

# Preparation and Physical Properties of Polyurethane Modified with Poly(4,4'-diphenylsulfone Terephthalamide)

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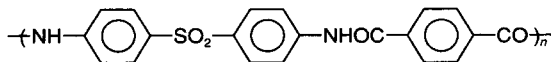
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## SYNOPSIS

Three conventional polyurethane (PU) elastomers were blended physically with various ratios of high molecular weight of poly(4,4'-diphenylsulfone terephthalamide) (PSA) to form 12 PU/PSA polyblends in order to modify their physical properties. Also three new polyurethanes were synthesized with a low-molecular-weight PSA prepolymer as a hydrogen donor for chain extending. From dynamic properties, it showed that both the blends and the new polyurethanes (or polyurethane-ureas) exhibited a glass transition temperature ( $T_g$ ) below 0°C and had a higher modulus  $E'$  than those of the conventional PU. Based on the analysis of X-ray diffraction of the conventional and the new PU, it was shown that the degree of stress-induced crystallization was dependent on the segmental composition of the soft and hard segments and also the degree of its stretching. On the morphological observation, it was revealed that both the blends and the new polyurethanes were in a dispersed phase structure, although new PU exhibited a better compatible state. For tensile properties, it was found that both tensile strength and elongation of the new polyurethanes were better than those of the blends and conventional PU. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

In polyurethane- (PU) based polyblends, a thermoplastic hard component such as ABS, SAN, or poly(vinyl chloride) PVC is generally added for the purpose of increasing their tensile strength, initial modulus, impact strength, and dimensional stability. According to Howe,<sup>1</sup> ABS resin may be used as a second component to reduce the costs of PU without deteriorating their original properties. Thermofil Inc. manufactured a PU/ABS polyblend, which could be used for making goods such as take-ups for cinematographic projectors. In this work, the wholly aromatic poly(4,4'-diphenylsulfone terephthalamide) (PSA) was selected as a reinforcement agent for conventional PU for strengthening the mechanical and thermal properties of PU, owing to its excellent solubility<sup>2,3</sup> and thermal stability.<sup>4</sup> The chemical structure of PSA is:



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Another reason for selecting PSA as the reinforcing agent was that the PSA could easily form a strong intermolecular hydrogen bonding with PU, and therefore a good molecular compatibility would be expected.

## EXPERIMENTAL

### Materials

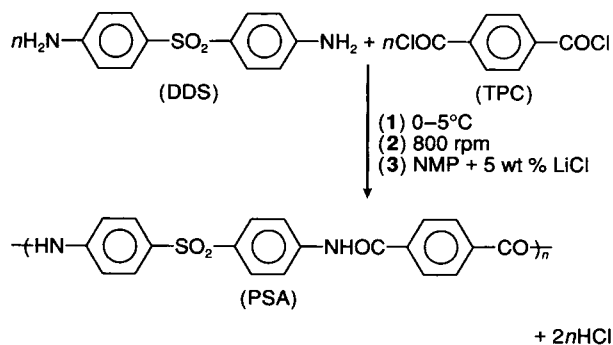
4,4'-Diphenylmethane diisocyanate (MDI) was kindly supplied by the Dynasty Chemical Co. Polytetramethylene glycols (PTMG 650, 1000, 2000) were provided by Evermore Chemical Co. 1,4-Butanediol (BD) was obtained by Ferak Berlin Chemical Co. Both analyzed reagent-grade 4,4'-diaminodiphenyl sulfone (DDS), terephthaloyl chloride (TPC), and spectrophotometric grade *N*-methyl-2-pyrrolidone (NMP), dimethyl acetamide (DMAc) were purchased from Merck Co. Lithium chloride (LiCl) was obtained by Hayashi Pure Chemical Co. All materials were used as received.

### Preparation of Conventional Thermoplastic Polyurethanes

The conventional polyurethanes were prepared by the following procedures. In a 250-mL five-necked flash equipped with a dropping funnel, a nitrogen gas inlet, a mechanical stirrer, and a thermometer, 12.5 g (50 mmol) of MDI was dissolved in 30 mL DMAc and heated to 65°C. Then 25 mmol of PTMG in 15 mL of DMAc was slowly added to the solution with vigorous stirring over a period of 0.5 h. The temperature was further raised to 70°C. The reaction time was varied depending on the molecular weight of PTMG. For molecular weight of 650, 1000, or 2000, the reaction time of 30, 50, or 80 min was adopted, respectively. Finally 2.25 g (25 mmol) of BD in 5 mL of DMAc was added slowly and allowed to react at 80°C for 45 min. The solution was slightly cooled and stirred for 90 min. The polyurethanes were obtained.<sup>5</sup>

### Blends of Conventional Polyurethanes and PSA

High-molecular-weight PSA was prepared by low-temperature polymerization of 24.8 g (100 mmol) of DDS with 20.3 g (100 mmol) of TPC in 200 mL of NMP containing 5 wt % LiCl under the stirring rate of 800 rpm. The scheme is<sup>3</sup>:



