

# Structure–Property Relationship of Modified Polypropylene–Polycaproamide Fiber

I. GROF,\*<sup>1</sup> M. M. SAIN,<sup>1</sup> and OLGA DURČOVA<sup>2</sup>

<sup>1</sup>Department of Plastics and Fibre, Chemical Technology Faculty, Technical University, Bratislava, Czechoslovakia, and <sup>2</sup>Research Institute of Fibre, SVIT, Czechoslovakia

## SYNOPSIS

The effect of the addition of polyamide on the structure and properties of polypropylene fiber has been studied. Although a good fiber is obtained with a composition containing only a very low concentration of polycaproamide in polypropylene, the increase in polyamide content decreases the drawing strength of the mixed polymer melt due to sudden lowering of melt viscosity and strength. The poor melt strength of the studied polymer mixture is attributed to increased heterogeneity induced in the system with increased concentration of polyamide. Use of an effective interphase modifier, maleic anhydride-grafted polypropylene, however, was found to improve fiber properties of the studied polymer mixtures even with a very high concentration of polyamide as the dispersed phase. Thus, addition of a 1–4 wt % interphase modifier facilitates the formation of good fiber even with 30 wt % polycaproamide in the blend. This improvement is attributed to the improved dispersity of polyamide in the polypropylene matrix as well as improved phase compatibility due to the formation of a chemically modified polyamide during melt extrusion in the presence of maleic anhydride-grafted polypropylene.

## INTRODUCTION

The stability of the morphological structure in incompatible polymer blends is influenced by adding suitable interphase modifiers. Such compatibilizers improve blend morphology with a finer dispersion of the discontinuous phase in the dominant polymer matrix. It has been already reported that in polypropylene–polyamide blends the average particle size of the dispersed phase before melt extrusion is smaller than that of its size after extrusion.<sup>1,2</sup> The dispersed fine particles agglomerate during extrusion to form an unstable fiber structure that during spinning subsequently dissociates into smaller and deformed spherical particles. The improvement in structural stability in polymer blends is achieved by adding grafted polymers or copolymers that reduce the interfacial surface energy of the polymer mixture. A selective additive that essentially contains

components compatible to both the polymers in a studied mixture improves interphase adhesion.<sup>3,4</sup>

The effect of maleic anhydride-grafted polypropylene on the polypropylene–polyamide blend has been studied by Ide and Hasegawa.<sup>5</sup> The improvement in the physicomechanical properties of the blend is attributed to the formation of a stable interphase. Similar improvement in phase dispersion was also noted when surface active elements were used in mutually immiscible polymer mixtures.<sup>6</sup> In the recent past, a lot of work has been done to improve the blend compatibility, but very little is known about the fiber properties of such blends. In synthetic fiber preparation, the use of a small concentration of a second polymer is of interest to researchers. Past investigation revealed that a two-component polymer mixture of polypropylene and polycaproamide has inferior fiber-forming properties compared to polypropylene fiber.

This report summarizes some of our experimental results to improve the fiber property of polypropylene–polycaproamide blends by modifying the composition in presence of maleic anhydride-grafted polypropylene. A comparison of the fiber structure

\* To whom correspondence should be addressed.

**Table I Physicomechanical Properties of Undrawn PP-PA6 Fibers**

PA6 Content (wt %)	Tenacity (cN dtex <sup>-1</sup> )	Elongation (%)	Young's Modulus (cN dtex <sup>-1</sup> )
0	2.2	28	17.0
1	2.4	43	16.9
3	2.3	60	16.5
5	2.4	64	16.2
7	2.3	59	16.0
10	1.9	66	14.0

and useful properties are also made for an unmodified composition with maleic anhydride-grafted polypropylene-modified polypropylene-polycaprolactone blends.

