Effects of a Soft Segment Component on the Physical Properties of Synthesized Waterborne Polyurethanes by Using Triblock Ester-Ether Copolydiol as the Soft Segment

Meng-Shung Yen* and Shu-Chin Kuo

Textile and Polymer Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 10772, Taiwan, ROC

Abstract: This paper examines the effect of an ester-ether soft segment structure on the physical properties of synthesized WBPUs. The CET series, CPT series, and CMT series anionic waterborne polyurethane (WBPU) were prepared with PCL-PEG-PCL, PCL-PPG-PCL, and PCL-PTMG-PCL triblock copolydiol as the soft segment. These copolydiols were synthesized from polyethylene glycol (PEG), polypropylene glycol (PPG), or polytetramethylene glycol (PTMG), respectively, by end capping with caprolactone (CL). Particle size and its distribution, solvent absorption, thermal properties, and the mechanical properties of the WBPUs were studied. The particle size of WBPU dispersion was in the sequence of CET > CPT > CMT series. The CET series WBPU had better phase mixing between the soft and hard segment, whereas the CMT series WBPU had good phase separation and better mechanical properties. In addition, both the phase mixing and mechanical properties increased with PCL content, except for the CMT series WBPU.

Keywords: Waterborne polyurethane, Triblock ester-ether copolydiol, Phase mixing, Mechanical properties.

Introduction

Recently, the increasing acceptance of waterborne polyurethane (WBPU) for use in industry has been motivated by more stringent environmental requirements, such as the reduction of solvent emissions into the atmosphere. In the textile industry, WBPU has been widely used for suede, water vapor permeability (WVP), and non-formaldehyde durable press applications [1-6]. In general, the physical properties of WBPU are greatly affected by the hydrophilic segment [7-9], the composition of the hard segment [10-12], and the composition and molecular chain of the soft segment [13-17]. For example, past reports [8-9,12] showed that the type and content of the hydrophilic segment and the composition of the hard segment largely influenced the stability of the WBPU dispersion solution and tensile stress properties of the WBPU cast film. In terms of the soft segment, our laboratory [17] compared the physical properties of polyester based and polyether based polyurethane (PU), and showed that the polyether based PU had lower $T_{g,s}$ than the poly-

ester based PU. The polyether based PU films showed higher water vapor permeability (WVP), higher breaking elongation, and lower breaking strength.

To enhance the physical properties of PU, PU preparations with mixed polydiol have been widely studied recently. [18-24] The mixing procedure can be provided by mixing different PUs or blending different polydiols as the soft segment, or using the triblock copolydiol as the soft segment. For example, Ahn et al. [18] studied the properties of polyurethane urea (PUU) prepared from 4,4'-diphenylmethane diisocyanate with PTMG and poly-hexamethylene carbonate glycol (PHC) as the blending soft segments. As the PTMG composition of the soft segment was partly replaced by PHC, the modulus for a shorter soft segment was increased. Phase separation between hard and soft segments was also promoted as the PHC content increased. Xiu et al. [19,20] used an ester-ether copolydiol (polypropylene oxide and maleic anhydride) as the soft segment to study the influence of soft segment species and molecular weight on the physical prop-
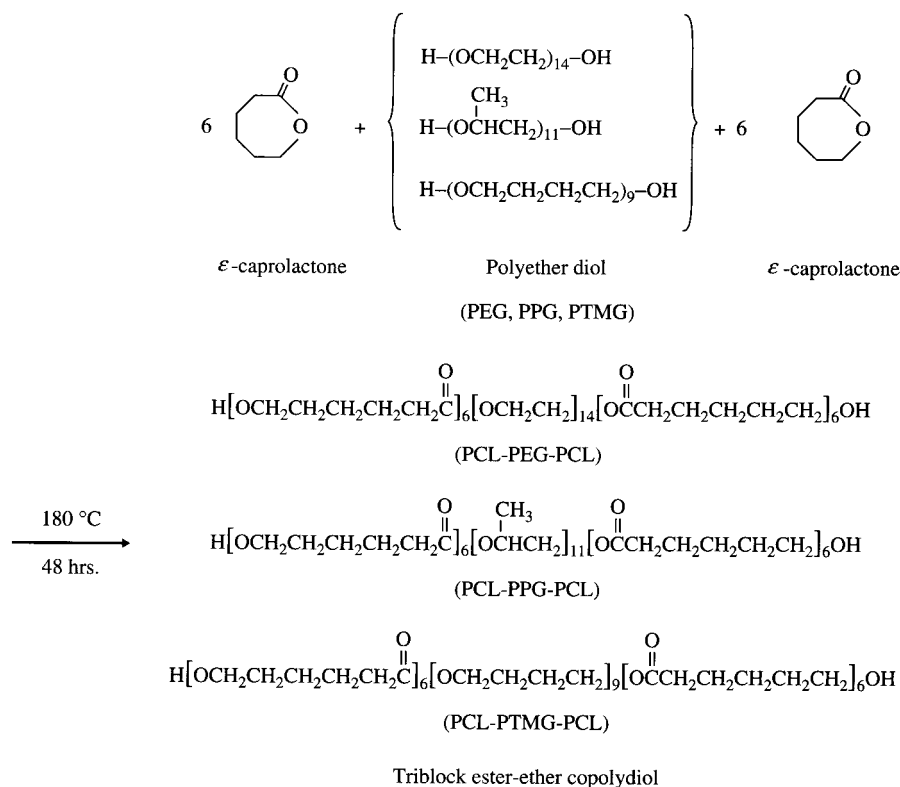

