

Synthesis and Characterization of Waterborne Polyurethane Adhesives Containing Different Amount of Ionic Groups (I)

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ABSTRACT: A series of waterborne polyurethanes (WBPU) containing different amount of 2,2-bis(hydroxymethyl) propionic acid (DMPA) were synthesized using prepolymer mixing process. Relationships between the DMPA content and physical, mechanical, and thermal properties as well as adhesive behavior at different condition were investigated. Stable aqueous dispersions of WBPU were obtained when the DMPA content was more than 10 mol %. At higher DMPA content, the particle size of the WBPU dispersion was lower but the viscosity of the dispersion was higher. Water swelling and tensile strength of the films increased with increasing of DMPA content. The optimum adhesive strength of WBPU adhesives was

found to be depended on the DMPA content, pressing temperature, and pressure on adhesion process. The adhesive strength of WBPU adhesives increased with increasing DMPA content. The optimum pressing temperature decreased with increasing DMPA content. The adhesive strength of WBPU adhesives increased with increasing pressure up to 15 kg f/cm² and then leveled off. The optimum pressing temperature of WBPU adhesives samples containing 24.02, 22.05, and 17.05 mol % DMPA was about 100, 120, and 140°C, respectively. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5684–5691, 2006

Key words: waterborne polyurethanes; adhesive

INTRODUCTION

The waterborne polyurethane (WBPU) formulation has been attracted much more due to environmental consideration. The preparation of WBPU is free from emission of organic volatile solvent, as a result the atmosphere is saved from pollution.^{1–4} Besides, WBPU has received considerable attention in the past few decades due to its tremendous usefulness in coatings and adhesives for various substrates.^{5,6} Their application includes areas such as construction, automotive, packing, transportation, electronics, textiles, tape, paper, and footwear.^{7,8}

One important feature of polyurethane ionomers is their ability to disperse or dissolve in water if a sufficient amount of ionic moiety is incorporated, which is a great advantage over conventional solvent borne polyurethane.^{1,9} It is well recognized that a minimum ionic content is required for the formation of a stable polyurethane ionomer, depending on the type of the ionic species. In addition, the interaction between ions and their counter ions is responsible for the effect on their properties. The degree of neutralization and content of ionic component has very significant effect to the properties of an ionomer.^{3,10} Yang et al. investi-

gated the particle size and mechanical properties of WBPU dispersion at different degree of neutralization using triethylamine and mixture of ammonium hydroxide and cupric hydroxide as neutralizing agent. The particle size decreased with increasing degree of neutralization. The fully neutralized WBPU dispersion using triethyl amine shows better mechanical properties, whereas mixture of ammonium hydroxide and cupric hydroxide shows less mechanical properties at same condition.¹⁰ Yang et al. also showed that the WBPU dispersion containing triethyl amine give better adhesive strength than sodium hydroxide or cupric acetate used as a neutralizing agent.¹¹

A lot of work has already been done in solvent based polyurethane adhesives.^{12–20} Sánchez-Adsúar et al. showed the adhesive strength increased with increased of high hard/soft segment ratio.¹² Nakamae et al. studied on different hard segment content and incorporated high amount of carboxyl group to increase the adhesive strength on aluminum plates.^{18,20} But the literature dealing with the synthesis and characterization of WBPU dispersion and its application in adhesion is relatively low and the majority of studies have been made in industrial laboratories, so they have not been published in the open scientific literature.

Therefore, the aim of this study is to investigate the thermophysical properties as well as adhesive strength of WBPU dispersion to contribute to the scarce litera-

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ture of WBPU adhesives. We synthesized a series of WBPU dispersion by changing 2,2-bis(hydroxymethyl) propionic acid (DMPA) content (5–25 mol %). At fixed poly (tetramethylene oxide) glycol (PTMG) ($M_n = 2000$) and ethylene diamine (EDA), the DMPA and 4,4-dicyclohexylmethane diisocyanate (H_{12} MDI) were raised. We focused the behavior of DMPA on stability, particle size and viscosity of WBPU dispersions and the water swelling and mechanical and thermal properties of cast films. Finally, we used these WBPU dispersions as adhesive on nylon fabrics at different condition. For this purpose, we changed the pressing temperature (80, 100, 120, and 150°C) and pressure (5, 10, 15, 20, and 25 kg f/cm²) during adhesive preparation. The adhesive test was conducted at room temperature and different elevated temperatures as 80, 100, 120, and 150°C. At elevated testing temperature, the specimen was set up at specific temperature and retained for 10 min at that temperature, after then the adhesive test was conducted.

