

# Miscibility of Segmented Polyurethane/Poly(vinyl chloride) Blends

SUDARYANTO, TAKASHI NISHINO, MASAKI UENO, SEIJI ASAOKA, KATSUHIKO NAKAMAE

Department of Chemical Science and Engineering, Faculty of Engineering, Kobe University, Rokko, Nada, Kobe 657-8501, Japan

Received 27 October 2000; accepted 22 March 2001

**ABSTRACT:** Miscibilities of segmented polyurethanes (SPUs) and poly(vinyl chloride) (PVC) or functionalized poly(vinyl chloride) (FPVC) were studied with dynamic mechanical analysis, differential scanning calorimetry, and X-ray diffraction. Mechanical properties of the blends were also studied with tensile measurements. The miscibility of the blends depended greatly on the hard-segment content of SPU and the existence of the functional groups. The combination of SPU with a low hard-segment content and PVC with functional groups made the blend system miscible. Moreover, controlling the blend composition of SPU/FPVC allowed us to modify the mechanical properties of SPU, where the elongation at break was multiplied without a significant change in its tensile strength. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3022–3029, 2001

**Key words:** segmented polyurethane; poly(vinyl chloride) (PVC); blends; miscibility

## INTRODUCTION

Segmented polyurethanes (SPUs), consisting of hard segment (HS) and soft segment (SS), are known as versatile polymers because of the great variety of their structures and properties.<sup>1</sup> Thermodynamic immiscibility between the HS and SS results in the formation of microphase separation, which leads to SPU being used in various applications such as adhesives, coatings, plastics, and elastomers. A considerable number of industrial and academic studies have been directed toward clarifying the microphase-separated structure and its effect on the bulk as well as the surface properties of SPU.<sup>1–6</sup>

Because of their unique properties, such as biocompatibility, frictional resistance, softness, and low-temperature properties, SPUs also find applications as components of polymer blends. For example, SPU have been blended with poly-

(vinyl chloride) (PVC),<sup>7,8</sup> chlorinated PVC,<sup>9</sup> poly(vinyl butyral),<sup>10</sup> poly(ethyl terephthalate),<sup>11</sup> and sulfonated polystyrene.<sup>12</sup> The SPU/PVC blend system has been used in several applications, such as coating materials<sup>13,14</sup> and magnetic recording media.<sup>15</sup> Therefore, understanding the miscibility of SPU/PVC blends is important for controlling their properties and developing another blend system as well. It has been reported that the microphase-separated structure of SPU is influenced by the SS structure and its molecular weight,<sup>16,17</sup> the HS content,<sup>18</sup> and the sample preparation method.<sup>19</sup> They are also supposed to play important roles in the miscibility of SPU/PVC blends.<sup>7</sup>

In this study, the miscibility of SPU with PVC was investigated on the basis of the effects of the HS content of SPU and the functional groups in PVC.

