

PCL-PEG-PCL Triblock Ester-Ether Copolydiol-Based Waterborne Polyurethane. II. Effect of NCO/OH Mole Ratio and DMPA Content on the Physical Properties

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Received 15 April 1997; accepted 27 June 1997

ABSTRACT: This article was focused on the effects of the NCO/OH molar ratio and 2,2-bis(hydroxyl methyl) propionic acid (DMPA) content during prepolymerization on the physical properties of synthesized waterborne polyurethane (WBPU) by using the polycaprolactone-poly(ethyl glycol)-polycaprolactone triblock copolydiol (PCL-PEG-PCL) as the soft segment. The results showed that the particle size of the WBPUs' dispersion decreased with a decreasing NCO/OH molar ratio or increasing DMPA content. Regarding thermal and mechanical properties, the WBPUs had a higher T_g 's and lower T_m 's and a higher breaking stress and a lower breaking strain of film with the NCO/OH molar ratio or DMPA content increase. The increasing NCO/OH molar ratio was advantageous to the water vapor permeability (WVP)-breaking stress balance, but the effect of the DMPA content on the WVP was not significant. The WBPU with PCL-PEG-PCL as the soft segment had a smaller particle size in dispersion and a better WVP-breaking stress balance than those of WBPU with the blending PCL and PEG as the soft segment. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1301-1311, 1998

Key words: waterborne polyurethane; ester-ether copolydiol; hydrophilic segment; water vapor permeability

INTRODUCTION

Waterborne polyurethane (WBPU) dispersions have been widely used in the textile industry for sueding, water vapor permeability (WVP), anti-static, and nonformaldehyde durable press applications.¹⁻⁸ The physical properties of WBPU are greatly affected by the composition and molecular chain of the soft segment.⁷⁻¹³ To enhance its physical properties, recently, WBPU was prepared by using mixed polydiols as the soft segment and the effects have been widely studied.¹²⁻¹⁵ In an effort to improve the mechanical properties and the WVP of WBPU, we used the polycaprolactone diol-poly-

(ethyl glycol)-polycaprolactone diol (PCL-PEG-PCL) triblock ester-ether copolydiol as the soft segment in the preparation of the WBPU. We found that the PCL-PEG-PCL-based WBPU had better film softness and fabric WVP properties than did the WBPU synthesized by blending the PCL polydiol and the PEG polydiol as the soft segment.^{16,17} We also found that the higher the soft-segment content (the higher the end cap of the PCL content on PEG) or the higher the PEG molecular weight in the soft-segment composition, the greater the improvements in the fabric WVP. However, the mechanical property of cast film decreased with increasing PEG molecular weight. The balance in physical properties between the WVP and the mechanical properties require further improvements.

The mechanical properties of the WBPU cast

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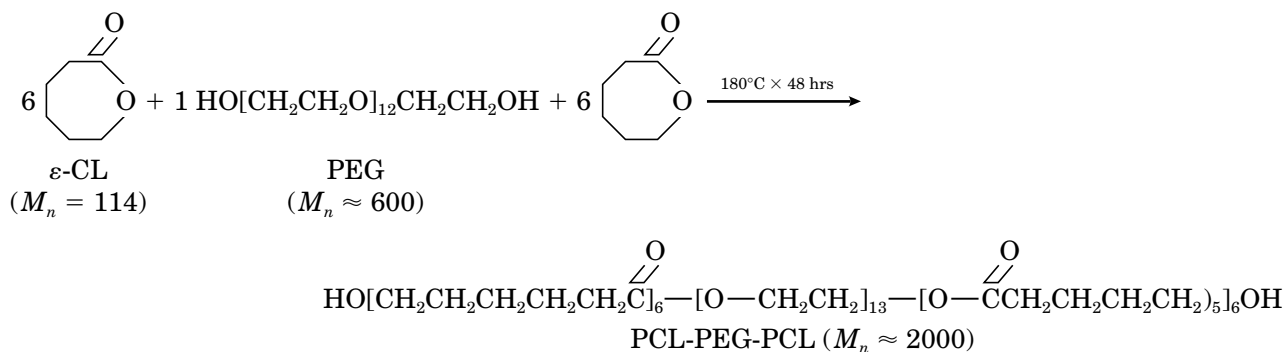
film is influenced not only by the soft-segment composition but also by the hard-segment composition and the hydrophilic segment. Past reports^{18–24} showed that the type and content of the hydrophilic segment largely influenced the stability of the WBPU dispersion and hardness and tensile-stress properties. For anionic WBPU dispersion, it was generally observed that when the Coulombic force in the PU intermolecular structure increased the particle size of the PU dispersion decreased and the hardness and tensile stress of the cast film improved due to the increasing amount of hydrophilicity.^{23,24} It was generally observed that the hardness and breaking stress increased as the NCO/OH mol ratio increased.^{25–27} This article was focused on the effects of the NCO/

