

Effect of Polyisocyanate Hardener on Waterborne Polyurethane Adhesive Containing Different Amounts of Ionic Groups

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Abstract: Waterborne polyurethane (WBPU) adhesive with varying amounts of dimethylol propionic acid (DMPA) was synthesized by prepolymer process and blended with polyisocyanate hardener. The mean particle size of the WBPU dispersion decreased with increasing DMPA content. ¹H NMR spectroscopy confirmed the formation of allophanate bonds and biuret bonds due to the reaction of hardener NCO with urethane/urea groups. The optimum NCO content with the greatest adhesive strength was dependent on the total content of urethane/urea groups in the WBPU molecules. The optimum NCO content increased with increasing number of urethane groups (DMPA content). The adhesion strength of WBPU adhesives was maximized at a molar ratio of hardener NCO to urethane/urea of about 0.28.

Keywords: waterborne polyurethane, hardener, adhesive strength.

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. In recent years, significant emphasis has been placed on the use of WBPU dispersions due to their health and environmental safety.¹⁻⁷

In the past few decades, much effort has been given on solvent based polyurethane adhesive⁸⁻¹⁶ which is now being restricted due to high solvent content. However, very few studies on WBPU adhesive, which is environment friendly, can be found in the open scientific literature. Kim and Kim¹⁷ studied different polyester based polyol of WBPU to their adhesive strength. Yang *et al.*¹⁸ studied different types of neutralizing agents on polycaprolactone based WBPU to their adhesive strengths. Rahman and Kim¹⁹ studied the effects of dimethylol propionic acid (DMPA) on their adhesive strength and showed adhesive strength increased with increasing DMPA content. Kwon and Kim²⁰ used different HMMM content to crosslink with WBPU to increase the adhesive strength. However the polyisocyanate hardener

which is used in many industrial coatings and adhesive applications has not been investigated widely in WBPU adhesives. The majority of studies have been made in industrial laboratories, so they have not been published in the literature.

It is usual to add very little amount of polyisocyanate hardener, but the influence of polyisocyanate hardener content on the adhesion of WBPU adhesive has not been considered yet. Study on the optimum molar ratio of hardener NCO to urethane/urea group for obtaining the high adhesive strength of WBPU adhesives can also hardly found. Therefore, in this study, we used various NCO content (0~5 mole) of hardener with synthesized WBPU which have different amount of DMPA, in order to find the optimum NCO content of hardener with respect of adhesive strength.

Experimental

Materials. Polytetramethylene oxide glycol (PTMG number-average molecular weight = 2,000 g/mol; Aldrich Chemical) was dried at 90 °C and 1-2 mmHg for 3 h before use. Dimethylol propionic acid (DMPA, Aldrich Chemical, Milwaukee, WI), Tri-ethyl amine (TEA; Junsei Chemical, Tokyo, Japan), *N*-methyl-2-pyrrolidone (NMP; Junsei Chemical), 4,4-dicyclohexylmethane diisocyanate (H₁₂MDI, 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 (ARF

