

Effects of Mixing Procedure on the Structure and Physical Properties of Ester–Ether-Type Soft Segment Waterborne Polyurethane

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SYNOPSIS

The effects of the mixing procedure for the preparation of ester–ether-type waterborne polyurethane (WBPU) on the structure and properties of the cast film are studied here. The following three types of WBPU processing are examined: film formed from WBPU mixing ether-type WBPU with ester-type WBPU (CEM series), film formed from WBPU synthesized with PEG2000 and PCL2000 polydiol as the soft segments (CEB series), film formed from WBPU synthesized with triblock ester-ether copolydiol (PCL-polyethylene glycol-PCL) as the soft segment (CET series). The water vapor permeability (WVP) for the application to nylon fabrics is also studied. The results show that the mixing procedure greatly affects the properties of the ester–ether-type WBPU. The CEB series has better phase mixing than the CET series, and the CEM series has a phase boundary between the ester- and ether-type WBPU. The CEM series has a better Young's modulus and breaking stress and poorer breaking strain than the CEB and CET series. In addition, samples with lower ethylene oxide (EO) content have better phase mixing and mechanical properties. On the other hand, the ester–ether-type WBPU has a higher WVP than the ester-type WBPU and the WVP increases with the EO content. The order of the mixing procedures for WVP is CET > CEB > CEM. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethane (PU) products are generally used in the automobile, paint, furniture, and the medical and textile industries. Recently, the increasing acceptance of waterborne polyurethane (WBPU) is motivated by more stringent environmental requirements, such as the reduction of solvent emissions into the atmosphere.¹ The applications for textiles² include suede processing, soft-hand processing, wrinkle-free processing, antistatic processing, sizing, and adhesives.

The variations in the compositions of the soft and hard segments give PU films a wide range of physical properties. In general, PU films using polyester diol as the soft segment have better tensile strength, and PU films using polyether diol as the

soft segment have improved water vapor permeability (WVP) and hydrolysis resistance.^{3,4} Xiu et al.⁵ investigated the differences in hydrogen bonding and crystallization behavior between polyether and polyester polyurethane-urea (PUU) and found that the hard segment crystallization behavior of polyether-based PUU is higher than that of polyester-based PUU with the same hard segment content. Hydrogen bonding in the polyether-based PU was formed mainly between the hard segments, which favored the formation of crystals in the hard segment, whereas the polyester-based PU formed bonds mainly between the soft and hard segments, which hindered the crystallization of the hard segment. Recently, Yen and Chen⁶ compared the physical properties of the PU with poly(tetramethylene glycol) (PTMG) and poly(butylene adipate) as the soft segment while varying the chain length and showed that the polyether-based PU had lower T_g s than the polyester-based PU. The polyether-based PU films

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

WBPU Code	Soft Segment Composition	WBPU Type	M_n ($\times 10^4$)	M_w ($\times 10^4$)	M_n/M_w
C-2000	PCL	Ester	5.4	8.9	1.7
E-2000	PEG	Ether	6.0	9.4	1.6
CEB-2000-33 ^a	PCL, PEG	Ester-ether	7.7	14.6	1.6
CEB-2000-50 ^a	PCL, PEG	Ester-ether	9.5	14.9	1.6
CET-2000-30 ^a	PCL-PEG-PCL	Ester-ether	7.2	11.9	1.7
CET-2000-50 ^a	PCL-PEG-PCL	Ester-ether	7.1	11.4	1.6

^a X and Y of the CEM-X-Y, CEB-X-Y, and CET-X-Y show the molecular weight and EO weight content of soft segments, respectively.

showed higher WVP, higher breaking elongation, and lower breaking strength.

To improve the physical properties, mixed polyols as soft segments of PU were studied recently. Xiu et al.⁷ used ester-ether copolydiol (polypropylene oxide and maleic anhydride) as mixed soft segments

to study the influence of soft segment structure and molecular weight on the physical properties of PU film. Polyester-ether based PUU displayed a higher Young's modulus and lower elongation than polyester-based or polyether-based PU, primarily due to the larger interface within domains. Ahn et al.⁸ also studied the properties of PUU prepared from 4,4'-diphenylmethane diisocyanate with PTMG and poly(hexamethylene carbonate glycol) (PHC) as mixed soft segments. As the composition of the soft segment was varied by partly replacing PTMG with PHC, the modulus for a shorter soft segment increased as the content of PHC increased. But the change in modulus becomes relatively small for a longer soft segment. It seemed that the phase separation between hard and soft segments was also augmented as the content of PHC increased.

