Structure–Property Relationships in Polyurethane–Poly(styrene-co-acrylonitrile) Blends

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SYNOPSIS

Blends of thermoplastic polyurethane (TPU) and poly(styrene-co-acrylonitrile) (SAN) (34% acrylonitrile and 24% acrylonitrile) and polyurethane ionomer (PUI) with SAN (34% acrylonitrile) were prepared in the melt. The structural properties and morphology of the blends were investigated. TPU and SAN blends were immiscible in the composition range 30–70 wt % of TPU or SAN. In TPU-rich blends, SAN propagates the separation of hard and soft segments in TPU. In SAN-rich blends, the interaction stage depends on acrylonitrile contents. SEM measurements showed that the blends of TPU/SAN were fine dispersions and clearly showed a continuous and disperse phase, whereas the morphology of the PUI/SAN blends were different. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The study of the multicomponent polymeric system is now one of the advanced domains in modern polymer science. The general characteristics of the multicomponent polymeric systems include the formation and transitions of the complex structure in blends of crystalline and amorphous components. Since the interactions between the blend components are of great importance, the coupling agent activity and the modification of contacts between the components as well as the general aspects of adhesion between polymers have been examined.

The chemical structure of blends of thermoplastic polyurethane (TPU) and poly(styrene-co-acrylonitrile) (SAN) is very complex, but the use of TPU as a modifier for rigid thermoplastics has recently increased. Nevertheless, there are several published studies on TPU and SAN blends.[1–5] The blending of TPU with SAN results in many property variations of TPU/SAN blends regarding the numerous combinations of different polyurethane types (hard and soft segment character, domain separation, etc.) with different SAN copolymers (weight % of acrylonitrile and different distributions of styrene and

acrylonitrile). In addition, numerous techniques for determining the (im)miscibility stage and miscibility studies of TPU/SAN blends may give somewhat discrepant results. The unmixing of the TPU/SAN solutions over all the composition ranges led to the conclusion of immiscibility of TPU/SAN blends.[1] Mechanical, thermal, and spectroscopic studies[2] of melt-blended TPU with SAN (20 wt % acrylonitrile) seem to confirm the idea of immiscibility within the investigated composition range, even though good mechanical properties are fairly well observed over the wide composition range. Contrary to the latter finding, this range gave better results in the composition range 20–30 wt % of TPU or SAN.[3]

Ratzsch et al.[4] established that 10 wt % SAN in blends with TPU results in an improvement in mechanical properties. At higher concentrations of SAN (like 10%), the tensile strength decreases. In this case, the typical structure of TPU is destroyed. That means that the phase separation of hard and soft segments and regions of higher order are disturbed. In studying the TPU/SAN system, Ratzsch and Pionteck[5] determined the interactions between matrix of TPU and the disperse phase SAN, which are not only van der Waals forces.

Miscibility, structure, and properties of polymeric pairs can be determined by different methods. In this paper, the structural properties and miscibility

as well as the morphology of TPU/SAN and PUI/SAN blends were investigated by wide angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM).

More thorough analyses of TPU/SAN systems, different series of blends of polyester-based TPU with two SAN (SAN24 and SAN34; with 24 and 34 wt % of acrylonitrile, respectively) were made. For a comparison, the blends of polyurethane ionomer (PUI) with SAN (34 wt % acrylonitrile) were also studied.

EXPERIMENTAL

Materials

In this work, commercial polyester TPU (Elastollan C 90 A, BASF) and commercial SANs (Luran 388 S, BASF, further on marked as SAN34 and Luran 368 R, BASF, further on marked as SAN24) were applied. By ^{13}C-NMR, it was found that Elastollan C 90 A was a polyester urethane on the basis of a polyester from adipic acid and 1,6-hexanediol, 1,4-butanediol (BD), and 4,4'-diisocyanato–diphenylmethane (MDI).

The molar masses of all the used polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards. A modular chromatograph consisting of a Waters 510 pump and a Varian Techtron 635 spectrophotometer set at 257 nm, μ-Styragel columns with pore sizes of 10^{-6} and 10^{-5} m, and tetrahydrofurane (1 mL/min) as a mobile phase were used. The values found were 170,000 for TPU, 130,000 for SAN34, and 160,000 for SAN24.

Polyurethane ionomer (PUI) was synthesized from polycaprolactone (CAPA, M_n = 2000, Solvay), MDI (Bayer), BD (Bayer), and 2,2'-(dihydroxymethyl)propionic acid (DMPA, Janssen) using a standard[6] prepolymer process: In the first step, the isocyanate prepolymer is formed from polymeric diol and an excess of diisocyanate. The prepolymer is then dissolved in a low boiling solvent (normally acetone) and chain-extended by low molar mass diols, part of them containing ionic groups. In the next step, the ionic groups are quaternized by a tertiary amine (triethylamine) and then a dispersion is formed by the addition of water while vigorously stirring. The still unreacted NCO groups react with water. The solvent is removed by vacuum distillation and a purely aqueous dispersion is obtained. The molar ratio of the components was CAPA : BD : DMPA : water 1 : 1 : 1.2 : 1. The synthesized PUI

contained 0.30 mmol/g of ionic groups and had a relative molar mass of 130,000 (GPC). To prepare the polymer blends, the PUI dispersion was dried into films at room temperature.

