

# Preparation and Properties of Waterborne Polyurethanes for Water-Vapor-Permeable Coating Materials

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**ABSTRACT:** Waterborne polyurethanes were prepared by polyaddition reaction using isophorone diisocyanate, dimethylol propionic acid, various polyols with a fixed molecular weight ( $M_n$  = about 2000), ethylene diamine as a chain extender, and triethylamine as a neutralization agent. Three types of polyols such as (1) solo glycols [polypropylene glycol (PPG) ( $M_n$  = 2000), poly(tetramethylene oxide) glycol (PTMG) ( $M_n$  = 2000), poly(tetramethylene adipate glycol) (PTAd) ( $M_n$  = 2000), or polycaprolactone glycol (PCL) ( $M_n$  = 2000)], (2) the polyol blends (PPG/PCL, PTMG/PCL, PPG/PTAd, PTMG/PTAd), and (3) a triblock glycol (TBG) ( $M_n$  = 1990) were used in this study. The triblock glycol (TBG) [(CL)<sub>4.5</sub>-PTMG ( $M_n$  = 1000)-(CL)<sub>4.5</sub> ( $M_n$  = 1990)] was synthesized from PTMG and  $\epsilon$ -caprolactone (CL) in this study. The triblock glycol was found to have two main melting peaks at about 13 and 40°C. This study was examined on the effect of the types of polyols on the particle size, viscosity, dynamic thermal properties, and water vapor permeability. The particle size of the aqueous polyurethane-urea dispersion increased in the order of polyol-blends-based samples (183–350 nm) > TBG-based sample (167 nm)

> solo-polyol-based sample (58–96 nm). By dynamic thermal mechanical analysis, the ester-type polyol- (PTAd and PCL) based samples were found to have higher storage modulus and  $T_g$  than those of ether-type polyol- (PPG and PTMG) based samples. The water vapor permeability (WVP) increased in the order of TBG-based sample > PCL/PTMG-based sample > PTAd/PTMG-based sample > PCL/PPG-based sample > PTAd/PPG-based sample > PTMG-based sample > PPG-based sample > PCL-based sample > PTAd-based sample. WVP was found to increase in the order of TBG-based sample > polyol-blend based samples > solo-polyol-based samples. It was also found that the samples containing ether-type glycols (PTMG, PPG) had higher permeability than samples having ester-type glycols (PCL, PTAd). PTMG-based samples were found to have higher permeability than PPG-based samples if other compositions were constant. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 123–129, 2003

**Key words:** polyurethane; coating; structure–property relations

## INTRODUCTION

The properties of polyurethane (PU) are remarkably affected by the content, chemical structure, and molecular weight of the soft segments.<sup>1–5</sup> It is well known that the ester-type polyol-based PU provides better mechanical properties, whereas the ether-type polyol-based PU shows better hydrolysis, softness, and water-vapor permeability (WVP). Generally, mixed polyols or special type polyols were used to impart special properties to PU. Yen et al.<sup>6</sup> used polyol blends such as binary [poly(ethylene glycol)/polypropylene glycol (PEG/PPG), PPG/poly(tetramethylene oxide) glycol (PTMG), and PEG/PTMG] or ternary (PEG/PPG/PTMG) systems for waterborne polyurethane (WBPU). They found that the WBPU having different polyol components had significantly different particle sizes and dispersion behaviors. Kim et al.<sup>7,8</sup> studied

the effects of poly(tetramethylene adipate glycol (PTAd)/PPG (ester/ether type soft segment) ratio on the mechanical properties. The mechanical properties were found to depend on the ratio of polyol blend. Xiu et al.<sup>9</sup> used ether-type polyol PPG and ester-type polyol PTAd with various molecular weight, and poly-ether-ester polyol [poly(propylene oxide–maleic anhydride)diol]. Ester-type polyol-based PU showed much better physical properties than those of ether-type polyol-based PU, due to their ability to crystallize and to stronger forces between the polymer chains. Polyester-ether-based PU displays a higher Young's modulus and lower elongation than polyester-based or polyether-based PU, primarily due to the larger interface within domains. Chen et al.<sup>10</sup> studied the PU properties with PPG/PEG as mixed soft segments of PU. As PEG content increased, the moisture permeability of the PU films increased. The mechanical properties were not changed. Poly(dimethyl siloxane)(PDMS)/PTMG as soft segments was used to investigate the changes in water absorption and moisture sensitivity with the different composition.<sup>11</sup> PDMS/PTMG-based materials had higher water absorption values than either the pure PTMG or pure

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PDMS-based material. Yen et al.<sup>12,13</sup> synthesized the polycaprolactone–poly(ethylene glycol)–polycaprolactone (PCL–PEG–PCL) triblock copolydiol from PEG and  $\epsilon$ -caprolactone under uncatalyzed reaction conditions according to Piero's synthesis method,<sup>14</sup> and examined the effects of length ratios of PEG/PCL chains on the WVP of WBPU-coated fabrics.