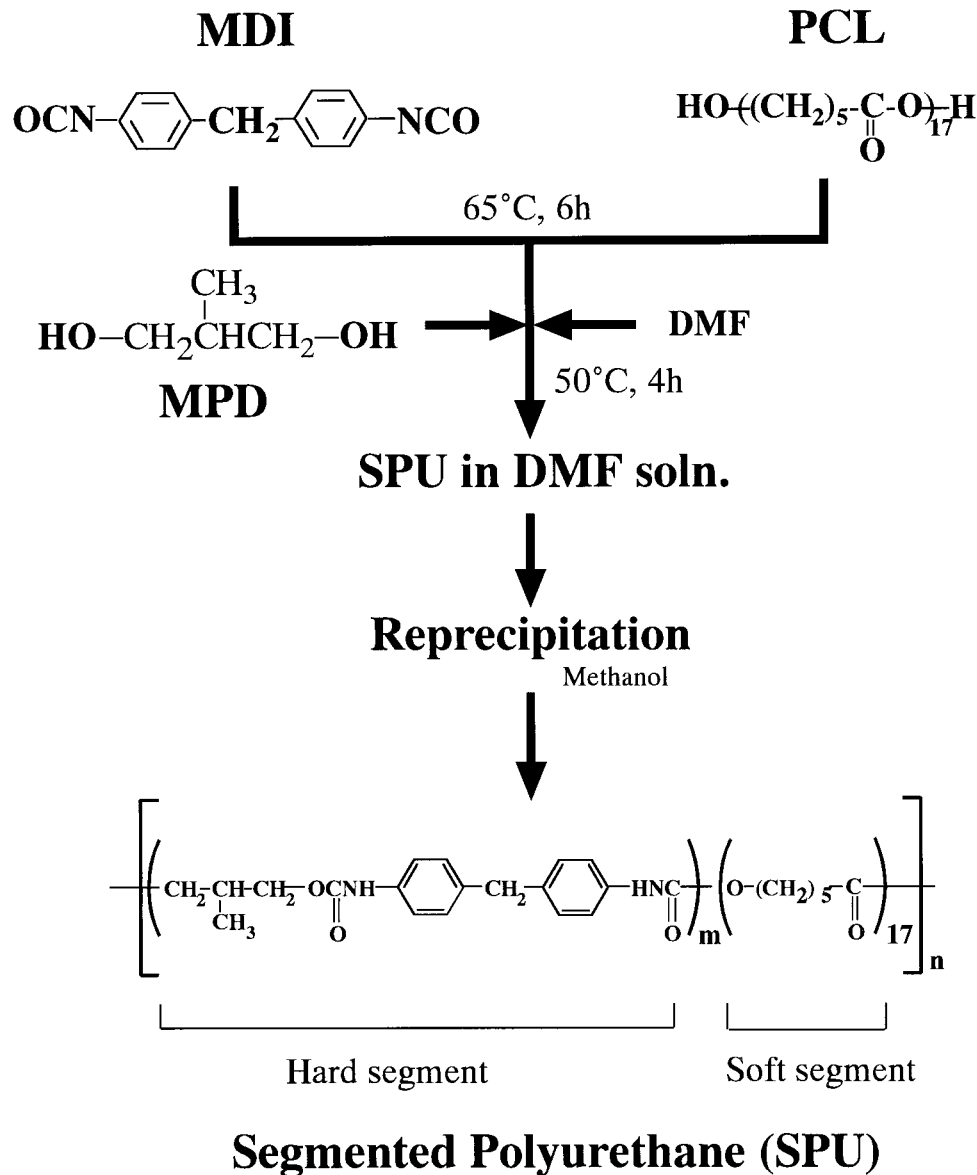
## EXPERIMENTAL

### Sample Preparation

A conventional prepolymer preparation method was used for the synthesis of SPU. 4,4'-Diphenyl

Correspondence to: T. Nishino (tnishino@kobe-u.ac.jp).

*Journal of Applied Polymer Science*, Vol. 82, 3022–3029 (2001)  
© 2001 John Wiley & Sons, Inc.



**Figure 1** Chemical formulas and experimental procedure for the synthesis of SPU.

methane diisocyanate (MDI; Mitsui Toatsu Chemical, Inc., Osaka, Japan) and polycaprolactone [PCL; number average molecular weight ( $M_n$ ) = 2000; Daicel Chemical Industries, Ltd. (Osaka, Japan); NCO/OH < 1] were added to the reactor. The reaction between MDI and PCL was performed at 65°C for 6 h under a nitrogen atmosphere. Then, the NCO-terminated prepolymer was diluted with *N,N'*-dimethyl formamide (DMF). 2-Methyl-1,3-propane diol (MPD; 99%; Aldrich Chemical Co., Sheboygan, WI) as a chain extender was added to the diluted prepolymer solution in a proper amount to achieve an NCO:OH molar ratio of 1:1. The chain-extension

**Table I** Recipes of SPU Synthesized

Composition (mol %)			HS Content (% w/w)
HS		SS	
MDI	MPD	PCL	
50	32	18	30
50	42	8	50
50	46	4	70

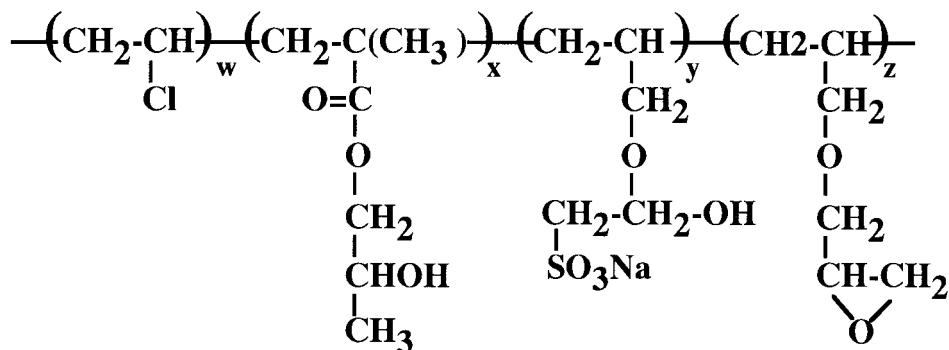


Figure 2 Chemical formula for FPVC.

