

# Polyurethane–Polypropylene Blends

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## SYNOPSIS

Five series of blends were obtained by mixing five polyurethanes (PUR), based on polypropyleneoxide, MDI, and butanediol, with polypropylene (PP). The structure of PUR was varied by varying soft segment length (MW = 1000 and 2000) and soft segment concentration (50, 60, and 70%). It has been shown that interaction between PUR and PP was better in the case of PUR with the polyol of MW = 1000. The addition of lower molecular weight PUR produced an easy flowing material in the molten state, comparable with the "control rheology PP." The morphology of the blends changed with PUR concentration. At 30% PUR the dispersed phase tended to agglomerate in the form of long cylinders. Mechanical properties generally were affected by the change of morphology.

## INTRODUCTION

Elastomers are frequently used as impact modifiers of polypropylene. Apart from imparting better impact properties, they can influence processing and other characteristics of the composite. Introduction of the very polar PUR to the nonpolar PP gives to composites some new properties, not found in the neat PP, such as the possibility of printing. Polyurethanes may act as stabilizers since urethane groups have properties of secondary amines. The effect of the elastomer depends on its chemical structure as well as the interaction between the two polymers. The conditions required for good impact behavior of the composite involve good phase separation of matrix and elastomer (i.e., immiscibility of the two phases), good dispersion of the elastomer in the matrix in the form of regular (round) particles, good bonding of either a physical or chemical nature between the phases, proper particle size of the dispersed phase, and proper viscoelastic properties of both phases during mixing.<sup>1</sup>

To obtain good phase separation and adhesion between the matrix and the dispersed elastomer, the difference between their solubility parameters must

not be great. Good adhesion may be obtained on account of partial mixing of the phases. Polypropylene is a nonpolar, semicrystalline polymer, immiscible with other polymers due to its high crystallinity. Although polyurethane (PUR) elastomers are block copolymers of very polar nature, their properties depending on the chemical nature of both blocks (segments), as well as their length and concentration. They are two phase polymers due to immiscibility of the soft and rigid (hard) segments. If the soft segments are based on polypropyleneoxide (PPO), then some similarity with the polypropylene matrix may be expected. In this work, diphenylmethane diisocyanate (MDI)/butanediol/PPG based polyurethane elastomers were mixed with polypropylene and the structure of the composites examined. The concentration of the polyurethanes (PUR) in polypropylene was varied. The structure of polyurethanes was varied by varying soft segment molecular weight (1000 and 2000), and soft segment concentration (50, 60, and 70%). However, polyurethanes based on PPO 1000, at 70% soft segment concentration (SSC), were semiliquid and thus unsuitable for mixing. Five series of blends were obtained by mixing PP with five polyurethanes at different concentrations. The effect of polyurethane composition, i.e., soft segment length and soft segment concentration, on phase interaction, blend morphology, and mechanical properties of these compounds will be presented in this work.

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**Table I Designation of Polyurethane Samples and Their Composition**

Designation	PUR I	PUR II	PUR III	PUR IV	PUR V
Composition	PPO1000 50% SSC	PPO1000 60% SSC	PPO2000 50% SSC	PPO2000 60% SSC	PPO2000 70% SSC
Intrinsic viscosity (dL/g)	0.1	0.3	0.3	0.2	0.1

## EXPERIMENTAL

### Materials

The polypropylene "Hipolen MA-3" is a commercial product of Hipol, Odžaci, Yugoslavia, having melt flow rate (MFR) of 11 g/10 min. The polyurethanes used in this study were synthesized from polypropyleneglycols, MDI, and butanediol. Two polyols, having nominal molecular weights 1000 and 2000 (PPO1000 and PPO2000), were produced by Soda-So, Tuzla, Yugoslavia. Their number average molecular weights were 870 and 1800, respectively. Suprasec MPR is distilled MDI produced by ICI (U.K.). It was used as delivered. Reagent grade butane diol was distilled before synthesis.

### METHODS

The synthesis of the polyurethanes was carried out using the prepolymer technique, where polyol and MDI were reacted for 1 h at 80°C and then butane diol was added. Heating was continued for 24 h at 100°C. Soft segment concentrations (SSC) were 50, 60, and with polypropyleneglycol MW = 2000 also 70%. Designation of the PUR samples and their composition is given in Table I. The resulting polyurethanes were of rather low molecular weight as

characterized by their intrinsic viscosities in dimethylformamide at 25°C. The polyurethanes were mixed with polypropylene at 180°C in a laboratory internal mixer, Haake Rheomix, Model EU-5 at 45 rpm, for 5 min. The blends were compression molded into plaques 0.5 and 3 mm thick, at 230°C for 2 min under pressure of 7 MPa, with subsequent cooling in the mold at natural rate. Designation of the blends and their composition is given in Table II.

Melt flow rate was measured according to ASTM D 1238-65T, at 230°C and the load of 19.62N (2 kg). Density was measured by immersion in alcohol using a Mohr balance. Tensile properties were measured on an Instron tensile machine, Model 1122. A DuPont differential scanning calorimeter, Model 910 was used to study thermal transitions. Dynamic mechanical analyses were carried out on the DuPont DMA, Model 981 and Polymer Laboratories MDTA machine. A DuPont thermomechanical analyzer, Model 943, was used to measure expansion coefficients. A heating rate of 10°/min was used in the DSC and 5°/min in DMA and TMA. Izod notched impact strength was measured according to ASTM D 256. Wide angle X-ray analysis was conducted using a Philips X-ray diffractometer while a Jeol scanning electron microscope was used to study the morphology of the broken surfaces of the nitrogen cooled samples.