## EXPERIMENTAL

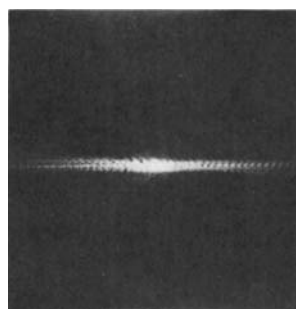
Our investigation involved two types of polymers: polypropylene (Tatren TF-411, Czechoslovakia)

and polycaprolactone; another additive used was maleic anhydride-grafted polypropylene (MAH-PP). This was a commercial product from Himont, Italy.

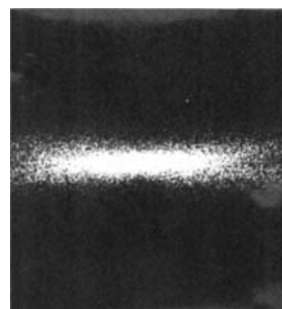
## Preparation of Blend

Polymer mixtures of polypropylene (PP) and polycaprolactone (PA6) with up to 30 wt % PA6 content were prepared by melt-mixing both components in a laboratory extruder (screw diameter 25 mm, temperature 260°C). The residence time of the polymer mixture in the extruder was 5 min. During melt mixing, 0.5 wt % calcium stearate was added as dispersing agent for all mixes that do not contain MAH-PP.

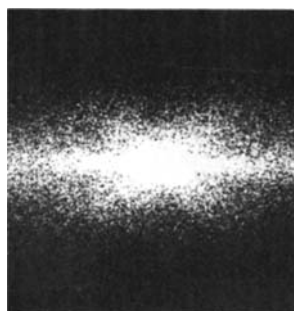
In another set of experiments, similar mixing of PP and PA6 was done with up to 30 wt % PA6 content, and in each batch, MAH-PP from 0.5 to 5.0 wt % was added during melt extrusion. All compositions were granulated to process further for fiber forming.



