

Polyamide–Polyurethane Interpenetrating Polymer Networks Prepared by Synthesis in the Melt

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Synopsis

Two types of interpenetrating polymer networks based on polyamide (nylon 12) and a polyurethane formed in the polyamide melt were prepared. The first type (A), which could be regarded as a semi-2-IPN, consisted of a polyurethane component crosslinked with trimethylolpropane whereas for the second type (B), which would meet the definition of a thermoplastic IPN, the polyurethane component was chain-extended with butane-1,4-diol only. The phase morphologies of these IPNs were investigated using electron microscopy, dynamic mechanical analysis, tensile testing, and sonic velocity measurements. Electron micrographs were compared by using the conventional TEM technique and a Robinson-type backscattered electron detector in combination with a SEM. It was concluded that the materials are phase separated, but with a fine continuous-dispersed phase structure. For a 44 wt % polyurethane IPN a cocontinuous phase structure with a subcellular texture was indicated. One physically blended sample was compared with the analogous IPN-type sample.

INTRODUCTION

An interpenetrating polymer network (IPN) may be defined as a material composed of a pair of polymeric networks which have been prepared in such a way that at least one of the networks has been synthesized and/or crosslinked in the presence of the other. Formation of IPNs is, therefore, the only way of intimately combining crosslinked polymers. Most polymer pairs show phase separation because of their thermodynamic immiscibility. However, if mixing is accomplished simultaneously with crosslinking, phase separation may be kinetically controlled by permanent interlocking of entangled chains. However, these entanglements of the component networks occur in most cases to the greatest extent only at the phase boundaries. Several reviews have now been written about IPNs.¹⁻³

A semi-IPN is formed when one of the polymers is a network and the other is linear. If the first-formed polymer is the linear component, then the material is referred to as a semi-2-IPN. A thermoplastic IPN^{4,5} is defined as a IPN in which chemical crosslinks have been replaced by physical crosslinks, as, for example, the crystalline portions of semicrystalline polymers.

In this study, two polyamide (PA)–polyurethane (PU) IPN-type systems are discussed from the morphological point of view. The first system (A) comprises a linear polyamide (nylon 12) and a crosslinked polyurethane based on an isocyanate-terminated polyether urethane prepolymer, crosslinked with trimethylolpropane. These blends can be defined as semi-2-IPNs.

The second system (B) comprises the same linear polyamide and a polyurethane based again on a isocyanate-terminated polyether urethane prepolymer but only chain-extended with butane-1,4-diol. Although some allophanate and acylurea linkages⁶ may be present to some extent in the final products, these may, in this case, be called thermoplastic IPNs since they exhibit thermoplastic behavior at elevated temperatures.

Additionally, one IPN sample from system B was compared with the analogous sample of a physical polyamide-polyurethane blend.

EXPERIMENTAL

Materials

The polyamide used was Grilamid L20 which was kindly donated by EMS Chemie AG. It is a nylon 12 with a viscometrically determined molecular weight of 16,500 g/mol.

Adiprene L-100 and L-700 were kindly provided by Uniroyal Ltd. These isocyanate-terminated polyether urethane prepolymers had number average molecular weights of 1990 g/mol⁷ and 1700 g/mol, respectively.

Trimethylolpropane (TMP), used for crosslinking the urethane prepolymers, was supplied by Aldrich Chemicals. Butane-1,4-diol (BD), used as a chain extender, was supplied by BDH Chemicals Ltd., and the urethane catalyst used was Stanclere T 220 from Akzo Chemie.

Synthesis

The polyurethanes for system A were prepared from Adiprene L-100, butane-1,4-diol, and trimethylolpropane (BD : TMP in molar ratio 3 : 2) with the overall ratio of isocyanate to hydroxyl being 1.05 : 1. The polyurethanes for system B were prepared from Adiprene L-700 and butane-1,4-diol with the same isocyanate to hydroxyl ratio.

The pure polyurethanes were formed by mixing the prepolymers, chain extenders, crosslinking agents, and catalyst. The degassed mixture was then poured in a mold and hot-pressed at 190°C for 25 min. The resulting uniform, transparent sheets were post-cured for 4 h at 100°C.

