Study on Polyethylene Glycol/Polydimethylsiloxane Mixing Soft-Segment Waterborne Polyurethane from Different Mixing Processes

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ABSTRACT: The surface structure and physical properties of polyethylene glycol series polyurethane (PEG-PU) membranes, in which were introduced hydrophobic polydimethylsiloxane (PDMS) component by the procedure of PU blending or of soft-segment copolymerization, were studied in this investigation. In the case of the blending process, the synthesized waterborne polyurethanes (WBPUs) of PEG–PU and of polydimethylsiloxane series polyurethane (PDMS–PU) were combined, whereas in the copolymerization process PEG and PDMS were taken as mixed soft segments to polymerize the WBPU. For the blending method, glass-transition and melting temperatures increased rapidly when a small amount of PDMS–PU was added to PEG–PU and reached a maximum with 5% PDMS–PU mixed in. However, in the case of the copolymer method, thermal properties closely followed predicted values. From dynamic mechanical analysis studies it was found that a low PDMS–PU content ratio could increase the rubbery elasticity of PEG–PU membrane and improve its strength simultaneously in the blending method, and the copolymer method only caused PU to gain some natural complementary strength and elasticity. Electron spectroscopy for chemical analysis studies indicated that PDMS migrated to the surface much more easily in the blending method than in the copolymer method. The SEM studies also found that, in the blending method, the numbers of pores were less than those in the copolymer method. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 233–243, 2003

Key words: waterborne polyurethane; polyethylene glycol; polydimethylslioxane; blending; copolymerization

INTRODUCTION

Polyurethane (PU) elastomers are block copolymers consisting of alternate soft and hard segments. Within the practical temperature range, the soft segment works like those existing in rubber that render the polymer elastic, and the hard segment makes that part of the polymer appear like glass or semicrystalline and possesses a coagulated structure. At the same time, because of the discrepancy between the compatibility of the soft and hard segments, it would form a double-phase separation or mixture. These properties make PU materials possess special features like elasticity, smooth to the touch, microphase separation, and so forth.[1,2] Currently, because waterborne polyurethane (WBPU) has no solvent vapor problems of toxicity and pollution, it has a processing advantage and hence WBPU has drawn much attention. However, WBPU has shortcomings, such as lacking resistance to water, surface hydrophilicity, and low strength. These properties need to be improved by using a different mixing composition of soft segments.

In general, polydimethylsiloxane (PDMS) has the following characteristics: (1) rather low glass-transition temperature (T_g; approximately $-123°C$)[3,4]; (2) excellent heat stability, oxidation resistance, is inert to high or low temperatures, and is weatherproof (this is attributed to its possessing very strong Si—O bonding energy at about 108 kcal/mol)[5]; (3) great molecular flexibility (attributed to its low intermolecular attraction)[4]; (4) high impact resistance[6,7]; (5) excellent resilience[8]; (6) good electric insulation; (7) high oxygen permeability[9]; (8) nontoxicity[10]; and (9) low surface energy (that can easily transfer around on the surface of the polymer and provide good hydrophobicity).[11–14] The introduction of the PDMS component into PU can be expected to improve the PU's integral and surface properties.

In previous studies, to enhance the mechanical properties of PU, PDMS was introduced into PU through both blending[11,12,15,16] and copolymerization[13,14,17–24] methods. For instance, Dwight et al.[12] determined the surface chemical composition of the poly(tetramethylene oxide) series polyurethane (PTMO–PU) membrane, formed by blending with a small amount of PDMS–PU, using electron spectroscopy for chemical analysis (ESCA), and verified that PDMS was spread in the top layer, whereas the hard segment stayed in the lowest layer. Hill et al.[15,16] also blended PTMO–PU and PDMS–PU in their study of surface

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structure and heat properties of membrane formation. Their results showed that the mechanical properties of the blends were more enhanced and the PU membrane was PDMS-rich in the surface structure and the separation extent of the soft and hard phases widened significantly because of the incompatibility between the hard and soft segments and the low surface energies of PDMS.

For the copolymerization study, Sakurai et al.[19] used block segments of PDMS and PTMG as soft segments, and MDI as the hard segment to synthesize the PU copolymer and study the fatigue and crystal properties with DMA, DSC, and small angle X-rays, and pointed out that PTMG crystals would lead the hard segment to microphase separation, and the addition of PDMS can lower the crystallization of PTMG and prevent the microphase separation of the hard segment. Fan et al.[13,14] recently employed a chain extender featuring a PDMS side chain and with PTMO as the soft segment in their synthesis of a WBPU to study the membrane properties. They found that the siloxane side chain would migrate to the surface and thus enhance the water repellency of the PU membrane, and also found that the breaking strength did not decrease as the PDMS content stayed at a low level of 6% (w/w). From the preceding results, it is clear that the introduction of PDMS into PU largely affects the crystalline structure and phase separation of polyurethane.

As mentioned above, the WBPU, especially using the polyethylene glycol (PEG) series, has many shortcomings such as low water resistance. In this study, to improve the properties of the PEG series WBPU, which is usually used in polymer finishing such as textile finishing, the hydrophobic PDMS component was introduced into the PEG series PU either by the procedure of PU blending or by mixed soft-segment copolymerization. The surface structure and thermal properties of the formed membranes for the different PDMS content of WBPU were compared for both blending and copolymerization methods. In the experiment, the anionic WBPU (PEG–PU or PDMS–PU) was synthesized by using dicyclohexylmethane diisocyanate (H_{12}MDI) as the hard segment, 2,2-bis(hydroxymethyl) propionic acid (DMPA) as the ionic center, and polyol (PEG or PDMS) as the soft segment. In the case of the blending process, PEG–PU and PDMS–PU WBPU were combined, whereas in the copolymerization process, PEG and PDMS were taken as mixed soft segments to polymerize the WBPU.