**Table II Designation and Composition of PP/PUR Blends**

% of PUR in the Blend	5	10	15	20	30	40	50
Series I (PPO1000 50% SSC)	I-1	I-2	I-3	I-4	I-5	I-6	I-7
Series II (PPO1000 60% SSC)	II-1	II-2	II-3	II-4	II-5	II-6	II-7
Series III (PPO2000 50% SSC)	III-1	III-2	III-3	III-4	III-5	III-6	III-7
Series IV (PPO2000 60% SSC)	IV-1	IV-2	IV-3	IV-4	IV-5	IV-6	IV-7
Series V (PPO2000 60% SSC)	V-1	V-2	V-3	V-4	V-5	V-6	V-7

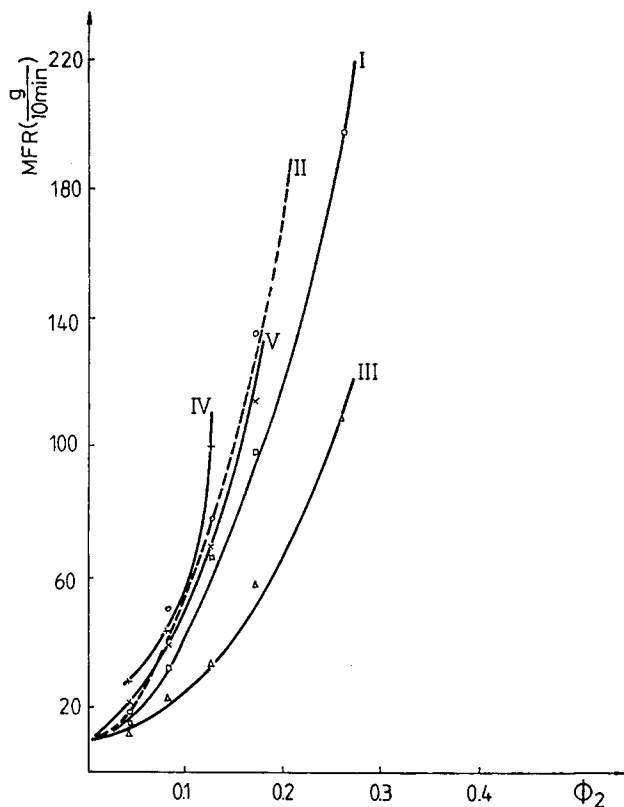


Figure 1 Melt flow rate vs. composition of blends.

## RESULTS AND DISCUSSION

### Physical and Mechanical Properties of Blends

The melt flow rate of the blends, as shown in Figure 1, increased drastically with the addition of the polyurethanes. This was explained by their low molecular weight and possibly a small amount of unreacted polyol acting as a lubricant. No particular effect of the polyurethane type could be observed

except that the series with 50% SSC, i.e., series I and III, displayed lower MFR values than the other series. It is interesting that in this way melt flow rates characteristic of "control rheology" polypropylenes can be easily obtained. This effect deserves more attention, but present results do not allow further elaboration.

Polypropylene/polyurethane blends could be processed only if the polyurethane content was below 30%. In some cases even that limit could not be reached because the polyurethane particles tended to agglomerate and to form a continuous phase, which sticks to the press platens and is consequently removed from the samples. The 0.5 mm sheets were slightly yellowish. The quality of the samples is seen from the density measurements and the departure from the calculated values. The density of the samples was compared to that of the linear mixture equation (LME):

$$\rho_m = \phi_1\rho_1 + \phi_2\rho_2 \quad (1)$$

where  $\rho_m$  is the density of the mixture,  $\rho_1$  and  $\rho_2$  are component densities, and  $\phi_1$  and  $\phi_2$  corresponding volume fractions. Density of the polyurethanes was about  $1.1 \text{ g/cm}^3$ , and did not vary appreciably with the structure.

Considerable differences between experimental and LME values exist. Figure 2 demonstrates the limited precision of the method, as well as probably the presence of air at the highest concentrations of polyurethane. However, density of the samples is close to that predicted by LME up to 30 wt % of PUR, i.e., in the range of concentrations used for other measurements.

Yield strength of the composites is expected to decrease with the increase of the volume concentration of PUR. Figure 3 shows that such behavior is

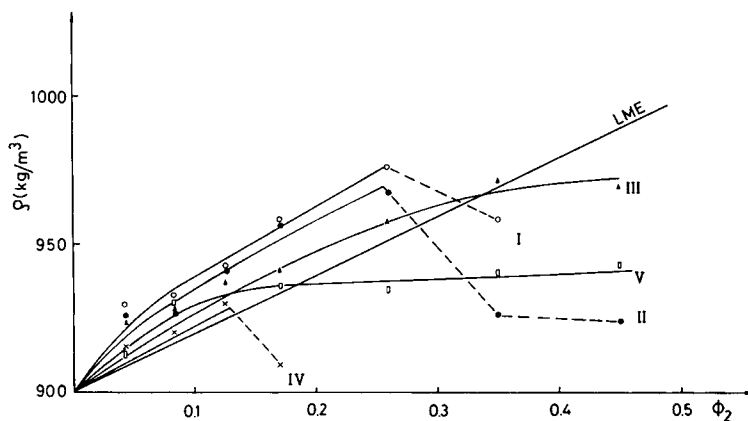


Figure 2 Dependence of density on the blend composition.

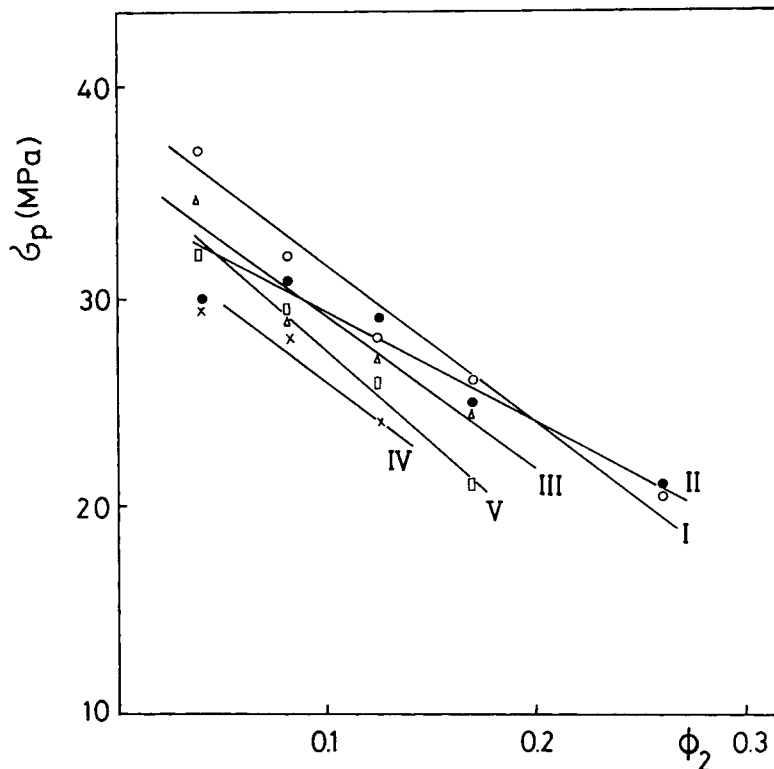


Figure 3 Yield strength vs. composition of the blends.