The IPNs were formed in a Brabender Plastograph (type PL3S) fitted with a type 50 roller mixer. To the polyamide melt at about 210°C, the polyurethane prepolymer/chain extender/crosslinker mixtures were added. A characteristic time until the uncatalyzed polyurethane-forming reaction started was 3 min, and the reaction was then allowed to proceed during the mixing process for 5 min more. The homogeneous-looking materials were hot pressed to uniform sheets and post-cured for 4 h at 100°C.

The physical blend was also formed in the Brabender plastograph. To the polyamide melt at about 210°C, the linear polyurethane polymer of system B was added and mixed for 5 min. The, again, homogeneous-looking material was hot pressed to provide uniform sheet for subsequent investigation.

Techniques

The dynamic mechanical data were obtained using a dynamic mechanical thermal analyzer (Polymer Laboratories) at a frequency of 10 Hz and a heating rate of 2°C/min.

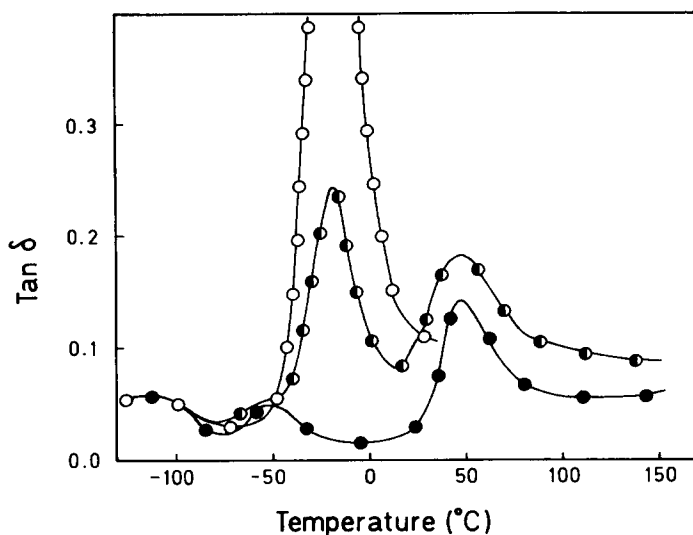


Fig. 1. $\tan \delta$ -temperature plots (10 Hz) of the polyamide (\bullet), the polyurethane (\circ), and of the IPN containing 44 (\ominus) wt % polyurethane from system A.

The stress-strain tests were conducted (20°C) on standard dumbbell specimens using a J. J. Lloyd tensile testing machine (type T5002) at a strain rate of 1.0 cm/min.

V_L , the longitudinal sonic velocity, was measured (20°C) with a Morgan pulse propagation meter (Model PPM-5R). This instrument operated at a resonant frequency of about 15 kHz.

Electron micrographs were obtained using a Hitachi HU-11B transmission electron microscope. The samples were hardened and stained with osmium tetroxide vapor prior to microtomy. The polyurethane phases are preferentially stained.⁸ A limited number of electron micrographs were also obtained with a scanning electron microscope employing a Robinson-type⁹ back-scattered electron detector.

RESULTS AND DISCUSSION

System A

Dynamic Mechanical Analysis

Four semi-2-IPNs were prepared containing 10, 27, 44, and 68 wt %, respectively, of the polyurethane network component. Figure 1 shows $\tan \delta$ vs. temperature plots for the homopolymers and for the 44 wt % PU IPN. The presence of three loss peaks is obvious for the polyamide component. The largest is the glass transition (T_g) at 49°C . Other investigators¹⁰ have recently determined it to lie at a temperature of 68°C , but their samples were specially dried before the measurements were made. It is known¹¹ that this α -peak is shifted to lower temperature by the absorption of water. The β -transition, which lies at -52°C , is believed to be a crankshaft-type motion involving a nonhydrogen-bonded amide group and several methylene carbon groups. Polymers with significant sequences of methylene groups exhibit transitions at