Blends Preparation

TPU and SAN components were dried for 6 h at 373 K. TPU/SAN34 and TPU/SAN24 blends of different weight ratios (100/0, 75/25, 50/50, 25/75, 0/100) were prepared by melting them in a Brabender kneading chamber (rotation speed 50/min) at 468 K for 10 min. PUI/SAN34 blends (60/40, 50/50, 40/60, 25/75, 10/90) were prepared by mixing, under the same conditions, for 5 min with an addition of 0.2 wt % of antioxidant Lovinox BHT. All blends were milled at room temperature. The milled samples were molded in a hydraulic press at 493 K and 15 MPa and then water-cooled to room temperature.

Methods

Wide-angle X-ray diffraction experiments were performed using a Phillips diffractometer with monochromatized CuKα radiation. Intensity was scanned in the diffraction angle range of 2θ = 4–60°.

The morphology of the TPU/SAN and PUI/SAN blends was investigated by a Jeol JSM scanning electron microscope. The samples, in the form of thin plates, were immersed in liquid nitrogen for 10 min, and then broken. The fractured surfaces were etched with methyl ethyl ketone and then metallized with a Au–Pd alloy. SEM measurements were performed only on broken and broken-and-etched samples.

RESULTS AND DISCUSSION

The WAXD curves of TPU/SAN and PUI/SAN blends are shown in Figures 1–3. (TPU/SAN34, Fig. 1; TPU/SAN24, Fig. 2; PUI/SAN34, Fig. 3). The TPU diffractogram shows two diffuse maxima with Bragg spacings $d \simeq 2.23$ Å ($40.4°$ 2θ), which corresponds to the intrachain distances, and $d \simeq 4.35$ Å ($20.4°$ 2θ), which corresponds to the interchain character. Weak discrete maxima on the TPU WAXD amorphous halo correspond to the reflections of crystalline hard segment microdomains[7,8] (Figs 1 and 2 and Table I). The WAXD curve of the SAN34 (Fig. 1) and the WAXD curve of SAN24 (Fig. 2) show three diffuse maxima that arose from
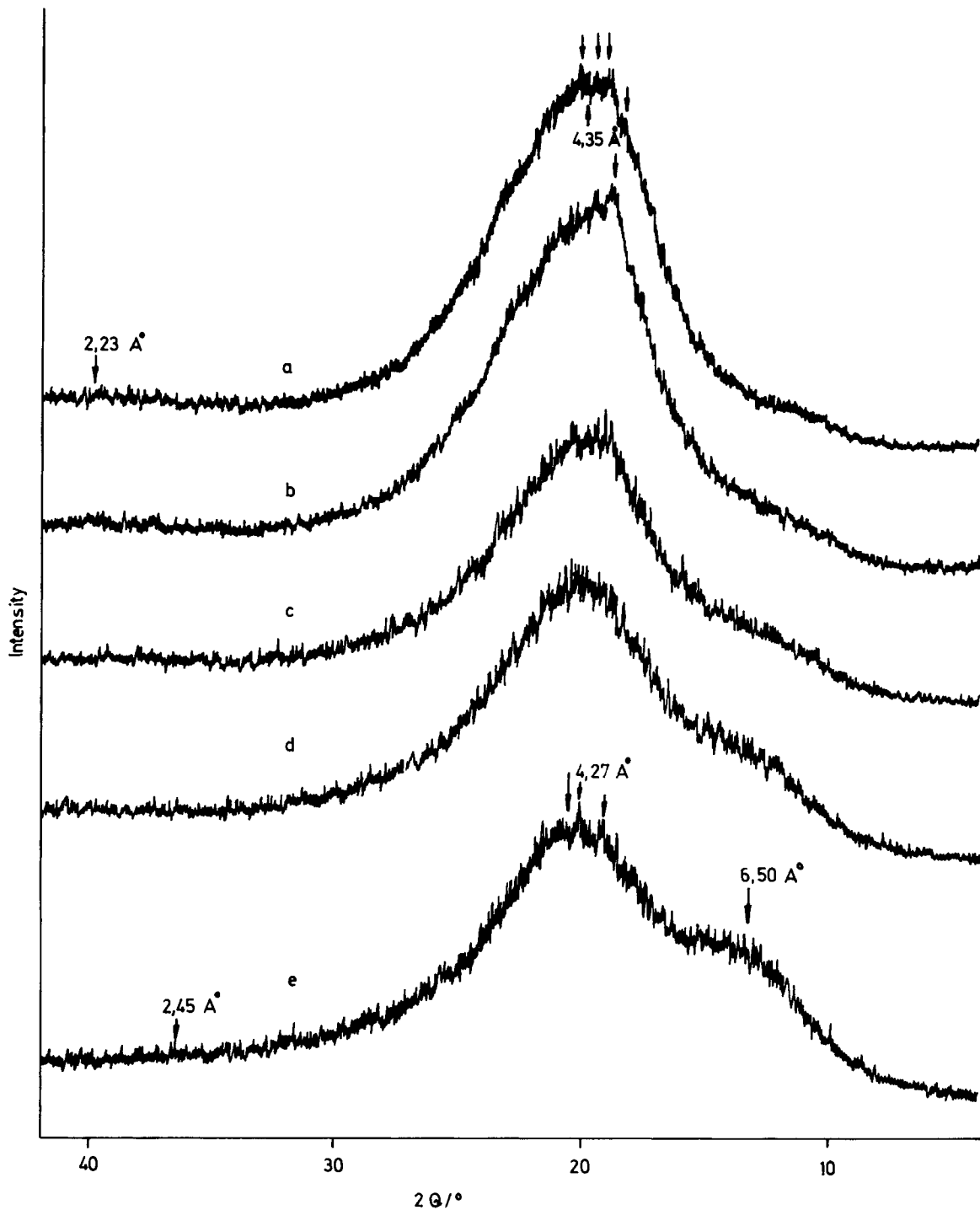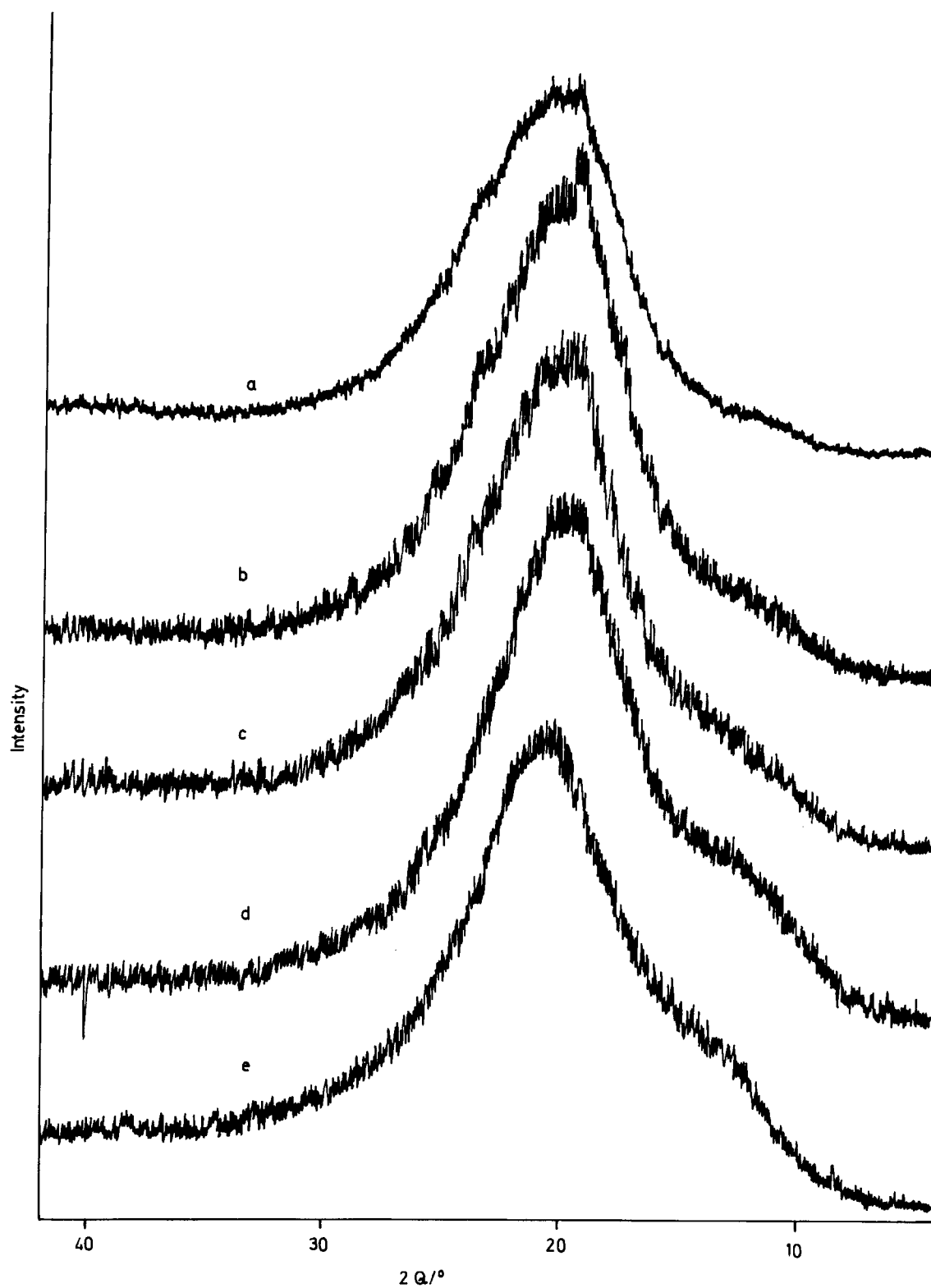
Figure 1   WAXD curves of TPU/SAN34 blends: (a) 100/0; (b) 75/25; (c) 50/50; (d) 25/75; (e) 0/100.

