

Synthesis and Properties of Waterborne Poly(urethane urea)s Containing Polydimethylsiloxane

Young-Hee Lee, Eun-Ji Kim, Han-Do Kim

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

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ABSTRACT: To obtain flexible waterborne poly(urethane urea) (WBPU) coatings with functionalities such as shape recovery and water resistance, we synthesized a series of WBPUs by a prepolymer mixing process from hexamethylene diisocyanate, polyol, 2,2-bis(hydroxymethyl) propionic acid, ethylenediamine, and triethylamine with polyol blends [hydroxyl-terminated polydimethylsiloxane (PDMS) with a number-average molecular weight of ≈ 550 and poly(tetramethylene oxide) glycol (PTMG) with a number-average molecular weight of 650] of different molar ratios. The effects of the PDMS content in PDMS/PTMG on the dynamic thermal and mechanical properties, hardness,

tensile properties, water resistance (water absorption, contact angle, and surface energy), and shape-memory properties of WBPU films were investigated. As the molar percentage of PDMS in WBPUs increased, the storage modulus, tensile strength and modulus, elongation at break, hardness, and shape-retention rate (30–15%) decreased; however, the water resistance and shape-recovery rate (80–90%) increased. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 212–219, 2011

Key words: polymer synthesis and characterization; polyurethanes; swelling; thermal properties

INTRODUCTION

Waterborne poly(urethane urea)s (WBPUs) are regarded as some of the most important industrial polymers nowadays because of their tremendous usefulness and environmental benefits in comparison with their counterparts, solvent-borne polyurethanes (PUs). WBPUs containing ionic moieties have been used for a wide range of commercial applications, such as adhesives and coatings for various substrates.^{1–8} One important feature of PU ionomers is their ability to disperse or dissolve in water if a sufficient amount of an ionic moiety is incorporated. Because of their ionomeric character and the absence of dispersants, WBPU systems have extremely good film-forming properties. Ionic monomers of WBPUs can improve mechanical properties, adhesive strength, and aqueous dispersion stability.⁹

However, dried films of WBPUs are generally water-sensitive because of the presence of ionic groups. Therefore, the ionic content should be kept to a minimum for the formation of water-resistant WBPUs. However, it is very difficult to obtain stable WBPU dispersions with low concentrations of ionic moieties (<10 mol % or 2 wt %).⁹ Thus, it is very important to adjust the water resistance and dispersion stability via the subtle control of the hydrophilic–

hydrophobic balance through the use of the hydrophobic component and enough ionic moieties for WBPUs.

Polydimethylsiloxane (PDMS) has many applications because of its unique properties, which arise mainly from the nature of the siloxane bond (Si–O). These properties include an extremely low glass-transition temperature (T_g ; -123°C), low surface tension, high flexibility, high permeability to gases, chemical inactivity, insulating stability, very good thermal stability, and UV stability.^{10–13} In the past, many studies were published in which PDMS was used as a component of PU to improve PU properties such as water resistance, flame resistance, and heat resistance.^{14–16} However, few studies on PDMS-modified WBPUs and UV-curable WBPUs have been reported recently.¹⁷

Shape-memory polymers (SMPs) are capable of changing their shape on exposure to a stimulus such as heat, electrical current, or photoenergy.^{18,19} Thermoresponsive SMPs are increasingly being investigated for use as smart materials in a variety of applications.²⁰ Characteristic advantages of SMPs, such as low densities, high shape-recovery rates, and easy processing conditions, make them very attractive research targets.^{21–25}

PU, polyester, and polystyrene are some of the successfully tested SMPs.^{26–33} SMPs are generally composed of fixed and reversible segments: the fixed segment forms domains by interchain interactions and works as a pivoting point for shape recovery, and the reversible segment forms a soft domain absorbing external stress applied to the polymer by

Correspondence to: H.-D. Kim (kimhd@pusan.ac.kr).
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unfolding. Among the SMP candidates, solvent-based PUs³⁴ and thermoplastic PUs are favored because of their distinct properties, such as high strain and high shape-recovery rates, if the hard-segment structure and chain length of the soft segment are carefully controlled. However, studies on WBPU with shape-memory functionality are rare in the open scientific literature.

