

# Preparation and Properties of Waterborne Polyurethanes Based on Triblock Glycol (CL)<sub>4,5</sub>-PTMG-(CL)<sub>4,5</sub> for Water Vapor Permeable Coatings: Effect of Soft Segment Content

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**Abstract:** A series of waterborne polyurethanes (WBPU) were prepared from 4,4-dicyclohexylmethane diisocyanate (H<sub>12</sub>MDI), 2,2-bis(hydroxymethyl) propionic acid (DMPA), ethylenediamine (EDA), triethylamine (TEA), and triblock glycol [TBG, ( $\epsilon$ -caprolactone)<sub>4,5</sub>-poly(tetramethylene ether) glycol (MW = 2000)-( $\epsilon$ -caprolactone)<sub>4,5</sub>: (CL)<sub>4,5</sub>-PTMG-(CL)<sub>4,5</sub>, MW = 3000] as a soft segment. Two melting peaks of TBG at about 14 °C and 38 °C were observed indicating the presence of two different crystalline domains composed of CL and PTMG dominant component. The effect of soft segment content (60-75 wt%) on the colloidal properties of dispersion, and thermal and mechanical properties of WBPU films, the water vapor permeability (WVP) and water resistance (WR) of WBPU-coated Nylon fabrics, and the adhesive strength of WBPU-coated layer and Nylon fabrics was investigated. As soft segment contents increased, the water vapor permeability of WBPU-coated Nylon fabrics increased from 3615 to 4502 g/m<sup>2</sup>day, however, the water resistances decreased from 1300 to 500 mmH<sub>2</sub>O.

**Keywords:** Polyurethane, Coatings, Triblock glycol, Water vapor permeability

## Introduction

Water dispersions (lattices or emulsions) of polyurethane monomers permit the application of polyurethane from an aqueous medium. Due to the absence of dispersants used in their formation and due to their ionomeric character, these systems show extremely good film-forming properties. WBPU dispersions have been used for a wide range of commercial application such as adhesives or coatings for various substrates[1-8]. The earliest use for WBPU dispersions, i.e., as a coating for textiles, is still one of the largest market areas for them. Recently, polyurethane films with high water vapor permeability were used in breathable coating fabrics, medical applications, and special adhesives[9,10]. In the applications of breathable coating fabrics, the water vapor permeability was the most important factor.

In general, particle size is governed by a number of internal and external factors. The hydrophilicity of polyurethane was the most important factor among them. With increased hydrophilicity, smaller particles results[2,11]. The physical properties of WBPU are significantly affected by segmental polarity difference, segmental length, crystallizability of these segment, intra- and intersegment interactions such as hydrogen bonding, overall composition, and molecular weight[12-15]. The phase separation between soft segment and hard segment is also determined by these factors.

The nature of the hydrogen bonding of hard segments causes a strong mutual attraction leading to domain formation. Infrared spectroscopy has been employed extensively to study the characteristics of hydrogen bonding in domains[16-18].

It is well known that the ester type polyol-based polyurethane gives better mechanical properties, whereas the ether type polyol-based polyurethane shows better hydrolysis resistance, softness, and water vapor permeability. To make better physical properties, a mixed or special type of polyol soft segment polyurethane was used for imparting polyurethane with specific properties[19-22]. Kim and Lee[14] investigated the effect of soft segment (PTAd) length (MW: 600-2000) on the emulsion characteristics and properties of emulsion-cast films. They found that polyurethane based on PTAd (MW: 2000) gave significantly improved strength over PTAd (MW: 1000) based polyurethane, and the highest elongation. The results were interpreted in terms of soft segment crystallization, and soft-hard phase separation, which was concluded from the lowered soft segment T<sub>g</sub>. Yen and Kuo [23] used the polycaprolactone diol-poly(ethyl glycol)-polycaprolactone diol (PCL-PEG-PCL) triblock ester-ether copolydiol as a soft segment in the preparation of the WBPU. They found that the PCL-PEG-PCL based WBPU had better film softness and fabric WVP properties than those of the WBPU based on PCL polydiol/PEG polydiol blend as a soft segment.