TABLE I
Dynamic Mechanical Data (10 Hz) for the Homopolymers and Semi-2-IPNs
from System A taken from the $\tan \delta$ -Temperature Curves

| Sample | T_g ($^{\circ}\text{C}$) | | $\tan \delta_{\max}$ | | Half-peak width ^a ($^{\circ}\text{C}$) | |
|-------------------|------------------------------|------|----------------------|------|---|----|
| | PU | PA | PU | PA | PU | PA |
| Polyamide (PA) | | + 49 | | 0.14 | | 42 |
| 10 wt % PU | | + 49 | | 0.14 | | 42 |
| 27 wt % PU | | + 50 | | 0.15 | | 47 |
| 44 wt % PU | - 18 | + 49 | 0.24 | 0.18 | 32 | 69 |
| 68 wt % PU | - 18 | | 0.77 | | 23 | |
| Polyurethane (PU) | - 18 | | 0.79 | | 24 | |

^aWidth of peak at half-height.

around -115°C . Dynamic mechanical data for various polyurethanes have been reported.¹² The glass transition of the soft segments is clearly seen at -18°C .

For the 44 wt % PU IPN, both glass transitions of the homopolymers occur at unshifted T_g values (see Table I), which is indicative of very substantial phase separation. However, a distinct broadening of the transitions (see Table I) suggests a certain degree of mixing at presumably, predominantly, the phase boundaries. The magnitude of the PU relaxation is considerably reduced. This may be attributed to the fact that the PA component is in the glassy state at this temperature. Consequently, certain PU segments intimately associated with PA-rich regions will experience restrictions to motion.

Figure 2 shows $\tan \delta$ vs. temperature plots for the 10, 27, and 68 wt % PU IPNs. The former two materials show only the polyamide loss peaks with

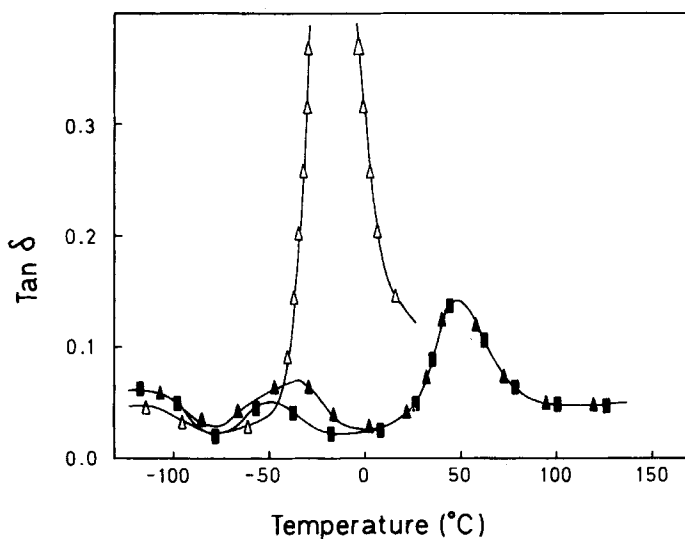


Fig. 2. $\tan \delta$ -temperature plots (10 Hz) of the IPNs containing 10 (■), 27 (▲), and 68 (Δ) wt % polyurethane from system A.

unshifted values of T_g (see Table 1), but for the 27 wt % PU sample also some peak broadening has occurred. In addition, the β -transition appears to have been split into a second component which lies at about -32°C . This could indicate some degree of mixing of the PU soft segments with methylene sequences in the PA. For both the 10 and the 27 wt % PU IPNs, the PU component is likely to be dispersed in the polyamide matrix. The 68 wt % PU IPN shows only the unaffected PU glass transition. Therefore, it will have a continuous PU phase. The occurrence of the unshifted transitions of only one component in each of these three cases indicates relatively poor interfacial adhesion. We have observed this phenomenon in other blends where a high level of incompatibility occurs. Therefore, the appearance of both components in the 44 wt % PU sample suggests at least more extensive mixing and possibly dual phase continuity.