(a) Pure PP Fibre

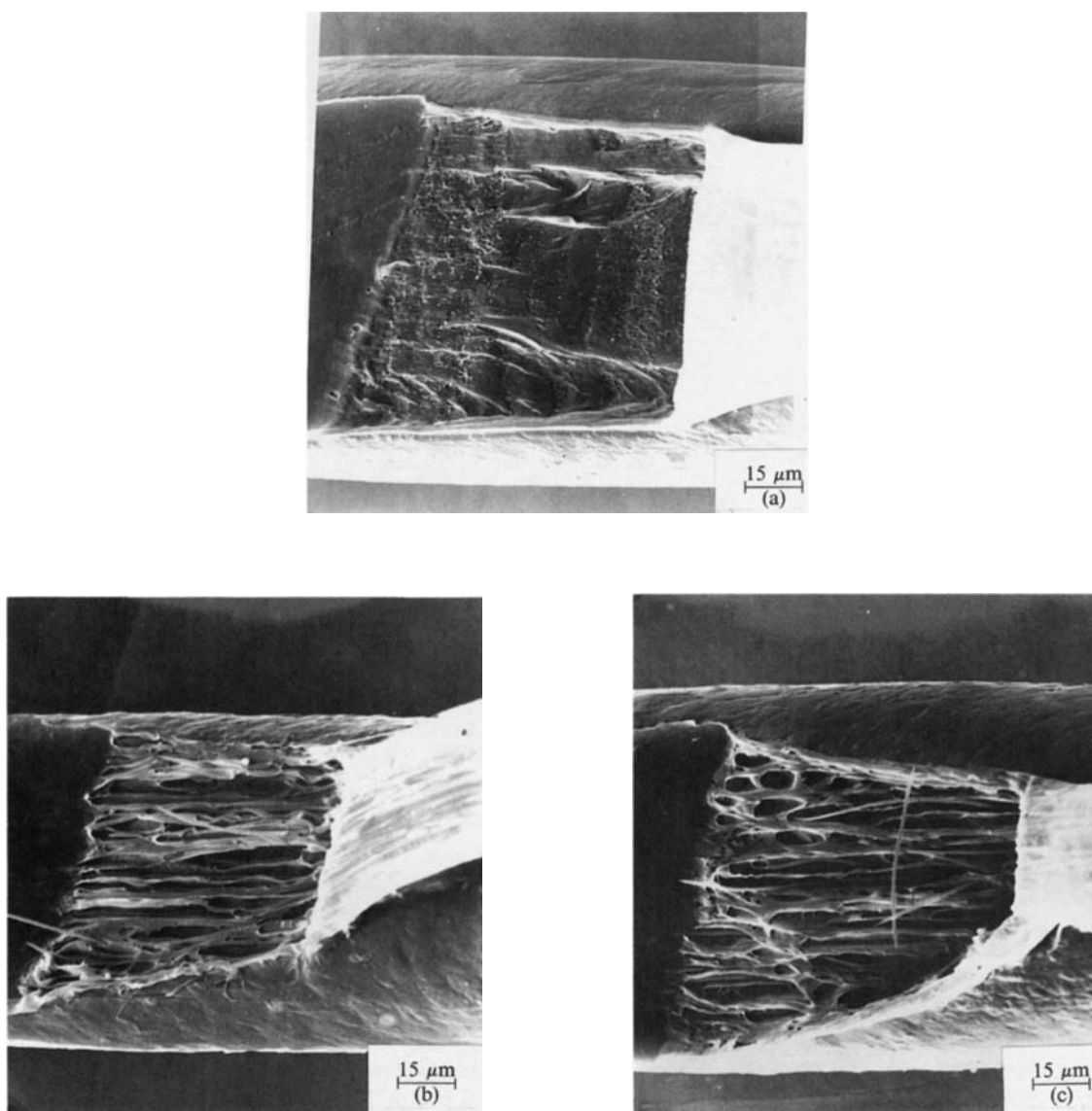


(b) PP-PA6 with 10 wt% PA6



(c) PP-PA6 with 20 wt% PA6

**Figure 1** SALS patterns of drawn PP and PP-PA6 fibers: (a) pure PP fiber; (b) PP-PA6 with 10 wt % PA6; (c) PP-PA6 with 20 wt % PA6. Magnification: (a) 1100×; (b) 900×; (c) 770×.



**Figure 2** Electron micrographs of undrawn fibers (peeled): (a) pure PP; (b) PP-PA6 with 10 wt % PA6; (c) PP-PA6 with 15 wt % PA6.

### Preparation of Mixed Fibers

Fibers were prepared from polymer blends in a laboratory spinning equipment fitted with a 32 mm extruder. The complete apparatus was equipped with a self-contained dynamic mixer with heating and mixing arrangements. The fiber-forming condition was as follows: temperature 295°C, pressure 4 MPa, feed rate 40 g min<sup>-1</sup>, drawing rate 400 m min<sup>-1</sup> (nozzle) and 1000 m min<sup>-1</sup> (fiber). Spun fibers were prepared at 120°C with a drawing ratio = 3. The