In this study, a series of flexible WBPU for smart coatings were prepared from hexamethylene diisocyanate (HDI) as a linear aliphatic diisocyanate, a poly(tetramethylene oxide) glycol [PTMG; number-average molecular weight (M_n) = 650]/PDMS (M_n ~ 550) blend as a soft segment, ethylenediamine (EDA) as a chain extender, 2,2-bis(hydroxymethyl) propionic acid (DMPA) as a contributor of ionic groups, and triethylamine (TEA) as a neutralization agent. The effects of the PDMS content on properties such as shape memory, water resistance, and thermal and mechanical properties were investigated.

EXPERIMENTAL

Materials

PTMG (M_n = 650 g/mol; Aldrich Chemical, Milwaukee, WI, USA) and hydroxyl-terminated PDMS (M_n = 550 g/mol; Aldrich Chemical) were dried at 85°C and 1–2 mmHg for several hours until no bubbling was observed. HDI (Aldrich Chemical), DMPA (Aldrich Chemical), *N*-methyl-2-pyrrolidone (Junsei Chemical), EDA (Junsei Chemical, Tokyo, Japan), and TEA (Junsei Chemical) were used without further purification.

Synthesis of the WBPU and their films

The WBPU were synthesized with a prepolymer mixing process.³⁵

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 vacuo* at 90°C for 30 min. DMPA and *N*-methyl-2-pyrrolidone (1/2 w/w) were added to the flask, and the mixture was allowed to cool to 45°C with moderate stirring (170–200 rpm). Then, HDI was added to the flask, and the mixture was heated to 85°C with moderate stirring (170–200 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 car-

boxyl groups of the NCO-terminated prepolymer. After 30 min of neutralization, distilled water (70 wt %) was added to the reaction mixture with vigorous stirring (ca. 1000 rpm). The neutralized prepolymer was chain-extended until the NCO peak (2270 cm^{-1}) in the IR spectra had completely disappeared. All the WBPU were obtained through the evaporation of acetone and the subsequent addition of an adequate amount of distilled water. The WBPU with PDMS were synthesized by the prepolymer mixing process shown in Scheme 1.³⁵ The compositions of the WBPU used in this study are presented in Table I. The soft-segment content of the WBPU samples was fixed at 69%, but the content of PDMS in PTMG/PDMS was 0, 25, or 50 mol %. The numbers of samples (WP-0, WP-25, WP-50) indicated the PDMS content. We prepared the WBPU films by pouring the aqueous dispersion onto a Teflon disk under ambient conditions for 48 h. The films (typically ca. 0.1 mm thick) were dried *in vacuo* at 50°C for 1 day and were stored in a desiccator at room temperature.