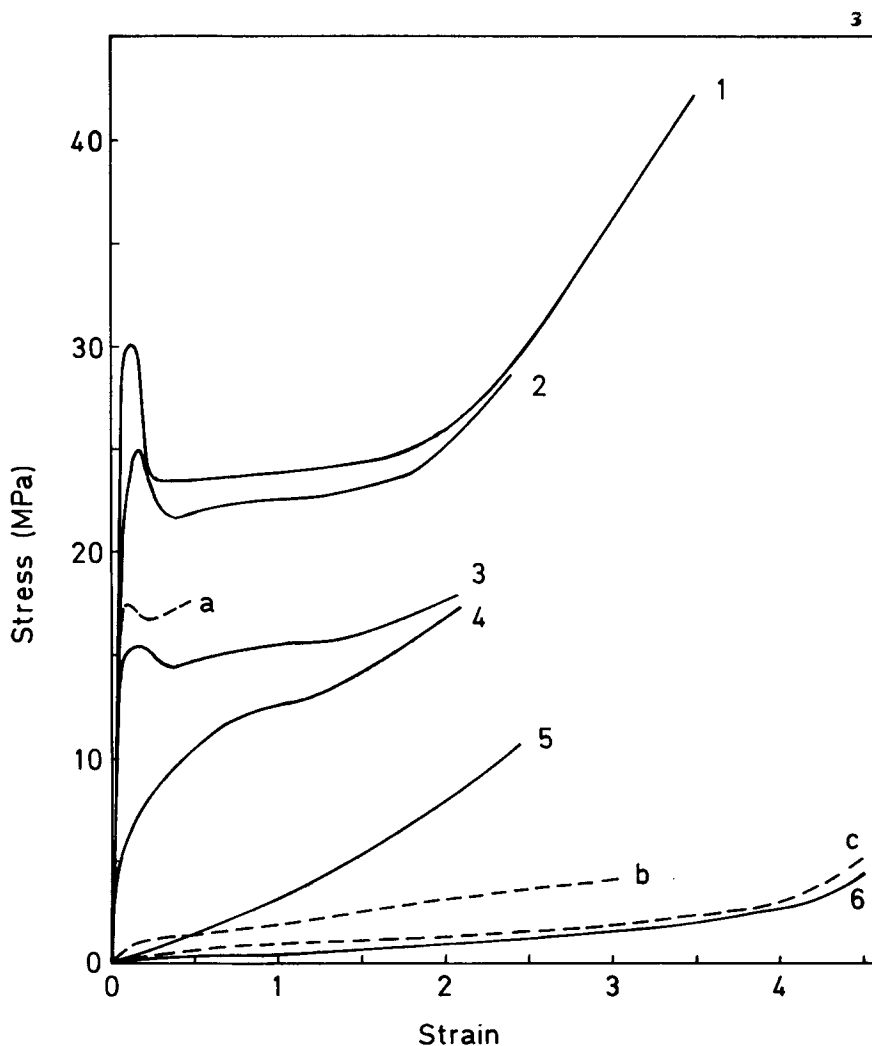


Fig. 3. Stress-strain curves (20°C) for the polyamide (1), the polyurethane (6), and the IPNs containing 10 (2), 27 (3), 44 (4), and 68 (5) wt % polyurethane from system A and polyurethane (c) and the IPNs containing 28 (a) and 79 (b) wt % polyurethane from system B.

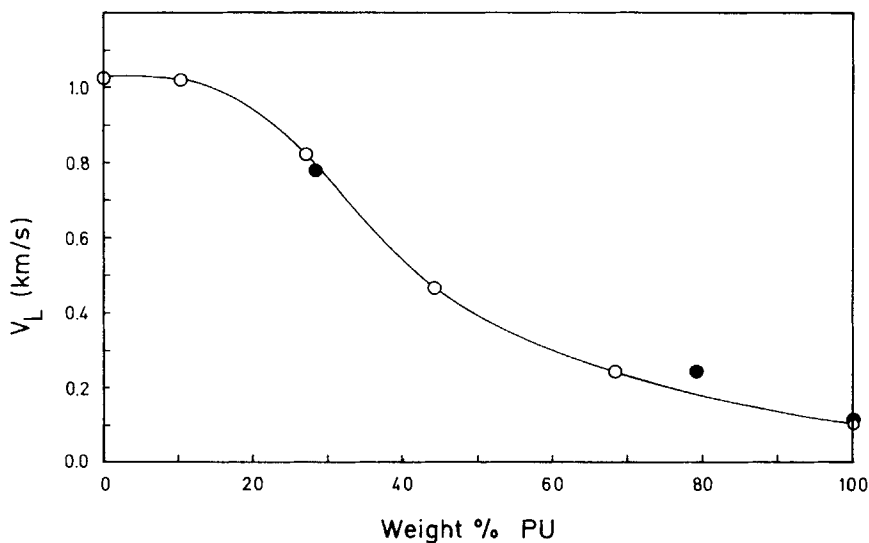


Fig. 4. V_L -composition data for the polyamide-polyurethane IPNs and for the constituent polymers from system A (○) and from system B (●).