The constitution of polydiols influences greatly the film structure and physical properties of PU. There are still few studies of mixed polydiols' effect on the behavior of WBPU. We study the effect of mixed polydiols on the physical properties and WVP of the cast films of WBPU and the variations in the procedure for its preparation. The following three types of WBPU possessing are examined: film cast by mixing ether-type WBPU with ether-type WBPU (CEM series), film cast from WBPU synthesized with polyethylene glycol (PEG) and polycaprolactone glycol (PCL) as mixed soft segments (CEB series), and film cast from WBPU synthesized with triblock ester-ether copolydiol (PCL-PEG-PCL) as the soft segment (CET series). The physical properties of the films and the WVP for the application to nylon fabrics are also studied.

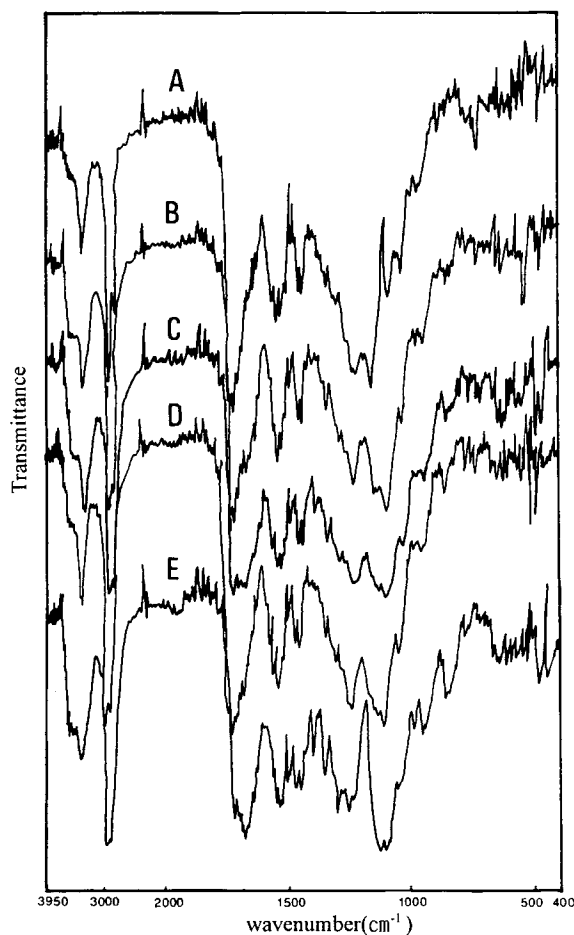


Figure 1 The IR spectra of WBPU. (A) C-2000; (B) CEM-2000-50; (C) CEB-2000-50; (D) CET-2000-50; (E) E-2000.

EXPERIMENTAL

Materials

The polydiols used in this study were PCL ($M_n = 2000$, PCL2000), PEG ($M_n = 2000$, PEG2000),

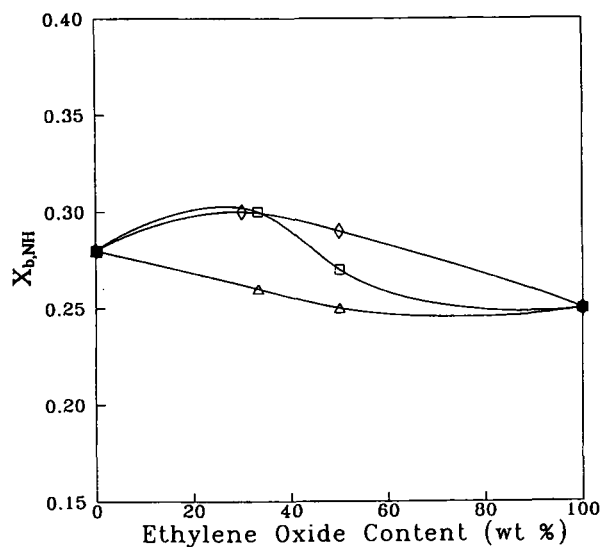


Figure 2 The hydrogen bonding index ($X_{b,NH}$) for the ester-ether-type WBPU with different EO content. ■, C-2000; ●, E-2000; □, CEM series; △, CEB series; ◇, CET series.

and triblock ester-ether copolydiol ($M_n = 2000$, PCL-PEG-PCL). PCL2000 and PEG2000 were from Hanawa, Japan. The PCL-PEG-PCL copolymers were synthesized from PEG ($M_n = 600$ or 1000) by reacting with ϵ -caprolactone at both ends under uncatalyzed reaction conditions according to the synthesis method of Piero et al.⁹ The methylene bis(cyclohexyl-diisocyanate) (H_{12} MDI, from Bayer) used as hard segments was vacuum dried at 80°C for 2 h. 2,2-Bis(hydroxyl methyl) propionic acid (DMPA, from Tokyo Chemical, reagent grade) was used to provide potential ionic centers. Triethylamine (TEA), ethylene diamine (EDA) (both from Hanawa, Japan, reagent grade), and 1-methyl-2-pyrrolidone (NMP, Ferak, reagent grade) used as neutralizer, chain extender, and solvent, respectively, were immersed in 4 \AA molecular sieves for more than a week before use.