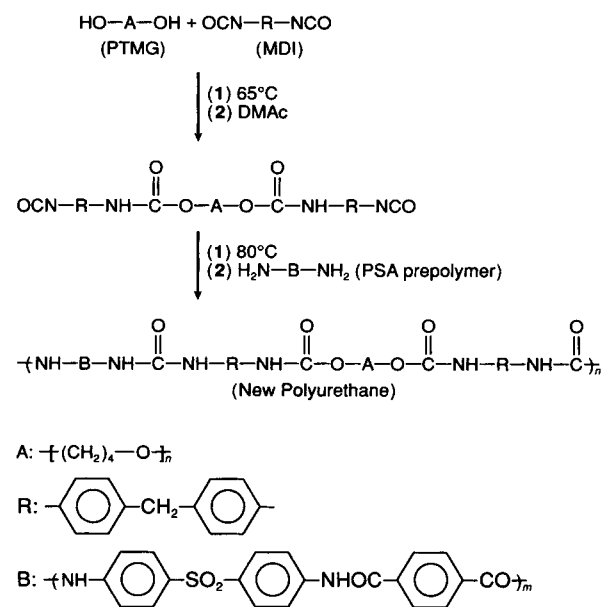
Three conventional polyurethanes (PU-650-BD, PU-1000-BD, and PU-2000-BD) were blended physically with high-molecular-weight PSA in different ratios (5, 10, 15, and 20 wt %) to form 12 PU/PSA polyblends. The mixture was dissolved in DMAc and stirred vigorously. Then the solutions were cast on a glass plate and dried under vacuum at 80°C for 16 h to prepare the films.

### Synthesis of New Polyurethanes

Low-molecular-weight amine-terminated PSA was prepared also by low-temperature polymerization, 24.8 g (100 mmol) of DDS with 10.2 g (50 mmol) of TPC in 180 mL of NMP containing 5 wt % LiCl. The inherent viscosity of PSA prepolymer in 98%

concentrated sulfuric acid was 0.04 dL/g at 30°C. The number-average molecular weight ( $\bar{M}_n$ ) of PSA prepolymer (DDS-TPC-DDS) was 600, which was measured from gel permeation chromatography (GPC).

The new polyurethanes were synthesized by following reaction scheme<sup>6</sup> by using PSA prepolymer as a hydrogen donor for chain extending. Five grams (20 mmol) of MDI was dissolved in 30 mL DMAc and then heated to 65°C. Then 10 mmol of PTMG in 15 mL of DMAc was slowly added to the solution with vigorous stirring over a period of 0.5 h. The temperature was further raised to 70°C. The reaction time was varied according to the molecular weight of PTMG. For molecular weights of 650, 1000, or 2000, the reaction time of 20, 40, or 60 min was used, respectively. Finally, 6 g (10 mmol) of PSA prepolymer in 30 mL of DMAc was added slowly and allowed to react at 80°C. After the reaction for 2 h, the solution was slightly cooled and stirred for 90 min. A viscous solution was finally obtained. The new polyurethanes were cast into films.<sup>5</sup>



Scheme 1

The molecular weight and the inherent viscosity of these polyurethanes are given in Table I. The  $\bar{M}_n$  and  $\bar{M}_w/\bar{M}_n$  were determined by Waters gel permeation chromatography (GPC). The polymer solution was first quenched in distilled water and dried in a vacuum oven over 2 days at 50–60°C. The solid polymer was then dissolved in dimethylformamide (DMF) containing 0.05 mol LiBr to make a 0.54% solution. The column ( $\mu$ . BONDAGEL E-Linear) was calibrated with monodisperse polystyrene standardized at a flow rate of 1 cm<sup>3</sup> min<sup>-1</sup>.

**Table I** Molecular Weight and Inherent Viscosity of New Polyurethanes

Polymer	$\bar{M}_n$ $\times 10^{-4}$	$\bar{M}_w$ $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$\eta$ inh
PU-650-BD <sup>a</sup>	3.60	5.14	1.43	0.41
PU-1000-BD	3.48	5.33	1.53	0.40
PU-2000-BD	3.08	5.13	1.67	0.38
PU-650-PSA <sup>b</sup>	3.69	5.26	1.43	0.42
PU-1000-PSA	3.67	5.77	1.57	0.42
PU-2000-PSA	4.13	6.24	1.51	0.47
PSA	7.31	14.41	1.97	0.60

<sup>a</sup> PTMG (650): MDI : 1, 4-BD = 1 : 2 : 1.<sup>b</sup> PTMG (650): MDI : PSA prepolymer = 1 : 2 : 1.

### Measurements

Infrared spectra of conventional and new polyurethanes were obtained by Hitachi Model 260-50 type, over a range of 250–4000  $\text{cm}^{-1}$ . The samples were films about 10  $\mu\text{m}$  thick.

Dynamic mechanical measurements were performed over the temperature range of  $-100^\circ\text{C}$  to room temperature and also from room temperature to  $200^\circ\text{C}$  in a Rheovibron DDV-II-C type. The samples were purged with a dry air cooled by liquid nitrogen in the former range, and a dry nitrogen gas in the latter range. Measurements were made at a heating rate of  $2^\circ\text{C}/\text{min}$  with the specimen of 20 mm length, 4 mm width, and 1 mm thickness.

Differential scanning calorimetry (DSC) was performed by Seiko SSC 5000 type at a heating rate of  $20^\circ\text{C}/\text{min}$  under nitrogen atmosphere to obtain the glass transition. The calibration standard was In in the measurement.