the amorphous phase. Calculated spacings from the Bragg equation are 2.45 Å (36.7° 2θ) for the smallest maximum, 4.27 Å (20.8° 2θ) for the largest maximum, and 6.50 Å (13.6° 2θ) for the medium maximum. In the SAN34 diffractogram, very weak crys-

talline reflections (4.60 and 4.37 Å) appeared that could not be assigned.

The weight contents of crystalline domains, i.e., degrees of crystallinity, X_{cr} are calculated as the integral degree of crystallinity for polyurethane[9] (Ta-

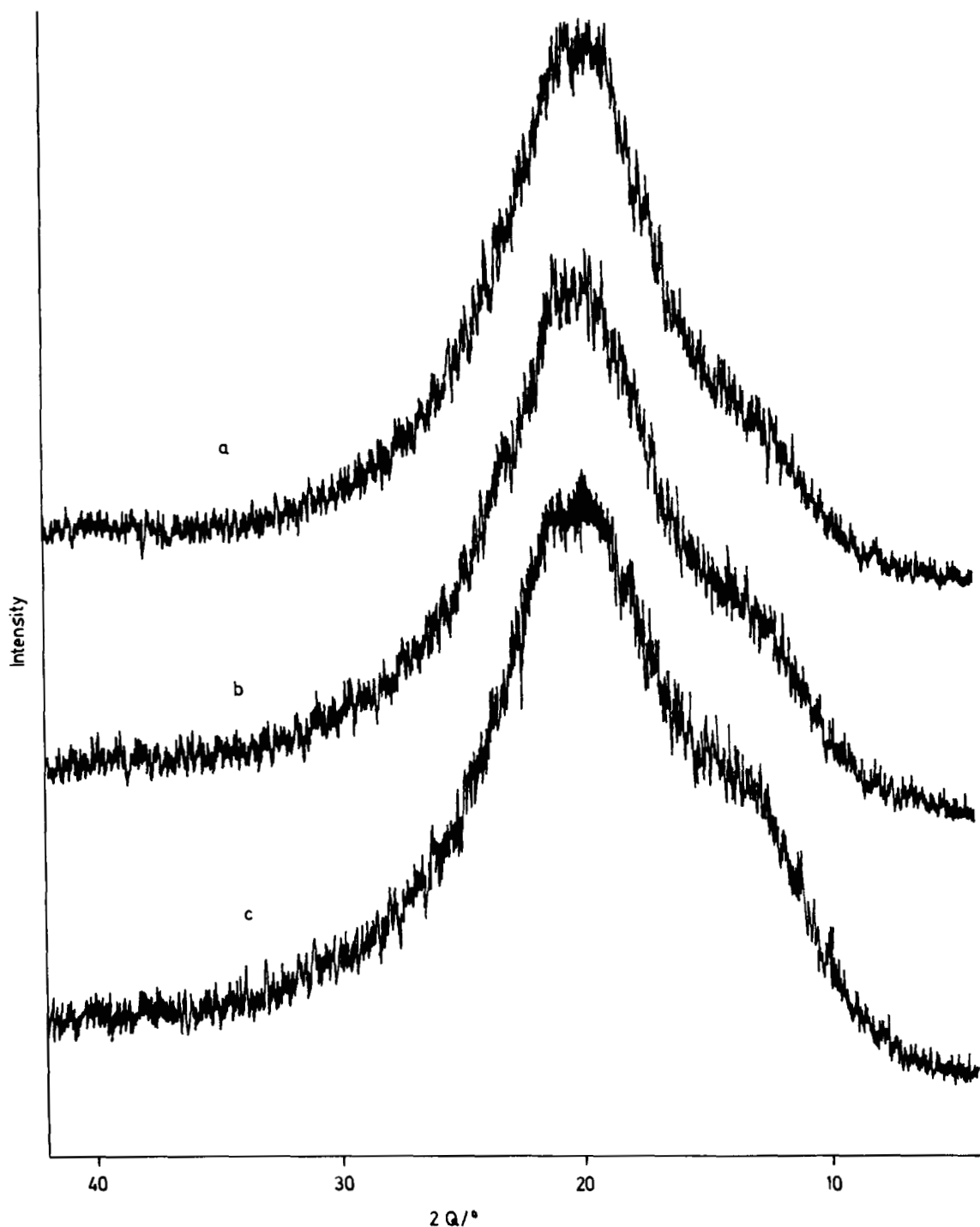**Figure 2**   WAXD curves of TPU/SAN24 blends: (a) 100/0; (b) 75/25; (c) 50/50; (d) 25/75; (e) 0/100.