Synthesis

The anionic WBPU was synthesized using the pre-polymer mixing process method.¹ The solution of polyol and DMPA dissolved in NMP was added to the reactor and heated to 80°C . H_{12} MDI and the catalyst di-*n*-butyltin dilaurate (DBTDL) were then added to the mixture and the reaction proceeded at 90°C for 3.5 h. The reaction was ended according to the determination of isocyanate (NCO) groups by dibutylamine back titration.¹⁰ The mixture was cooled to 70°C and neutralized with TEA. Aqueous

dispersion was obtained by the drip adding water with EDA/water for a period of 2 h.

Three types of WBPU for film casting were synthesized in this study. In the CEM series, WBPU C-2000 was synthesized with PCL2000 as the soft segment, and WBPU E-2000 was synthesized with PEG2000 as the soft segment. In the CEB series, WBPU CEB-2000 was synthesized with PCL2000 and PEG2000 as mixing soft segments, and in the CET series, WBPU CET-2000 was synthesized with triblock PCL-PEG-PCL copolydiol as the soft segment.

Film Casting and Nylon Fabric Coating

The films from the solvent evaporation method were obtained by casting the WBPU solution or mixing the WBPU solution evenly on a Teflon plate, followed by drying at 50°C for 3 days. The films were then removed and placed in a desiccator for testing. For the coating of nylon fabrics, the WBPU solution, including a thickening agent ($\text{NH}_4\text{OH}_{\text{aq}}$) and catalyst, was coated onto the nylon taffeta fabrics. After that, the fabrics were predried at 100°C for 3 min and cured at 130°C for 5 min. The molecular weights of the WBPUs were determined by a Waters RI-6000 gel permeation chromatator, and the results are listed in Table I.

Test

The IR spectra were analyzed with a JASCO Fourier transform IR spectrophotometer. SEM micrographs

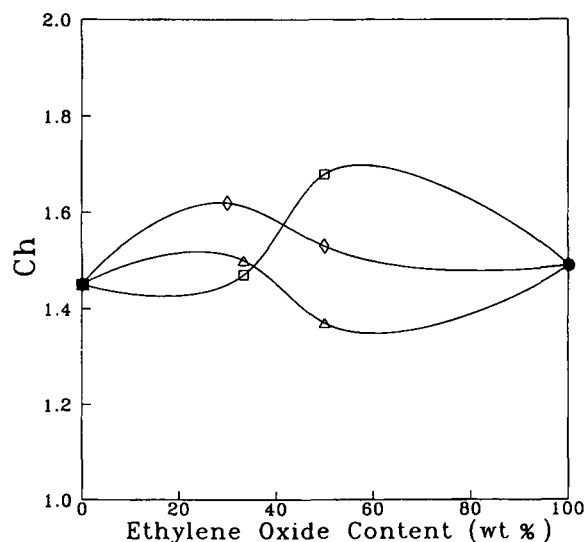


Figure 3 The cohesive force of hard segment (Ch) for the ester-ether-type WBPU with different EO content. ■, C-2000; ●, E-2000; □, CEM series; △, CEB series; ◇, CET series.

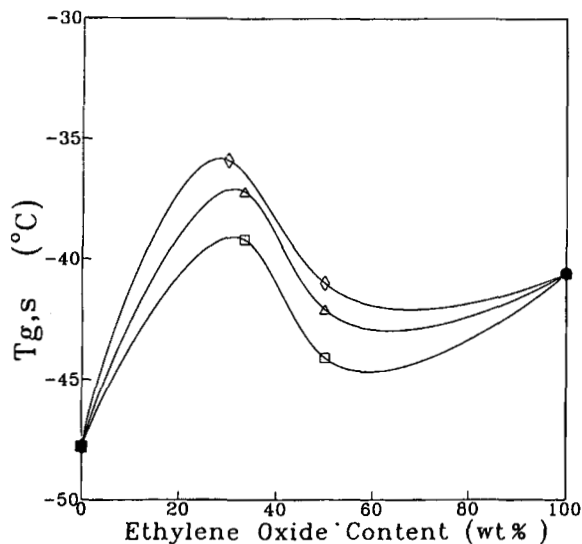


Figure 4 The glass transition temperature of soft segment for the ester-ether-type WBPU with different EO content. ■, C-2000; ●, E-2000; □, CEM series; △, CEB series; ◇, CET series.