The storage (E') moduli and the loss (E'') moduli data confirm the trends reported above for the $\tan \delta$ -temperature data.

Stress-Strain Analysis

Figure 3 shows the stress-strain behavior of both the homopolymers and of the four IPNs. The latter all exhibit a substantial decrease in the elongation to break compared to that of the pure components. In accordance with the DMA data, the curves for the 10 and 27 wt % PU IPNs reflect the existence of a continuous PA phase, whereas the curve for the 68 wt % PU IPN indicates a

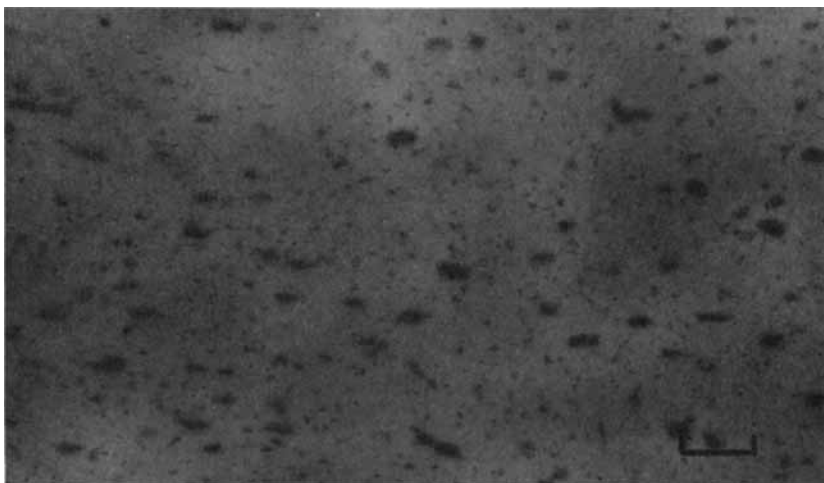


Fig. 5. Transmission electron micrograph of the polyamide-polyurethane IPN from system A containing 10 wt % polyurethane. The scale mark represents 500 nm.

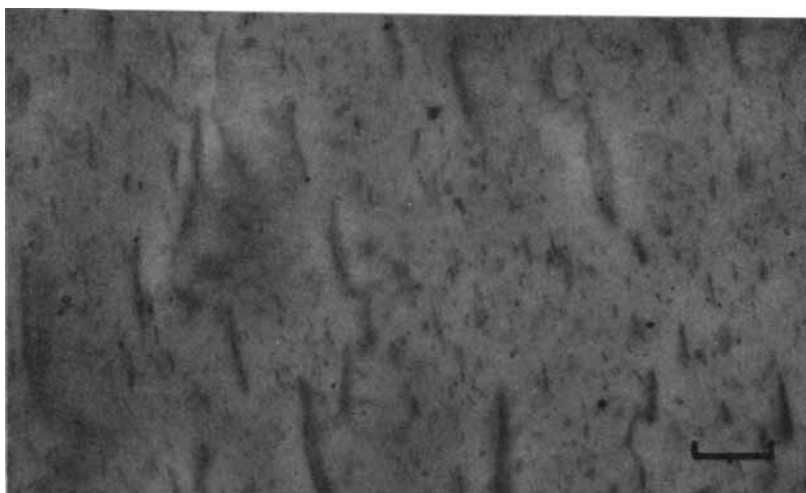


Fig. 6. Transmission electron micrograph of the polyamide-polyurethane IPN from system A containing 27 wt % polyurethane. The scale mark represents 500 nm.

continuous PU phase. The 44 wt % PU IPN shows an intermediate behavior. It exhibits a relatively high initial modulus, but does not show yielding.

Sonic Velocity Data

Rubbery materials have low longitudinal sonic velocities (below 0.5 km/s) relative to plastics. The V_L values of the homopolymers and of the four IPNs are shown in Figure 4. An S-shaped curve has been reported before for blended materials exhibiting phase inversion.^{13,14} The data for system A imply substantial phase separation.