Figure 3 WAXD curves of PUI/SAN34 blends: (a) 50/50; (b) 25/75; (c) 10/90.

ble II). The small crystallinity degree of TPU refers to a small amount of ordered crystalline hard segment microdomain separated from the amorphous matrix in TPU, but it does not inform us about the total amount of the hard segment. The relatively narrow great diffuse maximum ($\sim$4.35 Å) indicates that besides the amorphous matrix (probably hard–

soft segment mixture)[10] and the crystalline hard-segment domain, there also exists a tendency for ordering the soft segment into an unoriented, isotropic polyurethane film.

The degree of crystallinity keeps a constant value by the dilution of TPU with 25 wt % SAN34 or SAN24 (75/25 TPU/SAN). Truly, these very low

Table I Comparison of the Literature[8,9] and Observed Values (obs.) of the Bragg Spacings, *d*, for the Crystalline MDI/BD Hard-segment Domain

hkl	$d/\text{Å}$ (Ref. 7)	$d/\text{Å}$ (Ref. 8)	$d/\text{Å}$ (obs.)
004	7.65	8.67	
$\bar{1}02$	4.91	4.93	
$\bar{1}01$	4.75	4.70	4.77
$0\bar{1}4$	4.60	4.53	4.60
$\bar{1}06$	4.53		
101	4.25		4.28
$\bar{1}07$	4.15	4.17	4.13
102	3.89	3.80	
$0\bar{1}8$	3.75		3.73
103	3.56	3.53	
$\bar{1}\bar{1}9$	3.42		
104	3.30		

crystallinity values (1%) can be considered as a limit of method resolution, but the higher $0\bar{1}4$ reflection (4.60 Å, 19.3° 2θ) in 75/25 TPU/SAN34 and in 75/25 TPU/SAN24 blends is more obvious than in the pure polyurethane (100/0 TPU/SAN). Simultaneously, intensities of other TPU reflections decrease. The increasing of the $0\bar{1}4$ reflection intensity, which is assigned to the interchain separation distance of 4.7 Å in a hard-segment domain,[11,12] supports the hypothesis that the interaction between TPU and SAN in a 75/25 TPU/SAN blend propagates further separation of the hard and soft TPU

segments. This is possible because of the relatively great chain mobility in the TPU matrix.

Every WAXD curve of the TPU/SAN34 and the TPU/SAN24 series fits the curve calculated by a linear combination of TPU and SAN34 (or TPU and SAN24)-normalized WAXD curves in the angle range of $2\theta = 8$–$34°$ (Figs. 1 and 2).

The WAXD curves of both TPU/SAN blends fit well with the calculated curves, which may indicate immiscibility of both of the TPU/SAN series in the whole composition range, just like the conclusion from the miscibility studies of TPU/SAN solutions.[1] Especially close-fitting WAXD curves achieved with a 50/50 TPU/SAN34 and with a 50/50 TPU/SAN24 agree with the proposed immiscibility in the composition range 30–70 wt % TPU.[2]

The intensity ratio values α, calculated as $I(21°)/I(16°)$, $I(16°)/I(14°)$, and $I(16°)/I(12°)$, as a measure for ratio two interchain maxima $\alpha = I_{4.27}/I_{6.50}$, increase in the series $\alpha(\text{PUI/SAN34}) < \alpha(\text{TPU/SAN34}) < \alpha(\text{TPU/SAN24})$ and $\alpha(\text{SAN34}) < \alpha(\text{SAN24})$. These results indicate differences between SAN34 and SAN24 and between their interaction with TPU and PUI in the SAN-rich composition range. Because of the result $\alpha(\text{SAN34}) < \alpha(\text{SAN24})$, amorphous maximum at 6.50 Å could be assigned mainly to the interchain character of the acrylonitrile sequences. Analogously, the effect of acrylonitrile sequences increases in the series (TPU/SAN24) < (TPU/SAN34) < (PUI/SAN34).

