

Influence of Spinning Velocity on Mechanical and Structural Behavior of PET/Nylon 6 Fibers

S. ASLAN,¹ P. LAURIENZO,¹ M. MALINCONICO,¹ E. MARTUSCELLI,^{1*} F. POTA,² R. BIANCHI,³
G. DI DINO,³ and G. GIANNOTTA⁴

¹Istituto di Ricerca e Tecnologia delle Materie Plastiche del C.N.R., via Toiano 6, 80072 Arco Felice, Naples, Italy; ²Consorzio sulle Applicazioni dei Materiali Plastici e sui problemi della Corrosione (CAMPEC), Naples, Italy; ³Centro Ricerche Montefibre, Acerra, Naples, Italy; and ⁴Istituto G. Donegani, Novara, Italy

SYNOPSIS

Influence of spinning velocities on the mechanical and structural properties of polyethylene terephthalate (PET)/nylon 6 blend fibers have been reported. Fibers of PET/nylon 6 containing a small percentage of nylon (5% by weight) have been melt-spun at 3 different spinning velocities (2,900; 3,200; 3,600 m/min). The fibers have been characterized by thermal, morphological, structural, and mechanical analysis. Various techniques such as SEM, DSC, X-ray diffraction, hot water shrinkage (HWS), viscosity, and birefringence have been used. SEM analysis revealed that in the blend, nylon 6 is well-dispersed as spheres in the PET matrix. The blend shows a marked decrease in the melt-flow index, which in turn leads to a beneficial effect on the rheological properties of the PET without negatively influencing its mechanical characteristics. This finding results in a saving on energetical requirements of the processing, as both temperature and pressure of spinning can be decreased. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In fiber technology, two or more polymers may be formed into a product to obtain combinations of individual material characteristics or new ones by either of two distinctly different routes, both of which are referred to as blending. The former is more well-developed, and an older concept of fiber-fiber blending in which conventional synthetic or natural fibers are mixed. These fibers, which are referred to as fiber blends, give combinations of such characteristics as comfort, ease of care, durability, and appearance in a product not available with a single fiber type. Well-known examples are polyester-cotton and nylon-wool fiber blends. On the other hand, when the polymer-polymer blends comprise the individual filaments, they are referred to as blend fibers. Basically, blend fibers are best suited when *each fiber* needs to have the desired characteristics,

whereas fiber blends are more appropriate when only *the product as a whole* needs to have these characteristics.¹

In fiber production, polyester accounts for almost half of all synthetic fibers and one-seventh of all textile fibers. Factors for the growth of the polyester fibers in the market are favorable interfiber economics resulting from increased volumes, expanding uses and new products, and, most important, the substitution of polyester for cotton.

From an industrial point of view, blends of polyester fibers with other synthetic and natural polymers are of great interest. An extensive effort has been made to enlarge the range of applications for polyester fibers by blending with other polymers to improve their properties.

Despite the large industrial activity in blend fibers, there is insufficient detailed scientific literature available. Many of the significant ideas and most of the details are proprietary and are only available through the patent literature. Among possible second components, polyamides seem particularly suited to impart a number of interesting properties to PET. In scientific literature, PET/nylon 6 bi-

* To whom correspondence should be addressed.

component fibers have been studied both in PET²⁻⁴ and nylon 6 matrix. Since our study concerns PET matrix, the latter is not going to be discussed here. Moreover, in both cases, two-phase morphology of the blend has been stated by the authors. Addition of nylon 6 into PET matrix decreases the melt viscosity up to a certain point. Further addition of nylon 6 (more than 40%) leads to phase inversion, and the viscosity starts to increase. Papero et al. have studied the tensile properties of blend fibers, and they found that the blend fibers had almost the same tenacities as the fibers of the parent polymers. According to patent literature, depending on the PET and nylon 6 content, one can increase the conductivity⁵⁻⁹ and water resistivity,^{10,11} improve crimpability,^{12,13} dyeability,^{13,14} and spinnability¹⁵⁻¹⁸ of PET fibers. Improvement of the electroconductivity to increase the antistatic properties is an extensive research area for the carpet and garment manufacturers. Static electricity is normally generated when two different materials are rubbed together. PET fibers have a tendency to accumulate static electricity; this may create a number of problems, like interfering with textile processing (inability to card, spin, etc.) or being objectionable to a person wearing the material because of its clinging, sparking, etc. To solve this problem, the electroconductivity of PET fibers can be accomplished by blending the material with nylon 6 and conductive powders such as mostly carbon black and SnO₂ coated powder TiO₂ (in the proportion of 35%). The process is performed by melt-spinning of a system in the form of sheath and core structure where the former consists of PET and the latter nylon 6 and electroconductive powder.

