

Effects on the Structure and Properties of Membranes Formed by Blending Polydimethylsiloxane Polyurethane into Different Soft-Segment Waterborne Polyurethanes

Meng-Shung Yen, Ping-Yuan Tsai

Department of Polymer Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Section 4, Taipei, Taiwan, Republic of China

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ABSTRACT: Polydimethylsiloxane polyurethane (PDMS-PU), which was synthesized from PDMS as the soft segment, was blended into a variety of ester- or ether-based soft-segment waterborne polyurethanes with different concentrations to investigate the crystallization, thermal, and physical properties of the membrane formations. According to X-ray analysis, the ether-based PUs, synthesized from soft segments of poly(propylene glycol) (PPG1000) or poly(ethylene glycol) (PEG2000), were found to have maximum crystallinity at a 5% blending ratio of PDMS-PU, but the ester-based PU, synthesized from soft segments of polycaprolactone (PCL1250), had decreased crystallinity at a 5% blending ratio. Differential scanning calorimetric analysis revealed that the $T_{g,s}$ values of PUs were highest when the blending ratio of PDMS-PU was 5%–10%, except for PU from PCL1250. Moreover, ether-based PUs showed maxi-

imum $T_{m,h}$ values, but the $T_{m,h}$ of the ester-based PU was greatly reduced when PU with PCL1250 was blended with PDMS-PU. In addition, the PU from PEG2000 had the highest melting entropy. Mechanical property analysis showed that the stress of ether-based PUs would be increased when PUs were blended with a small amount of PDMS-PU and that the stress of PU from poly(tetramethylene glycol) (PTMG1000) increased to its greatest value (20–30 MPa). On the other hand, the ester-based PU, from PCL1250 blended with PDMS-PU, would have reduced stress. On the whole, the stress and strain of PU from PEG1000 had excellent balance. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 210–221, 2006

Key words: polyurethanes; polysiloxanes; blending; thermal properties; mechanical properties

INTRODUCTION

Polydimethylsiloxane (PDMS), obtained by hydrolytic condensation from dimethyldichlorosilane or ring-opening polymerization from cyclic siloxane (mainly trimers or tetramers),¹ offers the advantages of low surface tension, unique flexibility, low glass-transition temperature, low elasticity change versus temperature, high thermal stability, chemical inertness, dielectric stability, shear stability, and high compressibility.² In a PDMS thermal degradation kinetic study, PDMS when decomposed in a nitrogen atmosphere was resistant to temperatures greater than 400°C, so it offered high thermal stability.³ Crystallization studies found that the T_g (–123°C) of PDMS was unaffected by the cooling rate or the molecular weight of PDMS, so it maintained its low-temperature properties.⁴

Polyurethanes (PU), which possess good flexibility and microphase separation, have been widely used in elastic fibers, coating materials, bonding agents, and

artificial leather.⁵ However, PUs also possess some disadvantages such as yellowing, low strength, and poor weathering and heat endurance. In past research, PUs showed improved characteristics when a PDMS component was introduced into them.^{6–12} For instance, Bayer⁶ synthesized a PU resin, using PDMS and polyester as the mixing soft segment, and found that the PU possessed higher wet membrane tensile strength and vapor permeability. Sha'aban et al.⁷ studied the surface structure and thermal properties of formed membranes that were produced by blending poly(tetramethylene glycol) polyurethane (PTMG-PU) with polydimethylsiloxane polyurethane (PDMS-PU). They found that the incompatibility of the soft and hard segments of PU and the low surface energy of PDMS could help the PDMS migrate to the surface of the PU film and enhance the phase separation of the soft and hard segments during the process of PU formation. To improve the mechanical properties of oil-soluble PU, Adhikari et al.^{10,11} synthesized oil-soluble PU by mixing the soft segments of PDMS and polyethers or polycarbonates. Previously, in our laboratory,¹² waterborne polyurethane (WBPU) was blended with PDMS-PU to investigate the thermal properties of PUs and the surface composition and

Correspondence to: M.-S. Yen (D9004103@mail.ntust.edu.tw).

physical properties of formed membranes. Our research also found that, by blending a small amount of PDMS-PU into WBPU, the PDMS would migrate to the surfaces of PU formed membranes and alter the crystallinity of PU; hence, the addition of PDMS resulted in significant enhancement of the thermal properties and modulus of PU.

The soft segments in PU play an important role in determining its properties. Previous studies of the effect of soft segments on PU properties reported that the crystallinity of ether-based PU was higher than that of the ester-based PU with identical hard-segment concentrations.¹³ Previous studies in our laboratory¹⁴ confirmed that the glass-transition point of the soft segments ($T_{g,s}$) of waterborne PU from ether-based poly(tetramethylene glycol) (PTMG) was lower than that from ester-based poly(tetramethylene adipate) (PBA). Moreover, our laboratory found that $T_{g,s}$ of WBPU from ether-based poly(tetramethylene glycol) resulted in PU having greater breaking elongation but lower breaking strength; however, fabric treated by the PU had higher moisture penetrability. As mentioned above, soft segments play an important role in the physical properties of PU, so further investigation is needed into the effect of PDMS-PU by blending it with different kinds of ester- or ether-based soft segments of WBPUs.

The present study synthesized various types of ester- or ether-based waterborne PUs using ester-based polyol (PCL) or ether-based polyol (PEG, PPG, PTMG) as the soft segment, H_{12} MDI as the hard segment, and DMPA as an ionic center. PDMS-PU, which was synthesized from PDMS as the soft segment, was blended into ester- and ether-based WBPUs with varied concentrations in order to investigate the crystallinity, thermal, and physical properties of formed membranes.

EXPERIMENTAL

Materials

Polyols of poly(ethylene glycol) (PEG, M_n 600, 1000, or 2000; Merck, Darmstadt, Germany), poly(propylene glycol) (PPG, M_n 1000; Merck, Darmstadt, Germany), poly(tetramethylene glycol) (PTMG, M_n 1000; Merck, Darmstadt, Germany), polycaprolactone (PCL, M_n 1250; Merck, Darmstadt, Germany), or polydimethylsiloxane (PDMS, M_n 2000; SF-8427, Dow-Corning, Midland, MI) were used as the soft segments, and dicyclohexylmethane diisocyanate (H_{12} MDI; Bayer, Leverkusen, Germany) and 2,2-bis(hydroxymethyl) propionic acid (DMPA; reagent grade; Acros, Geel, Belgium) were used as the hard segment and the potential ionic center, respectively, for the synthesis of anionic waterborne polyurethane (WBPU). All the materials were vacuum-dried at 80°C for 2 h. Triethyl-

amine (TEA, reagent grade; Acros), ethylene diamine (EDA, reagent grade; Acros, Geel, Belgium) and 1-methyl-2-pyrrolidone (NMP, reagent grade; Acros) were used as the neutralizer, chain extender, and solvent, respectively, all of which 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.¹⁵ First, for the synthesis of each soft-segment WBPU, 1 mol polydiol (PEG, PPG, PTMG, PCL, or PDMS) and 1 mol DMPA dissolved in NMP were added to the reactor and heated to 80°C. Second, 4 mol H_{12} MDI and the catalyst (di-*n*-butyltin dilaurate; DBTDL, 0.05 wt %) were added to the mixture and prepolymerized at 90°C for 4 h. The prepolymerization came to completion as the NCO value of H_{12} MDI was reduced by half. The change in the NCO value in the prepolymerization was determined using a standard dibutylamine back-titration method.¹⁶ Third, the prepolymer was cooled to 70°C, neutralized by TEA, and diluted with water. Then, after 1 mol EDA aqueous was added into the prepolymer drop by drop, the chain extension lasted for 2 h. Finally, the final dispersion solution was diluted to a 30% aqueous solution. The compositions of the WBPUs are listed in Table I. The infrared spectra of the synthesized WBPUs were analyzed with a Fourier transform infrared (FTIR) spectrophotometer (Jasco, Tokyo, Japan). The molecular weights of WBPUs were identified by gel permeation chromatography (GPC, PL-GPC 220; Polymer Laboratories, UK) with polystyrene standards and are listed in Table I.

