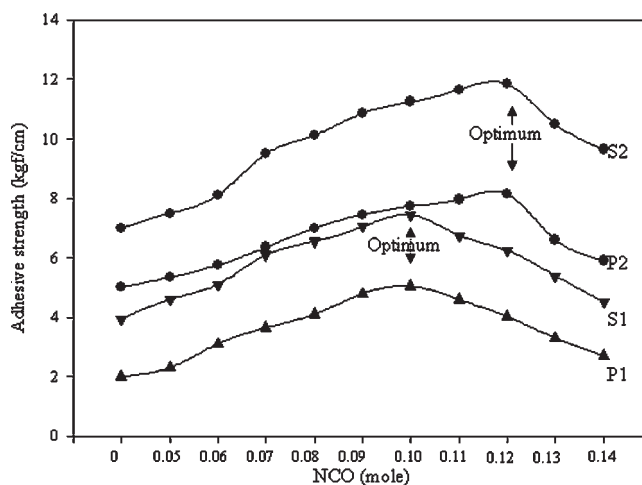
Sample designation	Tensile strength (kgf/cm <sup>2</sup> )	Initial modulus (kgf/cm <sup>2</sup> )	Elongation at break (kgf/cm <sup>2</sup> )
P1	218	27	1136
P2	291	36	1016
S1	324	340	1018
S2	364	426	926

lus than PTMG polyol based WBPU (P1, P2). This is due to more polar character of PTAd than PTMG which significantly increased the tensile strength and initial modulus of the film. DMPA content is also an important factor to increase the tensile strength. Generally, the tensile strength and initial modulus increased with increasing of DMPA content.<sup>8,12</sup> Because of to high DMPA content, the sample P2 and S2 show the high tensile strength and initial modulus than P1 and S1, respectively.

The NCO group of polyisocyanate hardener reacts with urethane and urea group of WBPU to form allophanate and biuret bond, which changed the structure of WBPU, linear to crosslinked and increased the adhesive force of WBPU material. It was found that the adhesive layer was torn instead of breaking the nylon fabric-adhesive interface for all samples. This indicates that the bond strength of WBPU adhesives mainly depend on the adhesive thin layer prepared from WBPU dispersion with hardener. The adhesive force could be increased by increasing the strength of the thin film in between the nylon fabrics. The types of hardener and its number ratio (molar ratio) of NCO group to urethane/urea group, on adhesive force of WBPU adhesive with nylon fab-

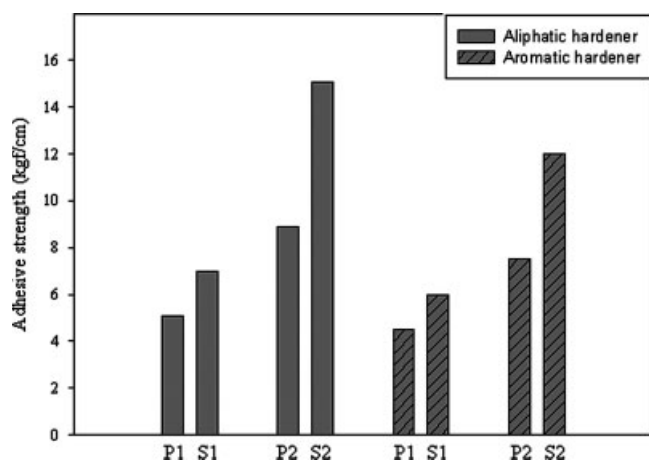


**Figure 6** Effect of NCO group (mole) of aliphatic hardener on adhesive strength of WBPU adhesive based on PTMG (P1, P2) and PTAd (S1, S2).



**Figure 7** Effect of NCO group (mole) of aromatic hardener on adhesive strength of WBPU adhesive based on PTMG (P1, P2) and PTAd (S1, S2).

ric is shown in Figures 6 and 7. The adhesive force significantly increased up to the optimum NCO content of hardener. The optimum number ratio (molar ratio) of NCO group is constant with two different types of soft segment (polyol) of WBPU at fixed urethane/urea group using aliphatic/aromatic hardener. However, the optimum number ratio (molar ratio) of NCO group to urethane/urea group was increased with increasing of urethane/urea group. Moreover, the optimum number ratio (molar ratio) of NCO group is different for two different types of hardener with constant urethane/urea group. It was found that the number ratio (molar ratio) of aliphatic hardener NCO to urethane/urea was about 0.010 to reach the highest adhesion force of WBPU adhesives. This indicated that almost 3% of urethane/urea group of WBPU could participate in crosslinking reaction with hardener NCO group. However, the optimum molar ratio of aromatic hardener NCO group was increased at same urethane/urea content (0.011). There are two possible reasons to increase the hardener content. Either it could react more with urethane/urea group or participate more side reactions. We used 40 wt % solid content of WBPU. When NCO group is attached with aromatic group then its reactivity increases with not only to urea/urethane group but also water in WBPU dispersion. As a result, more carbamic acid formed which is very unstable and finally it converted to carbon dioxide and urea. This urea further participate reaction with NCO group. Therefore, more NCO group is needed and optimum NCO content subsequently increased. Using aliphatic hardener, the carbon dioxide and urea formed is less due to less reactivity of NCO group with water. However, the adhesive strength is low using aromatic hardener than aliphatic hardener at optimum number ratio (molar ra-



**Figure 8** Comparison of the adhesive strength of different samples [PTMG based samples (P1, P2) and PTAd based samples (S1, S2)] with aliphatic and aromatic hardener.

tio) of NCO content to fixed urethane/urea group. The carbon dioxide entrapped in the adhesive layer forming some gaps or voids with possible detrimental effects on the interface strength and decreased the adhesive strength.<sup>16</sup> Excess polyisocyanate hardener decreased the adhesive strength little in both cases. This might be due to the increase of voids in the adhesive layer as well as low molecular weight molecules.

The optimum number ratio of NCO group (molar ratio) to urethane/urea is almost same at fixed DMPA content in PTMG and PTAD based-WBPU adhesives. But, the effect of hardener to increase the adhesive force of WBPU based on different polyol (PTMG/PTAd) is different. The PTAd polyol-based WBPU (S series) show high adhesive strength than PTMG polyol-based WBPU (P series) (Fig. 8). This is due to highly polar nature of the PTAd soft segment and strong mechanical interlocking of polyester-based WBPU adhesive. The highest adhesive strength among all of the samples was obtained by mixing of aliphatic hardener with PTAd polyol based WBPU which contain maximum number ratio of NCO group (molar ratio) (S2).

## CONCLUSIONS

The adhesive force of WBPU increased with increasing of hardener content up to the optimum point and then decreased. The optimum number ratio of (molar ratio) of NCO group of hardener to urethane/urea group (DMPA content) depends on the hardener types and DMPA content in WBPU. Optimum hardener content increased with increasing of DMPA content (urethane/urea group). At fixed DMPA content (urethane/urea group) the optimum hardener content decreased using aliphatic hardener than aromatic hardener. However, the aliphatic hardener increased more adhesive force than aromatic hardener at optimum number ratio of (molar ratio) NCO group to urethane/urea group. PTAd polyol based WBPU show higher adhesive force than PTMG polyol based WBPU, at the optimum number ratio of NCO group (molar ratio) to urethane/urea group, using, aliphatic, and aromatic hardener.

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