generally observed. A change in the trend at  $\phi_2 = 0.25$  may be explained by the change in morphology. Tensile properties were examined on the nonstandard, 0.5 mm thick samples. Elongation at break of the neat PP was only a few percent and tended to decrease with the addition of PUR.

The moduli of elasticity of the composites were modeled by the Nielsen model<sup>2</sup>:

$$\frac{M}{M_1} = \frac{1 + AB\phi_2}{1 - B\psi\phi_2} \quad (2)$$

where

$$A = k_E - 1$$

$$B = [(M_2/M_1) - 1]/[(M_2/M_1) + A]$$

$$\psi = 1 + [(1 - p_f)/p_f^2] * \phi_2$$

with the  $\psi$  parameter characterizing filling properties of the dispersed phase.  $p_f$  is the packing coefficient, being 0.64 for dense statistical packing of monodisperse sphere.  $k_E$  is Einstein's parameter. Here,  $M$ ,  $M_1$ , and  $M_2$  refer to the moduli of the blend, matrix, and the dispersed phase.

As can be seen from Figure 4, moduli of series III and V follow Nielsen's predictions whereas those for the other three series are higher than expected, which can be ascribed to the higher crystallinity of PP, probably due to the more favorable crystallization conditions during sample preparation. Notched Izod impact strength is one of the key properties of the composites. Figure 5 shows that it increases with the volume fraction of PUR up to about 15% and then drops. This was associated with increased particle size above 15% PUR and the change of morphology of the composites. It has been found<sup>3</sup> that the optimal size for elastomer particles as an impact modifier is about 0.5  $\mu\text{m}$ , with distribution between 0.1 and 1  $\mu\text{m}$ . In this case, average particle size was above this critical level and the distribution also wider. An increase of SSC led to a decrease of impact strength. With the exception of series IV, longer soft segments reduced impact strength.

#### Phase Interaction in PP/PUR Blends

The properties of the polyurethane/polypropylene blends are largely dependent on the interaction between the two phases. The scale of interaction can

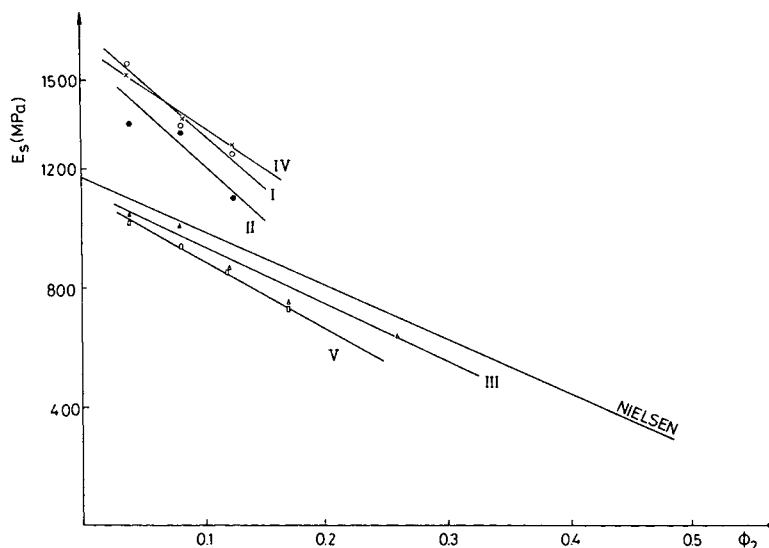


Figure 4 The effect of composition on the flexural modulus of the blends.

be assessed from the solubility parameters of the components in the mixture. The solubility parameter  $\delta$  of polypropylene was calculated, using the group contribution method<sup>4</sup> and Hoy tables, to be  $16.8 \text{ (J/cm}^3\text{)}^{1/2}$ , whereas that for polyurethanes (70% SSC) is  $19.2 \text{ (J/cm}^3\text{)}^{1/2}$  and varies slightly with the soft segment concentration (SSC) of the

polyurethane. However, polyurethanes themselves are two-phase systems consisting of rigid hard segments, having in our case  $\delta = 23.4\text{--}24.1 \text{ (J/cm}^3\text{)}^{1/2}$  and polypropyleneoxide (PPO) soft segments whose calculated solubility parameter is  $17.2 \text{ (J/cm}^3\text{)}^{1/2}$ . The solubility parameters of similar polyurethanes are discussed in the literature.<sup>5</sup> In a three-component system, such as the mixture of a homopolymer with a copolymer, miscibility is possible even if individual components are immiscible, since the effective  $\chi$  parameter,  $\chi_{ef}$ , is a complex function of individual interaction parameters<sup>6,7</sup>:

$$\chi_{ef} = \phi_2 * \chi_{12} + \phi_3 * \chi_{13} - \phi_2 * \phi_3 * \chi_{23} \quad (3)$$

where  $\phi$  is the volume fraction of the component in the index and  $\chi$  is an individual interaction parameter between components given in the index. In our case, index 1 may refer to polypropylene, 2 to PPO, and 3 to the hard segment in the polyurethane.