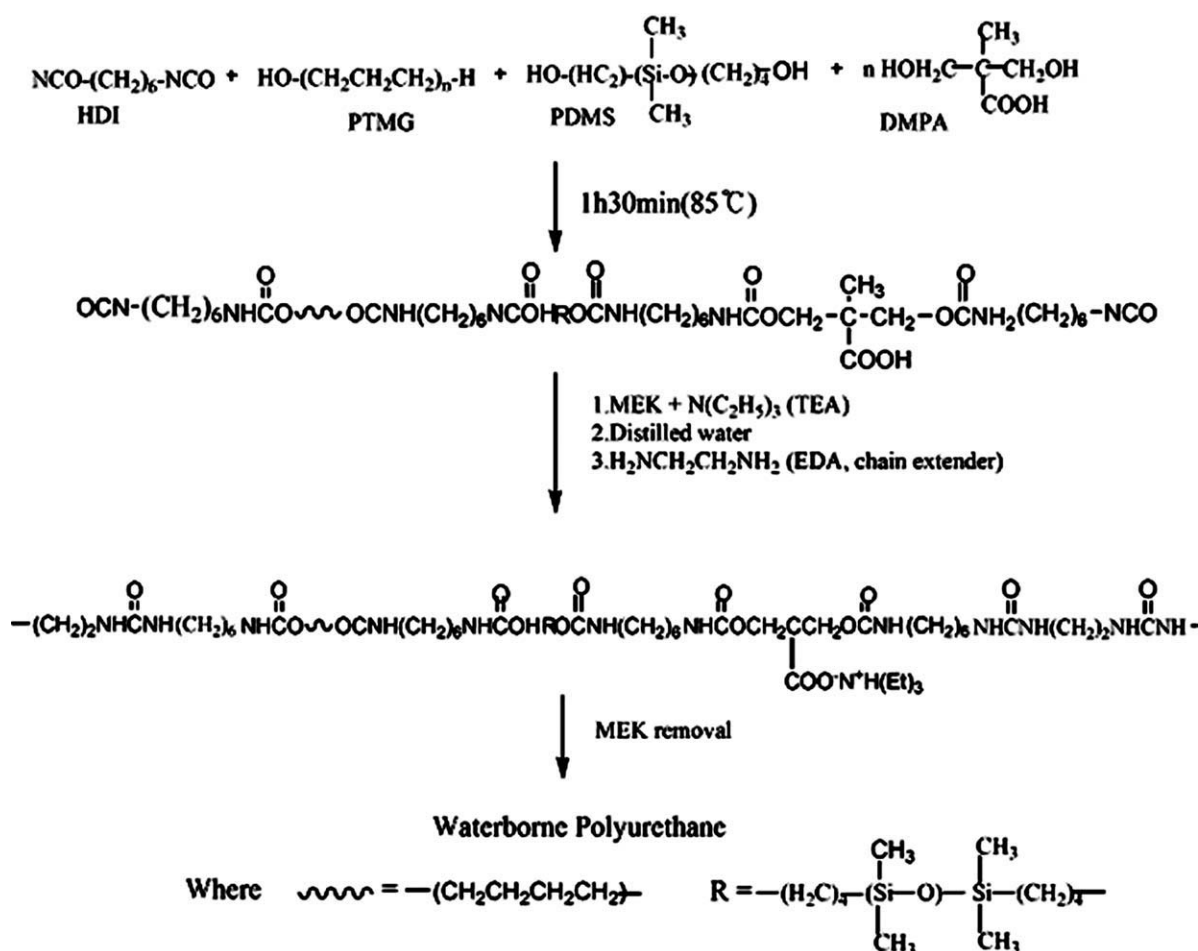
Characterization

IR spectra were obtained with a Nicolet Impact 400D computerized Fourier transform infrared (FTIR, JASCO, Japan) spectrometer. For each sample, 32 scans at a resolution of 2 cm^{-1} were collected in the transmittance mode.

The inherent viscosity (dL/g) of WBPU was determined from the ratio of the natural logarithm of the relative viscosity (t/t_0 , where t is the flow time of the solution and t_0 is the flow time of the solvent) to the concentration (g/dL) of the polymer with respect to the solvent (DMF). The inherent viscosity of the WBPU prepared here decreased a little with increasing PDMS content.

The thermal dynamic mechanical behavior of WBPU was measured at 3 Hz with a 20- μm amplitude in a tension mode with a DMA Q800 (TA Instrument, Keyworth, Nottinghamshire, UK) at a heating rate of 5°C/min in the temperature range of –140–150°C. The dimensions of the films were 15 × 5.3 × 0.2 mm^3 for dynamic mechanical analysis (DMA) measurements. The T_g values of WBPU also were measured with the DMA Q800 according to ASTM E 1640-04. DMA temperature calibration was performed with indium (melting temperature = 156.6°C). The mechanical measurements were made in simple extension on dumbbell specimens with an Instron 5582 tensile tester (Instron, Co., Ltd., Canton, Ohio, USA). A crosshead speed of 500 mm/min was used throughout these investigations to determine the ultimate tensile modulus and strength for all the samples. The quoted values are averages of five measurements.

To measure the water swelling of the WBPU film samples, the films were immersed in distilled water



Scheme 1 Preparation process of WBPU.

at room temperature for 48 h, and the percentage of swelling was determined by the measurement of the weight change. The water swelling of the films was calculated according to eq. (1):

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

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

The contact angles of water and benzene were measured at 25°C with a contact-angle goniometer (SEO, Phoenix 450, Suwon, Korea), and the reported results are mean values of five measurements. The contact angle, a measure of the surface wettability, was used to determine the water resistance. The sur-

face energy of the solid film (γ_s) was calculated with the following equation:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

where γ_s^d represents the dispersion force and γ_s^p represents the polarity force. γ_s^d and γ_s^p were calculated as follows:

$$\begin{aligned} \gamma_{11}(1 + \cos \theta_1) &= 2(\gamma_{11}^d \gamma_s^d)^{1/2} + 2(\gamma_{11}^p \gamma_s^p)^{1/2} \\ \gamma_{12}(1 + \cos \theta_2) &= 2(\gamma_{12}^d \gamma_s^d)^{1/2} + 2(\gamma_{12}^p \gamma_s^p)^{1/2} \end{aligned} \quad (3)$$

where γ_{11} and γ_{12} represent the surface tensions of the two testing liquids and include the dispersion

