Preparation and Properties of Waterborne Poly(urethane urea)s for Adhesives: The Effects of the 2,2-Bis(hydroxylmethyl)propionic Acid Content on the Properties

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ABSTRACT: A series of waterborne poly(urethane urea)s (WBPUs) containing various concentrations (8.3–15.5 mol %) of 2,2-bis(hydroxylmethyl)propionic acid (DMPA) were prepared from isophorone diisocyanate, poly(tetramethylene adipate) glycol, DMPA, ethylenediamine, and triethylamine. The length of the hard segment with the DMPA content was varied from 18.7 to 22.6 wt % at a fixed soft-segment length (2000 g/mol). The effect of the DMPA content on the colloidal properties of WBPU dispersions, the hydrogen-bonding index, water swelling, dynamic mechanical thermal properties, and mechanical properties of WBPU films, and the adhesive strengths of substrates such as chloroprene rubber (CR)/CR, CR/polyurethane foam, CR/ethylene vinyl acetate foam, and thermoplastic olefin sheet/polypropylene foam were investigated. Stable aqueous dispersions of WBPU were obtained when the DMPA concentration was greater than 10 mol %. As the DMPA content increased, the particle size of the WBPU dispersion decreased, but the viscosity of the WBPU dispersion increased. The hydrogen-bonding fraction, water swelling, dynamic storage modulus and relaxation temperature, and tensile strength of the films increased with increasing DMPA content. According to an adhesion test, the substrates adhering to WBPU with greater than 10 mol % DMPA tore at about 8.0 kgf/cm^2 instead of breaking the adhered region. These results suggested that the WBPUs prepared in this study could have potential for adhesive use. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1743–1751, 2004

Key words: adhesives; polyurethanes

INTRODUCTION

One of the most important characteristics of many polyurethane (PU) ionomers is their ability to disperse or dissolve in water. To be dispersible in water, PU should contain ionic and/or nonionic hydrophilic segments in its structure.[1–6] Waterborne poly(urethane urea)s (WBPUs) are usually prepared in the forms of ionomers with a molecular weight high enough to form films with excellent performance solely upon physical drying. The ionic centers are located in hard segments because ionic diols are incorporated as chain extenders.

PU anionomers are usually prepared by the addition of a pendant acid group such as 2,2-bis(hydroxylmethyl)propionic acid (DMPA) into the backbone of the PU prepolymer. The pendant carboxylic acid groups are neutralized with a base to form internal salt-group-containing prepolymers that can easily be dispersed in water. The degree of neutralization, the counterion[7–9], and the type of ionic component[10] contribute significantly to the properties of PU ionomers. In general, properties such as adhesion, toughness, tear strength, and abrasion resistance are improved by ionization.

The properties of poly(urethane urea) dispersions are dependent on the chemical structure and compositional variation, the block length, and the ionic and urea group content. Primarily because of inter-urethane/urea hydrogen bonding, the two segment types tend to phase-separate in PU, forming microdomains.[11,12] The driving force for microdomain formation includes hydrogen bonding in urethane/urea groups, the electrostatic interaction (Coulombic forces) between the ionic groups, and the crystallization of both hard and soft segments. WBPU has extremely good cohesion and adhesion and mechanical properties because of the presence of microdomains.

The applications of PU adhesives include substrates such as glass, wood, leather, plastics, rubber, metals, concrete, and ceramic.[13–15] Anionic WBPUs have been most frequently used in the coating and adhesive industries.[14,16] Most studies on WBPUs for adhesives have in the past been carried out in industrial laboratories,[17] and systematic data on the properties of adhesive polymer are rarely available in the open literature.

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This study considers the preparation and properties of WBPUs based on isophorone diisocyanate (IPDI), poly(tetramethylene adipate) glycol (PTAd), DMPA, ethylenediamine (EDA), and triethylamine (TEA). The moles of PTAd and EDA were kept constant, whereas the moles of DMPA, TEA, and IPDI were raised; this provided higher hard-segment and salt-group contents. DMPA (8.3–15.5 mol %) was incorporated into WBPUs at the fixed soft-segment length (PTAd; 2000 g/mol); therefore, the hard-segment content was varied in the range of 18.7–22.6 wt %. We studied the effects of the DMPA content on the stability and particle size and viscosity of WBPU dispersions and the water swelling and mechanical and dynamic mechanical thermal properties of cast films. The performance of the WBPU dispersions as adhesives for various substrates such as chloroprene rubber (CR)/CR, CR/PU foam, CR/ethylene vinyl acetate (EVA) foam, and thermoplastic olefin (TPO) sheet/polypropylene (PP) foam was examined.