For the case of a mixture containing PP and PUR with 50% SSC,  $\chi_{ef}$  is 0.174 while  $\chi_{12}$  is 0.0030, and  $\chi_{13}$  is 0.987 while  $\chi_{23}$  is 1.093. Application of eq. (3) is correct if the copolymer is random and not segmented as is the case with polyurethanes. If the blocks are long enough, they may behave as homopolymers. The interaction parameter between PP and PPO is rather small and close to zero, suggesting that some degree of mixing may take place. Only the amorphous part of the polypropylene, which accounts for 40% of the PP mass, may be mixed on the molecular level with another polymer or segment

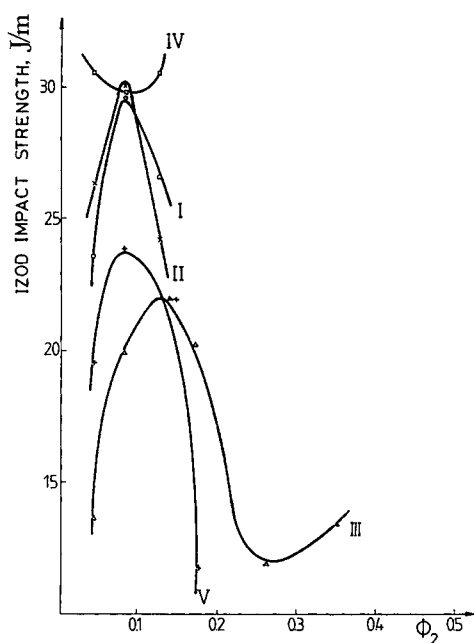


Figure 5 Dependence of notched Izod impact strength on the composition of the blends.

of a polymer. The interaction between the two phases in the immiscible blend can be estimated from the mechanical or dielectric behavior or observed directly by electron microscopy.

Polyurethanes with 50% SSC are hard elastomers while those with 60 and 70% SSC have considerably lower hardness due to the transition from bicontinuous phases to a continuous soft phase at higher SSC. Better phase separation in the polyurethanes is expected in samples with lower SSC which have longer hard segments. In the case of partial mixing of PP and polyurethanes,  $T_g$  of the PPO in polyurethanes (which is about  $-20^\circ\text{C}$  for the PPO1000 and  $-40^\circ\text{C}$  for PPO2000) is expected to rise and that of PP (about  $-10^\circ\text{C}$ ) to decrease. The DSC curves of all the samples were relatively featureless.  $T_{g\text{PPO}}$  was unclear due to the low concentration of the species in the sample, whereas the PP displayed transition in the region at  $40\text{--}60^\circ\text{C}$  ascribed to the presence of the atactic component and to melting at about  $165^\circ\text{C}$ . The maxima of the melting endotherms were at  $167^\circ\text{C}$  and did not vary with the type of blends.

In principle, better information about any interaction is obtained from dynamic mechanical analysis (DMA). On  $\tan \delta$  vs. temperature curves for series

I, using neat PP as reference, a characteristic  $\alpha$ -peak for the PP glass transition is observed at  $24^\circ\text{C}$  and shoulders at between  $-7$  and  $-15^\circ\text{C}$ , characterizing the glass transition of the soft segment in the polyurethanes. In samples based on PUR with PPO2000, soft segment glass transition ( $\beta$ -peak) appeared as a distinct peak at about  $-30^\circ\text{C}$ . In most polymers, a peak at about  $90^\circ\text{C}$  (designated  $\alpha'$ ) appeared. The origin of this maximum was puzzling since it did not exist in the other samples in the series or in the PP. This temperature, however, coincides with the hard segment glass transition. The peak may be also caused by decrease of modulus combined with a softening of the polyurethanes. Direct comparison of the transition temperatures obtained by the resonance type of dynamic measurements, such as in DMA, may be misleading if they are measured at different frequencies (which are continuously changing). By increasing the fraction of polyurethane in the PP matrix, modulus of the mixture decreases more rapidly with temperature and a shift to lower temperatures is expected. Roughly, this trend was observed.

$T_\alpha$  for neat PP is  $24^\circ\text{C}$ , whereas in the blends this peak was shifted to lower temperatures a few degrees but no clear trend could be observed. In most

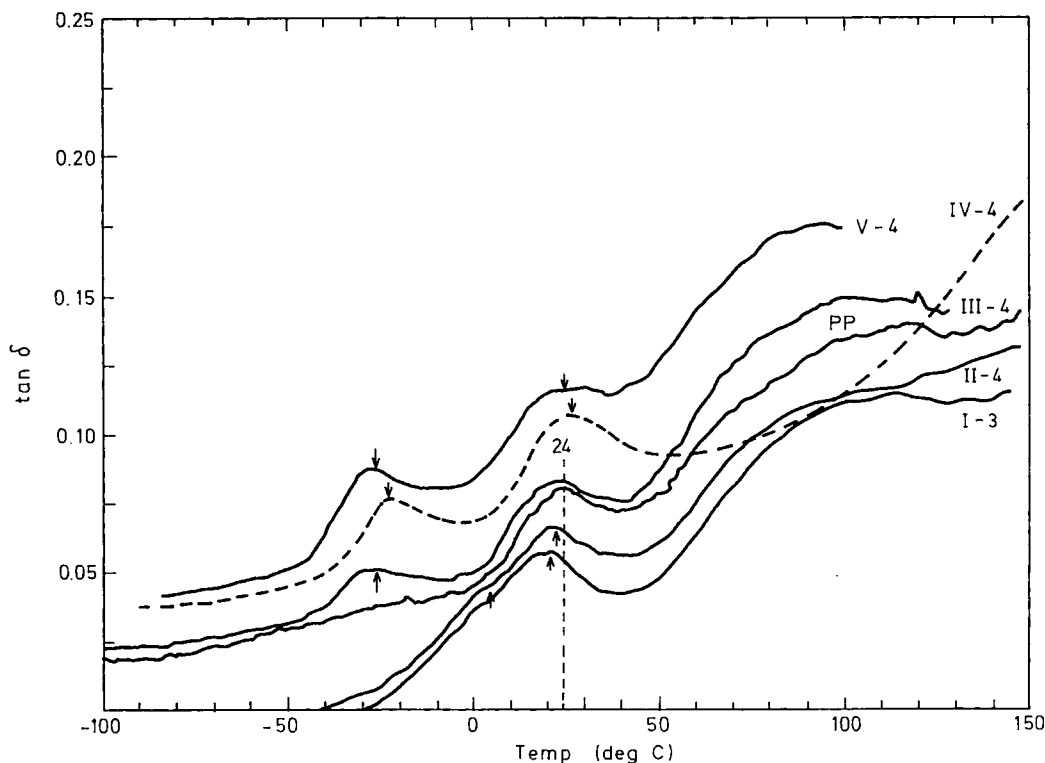


Figure 6  $\tan \delta$  curves at 10 Hz of selected PP/PUR blends.

