

PCL-PEG-PCL Triblock Copolydiol-Based Waterborne Polyurethane. I. Effects of the Soft-Segment Composition on the Structure and Physical Properties

MENG-SHUNG YEN, SHU-CHIN KUO

Department of Textile Engineering, National Taiwan Institute of Technology, 43, Keelung Road, Section 4, Taipei, Taiwan, Republic of China

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ABSTRACT: This article examines the effects of the soft-segment composition on the structure and physical properties of waterborne polyurethane (WBPU) based on polycaprolactone-poly(ethylene glycol)-polycaprolactone (PCL-PEG-PCL) triblock copolydiol as the soft segment. The molecular weight of PEG in the soft-segment composition and soft-segment content (SSC) are varied in this study. The water-vapor permeability (WVP) for the WBPU-coated nylon fabric is also studied. The results showed that the glass transition temperatures (T_g 's) of the soft segment decreased and its temperature range (ΔT_g 's) narrowed with increase of SSC up to 63 wt % and decrease of the PEG molecular weight. The dynamic mechanical analysis results showed that the α -peak height of the soft segment increased with SSC when the SSC was less than 63 wt %. However, when SSC was more than 63 wt %, the α -peak height became smaller with increasing SSC due to the crystallization of the soft segment. At the same SSC, the number of spherulites was reduced and the spherulites become larger with decrease of the PEG molecular weight. As for the mechanical properties of the WBPU cast film, the breaking stress decreased and the breaking elongation increased with increasing SSC or decreasing PEG molecular weight. For the WBPU-coated nylon fabrics, either higher SSC or higher PEG molecular weight improves the WVP. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 883–892, 1997

Key words: waterborne polyurethane; PCL-PEG-PCL ester-ether triblock copolydiol; crystallization; phase separation; water vapor permeability

INTRODUCTION

The physical properties of polyurethane (PU) is significantly affected by the compositions of the soft segments.^{1–3} In general, the ester-type polydiol-based PU displays better mechanical properties, whereas the ether-type PU displays better hydrolysis resistance, softness, and water-vapor permeability (WVP). To improve the physical properties, a mixed or special type of polyol soft-

segment PU was used for imparting PU with specific properties.^{4–12} Chen et al.⁴ studied the PU properties with poly(propylene glycol)-poly(ethylene glycol) (PPG-PEG) as mixed soft segments of PU and showed that PU with higher PEG content could increase the moisture permeability of the PU films while the mechanical properties were not affected. Cooper et al.^{5,6} used poly(dimethyl siloxane) (PDMS) and poly(tetramethylene glycol) (PTMG) as mixed soft segments and found that the PU had a better water absorption and moisture sensitivity than did PU with PDMS as the soft segment. They also found that as the PDMS component was replaced by a cyanoethyl group-modified PDMS (PCEMS) both the ultimate stress and elongation at break improved

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with increased PTMG content. Kim and Kim⁷ mixed poly(tetramethylene adipate) (PTAd) and PPG as an ester-ether polydiol soft segment and found that the initial modulus and tensile strength increased slowly at low PPG content, but increased rapidly at higher PPG content.

Waterborne polyurethane dispersions (WBPU) have been widely used in the textile industry for water-vapor permeability (WVP), sueding, anti-static, and nonformaldehyde applications.^{2,13,14} The ether-type WBPU has better softness, WVP, and hand, while the ester-type WBPU displays better adhesion, dyeability, and mechanical properties.² To obtain a better physical property balance, study using mixed ester and ether polyol soft segments for WBPU may be an appropriate route. In our previous article,¹² we focused on the effects of a soft-segment mixing procedure for the WBPU study: films formed from mixed ether and ester-type WBPU (CEM series), films from WBPU synthesized with PEG and PCL as mixed soft segments (CEB series), and films formed from WBPU synthesized with ester-ether triblock copolydiol (PCL-PEG-PCL) as the soft

segment (CET series). The results showed that the CEM series WBPU had better mechanical properties and a clear phase boundary between the ester-type and ether-type WBPU, the CEB series WBPU had better phase mixing, and the CET series WBPU had better softness, elongation, and WVP. For textile-coated fabrics, the softness, handle, permeability, and mechanical properties are required. From the previous studies, it suggests that the mixing procedure of the CET series WBPU would be more suitable for the coated finishings. However, the CET series WBPUs revealed weaker mechanical strength; thus, a detailed examination of this procedure must be studied further.