Membrane casting

The blending series of PUs was used for membrane casting. In the blending method, different weight ratios of PDMS-WBPU were blended into ester-based polyol (PCL) WBPU or ether-based polyol (PEG, PPG, or PTMG) WBPU by stirring. The membranes were prepared by pouring WBPU on a Teflon plate and then drying the membranes at 50°C for 72 h (the thickness of PU membrane was about 150 μm).

Procedures of testing

Wide-angle X-ray diffractograms of the rotated samples were obtained with an X-ray diffractometer (D/Max-RC, Rigaku, Japan) using monochromatic $\text{CuK}\alpha$ radiation in the diffraction range of $2\theta = 5\text{--}40^\circ$. The scanning rate was $5^\circ/\text{min}$. Thermal analysis of the samples was carried out with a differential scanning calorimeter analyzer (DSC; DuPont 930 thermal analyzer 2000; DuPont, Boston, MA), at a heating rate of

TABLE I
Synthetic Composition of WBPU Polymers

Symbol	Type of soft segment	PU composition (wt %)				Molecular weight		
		Hard segment	Soft segment	Dispersing center	Chain extender	M_w	M_n	M_w/M_n
E600	PEG 600	55.1	31.5	7.0	6.3	64493	31081	2.075
E1000	PEG 1000	45.5	43.4	5.8	5.2	64697	32992	1.961
E2000	PEG 2000	31.7	60.6	4.1	3.6	69004	31887	2.164
P1000	PPG 1000	45.5	43.4	5.8	5.2	66377	32458	2.045
T1000	PTMG 1000	45.5	43.4	5.8	5.2	67498	34403	1.962
C1250	PCL 1250	41.1	48.9	5.3	4.7	72137	33397	2.160
S2000	PDMS 2000	31.7	60.6	4.1	3.6	61494	31763	1.936

Hard segment : soft segment : dispersing center : chain extender (molar ratio) = 4 : 1 : 1 : 2. Hard segment : H_{12} MDI; dispersing center: DMPA; chain extender: EDA.

20°C/min. The membrane stress-strain test was carried out according to the ASTM D 638M-93 method with a Tensilon Testing machine (RTA-1T, ORIEN-TEC).

RESULTS AND DISCUSSION

Synthesis and characterization of WBPU

Figure 1 shows the FTIR spectra of WBPU from different soft-segment types, where for synthesized PUs, the absorption peak of the NCO group did not appear around 2200 cm^{-1} and the OH absorption peak around $3300\text{--}3500\text{ cm}^{-1}$ narrowed. The absorption peak of the narrower NH group appeared at 3300 cm^{-1} , the absorption peaks of the C=O groups of urethane and of urea appeared at 1730 and 1690 cm^{-1} , respectively, and the absorption peak of the formation of the —CNH group was at 1540 cm^{-1} . The urethane structure of PU was proved from the above. In addition, ether-based WBPU (E600, E1000, E2000, P1000, and T1000) had strong ether-group C—O—C absorption peaks of the soft segment between 1000 and 1112 cm^{-1} .¹⁷ The ether group C—O—C absorption peaks from the PEG series tended to be stronger with increased PEG molecular weight. The sharp absorption peaks of the —CH₂— groups were around $2850\text{--}2930\text{ cm}^{-1}$, and the absorption peaks became relatively stronger with increased molecular weight of PEG. P1000 had three absorption peaks of —CH₂— groups because of a side chain of methyl in the PPG1000 soft segment.¹⁸ In addition, T1000 had two absorption peaks with an obvious separation. The ester-based WBPU (C1250) showed a sharper absorption peak of C=O (ester group) around 1690 cm^{-1} and no absorption peak of the ether-based C—O—C group between 1000 and 1112 cm^{-1} . Furthermore, the absorption peaks of the C=O ester group in C1250 shifted to lower frequencies because hydrogen bonding in the ester group of the ester-based PU occurred between the soft and hard segments, but in the ether-based PU

hydrogen bonding occurred between the hard segments. Therefore, hydrogen bonding in the ester-based PU was stronger than that in the ether-based PUs.^{13,19} PDMS-PU (S2000) showed symmetrical Si—O—Si stretching between $1000\text{--}1130\text{ cm}^{-1}$; —CH₃ bending within CH₃—SiO—CH₃ symmetry bending, and CH₃—Si rocking around 805 and 885 cm^{-1} .²⁰

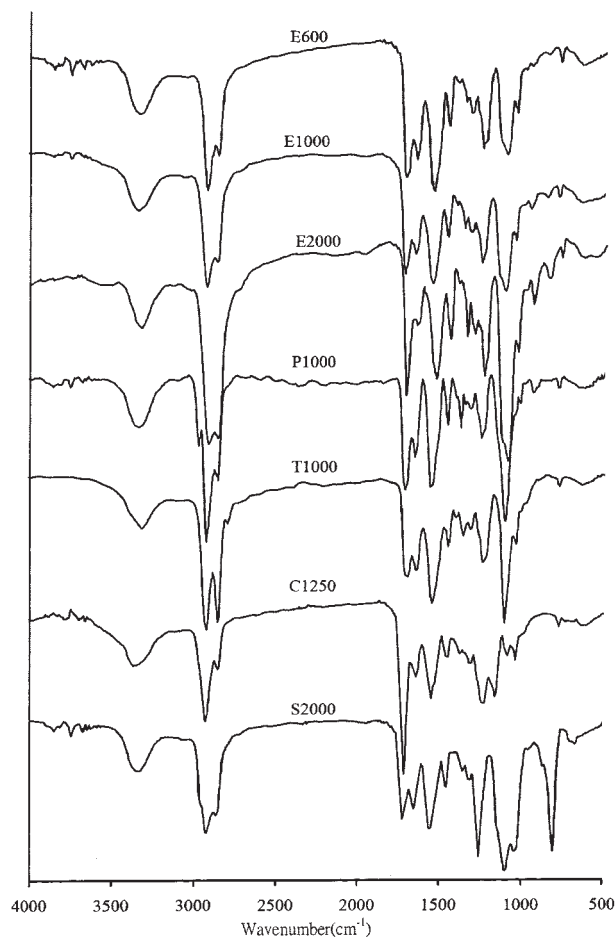


Figure 1 FTIR spectra of WBPU of different soft-segment types.

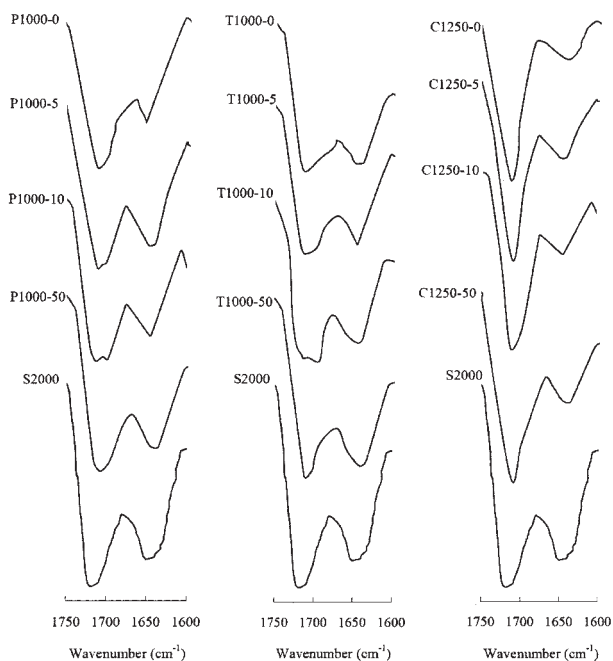


Figure 2 FTIR analysis of WBPU membranes analyzed by blending WBPU of different soft-segment types with PDMS-PU.