OH mol ratio and DMPA content in the prepolymerization on the physical properties of the synthesized WBPU by using the PCL–PEG–PCL triblock ester–ether copolydiol as the soft segment.

EXPERIMENTAL

Materials

The PCL–PEG–PCL triblock ester–ether copolydiol (M_n about 2000), used as the soft segment for the WBPU was synthesized from a PEG (M_n 600) end-capped with ϵ -caprolactone (ϵ -CL) according to the synthesis method of Piero et al.²⁸ The reaction equation is listed as follows:



Methylene bis(cyclohexyl–diisocyanate) (H_{12} MDI, from Bayer) was dried at 80°C for 2 h in a vacuum. 2,2-Bis(hydroxyl methyl)propionic acid (DMPA, from Tokyo Chemical, reagent grade) was used as the potential ionic center. Triethylamine (TEA) and ethylene diamine (EDA) (both from Hanawa, Japan, reagent grade) and 1-methyl-2-pyrrolidone (NMP, Ferak, reagent grade) were used as the neutralization agent, chain extender, and solvent, respectively. They were dried with 4 Å molecular sieves.

Synthesis

The CET series anionic waterborne polyurethane (CET series WBPU) was prepared with the PCL–PEG–PCL triblock copolydiol as the soft segment by the prepolymer mixing method.²⁹ The polydiol and DMPA were dissolved in NMP and added to the reactor and heated to 80°C. H_{12} MDI and di-*n*-butyltin dilaurate were then added to the mixture and the reaction was kept at 90°C for 3.5 h. The mixture was then cooled to 70°C and neutralized with TEA. An aqueous dispersion was obtained

by adding water drop by drop and the chain-extension process with EDA/water was continued for 2 h. The final dispersion solution was diluted to 30% with water. For comparison, another type of WBPU (CEB series WBPU) was prepared by blending PEG polydiol and PCL polydiol as the soft segment.

Film Casting and Nylon Fabric Coating

Films were prepared by casting WBPU on a Teflon plate, followed by drying at 50°C for 72 h. The films were then removed and placed in a desiccator before testing. A 2% melamine resin, thickening agent [$\text{NH}_4\text{OH}_{(\text{aq})}$], and 0.5% catalyst were added to the WBPU and this solution was used to coat the nylon fabrics. A 50 g/sq m piece of nylon taffeta fabric was coated with the solution. After coating, the fabric was predried at 100°C for 3 min and cured at 130°C for 5 min.

Characterization

The molecular weights of the WBPUs were determined by a Waters RI-6000 gel permeation chro-

Table I The Molecular Weight and its Distribution of the Synthesized WBPU

WBPU Code	NCO/OH ^a Molar Ratio	DMPA ^b		H ₁₂ MDI (g)	Polydiol (g)	Molecular Weights of WBPU		
		Wt %	g			$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n
CET ^c -1	1.37	4.50	1.34	7.39	20.66	3.9	9.8	2.51
CET-2	1.60	3.56	1.05	7.67	20.66	6.9	14.3	2.06
CET-3	1.60	4.50	1.34	8.38	19.68	6.9	12.7	1.85
CET-4	1.60	5.51	1.63	9.14	18.89	8.4	18.1	2.10
CET-5	1.83	4.50	1.34	9.36	18.70	9.2	16.4	1.78
CET-6	2.07	4.50	1.34	10.32	17.71	9.4	16.5	1.74
CEB ^d -1	1.37	4.50	1.34	7.39	20.66	2.3	6.9	3.3
CEB-2	1.60	3.56	1.05	7.67	20.66	6.9	17.2	2.50
CEB-3	1.60	4.50	1.34	8.38	19.68	6.8	14.9	2.19
CEB-4	1.60	5.51	1.63	9.14	18.89	6.0	14.5	2.41
CEB-5	1.83	4.50	1.34	9.36	18.70	8.5	17.0	2.00
CEB-6	2.07	4.50	1.34	10.32	17.71	8.7	16.9	1.94

^a The NCO/OH molar ratio represents the molar ratio of H₁₂MDI(polydiol + DMPA) in the prepolymerization.