This article was focused on the effects of the soft-segment composition on the structure and physical properties of synthesized WBPU by using the PCL-PEG-PCL triblock copolydiol as the soft segment. In the synthesis of the PCL-PEG-PCL triblock copolydiols from fixed molecular weights of PEG by end-capped ϵ -caprolactone (ϵ -CL), the molecular weight was from 430 to 3300. The ϵ -CL/PEG mol ratio varied from 2 to 24 and

Table I Soft-segment Compositions of PCL-PEG-PCL Triblock Copolydiol WBPUs^a

PU Code	Soft-segment Composition				
	M_n of PEG	ϵ -CL/PEG Molar Ratio	M_n of Triblock Copolydiol		Soft-segment Content in WBPU (SSC Wt %) ^c
			Calculated	Experimental ^b	
CET-600-42 ^d	600	2	828	841	41.9
CET-600-53		6	1284	1273	52.9
CET-600-63		12	1968	2011	63.1
CET-600-70		18	2652	2668	69.5
CET-600-74		24	3331	3300	74.3
CET-400-42	400	4	856	839	42.4
CET-400-53		8	1312	1296	53.1
CET-400-60		12	1768	1750	60.2
CET-400-63		14	1996	1954	62.9
CET-400-66		16	2224	2234	65.8
CET-200-27	200	2	428	435	27.3
CET-200-34		4	656	663	33.5
CET-200-44		6	884	894	44.0
CET-200-50		8	1112	1155	49.7
CET-200-54		10	1340	1375	53.9
CET-200-63		16	2024	1981	63.0

^a H₁₂MDI : copolydiol : DMPA : EDA = 1.6 : 0.5 : 0.5 : 0.5 (molar ratio).

^b Molecular weights of the PCL-PEG-PCL ester-ether triblock copolydiols were determined by the ASTM D 1638 method.

^c SSC (wt %) = 100 × (mass of the soft segment/total mass).

^d The X and Y of the CET-X-Y show the PEG molecular weights and SSC in WBPU with the PCL-PEG-PCL ester-ether triblock copolydiol as the soft segment, respectively.

Table II Thermal Properties and Relative Crystallinity of the CET Series WBPU with the PCL-PEG-PCL Triblock Copolydiol as the Soft Segment

PU Code	DSC					DMA T_{α} (°C)	Relative Crystallinity ^a (%)
	T_g (°C)	ΔT_g (°C)	T_m (°C)	ΔH (J/g)			
CET-600-42	-17	42	—	—	Broad	0 ^b	
CET-600-53	-36	31	—	—	-30	5	
CET-600-63	-47	15	34	11	-44	21	
CET-600-70	-48	10	46	43	-48	36	
CET-600-74	-48	8	47	51	-47	40	
CET-400-43	-19	37	—	—	Broad	0 ^b	
CET-400-53	-37	20	—	—	-36	7	
CET-400-60	-46	15	—	—	-44	15	
CET-400-63	-47	12	35	14	-48	22	
CET-400-66	-48	10	47	37	-48	31	
CET-200-27	Broad	Broad	—	—	Broad	—	
CET-200-33	-4	34	—	—	Broad	—	
CET-200-44	-24	24	—	—	-26	0 ^b	
CET-200-50	-34	18	—	—	-32	2	
CET-200-54	-40	13	—	—	-46	14	
CET-200-63	-48	9	34	20	-48	28	

^a The relative percentage crystallinity (X_c) used by the wide-angle X-ray analysis is $X_c = \frac{\int_{\theta_1}^{\theta_2} lc(x)dx}{\int_{\theta_1}^{\theta_2} l(x)dx}$, where the $\int_{\theta_1}^{\theta_2} lc(x)dx$ is the area of the crystal region, $\int_{\theta_1}^{\theta_2} l(x)dx$ is the total area of the crystal and amorphous region, and the diffraction angles θ_1 and θ_2 are 10° and 40°, respectively.

^b It is assumed that the SSC is 43 ± 1 wt %, as a completely amorphous polymer in any series of WBPU.

molecular weights of PEG were 200, 400, and 600, and of PCL, between 228 and 2736.

EXPERIMENTAL

Materials

The waterborne polyurethane (WBPU) used the PCL-PEG-PCL ester-ether triblock copolydiol as the soft segment. The PCL-PEG-PCL ester-ether triblock copolydiol was synthesized from a fixed molecular weight of PEG by end-capped ϵ -caprolactone (the molecular weight of ϵ -CL is 114) according to the synthesis method of Piero et al.¹⁵ and the soft-segment molecular weight shown in Table I. The ϵ -CL/PEG mol ratio varied from 2 to 24 and the molecular weights of the PEG used were 200, 400, and 600, and that of the PCL, between 228 and 2736. Methylene bis(cyclohexyl-diisocyanate) (H_{12} MDI, from Bayer) as the hard segment was vacuum-dried at 80°C for 2 h. 2,2-Bis(hydroxyl methyl)propionic acid (DMPA, from Tokyo Chemical, reagent grade) was used

as potential ionic centers. Triethylamine (TEA) and ethylene diamine (EDA) (both from Hanawa, Japan, reagent grade) and 1-methyl-2-pyrrolidone (NMP, Ferak, reagent grade), used as the neutralizer, chain extender, and solvent, respectively, were immersed in 4 Å molecular sieves for more than 1 week before being used.

Synthesis

The anionic WBPU was synthesized by a prepolymer mixing method.¹⁶ The synthesized ester-ether triblock copolyols and DMPA dissolved in NMP were added to the reactor and heated to 80°C; H_{12} MDI and the catalyst (di-*n*-butyltin dilaurate) were then added to the mixture and the reaction proceeded at 90°C for 3.5 h. The mixture was cooled to 70°C and neutralized with TEA. An aqueous dispersion was obtained by the drip addition of water with EDA/water for a period of 2 h.