However, interactions between PUI and SAN are of a different character than the interactions between TPU and SAN. Although the difference be-

**Table II Degree of Crystallinity (X_{cr}) and Intensities Ratios**

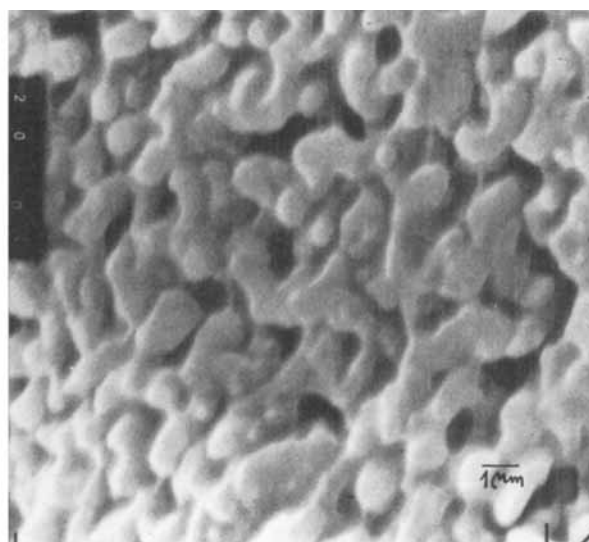| Composition (g/g)	$X_{cr}/\%$	$I(21°)/I(16°)$	$I(21°)/I(14°)$	$I(21°)/I(12°)$
TPU/SAN34				
100/0	1.4	3.40	5.84	8.59
75/25	1.8	2.78	4.48	6.95
50/50	0.4	2.32	3.09	4.43
25/75	0.0	2.08	2.44	3.14
0/100	0.0	1.68	1.82	2.32
TPU/SAN24				
100/0	1.4	3.40	5.84	8.59
75/25	1.3	2.87	4.44	5.91
50/50	0.0	2.51	3.41	5.08
25/75	0.0	2.03	2.64	3.33
0/100	0.0	1.93	2.56	3.29
PUI/SAN34				
50/50	0.0	2.07	2.77	3.94
25/75	0.0	1.87	2.32	3.15
10/90	0.0	1.56	2.00	2.63
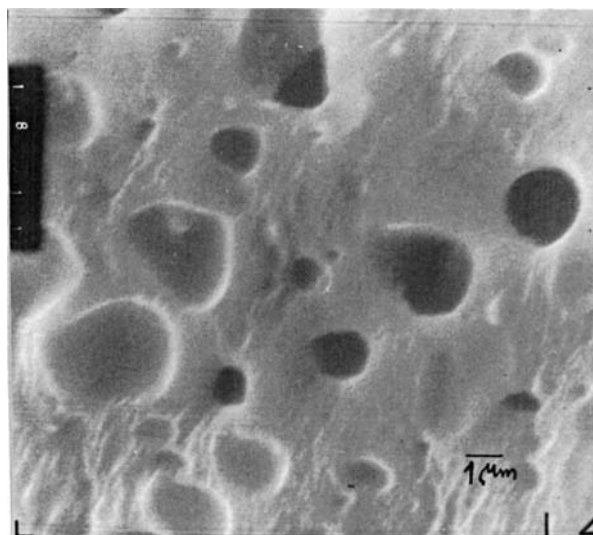
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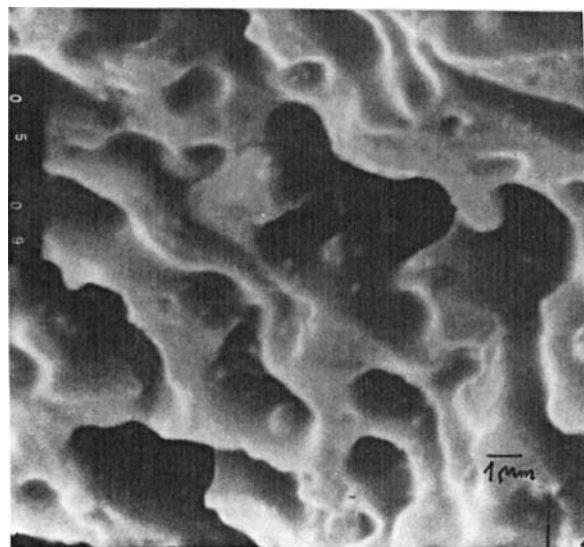
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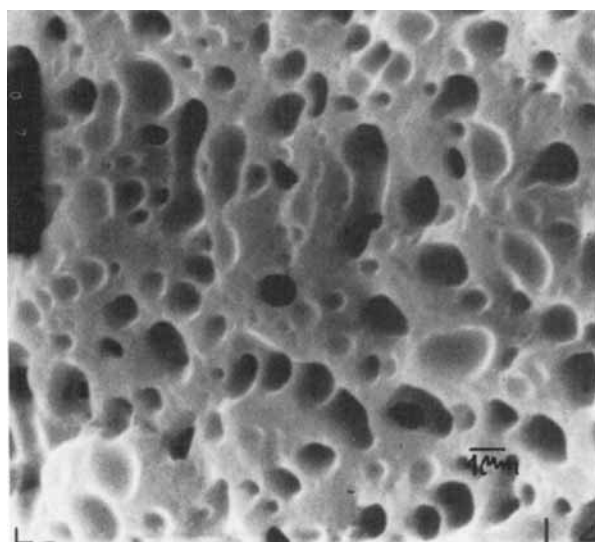
c

d

Figure 4 Micrographs of etched samples of TPU/SAN blends: (a) TPU/SAN34 75/25; (b) TPU/SAN34 50/50; (c) TPU/SAN24 75/25; (d) TPU/SAN24 50/50.

tween α (TPU/SAN34) and α(TPU/SAN24) increases with SAN content, small differences between α(PUI/SAN34) and α(TPU/SAN34) slightly increase with PUI (TPU, respectively) content.