EXPERIMENTAL

Materials

The polyethylene glycol (PEG, $M_n \sim$ 2000; Merck, Darmstadt, Germany) and polydimethylsiloxane
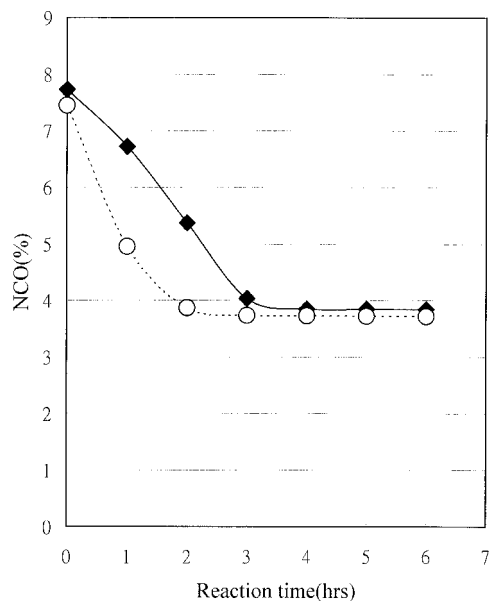

Figure 1 NCO(%) in PU prepolymer for different reaction times in the prepolymerization step (—◆— PDMS–PU and - - ○ - - PEG2000–PU).

(PDMS, $M_n \sim$ 2000; SF-8427, Dow-Corning, Midland, MI) were used as the soft segment, and dicyclohexylmethane diisocyanate (H_{12}MDI; Bayer, Germany) and 2,2-bis(hydroxymethyl) propionic acid (DMPA; reagent grade; Acros, Belgium) were used as the hard segment and potential ionic centers, respectively, for the synthesis of anionic waterborne polyurethane (WBPU). All the materials were vacuum-dried at 80°C for 2 h. Triethylamine (TEA, reagent grade; Acros), ethylene diamine (EDA, reagent grade; Acros) and 1-methyl-2-pyrrolidone (NMP, reagent grade; Acros), which were used as 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 (PEG2000 PU or PDMS 2000 PU) was synthesized by a prepolymer mixing method.[25] For the synthesis of separate PEG 2000 WBPU and PDMS 2000 WBPU, 1 mol PEG ($M_n \sim$ 2000) or PDMS ($M_n \sim$ 2000) and 1 mol DMPA dissolved in NMP were added to the reactor and heated to 80°C; 4 mol H_{12}MDI and then the catalyst (di-n-butyltin dilaurate) were added to the mixture and the prepolymerization proceeded at 90°C for 4 h, reaching the half NCO residue value of H_{12}MDI. The change of the NCO value during the prepolymerization was determined by using the standard dibutylamine back-titration method of David et al.[26] The prepolymer was cooled to 70°C and neutralized with TEA. The prepolymer aqueous dispersion was obtained by adding water, drop by drop, and the chain-extension process with 2
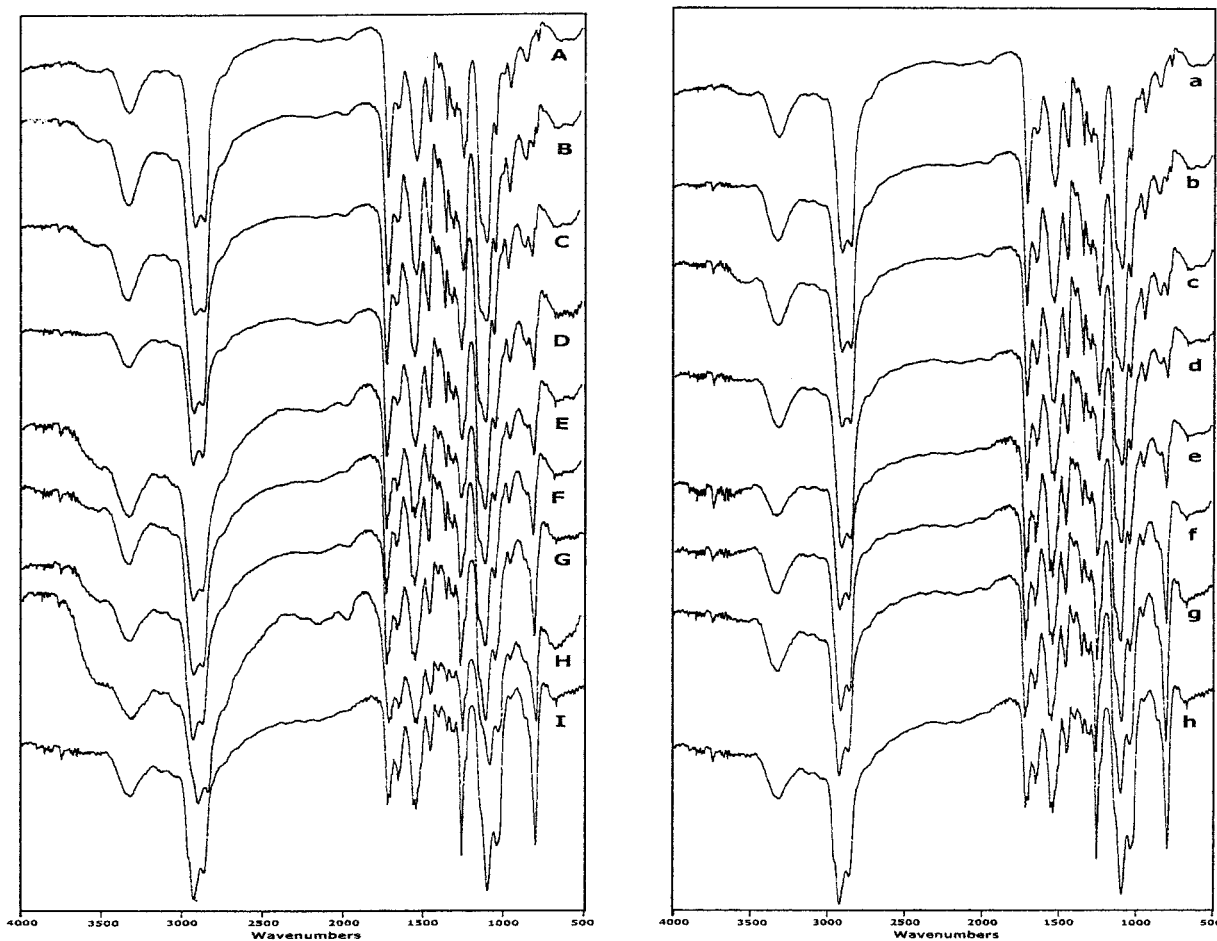
Figure 2 FTIR analyses of WBPU membranes formed by blending different weight ratios of PDMS–PU with PEG–PU (A: PEG2000, B: B2000–5%, C: B2000–10%, D: B2000–15%, E: B2000–20%, F: B2000–25%, G: B2000–50%, H: B2000–75%, I: PDMS2000) or from the mixed PEG and PDMS soft segments copolymerized PU with various PDMS content weight ratios (a: PEG2000, b: C2000–5%, c: C2000–10%, d: C2000–15%, e: C2000–25%, f: C2000–50%, g: C2000–75%, h: PDMS2000).