Film Casting and Nylon Fabrics Coating

The films from the solvent evaporation method were obtained by casting the WBPU resins evenly

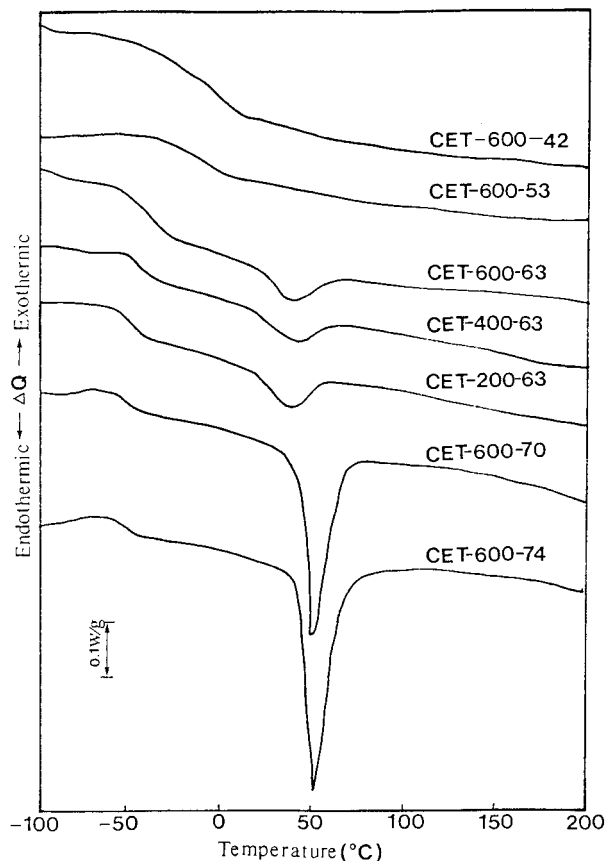


Figure 1 DSC thermograms of the CET series of WBPU.

on a Teflon plate, followed by drying at 50°C for 3 days. The films were then removed and placed in a desiccator ready for testing. For the coating of nylon fabrics, the WBPU dispersion was blended with melamine resin, a thickening agent [$\text{NH}_4\text{OH}_{(\text{aq})}$], and a catalyst was coated onto the nylon taffeta fabrics. After coating, the fabric was pre-dried at 100°C for 3 min and cured at 130°C for 5 min. The synthesized WBPU resins are coded in Table I.

Test

The IR spectra of the samples were analyzed with a JASCO FTIR spectrophotometer. Polarized microscopy was examined with an Olympus BH-2-UMA-type polarized microscope at magnifications of 100 \times . The wide-angle X-ray scattering profiles (WAXS) were taken with a Philips PW 1050 diffractometer, employing nickel-filtered $\text{CuK}\alpha$ radiation and the 2θ scanning rate was 2°/min with a sample thickness of 150 μm . The relative percentage crystallinity (X_c) used by the wide-angle X-ray analysis is

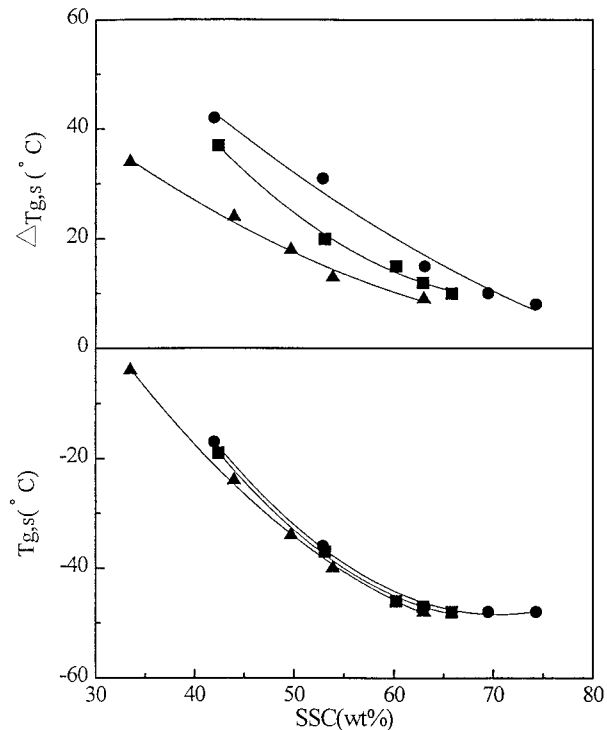


Figure 2 T_g 's and ΔT_g 's of the soft segment vs. the SSC of the WBPU: (●) CET-600 series; (■) CET-400 series; (▲) CET-200 series.