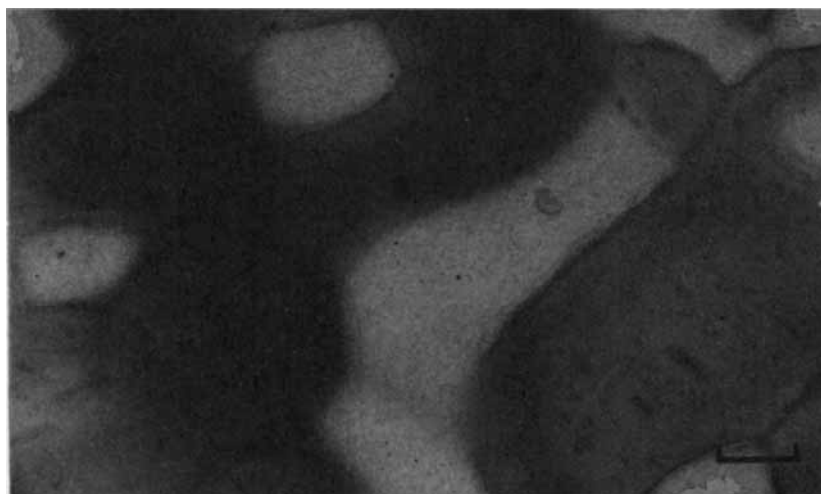


Fig. 7. Transmission electron micrograph of the polyamide-polyurethane IPN from system A containing 44 wt % polyurethane. The scale mark represents 500 nm.

Electron Microscopy

Figures 5, 6, and 7 are transmission electron micrographs of the 10, 27, and 44 wt % PU IPNs, respectively. The dark areas in the micrographs are PU-rich regions.⁸ It is clear from Figure 6 that the PU at the 10 wt % level is present as discrete phases in a PA matrix. When the PU concentration is raised to 27 wt %, the PU-rich regions still appear to be discrete, but are elongated. This is not surprising for a situation in which the PU has formed under fairly high shear conditions. The 44 wt % PU IPN (Fig. 7) shows an interesting morphology. Large, elongated PU-rich domains are interspersed by PA-rich regions. It was not possible to decide from the electron microscopic evidence whether dual-phase continuity had been achieved in this material.

Electron micrographs of fracture surfaces taken with a scanning electron microscope equipped with a Robinson-type backscattered electron detector showed rather poor contrast compared to that obtainable by TEM.

System B*Dynamic Mechanical Analysis*

Two thermoplastic IPNs were prepared containing 28 and 79 wt % PU, respectively. It was not possible to form a macroscopically homogeneous IPN with about a 50 wt % PU content. Figure 8 shows $\tan \delta$ vs. temperature plots for the homopolymers and the two IPNs. Certain dynamic mechanical data are also presented in Table II. The occurrence of only one T_g in each IPN indicates for both cases, similar to system A, a continuous-dispersed phase morphology with the same low level of mechanical coupling between the components. The origin of the transition around -32°C for the 28 wt % PU IPN has already been speculated about for system A.

The data in Table II are consistent with a high degree of incompatibility.

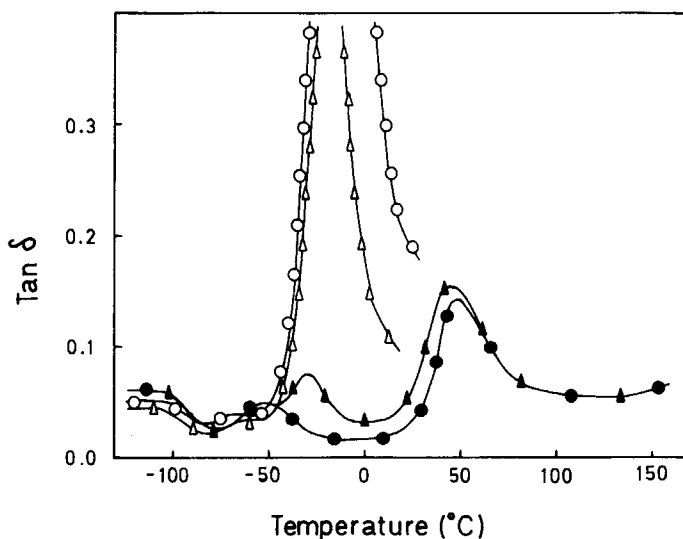


Fig. 8. $\tan \delta$ -temperature plots (10 Hz) of the polyamide (●), the polyurethane (○), and of the IPNs containing 28 (▲) and 79 (△) wt % polyurethane from system B.