were observed using a Cambridge S360. The soft segment on the surface of the WBPU was films selectively etched by dimethylformamide vapor for 2 weeks, and the surface of the samples was coated with gold before examination.⁷ The physical properties of the films were measured by a tensile tester, thermal analyzer, and dynamic mechanical analyzer. Tensile testing was performed according to the ASTM D412 Die C standard method. The DuPont Thermal Analyst 2000 was used for differential scanning calorimeter (DSC) thermal analysis, using liquid nitrogen for cooling and with a heating rate of 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, prestress of 1.8 MPa, and a temperature range of -120–50°C. The WVP study was based on the JIS-1099 CaCl₂ method at 40°C with relative humidity at 90%.

RESULTS AND DISCUSSION

Structural Analysis

The IR absorbance peaks appearing at 3300, 1730, and 1690 cm⁻¹ show the existence of the —NH—, and the C=O of urethane, and the C=O of urea groups, respectively (Fig. 1). These peaks shift to lower frequencies due to the formation of hydrogen bonding between PU molecular chains. The NH hydrogen bonding coupling force of urethane ($X_{b(\text{NH})}$) can be expressed using an equation^{11–13} by

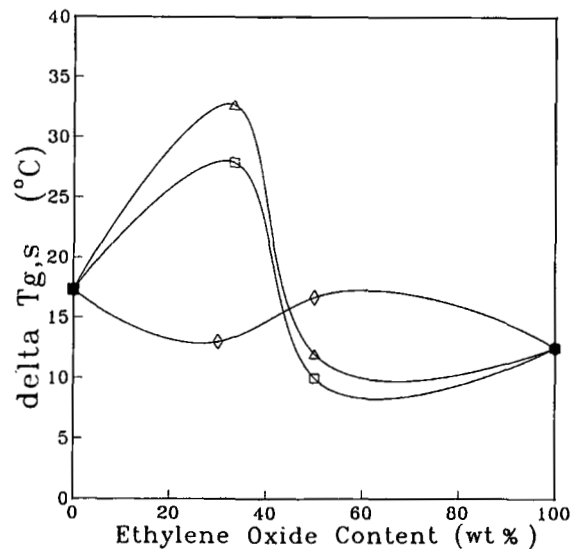


Figure 5 The range of glass transition temperature of soft segment for the ester-ether-type WBPU with different EO content. ■, C-2000; ●, E-2000; □, CEM series; △, CEB series; ◇, CET series.

$$\{X_{b(\text{NH})} = [1 + 3.46 \times (A_b/A_f)_{\text{NH}}]^{-1}\}$$

where $A_{b,\text{NH}}$ and $A_{f,\text{NH}}$ are the absorbance of bonded and free NH groups, respectively. The cohesive force index of the hard segment (Ch) can be expressed using an equation¹⁴ by

$$\{Ch = A_{(\text{urea})}/A_{(1600)}\}$$

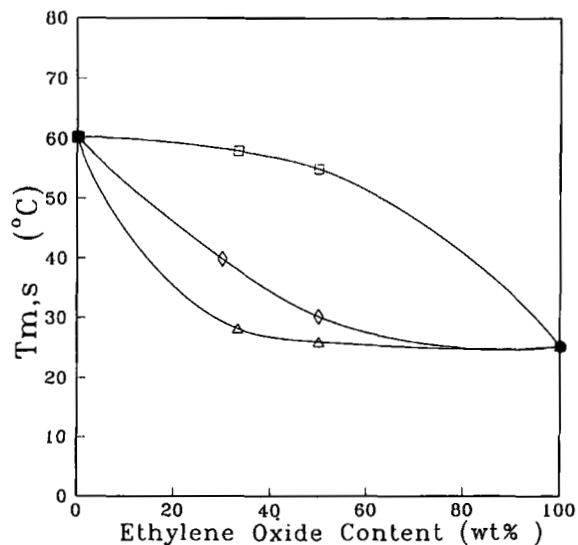


Figure 6 The melting temperature of soft segment for the ester-ether-type WBPU. ■, C-2000; ●, E-2000; □, CEM series; △, CEB series; ◇, CET series.