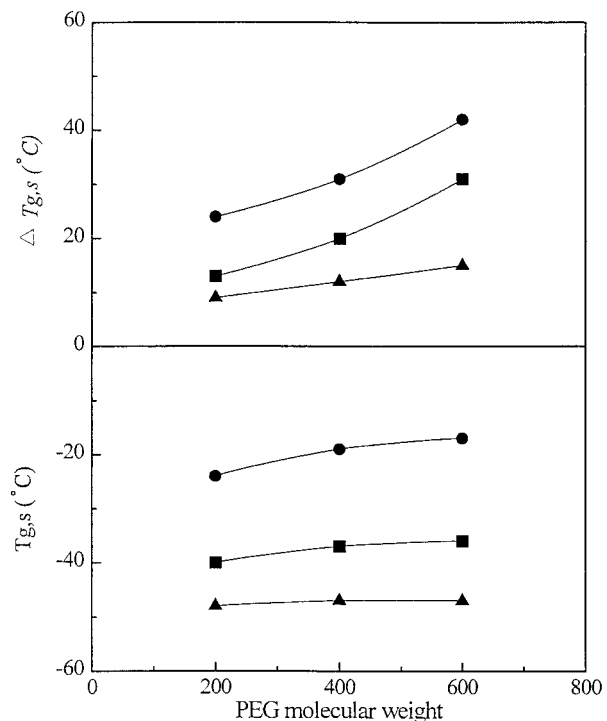


Figure 3 T_g 's and ΔT_g 's vs. the PEG molecular weight in the soft-segment composition for the WBPU. Average soft-segment molecular weight: (●) 850 \pm 50; (■) 1300 \pm 50; (▲) 2000 \pm 50.

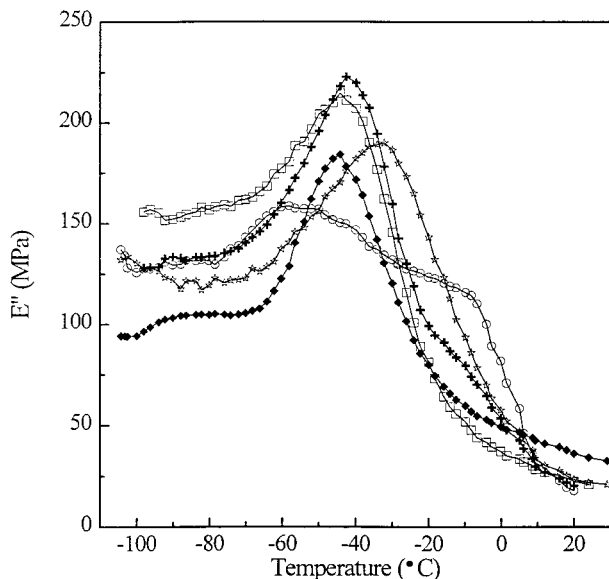


Figure 4 The loss modulus of the CET-600 series WBPU-casted films: (○) CET-600-42; (☆) CET-600-53; (⊕) CET-600-63; (□) CET-600-70; (◆) CET-600-74.

$$Xc = \frac{\int_{\theta_1}^{\theta_2} lc(x) dx}{\int_{\theta_1}^{\theta_2} l(x) dx}$$

where the $\int_{\theta_1}^{\theta_2} lc(x) dx$ is the area of the crystal region, $\int_{\theta_1}^{\theta_2} l(x) dx$ is the total area of the crystal and amorphous region, and the diffraction angles θ_1 and θ_2 are 10° and 40° , respectively. At the same time, it is assumed that the SSC is 43 ± 1 wt % as a completely amorphous polymer in any series of WBPU. The relative percentage crystallinity

data is listed in Table II. The physical properties of the films were measured by a tensile tester (Toyo Baldwin Tensilon UTM-3-500), a differential scanning calorimeter analyzer (DSC, DuPont thermal analyzer 2000), and a dynamic mechanical analyzer (DMA, GABO qualimeter). The testing conditions of these samples were described in the previous article.¹²

RESULTS AND DISCUSSION

Thermal Properties

Figure 1 shows differential scanning calorimeter (DSC) diagrams of the synthesized WBPU resins. The glass transition temperature (T_g) of the soft segment and its temperature range (ΔT_g) in the WBPU are significantly affected by the SSC, and the crystallization occurs as the SSC is above 63 wt %. The thermal properties of the WBPU are listed in Table II, and the effects of the soft-segment composition on the thermal properties are illustrated in Figure 2 and 3. Figure 2 shows the effects of the SSC on the T_g and ΔT_g . A higher SSC, suggesting a larger amount of the PCL component in the soft segment, resulted in a lower T_g value and a narrower ΔT_g range, and the curve leveled off when the SSC was above 63 wt %. This is because a higher SSC (longer PCL chain length) sample is not easy to mix with the hard segment, resulting in phase separation between the soft and hard segments and promoting crystallization of the soft segments. Cooper et al.'s¹⁷