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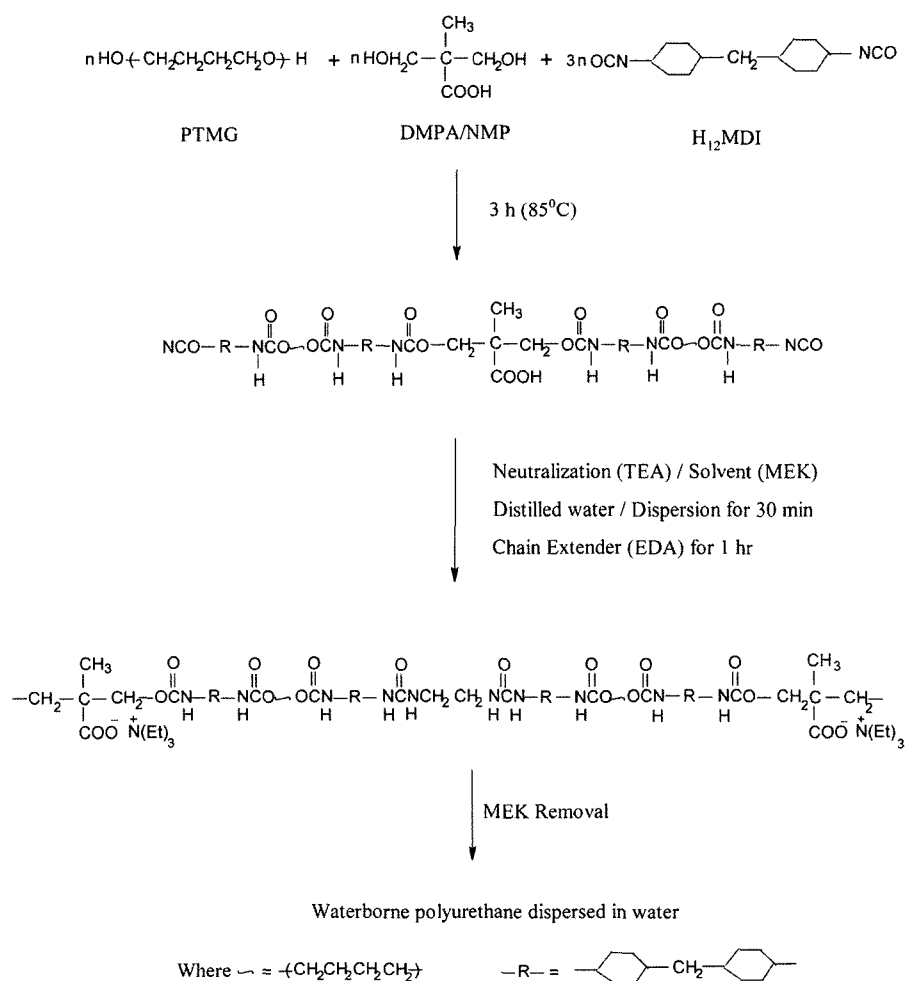
30) were used without further purification. NCO content in the hardener is 20%.

Synthesis of the Waterborne Polyurethanes. The WBPU were synthesized with the prepolymer mixing process (Scheme I). PTMG 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, H₁₂MDI 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 PU prepolymer. After 30 min of neutralization, distilled water (60 wt%) was added to the reaction mixture with vigorous stirring (1,300~1,500 rpm). The neutralized prepolymer was chain-extended by the dropping of EDA at 40°C for 1 h, and the reaction continued until the NCO peak (2270 cm⁻¹) in the IR spectra had completely disappeared. All the WBPUs (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 which was cured at 100°C. The films (typically about 0.5 mm thick) were dried in vacuum at 50°C for 1 day and stored in a desiccator at room temperature. WBPU adhesive materials were formulated from WBPU, a thickener (L75N, 0.5 wt%), and a polyisocyanate hardener (ARF 30, NCO content in the hardener is 20%) which was stirred at (200~250 rpm) at room temperature about 6 h. The WBPU adhered material was coated on the nylon fabrics and another nylon fabric was laid on the coated surface



Scheme I. The preparation process for waterborne polyurethane.

and then dried at 100 °C under certain pressure (15 kgf/cm²) for 10 min.

Characterization. The mean particle size of the WBPU dispersion was measured using laser-scattering equipment (Autosizer, Melvern IIC, Malvern, Worcester, UK). A small amount of aqueous dispersion was added in a deionised water tank and this was followed by the pinhole being set at 200 μ m. The average particle diameters were measured at 25 °C. ¹H-NMR spectra of the polyurethane ionomers were recorded on Varian Unity Plus 300 spectrometer operating at 300 MHz. 30 mg polyurethane ionomer was dissolved in 4 mL of deuterated chloroform. TMS was used as an internal reference. Thermal gravimetry analysis was performed in a Pyris 6 TGA (Perkim Elmer, USA). 5.0 mg polyurethane ionomer films were placed in a platinum pan and heated from 30 to 500 °C under nitrogen gas, at a heating rate of 10 °C/min. The tensile properties were measured at room temperature with a United Data System tension meter (SSTM-1 United Data Systems, Instron, Japan) according to the ASTM D 638 specifications. A crosshead 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

Particle Size. Sample designations and compositions of WBPU adhesive is given in Table I. The mean particle size of the WBPU dispersions containing different amount of DMPA has been shown in Figure 1. The mean particle size was decreased with increase of DMPA content.²¹ Though the mean particle size is not directly related to the physical properties of WBPU cast films, but the control of the mean particle size is important with respect to the particular application of WBPU dispersion. It is well known that relatively larger particles are preferred in surface coatings for rapid drying, and smaller ones are desirable when the deep pene-