^b The DMPA wt % represents the weight percent of DMPA weight/total prepolymer weight $\times 100\%$.

^c The CET series' WBPU was synthesized with the PCL-PEG-PCL triblock copolydiol ($M_n = 2000$) as the soft segment.

^d The CEB series' WBPU was synthesized by blending PCL and PEG ($M_n = 2000$) as the soft segment.

matograph using polystyrene standards. The particle size and its distribution of the WBPU were measured by light scattering (MALVERN, a He-Ne-type laser with wavelength of 633 nm

was used). The sample was first diluted with deionized water to 0.5%, followed by ultrasonic wave treatment. The differential scanning calorimeter analyzer (DSC, DuPont thermal analyzer 2000)

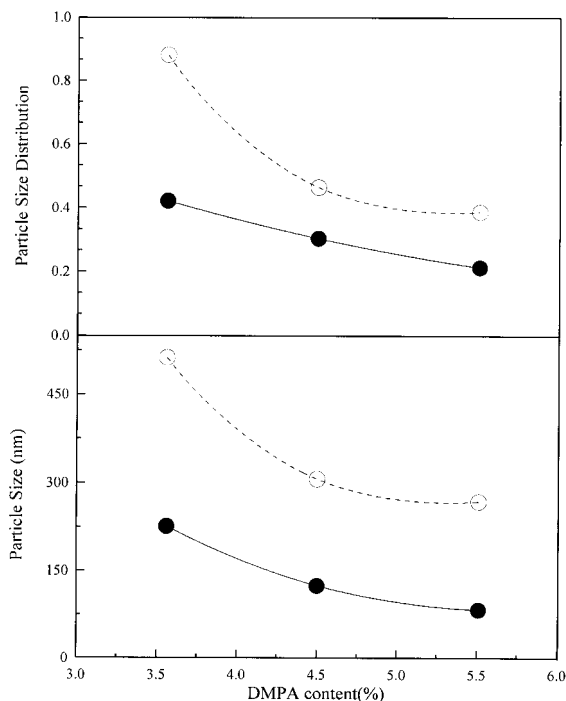


Figure 1 The influence of DMPA contents on the particle size and its distribution of the WBPU dispersion: (●) CET series; (○) CEB series.

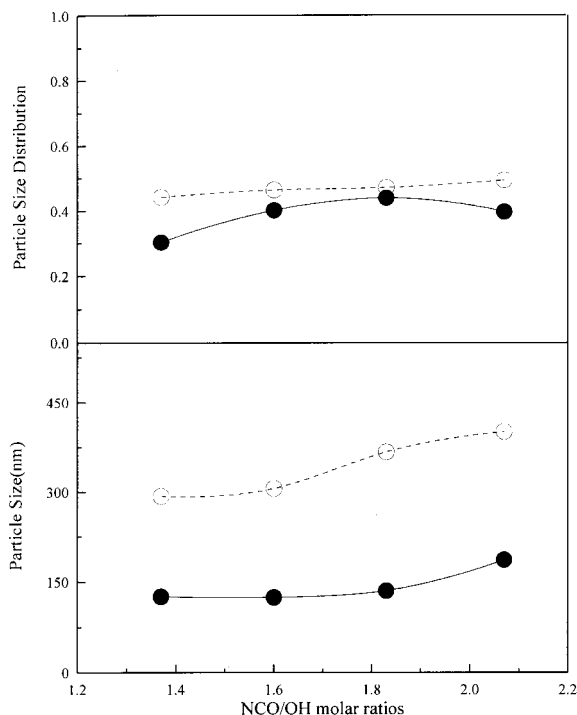


Figure 2 The influence of the NCO/OH molar ratio on the particle size and its distribution of the WBPU dispersion: (●) CET series; (○) CEB series.