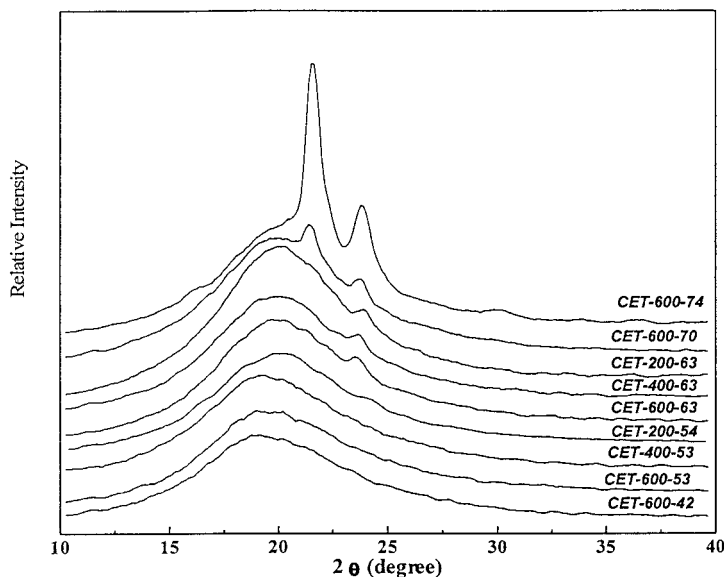


Figure 5 WAXS patterns of the CET series WBPU-casted films.

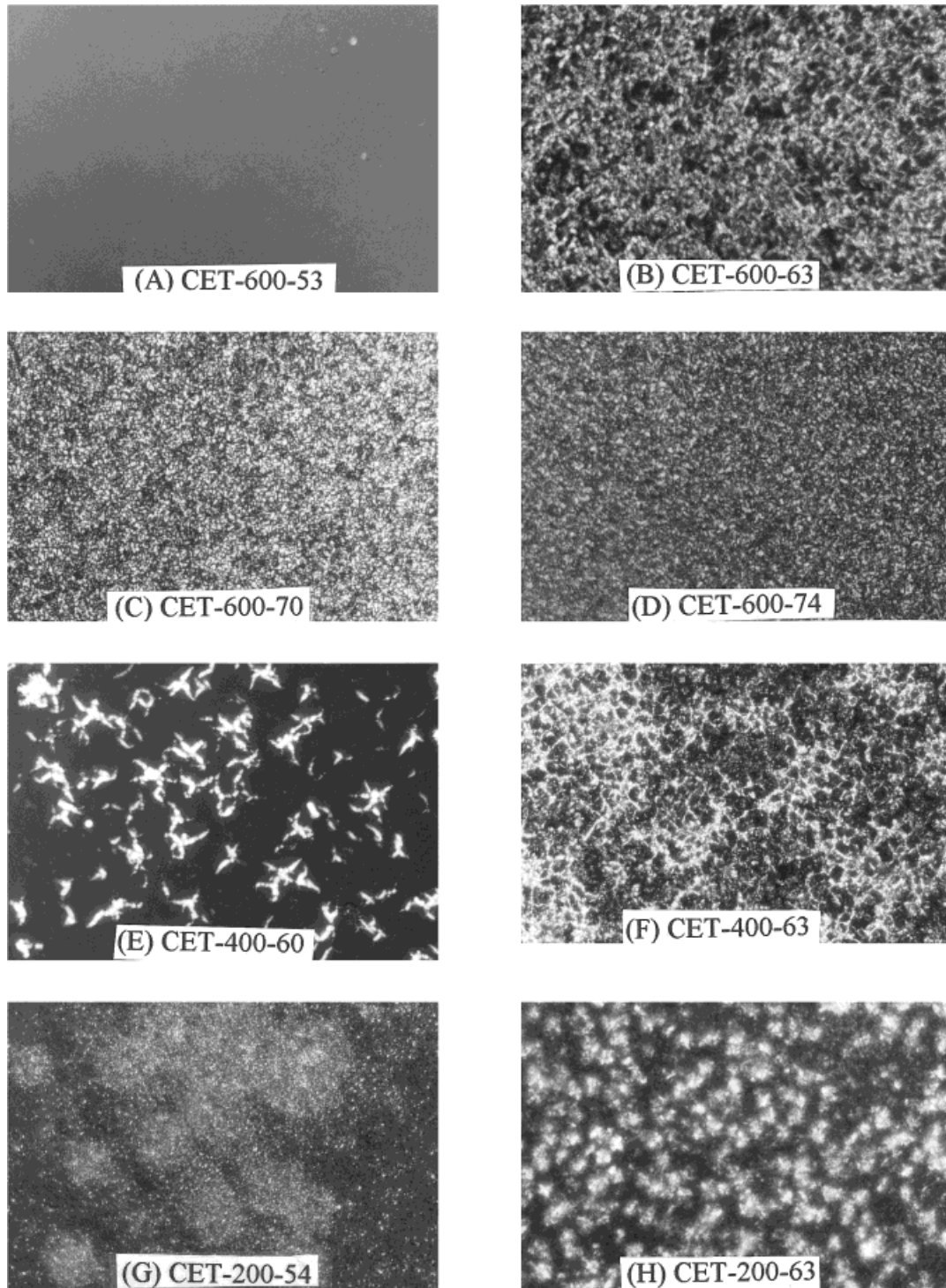


Figure 6 Polarization micrographs of the CET series WBPU-casted films.

studies showed that the T_g becomes lower and a better phase separation could be observed as the soft-segment molecular weight is increased.