mol EDA aqueous was continued for 2 h. For the mixed soft-segment copolymerization series WBPU, the procedure was the same as that for the separate soft segment WBPU except that the mixture of PEG and PDMS with different weight ratios was used as the soft segment. The final dispersion solution was diluted to 30% aqueous solution. The infrared spectra of the final samples were analyzed with a Jasco Fourier transform infrared (FTIR) spectrophotometer (Jasco, Tokyo, Japan).

Membrane casting and nylon fabric coating

The blending PU from PEG–WBPU and PDMS–WBPU or the copolymer series PU were used for the membrane casting and nylon fabrics coating. In the blending method, different weight ratios of PDMS–WBPU were blended into PEG–WBPU with stir mixing, and the membranes were prepared by casting WBPU onto a Teflon plate, followed by drying at 50°C for 72 h (PU membranes thickness was about 150 μm). Then the

membranes were removed and placed in a desiccator ready for testing. For the coating of nylon fabrics, the WBPU dispersion added with melamine resin, a thickening agent [NH_4OH (aq)] and a catalyst were coated onto the nylon taffeta fabrics. After coating, the fabrics were predried at 100°C for 3 min and cured at 130°C for 5 min.

Testing

Thermal analysis of the samples used a differential scanning calorimeter analyzer (DSC; DuPont 930 thermal analyzer 2000; DuPont, Boston, MA), at a heating rate of 20°C/min. The dynamic mechanical analysis (DMA) of the samples was obtained with a DuPont 2980 thermal analyzer 2000 with liquid nitrogen for cooling, at a frequency of 1 Hz and the heating rate of 5°C/min. The electron spectroscopy for chemical analysis (ESCA) spectra used a VG. Microtech MT-500 spectrometer equipped with a monochromatic Mg–K_α (1253.6 eV) X-ray source (UK), and samples were fur-
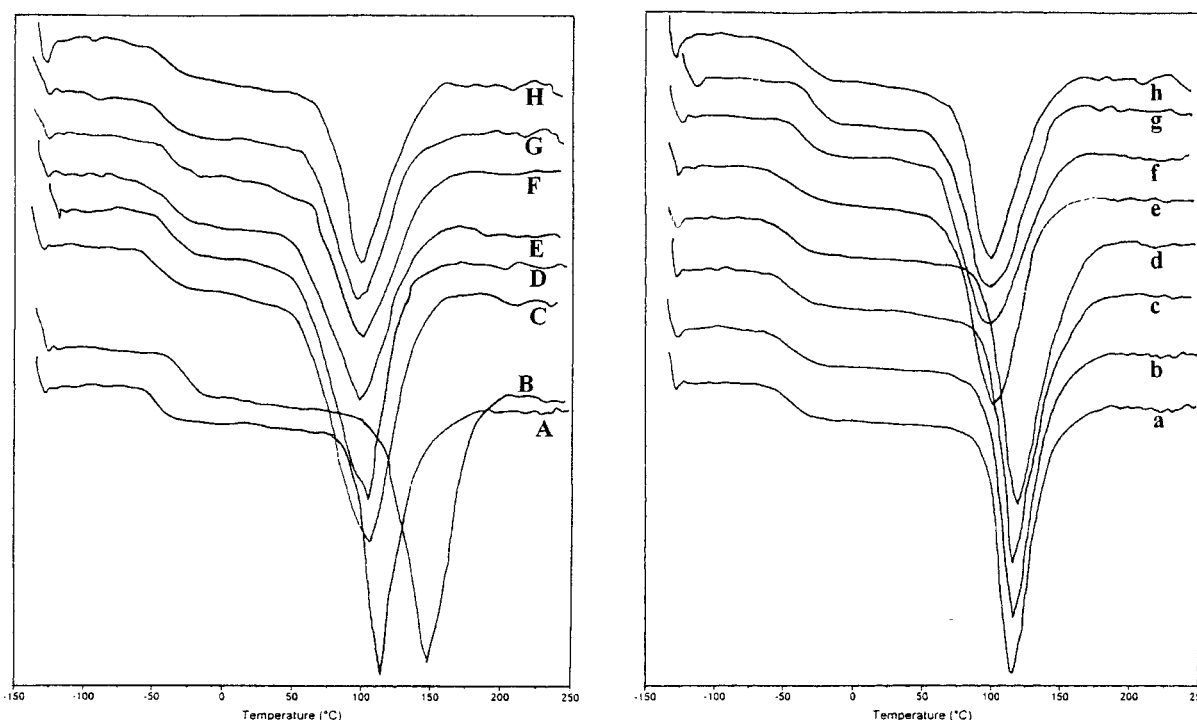
Figure 3 DSC analysis of WBPU of PEG and PDMS mixture soft segment with blending method (A: PEG2000, B: B2000–5%, C: B2000–10%, D: BE2000–15%, E: BE2000–25%, F: BE2000–50%, G: BE2000–75%, H: PDMS2000) and copolymer method (a: PEG2000, b: C2000–5%, c: C2000–10%, d: C2000–15%, e: C2000–25%, f: C2000–50%, g: C2000–75%, h: PDMS2000).

ther vacuum dried at 3 days before being tested. All binding energies (BEs) used for analysis were C1s, 285 eV; Si2p, 103 eV; N1s, 400 eV; O1s, 533 eV. The scanning electron microscope (SEM) surface section pictures of the WBPU-coated nylon fabrics were taken with a Cambridge s360-type scanning electron microscope (UK).