In this study, triblock glycol (TBG) [(CL)<sub>4.5</sub>–PTMG ( $M_n = 1000$ )–(CL)<sub>4.5</sub>,  $M_n = 1990$ ] was synthesized from PTMG and  $\epsilon$ -caprolactone according to the similar method of Piero synthesis. WBPU were prepared by polyaddition reaction using isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA), various polyols with a fixed molecular weight ( $M_n =$  about 2000), ethylene diamine (EDA) as a chain extender, and triethylamine (TEA) as a neutralization agent. Three types of polyols—(1) solo polyols [PPG ( $M_n = 2000$ )], [PTMG ( $M_n = 2000$ )], [PTAd ( $M_n = 2000$ )], [PCL,  $M_n = 2000$ ]]; (2) the polyol blends (PPG/PCL, PTMG/PCL, PPG/PTAd, PTMG/PTAd); and (3) a triblock polyol (TBG) [(CL)<sub>4.5</sub>–PTMG ( $M_n = 1000$ )–(CL)<sub>4.5</sub>,  $M_n = 1990$ ]]—were used in this study. The effect of types of polyols with fixed molecular weight ( $M_n = 2000$ ) on the particle size, viscosity, dynamic thermal properties, and WVP of WBPU was investigated.

## EXPERIMENTAL

### Materials

CL (Sigma, MO) and PTMG (Union Carbide, VA,  $M_n = 2000$ ) were dried over calcium hydride at room temperature for 24 h. CL was distilled at 96°C under vacuum (15 mm Hg) before use. DMPA (Aldrich Chemical, WI), PCL (Union Carbide,  $M_n = 2000$ ), PPG (Union Carbide,  $M_n = 2000$ ), and PTAd (Union Carbide,  $M_n = 2000$ ) were dried in a vacuum oven (100°C) for at least 5 h. IPDI (Aldrich Chemical), EDA (Aldrich Chemical), TEA (KASEI, Japan), methyl ethyl ketone (MEK, Aldrich), and *N*-methyl-2 pyrrolidone (NMP, Aldrich) (Aldrich Chemical) were used after dehydra-

tion with 4 Å molecular sieves for one day. Dibutyl tin dilaurate (DBTDL, Aldrich), thickner (L75N, Bayer, Germany), stiffener (Desmodur DA, Bayer), and slipping agent (BYK333, BYK, Germany) were used without further purification.

### Synthesis of triblock polyol and WBPUs

Synthesis of triblock polyol (TBG) [(CL)<sub>4.5</sub>–PTMG ( $M_n = 1000$ )–(CL)<sub>4.5</sub>, theoretical  $M_n = 2000$ , measured  $M_n = 1990$ ]

TBG was synthesized by the reaction of the stoichiometric amount of PTMG ( $M_n = 1000$ ) (50 g, 0.05 mole) and  $\epsilon$ -caprolactone (CL) (51 g, 0.45 mole) under mild stirring (150 rpm) with nitrogen gas atmosphere for 48 h at 180°C. Then the reaction mixture was distilled to remove the unreacted component CL in vacuum condition at 190°C. The CL/PTMG mol ratio was about 9. TBG obtained with the yield about 95% was dried in a vacuum oven at 100°C for one week. The average molecular weight ( $M_n = 1990$ ) of TBG was determined by titration and its molecular weight ( $M_n = 1990$ ) was almost same as theoretical molecular weight ( $M_n = 2000$ ).