reaction was performed at 50°C for 4 h and allowed to stand overnight at room temperature. The reactant was purified by reprecipitation into methanol, followed by drying under vacuum for at least 24 h at 60°C. The experimental procedure and the chemical formulas of the synthesized SPUs are shown in Figure 1. SPUs with different

HS content were prepared with changes in the composition of PCL and MPD, as shown in Table I. The HS content (wt %) was defined as follows:

$$\text{HS content} = \frac{\text{weight of (MDI + MPD)}}{\text{weight of (MDI + MPD + PCL)}} \times 100$$

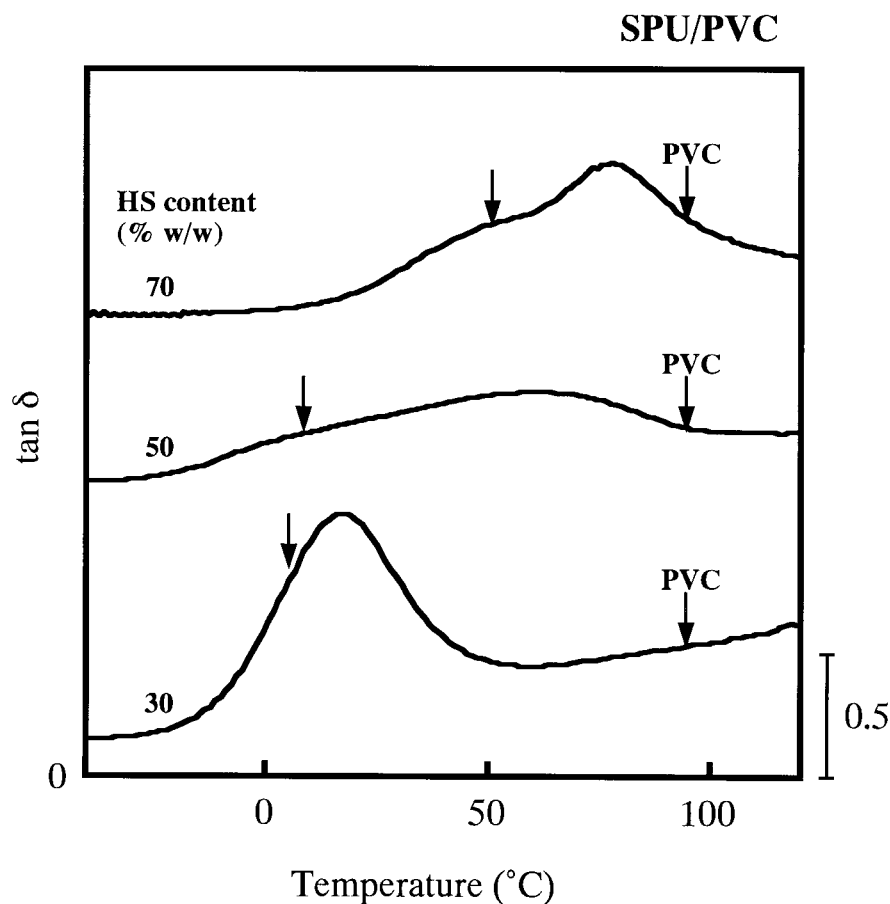
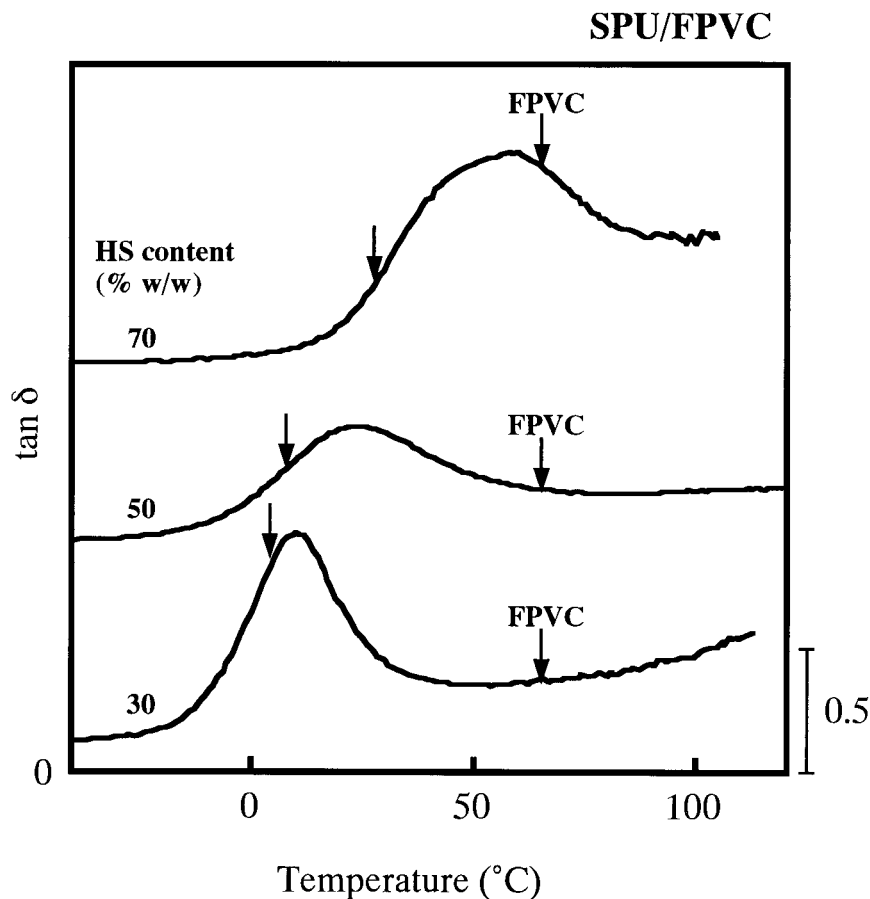