The soft segment in polyurethane is normally in the amorphous state, despite the fact that the melting temperatures of the polyol are mostly above room temperature. The soft segment crystallizes only at very low levels of hard segments or prolonged cooling. The crystallization is noticeable as an increase in hardness. The low temperature properties of polyurethane are governed by the broadness and location of the glass transition range. Improved low temperature flexibility [24,25], characterized by the lower end of T<sub>g</sub> and a narrow T<sub>g</sub> range, is obtained through the use of soft segments which

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are less miscible with the hard segment as by the use of polyethers. The immiscibility, which induced phase separation between soft segments and hard segments, is also increased by increasing the molecular weight of soft segment[24,26, 27] or by annealing the elastomer[28]. Therefore, the character of the soft segment must be carefully adjusted to match the required property profile of the final application. However, research on the influences of block copolymer type soft segment and their content on the properties of WBPU can hardly be found.

In this study, TBG [(CL)<sub>4,5</sub>-PTMG-(CL)<sub>4,5</sub>, MW = 3000] was synthesized by end capping reaction of PTMG (MW = 2000) and CL according to the Piero's synthesis method[29]. A series of waterborne polyurethanes were prepared from 4,4-dicyclohexylmethane diisocyanate (H<sub>12</sub>MDI), 2,2-bis(hydroxymethyl)propionic acid (DMPA), ethylenediamine (EDA), triethylamine (TEA), and TBG (CL)<sub>4,5</sub>-PTMG-(CL)<sub>4,5</sub> MW = 3000] as a soft segment. This article was focused on the effect of soft segment content (60-75 wt%) with a fixed molecular weight (MW = 3000) of TBG on the colloidal properties of dispersion, hardness and thermal/mechanical properties of WBPU films, the water vapor permeability and water resistance of WBPU-coated Nylon fabrics, and the adhesive strength of WBPU-coated layer and Nylon fabrics.

## Experimental

### Materials

Poly(tetramethylene ether) glycol (PTMG, MW = 2000, BASF Korea) and  $\epsilon$ -caprolactone (CL, Aldrich Chemical) were distilled at 95 °C under vacuum before use. 4,4-dicyclohexylmethane diisocyanate (H<sub>12</sub>MDI, Aldrich Chemical), 2,2-bis(hydroxymethyl)propionic acid (DMPA, Aldrich Chemical), ethylenediamine (EDA, Junsei Chemical), triethylamine (TEA, Junsei Chemical), and N-methyl-2-pyrrolidone (NMP, Junsei Chemical) were used after dehydration with 4 Å molecular sieves for one week. Dibutyltin dilaurate (DBTDL, Aldrich Chemical), thickener (L75N, Bayer), and hardener (Desmodur DA, Bayer) were used without further purification.

### Synthesis of Triblock Glycol (TBG)

The TBG [(CL)<sub>4,5</sub>-PTMG (MW = 2000)-(CL)<sub>4,5</sub>] was obtained by the reaction of the stoichiometric amount of PTMG (MW = 2000, 0.05 mol) and CL (0.45 mol) under mild stirring with nitrogen gas atmosphere for 48 hrs at 180 °C. Then the reaction mixture was distilled to remove the unreacted component CL in vacuum condition for 2 hrs at 150 °C. The yield was about 95 %. The average molecular weight was about 3000 g/mol of TBG determined according to ASTM E 222-00.

### Synthesis of Waterborne Polyurethane (WBPU)

The WBPU was synthesized using the prepolymer mixing

process method[1]. The TBG was placed in a 4 necks round-bottom flask equipped with a thermometer, a stirrer, an inlet of dry nitrogen, a condenser, and a heat jacket, and degassed under vacuum at 90 °C for 30 min. Then DMPA/NMP (1/1 wt ratio) was added to the flask, and the mixture was allowed to cool to 45 °C under moderate stirring. Then H<sub>12</sub>MDI was added to the flask, and then 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 of NCO content during reaction was determined using a standard dibutylamine back-titration method (ASTM D1638). MEK (20 wt%) was added to the NCO-terminated prepolymer mixture to adjust the suitable viscosity of solution. And then TEA was added to the reaction mixture for neutralizing the carboxyl group of the NCO-terminated polyurethane prepolymer. After 30 min of neutralization reaction, distilled water (60 wt%) was added to the reaction mixture under vigorous stirring. The neutralized prepolymer was chain-extended by dropping EDA at 40 °C for 1 hour and the reaction continued until NCO peak (2270 cm<sup>-1</sup>) in IR spectra had completely disappeared. All the aqueous dispersions (40 wt% solid) were obtained by evaporating MEK and then by adding the adequate amount of water.