TABLE I
Sample Designation, Composition, and Inherent Viscosity ($[\eta]$) of the WBPUs

Sample designation	Composition (mol)						$[\eta]$
	HDI	PTMG	PDMS	DMPA	EDA	TEA	
WP-0	3	2.2	0	0.6	0.2	0.6	0.62
WP-25	3	1.65	0.55	0.6	0.2	0.6	0.59
WP-50	3	1.1	1.1	0.6	0.2	0.6	0.55

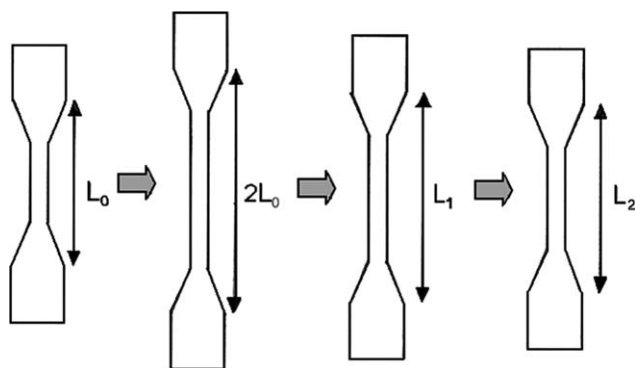


Figure 1 Specimen for the shape-memory test.

and polar components (indicated by the d and p superscripts, respectively). They have the following relationships: $\gamma_{11} = \gamma_{11}^d \gamma_{11}^p$ and $\gamma_{12} = \gamma_{12}^d \gamma_{12}^p$. Under the conditions for which the values of γ_{11}^d , γ_{11}^p , γ_{12}^d , and γ_{12}^p were given, γ_s^d and γ_s^p could be obtained by the determination of θ_1 and θ_2 . Therefore, γ_s could be obtained. The testing liquids were water (L1) and benzene (L2), and γ_{11}^d , γ_{11}^p , γ_{12}^d , and γ_{12}^p were 21.8, 51.0, 28.9, and 0 mN/m, respectively.³⁶

Thermogravimetric analysis (TGA) was performed with a Pyris 6 thermogravimetric analyzer (Perkin-Elmer, Waltham, MA, USA) under N_2 at a heating rate of $10^\circ\text{C}/\text{min}$ over a temperature range of $30\text{--}650^\circ\text{C}$.

The tensile properties were measured at room temperature with a United Data System SSTM-1 tension meter (Instron, Canton, Ohio, USA) according to ASTM D 638 specifications. A crosshead speed of $200\text{ mm}/\text{min}$ was used throughout these investigations to determine the ultimate tensile strength, modulus, and elongation at break for all the samples. The quoted values are averages of five measurements.

The Shore A hardness was measured with a durometer (Kobunshi Keiki, Kyoto, Japan) according to ASTM D 2240.

Shape-memory test

A DS-UTM-500 universal testing machine (Daesan Engineering, Kimhae, Korea) equipped with a temperature-controlled chamber was used to measure stress and strain at various temperatures for the investigation of the shape-memory properties. For the measurement of the shape-retention rate, a specimen with length L_0 was strained to 100% at 20°C above T_g and kept at that temperature for 5 min. The specimen under strain was cooled back to 20°C below T_g and left at that temperature for 30 min after the removal of the load; this was followed by the measurement of the deformed length (L_1). For the measurement of the shape recovery, the specimen was heated again to 20°C above T_g , kept at that temperature for 10 min, cooled back to 20°C below T_g ,

and kept at that temperature for 10 min, and then the final specimen length (L_2) was measured (Fig. 1). The measurements were repeated three times, and the shape-retention rate and shape-recovery rate were calculated with the following equations:³⁷

$$\text{Shape-retention rate} = (L_1 - L_0)/L_0 \times 100 (\%) \quad (4)$$

$$\text{Shape-recovery rate} = (2L_0 - L_2)/L_0 \times 100 (\%) \quad (5)$$

RESULTS AND DISCUSSION

Confirmation of WBPUs containing PDMS

Figure 2 shows the FTIR spectra of the WBPUs samples in this study. The urethane urea of WBPUs was identified by characteristic IR peaks, such as the N—H stretching vibration peak near 3330 cm^{-1} , the C=O stretching group at 1700 cm^{-1} , the C—N—H stretching band at 1540 cm^{-1} , and the —CH₂— stretching band at 1460 and 770 cm^{-1} . Symmetric CH₃ bending at 1258 cm^{-1} , Si—O—Si stretching at 1020 cm^{-1} , and CH₃ rocking at 803 cm^{-1} were assigned to PDMS in the WBPUs.