The dyeability of PET fibers can be improved to a large extent when it is melt-spun together with nylon 6. The chemical or physical modifications on the structure of fibers given by nylon 6 lead to an excellent dyeing when the blends of nylon 6 and 5% ethylene glycol-sodium 5-sulfoisophthalate-terephthalic acid copolymer and PET were melt-spun together at 10 : 90 wt ratio. The resulting fibers had good hygroscopic properties and good dyeing yield.

Excellent spinnability has also been patented together with the good antistatic properties and good color-fastness to washing when PET is co-spun together with polyamide containing poly(oxyalkylene) compound containing amido-forming functional groups and N,N'-bis(aminopropyl) piperazine.

These examples can be increased through the patent literature. All these studies indicate that the properties of PET fibers can be tailored according

to the manufacturers' wishes by blending the stated fiber with nylon 6.

In this study, the effect of nylon 6 on PET fiber properties was studied as a function of spinning velocity. For each spinning velocity, physical and mechanical properties of the filaments were investigated. Moreover, a morphological characterization on mode and state of dispersion of blend components was reported.

EXPERIMENTAL

The polymers used were PET (Montefiber, code S93; $\eta = 0.655$ dL/g in *o*-chlorophenol) and nylon 6 (nylon 6 SNIA-FIAT, code ASN27; $\eta = 2.9$ dL/g in concentrated H₂SO₄) chips. Before melt-spinning, the chips of PET and nylon 6 were dried separately in a vacuum tumble drier for 4 h at 180°C and 24 h at 130°C, respectively. The dried polymer chips were melt-blended on a laboratory scale counterrotating twin screw extruder (Haake TW-100; D = 20–31 mm, L = 330 mm) using the following parameters: screw speed = 70 rpm, feeding rate = 2 kg/h, temperature zones 1, 2, 3, and the die zone corresponding to 230, 250, 260, 280°C, respectively. The extrudate was cooled in water and cut into chips from the die, and the chips were spun into fibers using a melt-spinning unit. During the spinning operation, 4 different spinning velocities were used: 2,900; 3,200; 3,600; and 4,000 m/min. The temperature was controlled at 5 different zones during the spinning of PET STD: 285, 285, 285, and 294°C, and the head temperature 294°C. For a blend of PET with 5% nylon 6, the following temperatures were recorded: 280, 280, 280, and 283°C, and the head temperature 283°C. Before spinning, the chips were dried up to a moisture content of 9 ppm.

Tensile Properties

Automatic dynamometer (Calderara and Bossi) was employed to measure tenacity, % elongation, and modulus of preoriented yarns (POY). The measurement of dynafil (i.e., the force required to maintain a prefixed draw ratio) was performed with another automatic dynamometer (Textechno) at draw ratio = 1.7. The yarns that are obtained at the spinning velocity of 2,900 m/min were subjected to three different draw ratios (1.6, 1.7, 1.8). The drawing conditions are: drawing velocity = 800 m/min, $T = 185^\circ\text{C}$.

Birefringence

The birefringence of the filaments was measured with an optical microscopy (Leitz, Laborlux 11POL S.) with MgF_2 crystal compensator.

Hot Water Shrinkage (HWS)

HWS measurements were performed in water at $65^\circ C$ for 30 min.

DSC Analysis

The thermal analysis was performed by DSC Mettler T.A. 3000 under nitrogen atmosphere. The applied temperature range is $-50^\circ C$ to $300^\circ C$ with a heating rate of $20^\circ C/min$.

Viscosity

Viscosity of the PET was measured with an Ubbelohde type viscosimeter in orthochlorophenol at $35^\circ C$ with a concentration of 1.2 g/dL. PET from blend was recovered by formic acid extraction of the nylon 6 component.

Scanning Electron Microscopy

The photomicrographs of the starting blend and the fibers were taken by Philips SEM 500. Chips of the original blend were fractured in liquid N_2 , while yarns were embedded in epoxy resins and then fractured in liquid N_2 . All samples were coated with Au/Pd before SEM analysis.