Figure 2 shows the FTIR spectra of WBPU membranes. WBPU membranes of various soft-segment types were blended with PDMS-PU at different blending ratios. The ether-based WBPU membranes (P1000 and T1000) showed absorption from C=O groups at 1710 cm^{-1} , and absorption peaks were split in two as PDMS-PU was blended into WBPU membranes. This division occurred most obviously at a 10% blending ratio of PDMS-PU. Moreover, the C=O absorption peak, which showed hydrogen bonding at low frequencies, tended to increase its strength because 10% PDMS-PU blended into ether-based WBPU caused PDMS of low surface energy to migrate to the surface of the WBPU formed membranes. Hence, this migration resulted in the packing of hydrophilic ether-based WBPU, leading to an increase in the order of each soft segment and hard segment in WBPU and to increased hydrogen bonding in the hard segments.¹² With the ester-based WBPU (C1250) blended with PDMS-PU, there were no obvious changes in the peaks of the C=O groups because the stronger hydrogen bonding between the soft and hard segments would not be affected by the blending of PDMS-PU.

Figure 3 shows the FTIR spectra of WBPU membranes, indicating that WBPU membranes were made by blending PU containing PEG soft segments of different molecular weights with PDMS-PU at various blending ratios. When E600 and E1000 of ether-based PUs were at a 10% PDMS-PU blending ratio, the absorption peaks of the C=O groups ($1690\text{--}1730\text{ cm}^{-1}$) shifted from the high-frequency area to the low-frequency area. The result of this shift was similar to those for P1000 and T1000 shown in Figure 2. However, the E2000 series shifted

to the low-frequency peak when they were blended with PDMS-PU at a lower blending ratio (5%). E2000 had the highest soft-segment content; hence, it was easier for PDMS to migrate and E2000 easily carried out the packing of the soft and hard segments.

Composition of WBPU blended membranes formed

X-ray analysis of the WBPU membranes with different soft-segment types is shown in Figure 4. Crystallization peaks were found at 14.3° and 17° for both ether- and ester-based PUs. However, only a small crystallization peak of S2000 was found at 17° . Crystallization peaks in the ether-based PUs of the PEG series were found at 25.4° ; for E2000, in particular, the peaks were found not only at 25.4° but also at 21.3° . When the study focused on the main crystallization peak, at $2\theta = 17^\circ$, and a soft-segment molecular weight of 1000, the crystallinity of the ester-based PU would be stronger than that of the ether-based PUs. When all types of ether-based PUs were compared, crystallization was ranked: T1000 > P1000 > E1000. The greater crystallization in the ester-based PU could be attributed to the strong hydrogen bonding between the soft and hard segments. Moreover, with changes in molecular weight in the identical PEG series, E2000 was found to have the highest crystallinity, E600 the second highest, and E1000 the smallest crystallization. E2000 had higher hydrophilicity in the PEG2000 soft segment, so E2000 underwent phase separation between the hard

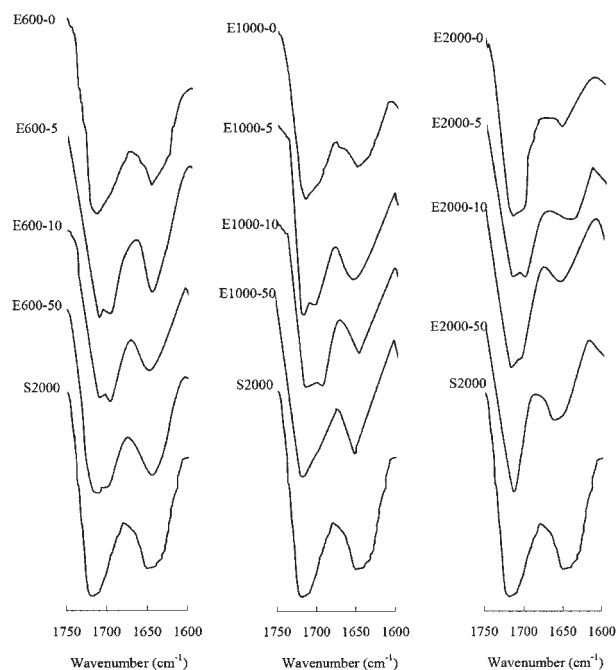


Figure 3 FTIR analysis of WBPU membranes analyzed by blending WBPU of PEG soft segments of different molecular weights with PDMS-PU.

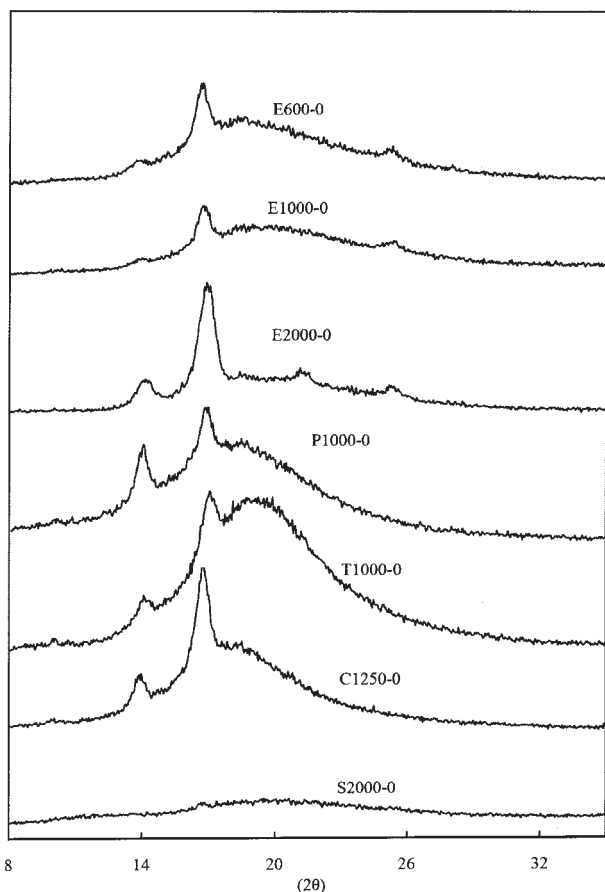


Figure 4 X-ray analysis of WBPU membranes of different soft-segment types.

and soft segments more readily. Phase separation made the hard segments prone to crystallization, so the crystallinity of the PUs increased.

Figure 5 shows the X-ray analysis of the PDMS-PU blended compounds, in which P1000 was found to have maximum crystallization at a 5% ratio, above which, the crystallization of P1000 decreased with an increase in the amount of PDMS-PU blended. With an increase in PDMS-PU, the crystallinity of T1000 increased; however, above a 50% blending ratio, it decreased. The crystallinity of C1250 initially decreased, but above a 5% blending ratio, it increased. The crystallization of C1250 increased, reaching its maximum at a 50% blending ratio. A major difference between ester- and ether-based WBPUs was that when blended with a large amount of PDMS-PU at 50%, the ester-based WBPU had strong crystallinity, whereas the ether-based WBPUs showed reduced crystallinity. This can be attributed to the strong hydrogen bonding between the soft and hard segments of the ester-based WBPU. At a 50% concentration of PDMS-PU in the blends, phase separation between the PDMS soft segments and the PCL soft segments increased in the ester-based WBPU, leading to increased WBPU crystallinity.