Figure 1. Reaction equation of the triblock ester-ether copolydiol.

erties of PUU film. Polyester-ether based PUU displayed higher Young's modulus and lower elongation than polyester based or polyether based PU, due primarily to the larger interface within domains. We have compared [24] the effects of the mixing procedure on the physical properties of preparations of ester-ether type WBPUs, and found that the mixed type WBPU had macrophase separation and better breaking strength, the WBPU using blended polydiols as the soft segment had good phase mixing between the soft and hard segments, and the WBPU using the triblock ester-ether copolydiol (PCL-PEG-PCL) as the soft segment had better softness, elongation, and WVP. For textile-coated fabrics, softness, permeability, and mechanical properties are required. We also found [25,26] that increasing the soft segment content or NCO/OH molar ratio results in better mechanical properties and WVP for the triblock PCL-PEG-PCL copolydiol based WBPU.

In this paper, the effect of the soft segment component on the physical properties of synthesized WBPU by using triblock ester-ether copolydiols as the soft segment was studied. The triblock ester-ether copolydiols were synthesized from different carbon numbers of ether polydiol (polyethylene glycol (PEG), polypropylene glycol (PPG), and polytetramethylene glycol (PTMG)) with caprolactone (PCL). The characteristics of WBPU

that were studied include particle size and its distribution, solvent absorption, thermal properties, and mechanical properties.

Experimental

1. Materials

The PCL-PEG-PCL , PCL-PPG-PCL, and PCL-PTMG-PCL triblock ester-ether copolydiols (Mn about 2000), used as the soft segments for the waterborne polyurethane (WBPU), were synthesized from polyethylene glycol (PEG), polypropylene glycol (PPG),and polytetramethylene glycol (PTMG) ($M_n \cong 600$ and 1000) end capped with ε-caprolactone (ε-CL) according to the synthesis method of C. Piero et al. [27]. The reaction equation is shown in Figure 1. Methylene bis(cyclohexyldiisocyanate) (H_{12}MDI, from Bayer) was dried at 80 °C for 2 hrs 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), ethylene diamine (EDA) (both from Hanawa, Japan, reagent grade), and 1-methyl-2-pyrrolidone (NMP, Ferak, reagent grade) were used as neutralization agent, chain extender, and solvent respectively. They were dried with 4 Å molecular sieves.

Table I. The component and moleuclar weight[a] of the triblock ester-ether copolydiols.