WAXS Analysis

Wide-angle X-ray diffraction measurements were done on a (PW 1050 model) Philips powder diffractometer (nickel-filtered CuK_α radiation; $R = 1,000$; scanning rate = $1^\circ/min$).

RESULTS AND DISCUSSION

Blend Preparation and Characterization

Fiber melt-spinning is a highly technological field. Complex physical processes come into operation, like crystallization, orientation, and drawing. For instance, it is much more complex than simple injection molding. Besides, the size of fibers is normally of few microns, and this severely restricts the

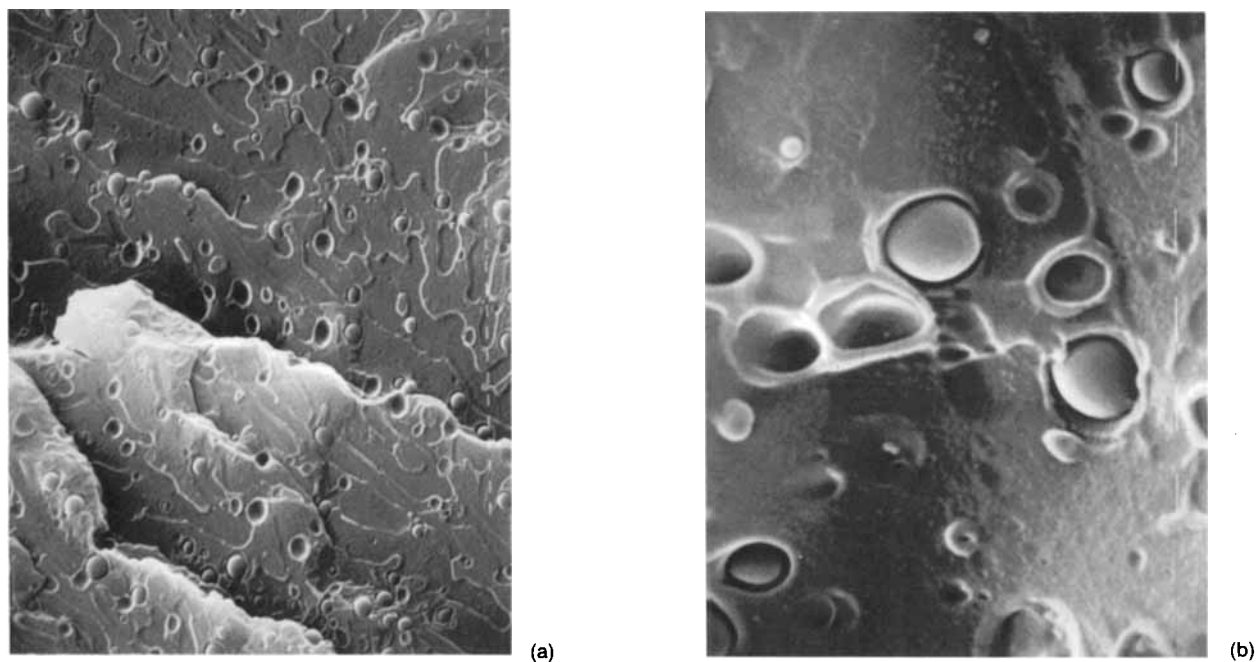


Figure 1 (a) SEM micrograph of PET/nylon 6 (95 : 5) chips, fractured in N_2 , $\times 2,500$.
(b) SEM micrograph of PET/nylon 6 (95 : 5) chips, fractured in N_2 , $\times 10,000$.

Table I Mechanical Data and Birefringence of Homopolymer and Blend Fibers

	POY 133/36 SO STD					POY 133/36 SO + 5% NYLON		
	2,900	3,200	3,600	4,000	4,400	2,900	3,200	3,600
Spin velocity (m/min)	2,900	3,200	3,600	4,000	4,400	2,900	3,200	3,600
Fiber fineness (dtex)	134.0	137.5	137.8	138.2	138.6	130.4	133.8	128.1
Tenacity (cN/tex)	23.7	23.9	24.7	25.7	27.6	22.6	23.0	23.4
Elongation (%)	148.8	130.8	115.3	101.1	93.0	135.8	123.6	143.1
Modulus (cN/tex)	140		193.5	218.4	254.4	142.7	157.7	199.1
HWS (%)	47.8	28.4	11.2	6.1	4.3	40.8	28.6	12.7
Dynafil (cN) DR = 1.7	59.7	96.5	139.2	179.2	224.4	74.1	104.0	143.1
Dynafil spin (cN/tex)	4.5	7.0	10.1	13.0	16.2	5.7	7.8	11.2
Birefringence	0.0308	0.0397	0.0519	0.0593	0.0702	0.0340	0.0356	0.0469