The X-ray analysis diagram of WBPU membranes is shown in Figure 6, where the WBPU membranes have different molecular weights of the PEG soft segment. With an increase in PDMS-PU, the crystallinities of E600, E1000, and E2000 increased, except that E1000

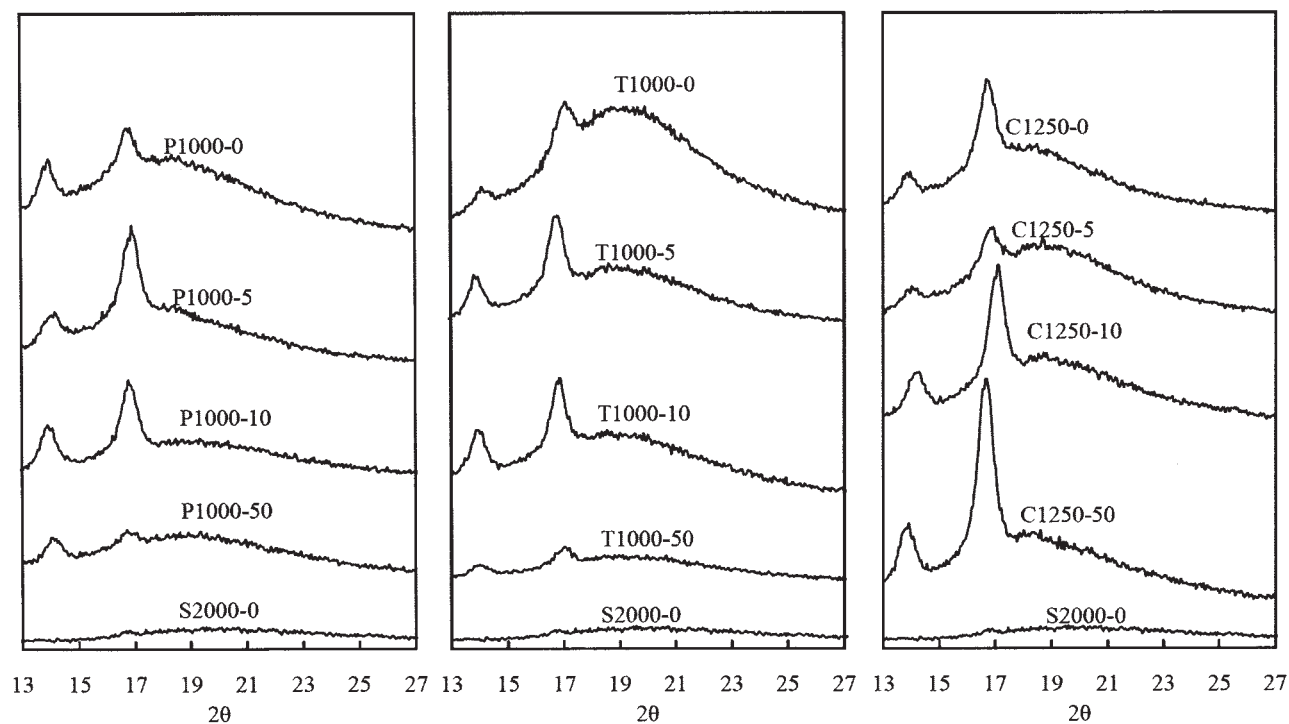


Figure 5 X-ray analysis of WBPU membranes analyzed by blending WBPUs of different soft-segment types with PDMS-PU.

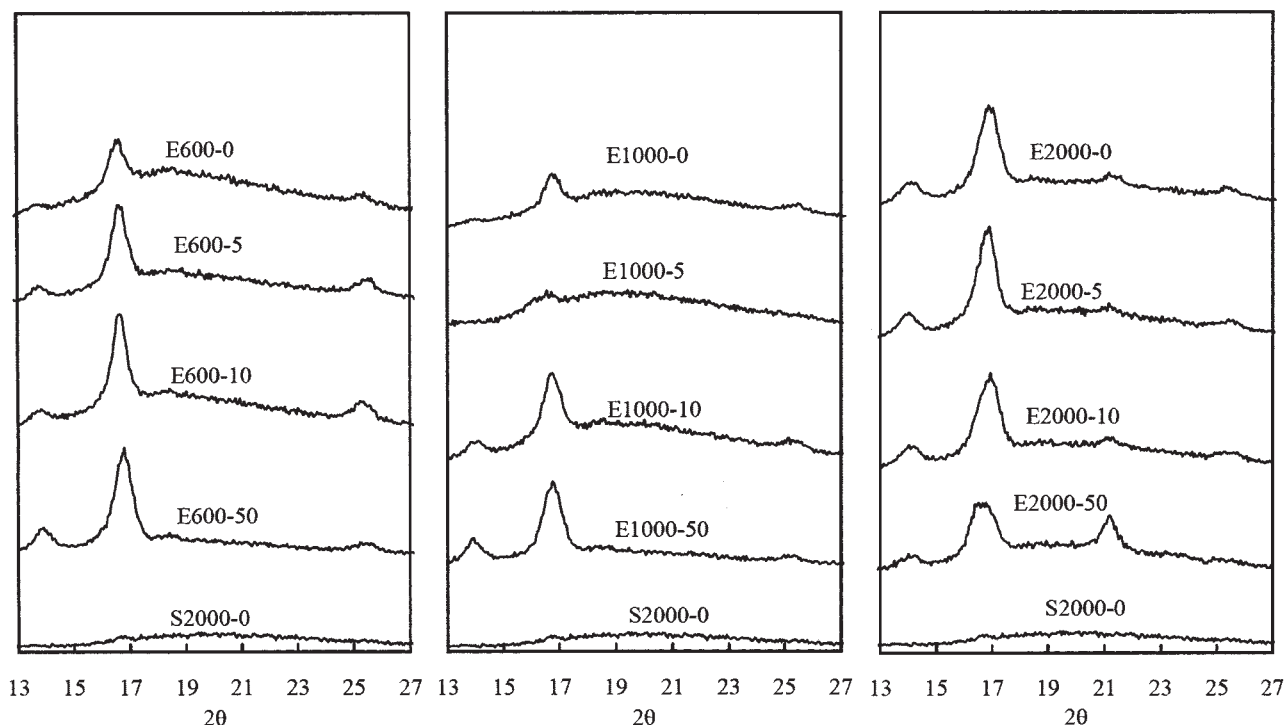


Figure 6 X-ray analysis of WBPU membranes analyzed by blending WBPU of PEG soft segments of different molecular weights with PDMS-PU.

had lower crystallinity at a 5% blending ratio and that E2000 showed a leveling trend above a 10% blending ratio. Among the WBPU of various molecular weights of PEG, E1000 and its blended compounds had the smallest crystallinity, which was attributed to a longer distance between the hard segments of PUs hindering the hard segments from crystallizing. The incompatibility between its soft and hard segments in E2000 increased the phase separation, whereas the foldable and flexible PEG2000 soft segments shortened the distance between the hard segments. Hence, a shortened distance between hard segments enhanced crystallinity.²¹

Thermal property analysis of WBPU blended membranes

Figure 7 shows the DSC curves of WBPU with various soft-segment types and PDMS-PU blends. The DSC thermal property analysis of unblended and blended WBPU membranes with different soft-segment types is shown in Figure 7(a,b), respectively. The melting peaks between 100°C and 160°C were the melting points of the hard segments of the PUs ($T_{m,h}$). The effect of unblended PUs of various soft-segment types on $T_{m,h}$ [Fig. 7(a)] was observed in a wider range of $T_{m,h}$ values in the ester-based PU than in the ether-based PUs; however, the area of the melting peak in the ester-based PU was smaller than that in the ether-

based PUs. This is because the dissolution parameters of the ester-based soft segments were closer to those of the hard segments; hence, in PUs phase mixing of the soft and hard segments was prone to occur. Concerning the effect of molecular weight of PEG soft segments on $T_{m,h}$, the melting peaks were widest in E600, and largest in area in E2000, indicating that E600 offered relatively less phase separation and that E2000

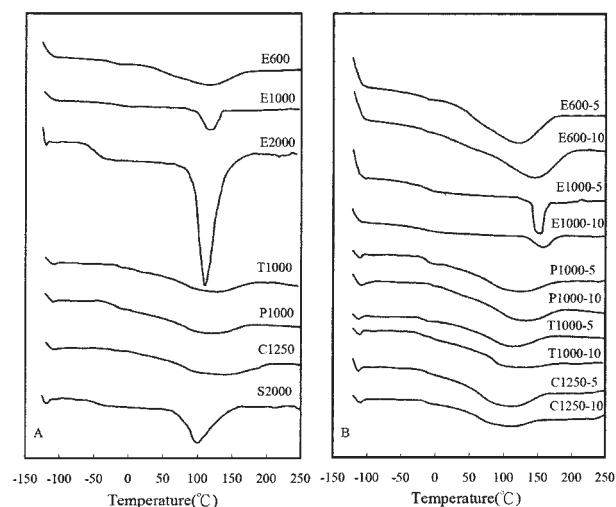


Figure 7 DSC analysis of WBPU of various soft-segment types and PDMS-PU blends.