Figure 3 Temperature dependence of mechanical  $\tan \delta$  for 70/30 SPU/PVC blends. Arrows indicate the  $\tan \delta$  peaks of each polymer before blending.



**Figure 4** Temperature dependence of mechanical  $\tan \delta$  for 70/30 SPU/FPVC blends. Arrows indicate the  $\tan \delta$  peaks of each polymer before blending.

PVC ( $M_n = 75,000$ ; Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used as received. PVC functionalized with sulfonate and epoxy groups [functional poly(vinyl chloride) (FPVC);  $M_n = 38,000$ ; Nippon Zeon Co., Ltd., Kawasaki, Japan], with its chemical formula shown in Figure 2, was also used.

DMF was used as the solvent for the solution blending because it was a good solvent for both PVC and FPVC as well as SPU. A 10 wt % DMF solution of SPU was mixed with that of PVC or FPVC. The mixed solution was stirred sufficiently and allowed to stand for 24 h at room temperature. Then, it was precipitated into methanol and vacuum-dried at 60°C for at least 24 h. The samples used for the experiments were prepared by melt pressing of the precipitate at 180°C and 5 MPa for 5 min followed by quenching into ice water. The films were stored in a desiccator.

The miscibilities of SPU/PVC and SPU/FPVC blend films were investigated with dynamic me-

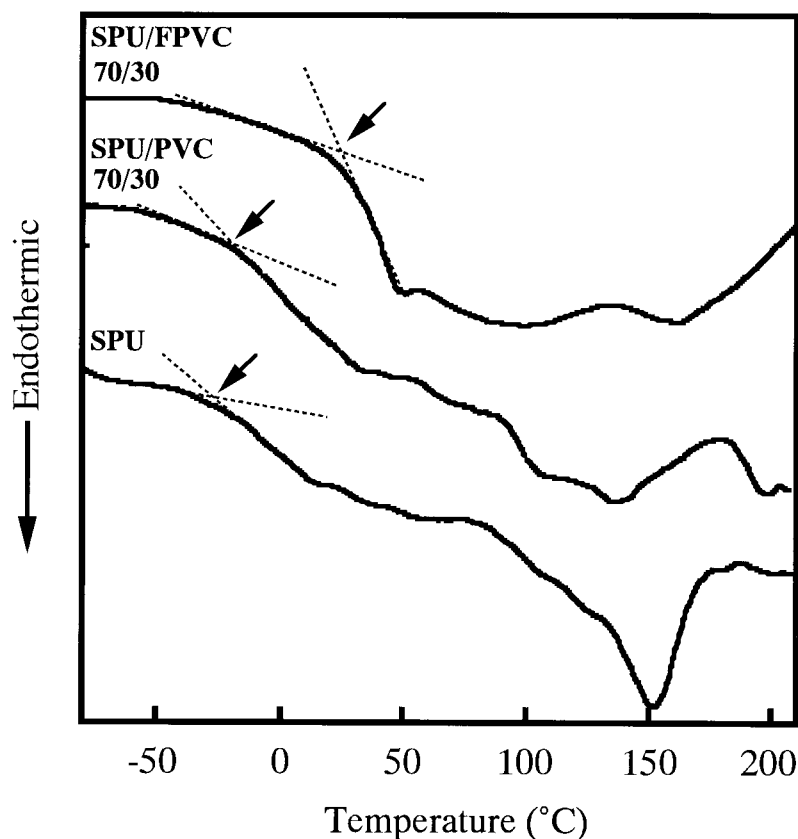
chanical analysis (DMA), differential scanning calorimetry (DSC), and X-ray diffraction measurements.