EXPERIMENTAL

Materials

PTMG (number-average molecular weight = 2000 g/mol; Aldrich Chemical) was dried at 90°C and 1–2 mmHg for 3 h before use. DMPA (Aldrich Chemical, Milwaukee, WI), Tri-ethyl amine (TEA; Junsei Chemical, Tokyo, Japan), *N*-methyl-2-pyrrolidone (NMP; Junsei Chemical), H_{12} MDI (Aldrich Chemical), and EDA (Junsei Chemical) were used after dehydration with 4-Å molecular sieves for 1 week. Dibutyltin dilaurate (Aldrich Chemical), a thickener (L75N, Bayer, Leverkusen, Germany), and hardener (Desmodur DA, Bayer), were used without further purification.

Synthesis of the waterborne polyurethanes

The waterborne polyurethanes (WBPU) were synthesized with the prepolymer mixing process.²¹ 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, 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 PU 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 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 films

WBPU films were prepared by pouring the aqueous dispersion on a Teflon disk under the ambient conditions for 48 h. 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 adhered materials were formulated from WBPUs, a thickener (L75N, 0.5 wt %), and a hardener (Desmodur DA, 5.0 wt %). The WBPU adhered material was coated on the nylon fabrics, and another nylon fabric was laid on the coated surface and then dried at different temperatures (80, 100, 120, and 150°C) under various pressing conditions (5, 10, 15, 20, and 25 kg f/cm²) for 10 min.

Characterization

The mean particle size of the WBPU dispersion was measured using laser-scattering equipment (Auto-sizer, 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 μm. The average particle diameters were measured at 25°C. The viscosity of the WBPU dispersions was measured at 25°C with a Brookfield (MA) LVDV-II+ digital viscometer, Brookfield, Middleboro, MA. The spindle number and speed rate of the spindle was 4 and 100 rpm, respectively.

A Fourier transform infrared spectrometer (Impact 400D, Nicolet, Madison, WI) was used to identify the WBPU structure. The dispersion sample was coated as a thin liquid film and dried for examination. For each IR spectrometer sample, 32 scans at a 4 cm⁻¹ resolution were collected in the transmittance mode.

¹H-NMR and ¹³C-NMR spectra of the polyurethane ionomers were recorded in a Fourier transform Bruker 300 MHz spectrometer model AC-300. Thirty milligrams of polyurethane ionomer was dissolved in 4 mL of deuterated chloroform. TMS was used as internal reference.

For swelling test of WBPU cast films in water, the films were immersed in water for 48 h at 30°C and the

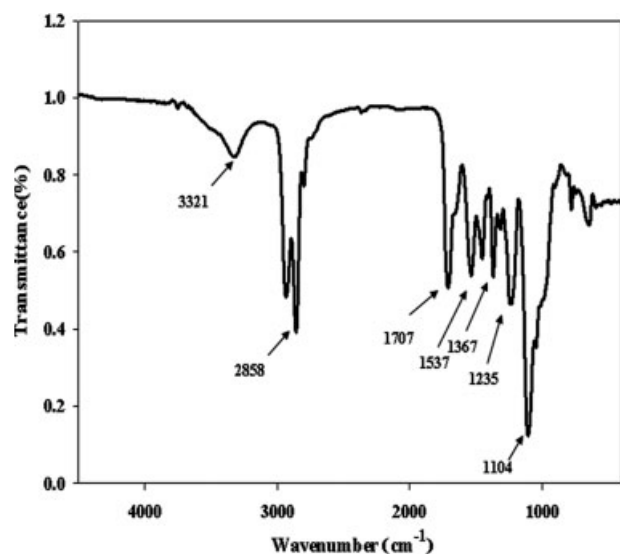


Figure 1 FT-IR spectra of the polyurethane ionomer containing 13.78 mol % DMPA.

(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).