WBPU code			Triblock ester-ether copolydiol			
	Components	PCL (wt%)	Cal. M_n	Exp.[b] M_n	M_w/M_n	Yield (%)
C-2000[c]	PCL	100	2000	–	–	–
E-2000[c]	PEG	0	2000	–	–	–
P-2000[c]	PPG	0	2000	–	–	–
M-2000[c]	PTMG	0	2000	–	–	–
CET-1000-63[d]	PCL-PEG-PCL	50	1912	1742	1.48	84
CET-600-63[d]	PCL-PEG-PCL	67	1968	1789	1.54	87
CPT-1000-63[e]	PCL-PPG-PCL	50	1912	1880	1.27	73
CPT-700-63[e]	PCL-PPG-PCL	68	2068	1964	1.65	94
CMT-1000-63[f]	PCL-PTMG-PCL	50	1912	1894	1.59	91
CMT-650-63[f]	PCL-PTMG-PCL	67	2018	1863	1.54	94

(a) The molecular weight of copolydiols were measured by GPC.

(b) $H_{12}MDI$: Polydiol : DMPA : EDA = 16 : 0.5 : 0.5 : 0.6 (molar ratio).

(c) The C-2000, E-2000, P-2000, and M-2000 show the synthesized WBPU with the PCL2000, PEG2000, PPG2000, and PTMG2000 as the soft segment, respectively.

(d) The X and Y of the CET-X-Y show the PEG moleular weights and soft segment content in WBPU with the PCL-PEG-PCL triblock ester-ether copolydiol as soft segment, respectively.

(e) The X and Y of the CPT-X-Y show the PPG molecular weights and soft segment content in WBPU with the PCL-PPG-PCL triblock ester-ether copolydiol as soft segment, respectively.

(f) The X and Y of the CMT-X-Y show the PTMG molecular weights and soft segment content in WBPU with the PCL-PTMG-PCL triblock ester-ether copolydiol as soft segment respectively.

2. Synthesis

The CET series, CPT series, and CMT series anionic waterborne polyurethane (WBPU) were prepared with PCL-PEG-PCL, PCL-PPG-PCL, or PCL-PTMG-PCL triblock copolydiol as the soft segment by the prepolymer mixing method [28]. The polydiol and DMPA were dissolved in NMP, then 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 hrs. 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 hrs. The final dispersion solution was diluted to 30% with water. The soft segment component of the ester-ether based WBPUs are listed in Table I.

3. Film casting

Films were prepared by casting WBPU on a Teflon plate, followed by drying at 50 °C for 72 hrs. The films were then removed and placed in a desiccator before testing.

4. Measurements

Particle size and distribution of WBPUs were measured by light scattering (MALVERN, a He-Ne type laser with a wavelength of 633 nm was used). The sample was first diluted with deionized water to 0.5%, followed by ultrasonic wave treatment. PU films with a thickness of 0.1 mm and size of 2 × 2

cm² were 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 of $\{(W - W_0)/W_0\} \times 100$. This value was taken as the percentage equilibrium absorption, and W and W_0 were the final weight and the initial weight respectively. Polarized microscopy was conducted with an Olympus BH-2-UMA type polarized microscope at magnifications of 100×. The differential scanning calorimeter analyzer (DSC, Du Pont Thermal Analyzer 2000) was used with liquid nitrogen for cooling, and the heating rate was 20 °C/min. Dynamic mechanical data were obtained using a GABO QUALIMETER at a frequency of 3.5 Hz, a constant heating rate of 2 °C/min, a prestress of 1.8 MPa, and a temperature range of -120 ~ 50 °C. Mechanical properties of the cast film were determined by using an Instron tensile tester, according to ASTM D-412 Die C.