The dynamic mechanical properties were measured with DMA (ITK Co., DVA-200, Kyoto, Japan). Rectangular strips (5 mm  $\times$  20 mm  $\times$  0.2 mm) were tested at 10 Hz in a stretching mode from  $-100$  to 230°C at a heating rate of 6°C/min.

**Table II** Miscibilities of SPU/PVC and SPU/FPVC Blends

HS Content of SPU (% w/w)	PVC Content (% w/w)			FPVC Content (% w/w)		
	30	50	70	30	50	70
30	m	m	m	m	m	m
50	i	i	i	m	m	m
70	i	i	i	p	p	p

m = miscible; p = partially miscible; i = immiscible.



**Figure 5** DSC thermograms of SPU and the blends. The HS content of SPU was 70 wt %.

The DSC thermograms were measured with a DSC220CU (Seiko Instruments, Tokyo, Japan). Samples weighing 15 mg were encapsulated in an aluminum pan, cooled rapidly from room temperature to  $-100^{\circ}\text{C}$  in the cell, and then heated to  $220^{\circ}\text{C}$  at a heating rate of  $20^{\circ}\text{C}/\text{min}$ . The glass-transition temperature ( $T_g$ ) was taken as the inflection point of the thermogram, and an endothermic peak temperature was taken as a melting point ( $T_m$ ). Sn was used as a standard sample.

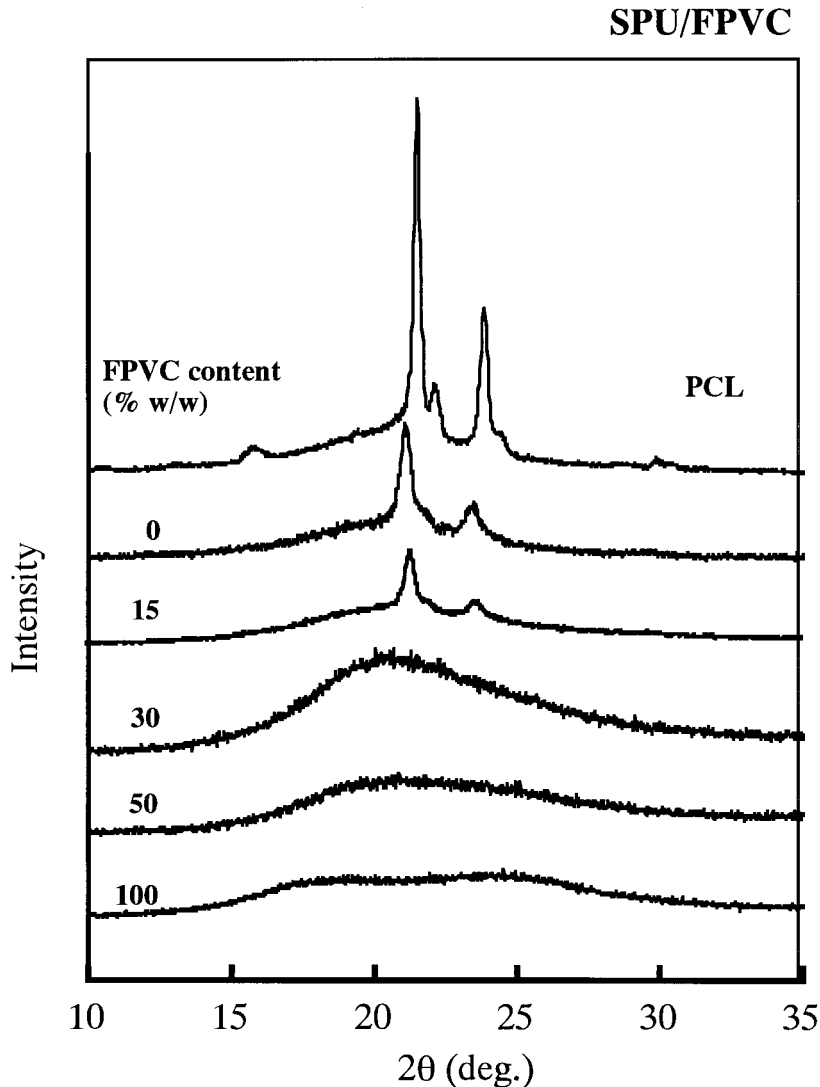
The X-ray diffraction profile was taken with a diffractometer (MAC Science, M18XHF, Yokohama, Japan) with nickel-filtered Cu  $K\alpha$  radiation generated at 40 kV and 200 mA. Reflectional diffraction profiles were obtained at a scan speed of  $1^{\circ}/\text{min}$ .