RESULTS AND DISCUSSION

WBPUs having various DMPA contents were synthesized by prepolymer mixing process in this study illustrated in Scheme 1.²¹ The moles of PTMG (number-average molecular weight = 2000 g/mol)

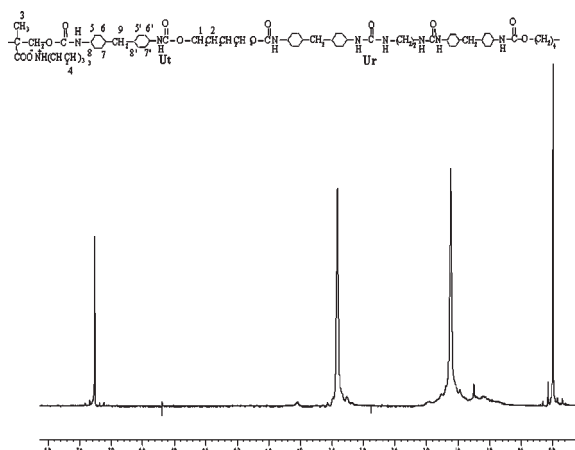


Figure 2 ¹H-NMR spectra of the polyurethane ionomer containing 13.78 mol % DMPA.

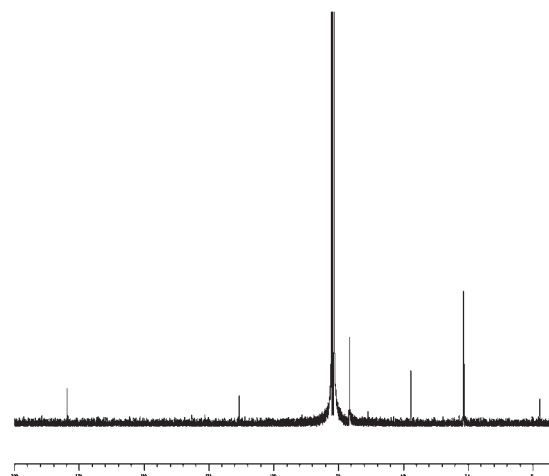


Figure 3 ¹³C-NMR spectra of the polyurethane ionomer containing 13.78 mol % DMPA.

and EDA were kept constant, whereas the moles of DMPA (4.88–24.02 mol %) and H₁₂MDI were raised; this provided higher hard-segment and salt-group contents. Therefore, the hard-segment content was varied in the range of 19.26–32.26 wt % at a fixed soft-segment length (2000 g/mol). The solid content of WBPUs prepared in this study was fixed at 40 wt %.

The sample designations, compositions, DMPA and hard-segment contents, and stability of WBPUs synthesized in this study are shown in Table I. The stability of the WPU dispersion was based on phase separation of the dispersion and physical changes of the prepared film. It was found that samples P1 and P2, containing lower contents of DMPA (< 10 mol %), were not stable, but samples P3, P4, P5, P6, and P7 having higher contents of DMPA (12.12–24.02 mol %), were stable after 4 months. The WPU dispersion of samples P1 and P2 are totally separated into two phases within 10 days. Besides the film of the two samples are softened within 1 week. But other WPU dispersion samples (P3, P4, P5, P6, and P7) showed no phase separation even after 4 months which indicated the stability of the dispersion. The film obtained from

TABLE II
Assignment of ¹H-NMR and Chemical Shift of Waterborne Polyurethane Ionomers

Assignment	Chemical shift (ppm)
NH(Ut) ^a	7.2
NH(Ur) ^b	7.1
H1	3.40
H2	1.65
H3 + H4	1.25
H5 ~ H8	1.0 ~ 1.2
H5' ~ H8	
H9	3.27

^a Ut = Urethane.

^b Ur = Urea.