RESULTS AND DISCUSSION

Synthesis and characterization of WBPU

Figure 1 shows the reaction time versus NCO residue value of $H_{12}MDI$ by the standard dibutylamine back-titration method. The figure shows that the prepolymerization reaction times of the PEG2000–WBPU and PDMS–WBPU were 2 and 3.5 h, respectively, to arrive at half of the NCO theoretical residue value. This indicates that –OH groups of soft segments were reacted completely with –NCO groups of hard segments. Therefore, the chain-extending reaction proceeded after prepolymerization at 4 h for the reaction time.

Figure 2 shows the FTIR spectrum analysis diagrams of blended PUs from the separated polyol polymerization and of the copolymer PUs with mixed polyol as soft segment; it was found that absorption bands around 2200 cm^{-1} (NCO groups) for isocyanate and 3300–3500 cm^{-1} (–OH groups, wide) for polyol had disappeared. In addition, the absorption band

around 3300 cm^{-1} (NH groups, narrow) for the PU structure appeared. The peaks at 1730 cm^{-1} (C=O groups of urethane), 1690 cm^{-1} (C=O groups of urea), 1540 cm^{-1} (C—NH groups),[27] 2850 cm^{-1} (–CH$_2$ groups, strong), and 1100–1112 cm^{-1} (ether groups of soft segments, strong)[28] confirmed the formation of the products of PU structure. With the increase of the PDMS content in WBPU, no matter whether the blending PUs or copolymer PUs, the intensity of the peaks of 1080 cm^{-1} (Si—O—Si, stretching), 1260 cm^{-1} (CH$_3$ in Si—CH$_3$ symmetry bending), and 885 cm^{-1} (CH$_3$—Si rocking)[14] increased simultaneously.

Thermal property of the mixed WBPUs from blending and copolymer

Figure 3 shows the DSC thermal analysis diagram of the mixed WBPU membranes formed by blending PEG–PU with PDMS–PU or from the two soft segments copolymerized PU membrane for various PDMS content weight ratios. The figure shows that the case of the blending was obviously different from that in the copolymer at PDMS content 5%. All the thermal property data are listed in Table I.

Figure 4 shows the effect of PDMS content weight ratio on the thermal properties of the formed membranes. First, in the blending method, when a small amount of PDMS–PU was added to PEG–PU, T_g and melting temperature (T_m) values increased rapidly

TABLE I
Thermal Properties of WBPU with PEG and PDMS Mixture Soft Segment by the Procedure of PU Blending and by Soft-Segment Copolymerization

Symbol	Mixing method	PDMS content ratio (%)	T_g (°C)	T_m (°C)	Energy (J/g)
E2000	—	0	−49.7	111.4	244.1
S2000	—	100	−39.8	101.1	136.4
BE2000–1[a]	Blending	1[b]	−44.08	112.6	239.5
BE2000–2		2	−41.8	115.9	229.8
BE2000–3		3	−41.3	121.0	229.8
BE2000–4		4	−40.3	124.6	227.1
BE2000–5		5	−30.3	146.0	215.5
BE2000–10		10	−39.4	108.0	196.6
BE2000–15		15	−39.4	102.4	168.7
BE2000–20		20	−39.1	100.5	137.6
BE2000–25		25	−39.6	100.5	131.7
BE2000–50		50	−39.4	101.8	131.3
BE2000–75		75	−38.6	97.9	137.5
CE2000–5	Copolymerization	5[c]	−49.3	112.6	242.3
CE2000–10		10	−48.6	113.5	240.1
CE2000–15		15	−48.1	113.5	227.8
CE2000–25		25	−47.2	100.3	163.4
CE2000–50		50	−46.6	93.1	127.7
CE2000–75		75	−44.0	95.5	124.5

[a] In symbol XE2000-Y, the component of X represents the mixture method with Blending (B) or Copolymerization (C), Y represents PDMS content ratio in WBPU. E shows the polyol of PEG; 2000 shows the molecular weight.
[b] PDMS content weight ratio in blending is calculated with [PDMS2000 WBPU/(PDMS2000 WBPU + PEG2000 WBPU)] × 100%.
[c] PDMS content weight ratio in copolymerization is calculated with [weight of PDMS2000 soft segment/(weight of PDMS2000 soft segment + weight of PEG2000 soft segment)] × 100%.

and reached a maximum at a PDMS–PU mixed-in amount of 5%. As the blending ratio of PDMS–PU increased and exceeded 10%, T_g and T_m changed and decreased to the level of the pure PDMS–PU. The thermal energy decreased as the mixed-in amount increased, and fell to the level of pure PDMS–PU as the mixed-in amount reached 20%. The reason for the phenomenon of sharp increases of T_g and T_m, caused by the addition of a tiny amount of PDMS–PU, is the fact that the surface energy of PDMS is relatively low and PDMS migrates to the surface of the membrane while the membrane is formed. The result could be attributed to better packing of hydrophilic PEG–PU,[16] which leads to an increase in the order of the PEG soft segment in the PEG–PU and greater T_g and T_m.

As the PDMS–PU mixed-in amount increased and reached 5%, the surface silicon content approached its saturation amount as well, so T_g and T_m reached the maximum value. However, when the PDMS–PU mixed-in amount exceeded 10%, PDMS–PU deposited accumulatively on top of PEG–PU, and part of the hydrophobic PDMS–PU mixed into the hydrophilic PEG–PU region to effect the amorphous arrangement of the PEG soft segment. That is why the T_g of the PEG soft segment decreased immediately. For the same reason, crystallinity was also affected by gradually increasing the mixed-in amount, and lowered the orig-

inal T_m level of PDMS–PU as that amount exceeded 20%. As for the thermal energy of the crystalline content, a clear maximum value does not appear because the content of PEG–PU in the membrane decreases relatively as the PDMS–PU mixed-in amount increases. The thermal energy decreased to the PDMS–PU level when the mixed-in amount reached 20%, although the decrease in energy was limited at the mixed-in amount of 5%.