PUI, as a microheterogeneous system, consists of diffuse phase-separated microregions of ionomer and interacts more closely with the SAN copolymer to enhance chain mobility. More considerable separation of acrylonitrile sequences in the microdomain follows as the result.

The results of scanning electron microscopy on unetched samples gave a few results. The pure TPU

a

b

c
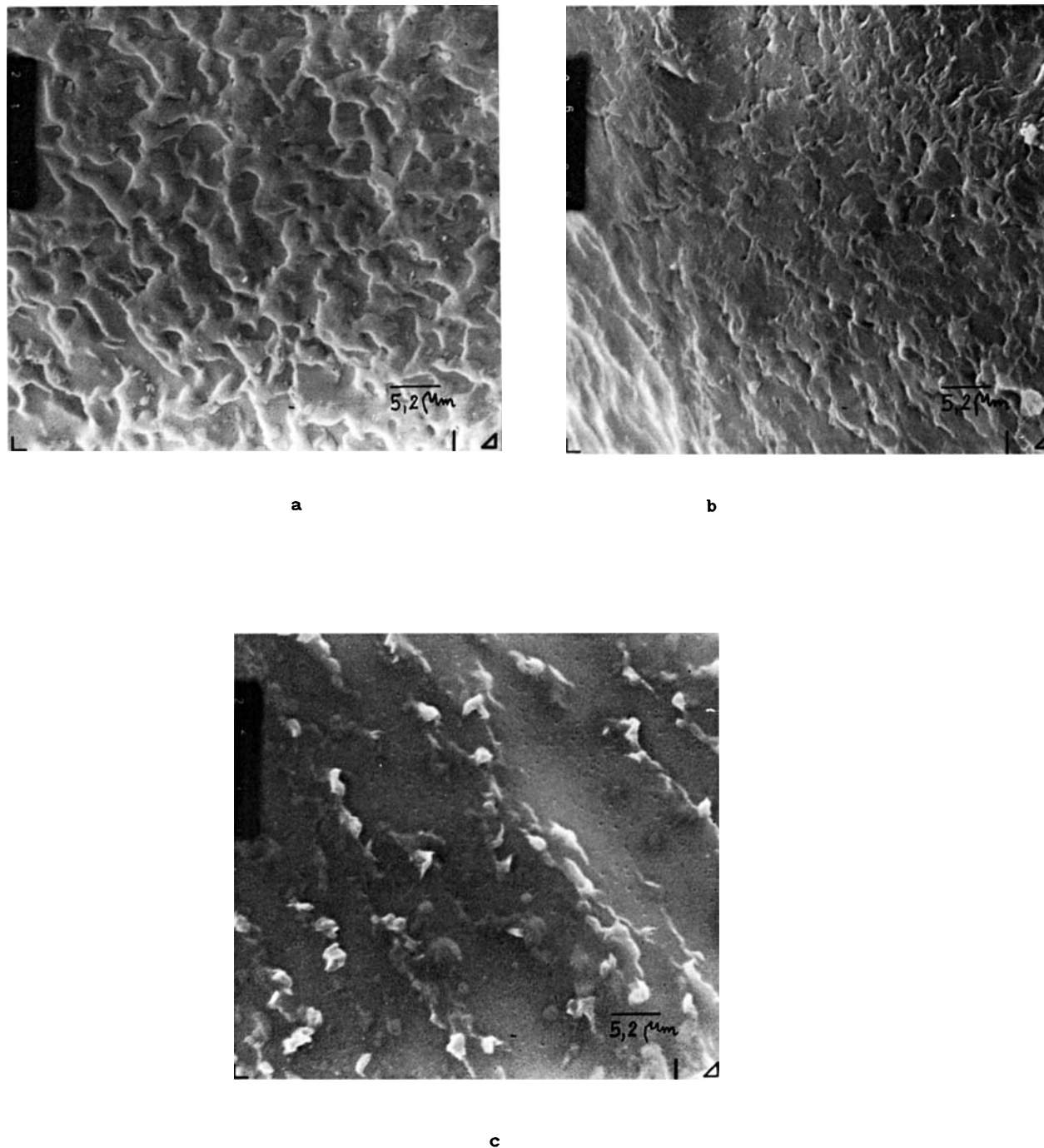
Figure 5   Micrographs of etched samples of PUI/SAN34 blends: (a) 60/40; (b) 50/50; (c) 40/60.

shows a two-phase structure; SAN34 and SAN24 are then rough on the surface.