EXPERIMENTAL

Materials

PTAd (number-average molecular weight = 2000 g/mol; Hosung Chemex, Ulsan, Korea) was dried at 90°C and 1–2 mmHg for 3 h before use. Other extra grades of DMPA (Aldrich Chemical, Milwaukee, WI), TEA (Junsei Chemical, Tokyo, Japan), *N*-methyl-2-pyrrolidone (NMP; Junsei Chemical), IPDI (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), a hardener (Desmodur DA, Bayer), and the primer sodium dichloroisocyanurate (Aldrich Chemical) were used without further purification.

Synthesis of the waterborne PUs

The WBPUs were synthesized with the prepolymer mixing process.[18] PTAd 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 vacuo* 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. Then, IPDI was added to the flask, and the mixture was heated to 85°C under moderate stirring. 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. 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. The NCO content was the same as the contents of OH and NH$_2$.

Preparation of the WBPU films

WBPU films were prepared by WBPUs being poured onto a Teflon disk under the ambient conditions. The films (typically ca. 0.5 mm thick) were dried *in vacuo* at 50°C for 3 days and stored in a desiccator at room temperature.

WBPU coating materials were formulated from WBPUs, a thickener (L75N, 0.5 wt %), and a hardener (Desmodur DA, 5 wt %). Various substrates such as CR/CR, CR/PU foam, CR/EVA foam, and TPO sheet/PP foam were buffed and treated with a primer. The WBPU coating materials were put on the substrates by brushing, and then they were dried at 85°C

TABLE I
Sample Designation, Composition, DMPA, Hard-Segment Contents, and Stability of the WBPU Samples

Sample designation[a]	Composition (mol)					DMPA		Hard-segment content (%)	Stability of WBPU
	IPDI	PTAd[b]	DMPA	EDA	TEA	mol %	wt %		
D-0.5	3.0	1.7	0.5	0.8	0.5	8.3	(2.8)	18.7	Unstable
D-0.6	3.1	1.7	0.6	0.8	0.6	9.7	(3.3)	19.4	Unstable
D-0.7	3.2	1.7	0.7	0.8	0.7	10.9	(3.8)	20.1	Stable
D-0.8	3.3	1.7	0.8	0.8	0.8	12.1	(4.3)	20.7	Stable
D-0.9	3.4	1.7	0.9	0.8	0.9	13.2	(4.8)	21.4	Stable
D-1.0	3.5	1.7	1.0	0.8	1.0	14.3	(5.3)	22.0	Stable
D-1.1	3.6	1.7	1.1	0.8	1.1	15.5	(5.8)	22.6	Stable

[a] The solid content and pH of the samples were 40 wt % and 8–9, respectively.
[b] The molecular weight of PTAd was 2000 g/mol.
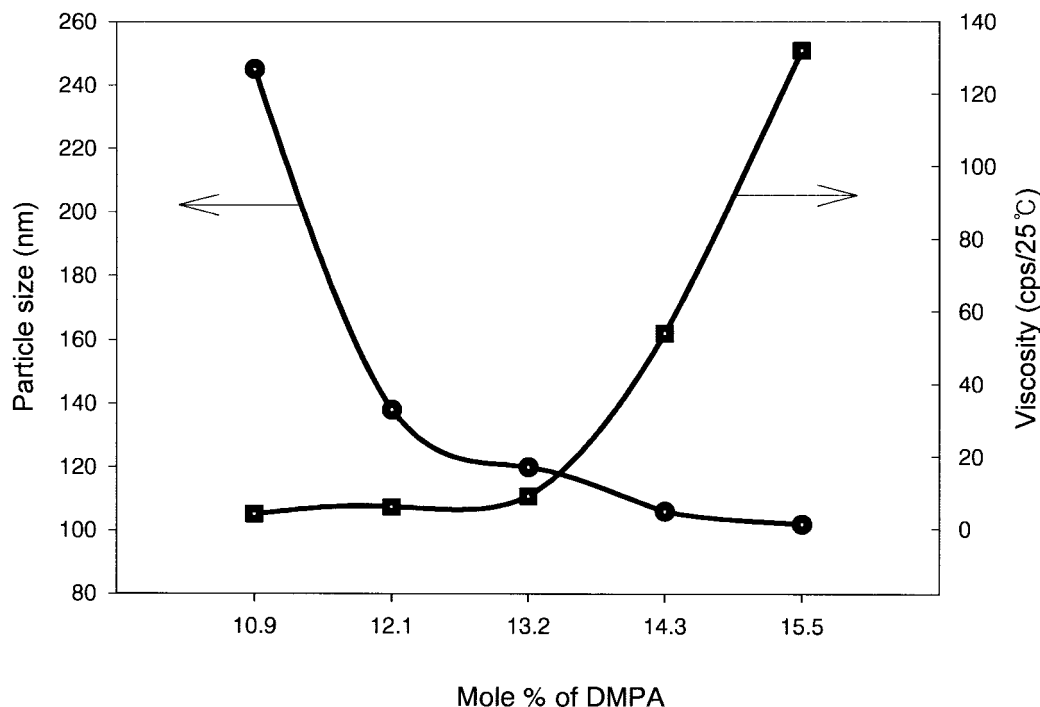
Figure 1 Effect of the DMPA content on (●) the particle size and (■) the viscosity of waterborne PUs.

for 5 min. These substrates adhered under an pressure of 5 kgf/cm^2.