### Synthesis of WBPU

Three types of WBPUs based on (1) solo glycols [PPG ( $M_n = 2000$ ), PTMG ( $M_n = 2000$ ), PTAd ( $M_n = 2000$ ), or PCL ( $M_n = 2000$ )], (2) the polyol blends (PPG/PCL, PTMG/PCL, PPG/PTAd, PTMG/PTAd), and (3) a triblock polyol (TBG) [(CL)<sub>4.5</sub>–PTMG [ $M_n = 1000$ ]–(CL)<sub>4.5</sub>,  $M_n = 1990$ ] were prepared as follows. DMPA was dissolved in NMP (50/50 w/w) in a four-necked round-bottom flask equipped with a thermometer, a stirrer, an inlet of dry nitrogen, a condenser, and a heat jacket. Then polyol was placed in the flask and degassed under vacuum at 60°C for 1 h. IPDI/MEK (12 g/5.6 g) was added slowly under moderate stirring, and the mixture was allowed to react at 80°C until the theoretical NCO content was reached. MEK

TABLE I  
Sample Designation and Composition (Mole Ratio) of WBPUs<sup>a</sup>

Sample designation	Polyol ( $M_n = 2000$ )	IPDI	DMPA	EDA	TEA
S-PPG	PPG (1.2)	3	0.8	1	0.8
S-PTMG	PTMG(1.2)	3	0.8	1	0.8
S-PCL	PCL (1.2)	3	0.8	1	0.8
S-PTAd	PTAd (1.2)	3	0.8	1	0.8
T-TBG	TBG (1.2)	3	0.8	1	0.8
B-CL/PPG	PCL/PPG (0.6/0.6)	3	0.8	1	0.8
B-PCL/PTMG	PCL/PTMG (0.6/0.6)	3	0.8	1	0.8
B-PTAd/PPG	PTAd/PPG (0.6/0.6)	3	0.8	1	0.8
B-PTAd/PTMG	PTAd/PTMG (0.6/0.6)	3	0.8	1	0.8

<sup>a</sup> The solid content of all samples: 30%.

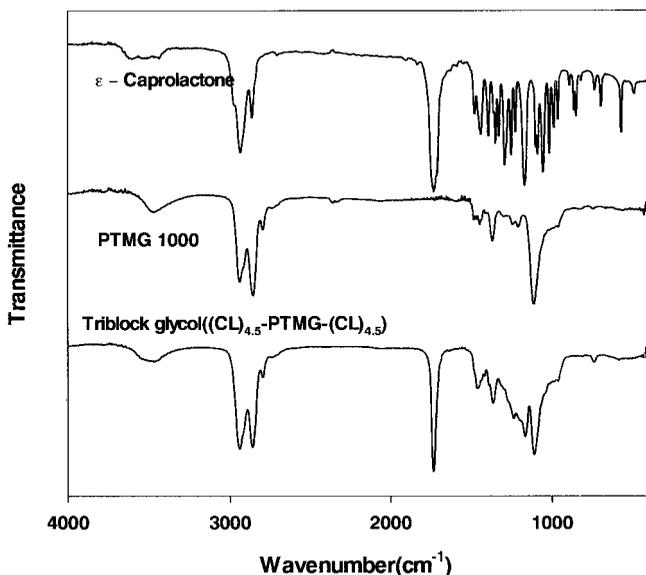


Figure 1 IR spectra of CL, PTMG, and triblock glycol [(CL)<sub>4.5</sub>-PTMG-(CL)<sub>4.5</sub>].

(18 wt % per polymer) was added to the NCO-terminated prepolymer mixture to adjust the suitable viscosity of solution. And then triethylamine was added to the reaction mixture for neutralizing the carboxyl groups of the NCO-terminated PU prepolymer. After 30 min of neutralization reaction, distilled water (70 wt % per polymer) was added to the reaction mixture.

The neutralized prepolymer was chain extended by dropping EDA at 40°C for 1 h and the reaction continued until NCO peak (2270 cm<sup>-1</sup>) in infrared (IR) spectra had completely disappeared. All the aqueous dispersions (30 wt % solids) were obtained by evaporating MEK and then by adding the adequate amount of water. The various samples of waterborne polyurethane (WBPU) prepared in this study are identified in Table I. The S-series samples are polyurethanes based on solo glycols, and sample T and B-series samples are based on the triblock glycol (TBG) and polyol blends, respectively.