Figure 3 shows the effects of the PEG molecular weight in the soft-segment composition on T_g and ΔT_g for various SSC. It is found that the T_g and

ΔT_g increase slightly as the PEG molecular weight was increased at the same SSC. With lower PEG molecular weight, the longer PCL chain length displays a higher degree of molecular aggregation and a lower T_g , which supposedly result from the crystallization. Figure 3 also shows

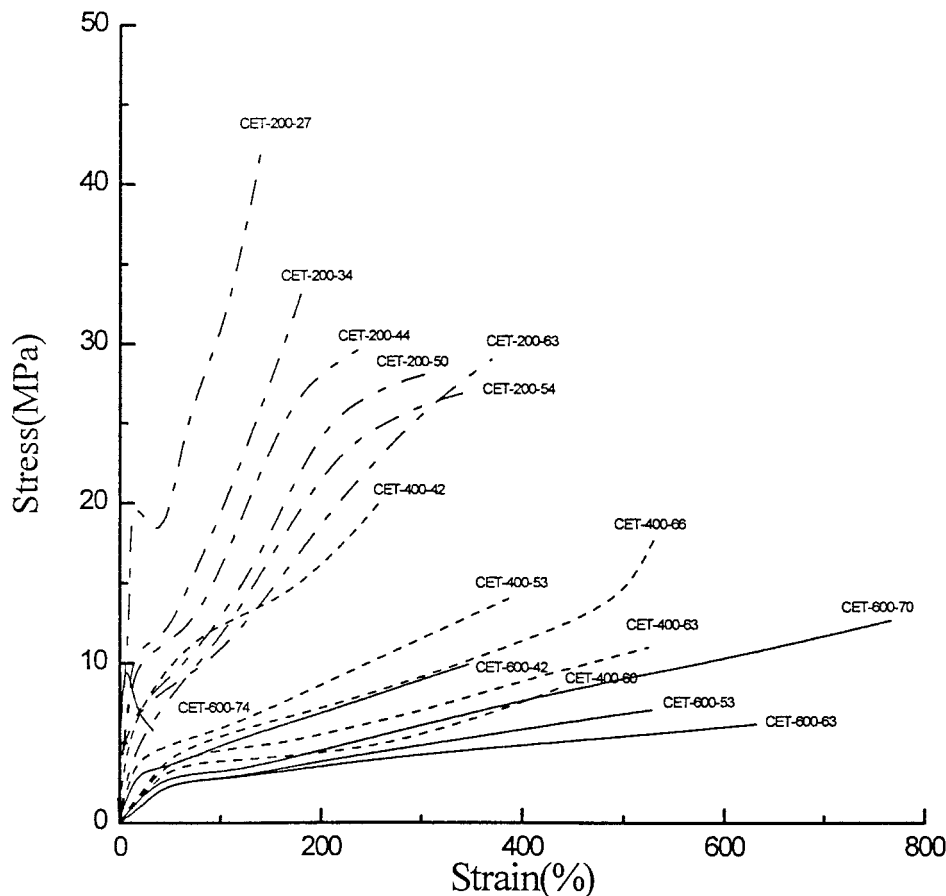


Figure 7 Stress-strain curves of the CET series WBPU-casted films.

that for a smaller molecular weight of the soft segment the effects of the PEG molecular weight on T_g and ΔT_g become larger.

Dynamic Mechanical Property

Figure 4 is the loss modulus diagram of the CET-600 series WBPU cast films as determined from DMA. It is shown that for increased SSC (longer PCL chain length) the sample α -peak width of the soft segment becomes narrower and its maximum position (T_α , α -peak temperature) shifted to lower temperatures. This is because with increase of the SSC the PCL composition (ester's group) increases; the cohesive energy of the ether group ($-\text{O}-$, 1000 cal/mol) is much lower than the cohesive energy of ester group ($-\text{COO}-$, 2900 cal/mol), which resulted in the better molecular order of the soft segments; and the intermolecular force between the soft and hard segments decreased with the SSC increase. These results are consistent with the DSC analysis results. Senich and Macknight¹⁸ pointed out that the extent of phase separation could be approximated by the

shift of the α -peak with SSC, assuming that T_α would decrease with increase in the phase separation. Figure 4 also shows that the α -peak height also changes significantly with the SSC. The α -peak height increases as the SSC increases from 42 to 63 wt %, which might arise from the intermolecular force of the flexible soft segment increase with SSC. However, the α -peak height reduces as the SSC was further increased up to 74 wt %. These results are correlated with the phenomena of crystallinity of the soft segments, i.e., as the SSC is above 63 wt %, the soft segment is able to aggregate and starts to crystallize. During the crystallization process, the molecular motion of the soft segment is increasingly restricted as its content varies from 63 to 74 wt %, which, consequently, reduces the α -peak height. Details about the crystalline state will be discussed further in the next section.

Crystallization Property

Figure 5 and Table II shows the X-ray diffraction pattern and the relative crystallinity of WBPU.

The WBPU with higher SSC show sharp and clear diffraction peaks at $2\theta = 21.5^\circ$ and 23.9° as shown for samples CET-600-70 and CET-600-74. This is due to the crystallization formation resulting from the PCL component in the soft segment. Comparing the samples with different PEG molecular weight in Figure 5, it is found that the diffraction intensity between $2\theta = 14^\circ$ and 26° slightly increases as the molecular weights of PEG decrease for the same SSC. This is because the decreasing molecular weight of PEG increases the PCL content relatively in the soft-segment composition for the same SSC. It also indicated that a higher PCL content has a better molecular order of the soft segment.