Characterization

The particle size of the dispersions was determined with a Malvern (Worcs, United Kingdom) IIC autosizer. Approximately 0.15 mL of emulsion was diluted with distilled water to an appropriate concentration in the cell, 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, Broakfield, Middleboro, MA.

A Fourier transform infrared spectrometer (Impact 400D, Nicolet, Madison, WI) was used to identify the WBPU structure. For each IR spectrometer sample, 32 scans at a 4-cm^{-1} resolution were collected in the absorbance mode.

WBPU cast films were immersed in water for 48 h at 30°C to measure the swelling in water, and the swelling percentage was determined from the weight increase:

$$\text{Swelling (\%)} = \frac{W - W_0}{W_0} \times 100 \qquad (1)$$

where W_0 is the weight of the dried film and W is the weight of the film at equilibrium swelling.

The thermal property of WBPUs was examined with differential scanning calorimetry (DSC; model 220C, Seiko, Chibas, Japan) at a heating rate of 10°C/min under a nitrogen atmosphere.

The dynamic mechanical thermal properties of the film samples were measured at 5 Hz with a DMTA MK III (Rheometric Scientific, United Kingdom) at a heating rate of 2°C/min from −100 to 100°C. The dimensions of the film samples were 5 mm × 5 mm × 0.5 mm for the DMTA measurements.

The tensile properties were measured at room temperature with a United Data System tension meter (SSTM-1 United Data Systems, Instrom, 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. The adhesion property was measured with the United Data System tension meter according to ASTM D 1876-01 (the peel resistance of adhesives, i.e., the T-peel test).

RESULTS AND DISCUSSION

A series of WBPUs based on IPDI, PTAd, DMPA, EDA, and TEA were synthesized with the prepolymer mixing process.[18] The moles of PTAd (number-average molecular weight = 2000 g/mol) and EDA were kept constant, whereas the moles of DMPA and TEA (8.3–15.5 mol %) and IPDI were raised; this provided higher hard-segment and salt-group contents. There-
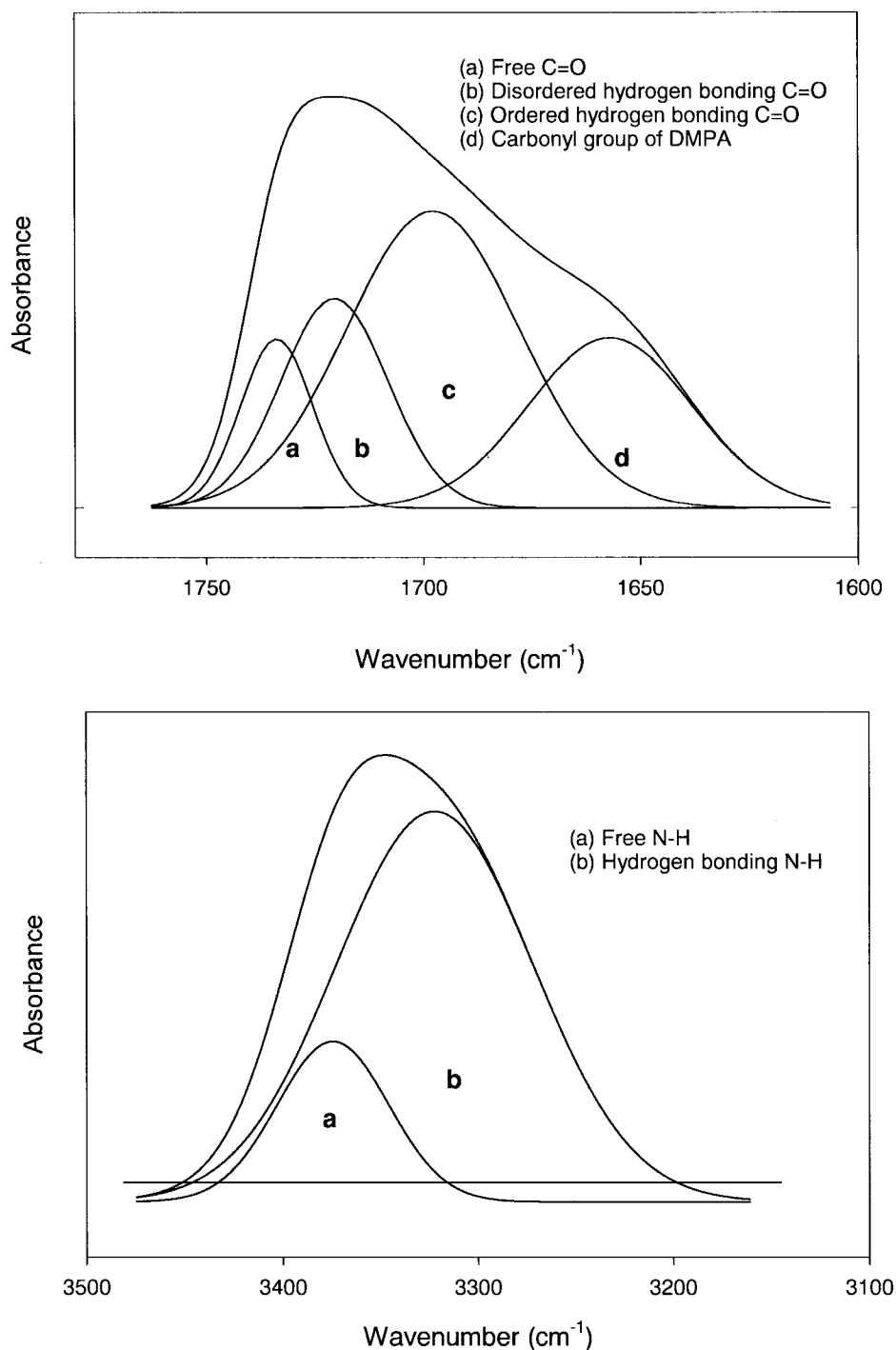
Figure 2 Decomposition of C=O and N—H stretching for sample D-0.8.