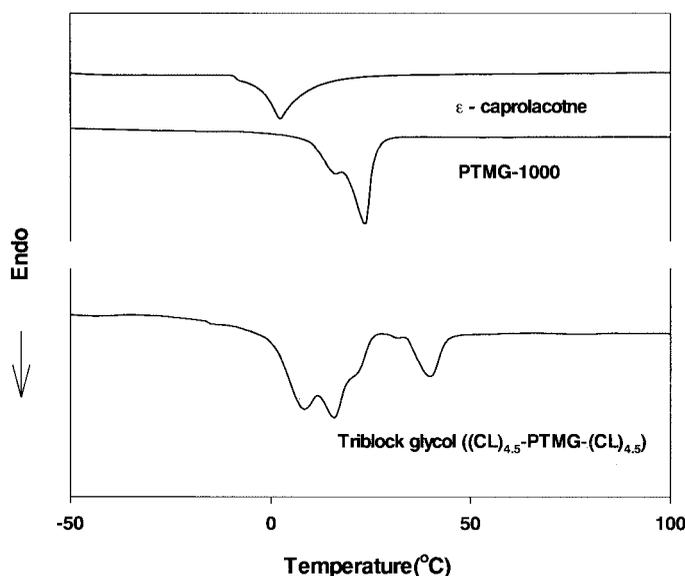
**Preparation of films and WBPU coated nylon fabrics**

**Preparation of films**

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 2 days and stored in a desiccator at room temperature.

**Preparation of WBPU-coated nylon fabrics**

Coating material was formulated from WBPU, thickener (L75N, 0.5 wt %), stiffener (Desmodur DA, 0.5 wt %), and slipping agent (BYK333, 0.1 wt %). The coating material was coated to nylon fabrics using steel



Sample	M <sub>n</sub> (theory)	M <sub>n</sub> (measurement)	Yield(%)	T <sub>m</sub> (°C)
Triblockglycol	2000	1990	95	13 : 40

Figure 2 DSC curves of CL, PTMG, and triblock glycol [(CL)<sub>4.5</sub>-PTMG-(CL)<sub>4.5</sub>], and reaction yield (%) and number average molecular weight (M<sub>n</sub>) of triblock glycol.

bar and filler, and then predried at 100°C for 2 min and cured at 130°C for 5 min. The thickness of coated PU layer was about 0.08 mm.

### Characterization

Particle size analysis was done using laser-scattering equipment (Autosizer, Melvern IIC, Malvern, Worcester, UK). A few drops of the dispersion were diluted in nonionized water before the measurement. The viscosity of WBPU dispersions was measured at 25°C using a Brookfield digital viscometer (model LVDV-II+, MA). A FTIR (Nicolet Impact 400D, Madison, WI) spectrometer was used to identify the structure of TBG. For each IR spectrometer sample, 32 scans at 4  $\text{cm}^{-1}$  resolution were collected in the transmittance mode. The thermal behavior of TBG was examined by using a differential scanning calorimeter (DSC, 220C Seiko, Japan) 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 dynamic mechanical thermal analyzer (DMTA) MK III (Rheometric Scientific, UK) with a heating rate of 3°C/min in the temperature range from -80 to 100°C. The dimension of film was a 8 × 5 × 0.5 (mm/mm/mm) for DMTA measurement. The WVP was examined by using an evaporation method described in ASTM E 9663-T.

## RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of CL, PTMG ( $M_n = 1000$ ), and the triblock glycol (CL<sub>4.5</sub>-PTMG-CL<sub>4.5</sub>,  $M_n = 1990$ ). The triblock glycol was identified by the characteristic peaks around 1730  $\text{cm}^{-1}$  of CL (carbonyl group) and 1112  $\text{cm}^{-1}$  of PTMG (ether group). The DSC curves of CL, PTMG, and TBG are shown in Figure 2. The melting temperatures of CL and PTMG were near 2 and 23°C, respectively. However, the triblock glycol was found to have two melting peaks such as a broad peak (peak containing three peak) around 13°C and a single peak at 40°C, which was indicated the presence of multiphase structure in the TBG.