Wide-angle X-ray photographs were taken with Ni-filtered  $\text{CuK}\alpha$  radiation using Rigaku D/max-II type X-ray diffractometer.

A scanning electron microscope, Cambridge Steroscan-600, was also used to examine the morphological structure of samples, which were sputter-coated with Au to prevent their oxidation.

All stress-strain data were obtained on a Instron 1122 type testing instrument at an extension rate of  $10 \text{ mm min}^{-1}$  with the specimen of 50 mm length, 10 mm width, and 0.5 mm thickness.

## RESULTS AND DISCUSSION

### Analysis of Infrared Spectra

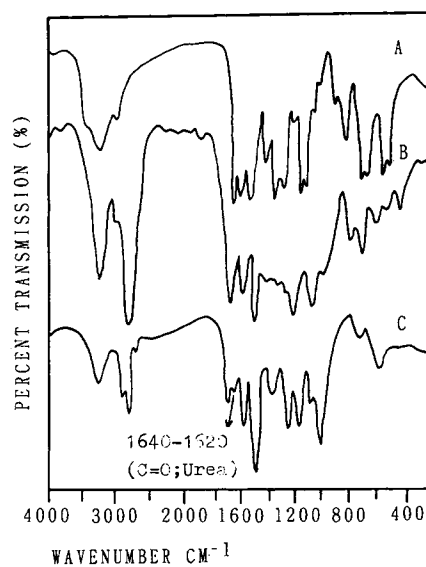
Infrared spectra were obtained by using the thin-film technique. The transmission IR spectra of

polymers are shown in Figure 1. The IR spectra of PSA (curve A) are characterized by the peaks at  $3400 \text{ cm}^{-1}$  ( $-\text{NH}-$  stretch vibration),  $1680 \text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ),  $1610 \text{ cm}^{-1}$ , and  $1540 \text{ cm}^{-1}$  ( $\text{C}\cdots\text{C}$ ), and  $1340 \text{ cm}^{-1}$  ( $-\text{SO}_2-$ ), whereas the characteristic absorption peaks of the conventional PU (curve B) are characterized at  $3400 \text{ cm}^{-1}$  ( $-\text{NH}-$  stretch vibration),  $1700 \text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ),  $2940 \text{ cm}^{-1}$  ( $-\text{CH}-$  stretch vibration), and  $1560 \text{ cm}^{-1}$  ( $-\text{NH}-$  deformation) absorptions.

Noticeably, a characteristic absorption of the  $\text{C}=\text{O}$  of urea group ( $-\text{NHCONH}-$ ) was found at  $1620\text{--}1640 \text{ cm}^{-1}$  for the reaction of  $-\text{NCO}$  with  $-\text{NH}_2$  group of PSA prepolymer.

### Dynamic Mechanical Measurements

The temperature dependence of loss tangent ( $\tan \delta$ ) and storage modulus ( $E'$ ) for PU-650-BD/PSA polyblend in the higher temperature range are shown in Table II and Figure 2. It was indicated that the primary dispersion temperature of  $M_1$ , which corresponds to glass transition temperature of the hard butyl segment (the short ( $-\text{MDI-BD}-$ )<sub>n</sub> segment) ( $T_{gh}$ ), was shifted to a higher temperature range with the increase of semirigid PSA part. Besides, the storage modulus  $E'$  of polyblends was also found to be increased with the increasing content of PSA. These indicated that the presence of PSA segment in the main chain could restrain the chain mobility of the hard butyl segment and consequently a higher  $T_{gh}$  and modulus resulted. Similarly, the



**Figure 1** Infrared spectra of polymers: (a) PSA, (b) PU-650-BD, (c) PU-650-PSA.

**Table II Thermal Properties of Polyblends and New Polyurethanes**

Code	Polymer	wt % of PSA	$T_g^a$		$T_m^c$	$T_{gh}^d$		$T_m$	$T_d^e$
			R <sup>b</sup>	DSC		R	DSC		
M1	PU-650-BD/PSA	0	-36	-30	—	64	78	151	280
M2	PU-650-BD/PSA	5	-32	-26	—	72	82	152	280
M3	PU-650-BD/PSA	10	-22	-18	—	80	89	152	281
M4	PU-650-BD/PSA	15	-14	-9	—	88	97	152	281
M5	PU-650-BD/PSA	20	-4	-2	—	98	105	153	281
M6	PU-1000-BD/PSA	0	-46	-42	—	63	75	160	267
M7	PU-1000-BD/PSA	5	-38	-35	—	71	79	160	267
M8	PU-1000-BD/PSA	10	-32	-28	—	77	85	160	267
M9	PU-1000-BD/PSA	15	-26	-20	—	84	90	161	268
M10	PU-1000-BD/PSA	20	-20	-14	—	90	98	161	268
M11	PU-2000-BD/PSA	0	-50	-44	12	62	72	175	250
M12	PU-2000-BD/PSA	5	-46	-40	13	66	75	175	251
M13	PU-2000-BD/PSA	10	-38	-32	13	72	79	175	251
M14	PU-2000-BD/PSA	15	-32	-26	13	80	84	176	251
M15	PU-2000-BD/PSA	20	-28	-22	14	86	90	176	251
B1	PU-650-PSA	34	-44	-35	—	—	252	341	329
B2	PU-1000-PSA	28	-46	-39	—	—	264	342	330
B3	PU-2000-PSA	20	-48	-42	9	—	276	345	330
—	PSA	100	—	—	—	—	335	503	—

<sup>a</sup>  $T_g$  of soft segment.<sup>b</sup> Rheovibron.<sup>c</sup>  $T_m$  of soft segment phase.<sup>d</sup>  $T_g$  of hard segment (the butyl or PSA segment).<sup>e</sup> Decomposition temperature, measured by TGA.

thermomechanical properties of other polyblends (M6-M15) were also found to have the same tendency in the high-temperature range.