Results and Discussion

1. Particle size and distribution

Table II shows the particle size and solvent absorption of the ester-ether type WBPUs, it is found that the CET series WBPU dispersions have a larger particle size than the CPT and CMT series. The ethylene oxide groups ($-CH_2CH_2O-$) in the soft seg-

Table II. Particle size (nm) and solvent absorption (%) of the ester-ether based WBPUs.
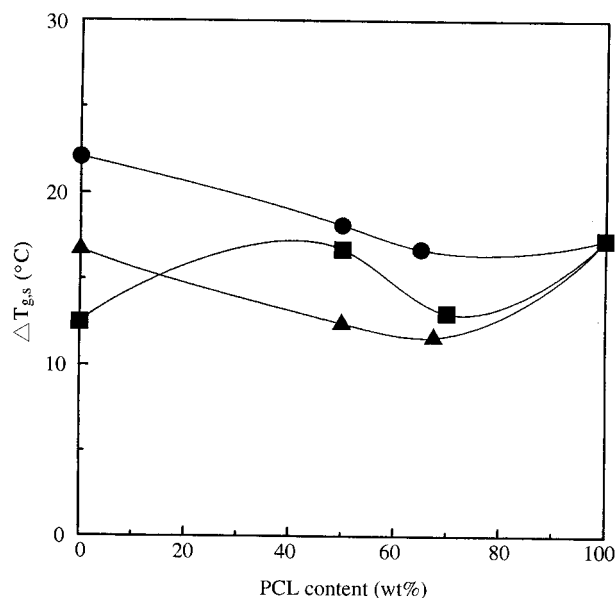
WBPU code	PCL contents in soft segment (%)	Particle		Solvent absorption (%)
		size (nm)	distribution	
C-2000	100	54	0.206	416
E-2000	0	102	0.523	124
P-2000	0	33	0.126	284
M-2000	0	66	0.341	134
CET-1000-63	50	100	0.512	165
CET-600-63	67	103	0.403	171
CPT-1000-63	50	67	0.371	386
CPT-700-63	68	33	0.130	498
CMT-1000-63	50	40	0.103	342
CMT-650-63	67	36	0.143	253
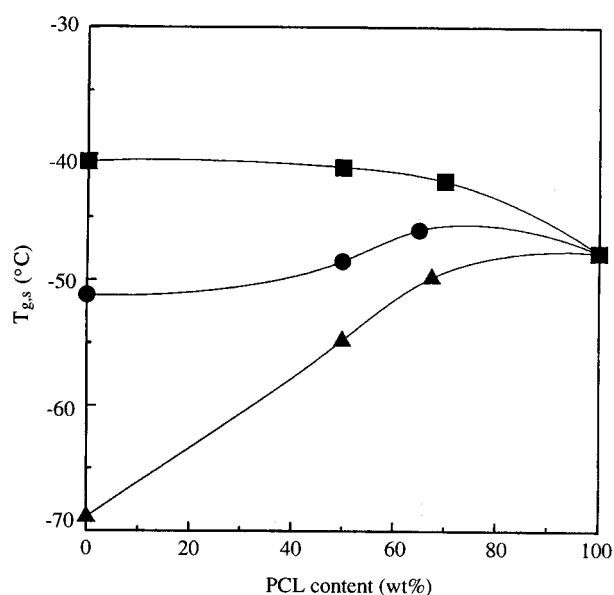
Figure 2. Glass transition temperature of soft segment for the ester-ether based WBPUs: (■) CET series, (●) CPT series, and (▲) CMT series.

Figure 3. Glass transition temperature range of soft segment for the ester-ether based WBPUs: (■) CET series, (●) CPT series, and (▲) CMT series.

ment of the CET series WBPU readily formed a hydrogen bond with water and coagulated with each other [29]; therefore, the particle size and distribution were larger and broader. On the other hand, the CPT series WBPU did not coagulate due to the distance between molecules and the presence of side groups (propylene oxide groups $-CH_2(CH_3)CHO-$) on its soft segment. As for the CMT series WBPU, it had weaker hydrophilicity than the two other series WBPU because it had a tetramethylene oxide group ($-CH_2CH_2CH_2CH_2O-$) in the soft segment, resulting in small particle size and narrow particle size distribution.
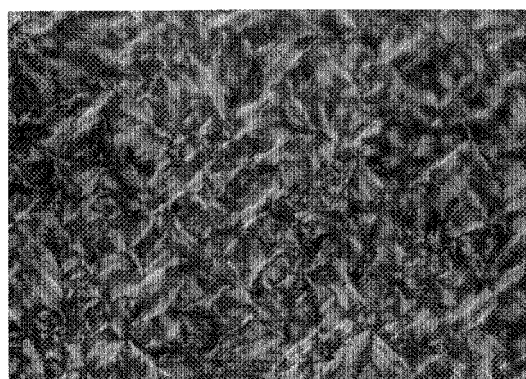
2. Solvent absorption