The particle size, viscosity, and WVP of various WBPU dispersions at 25°C and WVP of WBPU coated nylon fabrics at 40°C are shown in Table II. The particle size of solo glycols based WBPU (S-series samples) are in the range of 58–96 nm, the particle size of TGB based WBPU (T sample) is 167 nm, and those of blend glycols based WPU (B-series samples) are in the range of 183–350 nm. The particle size of WBPU prepared in this study increased in the order of B-series samples (183–350 nm) > T sample (167 nm) > S-series samples (58–96 nm). The B-series samples had the highest particle size values. The particle size of the T-sample-containing triblock copolymer was higher

**TABLE II**  
Particle and Viscosity of Dispersion at Room Temperature, and WVP of WBPU-Coated Fabric at 40°C

Sample	Particle size (nm)	Viscosity (cps/25°C)	WVP (g/m <sup>2</sup> day) at 40°C
S-PPG	58	34	1660
S-PTMG	73	29	2010
S-PCL	85	30	1520
S-PTAd	96	26	1490
T-TBG	167	8	3930
B-PCL/PPG	183	17	2600
B-PCL/PTMG	233	12	2760
B-PTAd/PPG	190	11	2530
B-PTAd/PTMG	350	10	2690

value than those of S-series samples having solo polyols. Generally, it is well known that random copolymers have higher random bulky structure compared with corresponding homopolymer. The larger particle size of B samples could be due to the random bulky structure of polymer composed of two different polyols. The viscosity increased in the order of S-series samples (26–34 nm) > B-series samples (10–17 cps) > T samples (8.1 cps). In general, the polymer dispersion of lower particle size has higher viscosity than that of higher particle size. Therefore, the higher viscosity of S-series samples is caused by relatively lower particle sizes. However, the reason for the lower viscosity of T sample than B-series samples is not understood clearly.

Figure 3 presents the storage modulus of (a) S-series samples/T sample and (b) B-series samples. It was found that the ester-type polyol- (PTAd, and PCL) based samples have higher storage modulus than those of ether-type polyol- (PPG and PTMG) based samples. The PTAd-based samples has higher storage modulus than PCL-based samples in the whole temperature range measured. The storage modulus of the PTMG-based sample was higher than those of PPG- and TBG-based samples at above -30°C; however, the storage modulus was in the order of PPG-based sample > TBG-based sample > PTMG-based sample at below -30°C. The decrease of storage modulus may be related to the decreased structural order resulting from the difficulty in regular molecular packing, which was depended on the molecular flexibility and regularity in the given temperature range. Especially, the storage modulus of TBG-based sample began to drop sharply at -30°C. Therefore, the TBG-based sample has the lowest storage modulus at room temperature. This result may be due to the lower regularity of TBG structure. Figure 4 shows the dynamic loss modulus of (a) S-series samples/T sample and (b) B-series samples. Most samples prepared in this study have a single loss modulus peak in the lower

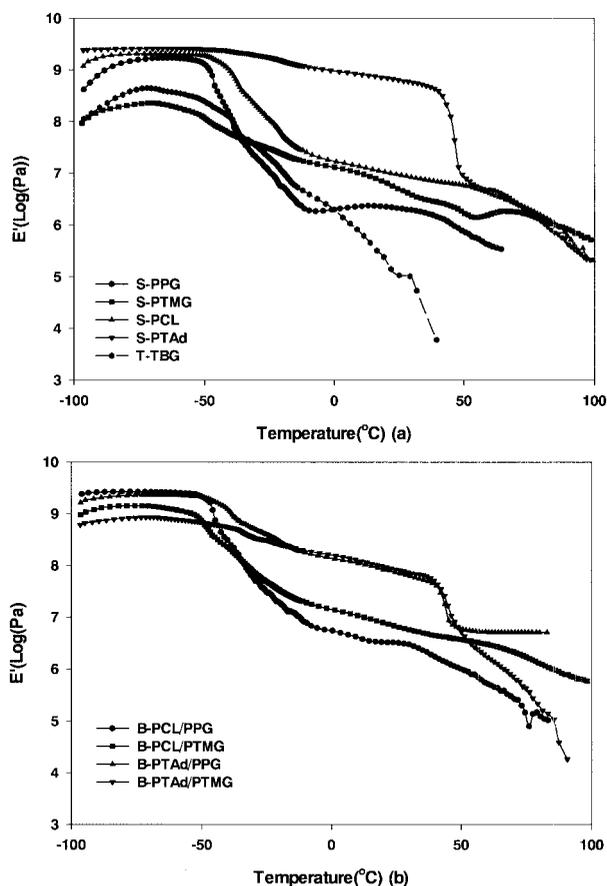
**TABLE III**  
DMT Properties of WBPU

Sample designation	$T_{gs}$ (°C)	$T_{gh}$ (°C)	Storage modulus at 20°C [Log(Pa)]
S-PPG	-47		6.35
S-PTMG	-50		6.81
S-PCL	-40		7.03
S-PTAd	-25	40	8.86
T-TBG	-50	-39(shoulder)	5.39
B-PCL/PPG	-47	-40(shoulder)	6.51
B-PCL/PTMG	-49	-40(shoulder)	6.90
B-PTAd/PPG	-41	-25(shoulder)	7.92
B-PTAd/PTMG	-50	-25(shoulder)	7.99