series, samples with 20% PUR showed higher  $T_\alpha$  than samples with 10 and 30% PUR. This fact has no clear explanation. Heterogeneity of the samples which could not be controlled, the complex structure of polyurethanes with the high fraction of low molecular species, even monomers, and any experimental error may all have contributed to the overall unclear picture. The  $\beta$  temperature also did not change regularly with PUR concentration. Those few measurements carried out at constant frequency of the DMTA machine (Fig. 6) showed that  $T_\alpha$  decreased by a few degrees in the presence of PPO1000-based polyurethanes. This indicates that some degree of interaction between PP and PUR exists. However, no effect was observed with PPO2000-based polyurethanes.

Thermomechanical curves of PP/PUR blends show a transition in the region between 40 and 80°C and softening prior melting, at about 150°C. The transition at about 40°C is one observed in DSC, and it was ascribed to the presence of atactic PP. Although no clear indications of the PP and PUR glass transitions were observed, additional information on the interaction between phases can be obtained from the slope of the TMA curves, i.e., from coefficients of expansion. In the case of good adhesion between phases, the composite coefficient of expansion should follow the linear mixture equation (LME):

$$\alpha_m = \phi_1\alpha_1 + \phi_2\alpha_2 \quad (4)$$

where  $\alpha_m$ ,  $\alpha_1$ , and  $\alpha_2$  are linear expansion coefficients of the mixture, component 1, and component 2 and  $\phi$  their corresponding volume concentrations.

The effect of polyurethane volume concentration on the linear expansion coefficient at 20°C, in all series was complex and did not obey a linear mixture equation. At -20°C this relationship was more regular. This could be explained by the heterogeneity of the samples or complexity of the systems above the glass transition of polyurethanes and in the region of  $T_g$  of the PP, or even by a combination of both causes. In addition, the poor adhesion of the phases may cause departure from the LME. Interphase bonding will be assessed more directly by electron microscopy.

Calculations show that the introduction of the polyurethanes in the polypropylene will produce a two-phase system with the possibility of good interactions between PPO on the particle surface and PP, which should be reflected in the properties and the morphology of the samples.

## Morphology of PP/PUR Blends

The morphology of the blends can be considered at two levels: At the level of the matrix where addition of PUR may affect the degree of crystallinity and the size of the crystalline forms of the PP matrix, and at the level of the composite where the size and the shape of PUR particles play the major role.

The degree of crystallinity of the sample is expected to decrease due to the addition of the generally noncrystalline PUR. Figure 7 displays the decrease of the degree of crystallinity of the composite with increase in PUR weight concentration. Assuming that the contribution of PUR to the amorphous halo is proportional to its weight fraction, the degree of crystallinity of the PP matrix can be calculated. These values show that the degree of crystallinity of PP stays constant or even increases slightly as the concentration of PUR is increased. This fact suggests that crystallization of the two phases was carried out separately at all stages, and there was no mixing between PUR and PP even in the molten state (180°C). The degree of crystallinity of the matrix was about 60%. The morphology change of the mixture can be easily followed by the polarizing microscope.

Figure 8 shows a series of microphotographs illustrating the effect of increasing concentration of PUR. At 5% PUR, spherulites are clearly discernible. At 10 and 15% PUR and partly crossed polarizers, PUR particles become visible. They are well dispersed throughout the crystalline matrix. At 20% PUR and higher, PUR particles assume elongated shapes and their size increases, tending to form the continuous phase at 40% PUR. The effect of increased concentration is clearly seen by the electron micrograph in Figure 9. Here, PUR particles on the broken surface (in liquid nitrogen) were washed out