In Figure 4, the dotted line represents the thermal properties of the mixed soft-segment copolymer series WBPU with mixtures of PEG and PDMS at different weight ratios used as the soft segment. The effect of PDMS content on T_g and T_m of the copolymer membrane was largely different from that of the blend membrane. With the increase of PDMS content in the soft segment, the T_g rose gradually toward that of pure PDMS–PU and no maximum value appeared. On the other hand, T_m increased slightly when there was a small amount of PDMS soft segment present, but after that it changed and decreased to even out. The effect on thermal energy was not quite as evident with small amounts of PDMS soft segment content as it was for the blend, but as the copolymer content reached 15% it started to decrease and at 50% reached a plateau. In the case of the copolymerization approach, the PDMS soft segment and the PEG soft segment coexist
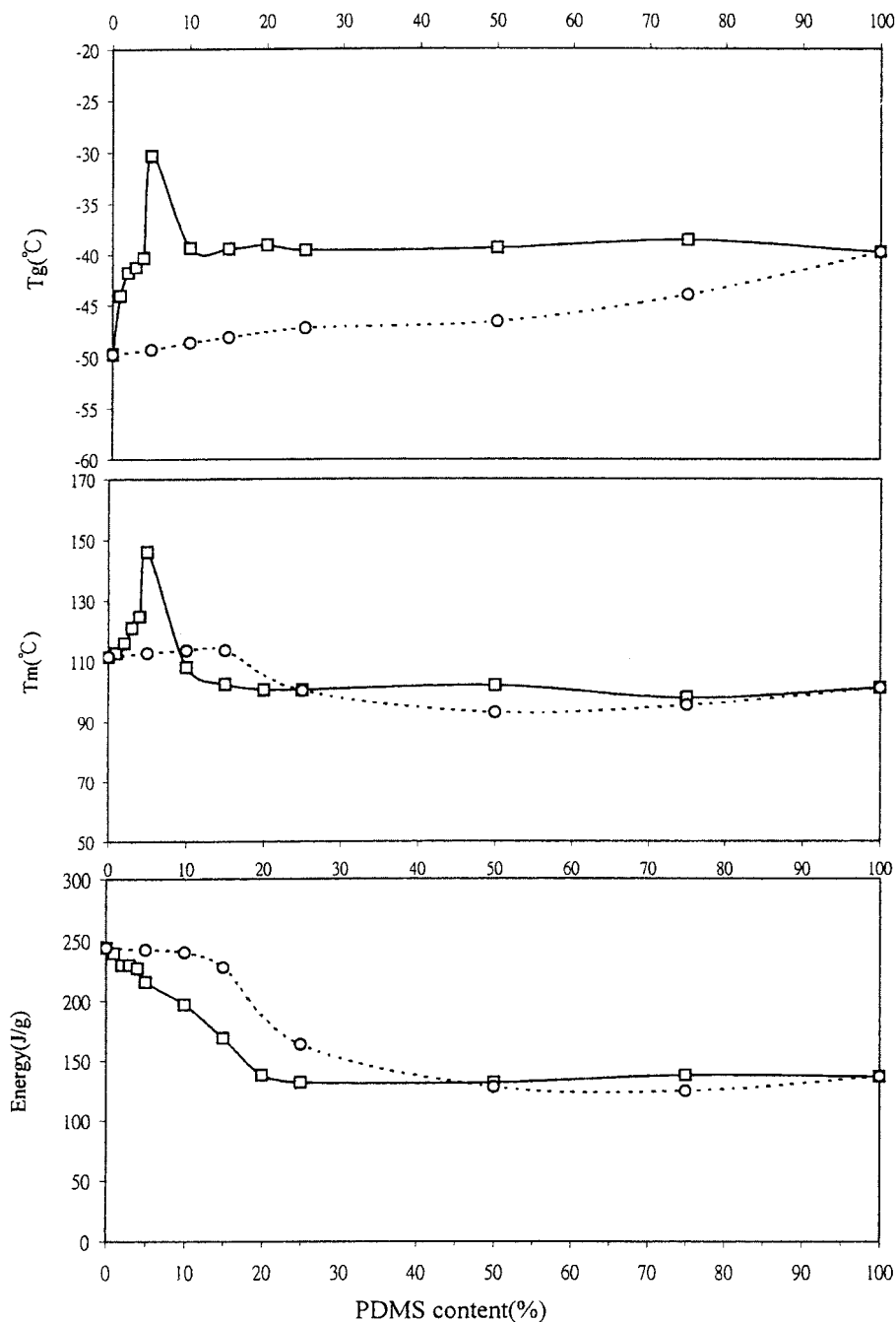
Figure 4   Thermal property of WBPU with PEG and PDMS mixture soft segment by the procedure of PU blending and by soft-segment copolymerization: (—□—) blending (- - ○ - -) copolymerization.

in the main chain of the polymer and influence the movement of the main chain. Because the PDMS segment was less likely to migrate to the surface, the introduction of PDMS on T_g, T_m, and thermal energy tended to follow the predicted values closely.

Figure 5 shows the dynamic mechanical thermal analysis of the membrane of the WBPU formed from both methods as related to the PDMS soft-segment content ratio. All the experimental data are listed in Table II. First, regarding the blending method by mixing in PU, it is shown in Figure 5 that tan δ of pure