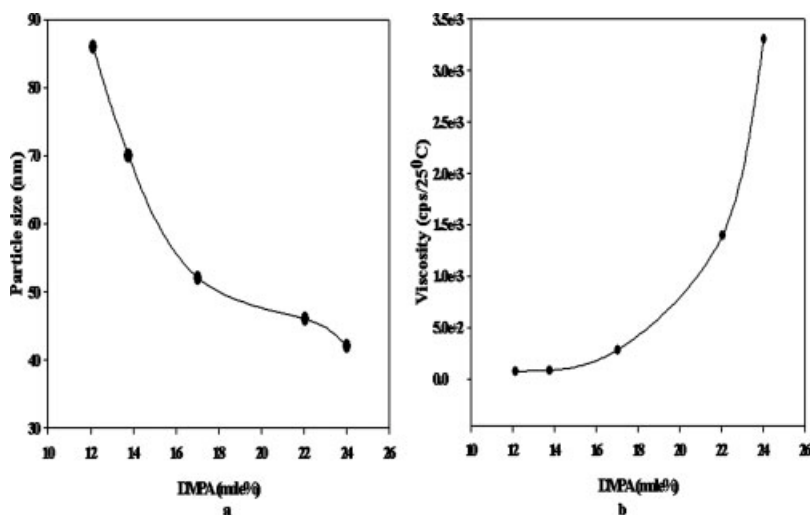


Figure 4 Effect of the DMPA content on the particle size (a) and the viscosity (b) of waterborne polyurethane dispersions.

those samples not softened in 4 months. This behavior indicated that the stability of the aqueous dispersions of WBPU was primarily dependent on the content of the hydrophilic ionic component DMPA.

The WBPU were identified by characteristic IR and NMR peaks. Figure 1 shows the characteristic IR peaks, such as the N-H stretching vibration peak near 3321 cm^{-1} and the C=O peak 1707 cm^{-1} . The ^1H -NMR and ^{13}C solution NMR spectra of WBPU in CDCl_3 at room temperature are shown in Figures 2 and 3, respectively. The chemical shift assignments are listed in Table II. There exist two kinds of —NH groups in the polymer: one is in the urethane unit and the other is in the urea unit. The 1H peak at 7.1 ppm is assigned to the —NH group of the urea unit. The downfield 7.2 ppm is assigned to the —NH group in the urethane unit since the —NH group is attached to the carboxylic group. The ^{13}C peaks appearing at 178.10 and 178.75 ppm is assigned to the carbonyl carbons in the urea and urethane groups, respectively. Beside 47.6 ppm for the *tert*-carbon of DMPA is appeared.

The effects of the DMPA content on the mean particle size and viscosity of the WBPU dispersions are shown in Figure 4. Previous studies^{22–26} have demonstrated that increase in the ionic group content increases the viscosity of the polyurethane dispersion. By increasing the DMPA content, the mean particle size decreased from ~ 86 to 42 nm , but the viscosity increased from 75 to 3302 cps at 25°C . This happened due to an increase of the hydrophilic structure through the addition of more salt groups and urethane linkages. The viscosity of the WBPU was governed by the hydrophilicity and some external factors such as the shear force and temperature. An increasing amount of ionic groups in a dispersion leads to smaller particles and hence more particles. Generally, smaller particles lead to larger hydrodynamic vol-

umes and, therefore, induce higher viscosities.^{2,27} However, depending on the specific application, an optimum mean particle size and viscosity exist, and so it is important to be able to control these values via the chemical composition. It is generally known that the mean particle size is not directly related to the physical properties of WBPU cast films. However, the control of the mean particle size is important with respect to the particular application of WBPU dispersion. For example, 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. The lower mean particle size of the WBPU dispersions prepared in this study indicated that these dispersions were applicable to adhesives for various substrates.

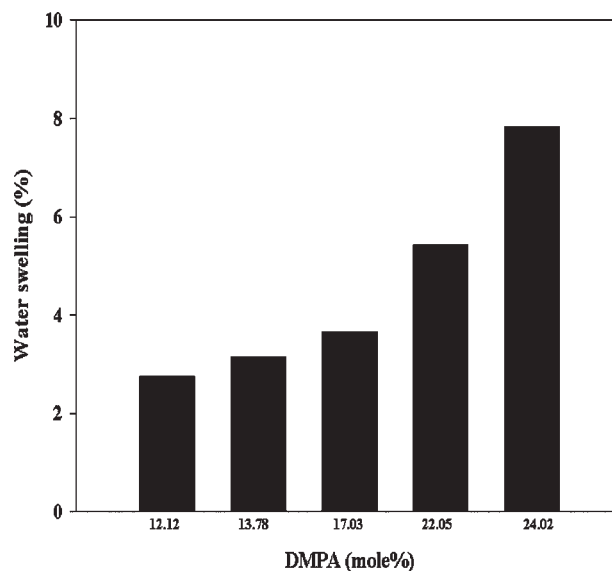


Figure 5 Effect of the DMPA content on water swelling of waterborne polyurethane films.