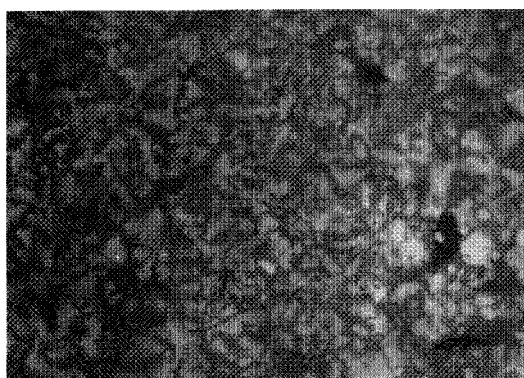The solvent equilibrium absorption of the three types of ester-ether series WBPU cast films is shown in Table II. The solvent absorption capacity is in the sequence of CPT series > CMT series > CET series. The CET series WBPU have higher cohesive energy than the CPT and CMT series. At the same time, the CPT series WBPU have a non-symmetric structure which allows the solvent molecule to enter into the PU molecular chain, so the CPT series have a higher solvent absorption capacity. Table II also shows that the PCL content in the soft segment increases as the solvent absorption of WBPU increases. This is because the solvent absorption capacity of the ester group is higher than that of the ether group.
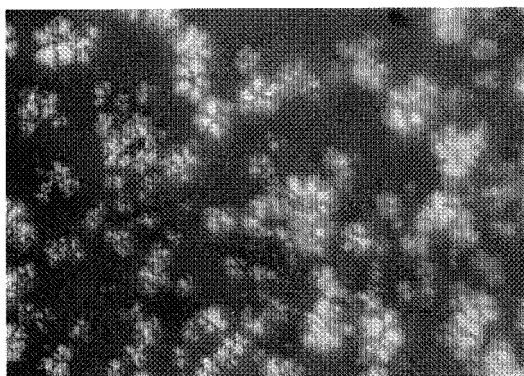
3. Thermal properties

Figures 2 and 3 show the glass transition temperatures ($T_{g,s}$) and range of glass transition temperatures ($\Delta T_{g,s}$) of the soft segment for the three series WBPUs. The order is CET series > CPT se-

(a) CET-600-63

(b) CPT-700-63

(c) CMT-650-63

Figure 4. The polarization micrographs of the ester-ether based WBPU cast films.

Table III. The thermal properties dates of the ester-ether based WBPUs.

WBPU	DSC				DMA
code	T_g (°C)	ΔT_g (°C)	T_m (°C)	ΔH_m (cal/g)	T_α (°C)
C-2000	-47.8	17.3	60.3	18.1	-50.2
E-2000	-40.6	12.5	25.2	10.2	–
P-2000	-51.2	22.1	41.6	6.5	-41.1
M-2000	-68.9	16.7	40.5	7.6	-58.9
CET-1000-63	-41.0	16.7	24.0	5.7	–
CET-600-63	-42.1	13.0	47.5	11.3	-35.7
CPT-1000-63	-48.5	11.8	–	–	-46.9
CPT-700-63	-44.3	10.1	49.7	5.7	-38.4
CMT-1000-63	-54.8	12.4	–	–	-58.7
CMT-650-63	-49.8	11.6	41.3	6.8	-44.3

series, so its $T_{g,s}$ is lower and its $\Delta T_{g,s}$ is narrower. The above results suggest that the CET series WBPU have higher phase mixing between the soft and hard segments and the CMT series have good phase separation. Figures 2 and 3 also show that the $T_{g,s}$ increases and $\Delta T_{g,s}$ decreases when the PCL (ester groups) content in the soft segment increases, except for the CET series WBPU. This is because more PCL chains increase the polarity of the soft segment and increase the soft and hard segment intermolecular action force, which results in a $T_{g,s}$ increase with ester content. On the other hand, the $T_{g,s}$ and $\Delta T_{g,s}$ of the CET series decrease slightly as the PCL content increases, because the $-CH_2CH_2O-$ composition in the soft segment easily form the hydrogen bond with the hard segment (urethane group). As the $-CH_2CH_2O-$ composition (PEG molecular weight) decrease, the intermolecular force between the soft and hard segment decrease, causing the $T_{g,s}$ and $\Delta T_{g,s}$ of the CET series to decrease slightly.