drawn fibers were subsequently textured by mechanical crimping.

### TESTING

The mechanical properties of fibers made from polymer mixtures were measured in an INSTRON Type 1122. The stretching rate was 100 mm min<sup>-1</sup>. The morphology of the fiber was evaluated using spectroscopic as well as microscopic techniques. IR

**Table II Dynamic-mechanical Properties of Undrawn PP-PA6 Fibers**

Composition PP/PA6/MAH-PP	$\tan \delta_{\max}$ PP	$T_{\max}$ PP (°C)	$\tan \delta_{\max}$ PA6	$T_{\max}$ PA6 (°C)	$E'_{20^\circ\text{C}}$ (GPa)
100/0/0	0.118	23.0	—	—	1.45
0/100/0	—	—	0.176	84.0	2.36
85/15/0	0.082	20.7	—	—	1.92
85/15/1	0.078	20.2	—	—	2.19
85/15/2	0.074	19.6	0.107	90.0	2.39
80/20/0	0.076	20.5	0.114	103.3	1.84
80/20/0.5	0.070	18.9	0.112	92.3	1.98
80/20/1	0.068	17.4	0.105	92.1	2.08
80/20/2	0.070	18.2	0.107	87.2	2.13
80/20/4	0.065	16.7	0.107	83.3	2.19
70/30/0	0.067	20.2	0.119	97.5	2.01
70/30/1	0.060	18.6	0.109	91.7	2.35