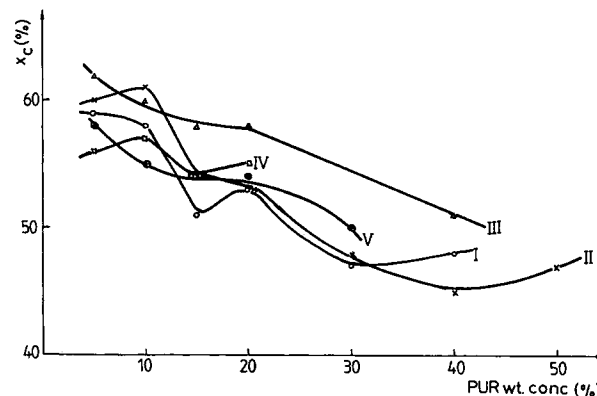
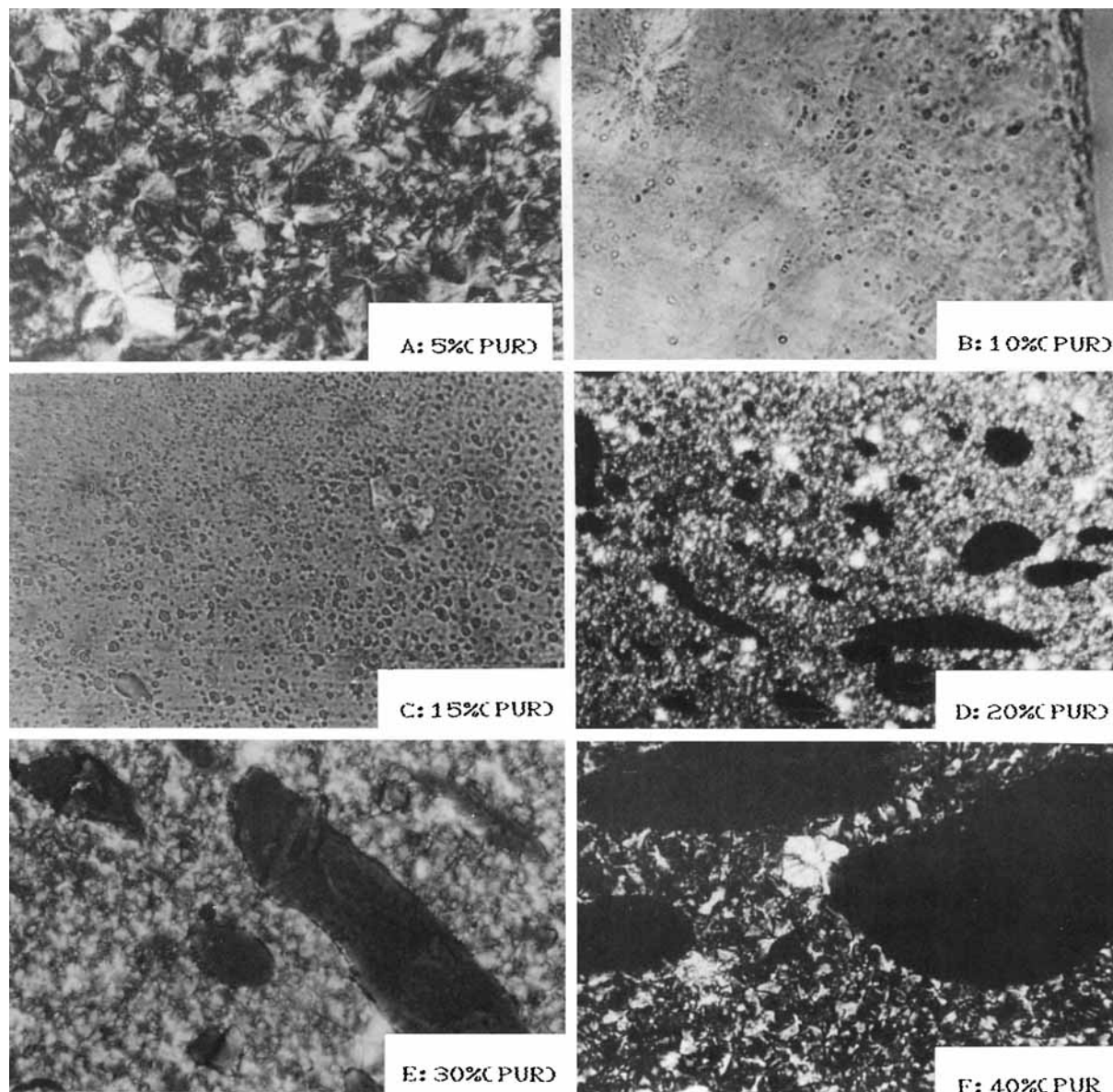


Figure 7 The effect of PUR concentration on the degree of crystallinity of blends.



**Figure 8** Microphotographs of the series of blends with the increasing PUR concentration obtained under polarized light.

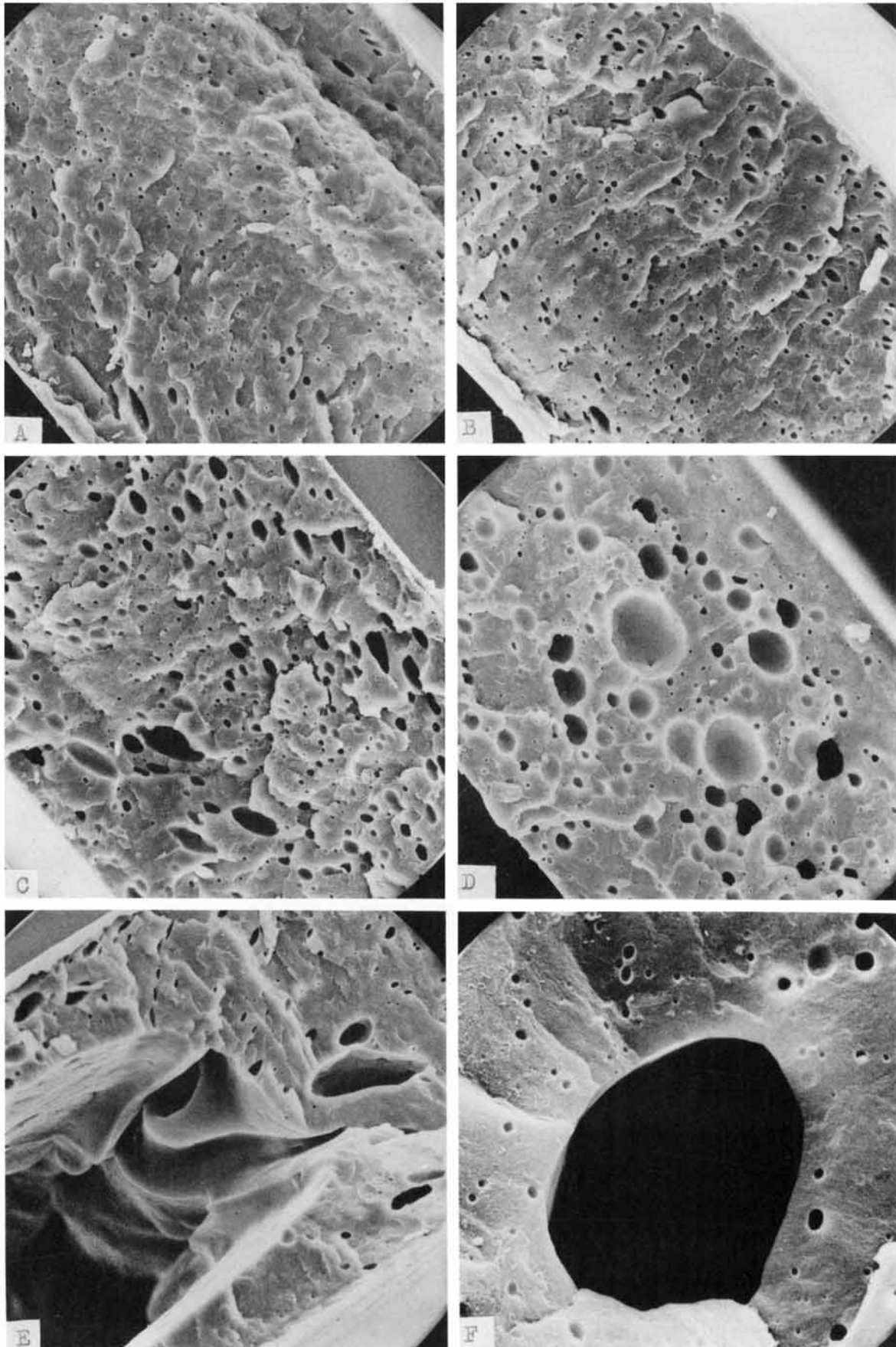
by dissolution in the dimethylformamide. By increasing the concentration, the shape, and the size of the PUR particles changes to reach a stage of bicontinuous phases at 40% PUR. Such samples could not be used in most tests. Electron micrographs of the samples with PUR particles reveal the interphase bonding.