TGA

Figure 3 shows TGA curves of the WBPUs. Several studies^{32,33} have reported that segmented PUs show two-stage degradation. The first stage, occurring between 200 and 370°C , is due to the depolycondensation process associated with the degradation of the urethane/urea hard segment. The second stage, occurring between 370 and 500°C , is the degradation of the soft segment by depolycondensation of polyol. All the samples prepared in this study also showed two-stage degradation. As the PDMS content of WBPUs increased, the first-stage temperature decreased; however, the temperature of the second stage of degradation increased. The residue at

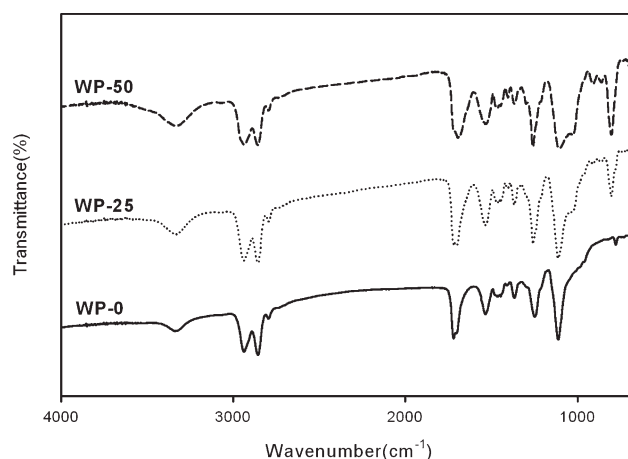


Figure 2 FTIR spectra of the WBPUs samples.

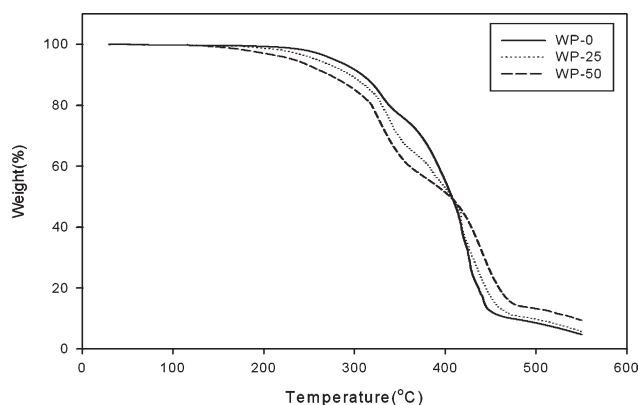


Figure 3 TGA curves of the WBPU samples.

530°C increased with increasing PDMS content. This should be attributed to the higher thermal stability of the PDMS component.

DMA

DMA measures stiffness and damping, and these are reported as the modulus and $\tan \delta$ (a measure of the energy dissipation of a material). Modulus values change with the temperature, and transitions in materials can be seen as changes in the storage modulus or $\tan \delta$ curves. This includes not only the glass transition (the α transition) and the melt transition but also other transitions (β and γ transitions) that occur at the glassy or rubbery plateau. The DMA results for the WBPUs are shown in Figure 4. The storage modulus of the WBPUs decreased with increasing PDMS content. The storage modulus of samples WP-0 and WP-25 were almost constant up to the point of decline ($\alpha - T_g$); however, the storage modulus of sample WP-50, which had the highest PDMS content, markedly decreased from T_g (-123°C) of pure PDMS. In the loss modulus and $\tan \delta$ curves, samples WP-25 and WP-50 had the glass transitions of the PDMS matrix phases ($\beta - T_g \approx -115^\circ\text{C}$), but sample WP-0 did not. The $\alpha - T_g$ peak in both the loss modulus and $\tan \delta$ curves broadened with increasing PDMS content. The loss modulus curve of sample WP-50 showed two broad peaks in the temperature range of $\alpha - T_g$. This might be attributed to the phase separation of two different PTMG and PDMS matrix phases. In particular, the peak area and intensity of the $\tan \delta$ curve markedly increased with increasing PDMS content. These phenomena indicated that the content of the amorphous phase and the mixing of different amorphous phases [various amorphous phases with different orders and compositions (PDMS/PTMG)] increased with increasing PDMS content (50 wt %). $\alpha - T_g$ significantly increased to a higher tempera-

ture with increasing PDMS content. This might have been due to the formation of a higher order amorphous phase containing some urethane/urea groups by phase mixing. From these results, we found that the WBPUs containing PDMS were very flexible copolymers with multiple amorphous phases.