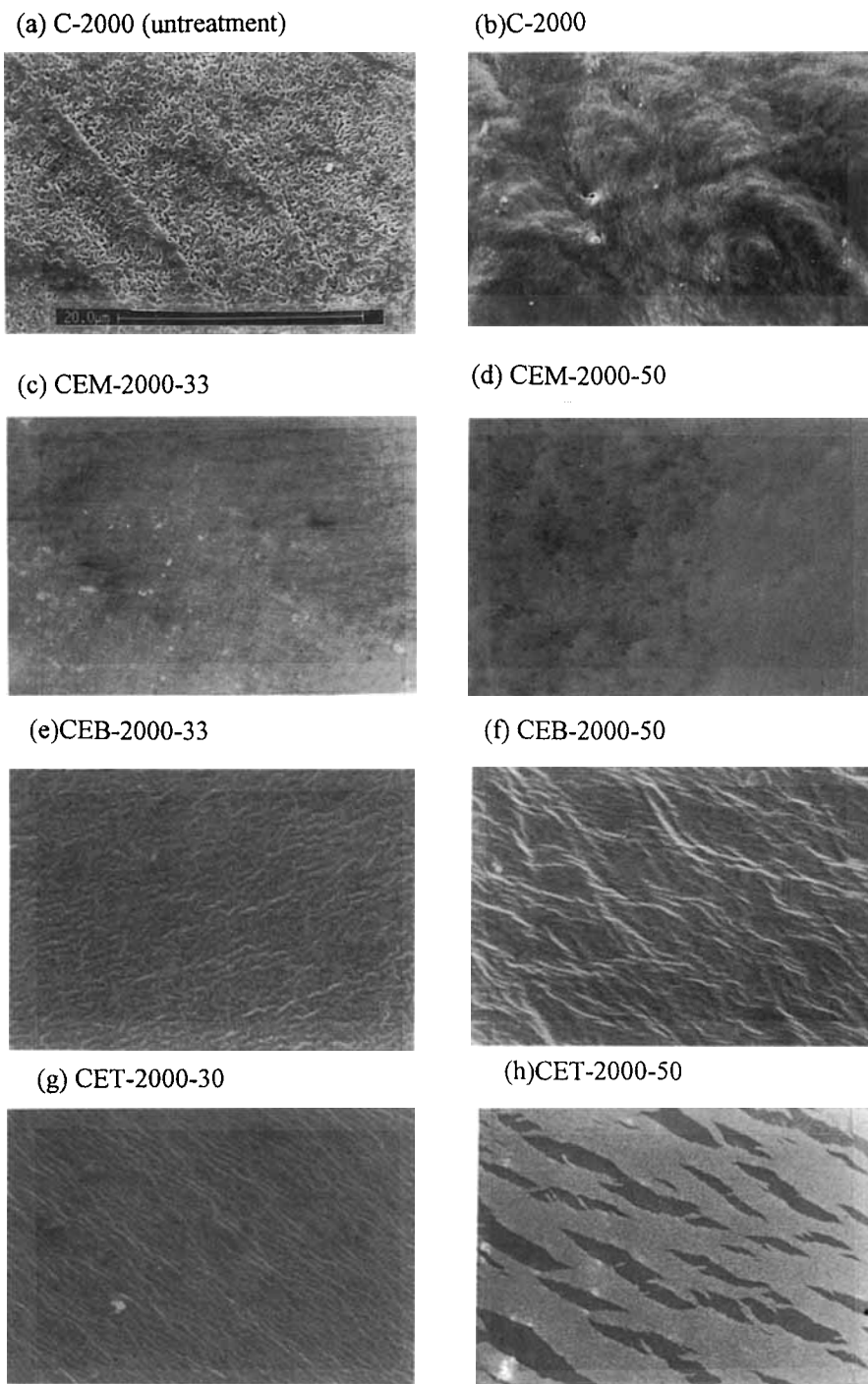


Figure 7 The SEM micrographs of the ester-ether-type WBPU films treated by DMF vapor. (a) C-2000 (untreatment); (b) C-2000; (c) CEM-2000-33; (d) CEM-2000-50; (e) CEB-2000-33; (f) CEB-2000-50; (g) CET-2000-30; (h) CET-2000-50.

where $A_{(\text{urea})}$ and $A_{(1600)}$ are the absorbance of bonded urea carbonyl groups and the peak at 1600 cm^{-1} , respectively.