The three series WBPU films were observed by a polarized microscope and are shown in Figure 4. The figure shows that the CET series have larger size spherulites than the CPT and CMT series. At the same time, Table III also shows that the CET series have higher crystal entropy (ΔH) and higher $T_{g,s}$, so the CET series have better crystallity of the soft segment and greater intermolecular force than the CPT or CMT series.

ries > CMT series for $T_{g,s}$, and CPT series > CET series > CMT series for $\Delta T_{g,s}$. It is generally accepted that the ester type PU has higher $T_{g,s}$ than the ether type PU. This is because the CET series have higher polarity of the soft segment than the CPT and CMT series. In addition, the CPT series have a non-symmetric structure in the soft segment which results in broader $\Delta T_{g,s}$. On the other hand, the CMT series have lower molecular cohesive energy of the soft segment than the CET and CPT

4. Dynamic mechanical property

Figure 5 shows the tanδ diagram of the three types of ester-ether series WBPU cast films as determined from DMA. The α-peak width of the ester-ether component in the soft segment becomes broader and its maximum position (T_α, α-peak temperature) shifts to a higher temperature than that of the ether-based WBPU, because two different kinds of cohesive forces are present in the soft segment of
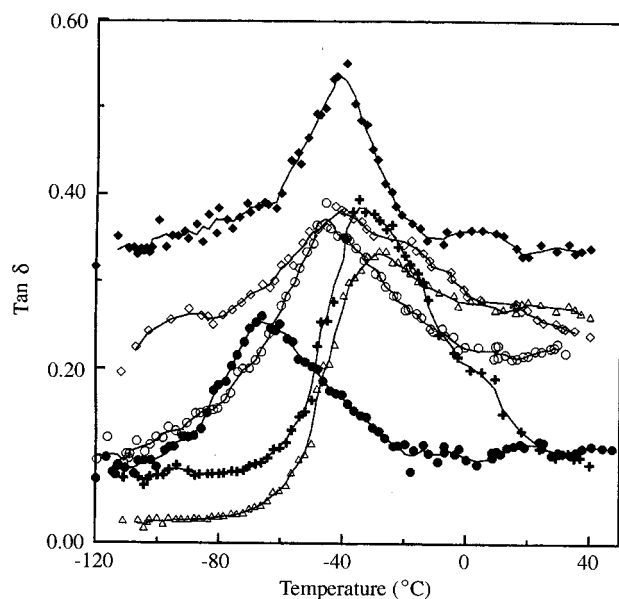
Figure 5. Dymatic mechanical analysis of the ester-ether based WBPU cast films: (◊) CET-600-63, (◊) CPT-700-63, (○) CMT-650-63, (+) C-2000, (♦) P-2000, and (●) M-2000.

Figure 6. Stress-strain curve of the ester-ether based WBPU cast films.

ester-ether-based WBPU. Since the CET series have a higher polarity and are hydrogen borne, then have a higher T_α and lower α-peak mountain, which results in phase mixing. The CPT series WBPU has in its soft segment side groups which produce an irregular PU molecular chain and result in the wider α-peak width. On the other hand, the CMT series WBPU has a lower T_α and narrower α-peak width because the PU has a higher intermilecular force between its soft segments and has a good phase separat.