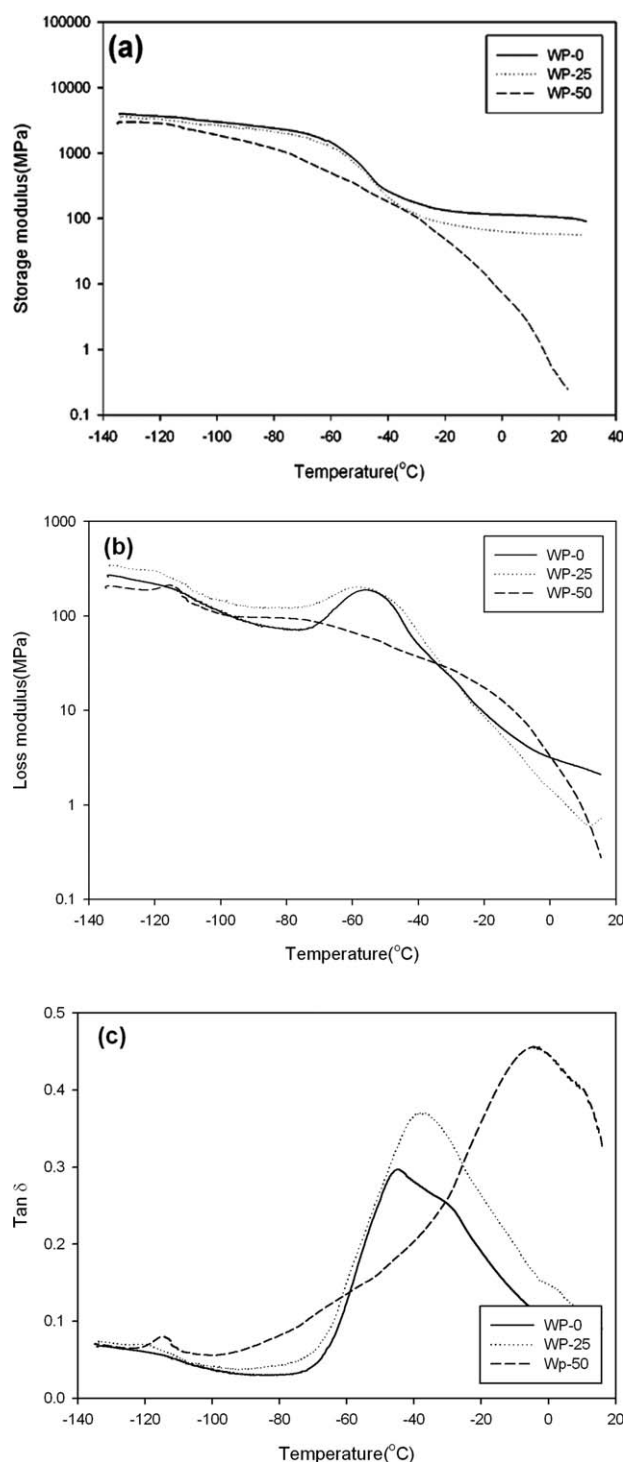


Figure 4 (a) Storage modulus, (b) loss modulus, and (c) $\tan \delta$ curves of the WBPU samples.

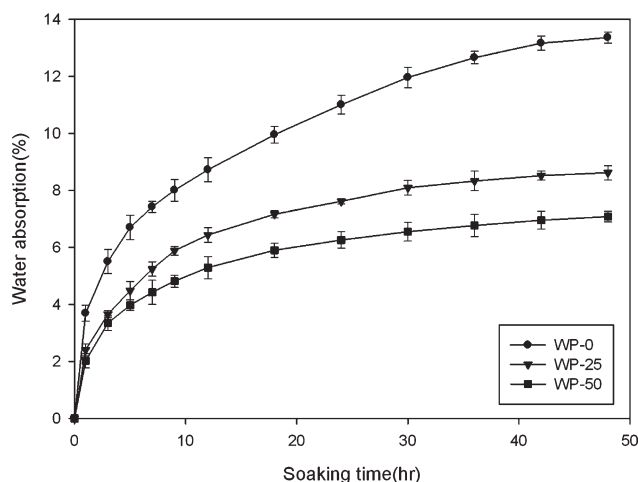


Figure 5 Relationship between the water absorption and the soaking time.