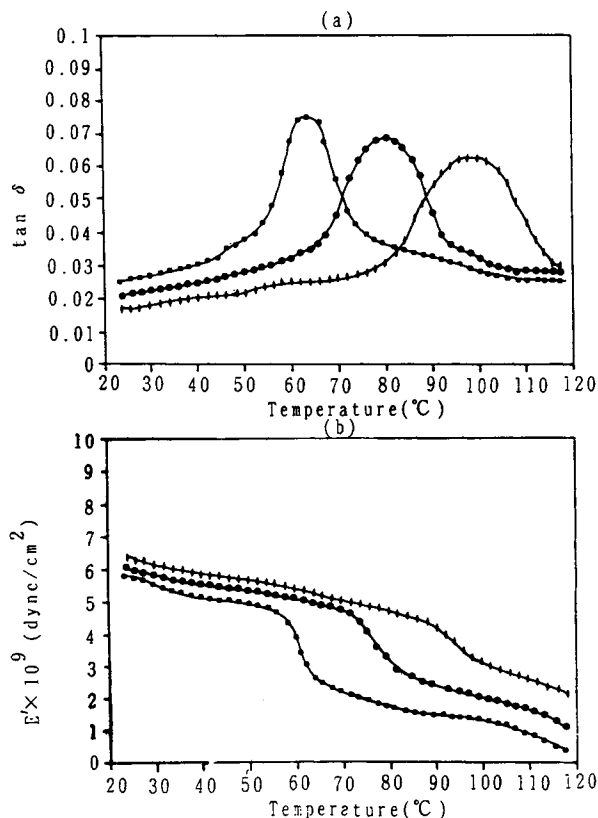
The second transition of polyblends in the low-temperature range corresponds to the glass transition temperature of the soft PTMG segment ( $T_g$ ), as shown in Table II and Figure 3. The  $T_g$  was also found to be elevated with the presence of PSA. The temperature shift was quite substantial due to the soft PTMG segment being immobilized by both the hard butyl and the semirigid PSA segment. Other dynamic mechanical behavior of other polyblends (M6-M15) was similar to those of the PU-650-BD/PSA polyblend series.

As seen in Table II and Figure 4, the new polyurethanes had a lower second transition temperature ( $T_g$ ), which was close to that of the pure soft PTMG segment, indicating that the soft matrix of new polyurethanes was self-aggregated. This could be verified by the effect of molecular weight of the soft segment on the degree of phase separation. It was found that the higher the molecular weight of PTMG, the greater the self-aggregation and consequently a lower  $T_g$ .

### Thermal Properties of Blends and New Polyurethanes

The thermal properties of blends and new polyurethanes are shown in Table II. Comparing the  $T_g$  of DSC and that of Rheovibron, it was found that the  $T_g$  of the former was higher than that of the latter. The heating rate was considered to be a contributing factor. It was 20°C/min in DSC, whereas 2°C/min in Rheovibron. It was also found in Figure 5 that the PU-650-BD/PSA blend series had an appreciable increase of  $T_g$  with the increasing weight percent of PSA. This indicated that the micro-Brownian motion of the hard butyl segment did suffer from the restraint of the semirigid PSA molecules, especially when the amount of PSA was large. The  $T_m$  of polyblends did not change. It remained at 152°C for PU-650-BD/PSA polyblend series. Similar results were also seen in our previous work for Nylon 6/PSA polyblends.<sup>3</sup>

The DSC scans for the new polyurethanes are shown in Figure 6 with variation of the molecular weight of the soft segment. It was evident from the results that the degree of phase separation of B3



**Figure 2** Temperature dependence of  $\tan \delta$  and storage modulus  $E'$  in higher temperature range for PU-650-BD/PSA polyblend series at 110 Hz: (■) M1 (0 wt % PSA); (●) M3 (10 wt % PSA); (+) M5 (20 wt % PSA).

(PU-2000-PSA) was greater than that of B1 or B2 (PU-650-PSA or PU-1000-PSA) due to lower  $T_g$  values. The melting endotherm peak ( $T_m$ ) of the soft segment appeared at 9°C in B3, whereas it was not seen in B1 and B2, indicating a long-chain crystallization of soft segment in B3. A similar thermal property occurred for the PU-2000-BD/PSA polyblend series. The  $T_m$  of these crystals appeared nearly 13°C. In general, the thermal stability of the new polyurethanes was superior to those of the blends.