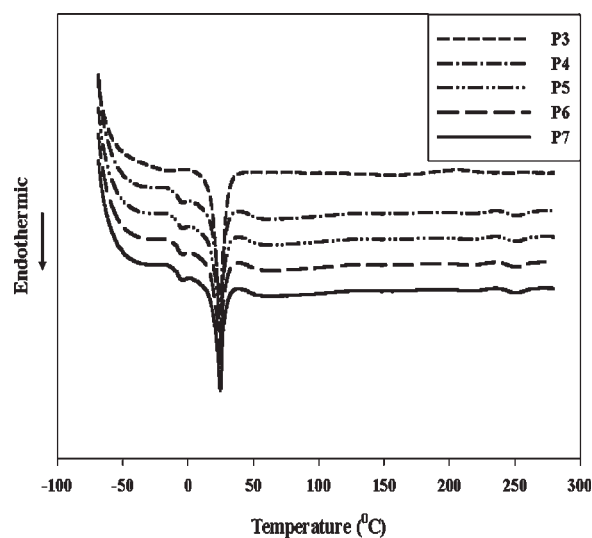


Figure 6 DSC curves of waterborne polyurethane films.

The water swelling of WBPU cast films are shown in Figure 5. With increasing of DMPA content, the water swelling of WBPU films also increases due to the enhancement of hydrophilic ionic DMPA moieties and urethane groups.

The thermal properties of the polyurethane ionomers containing PTMG ($M_n = 2000$ g/mol) as a soft segment were studied by differential scanning calorimetry (DSC). This analysis (Fig. 6) showed that the melting temperature of the soft segments near to 25°C was almost not changed with the DMPA content. This indicated that the phase mixing of soft segments with hard segments was almost not occurred. However, the melting temperatures of hard segments were almost not observed indicating the amorphous structure of hard segment region of WBPU prepared in this study.

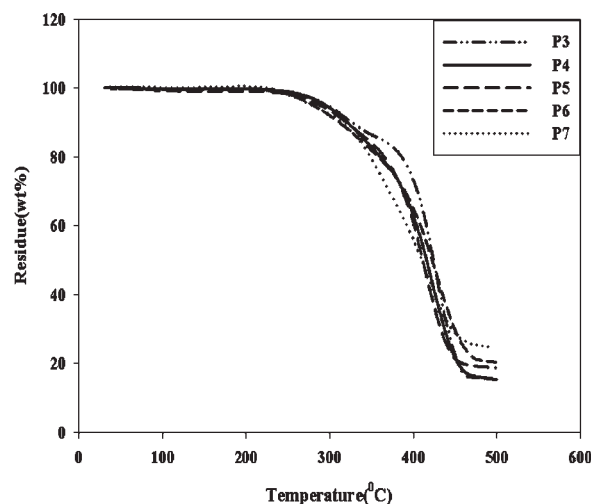


Figure 7 TGA thermographs of waterborne polyurethane films.

TABLE III
Temperature for 10% and 40% Weight Loss of Typical Waterborne Polyurethane Films Samples

Sample designation	Temperature at 10% weight loss	Temperature at 40% weight loss
P3	326.01	418.58
P4	321.75	405.38
P5	320.89	400.00
P6	313.52	396.00
P7	304.07	394.72

The thermal resistance of the polyurethane ionomers was analyzed by TGA that has been shown in Figure 7. 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.²⁸ 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. Table III shows the temperatures at 10 and 40% weight loss for typical WBPU film samples.

Figure 8 shows the stress-strain curves for WBPU with various DMPA 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 IV. These show that the mechanical properties of the polyurethane

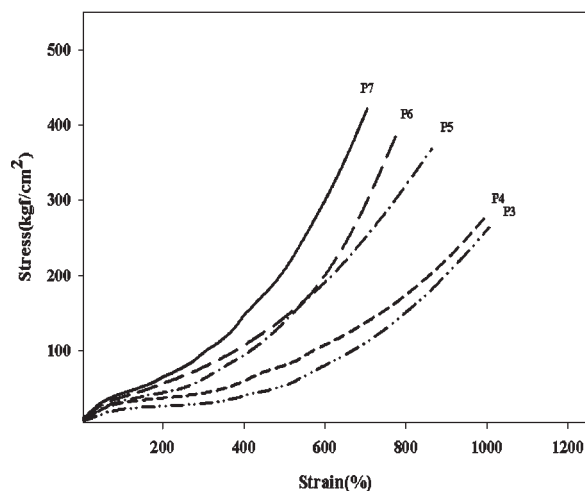


Figure 8 Effect of the DMPA content on the stress-strain curves of waterborne polyurethane films.