The $X_{b(\text{NH})}$ values from Figure 2 show that the hydrogen bonding coupling force resulting from

the ester-type WBPU (C-2000, ethylene oxide [EO] content is 0 wt %) is higher than that from the ether-type WBPU (E-2000, EO content is 100 wt %). Figure 3 shows that the urea hard segment cohesive force index value of the ether-type

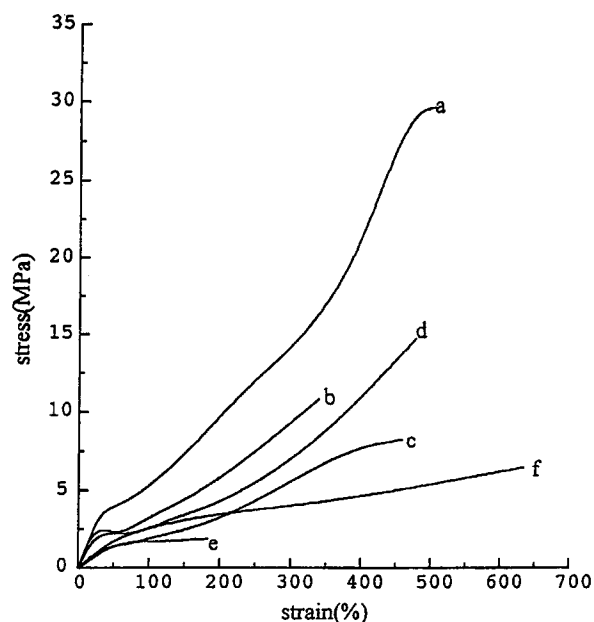


Figure 8 The stress-strain curves of the ester-ether type WBPU films. (a) C-2000; (b) CEM-2000-33; (c) CEM-2000-50; (d) CEB-2000-33; (e) CEB-2000-50; (f) CET-2000-30.

(E-2000) is slightly higher than that of the ester-type (C-2000). This is due to the fact that the $-\text{CONH}-$ group and $-\text{NHCONH}-$ group of the hard segments in the ester-type WBPU will form the hydrogen bonding mainly with the $-\text{COO}-$ groups of the polyester soft segments. On the other hand, the soft segments of the ether-type WBPU have the $-\text{CH}_2\text{CH}_2\text{O}-$ group, higher flexibility, and very different polarity from the hard segments; thus, the hydrogen bonding exists only between the hard segments,^{5,7} resulting in high conglomeration between the hard segments.

Samples CEM-2000-33 and CEM-2000-50 represent the films from the ester-type WBPU(C-2000)

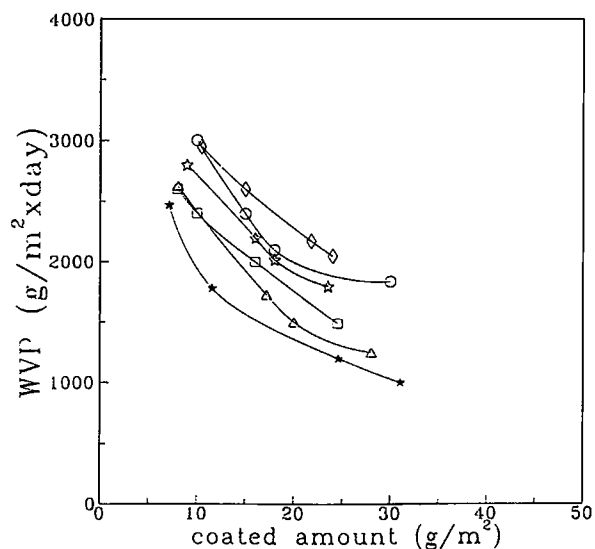


Figure 9 The WVP versus coated amount of the ester-ether-type WBPU on nylon fabrics. \star , C-2000; Δ , CEM-2000-33; \star , CEM-2000-50; \square , CEB-2000-33; \circ , CEB-2000-50; \diamond , CET-2000-30.

obtained by mixing with 33 and 50 wt % of the ether-type WBPU(E-2000), respectively. From Figures 2 and 3, we find that the CEM-2000-33 sample has more conspicuous hydrogen bonding. Conversely, the CEM-2000-50 sample has stronger conglomeration between the hard segments. It seems that adding a small amount of ether-type WBPU (E-2000) to the ester-type WBPU (C-2000) will increase the hydrogen bonding. The reason may be because that the ether-type PU chain dissolves into the ester-type PU molecular chain, resulting in the formation of phase boundary, hence increasing the surface area for the hydrogen bonding of the ester groups. However, as the EO content is increased further, macro-phase separation will emerge between the ether- and ester-type WBPU's molecular chains, inducing an