TABLE II
Physical Properties of WBPUs Measured by Blending WBPUs of Various Soft-Segment Types with PDMS-PU

WGPU ^a	Type of soft segment	PDMS content (%) ^b	Thermal properties			Strength properties		
			$T_{g,s}$ (°C)	$T_{m,h}$ (°C)	Energy (J/g)	Stress (MPa)	Strain	Young's modulus (MPa)
P1000	PPG 1000	0	-13.0	125.4	37.5	31.0 ± 0.5	0.2 ± 0.2	23.2 ± 0.6
P1000-5		5	-10.8	128.0	39.8	45.9 ± 0.7	4.6 ± 0.3	36.3 ± 0.6
P1000-10		10	-4.6	131.5	33.7	36.8 ± 0.4	3.8 ± 0.2	29.4 ± 0.1
P1000-15		15	-13.4	116.1	30.5	35.4 ± 0.6	3.6 ± 0.4	31.2 ± 0.9
P1000-20		20	-23.3	104.2	34.5	33.2 ± 0.5	3.5 ± 0.2	25.0 ± 1.1
P1000-25		25	-24.0	101.4	35.8	28.4 ± 0.2	3.1 ± 0.3	23.2 ± 1.1
P1000-50		50	-24.2	104.6	29.3	18.4 ± 0.6	2.8 ± 0.4	14.8 ± 0.1
P1000-75	75	-27.5	104.4	44.3	9.9 ± 0.6	2.3 ± 0.2	8.5 ± 0.3	
T1000	PTMG 1000	0	-20.3	116.9	41.9	40.8 ± 0.1	4.9 ± 0.2	0.8 ± 0.3
T1000-5		5	-20.8	119.9	51.9	73.4 ± 0.3	0.3 ± 0.2	83.0 ± 1.2
T1000-10		10	-17.3	125.1	21.8	55.1 ± 0.4	0.3 ± 0.1	55.1 ± 0.4
T1000-15		15	-20.2	109.0	21.8	54.7 ± 0.3	0.1 ± 0.1	54.7 ± 0.3
T1000-20		20	-25.2	102.4	22.3	40.0 ± 0.5	0.3 ± 0.3	40.0 ± 0.4
T1000-25		25	-30.5	104.4	29.1	35.3 ± 0.1	0.3 ± 0.3	48.2 ± 0.7
T1000-50		50	-31.1	105.2	48.8	20.3 ± 0.3	4.0 ± 0.4	21.2 ± 1.0
T1000-75	75	-34.0	103.7	50.3	11.3 ± 0.5	5.3 ± 0.2	16.1 ± 0.2	
C1250	PCL 1250	0	-8.9	135.2	43.4	48.1 ± 0.2	0.3 ± 0.1	53.7 ± 0.6
C1250-5		5	-9.7	111.6	48.4	37.5 ± 0.1	0.2 ± 0.1	41.5 ± 0.9
C1250-10		10	-10.5	106.4	24.0	34.5 ± 0.5	0.4 ± 0.3	38.5 ± 0.3
C1250-15		15	-12.8	105.2	25.3	33.9 ± 0.2	0.2 ± 0.1	36.0 ± 0.8
C1250-20		20	-14.5	103.2	27.5	30.4 ± 0.4	0.1 ± 0.1	31.5 ± 0.6
C1250-25		25	-16.2	101.9	31.8	28.6 ± 0.5	0.1 ± 0.1	33.7 ± 0.5
C1250-50		50	-17.8	102.4	42.9	21.8 ± 0.6	2.0 ± 0.1	23.5 ± 0.7
C1250-75	75	-37.7	100.1	57.7	19.1 ± 0.4	3.9 ± 0.3	15.1 ± 0.5	
S2000	PDMS2000	100	-39.8	101.1	136.4	8.7 ± 0.5	4.3 ± 0.1	4.6 ± 0.5

^a In designation of each WGPU, the letter indicates the type of segment, the four-digit number is the molecular weight of the soft segment, and the two-digit number is the content of PDMS (%).

^b PDMS content of blends was calculated by: moles of PDMS2000 soft segments in PDMS-PU/total (number of moles of soft segments in WGPU) × 100%.

was at maximal crystallization. Generally, the longer soft segment in WGPU increased the phase separation and crystallinity of WGPU.²² Regarding the state of blended WBPUs [Fig. 7(b)], the $T_{m,h}$ of the ether-based WGPU membranes tended to increase with increase concentrations of the PDMS-PU blends, except that C1250, the ester-based PU, was less affected by blending. The blends of ether-based PUs tended to pack because the PDMS, which had lower surface energy, migrated to the surface of the PU membrane. Moreover, the packing of ether-based PUs enhanced the order of hard segments in PUs, so $T_{m,h}$ would increase.¹² However, the hydrogen bonding of ester-based C1250 was stronger, so the $T_{m,h}$ of C1250 remained less affected by the blending of PDMS-PU.

The data on the PU thermal properties shown in Tables II and III were used to draw Figure 8, which shows the effect of various soft-segment types of WGPU and different blending ratios of PDMS-PU on the thermal properties. The $T_{g,s}$ unblended WBPUs showed a trend of C1250 > P1000 > T1000 > E1000, indicating the soft and hard segments of ester-based C1250 had greater hydrogen bonding, which made the ester-based soft segments rigid. However, P1000 had

the largest $T_{g,s}$ because the side-chain structures in the soft segments of P1000 were a barrier to spatial configuration. The order of the $T_{g,s}$ values of WBPUs with soft segments of different molecular weights was E600 > E1000 > E2000. E600 had the largest $T_{g,s}$ because its soft segment was shorter, so the movement of the soft segment declined.

In all the PDMS-PU blends shown in Figure 8, except C1250, the $T_{g,s}$ of PUs was highest when the blending ratio of PDMS-PU was 5%–10%. According to a previous study of our laboratory,¹² which focused on blending PDMS-PU with WGPU of PEG2000 soft segments (E2000), blending a small amount of PDMS with hydrophilic soft segments yielded better better packing, resulting in a maximum $T_{g,s}$. E2000 and E1000 had the highest $T_{g,s}$ values. This was because the unblended E2000 and E1000 had lower $T_{g,s}$ values and higher hydrophilicity of the soft segments. Moreover, the higher hydrophilicity of the soft segments was more susceptible to hydrophobic PDMS, so it brought about a higher range of $T_{g,s}$ values. In addition, as shown in Figure 8, the $T_{g,s}$ of P1000 was greatly reduced as P1000 was blended with PDMS-PU at a concentration above 10%. This is because PDMS and

TABLE III
Physical Properties of WBPU Measured by Blending WBPU of PEG Soft Segments of Different Molecular Weights with PDMS-PU