5. Mechanical properties

Figure 6 shows the stress-strain curve of the three types of ester-ether series WBPU casting films. The CMT series samples displayed a higher initial modulus and breaking stress, followed by the CPT series and CET series. The CMT series have good mechanical properties due to its phase separation and higher intermolecular force between soft segments. The CPT series have a poor breaking strain due to the non-symmetric molecular structure. The CET series have a higher breaking strain and lower breaking stress because of the flexing of the PEG molecular chain and higher phase mixing between soft and hard segments. Figure 7 shows the relationship between the mechanical properties and the PCL content in the soft segments for the three types of ester-ether based WBPU casting film. The breaking stress increases with an increase in the PCL content, except for the CMT series, since the increase of ester groups improves the breaking stress. The
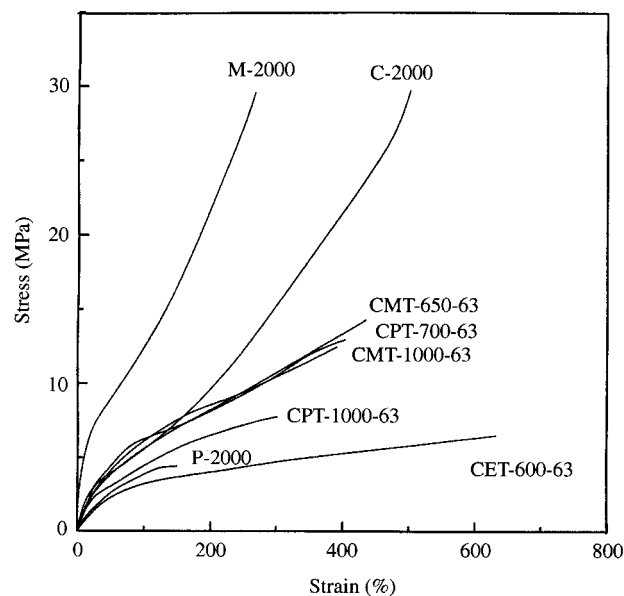

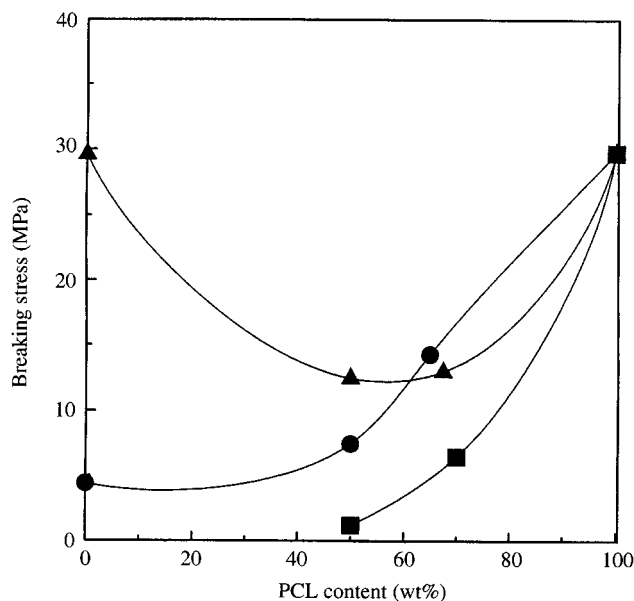**Figure 7.** Breaking stress of the ester-ether based WBPU cast films: (■) CET series PU, (●) CPT series PU, and (▲) CMT series PU.

breaking stress of the CMT series WBPU cast film decreases with PCL content increase because the good molecular arrangement of the PTMG chain is destroyed as the PCL chain increases.

Conclusion

This research studied the physical properties

of synthesized WBPUs with ester-ether copolydiols as the soft segment. The following results were observed:

1. The CET series easily formed hydrogen bonds and coagulated with each other, which resulting in the CET series having a larger particle size than the CPT and CMT series WBPUs.

2. The solvent absorption capacity was in the sequence of CPT series > CMT series > CET series. The CPT series WBPU had a non-symmetric structure which resulted in the solvent molecule entering into the PU chain.

3. The CET series had a higher $T_{g,s}$, the CPT series had a broader $\Delta T_{g,s}$, and the CMT series had a lower $T_{g,s}$, because the CET series WBPU easily formed hydrogen bonds with the hard segment, the CPT series WBPU had a non-symmetric structure, and the CMT series WBPU had a higher intermolecular force between the soft segment. Therefore, the CET series had better phase mixing between the soft and hard segment, whereas the CMT series had good phase separation.