spectroscopy was used to determine the purity of MAH-PP. Fiber structure was determined using a small-angle light scattering (SAL) technique. For a light source, a He-Ne laser T KG 203 was used. A Jeol JSM-35 scanning electron microscope (SEM) was also used for a detailed study of the morphology of prepared mixed polymer fibers. Samples were analyzed both by peeling off the fiber surface and by the longitudinally breaking of fibers by freezing them in liquid nitrogen. Dynamic mechanical properties were measured using a Rheovibron instrument at 110 Hz.

## RESULTS AND DISCUSSION

The melt viscosity of the polymer during extrusion and spinning plays an important role in determining the ultimate properties of the obtained fibers. Experimental investigation showed that the PP-PA6 polymer mixture could be continuously drawn into

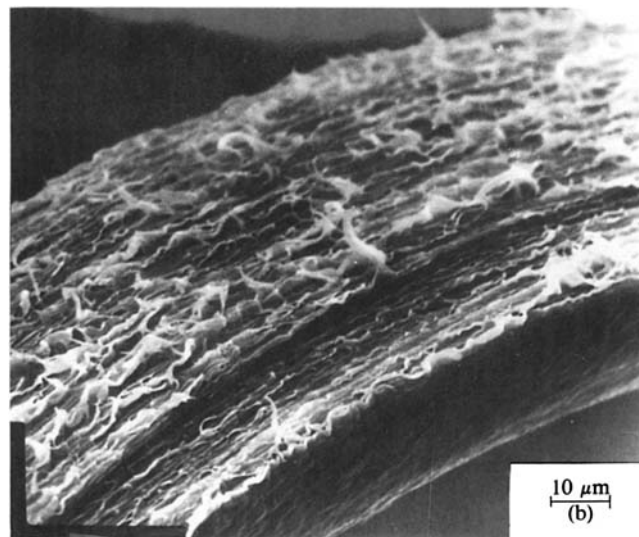
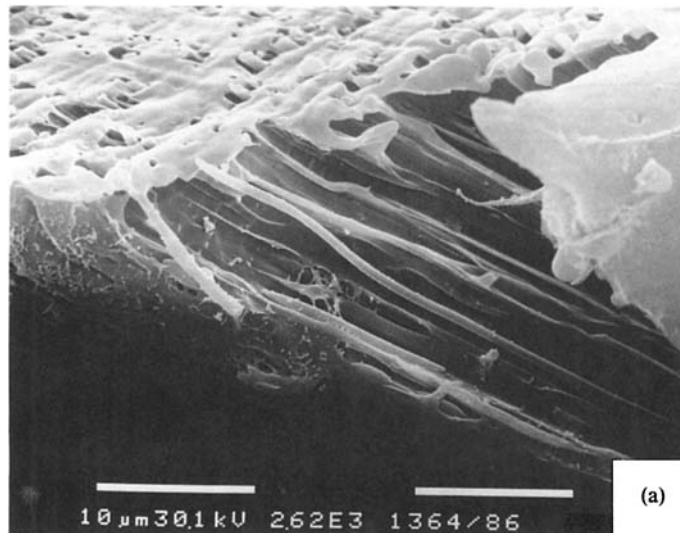
stable fibers with compositions containing up to 10 wt % PA6.<sup>7</sup> Above 7 wt % PA6 content in the polymer mixture, mechanical properties deteriorate, as is evident from Table 1. Moreover, compositions containing more than 10 wt % PA6 develop unusual broadening of the flow path at the spinnerate during melt spinning due to a sudden decrease in the melt viscosity of the PA6 phase when the melt is mixed with PP. Thus, an increase in PA6 concentration in the mixture reduces the axial stress applied during spinning of the fiber and results in loss of fiber orientation.