fore, the hard-segment content was varied in the range of 18.7–22.6 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 pH of all the WBPU dispersions indicated weak basicity (8–9). This might be due to the neutralization (formation of the carboxylate salt) of carboxyl acid in DMPA and amine in TEA.

The sample designations, compositions, DMPA and hard-segment contents, and stability of WBPUs syn-

thesized in this study are shown in Table I. From the stability results for the WBPU dispersions, we found that samples D-0.5 and D-0.6, containing lower contents of DMPA (<10 mol %), were not stable, but samples D-0.7, D-0.8, D-0.9, D-1.0, and D-1.1, having higher contents of DMPA (10.9–15.5 mol %), were stable after 4 months. This behavior indicated that the stability of the aqueous dispersions of WBPUs was primarily dependent on the content of the hydrophilic ionic component DMPA.
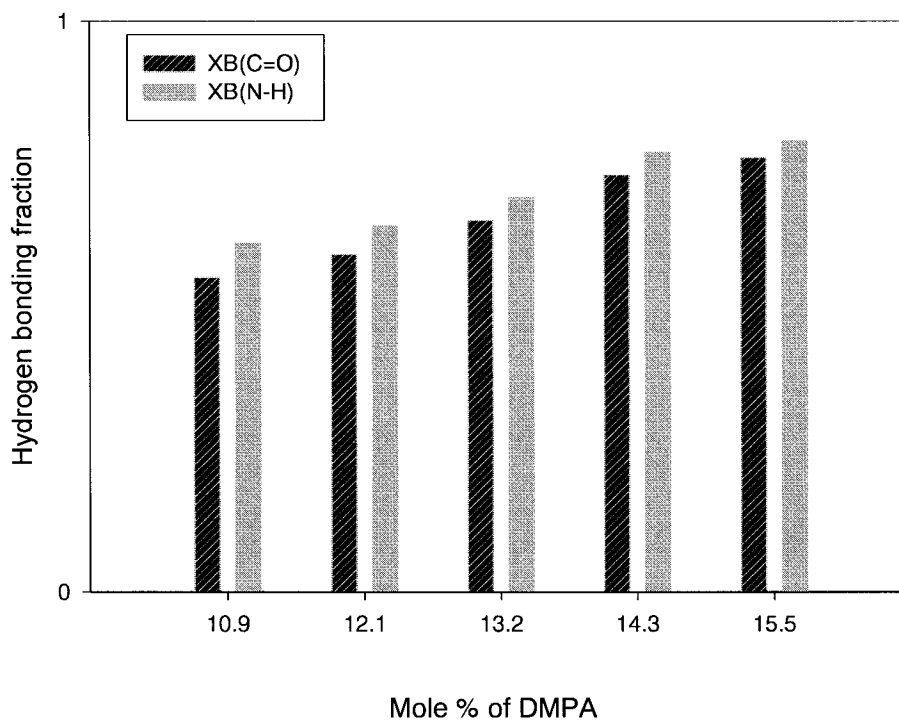
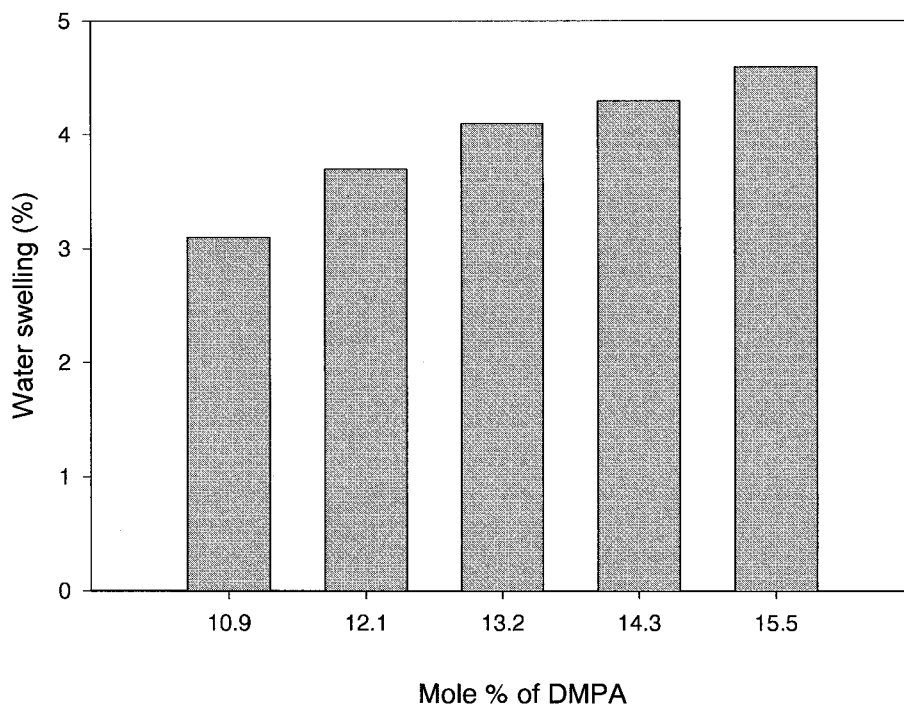**Figure 3** Effect of the DMPA content on X_B of waterborne PUs.

The effects of the DMPA content on the particle size and viscosity of the WBPU dispersions are shown in Figure 1. As the DMPA content increased from 10.9 to 15.5 mol %, the particle size decreased from approximately 245 to 102 nm, but the viscosity increased from 4 to 132 cps at 25°C. Smaller particles and higher viscosities resulted, with increased DMPA content. These phenomena were due to an increase in the hydrophilic structure through the addition of more salt groups and urethane linkages. The viscosity of WBPUs was governed by the hydrophilicity, in addition to external factors such as the shear force and temperature. Generally, smaller particles lead to larger hydrodynamic volumes and, therefore, induce higher viscosities.