### Preparation of Films and WBPU-coated Nylon Fabrics

Preparation of films were prepared by pouring the aqueous dispersion into a Teflon disk at ambient conditions. The films (typically about 0.5 mm thick) were dried in vacuum at 50 °C for 3 days and stored in a desiccator at room temperature.

Preparation of WBPU-coated Nylon fabrics were formulated from WBPU, thickener (L75N, 0.5 wt%) and hardener (Desmodur DA, 5 wt%). The coating materials were coated to Nylon fabrics using steel bar, and then cured at 85 °C for 5 min. The thickness of coated PU layer was about 0.04 mm.

### Characterization

Particle size analysis was done using laser-scattering equipment (Autosizer, Melvern IIC). A few drops of the dispersion were diluted in distilled water before the measurement. The viscosity of WBPU dispersions were measured at 25 °C using a Brookfield digital viscometer (Model LVDV-II+). FTIR (Nicolet Impact 400D) spectrometer was used to identify the structure of WBPU and TBG. For each IR spectrometer sample, 32 scans at 4 cm<sup>-1</sup> resolution were collected in the absorbance model. The thermal behavior of WBPU and TBG were examined by using a DSC 220C (Seiko) at a heating rate of 10 °C/min under a nitrogen atmosphere. The dynamic mechanical properties of film samples were measured at 5 Hz using DMTA MK III (Rheometric scientific) with heating rate of 3 °C/min in the temperature range from -90 to 100 °C. The dimension of film sample was 5 × 5 × 0.5 (mm) for DMTA measurement. The water vapor permeability was determined using an

**Table 1.** Sample designation and composition of waterborne polyurethanes

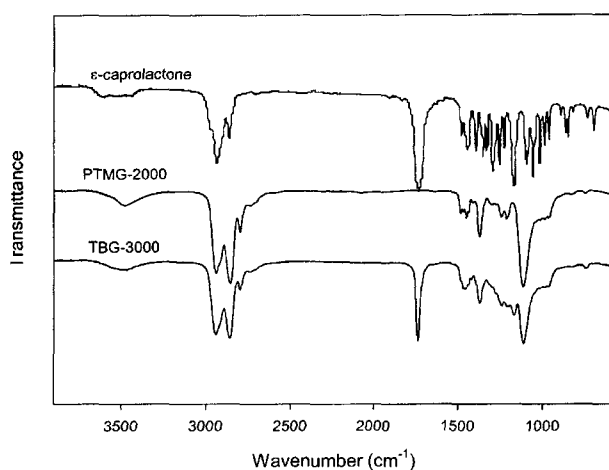
Sample <sup>1)</sup> designation	Composition (molar ratio) H <sub>12</sub> MDI/DMPA/EDA/TEA	SSC <sup>2)</sup> (wt%)	Molecular weight (g/mol)		Particle size (nm)	Viscosity (cps/25 °C)
			SS <sup>3)</sup>	HS <sup>4)</sup>		
S-60	3/0.78/1.65/0.78	60	3000	2000	76	45
S-65	3/0.78/1.53/0.78	65	3000	1615	78	44
S-70	3/0.78/1.35/0.78	70	3000	1286	98	40
S-75	3/0.78/1.11/0.78	75	3000	1000	170	38

<sup>1)</sup> Solid Content of Samples: 40 wt%.

<sup>2)</sup> Soft Segment Content: SSC.

<sup>3)</sup> Soft Segment: SS.

<sup>4)</sup> Hard Segment: HS.