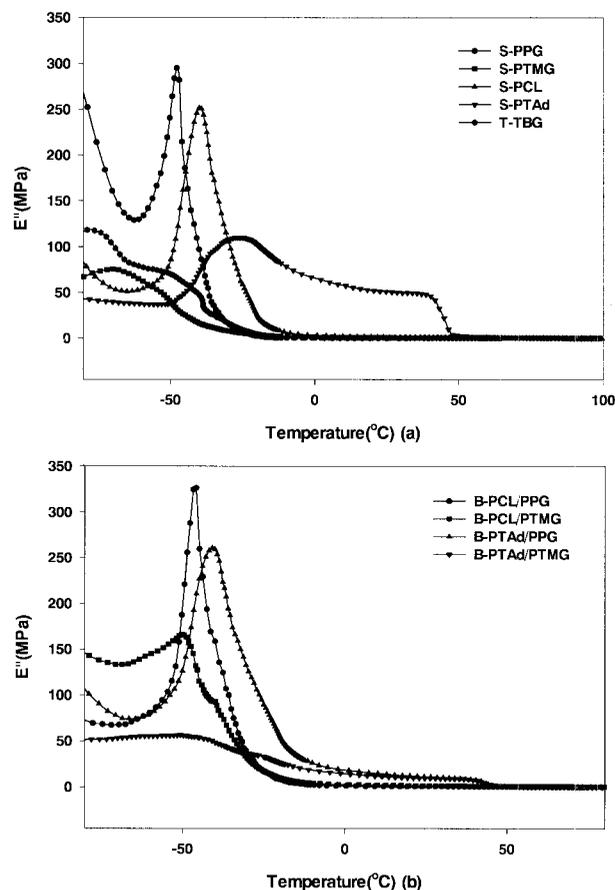
temperature range (glass transition temperature of soft segments:  $T_{gs}$ ). However, B-series samples have a peak containing a shoulder in the middle point of their two constituted component peaks (S-series samples). The TBG-based T sample has broad two peaks that could be assigned to PTMG and PCL components. The  $T_{gs}$ s of ester-type polyol-based samples was higher than those of ether-type polyol-based samples. It was found that the increasing

trend of  $T_{gs}$ s for various samples was almost same as the change of their storage modulus, while PTAd-based samples were solely found to have a glass transition temperature of hard segments at near 40°C. The higher  $T_{gs}$  values of ester-type polyol-based sample might be due to their higher ability to crystallize and to stronger intermolecular forces.

The WVPs (g/m<sup>2</sup>day) of WBPU-coated nylon fabrics as function of temperature are shown in Figure