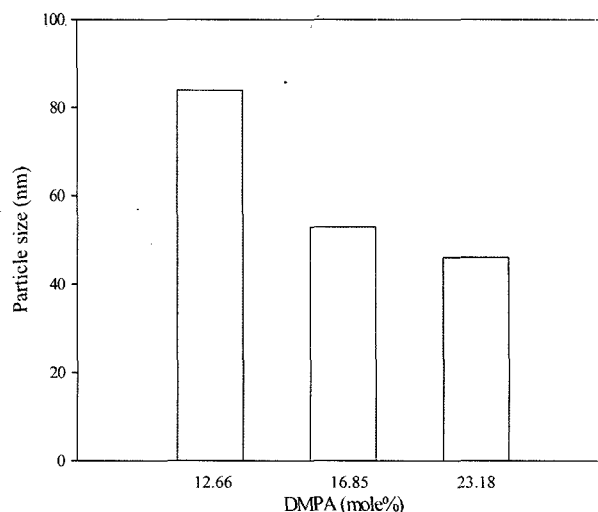


Figure 1. Relationship of particle size with DMPA of WBPU adhesives.

tration of the dispersion into a substrate is essential. The lower mean particle size in all of the dispersion prepared in this study indicated that these dispersions were applicable to adhesives with nylon fabrics.

Identification. The ¹H NMR allows a complete description of the structure of the cured WBPU adhesive which has been shown in Figure 2. 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 (Figure 2) of H₁₂MDI. 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 (Figure 2) respectively. There were two peaks at 6.82 and 6.86 ppm for urea and urethane respectively. The downfield 6.86 ppm is assigned to the -NH group in the urethane unit since the -NH group is attached to the carboxylic group. Using hardener, the new peaks appeared at 3.58, 3.74, 6.88, and 6.91 ppm which indicate some new bond formed by cross-linking of hardener NCO group with urethane and urea bond of polyurethane at high cured temperature 100 °C. Namely these peaks at 6.88 and 6.91 ppm were due to the allophanate and biuret bond respectively. Besides, the peak at 3.58 and 3.74 ppm were due to the proton of hardener. However, the unreacted urethane bond and

Table I. Sample Designation and Composition of WBPU Adhesive

Sample Designation	Composition (mole)					DMPA		Urethane/Urea (mole)	NCO (mole)	Optimum Hardener NCO (mole)	Optimum Molar Ratio*
	PTMG	DMPA	H12MDI	TEA	EDA	mol%	wt%				
P1	4.0	2.0	7.9	2.0	1.9	12.66	2.52	7.9	
P2	4.0	3.0	8.9	3.0	1.9	16.85	3.61	8.9	0/0.5/1/1.5/2/2.5/3/4/5	2.5	0.28
P3	4.0	5.1	11.0	5.1	1.9	23.18	5.53	11.0		3.0	0.27