[5,11] However, depending on the specific application, an optimum 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 average particle size is not directly related to the physical properties of WBPU cast films. However, the control of the particle size is important with respect to the particular application of a 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 particle size of the WBPU dispersions prepared in this study indicated that these dispersions were applicable to adhesives for various substrates.

The WBPUs were identified by characteristic IR peaks, such as the N—H stretching vibration peak near 3340 cm^{-1} and the C=O peak near 1730 cm^{-1}. Figure 2 shows the decomposition of the C=O and N—H stretching bands of an IR spectrum for typical film sample D-0.8. The hydrogen-bonding fraction (X_B) was calculated from the total peak area (C_T) and the peak area of hydrogen-bonding C=O or N—H groups (C_H) as follows: $X_B = C_H/C_T$, where $C_T = a + b + c$ for C=O, $C_T = a + b$ for N—H, $C_H = b + c$ for C=O, and $C_H = b$ for N—H.[19] $X_{B\ C=O}$ and $X_{B\ N—H}$ of the WBPU films increased with increasing DMPA content (see Fig. 3). These increases in X_B were due to the increase in the number of urethane groups with increasing DMPA. The fraction of carbonyl groups of DMPA (d) also increased with increasing DMPA content.

The water swelling of WBPU cast films with the DMPA contents are shown in Figure 4. As the DMPA content increased from 0.7 to 1.1 mol %, the swelling of the WBPU films increased from 4 to 6%. The WBPUs prepared in this study had greater swelling than nonionic PUs. The increase in the water swelling was due to the increases in the hydrophilic ionic DMPA moieties and urethane groups.