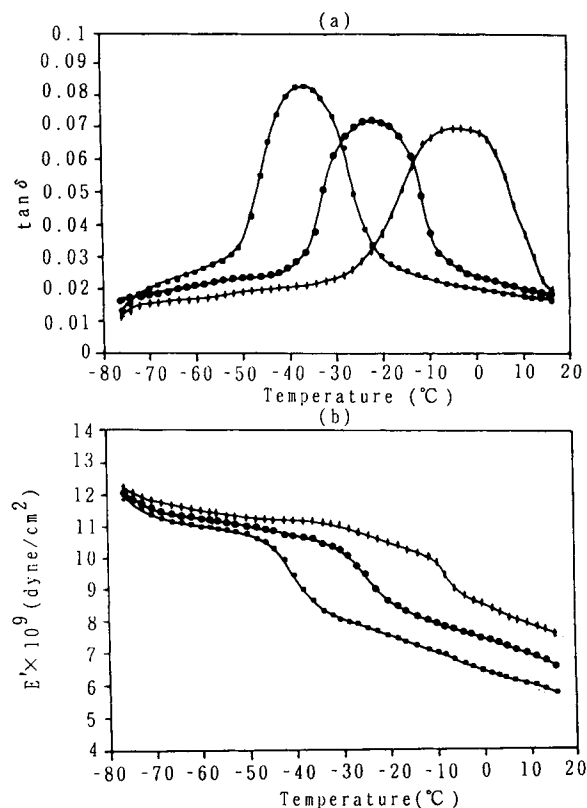
### Wide-Angle X-ray Diffraction

Wide-angle X-ray diffractions of conventional and new polyurethanes are shown in Figures 7 and 8. The unstretched conventional PU-2000-BD exhibited a diffraction peak at 20°. This was consistent with the results of other researchers.<sup>7-11</sup> Besides, unstretched PU-2000-PSA also possessed a diffraction peak at 20°. Hence, it was suggested that the diffraction peak at 20° could come from the diffrac-

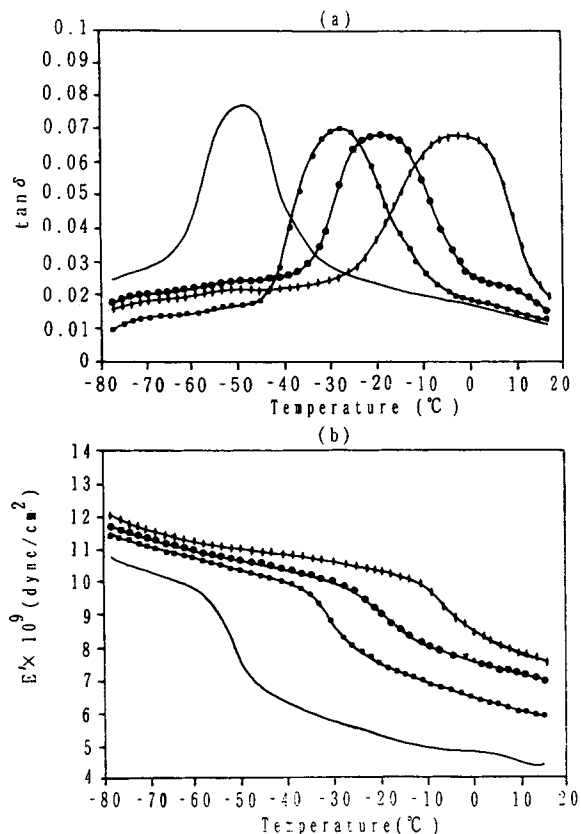
tion of soft PTMG segment at (100) plane.<sup>7</sup> Furthermore, a clear shoulder at about 24° was also found in the new polyurethanes under 500% stretching. This was believed to be the diffraction peak of (010) plane of the soft PTMG segment.<sup>7,8</sup> Furthermore, the half-width of the peak at 20° was found to be narrowed by its stretching. This demonstrated that the crystallization in the new polyurethane improved after its stretching.

### Morphological Observation by SEM

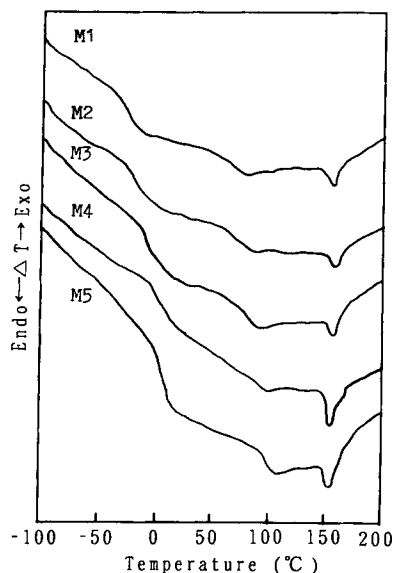
The scanning electron microscope was used to visualize the microstructure of the blends and the new polyurethanes. As shown in Figure 9, the conventional PU (PU-650-BD; 0 wt % PSA) had a uniform surface structure, but the blends exhibited a granular structure as the amount of PSA increased [Fig. 9(b)]. The granular structure was considered to be an aggregation of PSA. When the amount of PSA was up to 20 wt %, a large grain size from 3 to 5  $\mu\text{m}$  in diameter was observed. Other polyblends also



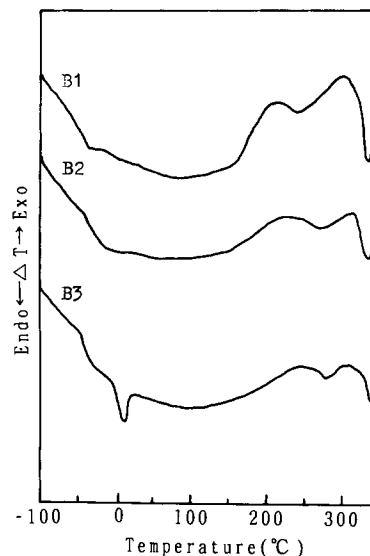
**Figure 3** Temperature dependence of  $\tan \delta$  and storage modulus  $E'$  in lower temperature range for PU-650-BD/PSA polyblend series at 110 Hz: (■) M1 (0 wt % PSA); (●) M3 (10 wt % PSA); (+) M5 (20 wt % PSA).