TABLE II
Dynamic Mechanical Data (10 Hz) for the Homopolymers and Thermoplastic IPNs
from System B taken from the $\tan \delta$ -Temperature Curves

| Sample | T_g (°C) | | $\tan \delta_{\max}$ | | Half-peak width ^a (°C) | |
|-------------------|------------|------|----------------------|------|-----------------------------------|----|
| | PU | PA | PU | PA | PU | PA |
| Polyamide (PA) | | + 49 | | 0.14 | | 42 |
| 28 wt % PU | | + 46 | | 0.16 | | 46 |
| 79 wt % PU | - 19 | | 0.51 | | 26 | |
| Polyurethane (PU) | - 15 | | 0.93 | | 28 | |

^aWidth of peak at half-height.

Stress-Strain Analysis

Figure 3 shows the stress-strain behavior of the homopolymers and of the two IPNs. The 28 wt % PU IPN shows a low elongation to break but was otherwise indicative of a situation where the PA component constituted a continuous phase. Clearly the PU component provides the continuous phase for the high PU-content IPN. The curves labeled a and 3 correspond to IPNs of virtually identical PU content, but in the latter case the PU is crosslinked. The most obvious difference is in extensibility. More work is, however, necessary to determine whether this always happens on crosslinking.

Sonic Velocity Data

The values of V_L for the two IPNs are shown in Figure 4. There are not enough data points to draw a final conclusion, but the behavior is apparently very similar to that of system A.

Physical Blend

A physical blend containing 30 wt % of a linear, preformed PU was prepared using the Brabender plastograph. It may be compared with the thermoplastic IPN containing 28 wt % PU. Figure 9 shows $\tan \delta$ vs. temperature plots for these two samples. As was the case for the IPN sample, the physically blended material showed evidence for a continuous-dispersed phase structure, but it showed no temperature shift for the glass transition of the polyamide component and a smaller shift of the β -transition. This indicates that there is even less mixing in the physical blend than is the case for the IPN.

Figures 10 and 11 are transmission electron micrographs of the 28 wt % PU IPN (system B) and the 30 wt % PU physical blend, respectively. The former shows a continuous-dispersed phase morphology with a wide range of domain sizes of the PU-rich component. Figure 11 shows a more strongly phase-separated morphology in which the PU-rich phases are somewhat more elongated than was the case for the IPN. In the latter case an already established PU was blended with the PA melt, while in the former the PU was polymerised in the PA melt. The elongated phases in Figure 11 are typical for melt-blended, incompatible polymers.

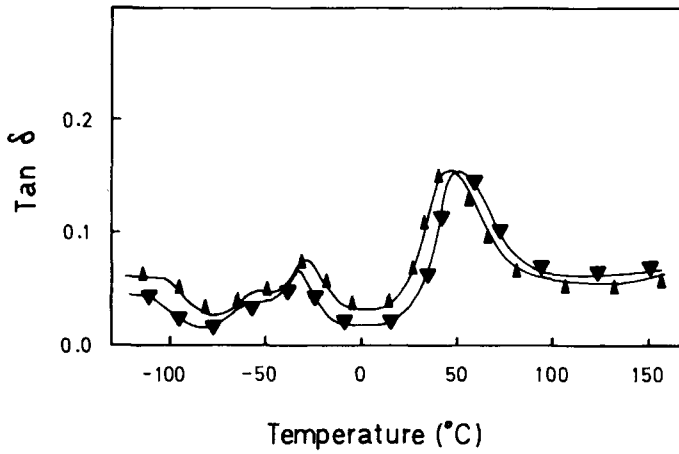


Fig. 9. Tan δ -temperature plots (10 Hz) of the IPN containing 28 (\blacktriangle) wt % polyurethane from system B and of the physical blend containing 30 (\blacktriangledown) wt % of a linear polyurethane.