was used with liquid nitrogen for cooling and the heating rate was 20°C/min. PU film with a thickness of 0.1 mm and 2 × 2 sq cm was used for the solvent absorption study. The polymer strips were immersed in toluene at 25 ± 0.1°C and the weight of the strips was monitored at regular time intervals to a constant weight. The extent of absorption was estimated from the equation $\{(W - W_0)/W_0\} \times 100$. The value was taken as the percentage equilibrium absorption, and W and W_0 are the final weight and the initial weight, respectively. The mechanical properties of the cast film were determined using an Instron tensile tester, according to ASTM D-412 Die C. The WVP study for the coated fabrics was based on the JIS-1099 CaCl₂ method at 40°C and 90% RH.

RESULTS AND DISCUSSION

Molecular Weight and Molecular Weight Distribution of WBPU

Table I shows the molecular weight and molecular weight distribution of the synthesized WBPUs. Here, the CET series and the CEB series WBPUs were synthesized by using the soft segment with the triblock ester-ether copolydiol (PCL-PEG-

PCL, $M_n = 2000$) and with blending PEG polydiol and PCL polydiol ($M_n = 2000$), respectively. The number-average molecular weight (M_n) increases and the molecular weight distribution (M_w/M_n) becomes narrower with an increasing NCO/OH molar ratio in the prepolymerization in the CET series and CEB series of WBPUs. This is due to increase of the —NCO residue groups in the prepolymer, which is favorable for the chain-extension reaction as the NCO/OH molar ratio increases. The effect of DMPA content on the molecular weight and its distribution of WBPU was not significant.

Comparison of the two WBPU series shows that the CET series has a higher M_n and a narrower M_w/M_n than those of the CEB series. This is because the soft segment of the CET series has better reactivity of the —OH group with the NCO group. In general, the ester-polydiol (PCL) has a higher reactivity than that of the ether-polydiol (PEG).

Particle-Size Analysis

Figure 1 shows the particle size and its distribution of the WBPU dispersion influenced by the DMPA content. The WBPU particle size de-

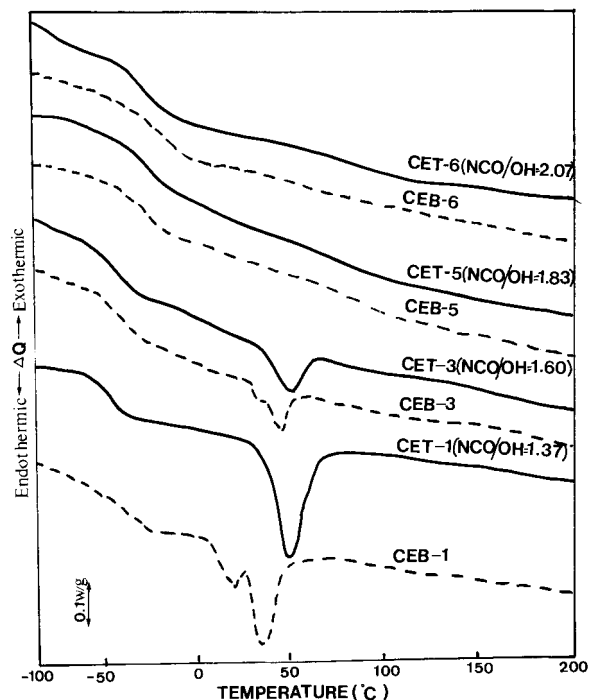


Figure 3 DSC thermographs of the WBPU with various NCO/OH molar ratios.

creased and its distribution became narrower with increasing DMPA content. This is because the particle size of the WBPU dispersion is affected by the hydrophilicity of the PU ionomer. Water enters more easily into the hard-segment domains to disperse the WBPU molecules as the ionic character (DMPA) of the hard segment is increased.^{29,30} Figure 2 shows the effect of the NCO/OH molar ratio on the particle size and its distribution of the WBPU. The WBPU particle size increases slightly and its distribution becomes slightly broader with an increasing NCO/OH molar ratio. As the NCO/OH mol ratio increases, the formation of urea groups in the PU molecule is also increased. The presence of hydrogen bonding results in the aggregation of the PU molecules. As a result, the free volume of WBPU will increase. The higher M_n of WBPU from the higher NCO/OH molar ratio is also a reason for the formation of a larger particle size.