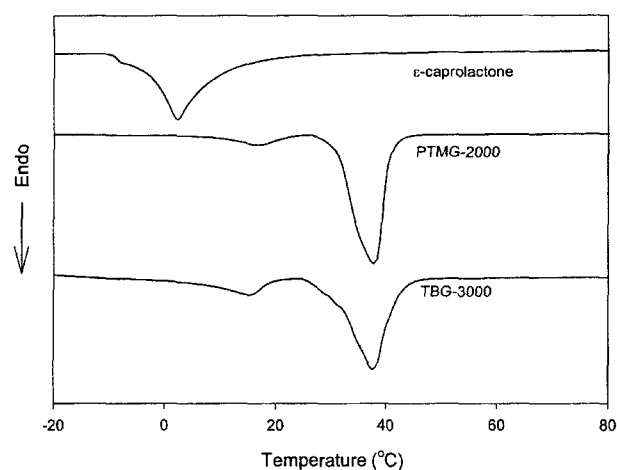
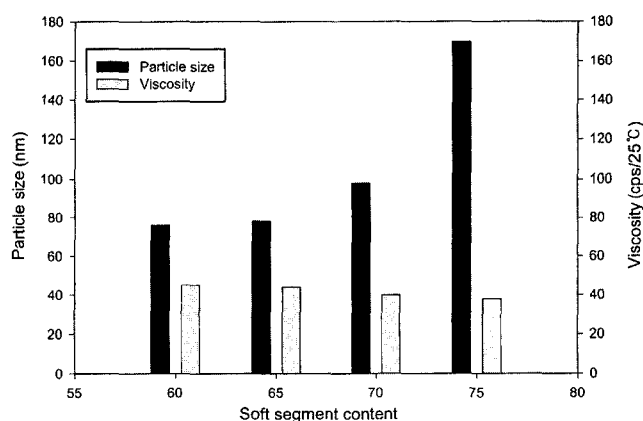
**Figure 1.** IR-Spectra of CL, PTMG, and TBG.

evaporation method described in ASTM E 9663-T. The water resistance was determined using a low range hydrostatic pressure method described in KS K 0591.

## Results and Discussion

The TBG [(CL)<sub>4.5</sub>-PTMG-(CL)<sub>4.5</sub>, MW = 3000] synthesized here was used to prepare WBPU. The WBPU had variable soft segment content (60-75 wt%) with a constant soft segment molecular weight of 3000 g/mol. As the soft segment content increases from 60 to 75 wt%, the average molecular weights of hard segments decreases from 2000 to 1000 g/mol. The sample designations, compositions, particle size and viscosity are shown in Table 1.

Figure 1 shows IR spectra of CL, PTMG (MW = 2000), and TBG (MW = 3000) prepared in this study. The TBG was identified by the characteristic CL's carbonyl group peaks at 1730 cm<sup>-1</sup> and PTMG's ether group peaks at 1112 cm<sup>-1</sup>. The DSC curves of CL, PTMG, and TBG are shown in Figure 2. The melting temperatures of CL and PTMG were near 2 °C and 38 °C, respectively. However, in the DSC curve of the TBG, two melting peaks at about 14 °C and

**Figure 2.** DSC curves of CL, PTMG, and TBG.**Figure 3.** Effect of soft segment content on the particle size and viscosity.

38 °C were observed indicating the presence of two different crystalline domains composed of CL and PTMG dominant components.

The particle size and viscosity of WBPU dispersions vs. soft segment content are shown in Figure 3. As soft segment

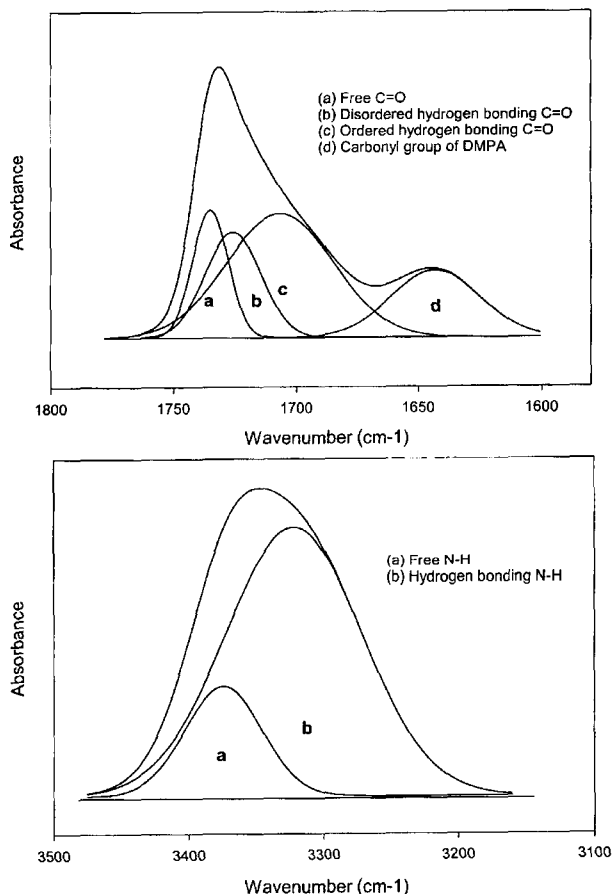
content increased, the particle size of the WBPU increased significantly, however, the viscosity of WBPU dispersion decreased a little. This behavior could be due to the decrease of hydrophilic groups content (hard segment content: the molecular weight of hard segment).