Figures 5 and 6 show the storage modulus and loss tangent (tan δ) of WBPU cast films, respectively. The storage moduli of the WBPU films were kept in the glassy plateau region from −100 to almost −30°C. These storage moduli increased with increasing DMPA content. The storage moduli decayed a little around the soft-segment glass-transition temperature (T_g; −30°C), but they sharply dropped in the melting-


Figure 4 Effect of the DMPA content on the water swelling of waterborne PU films in water.

temperature range of the soft segments. The melting-temperature range of the soft segments is discussed later.

The tan δ peak moved toward a higher temperature as the DMPA content increased. The lower relaxation

peak temperatures near $-30°C$ were assigned to T_g of the soft-segment-rich phase domains. T_g of the soft segment moved toward higher temperatures with increasing DMPA content. The increase in T_g of the soft segment indicated the presence of hard segments dis-
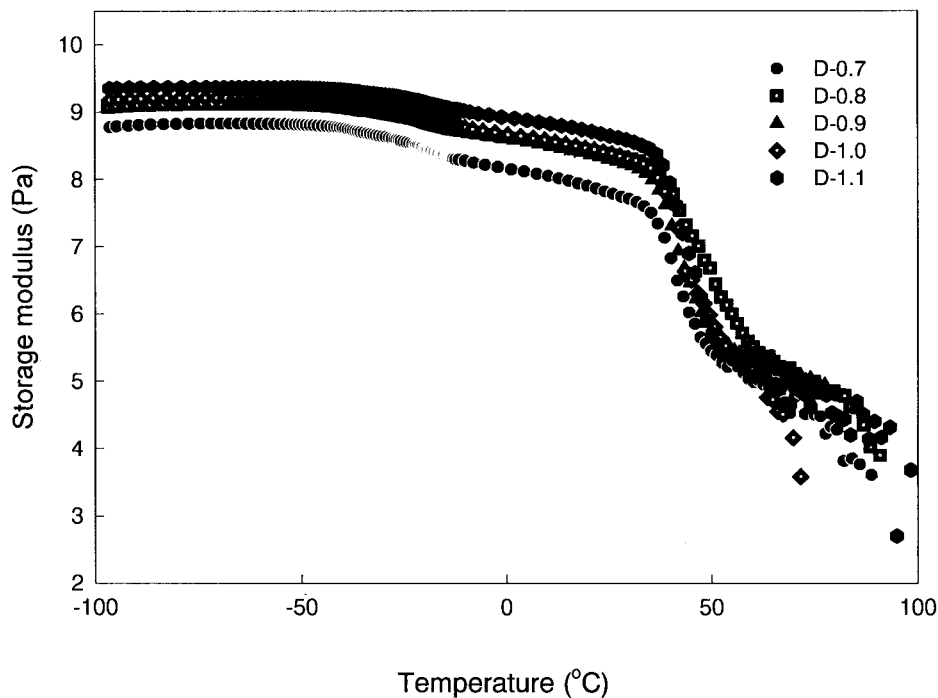
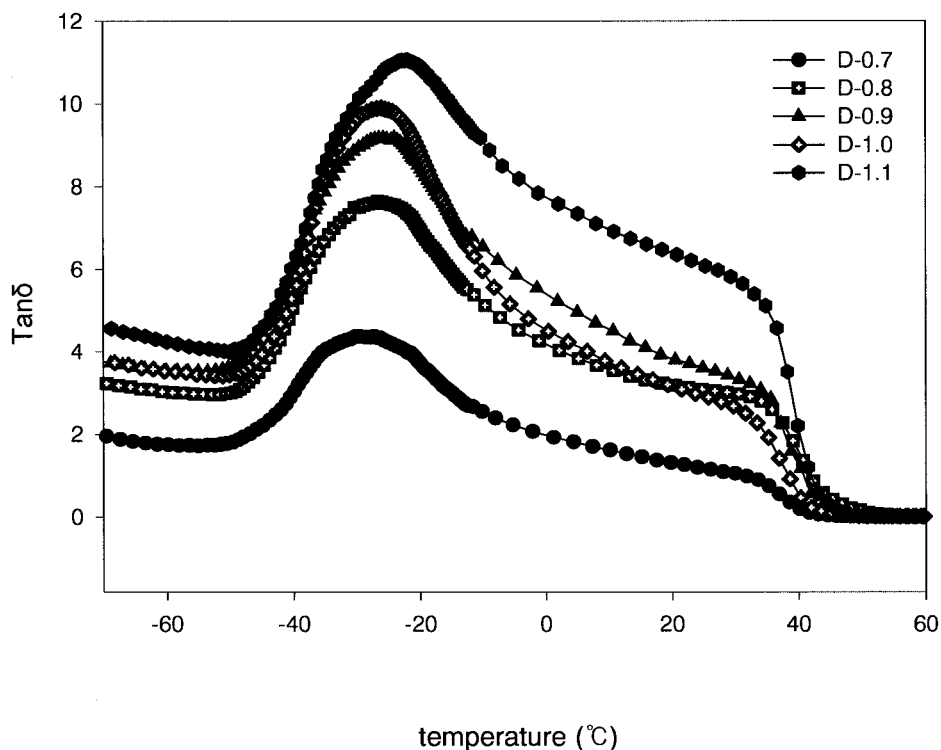**Figure 5** Storage modulus of waterborne PU films with various DMPA contents.