The spherulites of the soft segment in WBPU films was observed by the polarized microscope and are shown in the Figure 6. The figure shows that the spherulites increase as the SSC increases for all series of WBPU. It is also found that a lower PEG molecular weight induced a smaller number and a larger size of soft-segment spherulites for the same SSC. It is suggested that the required amount of SSC for spherulite formation increases with the PEG molecular weight in the soft segments. This result is well consistent with the thermal property testing.

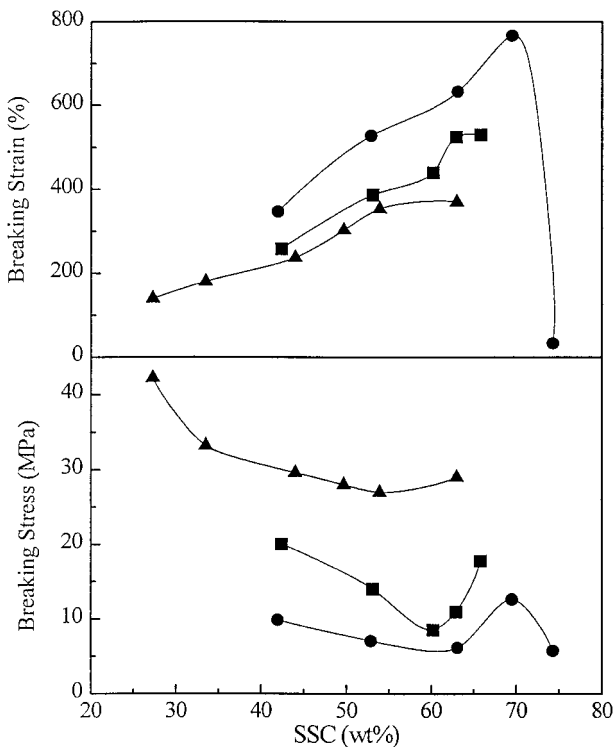


Figure 8 The breaking stress and breaking strain vs. the SSC for the WBPU-casted films: (●) CET-600 series; (■) CET-400 series; (▲) CET-200 series.

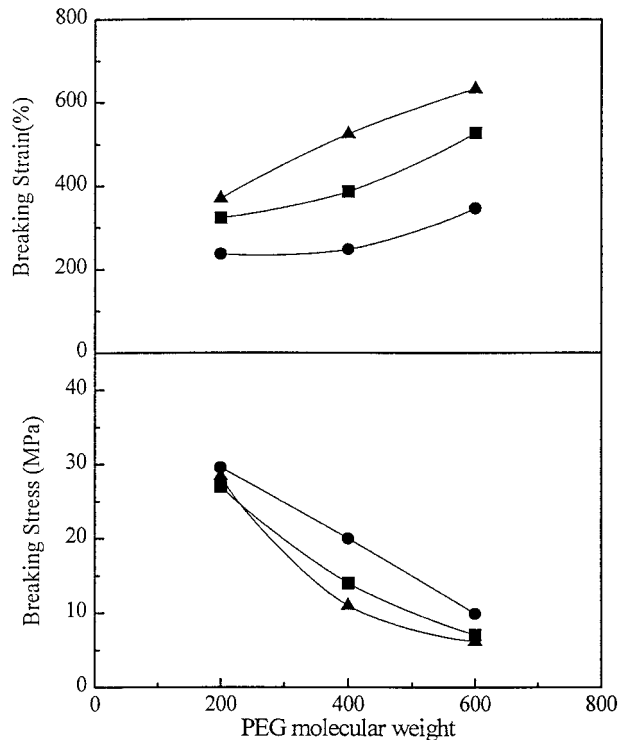


Figure 9 The breaking stress and breaking strain vs. PEG molecular weight in the soft-segment composition for the WBPU-casted films. Average soft-segment molecular weight: (●) 850 ± 50 ; (■) 1300 ± 50 ; (▲) 2000 ± 50 .

Tensile

Figure 7 is the stress–strain curve of the WBPU casting films. The CET-200 series samples displayed a larger initial modulus and breaking strength, followed by CET-400 and CET-600. Figure 8 shows the relationship between the mechanical properties and the SSC of the WBPU cast films. When SSC is below 60 wt %, the breaking stress became lower while the breaking strain increased with the SSC increase. This is because the intermolecular forces between the hard and soft segments decrease, which results in a lower breaking stress. However, as the SSC is over 60 wt %, both the breaking stress and strain increased (except for CET-600-74). This is because the spherulite's formation results in the intermolecular force between the soft segment, so the breaking stress increased. The CET-600-74 show a higher rigidity and friability due to its high relative crystallinity (shown in Table II). Figure 9 shows the effect of different PEG molecular weights on the mechanical properties of the WBPU cast films. As the molecular weight of PEG is lower, the PCL molecular aggregation increases