Hardness reflects the resistance to local deformation, which is complex property, related to cross-link density, plasticity/elasticity, strength/modulus and porosity of the matrix. The hardness of WBPU film prepared in this study was in the range of 90-66 Shore A (see Table 1). The hardness decreased significantly with increasing soft segment content. The decrease of hardness might be due to the increase of flexible soft segment matrix.

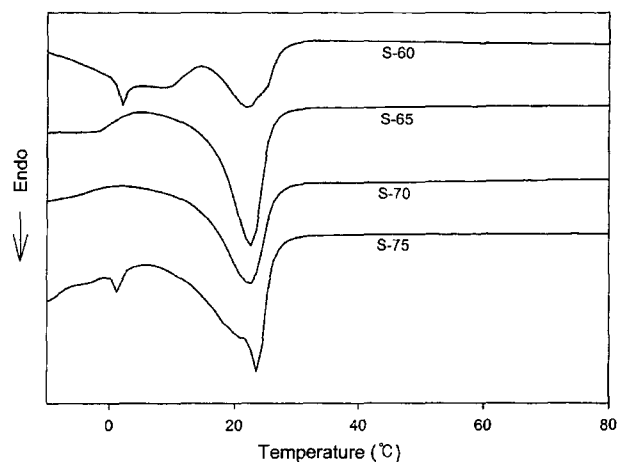
Figure 4 shows the decomposition of the C=O and N-H stretching bands of IR spectrum for typical film sample S-70. The hydrogen bonding fraction ( $X_B$ ) can be calculated from total peak area ( $C_T$ ) and the peak area of hydrogen bonding C=O or N-H groups ( $C_B$ ) as follows:  $X_B = C_B / C_T$ , where  $C_T = (a + b + c)$  for C=O and  $C_T = (a + b)$  for N-H, and  $C_B = (b + c)$  for C=O and  $C_B = (b)$  for N-H. The  $X_{B\ C=O}$  and  $X_{B\ N-H}$  of WBPU films increased with increasing soft segment content. Generally, the high length and content of

soft segment could induce the phase separation between soft segment and hard segment in polyurethane. These increases of  $X_B$  could be due to the increase of phase separation with increasing soft segment content.

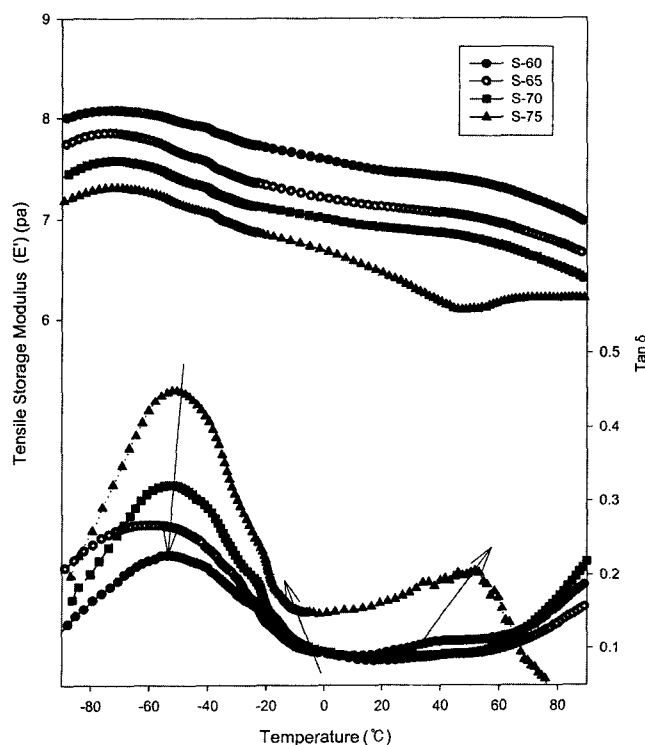
The differential scanning calorimeter (DSC) curves for the WBPU cast film samples are shown in Figure 5. Generally, the phase separation and soft segment crystallization is expected if soft segments are long enough. The soft segment TBG (MW = 3000) is believed long enough for crystallization.