Figures 10 and 11 reveal round particles at low concentration of PUR and a variable quality of interphase bonding. At high PUR concentration the imprint of the spherulite structure on the PUR particles could be observed, from which the thickness

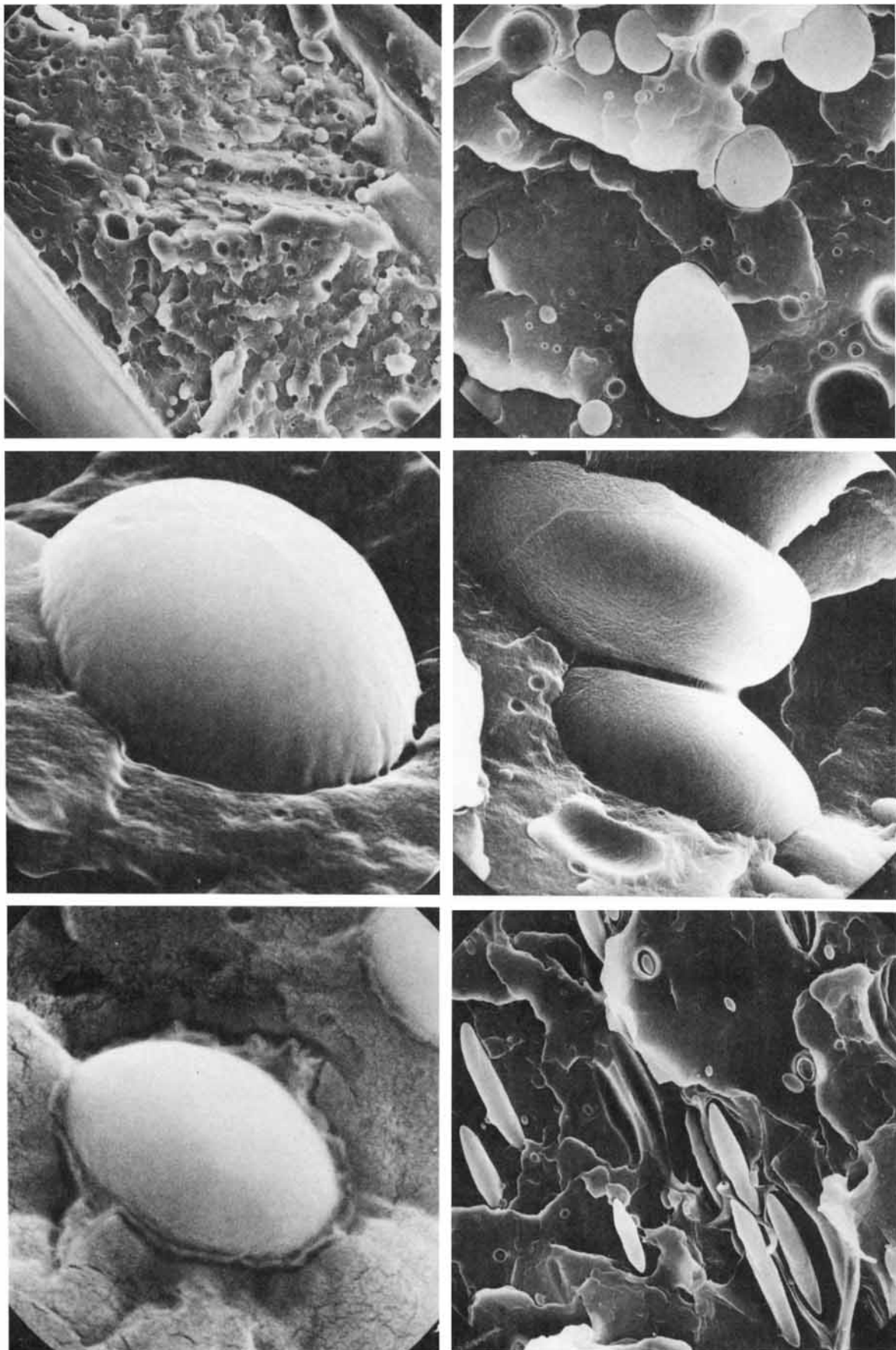
of the PP lamellae could be obtained. Such clear imprint can be obtained only if no adhesion between polymers exist. The fact that the imprint was observed in blends with 50% SSC polyurethanes and not with softer polyurethanes indicates that soft segment is responsible for increased interaction between the two polymers.

The PUR particle size distribution was extracted from the electron microphotographs. It turned out that the shape of the particle size distribution was bimodal or even multimodal. Number average  $\bar{d}_n$ , and volume average,  $\bar{d}_v$ , particle diameters increased