Symbol	Molecular weight of PEG soft segment	PDMS content (%)	Thermal properties			Strength properties		
			$T_{g,s}$ (°C)	$T_{m,h}$ (°C)	Energy (J/g)	Stress (MPa)	Strain	Young's modulus (MPa)
E600	600	0	-15.6	117.4	165.0	27.4 ± 0.4	3.6 ± 0.3	1.9 ± 0.9
E600-5		5	-12.7	120.2	164.6	30.8 ± 0.6	4.1 ± 0.2	2.2 ± 0.2
E600-10		10	-8.2	146.1	165.0	34.1 ± 0.4	4.5 ± 0.2	3.8 ± 0.7
E600-15		15	-10.6	114.4	110.3	24.6 ± 0.2	4.6 ± 0.3	3.9 ± 0.8
E600-20		20	-12.1	109.9	80.1	24.3 ± 0.2	4.6 ± 0.2	2.9 ± 0.9
E600-25		25	-12.4	108.0	55.4	21.6 ± 0.1	4.7 ± 0.3	2.7 ± 0.2
E600-50		50	-13.4	104.5	75.9	11.8 ± 0.6	4.5 ± 0.1	3.5 ± 0.5
E600-75	75	-15.8	102.2	76.1	6.2 ± 0.6	4.1 ± 0.1	3.8 ± 0.3	
E1000	1000	0	-23.8	118.2	77.2	17.1 ± 0.1	5.6 ± 0.2	25.3 ± 0.9
E1000-5		5	-16.0	153.0	76.7	36.0 ± 0.6	13.3 ± 0.2	25.3 ± 0.3
E1000-10		10	-10.9	160.3	32.6	43.0 ± 0.6	11.0 ± 0.2	28.8 ± 0.5
E1000-15		15	-21.6	134.1	33.1	32.2 ± 0.4	10.9 ± 0.1	22.8 ± 0.4
E1000-20		20	-21.2	124.0	32.4	24.3 ± 0.3	9.1 ± 0.3	18.3 ± 0.6
E1000-25		25	-22	113.2	33.3	23.2 ± 0.4	9.3 ± 0.3	14.9 ± 0.8
E1000-50		50	-22.6	106.6	32.8	16.0 ± 0.6	9.1 ± 0.2	8.0 ± 0.3
E1000-75	75	-24.9	100.7	33.4	11.2 ± 0.6	6.3 ± 0.1	3.6 ± 0.2	
E2000	2000	0	-49.73	111.4	244.1	0.4 ± 0.1	14.0 ± 0.3	—
S2000		100	-39.8	101.1	136.4	8.7 ± 0.3	4.3 ± 0.2	4.6 ± 1.0

PPG both have methyl-based side chains that make it difficult to arrange soft segments in order. On the other hand, there was no maximum $T_{g,s}$ when ester-based C1250 was blended with PDMS-PU because of less phase separation between the ester-based soft and hard segments. In other words, hydrogen bonding between the soft and hard segments of C1250 was greater, so the order of the soft segments was less affected by PDMS. Moreover, the maximum $T_{g,s}$ of E2000 was found with a 5% ratio because the amount and movement of the PEG soft segment in E2000 were higher. The effect on $T_{g,s}$ of the introduction of PDMS was consistent with the results of the infrared analysis.

It was found that the effect on $T_{m,h}$ of the various types of soft segments was greatest in the ether-based soft-segment series, which had the highest values, followed by, in order, E1000 > P1000 > T1000. The $T_{m,h}$ of C1250, the ester-based WBPU, was greatly reduced as C1250 was blended with PDMS-PU because the hydrophobic ester-based soft and hard segments tended to bring about phase mixing. According to the infrared analysis, there was strong hydrogen bonding between the hard and soft segments. C1250 had a compact composition and a higher $T_{m,h}$, so PDMS did not have enough strength to separate its soft and hard segments; thus, $T_{m,h}$ did not increase. Moreover, the effect of the molecular weight of the soft segments was to increase $T_{m,h}$ by blending in a small amount of PDMS-PU. E2000 had a maximum $T_{m,h}$ when it was blended with PDMS-PU in a 5% blending ratio, and E1000 and E600 had maximum values with a blend ratio of 10%. The maximum $T_{m,h}$ values were in the

order E1000 > E600 > E2000, which was consistent with the results of the infrared analysis. Because of blending, the blends of E1000 and PDMS-PU resulted in phase separation, which brought about increased hydrogen bonding.

Among the different compositions of soft segments, E1000 showed the highest entropy; the entropies of T1000, P1000, and C1250 were found to be approximately equal. In addition, among those composed of PEG soft segments of different molecular weights, E2000 had the greatest crystallinity in the hard segments, and the order of entropy was E2000 > E600 > E1000. E2000 had the greatest phase separation, which increased the order of the hard segments; thus, the crystallinity of PU increased. These results were validated by X-ray analysis, which showed that the hard segments of E2000 had the highest crystallization and those of E1000 the least. The influence of the blending of PDMS-PU was clearly found in that, when E2000 was blended with a small amount of PDMS-PU, the thermal energy of E2000 declined. Nevertheless, the thermal energies of E1000 and E600 were not affected by PDMS-PU blending at ratios of 5% and 10%, respectively.

Analysis of mechanical properties of WBPU blended membranes formed

The stress-strain curves of WBPU with various soft-segment types are shown in Figure 9, where WBPU were blended with PDMS-PU. The data in Figure 9 are summarized in Tables II and III. The order of Young's

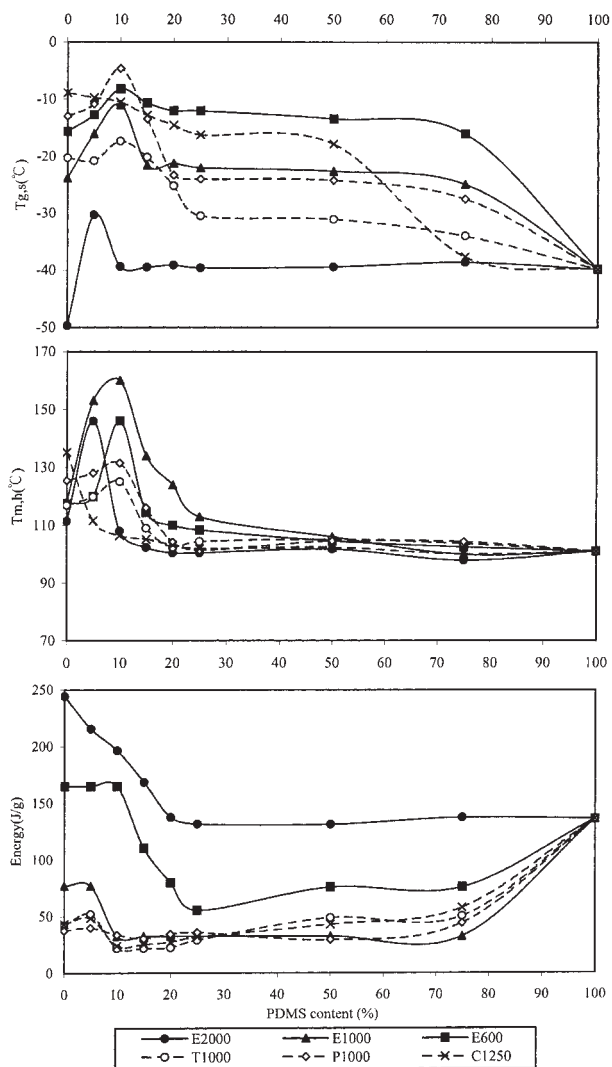


Figure 8 Thermal properties of WBPU membranes measured by blending WBPU of different soft segments with PDMS-PU at various blending ratios.

modulus values was $C1250 > T1000 > P1000$, the order of tensile stress values was $C1250 > P1000 > T1000$, and the order of strain values was $P1000 > T1000 > C1250$. After T1000 and P1000 were blended with PDMS-PU, the tensile stress and Young's modulus of the PUs were enhanced; stress was higher in the blends, which increased at blending ratios of 5%–20% than in those that were unblended, and the T1000 and P1000 blends had the highest stress with a blending ratio of 5%, but strain was reduced with further increases in the blending ratio. When C1250 was blended with PDMS-PU, its strain and Young's modulus indicated a brittle fracture; however, its strain showed no obvious change. The X-ray analysis mentioned above showed larger crystallization of C1250, which resulted in stress concentrations showing characteristics of rigidity and fragility.

Figure 10 illustrates the stress-strain curves of WBPU with PEG soft segments of various molecular

weights, showing a Young's modulus order of $E600 > E1000 > E2000$, a tensile stress order of $E1000 > E600 > E2000$, and a strain order of $E2000 > E1000 > E600$. Upon blending with a small amount of PDMS-PU (5% and 10%), the stress of E600 and E1000 at a 15% ratio first increased but then decreased. E2000 performed poorly under stress, as was evident near the strain axis; however, the strain performed at maximum extensibility. It can be extrapolated from the above that E600 showed rigidity and that there was recrystallization of its molecules during the stretching process, and on reaching the yield point, the tendency decreased and then increased until finally reach break. The tough fracture performance found in E1000 was attributed to the higher hydrophilicity of the PEG series, which tended to absorb moisture at room temperature. Moisture tended to increase its intermolecular distance, which increased the flexibility of its PU. Because the molecular weight of the soft segments of E1000 was between that of E600 and E2000, E1000 had a balanced performance in stress and strain.