Mechanical properties were measured with a tensile tester (Shimadzu, Autograph AGS-1kND, Kyoto, Japan) at room temperature. A rectangular strip was strained at  $2\text{ mm}/\text{min}$  with an initial length of 15 mm.

## RESULTS AND DISCUSSION

### Miscibilities of SPU/PVC and SPU/FPVC Blends

Figure 3 shows the temperature dependence of mechanical  $\tan \delta$  for the 70/30 (w/w) SPU/PVC blend system with various HS contents of SPU. Arrows in the figure indicate the  $\tan \delta$  peak of each component measured from the separated experiments. A single  $\tan \delta$  peak was observed for the blend with an HS content of 30 wt %, and the peak temperature was located between those of SPU and PVC. This means that this blend system is apparently miscible. However, two peaks could be observed for the blend with higher HS contents. The lower temperature peak agreed with that of the SPU component itself. The higher one is thought to correspond to that of the SPU/PVC partially miscible phase, in which the PVC component was dominant. This shows that they are not fully miscible, and the SPU component forms its original domain in the blend system. The miscibility of the SPU/PVC blend system decreased with the increasing HS content of SPU.

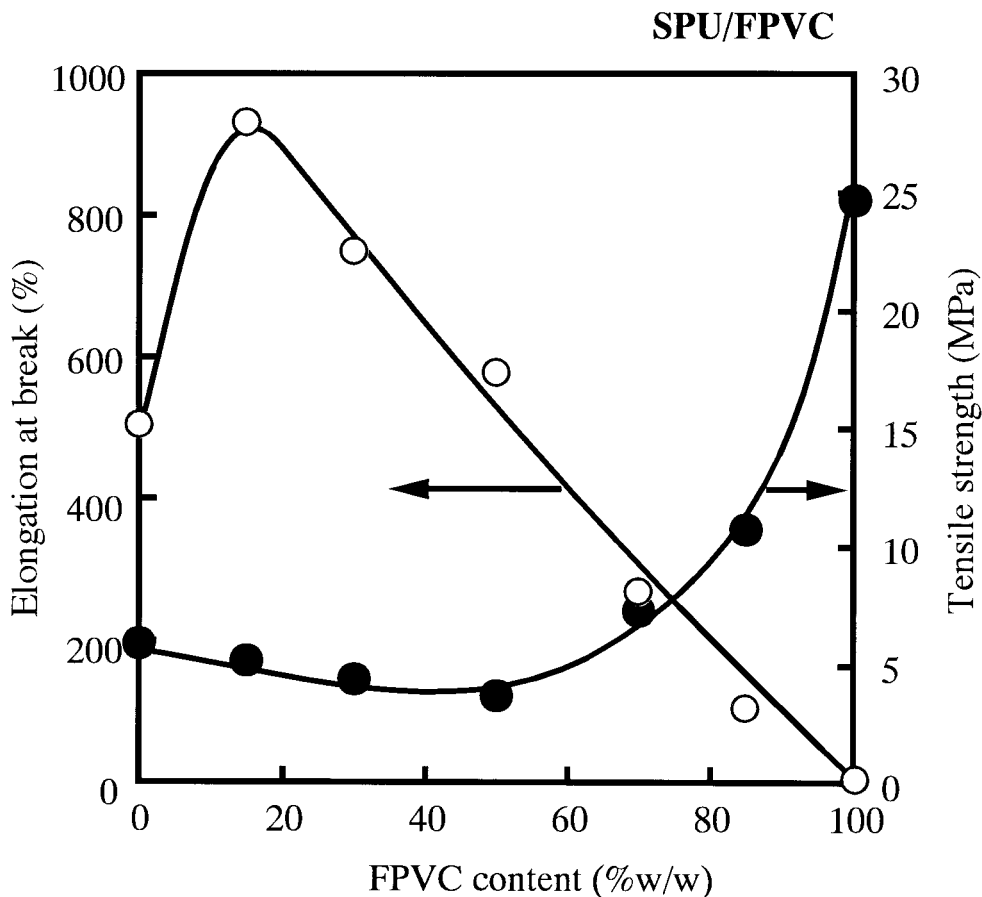


**Figure 6** X-ray diffraction profiles of SPU/FPVC blends. The HS content of SPU was 30 wt %.

Figure 4 shows the temperature dependence of mechanical  $\tan \delta$  for the 70/30 (w/w) SPU/FPVC blend system with various HS contents of SPU. The blends of FPVC and SPU with HS contents of both 30 and 50 wt % showed single  $\tan \delta$  peaks, which indicate they are miscible blend systems. However, the blend of FPVC and SPU with an HS content of 70 wt % gave at least two superimposed peaks, which reveals this is partially immiscible.

Table II summarizes the miscibility of SPU/PVC and SPU/FPVC blend systems on the basis of their dynamic mechanical behaviors, as shown previously. The SPU/PVC blend systems showed good miscibility at an HS content of 30 wt %, but

the increase in the HS content led the system to change into an immiscible one, independent of their blend compositions. The miscible window expanded for the SPU/FPVC blend system compared with that of SPU/PVC blends. This indicated that the functional groups in FPVC played important roles in the miscibility of the blends. If we consider the structures of SPU and FPVC, as shown in Figures 1 and 2, respectively, several possibilities can be considered for explaining the important roles of functional groups in the blend system. The polar functional groups in FPVC may interact with urethane bonds in the HS and/or ester bonds in the SS of SPU. An observation based on infrared spectroscopy