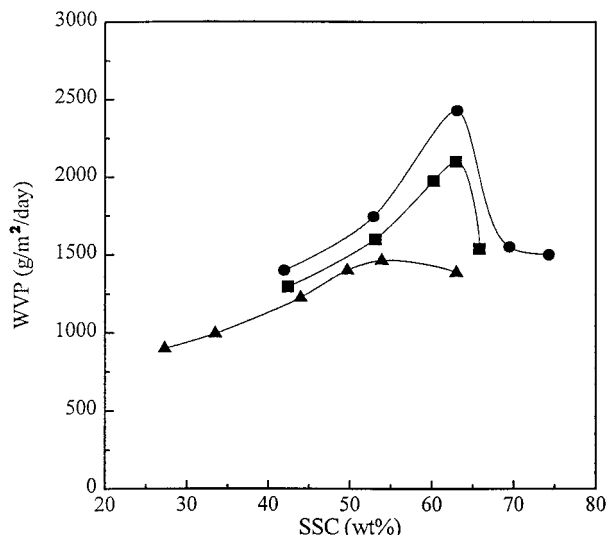


Figure 10 The WVP vs. the SSC for the WBPU resin-coated nylon fabrics: (●) CET-600 series; (■) CET-400 series; (▲) CET-200 series.

and the soft segments have higher rigidity, which increases the breaking stress but lowers the breaking strain.

In the previous study,¹² we compared the physical properties of film from three different procedures (CEM, CEB, and CET series) of WBPU. It was found that the WBPU cast films from the CET series had a poorer mechanical property than that of the others. From the results, we found that a better breaking strength of cast film can be obtained at appropriate SSC or lower PEG molecular weight in the soft-segment composition of the CET series WBPU.

Water-vapor Permeability

Figure 10 shows the effects of the SSC on the water-vapor permeability (WVP) of the WBPU resin-coated nylon fabrics. The results reveal that the WVP increases as the SSC increases and the maximum WVP value appears at the soft-segment crystallization formation region for all three series WBPU. Figure 11 shows the effects of PEG molecular weight on the WVP of the WBPU resin-coated nylon fabrics for the same SSC. Higher PEG molecular weight in the soft segment induced higher WVP due to its higher hydrophilicity. Reduced PCL content in the soft segment, which lessens the crystallization of the soft segments, also contributes to the higher WVP.

CONCLUSION

The WBPUs with different compositions of the PCL-PEG-PCL ester-ether triblock copolydiol

as soft segments were synthesized, and the physical properties and application on nylon-coated fabrics were investigated. The results produced the following observations:

1. For various SSC in the CET series WBPU, the T_g 's and ΔT_g 's become lower and narrower with SSC, resulting in phase separation between the soft and hard segments, and leveled off as the SSC is above 63 wt %. The breaking stress became lower while breaking strain increased with SSC increase for SSC below 60 wt %. However, as the SSC increased over 60 wt %, both the breaking stress and strain increased. This is due to the crystallization formation for SSC above 60 wt % for the CET series WBPU.
2. For various PEG molecular weights in the soft-segment composition, the T_g and ΔT_g increase slightly as the PEG molecular weight increased at the same SSC. As the molecular weight of PEG is lower, the PCL molecular aggregation increased and the soft segments have higher rigidity, which increases the breaking stress but lowers the breaking strain. Additionally, a lower molecular weight PEG induced a smaller number and a larger size of soft-segment spherulites.
3. For the WBPU-coated nylon taffeta fabrics, the WVP increased as the SSC increased

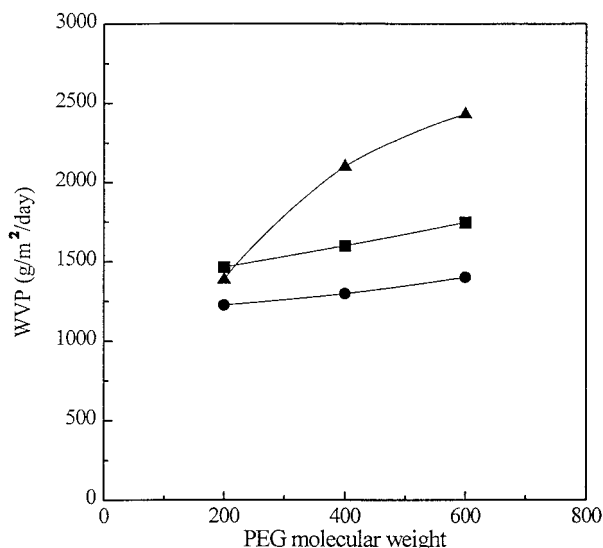


Figure 11 The WVP vs. PEG molecular weight of the soft-segment composition for the WBPU resin-coated nylon fabrics. Average soft-segment molecular weight: (●) 850 ± 50; (■) 1300 ± 50; (▲) 2000 ± 50.

and the maximum WVP value appeared at the soft-segment crystallization formation for all three series of WBPU. Higher PEG molecular weight in the soft-segment composition results in higher WVP due to its higher hydrophilicity.

4. From the above results, the WVP as well as the mechanical properties can be obtained at an appropriate SSC and PEG molecular weight in the soft-segment composition of the CET series of WBPU.

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