PEG–PU was higher than that of pure PDMS–PU, but the storage modulus (E') is the opposite above the glass-transition point temperature of the soft segment (T_{gs} −30°C). This is because PDMS has excellent heat stability and high molecular flexibility.[5] In the case of blending PDMS–PU and PEG–PU (Fig. 5, upper panel), as the mixed-in amount of PDMS–PU was in the range of 5–10% and at a temperature below T_{gs} (−50 to −30°C), tan δ values of the blends would not change much from that of pure PEG–PU and E' was higher than that of both pure PEG–PU and PDMS–PU. At
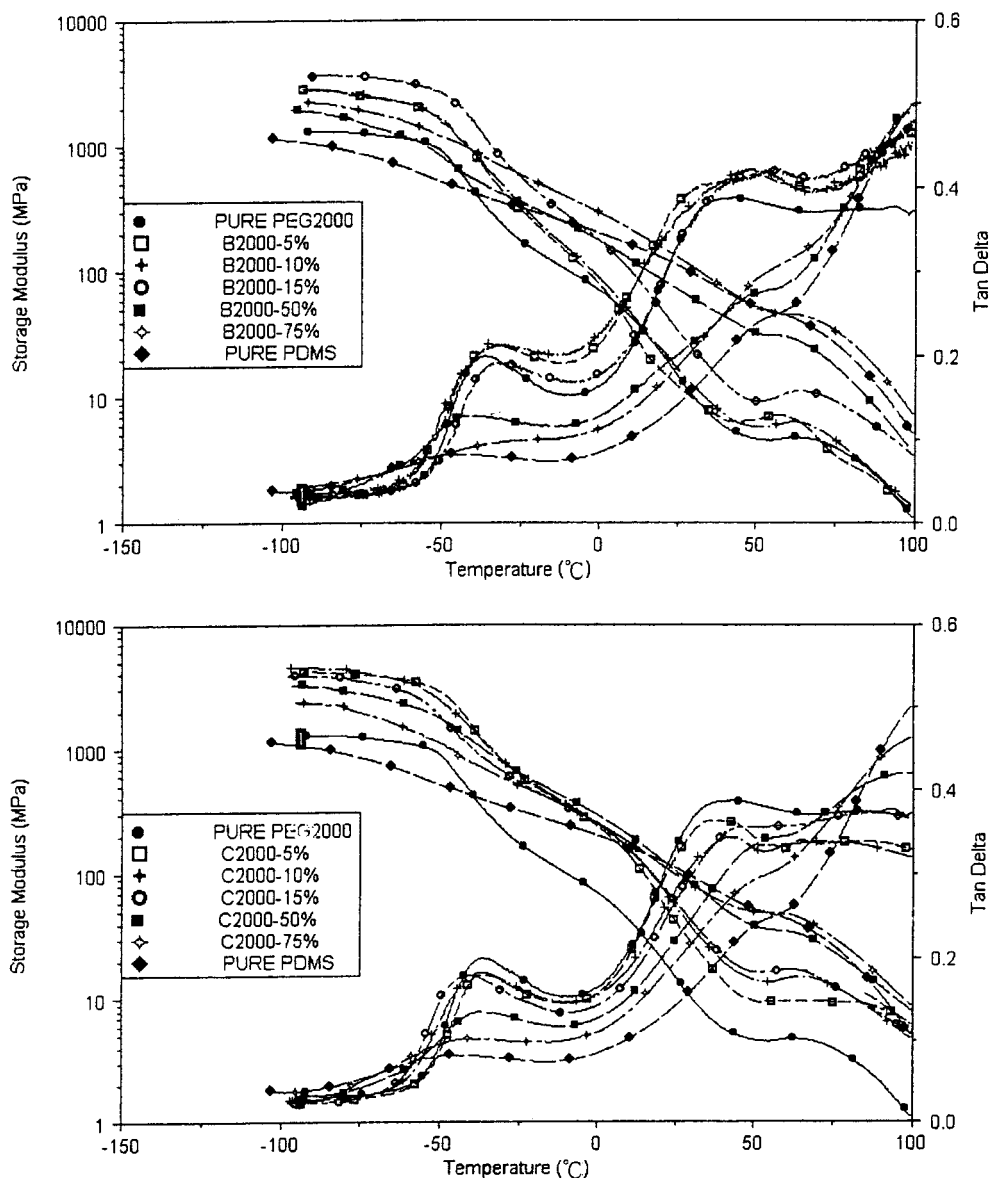
Figure 5 DMA analysis of WBPU with PEG and PDMS mixture soft segment by the procedure of PU blending (upper) and by soft-segment copolymerization (lower).

temperatures higher than T_{gs} (-30 to $100°C$), however, tan δ of the blends was greater than that of both the pure PEG–PU and pure PDMS–PU, which showed better rubbery elasticity. Furthermore, E' is almost larger than that of the pure PEG–PU and is located between that of the pure PEG–PU and pure PDMS–PU. Usually the higher the E', the stronger is the membrane's strength. In a previous report, Fan et al.[14] also came up with the same result of an increase in E' as they used a PDMS-containing chain extender to effectively improve the strength of PTMG–PU. From the above it is clear that, in the blending method, low PDMS–PU content ratio could increase the rubbery elasticity of PEG–PU membrane and improve its strength at the same time.

We also found, as shown in Figure 5, that at higher PDMS–PU mixed-in ratios (50–75%), independent of temperature, the tan δ and E' values were always located between those of pure PEG–PU and pure PDMS–PU, and came closer to the position of pure PDMS–PU with the increase in PDMS–PU mixed-in ratio. Above that, we also found, as shown in Table II, that when a small amount of PDMS–PU was added to the PEG–PU, the discrepancy between the T_{gs} of the soft segment and T_{gh} of the hard segment would increase and become larger when the PDMS–PU content increased. This showed that blending PDMS–PU in PEG–PU would aid the phase separation of the soft segment and the hard segment in PEG–PU, especially with a small amount of the soft segment of PDMS

TABLE II
Dynamic Mechanical Thermal Analysis of WBPU with PEG and PDMS Mixture Soft Segment by the Procedure of PU Blending and by Soft-Segment Copolymerization

Symbol	Mixing method	PDMS content ratio (%)	T_{gs} (°C)	T_{gh} (°C)	ΔT_g (°C)
E2000	—	0	−36.38	40.26	76.64
S2000	—	100	−44.60	53.20	97.80
BE2000–5	Blending	5	−31.61	49.08	80.69
BE2000–10		10	−34.91	50.14	85.05
BE2000–15		15	−31.55	55.71	87.26
BE2000–50		50	−43.23	48.15	91.38
BE2000–75		75	−41.53	51.47	93.00
CE2000–5	Copolymer	5	−33.93	43.98	77.91
CE2000–10		10	−37.12	43.72	80.84
CE2000–15		15	−40.03	44.35	84.38
CE2000–50		50	−37.53	46.87	84.40
CE2000–75		75	−45.62	47.93	93.55

having a larger surface energy. The reason that tan δ and E' varied so much above T_g at low PDMS mixed-in ratios is the fact that the hydrophobic groups of PDMS migrate to the surface, simultaneously causing better packing of PEG in PEG–PU, and the noncrystalline PEG soft segment starts dissociating and moving as the temperature becomes higher than T_g.