**Figure 4** Temperature dependence of  $\tan \delta$  and storage modulus  $E'$  in lower temperature range for polyblends (M5, M10, M15) and new polyurethane (B3) at 110 Hz: (+) M5 (20 wt % PSA); (●) M10 (20 wt % PSA); (■) M15 (20 wt % PSA); (—) B3 (20 wt % PSA).

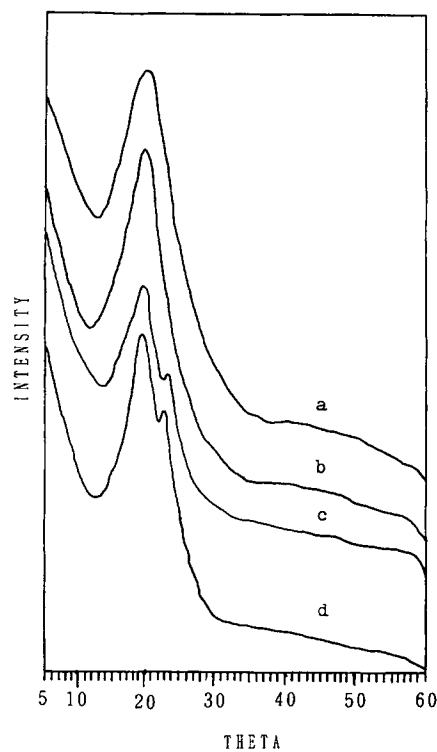


**Figure 5** DSC plots of polyblends of PU-650-BD with PSA in nitrogen: M1 (0 wt % PSA); M2 (5 wt % PSA); M3 (10 wt % PSA); M4 (15 wt % PSA); M5 (20 wt % PSA).

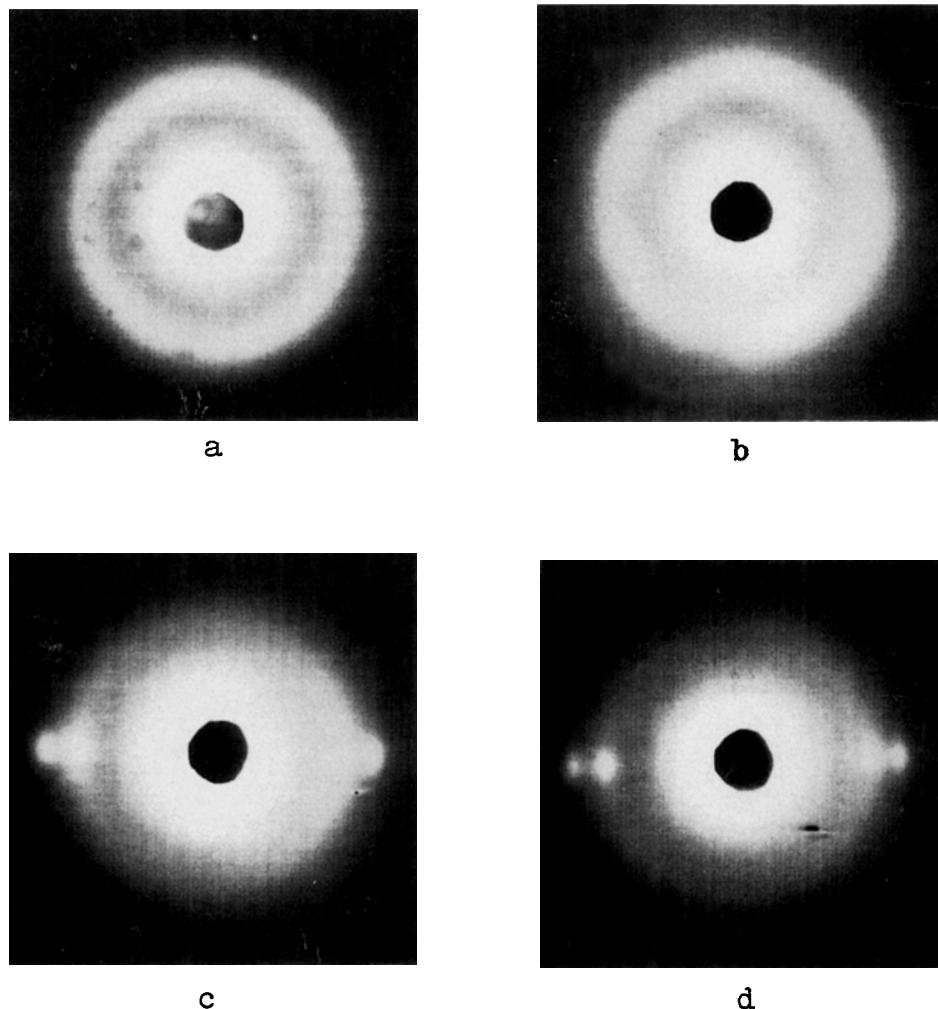


**Figure 6** DSC plots of new polyurethanes in nitrogen: B1 (PU-650-PSA); B2 (PU-1000-PSA); B3 (PU-2000-PSA).

showed similar morphological aggregation. With regard to the phase separation of polyblend, the blend of PU with 20 wt % PSA (M5) was extracted by