Figure 6 Tan δ of waterborne PU films with various DMPA contents.

persed in amorphous soft-segment microdomains. The chain mobility of the soft segments was restricted by the trapped hard segments, and this resulted in an elevated T_g value of the soft microdomain.

The DSC analysis showed that the melting temperature of the soft segments near 46°C was almost not changed with the DMPA content, as shown in Figure 7. This indicated that the hard-segment components
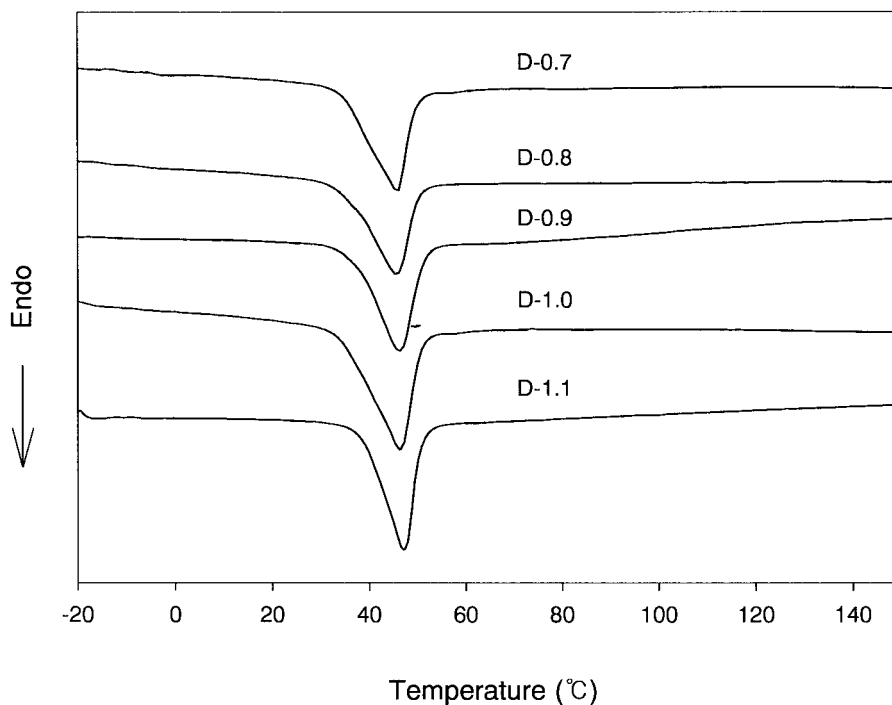

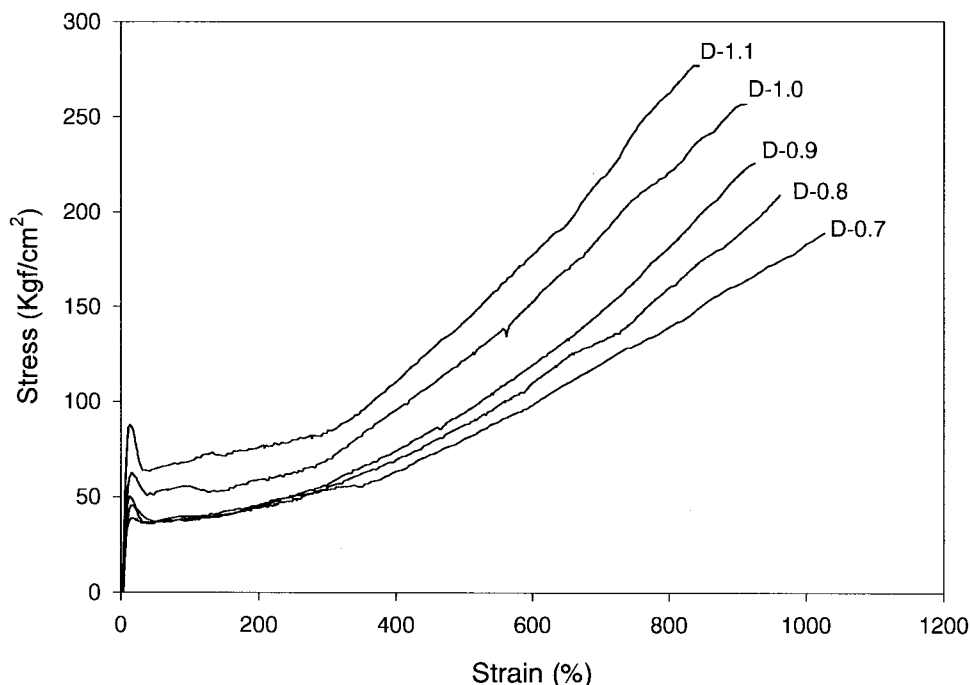**Figure 7** DSC curves of waterborne PU films.