Water resistance

Generally, it is very difficult to obtain stable WBPU dispersions with a low concentration of the ionic moiety. Therefore, it is very important to adjust the water resistance and dispersion stability of WBPUs through the subtle control of the content of the hydrophobic component (e.g., PDMS) with enough ionic moieties. Figure 5 shows the relationship between the water absorption and the soaking time for the WBPUs prepared in this study. The contact angles, surface energy, and water absorption of the WBPU films are shown in Table II. The water absorption increased with the soaking time and then leveled off. As the content of PDMS increased, the water absorption, maximum water adsorption, and surface energy of the films decreased significantly, whereas the water contact angle of the films increased. This should be attributed to the hydrophobicity of the PDMS molecules. In addition, PDMS had a much lower surface energy than PU, and the PDMS component might have migrated to the surface layer during the formation of a WBPU film.

Stress-strain behavior

The stress-strain curves and tensile properties of the film samples are shown in Figure 6 and Table III.

TABLE II
Contact Angles, Surface Energy, and Water Absorption of the WBPU Films

Sample designation	Contact angle (°)		Surface energy (mN/m)	Water absorption (%)
	Water	Benzene		
WP-0	56	19	47.9	13.4
WP-25	61	20	44.5	8.6
WP-50	69	27	38.8	7.1

The tensile strength, elongation at break, and modulus of WP-0, WP-25, and WP-50 were 15.5 MPa, 1588%, and 7.2 MPa, 9.1 MPa, 867%, and 3.4 MPa, 4.9 MPa, 500%, and 2.3 MPa, respectively. The tensile strength, elongation at break, and modulus of the WBPU samples decreased with increasing PDMS content in PTMG/PDMS. The decreases in the strength, modulus, and elongation might have been not only due to the broad, multiple amorphous phases [see the broad $\tan \delta$ peaks in Fig. 4(b)] but also due to the lower mechanical properties of the PDMS component.^{13,38} In addition, the decreases in these mechanical properties should be attributable to the decrease in the inherent viscosity (molecular weight).

Hardness

The Shore A hardness of the WBPU films prepared in this study is shown in Table III. The Shore A hardness of WP-0, WP-25, and WP-50 was 65, 56, and 48, respectively. The Shore A hardness decreased with increasing PDMS content. The decrease in the hardness should be attributable to the soft feature of PDMS and the large number of multiple amorphous phases, as described previously. As could be expected, the hardness decrease with the PDMS content should be directly attributable to the decrease in the moduli (the storage modulus and the tensile modulus) and the increase in the $\tan \delta$ peak area (which was related to the amount of the amorphous region). However, we could not find a dependence of the hardness on the T_g values of the waterborne PUs prepared in this study.

Shape-memory test

Generally, SMPs are composed of hard and soft segments: the hard segment keeps the original shape through chain interactions such as hydrogen bonding or dipole-dipole interactions together with the

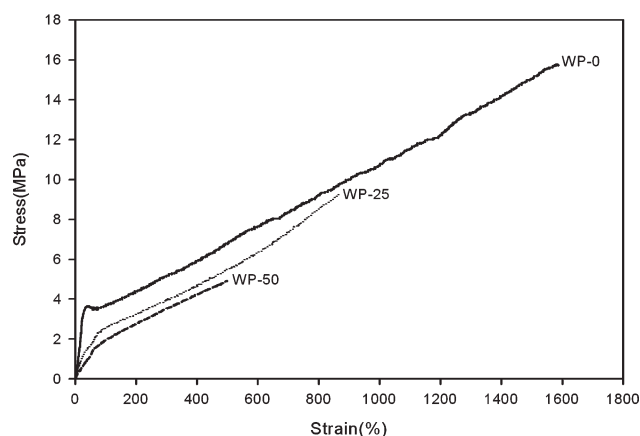


Figure 6 Stress-strain curves of the WBPU samples.