**Figure 7** The X-ray diagrams of conventional PU (PU-2000-BD) and new polyurethane (PU-2000-PSA): (a) unstretched conventional PU-2000-BD; (b) unstretched PU-2000-PSA; (c) stretched 300% PU-2000-PSA; (d) stretched 500% PU-2000-PSA.



**Figure 8** WAXD patterns of conventional PU (PU-2000-PSA): (a) unstretched conventional PU-2000-BD; (b) unstretched PU-2000-PSA; (c) stretched 300% PU-2000-PSA; (d) stretched 500% PU-2000-PSA.

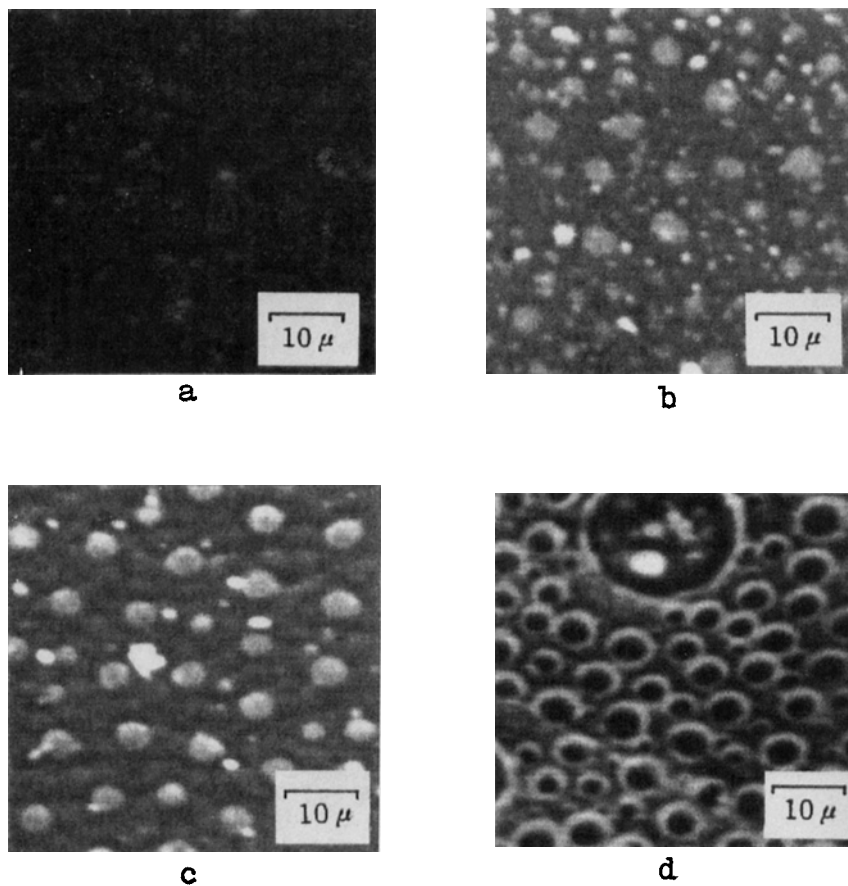
chloroform solvent to remove PSA part at room temperature for 8 h [Fig. 9(d)]. The result could infer that PU/PSA polyblend could be divided into two parts.

As shown in Figure 10, the morphology of the new polyurethanes also exhibited a two-phase structure similar to the blends. Nevertheless, the dispersed-phase texture of the new polyurethanes could not be separated by any solvents, since the PU and the PSA part in the polyurethane was chemically linked together by the covalent bonds.

#### Tensile Properties of Blends and New Polyurethanes

The results of tensile tests for cast films of polymers in room temperature are illustrated in Figure 11 and summarized in Table III. For PU-650-BD/PSA

polyblend series (M1–M5), it was found that the tensile strength increased initially and then decreased as the content of PSA increased. The results corresponded with previous morphological observations. At low content of PSA, the aggregation of PSA was small. Owing to intermolecular hydrogen bonding between the semirigid PSA and hard butyl segment, the tensile strength of blends was increased. Nevertheless, a further increase of PSA content could result in formation of large granular size of PSA and consequently a reduction of tensile strength, and finally reaching a complete brittleness. Initial modulus and elongation were found to be monotonically increased and decreased, respectively. Tensile properties of other polyblends (M6–M15) were found to be similar to those of PU-650-BD/PSA polyblend series.