Figure 11 shows the effect of varied WBPU soft-segment types and PDMS-PU blending ratios on stress. The order of the stress values in the unblended PUs was $C1250 > T1000 > P1000 > E600 > E1000$. The order of the stress values in the blended PDMS-PU of various soft-segment types was $T1000 > P1000 > C1250 > E1000$. When T1000 and P1000 were blended with PDMS-PU at a blending ratio of 5%, they had maximum stress values. With a PEG soft segment of various molecular weights, E600 and E1000 had maximum stress with a PDMS-PU blending ratio of 10%. At the low blending ratio (5%–15%), the stress of E1000 was higher than that of E600. At the low PDMS-PU blending ratio, the stress of the compounds increased to its greatest value (20–30 MPa). Among them, the rate of stress was most elevated in T1000, followed by E1000. The ester-based PU, C1250, blended with PDMS-PU reduced stress. Through the earlier infrared analysis, it was confirmed that stronger hydrogen bonding in C1250 inhibited movement of PDMS molecules. Moreover, the amount of C1250 decreased relative to an increase in the PDMS-PU blending ratio, thus, reducing stress.

Figure 12 shows the effect of different soft-segment types and PDMS-PU blending ratios on strain, with the order of the unblended PUs $E1000 > P1000 > E600 > T1000$ and $C1250$. Furthermore, the E1000 and P1000 compounds had extensibility and those of T1000 and C1250 were rigid. E1000 with 5% PDMS-PU had the maximum strain value, which gradually decreased to that of the PDMS-PU strain. When E600 was blended with PDMS-PU, the strain in the E600 compound increased to the level of the PDMS-PU strain. The compounds blended by P1000 and PDMS-PU revealed a gradual reduction in strain.

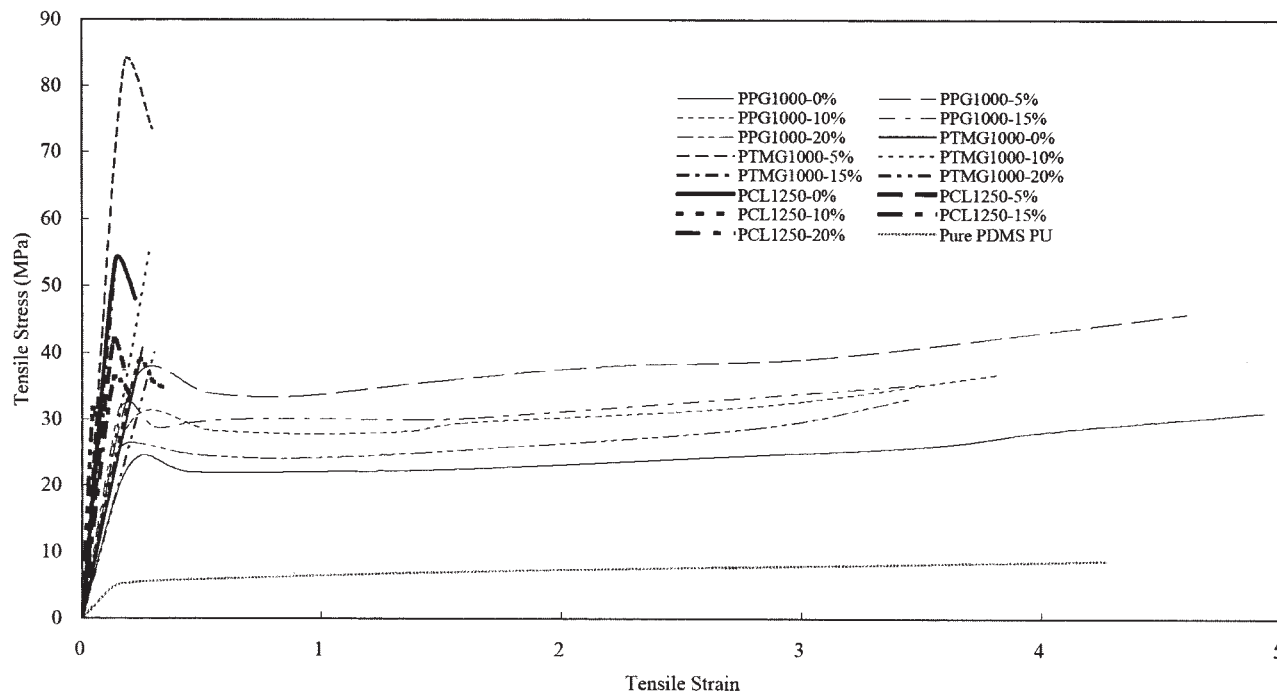


Figure 9 Stress-strain curves of WBPU membranes measured by blending WBPU of different soft-segment types with PDMS-PU.

CONCLUSIONS

PDMS-PU was blended into a variety of ester- or ether-based soft-segment WBPU, and the crystallization, thermal, and physical properties of the WBPU

membranes formed were compared. The major findings were:

1. FTIR analysis showed that when P1000, T1000, E600, and E1000 of ether-based PUs were at a

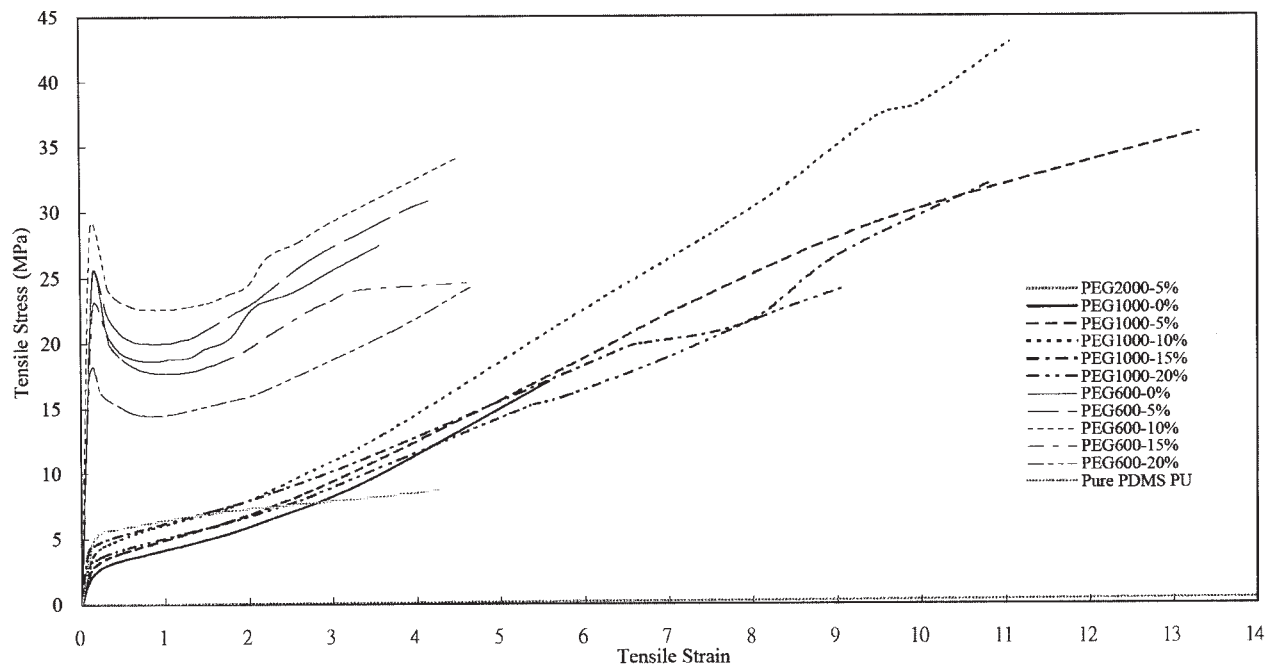


Figure 10 Stress-strain curves of WBPU membranes measured by blending WBPU of PEG soft segments of various molecular weights with PDMS-PU blends.