**Figure 4.** Decomposition of C=O and N-H stretching for typical sample S-70.



**Figure 5.** DSC curves of WBPU film samples.



**Figure 6.** Dynamic thermal mechanical properties for WBPU film samples.

It was found that the main melting peak temperatures of soft segment for all samples were appeared at around 23 °C. As the soft segment content increased, the main melting peak  $\Delta H_m$  increased significantly, however, their  $T_m$  was almost not changed.

Figure 6 shows the storage modulus and loss tan of WBPU cast films. The storage modulus decreased remarkably with increasing soft segment content in the whole temperature range measured. Generally, the longer the soft segment length and the greater the soft segment content in polyurethanes, soft-hard phase separation increases. Chen *et al.*[30] showed that increasing the hard and soft segment length for a fixed hard/soft segment composition ratio provides more complete phase separation, an increase in modulus, and a decrease in soft domain  $T_g$  (due to purer soft phase). As the soft segment content increased from 60 to 75 wt%, the main tan peak temperature (amorphous soft domain  $T_g$ s) at around -53 °C were almost not changed. However, the end temperature ( $T_e$ ) of main loss tand peak, which related with glass transition range ( $\Delta T_g$ ), decreased from -2 °C to -11 °C with increasing soft segment content. This narrower  $\Delta T_g$  also indicated that the increase of the phase separation occurred with increasing soft segment content. The very small tan  $\delta$  peak at higher temperature (due to amorphous

hard domain  $T_g$ ) increased with increasing soft segment content. This also suggested an increase of phase separation between the hard segment and soft segment with increasing soft segment content.

Figure 7 shows the stress-strain curves of the WBPU cast films: the mechanical data are further listed in Table 2. With TBG (MW = 3000), the soft segment is believed long enough for crystallization, and enhanced strength is expected. However, with increasing soft segment content, the tensile strength and Young's modulus of WBPU film samples decreased, while the elongation at break increased remarkably from 628 to 1389 %. This implies that the mechanical properties of WBPU prepared in this study are depended dominantly on the polar hard domain fraction (hard segment content) over soft domain crystallization.

The WVP and WR of the WBPU coated Nylon fabrics (WBPU coating layer: about 0.04 mm) are shown in Figure 8. The WVP and WR lie in the range of 3615-4502 g/m<sup>2</sup>day and 1300-500 mmH<sub>2</sub>O, respectively. The WVP of commercial products (very thin coating layer: about 0.01 mm) was in the range of 4000-5000 g/m<sup>2</sup>day. However their WR was below 500 mmH<sub>2</sub>O. Considering the thickness of WBPU coating layer and WR value, the WVP values of our samples were not bad compared with commercial product. As the soft segment increased, the WVP increased significantly, however,

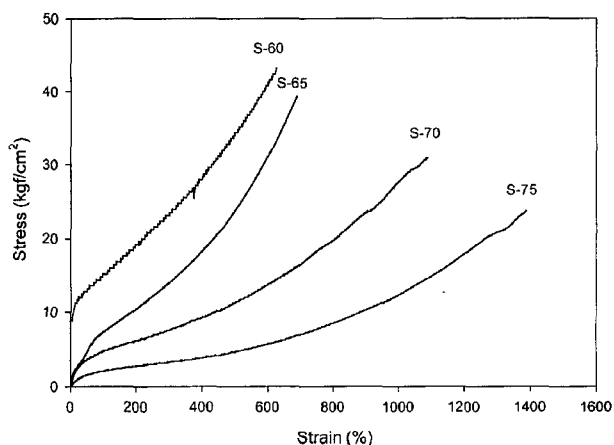


Figure 7. Stress-strain of WBPU film samples.