Figure 8 Effect of the DMPA content on the stress–strain curves of waterborne PU films.

could not invade the crystalline soft-segment regions. Those melting peaks appeared in the temperature range of 32–52°C.

The stress–strain curves of WBPU film samples are shown in Figure 8. As the DMPA content increased, the tensile strength and initial modulus of the WBPU films significantly increased, but the elongation at break decreased a little (see Table II). The increases in the strength and modulus with the DMPA content should be related to the increased interchain Coulombic forces between the ionic centers and hydrogen-bonding forces predominantly between the ionic centers and urethane linkages.

Adhesive testing was performed with CR/CR, CR/PU foam, CR/EVA foam, and TPO sheet/PP foam as substrates. The substrate polymers were torn instead of blocking the adhered polymer–polymer interfaces for all samples, and this indicated the excellent adhesion (>8.0 kgf/cm^2) of the WBPUs prepared in this study (see Table III). From these results, the WBPUs prepared in this study were found to have greater potential for use in adhesives of various polymer substrates, such as CR/CR, CR/PU foam, CR/EVA foam, and TPO sheet/PP foam.

CONCLUSIONS

WBPUs based on IPDI, PTAd (number-average molecular weight = 2000), DMPA, EDA, and TEA were prepared with the prepolymer mixing process. The moles of PTAd and EDA were held constant,

whereas the moles of DMPA, TEA, and IPDI were raised; this provided higher hard-segment and salt-group contents. DMPA (8.3–15.5 mol %) was added to WBPUs at a fixed soft-segment length (PTAd, 2000 g/mol), and the hard-segment content was varied from 18.7 to 22.6 wt %. The effects of the DMPA content on properties such as the particle size, thermal properties, mechanical properties, and adhesion strength of CR/CR, CR/PU foam, CR/EVA foam, and TPO sheet/PP foam were investigated. The WBPU dispersions (D-0.5 and D-0.6) containing lower DMPA concentrations were unstable, but the WBPU dispersions (D-0.7, D-0.8, D-0.9, D-1.0, and D-1.1) with higher DMPA concentrations were stable. With increased DMPA content, the particle size of the WBPU dispersions decreased, but its viscosity increased. The X_B value, water swelling, dynamic storage modulus and relaxation temperature, and tensile strength of the film samples in-

TABLE II
Mechanical Properties of Waterborne PU Films

Sample designation	Tensile strength (kgf/cm^2)	Young's modulus (kgf/cm^2)	Elongation at break (%)
D-0.7	189	289	1027
D-0.8	209	368	962
D-0.9	225	445	926
D-1.0	257	525	914
D-1.1	277	736	844

TABLE III
Adhesive Strength of the Samples for Various Substrates

Sample designation	Adhesion strength (kgf/cm^2)			
	CR^a/CR	CR/PU foam^b	CR/EVA foam^c	TPO sheet/ PP foam^d
D-0.7	7.7	7.7	2.9	1.8
D-0.8	7.9	8.0	3.1	2.2
D-0.9	7.8	7.9	3.0	1.8
D-1.0	7.8	7.8	3.0	1.7
D-1.1	7.8	7.8	3.0	1.8

^{a} Breakdown strength of CR rubber surface : 7.5–8.0 (kgf/cm^2)
^{b} Breakdown strength of PU foam surface : 7.5–8.0 (kgf/cm^2)
^{c} Breakdown strength of EVA foam surface : 2.5–3.2 (kgf/cm^2)
^{d} Breakdown strength of PP foam surface : 1.8–2.2 (kgf/cm^2)

creased with increasing DMPA content. According to the adhesion test, the substrates polymers were torn instead of blocking the adhered polymer–polymer interface for all samples, and this indicated that the WBPUs prepared in this study had excellent adhesion (>8.0 kgf/cm^2). The WBPUs prepared in this study were found to have greater potential for use in adhesives of various polymer substrates such as CR/CR, CR/PU foam, CR/EVA foam, and TPO sheet/PP foam.

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