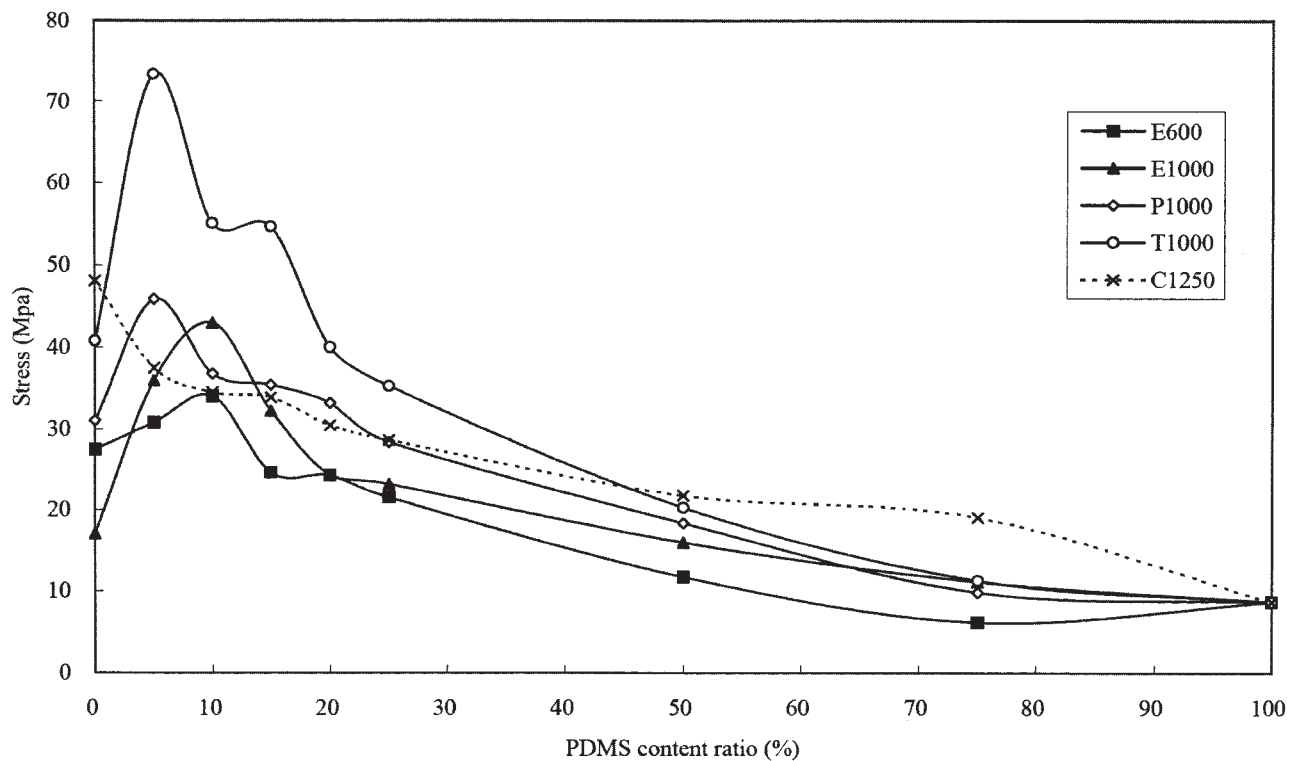


Figure 11 Stress of WBPU membranes measured by blending WBPU of different soft segments with PDMS-PU at various blending ratios.

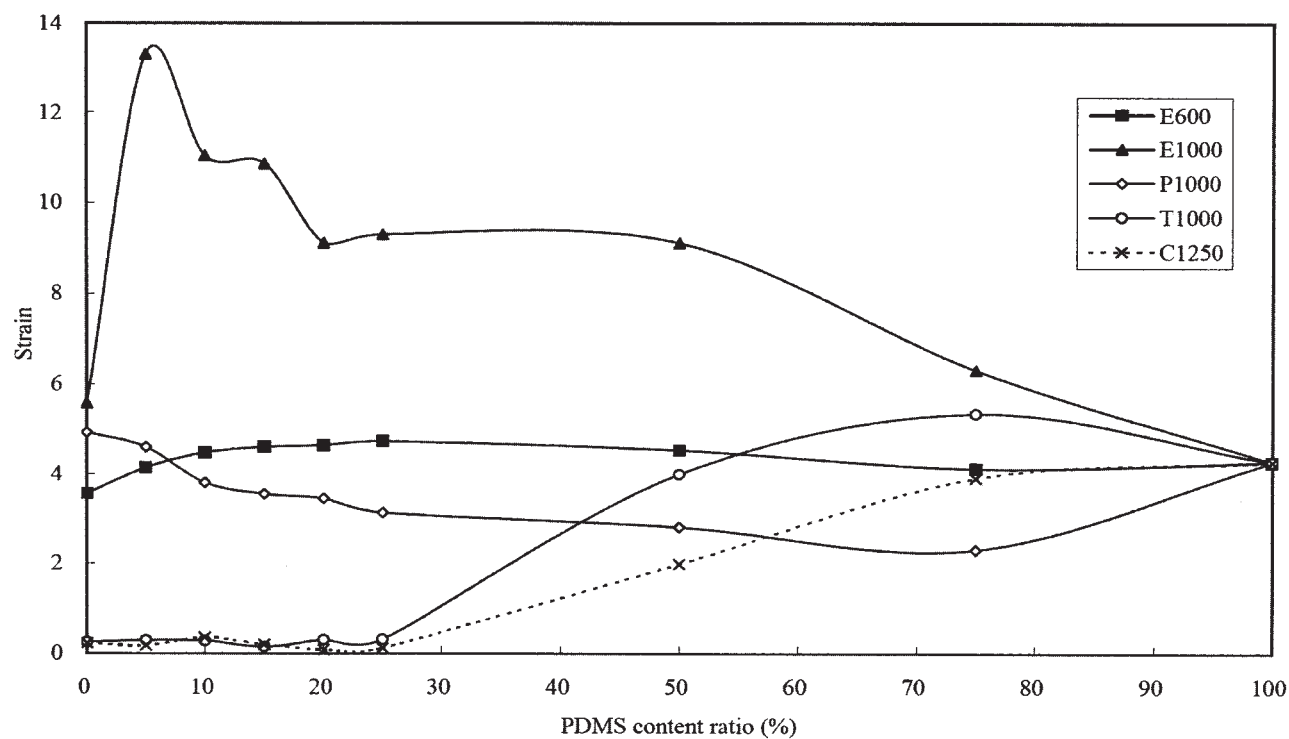


Figure 12 Strain of WBPU membranes measured by blending WBPU of different soft segments with PDMS-PU at various blending ratios.

10% PDMS-PU blending ratio and when E2000 was at a 5% blending ratio, there was stronger hydrogen bonding between the hard segments in the PUs. In addition, C1250, the ester-based PU, showed stronger hydrogen bonding between the soft and hard segments; however, the hydrogen bonding of C1250 was not affected by the blending of PDMS-PU.

2. X-ray analysis showed that P1000 and E2000 of the ether-based PUs had maximum crystallinity at a 5% blending ratio, but C1250, the ester-based PU, had decreased in crystallinity at that blending ratio.
3. Analysis of the DSC revealed that, except for PCL1250, the $T_{g,s}$ values of PUs were the highest when the PDMS-PU blending ratio was 5%–10%. The $T_{m,h}$ values of the ether-based PUs were at maximum, but the $T_{m,h}$ of the ester-based PU was greatly reduced as C1250 was blended with PDMS-PU. In addition, the PEG2000 series showed the highest entropy of PUs.
4. In terms of the mechanical property analysis, the stress of the compounds increased to its greatest value (20–30 Mpa) when T1000 was blended with a small amount of PDMS-PU. On the other hand, an ester-based PU (PCL 1250) blended with PDMS-PU would reduce its stress. On the whole, the stress and strain of E1000 had an excellent balance.

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