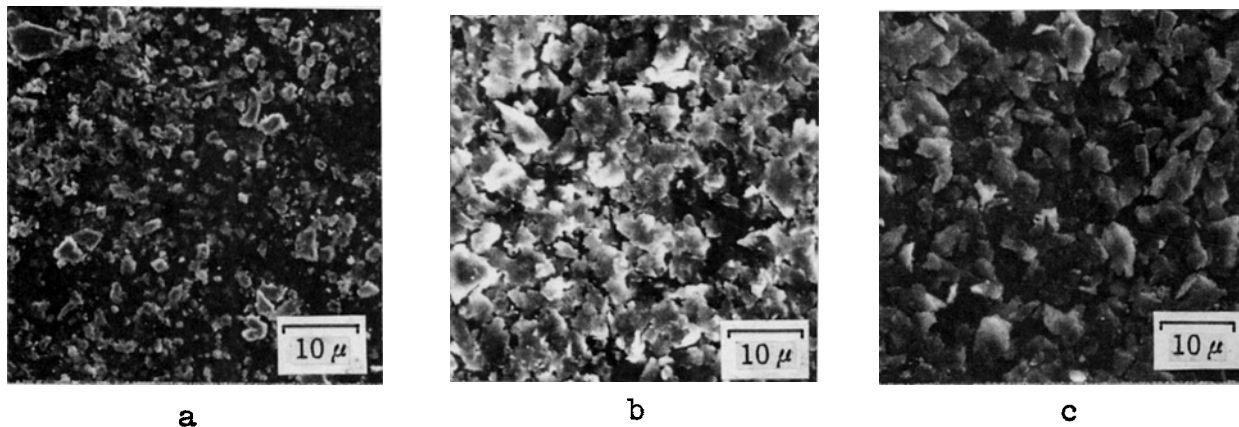


**Figure 9** SEM observations of PU-650-BD/PSA polyblend series for various amounts of PSA: (a) M1 (0 wt % PSA); (b) M3 (10 wt % PSA); (c) M5 (20 wt % PSA); (d) M5 but extracted PSA from polyblend with chloroform.

Also seen in Figure 11, it was found that the new polyurethanes had much better strength and elongation (better toughness) than those of blends with the same content of PSA. This result might come from a smaller macroscopic phase separation and the presence of urea linkage in the new polyurethane.

## CONCLUSIONS

The PU/PSA polyblends were prepared by physical blending and three new polyurethanes were synthesized by chemical extending. The reinforcement of PU with semirigid PSA instead of conventional hard

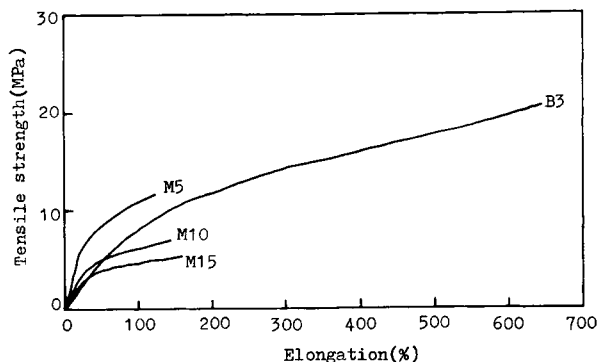


**Figure 10** SEM observations of new polyurethanes: (a) B1 (PU-650-PSA); (b) B2 (PU-1000-PSA); (c) B3 (PU-2000-PSA).



butyl segment proved to be successful. The new PU showed, on the same content of PSA, better tensile properties than those of polyblends. Nevertheless, by comparison of dynamic mechanical properties of new PU with polyblends, it showed that the transition temperature ( $T_g$ ) in the lower temperature region of new PU was lower than those of polyblends, and also storage modulus  $E'$ , which indicating a more self-aggregation of new PU in the soft segment.

For the morphological feature, it was demonstrated that the disperse-phase structure was observed in both of polyblends and new PU, although polyblends exhibited a better compatible state. By analysis of X-ray diffraction, it was suggested that the degree of stress-induced crystallization of conventional and new PU was dependent on the composition of the hard and soft segments, and also on the degree of its stretching. The  $20^\circ$  diffraction was correspondent to the soft PTMG segment for (100) plane, whereas the  $24^\circ$  was related to the diffraction peak of (010) plane of the soft PTMG segment. For thermal properties, the semirigid PSA reinforced PU polyblend exhibited a higher glass transition tem-



**Figure 11** Stress-strain curves for polyblends (M5, M10, M15) and new polyurethane (B3): M5 (20 wt % PSA); M10 (20 wt % PSA); M15 (20 wt % PSA); B3 (20 wt % PSA).

perature than that of pure conventional PU. Also, the  $T_{gh}$  and  $T_m$  of new PU were even higher than those of polyblends.

**Table III** Tensile Properties of Polyblends and New Polyurethanes

Code	wt % of PSA	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (MPa)
M1	0	9.54	426	37.72
M2	5	10.07	343	40.37
M3	10	11.67	268	48.26
M4	15	12.10	154	66.02
M5	20	10.72	114	78.34
M6	0	3.68	484	13.86
M7	5	4.03	408	16.91
M8	10	5.08	295	25.33
M9	15	4.92	202	33.34
M10	20	4.01	138	42.86
M11	0	3.20	510	6.61
M12	5	3.91	442	8.97
M13	10	4.22	338	13.45
M14	15	3.72	234	18.67
M15	20	3.06	172	27.56
B1	34	25.04	504	34.32
B2	28	22.51	592	30.54
B3	20	20.17	664	27.52
PSA	100	38.20	5	4326.20

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