4. The mechanical properties are in the sequence of CMT series > CPT series > CET series, because the CMT series WBPU had good phase separation and a higher intermolecular force between soft segment.

References

1. D. Dieterich, Leverkusen, U. S. Pat. 4,276,044 (1981).
2. J. T. Zermani, *J. Water Borne Coat*, 2 (1984).
3. R. E. Tirpak and P. H. Markusch, *J. Water Borne Coat*, 12 (1986).
4. K. Kuriyama, M. Ichihara, I. Misaizu and M. Kashimura, U. S. Pat. 4,746,684 (1988).
5. C. Prelini, A. Trovati, T. Gambini and V. Stefanoli, U. S. Pat. 5,024,674 (1991).
6. A. Watanabe, *Dyeing Industry*, **35**, 534 (1991).
7. K. Matsuda, H. Dhmura, Y. Tanaka and T. Sakai, *J. Appl. Polym. Sci.*, **23**, 141 (1979).
8. C. K. Kim, B. K. Kim and H. M. Jeong, *Colloid and Polym. Sci.*, **269**, 895 (1991).
9. T. K. Kim and B. K. Kim, *Colloid and Polym. Sci.*, **269**, 889 (1991).
10. S. L. Hsu, H. X. Xiao, H. H. Szmant and K. C. Frisch, *J. Appl. Polym. Sci.*, **29**, 2467 (1984).
11. J. Ferguson and D. Patsavoudis, *Eur. Polym. J.*, **8**, 385 (1972).
12. G. Spathis, M. Niaounakis, E. Kontou, L. Apekis, P. Pissis, and C. Christodoulides, *J. Appl. Polym. Sci.*, **54**, 831 (1994).
13. M. Xu, W. J. MacKnight, C. H. Y. Chen and E. L. Thomas, *Polymer*, **28**, 2183 (1987).
14. W. C. Chan and S. A. Chen, *Polymer*, **29**, 1995 (1988).
15. T. A. Speckhard, K. K. S. Hwang, C. Z. Yang, W. R. Laupan and S. L. Cooper, *J. Macrom. Sci. Phys.*, **B23**, 175 (1984).
16. B. P. Thapliyal and R. Chandra, *Polym. Int.*, **24**, 7 (1991).
17. M. S. Yen and K. L. Chen, *J. Appl. Polym. Sci.*, **52**, 1707 (1994).
18. T. O. Ahn, S. Jung, H. M. Jeong and S. W. Lee, *J. Appl. Polym. Sci.*, **51**, 43 (1994).
19. Y. Xiu, Z. Zhang, D. Wang, S. Ying and J. Li, *Polymer*, **33**, 1335 (1992).
20. Y. Xiu, D. Wang, C. Hu, S. Ying and J. Li, *J. Appl. Polym. Sci.*, **48**, 867 (1993).
21. B. K. Kim and T. K. Kim, *J. Appl. Polym. Sci.*, **43**, 393 (1991).
22. S. L. Cooper, R. A. Phillips, J. C. Stevenson and M. R. Nagoajan, *J. Macro. Sci. Phys.*, **B27**, 245 (1988).
23. S. L. Cooper, X. H. Yu, M. R. Nagoajan, T. G. Grasel, P. E. Grasel and P. E. Gibson, *J. Appl. Polym. Sci.*, **30**, 2319 (1985).
24. M. S. Yen and S. C. Kuo, *J. Appl. Polym. Sci.*, **61**, 1639 (1996).
25. M. S. Yen and S. C. Kuo, *J. Appl. Polym. Sci.*, **65**, 883 (1997).
26. M. S. Yen and S. C. Kuo, *J. Appl. Polym. Sci.*, in accept.
27. C. Piero, T. Mario, A. Fulvio, P. Maurizio and P. Massimo, *Polymer*, **30**, 338 (1989).
28. D. Dieterich, *Prog. Org. Coat.*, **9**, 281 (1981).
29. K. P. Antonse and A. S. Hoffman, *Poly(Ethylene Glycol) Chemistry*, J. M. Harris, ed., Plenum, New York, 1992.