Attempts have been made to explain the deterioration of mechanical properties with higher PA6 concentration by investigating the morphology of both undrawn and drawn fibers. Figure 1 shows the SAL pictures of pure as well as PA6-blended undrawn PP fibers. Evidently, the increase in PA6 concentration changes the crystallinity of pure PP components, as is indicated by diffuse scattering. Such a phenomenon in the SAL pictures confirms

**Table III Effect of MAH-PP on Mechanical Properties of Drawn\* PP-PA6 Fibers**

Composition PP/PA6/MAH-PP	Tenacity (cN dtex <sup>-1</sup> )	Elongation (%)	Young's Modulus (cN dtex <sup>-1</sup> )
100/0/0	1.5	70	19.5
0/100/0	2.9	61	11.8
80/20/0	1.4	40	18.0
80/20/0.5	1.7	61	21.0
80/20/1	1.5	54	18.5
80/20/2	1.5	63	19.2
80/20/4	1.6	60	20.2

\* Drawing ratio was 3 : 1.

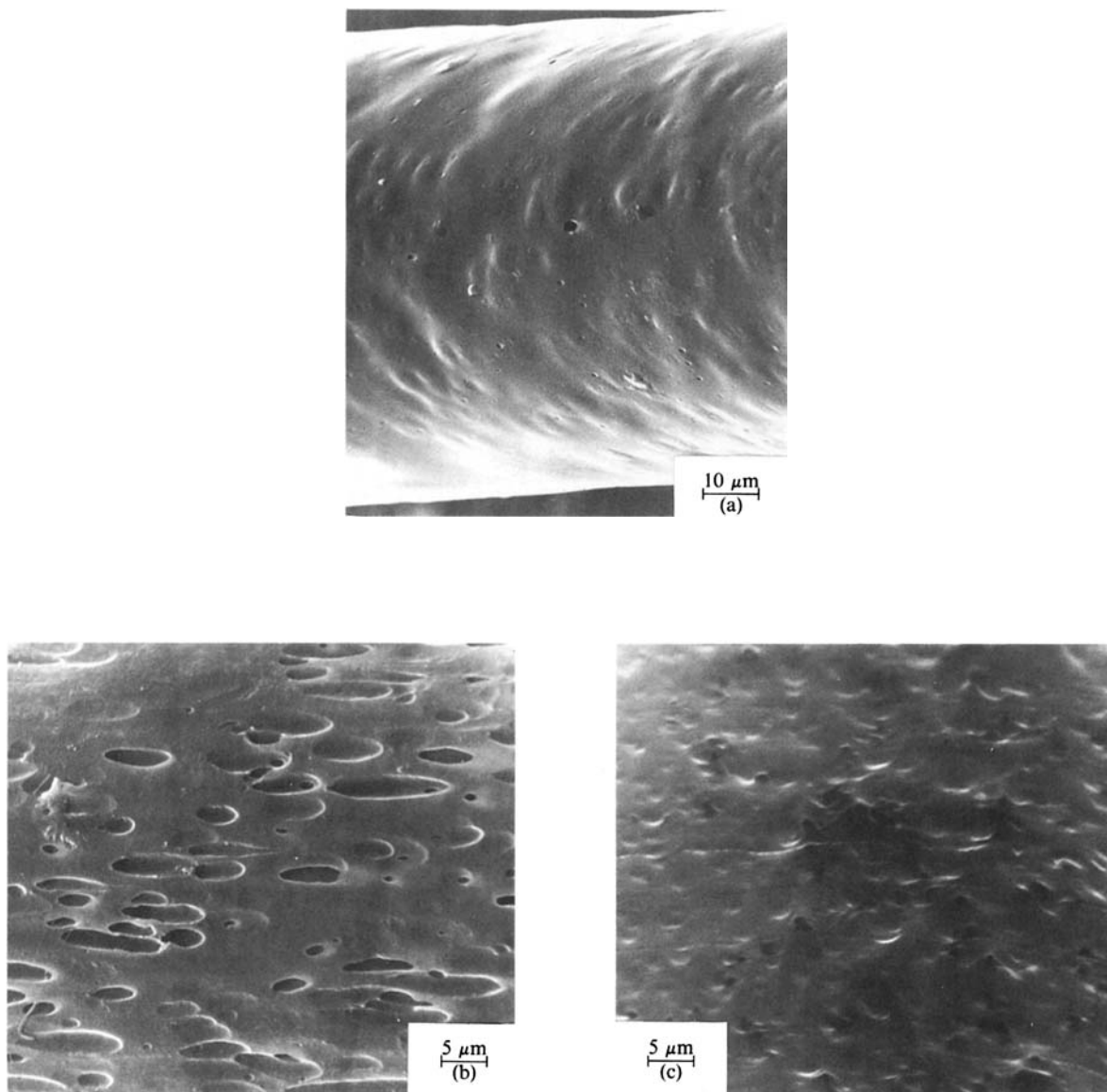


**Figure 3** SEM micrographs of etched PP-PA6 fibers: (a) unmodified PP-PA6 (80 : 20); (b) PP-PA6 modified with 1 wt % MAH-PP.

formation of amorphous and porous structure. This fact is in line with the work carried out by Ide and Hasegawa<sup>5</sup> where a reduced crystallinity of PP in the presence of polyamide has been demonstrated. Further study of the morphology of pure PP and PP-PA6 fibers (peeling method) using SEM in Figure 2 shows that the PA6 component is "coarsely" dispersed in the PP matrix in the form of thin fibrils oriented in the direction of the fiber axis and that the increase in PA6 concentration increases the micropore size by partially flattening in the direction

perpendicular to the fiber axis. Thus, PP fibrils had destroyed molecular orientation. Above 10 wt % PA6 content, the size of the micropores further increased and resulted in a further loss of compaction of the oriented PP matrix due to the formation of agglomerates.

Measurement of dynamic mechanical properties of the prepared mixture fibers suggests that obtained fibers are grossly heterogeneous in nature. From Table 2 it is confirmed that each polymer mixture has two peak temperatures, and with the increase