For the WBPUs prepared, the CET series has a far smaller particle size and a narrower particle distribution than those of the CEB series. In the CET series, the hydrophilic soft segment (PEG) is evenly distributed, which allows a favorable dispersion of water. The CEB series possesses a hydrophobic component (a long-chain PCL) in some soft segments, which will result in the ag-

gregation of the WBPU in the water to form a larger particle size.

Thermal Property

Figures 3 and 4 show the differential scanning calorimeter (DSC) diagrams of the cast films from the WBPU, with the thermal properties listed in Table II. In terms of the NCO/OH molar ratio (Fig. 3), the glass transition temperature of the soft segment (T_g 's) shifts to a higher temperature (-44.3 to -37.7°C) with an increasing NCO/OH molar ratio. This can be explained by Fox's law ($1/T_g = W_a/T_{g,a} + W_b/T_{g,b}$, where W_a and W_b are the weight percentage of the hard- and soft-segment components, respectively; T_g is the glass transition temperature of the polymer; and $T_{g,a}$ and $T_{g,b}$ are the glass transition temperature of the pure hard- and soft-segment components, respectively). In general, the T_g of the hard-segment component is far higher than that of the soft-segment component, so the T_g of the polymer increases with the hard-segment content. In addition, in urea-forming-type reactions, more chain extender (EDA) for the higher NCO/OH molar ratio will produce more urea linkages, which will result in more intermolecular force to increase the T_g 's. The results in Table II and Figure 3 also

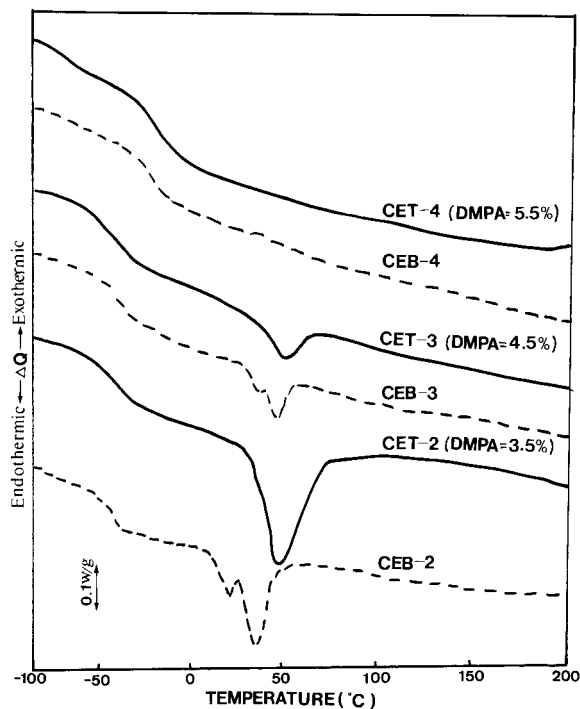


Figure 4 DSC thermographs of the WBPU with various DMPA contents.

show that the melting temperature (T_m) shifts to a lower temperature and the melt enthalpy (ΔH) becomes smaller with an increasing NCO/OH molar ratio and disappears when the NCO/OH molar ratio is above 1.8. The higher T_m 's and larger ΔH 's for the lower NCO/OH molar ratio is because the cohesive forces among the soft segments increase in accordance with the decrease of the intermolec-

ular forces between hard and soft segments. Under this condition, the crystallization of the soft segment and the phase separation can easily be formed. Figure 4 shows DSC diagrams of the synthesized WBPU with various DMPA contents. The T_g 's shift to higher temperatures (-42.6 to -36.0°C), the T_m 's shift to lower temperature, and the ΔH 's become smaller with increasing DMPA

Table II The Thermal Properties of the CET Series' WBPU with Various NCO/OH Molar Ratios and DMPA Contents