TABLE III
Thermal Properties, Mechanical Properties, and Shore A Hardness of the WBPU Film Samples

Sample designation	DMA		TGA: Residue at 530°C (%)	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)	Hardness (Shore A)
	αT_g (°C)	βT_g (°C)					
WP-0	-44.70	—	6.5	15.7	1588	7.2	65
WP-25	-35.92	-120.42	7.6	9.1	867	3.4	56
WP-50	-3.87	-114.86	11.2	4.9	500	2.3	48

physical crosslinking, and the soft segment absorbs external stress by unfolding or extension. When excess stress over the shape-memory limit is applied, the shape-memory property is lost, and the original shape cannot be recovered. Therefore, control over the kinds and contents of hard and soft segments is very important for improving the shape-recovery and shape-retention rates.³⁷

Figure 7 shows the shape-retention and shape-recovery rates of the WBPU samples prepared in this study. As the molar percentage of PDMS increased, the

shape-retention rate (30–15%) decreased; however, the shape-recovery rate (80–90%) of the WBPU films increased. This lower shape-retention rate should be attributable to the linear structure of the WBPU random copolymer. Therefore, we are going to investigate the improvement of shape memory via chemical crosslinking in another study in detail. Because the WBPU containing PDMS is a flexible linear polymer, it has a comparatively high shape-recovery rate. The high shape-recovery rate of the WBPU film samples might have been due to the phase separation of various components of the WBPU. These results showed that the increase in the PDMS content, which increased the flexibility and phase separation/mixing in segmented WBPU chains, significantly contributed to not only the increase in the shape-recovery rate but also to the decrease in the shape-retention rate.

CONCLUSIONS

A series of flexible WBPU were prepared from HDI as a linear aliphatic diisocyanate, a PDMS/PTMG blend as a soft segment, EDA as a chain extender, DMPA as a contributor of ionic groups, and TEA as a neutralization agent by a prepolymer mixing process. In this context, this study focused on the effects of the PDMS content in PDMS/PTMG on the thermal and mechanical properties, hardness, tensile properties, water resistance, and shape-memory properties of WBPU. The water resistance and shape-recovery rate (80–90%) of the WBPU films increased with the molar percentage of PDMS increasing in PDMS/PTMG. This should be not only due to the softness, hydrophobicity, and lower mechanical properties of PDMS but also due to the formation of multiple phases by phase separation/mixing of the various components of the WBPU.

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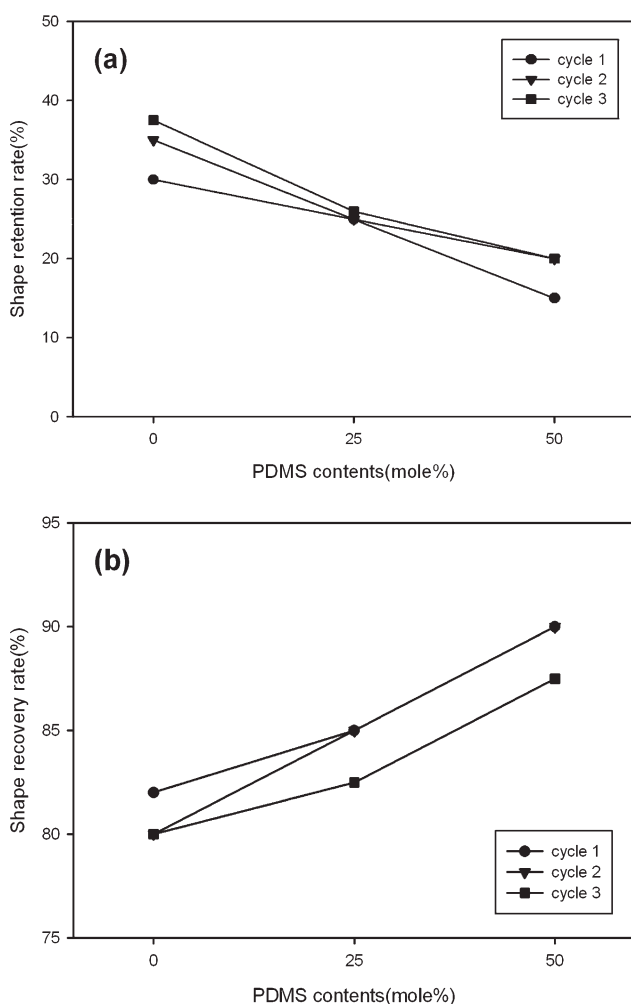


Figure 7 (a) Shape-retention rate and (b) shape-recovery rate of the WBPU samples.

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