possibility of applying blending technologies, where often the size of disperse phase is of the same order of magnitude as the whole diameter of fiber. General purpose spinning apparatus are made of single screw extruders, well-suited for the dispersion of pigments, additives of dyes, but insufficient when the second phase to be dispersed is another high molecular weight polymer. Because of this deficiency, we performed a prehomogenization step of PET and nylon 6 in the chosen ratio, in a twin screw extruder.

A preliminary drying cycle was affected, shorter at higher T for PET and longer at lower T for nylon 6, more sensitive to thermal degradation.

The chosen ratio of blend component PET/nylon 6 was 95 : 5 w/w. It was chosen as a compromise

between the need for sufficient modification of PET properties and the need for maintaining as much as possible the parameters of PET spinning.

Measurements of the melt-flow index (MFI) on the original polymers and their blend (95 : 5 w/w PET/nylon 6) showed the following results:

PET	64 g/10 min
Nylon 6	62 g/10 min
PET/Nylon 6	96 g/10 min

(MFI at 275°C and 2.16 kg).

The large increase in the MFI of blend was rather surprising. At first, we were convinced of an extensive degradation of PET during blending operation.

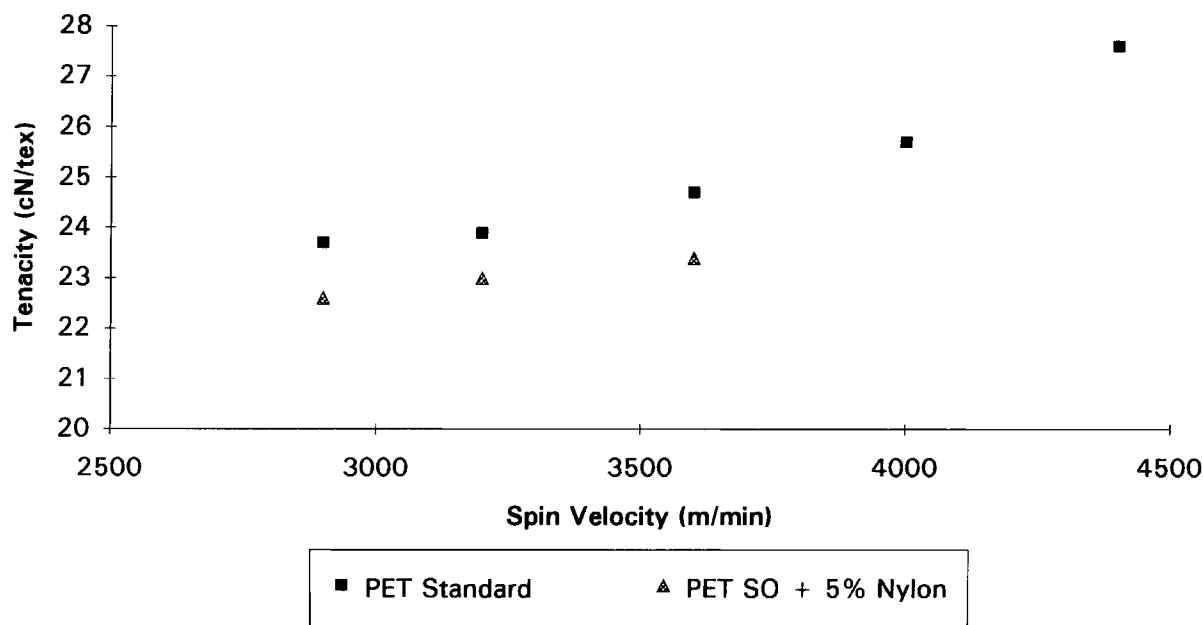


Figure 2 Tenacity vs. spin velocity of PET STD and PET/nylon 6 (95 : 5) blend fibers.