**Figure 7** Relationships between the FPVC content and (○) the elongation at break and (●) the tensile strength of SPU/FPVC blends. The HS content of SPU was 30 wt %.

shows that the formation of interurethane bonds of SPU was restricted by the existence of FPVC in the SPU/FPVC blend systems. Therefore, FPVC affects the formation of microphase separation of SPU.

#### Effect of PVC and FPVC on the Microphase Separation of SPU

Figure 5 shows DSC thermograms of SPU and the blends. The HS content of SPU was 70 wt %, and both the PVC and FPVC contents in the blend systems were 30 wt %. Pure SPU had a  $T_g$  at  $-38^\circ\text{C}$  and a  $T_m$  of the HS at  $152^\circ\text{C}$ . The position of  $T_g$  did not change significantly with blending with PVC; however, it shifted to  $12^\circ\text{C}$  by blending with FPVC.  $T_g$  corresponds to the molecular motion in the soft domain of SPU. Thus, no significant change in  $T_g$  showed immiscibility of SS and PVC. Despite the melting peak becoming broad and shifting to a lower temperature, the appearance of the melting peak for the SPU/PVC blend

shows the existence of a hard domain. These results coincided with the results obtained from the dynamic mechanical measurements, in which SPU/PVC was determined to be an immiscible system. However, a higher temperature shift of  $T_g$  and the disappearance of  $T_m$  for SPU/FPVC support this being a partially miscible system. The disappearance of  $T_m$  indicates that the hard domain was diminished and that a phase mixing with the soft domain occurred through blending with FPVC. This is thought to result in the increase of  $T_g$ .

The effect of blending FPVC onto the structure of the soft domain of SPU was also confirmed by X-ray diffraction.

Figure 6 shows the X-ray diffraction profiles of the SPU/FPVC blend system with various blend compositions. The HS content of SPU was 30 wt %. The profiles at the top and bottom of the figure refer to PCL as pure SS and FPVC, respectively. The pure SPU (the FPVC content was 0 wt %)

showed crystalline diffraction corresponding to the pure SS component. Crystalline diffractions were also observed for FPVC contents up to 15 wt %. However, the crystallinity decreased with increasing FPVC contents. This indicates that the crystallinity of the soft domain decreased with the blending of FPVC. In other words, FPVC was mixed with the SS of SPU; this resulted in the miscible blend.