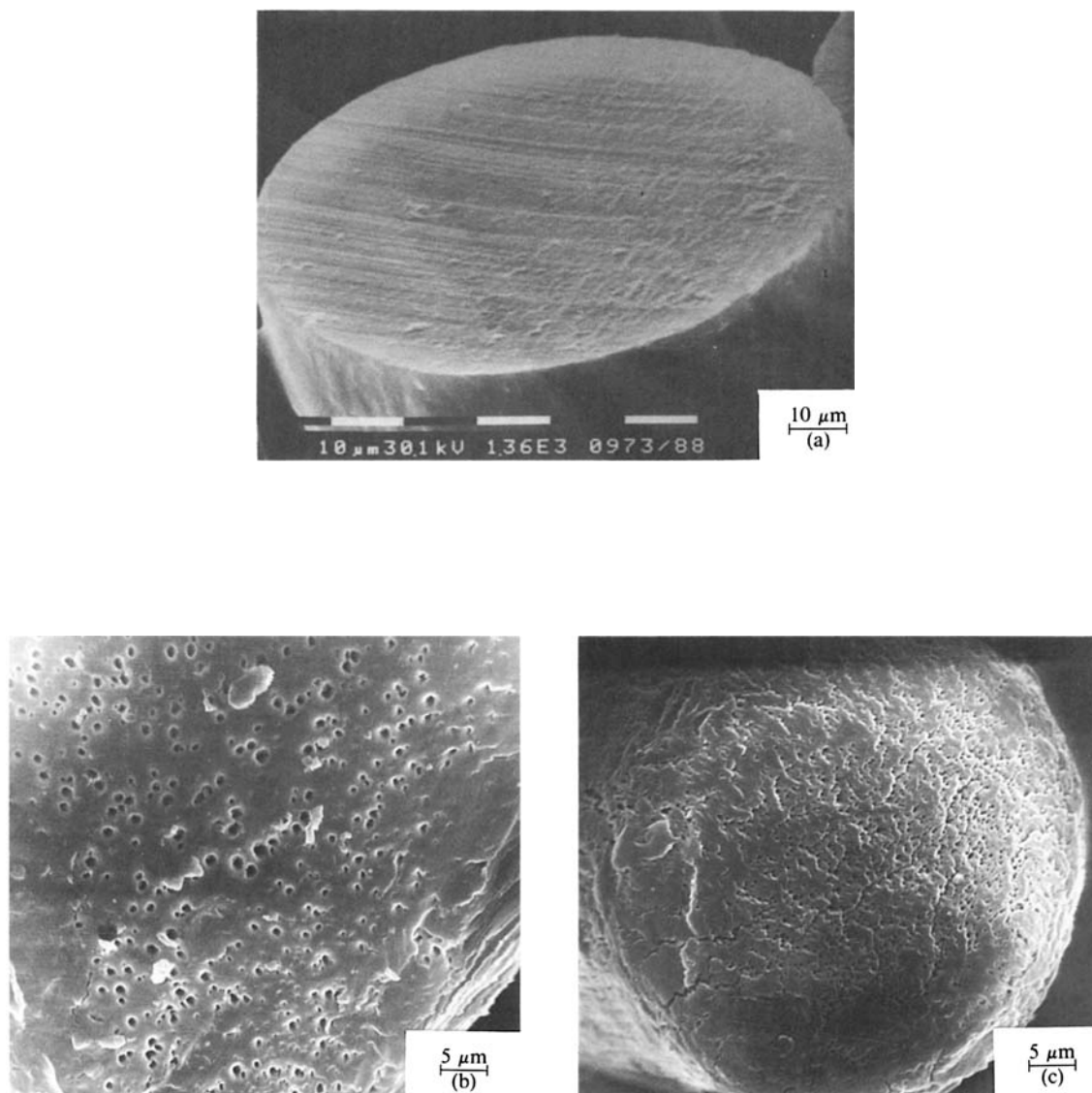


**Figure 4** SEM photographs of the surfaces of pure PP and PP-PA6 fibers; (a) pure PP; (b) PP-PA6 (80 : 20); (c) PP-PA6 (80 : 20) with 4 wt % MAH-PP.

in PA6 concentration, the peak temperatures of the two components in the mixture shift further apart, indicating growing heterogeneity in the system. Thus, in the preceding part of our discussion, we investigated the effect of MAH-PP on the studied polymer mixtures to improve fiber properties for compositions with more than 10 wt % PA6 content.

It is thought that the fiber property of the studied PP-PA6 polymer mixture can be improved by lowering the interfacial surface energy. Thus, addition of 1 wt % MAH-PP as the interphase modifier was found to improve the melt extrusion and subsequent

spinning behavior of the studied PP-PA6 polymer blend. As compared to our previous findings without MAH-PP, fibers with good drawing property were obtained even for a composition containing 30 wt % PA6. This improvement in melt strength of the polymer mix is also reflected in the mechanical properties of drawn fibers, as shown in Table 3. It is noted that a modified fiber with mechanical properties comparable to pure PP fiber has been achieved. A chemical reaction between PA6 and MAH-PP, as suggested by Ide and Hasegawa,<sup>5</sup> probably explains the improved phase interaction



**Figure 5** Electron micrographs of cross sections of pure PP and PP-PA6 fibers: (a) pure PP; (b) PP-PA6 (80 : 20); (c) PP-PA6 (80 : 20) with 4 wt % MAH-PP.

and, hence, the better melt strength and fiber properties of the studied blend. Furthermore, addition of MAH-PP in the polymer mixture was also found to influence the structural characteristics of the blend.