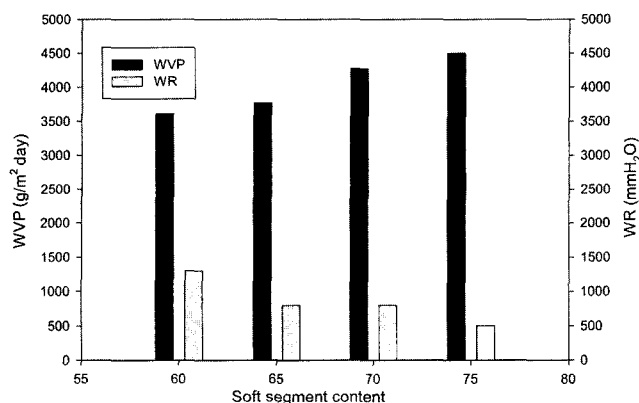


Figure 8. Effect of soft segment content on the WVP and WR.

Table 2. Physical properties of waterborne polyurethanes

Sample designation	Hydrogen bonding fraction <sup>1)</sup>		Adhesive strength (kgf/cm <sup>2</sup> )	Tg(s) (°C)	Te <sup>2)</sup> (°C)	Tg(h) (°C)	Young's modulus (Kgf/cm <sup>2</sup> )	Tensile strength (kgf/cm <sup>2</sup> )	Elongation (%)	Hardness (Shore A)
	X <sub>B(C=O)</sub>	X <sub>B(N-H)</sub>								
S-60	0.69	0.81	2.08	-52	-2.4	39	110	43	628	90
S-65	0.77	0.82	2.00	-53	-3.3	44	51	39	689	78
S-70	0.80	0.85	1.98	-53	-7.2	48	14	31	1091	74
S-75	0.83	0.91	1.96	-54	-11.0	53	5	24	1389	66

<sup>1)</sup> X<sub>B(C=O)</sub>: Hydrogen bonding fraction for C=O stretching.

X<sub>B(N-H)</sub>: Hydrogen bonding fraction for N-H stretching.

<sup>2)</sup> Te: End temperature of Tan  $\delta$ .

WR decreased. The increase of WVP might be attributed to the higher content of flexible soft segments and to the higher phase separation between soft and hard segments. The adhesive strength of WBPU-coated layer and Nylon fabrics decreased a little with increasing soft segment content. The adhesion strength of all the samples was near 2 kgf/cm<sup>2</sup>.

### Conclusions

The TBG (MW = 3000)  $\epsilon$ -caprolactone-poly(tetramethylene ether) glycol- $\epsilon$ -caprolactone (CL<sub>4.5</sub>-PTMG-CL<sub>4.5</sub>) synthesized in this study was used to prepare WBPU based on H<sub>12</sub>MDI/DMPA/EDA/TBG. Two melting peaks of TBG at about 14 °C and 38 °C were observed indicating the presence of two different crystalline domains composed of CL and PTMG dominant component. The WBPU had variable soft segment content (60-75 wt%) with a constant soft segment molecular weight of 3000 g/mol. The average molecular weight of hard segment decreased from 2000 to 1000 g/mol with increasing soft segment content. As the soft segment content increased, the particle size of dispersions increased significantly, however, the viscosity of the dispersions decreased a little. Hydrogen bonding fraction and the soft segment melting enthalpy ( $\Delta H_m$ ) increased significantly with increasing soft segment content. With increasing soft segment content, the tensile strength/modulus of WBPU film samples decreased, but the elongation at break increased significantly. As soft segment content increased, the WVP of WBPUcoated Nylon fabrics increased from 3615 to 4502 g/m<sup>2</sup>day, but the WR decreased from 1300 to 500 mmH<sub>2</sub>O. The significant changes of these properties were found to relate with the higher content of flexible soft segments and to the higher phase separation between soft and hard segments with increasing soft segment content. The adhesive strength of WBPU-coated layer and Nylon fabric was about 2.0 kgf/cm<sup>2</sup>.

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