WBPU Code	Thermal Properties				
	T_g ($^\circ\text{C}$)	ΔT_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH (W/g)	ΔT_m ($^\circ\text{C}$)
CET-1	-44.3	14	50.1	34	41
CET-2	-42.6	9	50.4	36	40
CET-3	-42.1	13	47.5	13	25
CET-4	-36.0	16	—	—	—
CET-5	-39.3	12	—	—	—
CET-6	-37.7	9	—	—	—
CEB-1	-45.1	16	40.2	24	45
CEB-2	-43.6	9	39.4	18	42
CEB-3	-43.1	15	38.7	12	30
CEB-4	-37.9	19	—	—	—
CEB-5	-40.2	12	—	—	—
CEB-6	-39.1	10	—	—	—

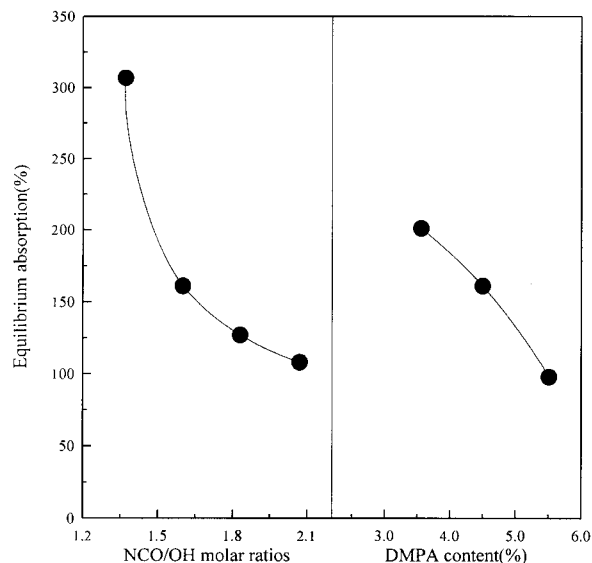


Figure 5 The equilibrium absorption of the CET series WBPU cast films with various NCO/OH molar ratios and DMPA contents.

content. This is because the ionic groups in the PU molecular chains bring more intermolecular Coulombic force and results in phase mixing between the hard and soft segments, whereby the movement of the PU molecular chain is limited.

Comparing the CET and CEB series of the WBPU prepared, we found that the CET series show a little lower T_g than that of the CEB series. However, the CET series possesses a higher T_m , a larger ΔH , and a narrower ΔT_g and ΔT_m than those of the CEB series. This indicates that the

intermolecular force between the soft segments and the phase separation for the CET series is larger than for those of the CEB series. This, in turn, may be due to the more regular and homogeneous arrangement of the soft segment in the PU molecular chains for the CET series.

Solvent Absorption

Figure 5 shows the equilibrium absorption vs. the NCO/OH molar ratio and the DMPA content of

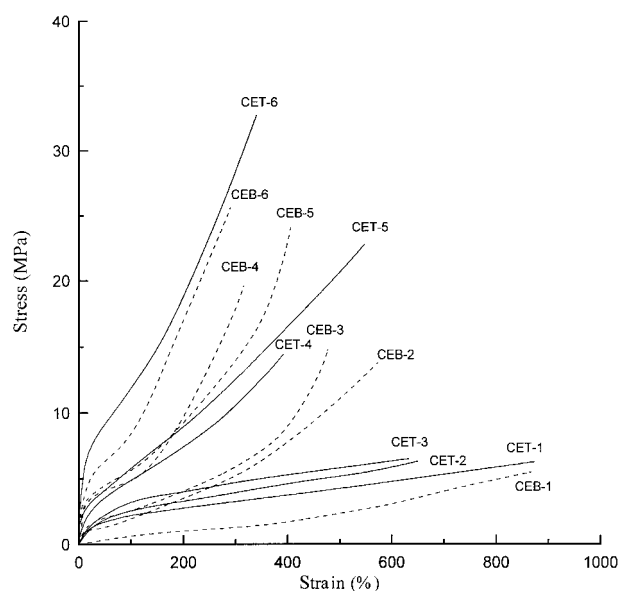


Figure 6 The stress-strain curves of the WBPU cast films.