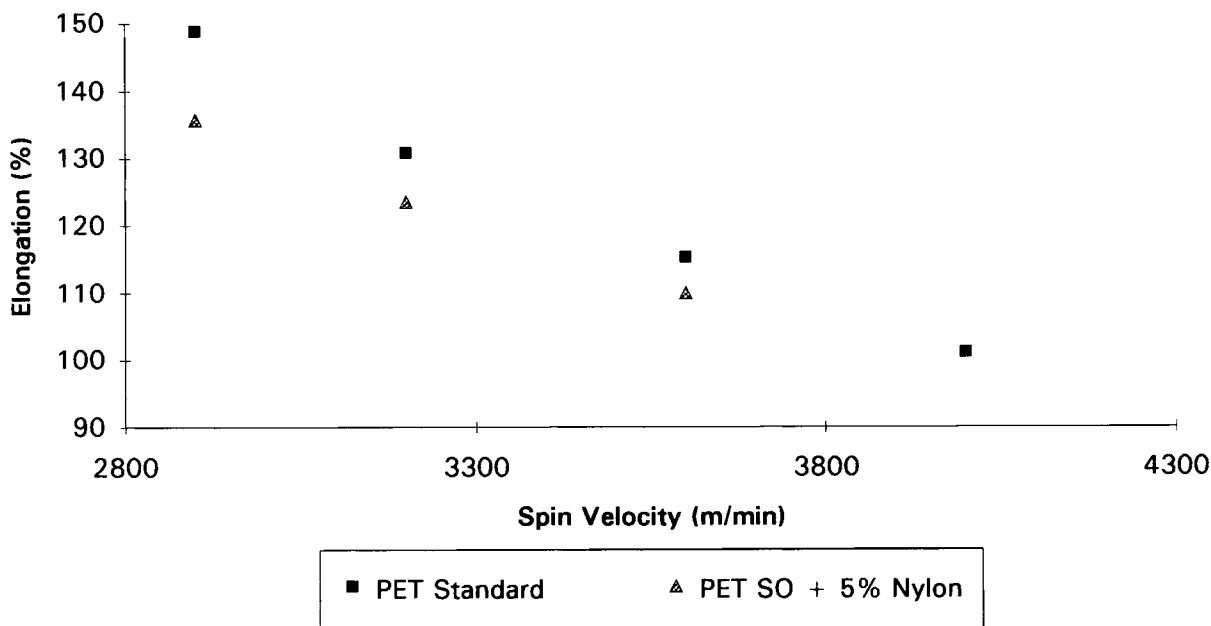


Figure 3 Elongation (%) vs. spin velocity of PET STD and PET/nylon 6 (95 : 5) blend fibers.

As a matter of fact, removal of nylon 6 from the blend with HCOOH left a PET which showed an intrinsic viscosity, η of 0.54, compared to a starting η of PET of 0.62. Such a reduction is not so large to explain a 50% reduction in melt viscosity.

The liquid N_2 fractured surfaces of the melt blended samples can be seen in Figure 1. As it is

observed from the micrographs, the blend is a two-phase heterogeneous system, in which nylon 6 is in the shape of droplets and PET constitutes the continuous phase. Smooth surfaces of particles seem to indicate a purely physical interaction between blend components. The diameter of nylon 6 particles ranges between 0.5 and 2 μm , they are of spherical