TABLE IV
Mechanical Properties of Waterborne Polyurethane Films

Sample designation	Tensile strength (kgf/cm ²)	Initial modulus (kgf/cm ²)	Elongation at break (%)
P3	264	2.95	1005
P4	276	5.21	994
P5	368	20.25	864
P6	384	29.25	774
P7	422	35.80	705

ionomers are highly dependent on the DMPA content, which agreed well with the previous work.²⁶ Kwak et al. in previous work showed that the tensile strength and initial modulus increased with increased of DMPA content, same behavior also observed here.

Figure 9 shows the relationship between the pressing temperature and the adhesive strength of WBPU dispersions with various DMPA content when the testing condition was room temperature. As the pressing temperature increased, the adhesive strength of each WBPU sharply rose up to a maximum strength and then decreased. There exists an optimal pressing temperature for high adhesive strength for each WBPU. Beyond the optimum pressing temperature, the adhesive strength dropped abruptly down with the increase in pressing temperature. The optimal pressing temperature (maximum adhesive strength temperature) decreases with the increase in DMPA content for high adhesive strength. It was found that the optimum pressing temperature of WBPU adhesives samples P7, P6, and P5 containing 24.02, 22.05, and 17.05 mol % DMPA was about 100, 120, and 140°C, respectively. The sample P3 has no significant adhesive strength due to very low amount of DMPA content (12.12 mol %). The sample P4 containing 13.78 mol % DMPA has lower adhesive strength, whereas

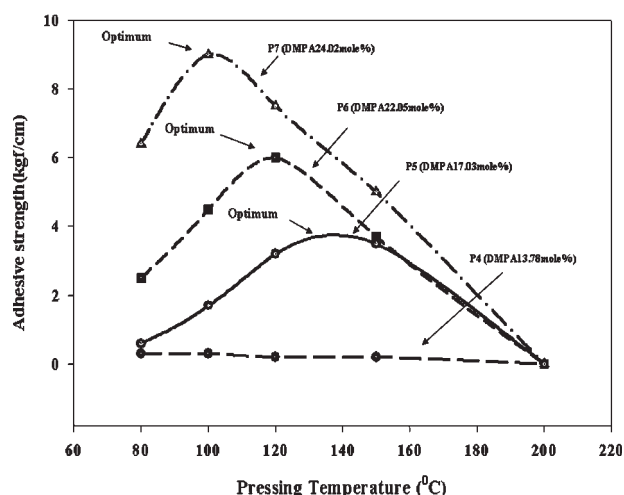


Figure 9 Relationship between the pressing temperature and adhesive strength of waterborne polyurethanes having various DMPA content.

P7 containing 24.02 mol % DMPA has greater adhesive strength. May be this is a tough job of formation of hydrogen and ionic bonds of hard segments at below or above the optimum temperature. In case of higher DMPA content the association of hard segments would be easier, therefore the optimum condition was shown at lower temperature. From this result, it was found that the best condition (the optimum temperature) of association of hard segments was dependent on the ionic moiety DMPA content in WBPU.

Figure 10 shows the effect of pressure of adhesion process on the adhesive strength of WBPU adhesives containing higher DMPA content (P5, P6, and P7). We fixed the optimal pressing temperature for each sample and changed the pressure during adhesive process. Initially the adhesive strength increased with increased of pressure, after then it does remain almost unchanged at about 15 kg f/cm² for various pressure and pressing temperatures 100, 120, and 150°C for P7, P6, and P5, respectively. From this result it is concluded that the optimum pressure of WBPU adhesives containing higher DMPA content at various pressure and temperatures (100, 120, and 150°C) was about 15 kg f/cm².