Next, regarding the soft-segment copolymerization mixing (Fig. 5, lower panel), whenever the temperature was below T_g, there was not much difference between the two methods. However, once the temperature became higher than T_g, tan δ was quite different in the copolymerization mixing method from that in the blending method. Both tan δ and E' of copolymer PU just stayed between that of the pure PDMS–PU and pure PEG–PU. Although the discrepancy between the soft- and hard-segment T_g increased along with the increase in PDMS content, the copolymerization phase separation was comparatively smaller (see Table II). Because the PDMS soft segment was introduced into the PEG–PU main chain in the case of the copolymerization method, the molecular chain restricted the PDMS segment from migrating toward the surface. Therefore the addition of PDMS into PEG–PU could only cause PU to gain some natural complementary strength and elasticity, and not provide outstanding specific tan δ elasticity as that in the case of the blending method with a small PDMS mixed-in amount.

Surface elemental analysis

To confirm that the siloxane chain was separated with the urethane group and migrated to the surface of the WBPU membrane, the surface elemental composition of the WBPU membrane was measured with ESCA. Table III shows the surface elemental analysis of the

WBPU membrane that contains various amount of PDMS. We took parameters in the table and made them into a diagram, as shown in Figure 6. In the blending method, when the PDMS–PU content was low, the silicon content increased quickly and the increasing magnitude was far beyond the theoretical value and approaching the saturated silicon content of pure PDMS–PU. Nitrogen content, by contrast, decreased to the saturated value along with the increase in PDMS–PU amount. Because the siloxane chain contains silicon and the urethane chain contains nitrogen, decreasing the content ratio of silicon to nitrogen indicates that the siloxane chain has migrated to the surface of the WBPU membrane as the membrane was formed. On the copolymerization side, the silicon content also increased with the introduction of PDMS soft segment, but the increasing magnitude was more reasonable according to the theoretical trend. This demonstrates that in the PU blending method, PDMS moved to the surface much more easily than in the case of copolymer method. All of these stemmed from the low surface energy of PDMS and the incompatibility of the soft and hard segments, which allowed PDMS to migrate to the surface in the formation of membrane, and the soft- and hard-segment phase separation to become broader under the blending PU

TABLE III
Element Composition Data Measured from the Surface of WBPU with PEG and PDMS Mixture Soft Segment by the Procedure of PU Blending and by Soft-Segment Copolymerization

| PDMS (%)	Type	Atomic percentage (%)			
		Carbon	Oxygen	Nitrogen	Silicon
0	Theoretical	63.80	30.65	5.55	0.00
	Real				
	Pure PEG–PU	63.76	30.43	5.51	0.30
5	Theoretical	63.54	29.99	5.55	0.92
	Real				
	Blending	71.46	17.40	2.12	9.01
	Copolymer	68.01	24.67	4.19	4.32
10	Theoretical	63.27	29.33	5.55	1.85
	Real				
	Blending	66.11	22.20	1.88	9.81
	Copolymer	68.24	25.02	2.37	5.17
25	Theoretical	62.46	27.36	5.55	4.63
	Real				
	Blending	61.19	25.79	0.22	10.95
	Copolymer	—	—	—	—
50	Theoretical	61.11	24.07	5.56	9.26
	Real				
	Blending	64.68	24.01	0.37	9.49
	Copolymer	74.76	15.49	2.69	7.06
75	Theoretical	59.76	20.78	5.56	13.90
	Real				
	Blending	59.56	26.15	0.31	13.97
	Copolymer	65.31	21.55	2.41	10.74
100	Theoretical	58.41	17.48	5.56	18.54
	Real				
	Pure PDMS–PU	62.38	23.59	2.07	11.97
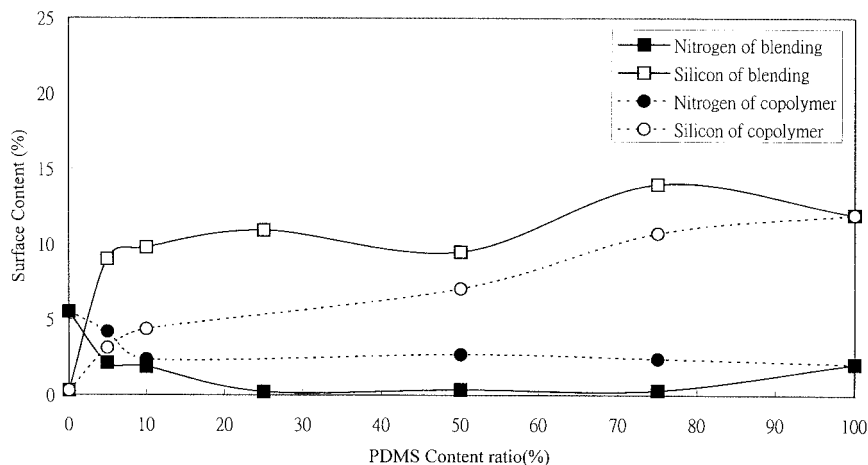
Figure 6 Surface element analysis of WBPU with PEG and PDMS mixture soft segment by the procedure of PU blending and by soft-segment copolymerization.

method.[11,12] In the copolymer method, on the other hand, because of the coexistence of PDMS soft segment and PEG soft segment in the polymer main chain, which interfered with main chain movement, the PDMS segment was less apt to migrate to the surface, and thus the effects of introducing PDMS on T_g, T_m, and energy appeared more natural. In short, PDMS migrated to the surface much more easily in the blend than in the copolymer, as was demonstrated by the silicon contents in the surface of the formed membranes.

Macrostructure of the blending and copolymer of WBPU

Figure 7 is a SEM diagram of nylon fabrics coated with WBPU containing various PDMS content ratios. It is evident from the figure that surface pores of pure PEG–PU coated were both few and small, and pure PDMS–PU could not form a continuous membrane on the fabric. However, when PDMS was added to the PEG–PU, the number of pores in the PEG–PU increased, along with the PDMS content ratio. In the blending method, when the PDMS content ratio was 5%, the numbers of pores were fewer and small, whereas the numbers of pores in the PEG–PU were greater and larger; with PDMS content > 25% the membrane started to crack and one could not form a continuous membrane. Compared to the blending method, in the copolymerization method at 5–10% PDMS soft-segment content ratio, the pores formed were smaller than those in the blending method. When the PDMS soft-segment quantity reached 25%, although pores of the membrane were larger, it was still able to form a continuous membrane.