Table III The Mechanical Properties of the WBPU with Various NCO/OH Molar Ratios and DMPA Contents

WBPU Code	Young's Modulus (MPa)	100% Modulus (MPa)	Breaking Stress (MPa)	Breaking Strain (%)
CET-1	6.7	2.2	6.3	873
CET-2	4.9	2.6	6.3	650
CET-3	5.9	3.2	6.5	633
CET-4	14.1	4.9	14.5	392
CET-5	20.1	5.9	22.8	547
CET-6	69.5	12.3	32.7	340
CEB-1	0.6	0.8	5.5	867
CEB-2	7.9	2.2	13.8	573
CEB-3	8.2	2.6	14.8	477
CEB-4	32.7	4.7	19.6	316
CEB-5	30.1	6.0	24.1	406
CEB-6	31.5	8.2	25.6	300

^a The WBPU cast film thickness is $120 \pm 10 \mu\text{m}$.

the cast films of the WBPU of the CET series. The solvent absorption decreases with the NCO/OH molar ratio and the DMPA content. Sreenivasan³¹ suggested that the lack of segment mobility in the hard-segment domain at the experimental temperature was the factor leading to the impermeability and that the soft segments possessed substantial chain mobility to facilitate the diffusion. Since the intermolecular forces between the hard and soft domains increase with the NCO/OH molar ratio, and the Coulombic force among the PU

molecules increases with the DMPA content, the mobility of the soft segment is restricted and the solvent absorption is decreased.

Mechanical Properties

Figure 6 shows the stress–strain curves of the WBPU cast films; the mechanical data are further listed in Table III. The Young's modulus and the breaking stress increase while the breaking strain decreases for the intermolecular force and the

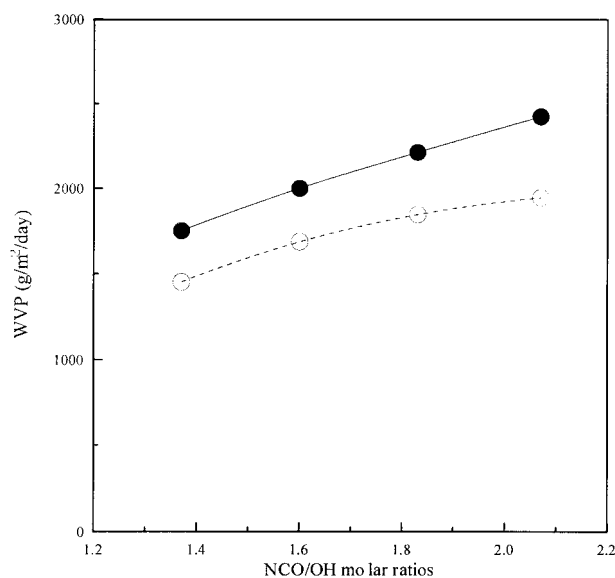


Figure 7 The WVP of the coated fabrics with various NCO/OH molar ratios of the WBPU: (●) CET series; (○) CEB series.

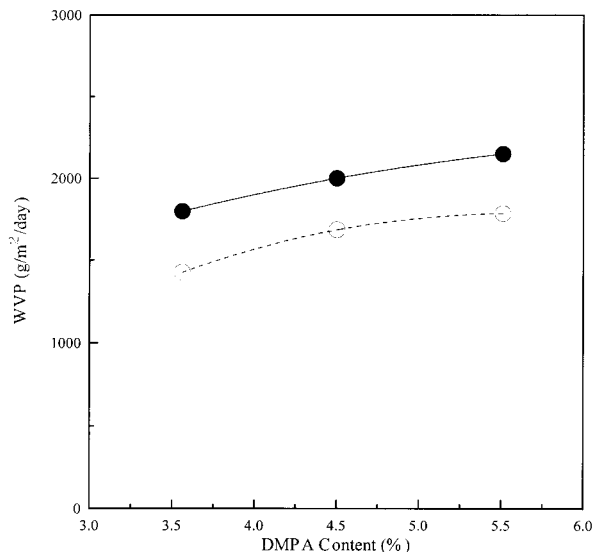


Figure 8 The WVP of the coated fabrics with various DMPA contents of the WBPU: (●) CET series; (○) CEB series.

phase mixing increases with the NCO/OH molar ratio. The Young's modulus and breaking stress also increase while the breaking strain decreases with increase in the DMPA content. This is due to the presence of the Coulombic force and the hydrogen-bond interaction between the molecular chains.^{18,29}