Figure 11 shows the behavior of adhesive strength when the testing condition was different (at high temperature). Though the sample P7 give good adhesive strength at room temperature testing condition (25°C), the adhesive strength decreased with increase in testing temperature (80, 100, 120, and 150°C). At very high testing temperature (150°C) the adhesive strength is almost negligible. Other samples also give same behavior at elevated testing temperature. May be at higher temperature the mechanical properties fall

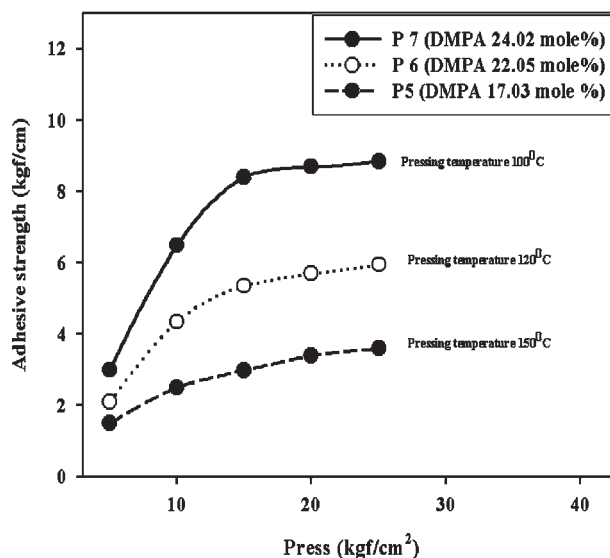


Figure 10 Effect of pressure on adhesive strength of waterborne polyurethane adhesives containing different amount of DMPA in nylon fabrics.

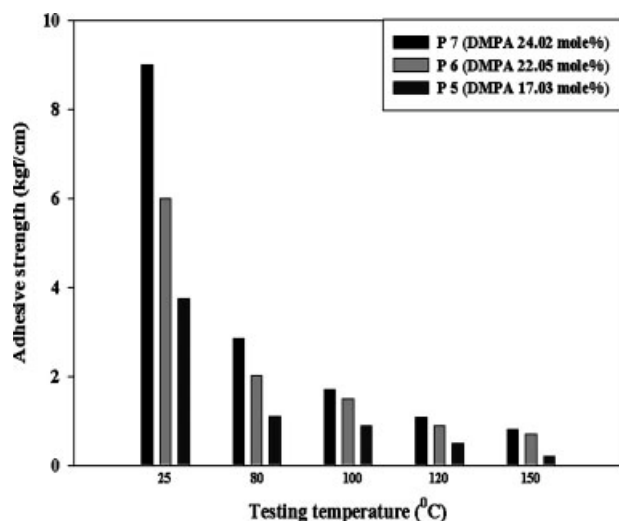


Figure 11 Effect of testing temperature on adhesive strength of waterborne polyurethane adhesives containing different amount of DMPA in nylon fabrics.

down due to the break up of hydrogen and ionic bonds in WBPU chains that causes adhesive strength lower. More detailed studies should be made for high temperature testing condition in the further study. So, concerning the results shown above, it is clear that by controlling the content of DMPA and optimum adhesive preparation condition gives a possibility of producing an optimum adhesive strength on nylon fabrics at various pressing temperature, pressure, and application temperature.

CONCLUSIONS

WBPU dispersions were prepared containing different amount of DMPA, and established the effect of DMPA content on their mechanical and physical property as well as adhesive strength on nylon fabrics at different condition. Decreases of mean particle size but increases of viscosity were produced as their DMPA content increased. Mechanical properties such as tensile strength and initial modulus of polyurethane films were affected by increasing of the DMPA content. Tensile strength and initial modulus increased significantly due to increased of DMPA content. With increasing of the DMPA content, the adhesive strength of WBPU on nylon fabrics also increased. The pressing temperature during adhesive processing has an interesting effect. First the adhesive strength increases with increases of pressing temperature. After optimum adhesive strength this started to decrease with increase of the pressing temperature. The optimum pressing temperature decreased with increased of DMPA content of WBPU adhesives. The adhesive strength is also dependent on the pressure during adhesive processing. The adhesive strength of WBPU adhesives at various pressures increased with increasing up to 15 kg f/cm²

and then leveled off. It was found that the optimum pressing temperature of WBPU adhesives samples P7, P6, and P5 containing 24.02, 22.05, and 17.05 mol % DMPA was about 100, 120, and 140°C, respectively, and the optimum pressure on adhesive process was found to be about 15 kg f/cm². All of the samples give good adhesive strength only at room temperature. But at higher application temperature the adhesive strength decreased significantly.

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