**Figure 3** Storage modulus of WPU films: (a) S-series samples/T sample, and (b) B-series samples.



**Figure 4** Loss modulus of WPU films: (a) S-series samples/T sample, and (b) B-series samples.

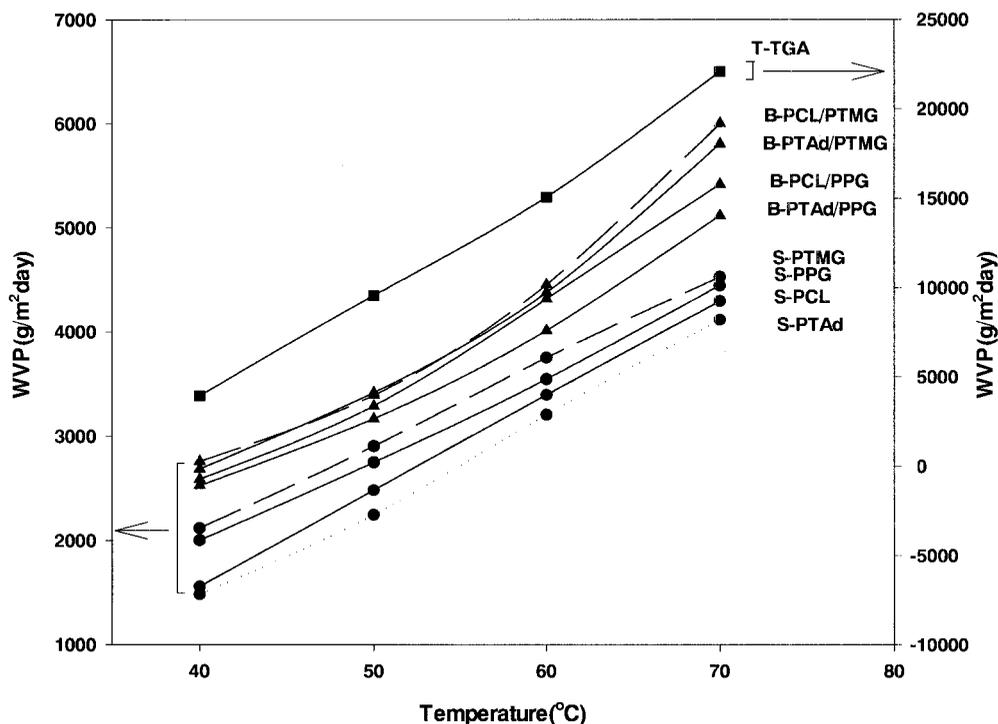


Figure 5 Effect of the type of various polyol on the WVP of WPU-coated nylon fabrics.

5. The WVP of fabrics increased with increasing temperature. The permeability increased in the order of T-TGB > B-PCL/PTMG  $\approx$  B-PTAd/PTMG > B-PCL/PPG > B-PTAd/PPG > S-PTMG > S-PPG > S-PCL > S-PTAd. It is noticeable that the triblock glycol (TBG)-based T-sample has the highest permeability (3930–23,000 g/m<sup>2</sup>day) in the temperature ranges of 40–70°C. From this result, it is concluded that the TBG prepared in this study is a good candidate to prepare waterborne polyurethanes for water-vapor-permeable coating materials. The permeability of B-series samples was higher than those of S-series samples. The ether-type glycol- (PTMG, PPG) based samples were found to have higher permeability than ester-type glycol- (PCL, PTAd) based samples. The samples containing the PTMG component were found to have higher permeability than samples having PPG component when other components were constant. The higher WVP might be attributed to the higher flexibility of soft segment and to the larger interface within domains. However, the root cause of the permeability difference between these samples is not clear at the present moment. More detailed studies should be made.

## CONCLUSIONS

WPU with three types of polyols such as (1) solo glycol [PPG ( $M_n = 2000$ ), PTMG ( $M_n = 2000$ ), PTAd ( $M_n = 2000$ ), or PCL ( $M_n = 2000$ )], (2) the blended polyols (PPG/PCL, PTMG/PCL, PPG/PTAd,

PTMG/PTAd), and (3) a triblock polyol (TBG) [(CL)<sub>4.5</sub>-PTMG ( $M_n = 1000$ )-(CL)<sub>4.5</sub>,  $M_n = 1990$ ] as soft segments were synthesized. The triblock glycol (TBG) was synthesized from PTMG and caprolactone in this study. The triblock glycol was found to have two melting temperatures of 13 and 40°C. This article has examined the effect of the types of polyols with fixed molecular weight ( $M_n = 2000$ ) on the particle size, dynamic thermal properties, and WVP. The particle size of the aqueous polyurethane-urea dispersion increased in the order of B-series samples (183–350 nm) > T sample (167 nm) > S-series sample (58–96 nm). By DMTA, it was found that the ester-type polyol- (PTAd and PCL) based samples have higher storage modulus and  $T_g$  than those of ether-type polyol- (PPG and PTMG) based samples. The WVP increased in the order of T sample > B-series samples > S-series samples. The permeability increased in the order of T-TGB sample > B-PCL/PTMG sample > B-PTAd/PTMG sample > B-PCL/PPG sample > B-PTAd/PPG sample > S-PTMG sample > S-PPG sample > S-PCL sample > S-PTAd sample. It is remarkable that the TGB-based T sample has the highest permeability, and the permeability of B-series samples is higher than those of S-series samples. It was also found that the samples containing ether-type glycols (PTMG, PPG) have higher permeability than samples having ester-type glycols (PCL, PTAd). The samples containing PTMG component were found to have

higher permeability than samples having PPG component when the other components were same.

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