Table II The Mechanical Properties of the Ester-Ether-Type WBPU

WBPU Code	EO of Soft Segment (wt %)	Young's Modulus (MPa)	Breaking Stress (Mpa)	Breaking Strain (%)
C-2000	0	11.76	29.69	502
E-2000	100	—	—	—
CEM-2000-33	33	9.80	10.88	339
CEM-2000-50	50	4.31	8.23	457
CEB-2000-33	33	8.23	14.80	477
CEB-2000-50	50	2.94	1.96	183
CET-2000-30	30	5.88	6.47	633
CET-2000-50	50	—	—	—

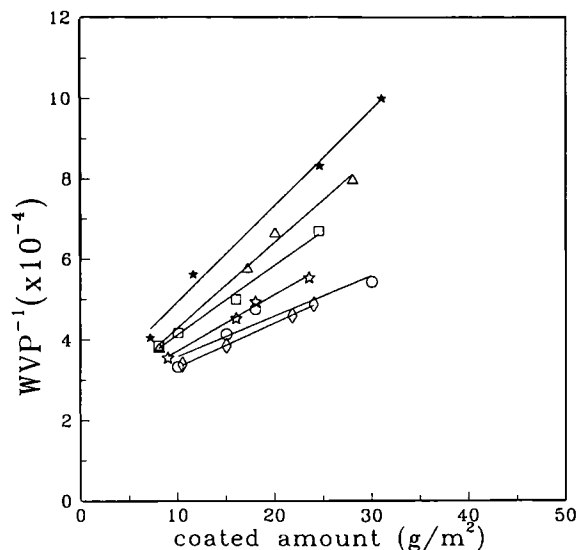


Figure 10 The inverse of WVP versus coating amount of the ester-ether-type WBPU on nylon fabrics. ★, C-2000; △, CEM-2000-33; ☆, CEM-2000-50; □, CEB-2000-33; ○, CEB-2000-50; ◇, CET-2000-30.

increase in the conglomeration between the hard segments of the individual types of WBPU. Xiu et al.⁷ compared the morphology of polyester-ether-based PUU with that of polyester-based and polyether-based PUU by using SEM micrographs and indicated that the polyester-ether-based PUU exhibited the morphology of both polyester-based and polyether-based PUU as well as having a larger domain size and a clear boundary between these two different morphologies. Because the film in the CEM procedure was cast by mixing ester-type and ether-type PU, the boundary phase between the ester-type and ether-type PU would be more distinct than in films cast using the other two procedures.

Samples CEB-2000-33 and CEB-2000-50 represent the WBPU synthesized by blending PEG2000 and PCL2000 as the soft segments, in which the EO content of the soft segment was at 33 and 50 wt %, respectively. The hydrogen bonding of NH and the cohesive force of the hard segment, especially for sample CEB-50, are less than the normal blending rule predicted. This phenomenon may be because the blended soft segment in the WBPU copolymer has an irregular arrangement of ester and ether segments in the molecular chains, which makes it difficult for them to interact with each other's molecular chains.

Samples CET-2000-30 and CET-2000-50 represent the WBPU films synthesized from triblock PCL-PEG-PCL copolydiols as the soft segment, in which the EO contents were 30 and 50 wt %, re-

spectively. The hydrogen bonding of NH and cohesive force of the hard segments, especially for sample CET-2000-30, are generally larger than those of normal blending rule predicted. Because of the symmetry, the regular arrangement of the soft segments, the orientation between the PU molecules is much better than that of the other series of WBPU studied here.

Thermal Properties

Shown in Figures 4–6 are the glass transition temperatures (T_g s), range of glass transition temperatures (ΔT_g s) and melting temperatures (T_m s) of the soft segment in the ester-ether type WBPU. The results show that E-2000 has a higher T_g , narrower ΔT_g , and lower T_m than C-2000. In general, the ester-type PU had a higher T_g than ether-type PU. The reason for the ether-type WBPU (E-2000) having a higher T_g is because the soft segment of the ether type (E-2000) used in this study is PEG (M_w is 2000), and the crystal formed will favor the increase of T_g . Antonsen et al.¹⁵ suggested that the PEG chain would begin to fold on itself and form segment-segment interactions when the molecular weight of the PEG is above 1200. The soft segment of the ester-type (C-2000) containing the $-\text{COO}-$ group has higher polarity and a more rigid molecular chain; thus, the T_m of C-2000 is higher.

As we increase the EO content of the ester-ether-type WBPU, the T_g increases and reaches the maximum value at 33 wt %, the T_m decreases, but ΔT_g is irregular. This suggests that the lower EO content may result in better phase mixing, a higher interacting force, and poorer arrangement of soft segments than with the ester-type (C-2000). However, the phase separation will take place at a higher EO content.