The phase separation of soft and hard segments for pure PEG–PU was very small, and thus the pores in the membrane formed were smaller. From DMA it

was proved that phase separation increased with PDMS content and the degree of phase separation for the blending method was greater than that for the copolymer method. In the blending method, however, when the PDMS–PU content ratio reached 5%, the silicon content in its surface rose unexpectedly against the calculated theoretical figure, approaching the saturated silicon content of the pure PDMS–PU. The degree of phase separation increased so that PDMS migrated to the surface, and the membrane surface displayed the property of PDMS–PU phase separation, resulting in pores of bigger size. Macroscopically, in the blending method, when the PDMS–PU content ratio was 5%, the numbers of pores were greater than those in the copolymer method, attributed to the greater degree of phase separation in the blending method than that in the copolymer method. In addition, in the blending method, when the content ratio was above 25%, because of phase separation, the membrane formed started to crack and, above 50% phase separation, became too large to form a continuous membrane. In the copolymer method, when the PDMS soft segment quantity reached 25%, its degree of phase separation was still small enough for PU to form a continuous membrane. It was not until it reached 50% that macroseparation resulted in a drop in PU membrane continuity.

CONCLUSIONS

Hydrophobic PDMS was introduced into PEG–PU either based on the procedure of PU blending or through mixed soft-segment copolymerization. The surface structures and thermal properties of the formed membranes were compared. The results produced the following observations:

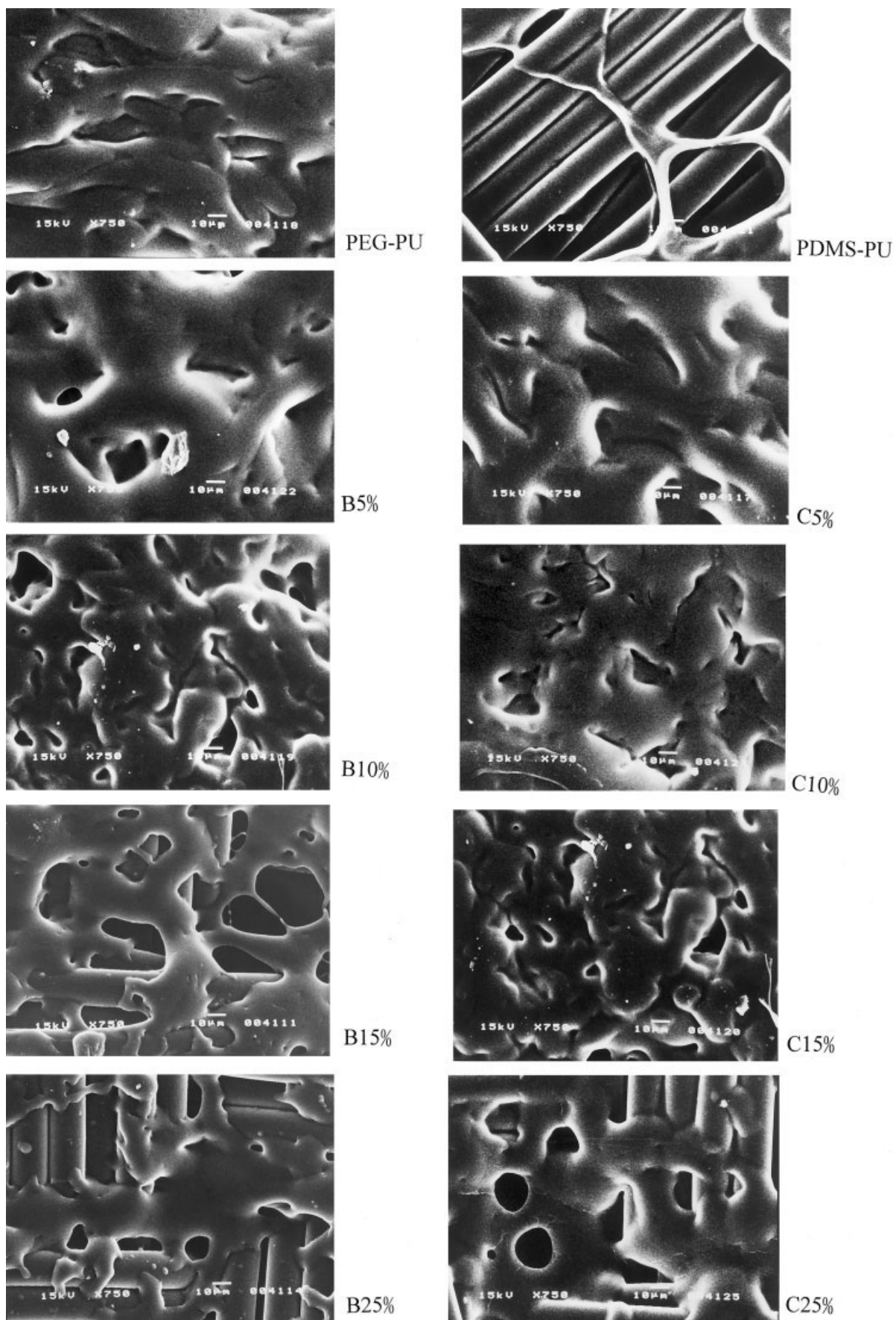1. From DSC, in the blending method, when a small amount of PDMS–PU was added to PEG–PU, T_g

Figure 7 SEM diagrams of nylon fabrics coated with PEG and PDMS mixture soft segment by the procedure of WBPU blending and by soft-segment copolymerization. The B% and C% show the PDMS content ratio in WBPU from mixture method (B: blending; C: copolymerization).

and T_m increased rapidly and reached a maximum at a PDMS–PU mixed-in amount of 5%. In the copolymer method, thermal properties tended to follow the predicted values closely.

2. From DMA studies it was found that, in the blending method, a low PDMS–PU content ratio could increase the rubbery elasticity of the PEG–PU membrane and improve its strength at the same time. In the copolymer method the addition of PDMS into PEG–PU only caused PU to gain some natural complementary strength and elasticity.

3. ESCA found that in the PU blending method, PDMS moved to the surface much more easily than in the case of the copolymer method.

4. From SEM studies it was also found that, in the blending method, the numbers of pores were less than those in the copolymer method.

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