*Hardener NCO mole
Urethane/Urea mole

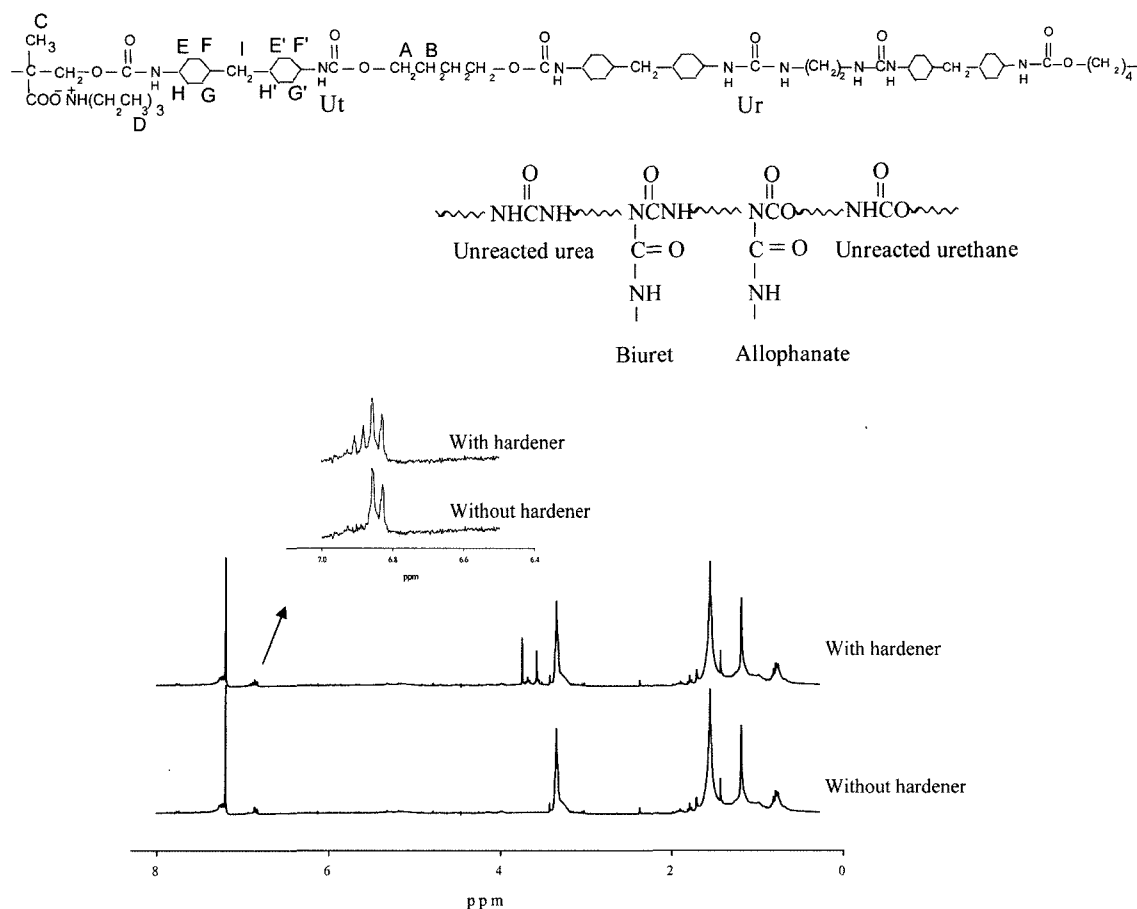


Figure 2. ^1H NMR spectra of the typical WBPU adhesive sample P3 containing optimum hardener and without hardener.

urea bond at 6.82 and 6.86 ppm respectively remained after curing. This indicated that all of the urethane and urea bonds couldn't react with hardener. Maybe this is due to the steric hindrance of crosslink structure of WBPU adhesives.

Thermal Property. The thermal resistance of the polyurethane ionomers was analyzed by TGA that has been shown in Figure 3. In a nitrogen atmosphere all TGA curves display a slower initial and then a more rapid degradation process, suggesting a two-step mechanism for degradation. It was found that the degradation temperatures decreased with increasing DMPA content. This indicates that the thermal stability of WBPU decreases due to the increase of COOH groups DMPA. From the TGA curves, it was found that degradation was comparatively slow in the solid polymers, indicating that they are reasonably stable up to their degradation points. The low thermal stability and two step mechanisms in nitrogen atmosphere were also reported by other.²² The increase of the DMPA content produces a slight decrease of the degradation temperature. This is due to the films low degradation temperature of urethane groups.

Mechanical Property. Figure 4 shows the stress-strain curves for waterborne polyurethanes with various DMPA

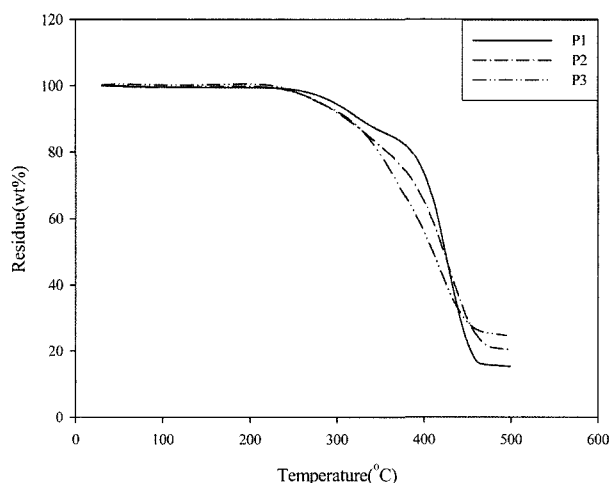


Figure 3. TGA thermographs of WBPU adhesive.