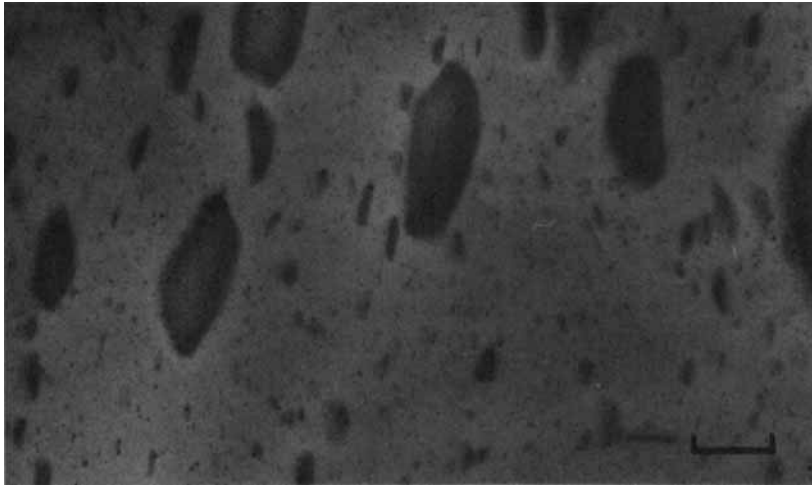


Fig. 10. Transmission electron micrograph of the polyamide-polyurethane IPN from system B containing 28 wt % polyurethane. The scale mark represents 500 nm.

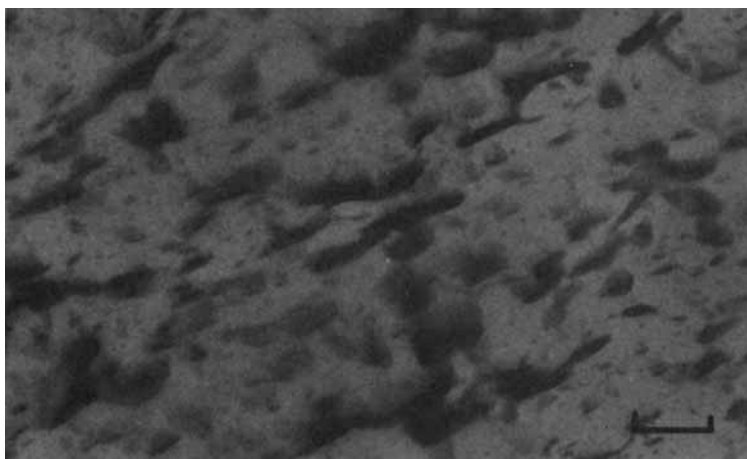


Fig. 11. Transmission electron micrograph of the polyamide-polyurethane physical blend containing 30 wt % of a linear polyurethane. The scale mark represents 500 nm.

References

1. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum, New York, 1981.
2. D. Klemperner, K. C. Frisch, H. X. Xiao, E. Cassidy, and H. L. Frisch, in *Advances in Chemistry Series 211*, D. R. Paul and L. H. Sperling, Eds., Am. Chem. Soc., Washington, DC, 1986.
3. L. H. Sperling, in *Advances in Chemistry Series 211*, D. R. Paul and L. H. Sperling, Eds., Am. Chem. Soc., Washington, DC, 1986.
4. W. P. Gergen, *Kautsch. Gummi*, **37**, 284 (1984).
5. J. M. Widmaier, J. Hubert, and G. Meyer, *Macromol. Chem.*, **183**, 249 (1982).
6. C. Hepburn, *Polyurethane Elastomers*, Applied Science, London, 1982.
7. D. J. Hourston and Y. Zia, *Polymer*, **20**, 1497 (1979).
8. S. C. Kim, D. Klemperner, K. C. Frisch, W. Radigan, and H. L. Frisch, *Macromolecules*, **9**, 258 (1976).
9. V. N. E. Robinson, *J. Phys. E: Sci. Instrum.*, **8**, 638 (1975).
10. E. S. Ong, Y. Kim, and H. L. Williams, *J. Appl. Polym. Sci.*, **31**, 367 (1986).
11. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, London, 1967.
12. J. Ferguson, D. J. Hourston, R. Meredith, and D. Patsavoudis, *Eur. Polym. J.*, **8**, 369 (1972).
13. D. J. Hourston and I. D. Hughes, *J. Appl. Polym. Sci.*, **21**, 3099 (1977).
14. D. J. Hourston and I. D. Hughes, *Polymer*, **18**, 1175 (1977).

Received July 29, 1987

Accepted October 13, 1987