From Table 2 it is clear that the dissipation factor ( $\tan \delta$ ) of the modified PP-PA6 blend obtained by dynamic mechanical measurement is less than that of the unmodified composition. The increase in MAH-PP concentration in the blend gradually decreases  $\tan \delta$  as well as the peak temperature ( $T_{\max}$ ) of PP. This result is due to an increase in the segmental movement of PP chains and improved ori-

entation of PP as well. On the other hand, for all the studied compositions, although the peak temperature ( $T_{\max}$ ) of the PA6 component was found to be higher than that of the pure PA6 with increasing MAH-PP concentration in PP-PA6 blend, a composition having the PA6 peak temperature close to that of pure PA6 (84°C) has been obtained.

These findings enable us to conclude that when the addition of PA6 develops heterogeneity in the system further modification by MAH-PP makes these blends more compatible. It is also interesting to note that the elastic modulus ( $E'$ ) of the modified mix is higher than that of the unmodified one. This

is attributed to the greater orientation effect of the mixed polymer fiber in the presence of MAH-PP compared to the unmodified PP-PA6 fiber.

The significant changes in physical, rheological, and dynamic mechanical properties of modified PP-PA6 fibers prompted us to investigate the detailed morphological changes in this system. In Figure 3, the SEM microstructures of unmodified and modified drawn fibers are compared. Evidently, unmodified fiber distinctly shows phase separation at the interface and modified fiber formed better-oriented fibrils, leading to a more compact structure. This orientation of the fibrils toward the direction of the applied drawing stress improved mechanical properties. Figure 4 presents drawn fiber surfaces of pure PP and unmodified as well as modified PP-PA6 mixtures. Addition of PA6 results in "coarse" dispersion of the dispersed PA6 particles on the fiber surface. Contrarily, further addition of an interphase modifier, MAH-PP, improves the dispersity of the PA6 phase and reduces the sizes of the micropores, as seen in Figure 4 (b) and (c). A similar conclusion is also drawn from the microphotographs of the cross-sectional area of selectively etched unmodified and modified PP-PA6 fibers, as shown in Figure 5. The PA6 microfibrils are distributed longitudinally along the micropores in the PP matrix. However, the addition of MAH-PP reduces the sizes of the micropores and develops a greater number of finer PA6 microfibrils, which prevents gross separation of two mutually incompatible polymer phases.

## CONCLUSION

The effect of addition of PA6 on the properties and structure of PP fibers has been studied. A good fiber

could be drawn from the PP-PA6 polymer mixture only with low PA6 concentration. Above 10 wt % PA6 content in the PP-PA6 composition, the prepared fibers show poor mechanical properties due to inferior orientation of PP fibrils in the fiber matrix compared to pure PP fiber and also due to the development of microporosity at the PP-PA6 interface. However, the addition of an interphase modifier, MAH-PP, in the PP-PA6 matrix improved the degree of dispersion of PA6 in PP matrix and also improved the fiber orientation. Thus, a fiber with good mechanical properties has been prepared even with 30 wt % PA6 content in the PP-PA6 blend in the presence of 4 wt % MAH-PP. The increase in MAH-PP concentration in the blend progressively improved the fiber drawing property of the studied compositions.

## REFERENCES

1. V. N. Kuleznev and J. P. Mirosnikov, *J. Kolloid*, **38**, 1120 (1979).
2. I. A. Kovalera, L. A. Suchareva, and N. I. Morozova, *Komp. Polim. Material*, **22** (24), 43 (1985).
3. J. Kovar, I. Fortelny, and M. Bohdanecky, *Plast. Kaucuk*, **19** (7), 193 (1982).
4. A. Y. Coran, in *Thermoplastic Elastomers, A Comprehensive Review*, N. R. Legge, G. Holden, and H. E. Schroeder, Eds., Hanser, Munich, 1987, p. 135.
5. F. Ide and A. Hasegawa, *J. Appl. Polym. Sci.*, **18**, 963 (1974).
6. N. K. Baramboin and V. F. Rakityanski, *J. Kolloid*, **36**, 706 (1974).
7. C. Duricova, I. Grof, and A. Marcincin, *Acta Polym.*, **41** (3), 164 (1990).

Received November 14, 1990

Accepted April 24, 1991