Micrographs of etched samples of TPU/SAN and PUI/SAN are shown in Figures 4 and 5 and they show clearly a continuous and disperse phase for all blends. The density and average dimensions of the cavities increase with the increasing amount of SAN in the blends of TPU/SAN34 and TPU/SAN24. The dimension of the cavities is higher in the TPU/SAN34 than in the TPU/SAN24 blends, with the

same composition of blends. The diameter of the cavities is around 1.6 μm in the TPU/SAN34 blends and around 0.8 μm in the TPU/SAN24 blends.

In the PUI/SAN34 blends, the morphology is different because of the additional interactions between PUI and SAN34. On the micrographs of the PUI/SAN34 blends, we cannot see the cavities. The surfaces are rough, and when a higher concentration of PUI is in PUI/SAN34 blends, the roughness increases.

The regular distribution of SAN in the TPU proves that the selected technological conditions in preparing the TPU/SAN blends are sufficient to obtain a fine dispersion of the two polymers. Immiscibility of thermoplastic polyurethane and poly(styrene-co-acrylonitrile) in TPU/SAN blends were supported by sigmoidal, step-shaped plots, by some mechanical properties (tensile strength at break, elongation at break, Shore D hardness),[13] and by dielectric as well as thermal properties.[14] Our results indicate immiscibility in the whole rather than in the 30–70% composition range.[3] In the composition range with less than 25 wt % of either component, different morphology and interactions between TPU (PUI) and SAN were visible. The character of interactions (or dominant interaction) in TPU and in the PUR-rich range, respectively, differs from that in SAN-rich range. In TPU and in the PUI-rich range, respectively, mechanical behavior, structural characteristics, and dielectric and thermal properties show that SAN particles act as stress concentrators[15] and plasticizer. In the SAN-rich range, the polar acrylonitrile sequences have a dominant effect. Some similar statements were also found in the literature.[15]

CONCLUSIONS

Thermoplastic polyurethane and poly(styrene-co-acrylonitrile) (TPU/SAN) blends are immiscible within the composition range 30–70 wt % of TPU or SAN. In TPU-rich blends (75/25 TPU/SAN), SAN copolymer propagates the separation of hard and soft TPU segments. In SAN-rich blends (25/75 TPU/SAN), the interaction stage depends on

the acrylonitrile contents, i.e., interaction is predominantly determined by polarity and mobility of the SAN chains. Interactions are identified by the acrylonitrile and ionomer contents and the system becomes partially miscible.

In the study of morphology by SEM for the TPU/SAN blends, both continuous and dispersed phases were observed. The results show that the density and the average dimensions of the cavities increase when the amount of SAN in the blends is increased.

REFERENCES

1. D. R. Paul and S. Newman, Eds., *Polymer Blends*, Academic Press, New York, 1978, Vol. 1, p. 35.
2. M. Iskandar, C. Tran, and J. E. McGrath, *Polym. Prepr. Am. Chem. Soc.*, **24**, 126–129 (1983).
3. H. W. Bonk, R. Drzal, C. Georgacopoulos, T. M. Shah, in *Antec' 85*, Washington, DC, April, 1985, pp. 1300–1303.
4. M. Ratzsch, G. Handel, G. Pompe, and E. Meyer, *J. Macromol. Sci. A*, **27**, 1631–1655 (1990).
5. M. Ratzsch and J. Pionteck, in *Conference of Reactive Production of Polymeric Goods, Conference Proceedings*, Zagreb, September, 1990, pp. 06/1–06/4.
6. J. W. Rosthauser and K. Nachtkamp, *Adv. Urethane Sci. Technol.*, **10**, 121 (1987).
7. J. Blackwell and M. Ross, *J. Polym. Sci. Polym. Lett. Ed.*, **17**, 447–451 (1979).
8. J. W. C. van Bogart, P. E. Gibson, and S. L. Cooper, *J. Polym. Sci. Polym. Phys. Ed.*, **21**, 65–95 (1983).
9. H. G. Kilian and E. Jenckel, *Koll.-Zeit Zeit. Polym.*, **165**, 25–31 (1959).
10. K. W. Chau and P. H. Geil, *Polymer*, **26**, 490–500 (1985).
11. J. Blackwell and K. H. Gardner, *Polymer*, **20**, 13–17 (1979).
12. J. Blackwell, M. R. Nagarajan, and T. B. Hoitink, *Polymer*, **22**, 1534–1539 (1981).
13. B. Žerjal, Ž. Jelčić, I. Šmit, and T. Malavašič, *Int. Polym. Process.*, **2**, 123–125 (1992).
14. B. Žerjal, to appear.
15. D. N. Fox and R. B. Allen, in *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1985, Vol. 3, p. 758.