The thermal properties are also affected by the procedure of the mixing process. The order is CET > CEB > CEM for T_g , CEM > CET > CEB for T_m , and CEB > CEM for ΔT_g (the ΔT_g of the CET series is hardly affected by EO content). This suggests that the CEB series shows better phase mixing than the CET and CEM series.

Surface Structure

Figure 7 shows the SEM micrographs of the WBPU film. The soft segments on the surface of the WBPU are etched by DMF, except for Figure 7(a). We find there are many micropores on the surface from Figure 7(a), and the corresponding relief could be observed after DMF vapor treatment [Fig. 7(b)–(h)].

For the ester-ether-type WBPU [Fig. 7(c)-(h)], it is clearly shown that the phase separation is obvious as the EO content increases. For the effect of the mixing procedure, the phase region of the CEM series is different from the CET and CEB series; it has a clear phase boundary, especially for CEM-2000-50, because the WBPU molecular chains in the CEM series can migrate and congeal. Figure 7 also shows that the CEB series has better phase mixing than the CET series. This is due to the hydrogen bonding and the cohesive force of the hard segment of the CEB series WBPU.

Mechanical Properties

Figure 8 shows the stress-strain curve of WBPU film, and the data are listed in Table II. The mechanical properties of E-2000 and CET-2000-50 are too weak and can be ignored. The Young's modulus is in the sequence of C-2000 > CEM-2000-33 > CEB-2000-33 > CET-2000-30 > CEM-2000-50 > CEB-2000-50, the breaking stress is in the sequence of C-2000 > CEB-2000-33 > CEM-2000-33 > CEM-2000-50 > CET-2000-30 > CEB-2000-50, and the breaking strain is in the sequence of CET-2000-30 > C-2000 > CEB-2000-33 > CEM-2000-50 > CEM-2000-33 > CEB-2000-50. This suggests that the EO content in the soft segment will negatively affect the mechanical properties of all ester-ether-type WBPU films. For the mixing procedures of the ester-ether-type WBPU, the CEM series has a better Young's modulus and breaking stress and poorer breaking strain than the CEB and CET series. The good mechanical properties of the CEM series may be due to the interface force between the ester-type and ether-type PU molecules. In addition, the CEB series has better phase mixing than the CET series and thus has a better breaking stress and Young's modulus than the CET series.

WVP

Figure 9 shows the WVP of the nylon fabrics treated with the ester-ether-type WBPU resins. It clearly shows that the WVP decreases with an increase in the amount of PU coating and is affected by the mixing procedures. Figure 10 is the inverse of the WVP plotted against the coating amount, and a straight line was obtained.

The ester-ether-type WBPU has a higher WVP than the ester-type WBPU (C-2000), and the WVP increases with the EO content in the ester-ether-type WBPU. This clearly shows that the EO functionality plays a role in increasing the WVP. For

the three procedures used in the WBPU samples, the sequence of the WVP is CET > CEB > CEM. That the CET series has a better WVP than the CEB series may be because it has good phase separation. On the other hand, the CEM series has better phase separation than the CEB series, but the WVP is lower. This is because the phase separation in the CEM series is in the macroscopical level of the ester- and ether-type WBPU molecules, which is different from the phase separation in the microscopical level of the other two series.

CONCLUSION

We primarily focus on the study of the structures and physical properties of ester-ether-type WBPU film cast using different mixing procedures. The WVP of the WBPU-coated nylon fabric is also examined. The results produce the following observations:

1. For the ester-ether-type WBPU, the phase separation will be generated as the EO content increases. The EO functional groups in the soft segment will negatively affect the mechanical properties of the ester-ether-type WBPU films.
2. For the effect of the mixing procedure,
 - a. The CEM series WBPU has a higher Young's modulus, breaking stress, and a clear phase boundary between the ester- and ether-type WBPU. The reason is that the WBPU molecular chains can migrate easily.
 - b. The CEB series WBPU shows a better phase mixing and weaker cohesive force of the hard segments, because of its irregular arrangement of molecular chains.
 - c. The CET series WBPU has a higher hydrogen bonding, cohesive force of the hard segments, and elongation, because of its symmetry and regular arrangement of molecular chains.
3. The thermal properties are also affected by the procedure of the mixing process. The order is CET > CEB > CEM for T_g and CEM > CET > CEB for T_m .
4. As for the WVP of treated nylon fabrics, the ester-ether-type WBPU has a higher WVP than the ester-type WBPU, and the WVP increased with the EO content in the ester-ether-type WBPU. For the three mixing pro-

cedures of WBPU, the sequence of the WVP is CET > CEB > CEM.

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