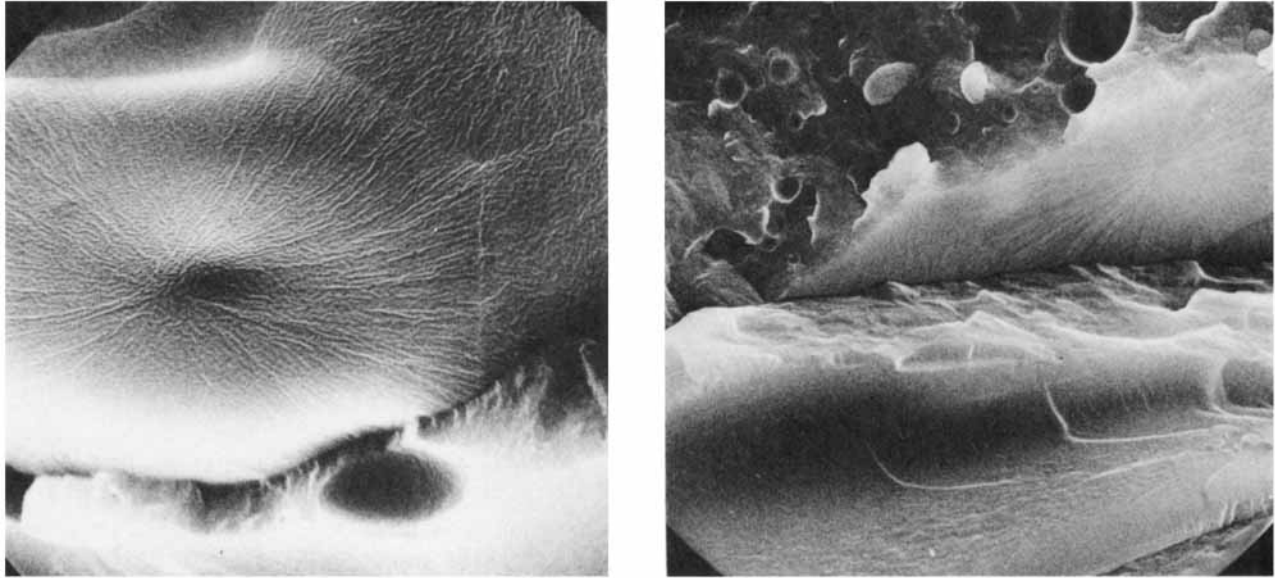




**Figure 9** Electron micrographs of the selected PP/PUR blends (PUR particles were washed out).



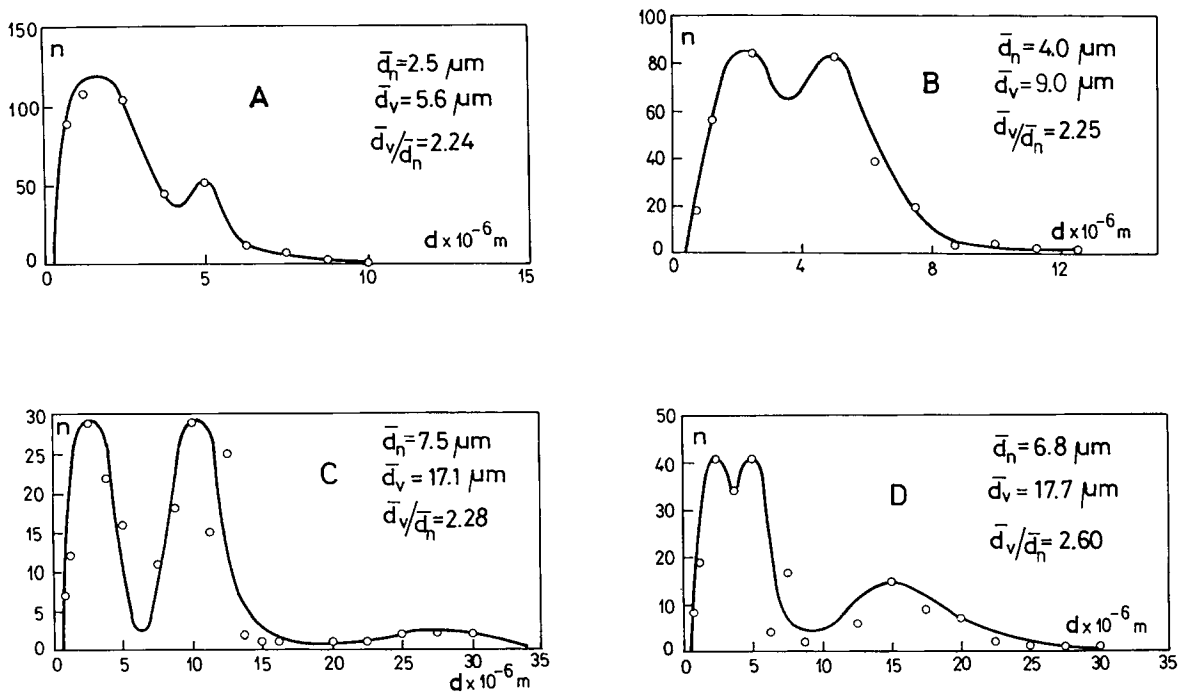
**Figure 10** Electron micrographs of the selected blends.



**Figure 11** Electron micrographs showing replica of the PP spherulite structure.

as the concentration of the PUR increased. Figure 12 shows particle size distribution (number of particles vs. diameter) for four samples in series I. The ratio of  $\bar{d}_v/\bar{d}_n$  is a measure of the breadth of distribution. It did not vary appreciably with the PUR concentration. Concerning the effect of the type of PUR on the blend morphology, polyurethanes with

higher SSC seem to offer better interphase adhesion than those with greater hard segment concentration. PPO2000 seems to offer poorer interphase adhesion than PPO1000. According to Galli et al.,<sup>8</sup> the higher the affinity between the elastomer and the PP, the better is the dispersion of the elastomer in the PP; thus, smaller particles have a better overall effect.



**Figure 12** Particle size distribution in the series I samples: (A) 5% PUR; (B) 10% PUR; (C) 15% PUR; (D) 20% PUR.

## CONCLUSION

Polyurethane/polypropylene blends were prepared by mixing five types of segmented polypropyleneoxide-based polyurethanes with PP in different concentrations. It was found that, in spite of the very different chemical nature of the two components, relatively good adhesion between the phases existed.

Polyurethane was dispersed in the form of round particles of the optimal size only at concentrations below 15% PUR in the matrix. At higher concentrations, the tendency to agglomeration of the PUR particles rendered these products less useful. Addition of the low molecular weight polyurethane produced an easy flowing melt with MFR in the range of "control rheology" polypropylenes.

Polypropylene/polyurethane blends with satisfactory mechanical properties were obtained only if the concentration of PUR was below 15%, which was explained by the "correct morphology" of the samples. Less phase-separated segmented PUR based on PPO1000 tended to give better compounds.

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