A comparison of the mechanical properties between the CET series and the CEB series of the WBPU cast film showed that, in general, the CET series had a higher modulus and breaking strain

than those of the CEB series, while the Young's modulus and breaking stress was lower for various DMPA contents (3.56–5.51 wt %) and at a lower NCO/OH molar ratio (1.60–1.83). However, as the NCO/OH molar ratio was increased to 2.07 (CET-6), the Young's modulus and breaking stress of the CET series became higher than those of the CEB series. Again, this may be due to the more regular molecular arrangement of the soft segments and good phase separation in the CET series, which resulted in the higher modulus and

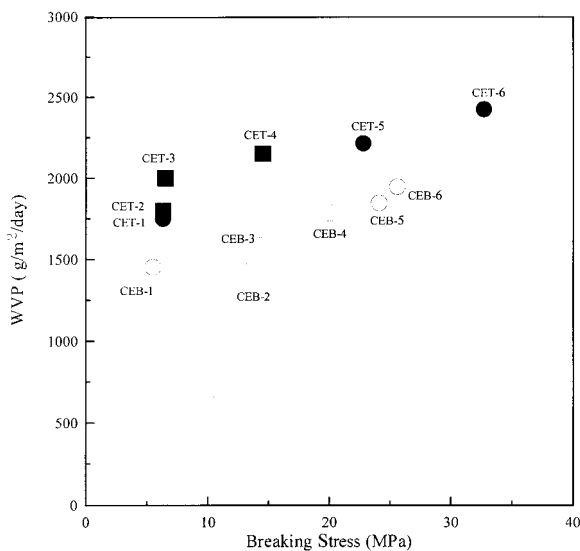


Figure 9 The relationship between the WVP of coated fabrics and the breaking stress of the WBPU films.

breaking strain. On the other hand, the CEB series possessed two different classes of soft segment. The PU molecular chains do not easily slip at the initial elongation and the soft-segment molecular arrangements became disordered after the yield point. Therefore, the Young's modulus and breaking stress were higher. The better mechanical properties of the CET series at a higher NCO/OH molar ratio may be because the WBPU in the CET series had better polymerization and had urea linkages to enter into the soft-segment region to support the domain.

WVP

Figure 7 shows the WVP of the coated fabrics with various NCO/OH molar ratios of WBPUs. The WVP increases with increasing of the NCO/OH molar ratio. Earlier theories suggest that the WVP becomes lower at a higher NCO/OH molar ratio. However, the partial dispersion of the hard-segment to the soft-segment domain retards the formation of the soft-segment crystal or may cause separation of the partial domains and support the soft-segment domains as the NCO/OH molar ratio is increased. Therefore, the water vapor can easily permeate the fabric surface with a higher NCO/OH molar ratio. Figure 8 shows the WVP of the coated fabrics treated with different DMPA contents of the WBPU. The hydrophilicity of the DMPA is favorable for increase of the WVP. In addition, the soft segment decreases as the DMPA contents increase (Table I), which results in a slight increase in the WVP. From Figures 7 and 8, we found that the CET series has a higher WVP than that of the CEB series. This is because the CET series WBPUs have better phase separation than that of the CEB series.

Figure 9 shows the relationship between the WVP of coat fabrics and the breaking stress of the WBPU film by comparing the WBPUs of the CET series and the CEB series. It is clear that the CET series' WBPU (especially CET-6) has a better WVP-breaking stress balance than that of the CEB series' WBPU. The increasing NCO/OH molar ratio is advantageous to the WVP-breaking stress balance, but the effect of DMPA content on the WVP is not significant.

CONCLUSION

The results can be summarized as follows:

1. A higher NCO/OH molar ratio yields a

larger particle size for the WBPU dispersion and better mechanical properties and WVP for the WBPU cast film. This is because the PU molecular aggregation and intermolecular force increases with the NCO/OH molar ratio.

2. A higher DMPA content yields a smaller particle size for the WBPU dispersion and better mechanical properties for the WBPU cast film. This is because the higher DMPA increases the hydrophilicity and Coulombic force of the WBPU.
3. A higher NCO/OH molar ratio is advantageous to the WVP-breaking stress balance, but the effect of the DMPA content on the WVP is not significant. Comparing the CET series and CEB series of the WBPU, the CET series yields a smaller particle size for the WBPU dispersion and better WVP-breaking stress for the WBPU cast film.

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