contents. As the DMPA content increased, the tensile strength, and initial modulus of the polyurethane ionomer films significantly increased but the elongation at break decreased a little that has been summarized in Table II. These show that

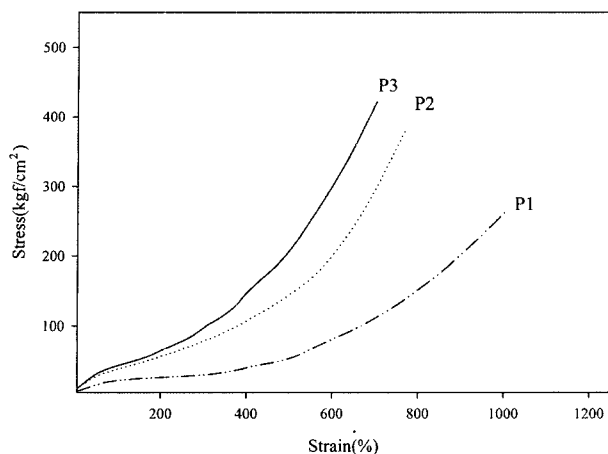


Figure 4. Stress-strain curves of WBPU adhesives.

Table II. Mechanical Properties of WBPU Adhesives

Sample Designation	Tensile Strength (kgf/cm ²)	Initial Modulus (kgf/cm ²)	Elongation at Break (%)
P1	264	2.95	1005
P2	384	29.25	774
P3	422	35.80	705

the mechanical properties of the polyurethane ionomers are highly dependent on the DMPA content, which agreed well with the previous work.^{19,21} Both confirmed that the tensile strength and initial modulus increased with increased of DMPA content, same behavior also observed here.

Adhesive Strength. It is well-known that hardener NCO group reacts with urethane and urea bond to form allophanate and biuret bond, which convert the WBPU linear structure to crosslinked structure and increase the strength of WBPU material. The effect of the hardener NCO content on adhesive strength of WBPU adhesive with nylon fabric was studied (Figure 5). It was found that the adhesive layer was torn instead of breaking the nylon fabric-adhesive interface for all samples. The adhesive strength significantly increased up to the optimum NCO content and then little decreased. However, the sample P1 having low DMPA content had very low adhesive strength. And it was very difficult to find the distinct optimum NCO mole of P1 sample. The optimum NCO mole increased with increasing of urethane bonds (DMPA content). The optimum NCO moles were 2.5 and 3.0 mole with respect of adhesive strength for P2 and P3 respectively. From these results, it was found that the molar ratio of hardener NCO to urethane/urea was about 0.28 to reach the highest adhesion strength of WBPU adhesives. This indicated that about 28% of urethane/urea groups could participate in crosslinking reaction with hardener NCO group. Moreover excess polyisocyanate hardener decreased the adhesive strength little. This might be due to the increase of low molecular weight molecules by adding excess hardener.

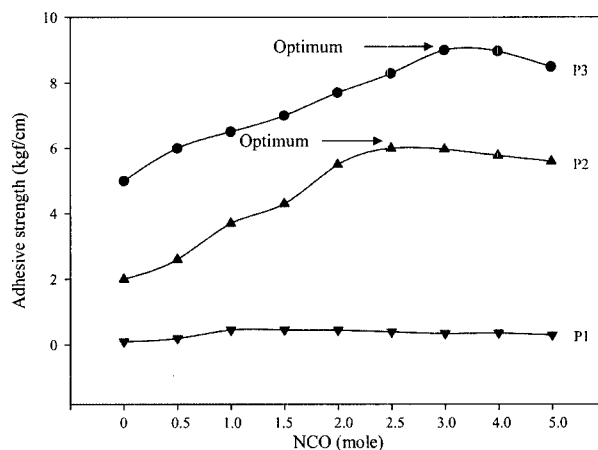


Figure 5. Adhesive strength of WBPU adhesive with various NCO groups.

Conclusions

Optimum NCO content which had the highest value of adhesive strength was depending on the DMPA content in WBPU adhesive. It was found that the optimum NCO content was increased with increasing DMPA content. NMR spectroscopy confirmed some allophanate and biuret bond formed in WBPU adhesive when it mixed with polyisocyanate and cured at 100 °C. This allophanate bond and biuret bond makes linear WBPU adhesive to crosslink structure and increase the adhesive strength. It was found that about 28% of urethane/urea group can participate in reaction with hardener NCO group.

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