The previous results lead to the conclusion that the FPVC mixed with both hard and soft domains and thereby improved the blend miscibility.

### Mechanical Properties of SPU/PVC Blends

Figure 7 shows the relationships between the FPVC content and the elongation at break and tensile strength of SPU/FPVC blends. The HS content of SPU was 30 wt %. With increasing FPVC content, the elongation of SPU rose up to the maximum value. This was caused by the decrease in the soft-domain crystallinity; that is, the soft domain changed to a more rubbery state. Beyond the maximum value, however, the elongation at break linearly decreased toward that of FPVC because the soft domain as well as the SPU concentration decreased with increasing FPVC content. The tensile strength showed an opposite tendency to the elongation at break. With increasing FPVC content up to 50 wt %, the tensile strength remained constant or even slightly decreased; this corresponded to the destruction of the hard domain. With further blending of FPVC, however, the tensile strength sharply increased because of the formation of the FPVC domain. This is an interesting phenomenon because the elongation of SPU could be doubled without a significant change in the tensile strength through the blending of a small amount of FPVC.

### CONCLUSIONS

The miscibility of SPU/PVC and SPU/FPVC blend systems were studied with DMA, DSC, and X-ray diffraction. The miscibility of the blends depended greatly on the HS content of SPU and the blend composition. The decrease in the HS content

made SPU miscible with PVC. FPVC mixed with both hard and soft domains of SPU; this destroyed the formation of the hard domain and the crystallinity of the soft domains. Therefore, SPU/FPVC had higher miscibility with SPU than SPU/PVC. Controlling the blend composition of SPU/FPVC allowed us to modify the mechanical properties of SPU.

### REFERENCES

1. Blackwell, J.; Lee, C. D. In *Advances in Urethane Science and Technology*; Frisch, K. C.; Klemperer, D., Eds.; Technomic: Lancaster, PA, 1984; Vol. 9, p 25.
2. Koberstein, J. T.; Stein, R. S. *J Polym Sci Polym Phys Ed* 1983, 21, 1439.
3. Yoon, S. C.; Ratner, B. D.; Ivan, B.; Kennedy, J. P. *Macromolecules* 1994, 27, 1548.
4. Nakamae, K.; Asaoka, S. *J Adhes Soc Jpn* 1995, 31, 38.
5. Nakamae, K.; Nishino, T.; Asaoka, S.; Sudaryanto. *Int J Adhes Adhes* 1996, 16, 233.
6. Nakamae, K.; Nishino, T.; Asaoka, S.; Sudaryanto. *Int J Adhes Adhes* 1999, 19, 345.
7. Wang, C. B.; Cooper, S. L. *J Appl Polym Sci* 1981, 26, 2989.
8. Bandyopadhyay, P. K.; Shaw, M. T. *J Appl Polym Sci* 1982, 27, 4323.
9. Wu, W.; Luo, X. L.; Ma, D. Z. *Eur Polym J* 1999, 35, 985.
10. Sincock, T. F.; David, D. J. *Polymer* 1992, 33, 4515.
11. Samios, C. K.; Gravalos, K. G.; Kalfaglou, N. K. *Eur Polym J* 2000, 36, 937.
12. Yang, W.; Shen, J.; Zhu, S. H.; Chan, C. M. *J Appl Polym Sci* 1998, 67, 2035.
13. Hepburn, C. *Polyurethane Elastomer*; Elsevier: London, 1992; p 19.
14. Enomoto, M.; Suehiro, K.; Muraoka, Y.; Inoue, K.; Sumita, M. *Text Res J* 1997, 67, 601.
15. Nakamae, K.; Yamaguchi, K.; Asaoka, S.; Karube, Y.; Sudaryanto. *Int J Adhes Adhes* 1996, 16, 277.
16. Xiu, Y.; Wang, D.; Hu, C.; Ying, S.; Li, J. *J Appl Polym Sci* 1993, 48, 867.
17. Wilkes, G. L.; Abouzahr, S. *Macromolecules* 1984, 14, 456.
18. Koberstein, J. T.; Leung, L. M. *Macromolecules* 1992, 25, 6205.
19. Hu, W.; Koberstein, J. T. *J Polym Sci Part B: Polym Phys* 1994, 32, 437.