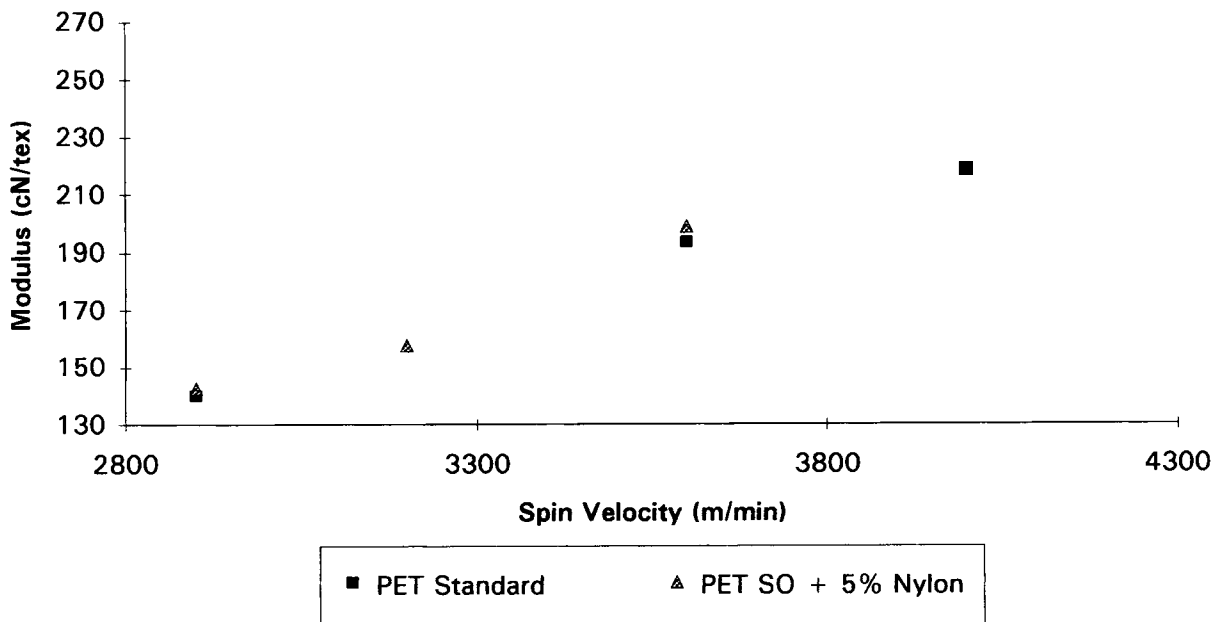


Figure 4 Modulus vs. spin velocity of PET STD and PET/nylon 6 (95 : 5) blend fibers.

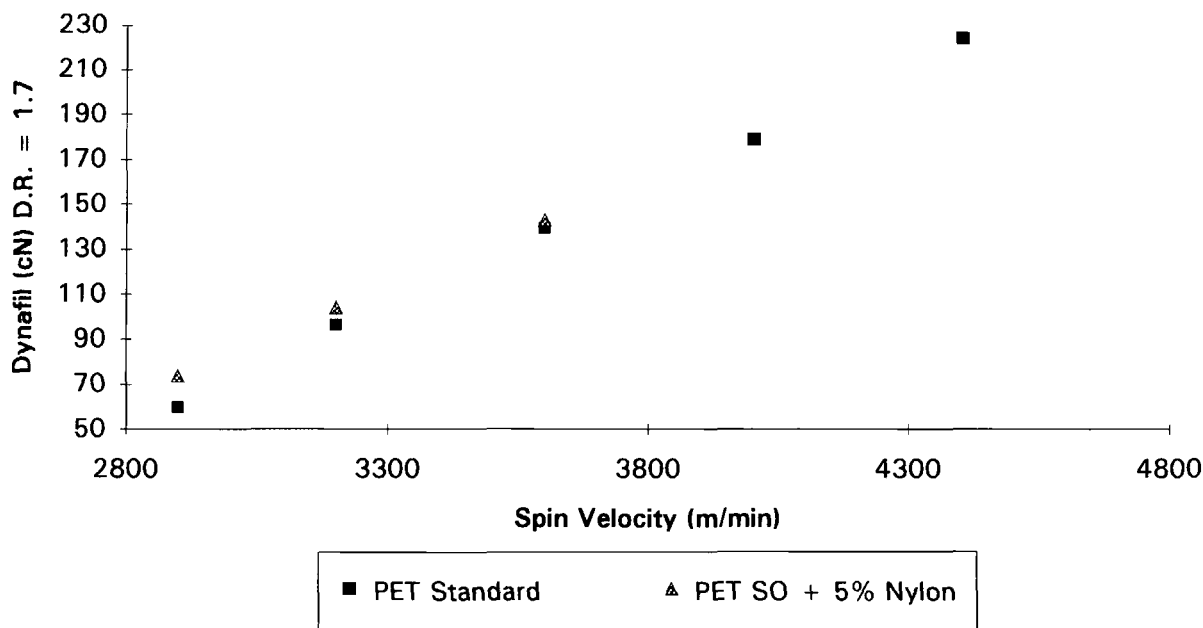


Figure 5 Dynafil vs. spin velocity of PET STD and PET/nylon 6 (95 : 5) blend fibers.

shape, and are regularly distributed. Such morphology may help to explain the previous findings on MFI increase. As a matter of fact, the rheology of molten PET containing small, well-dispersed, and freely rotating nylon 6 spheres must be completely different from plane PET, and the melt viscosity is likely to decrease.¹⁹ It has been also reported that a two-phase fluid which contains deformable droplets

will give lower apparent viscosity than a single-phase fluid or a two-phase fluid which contains nondeformable droplets.²⁰

Fiber Production and Characterization

In this research, only one blend was studied to see the effect of nylon 6 component on PET fibers. Ac-

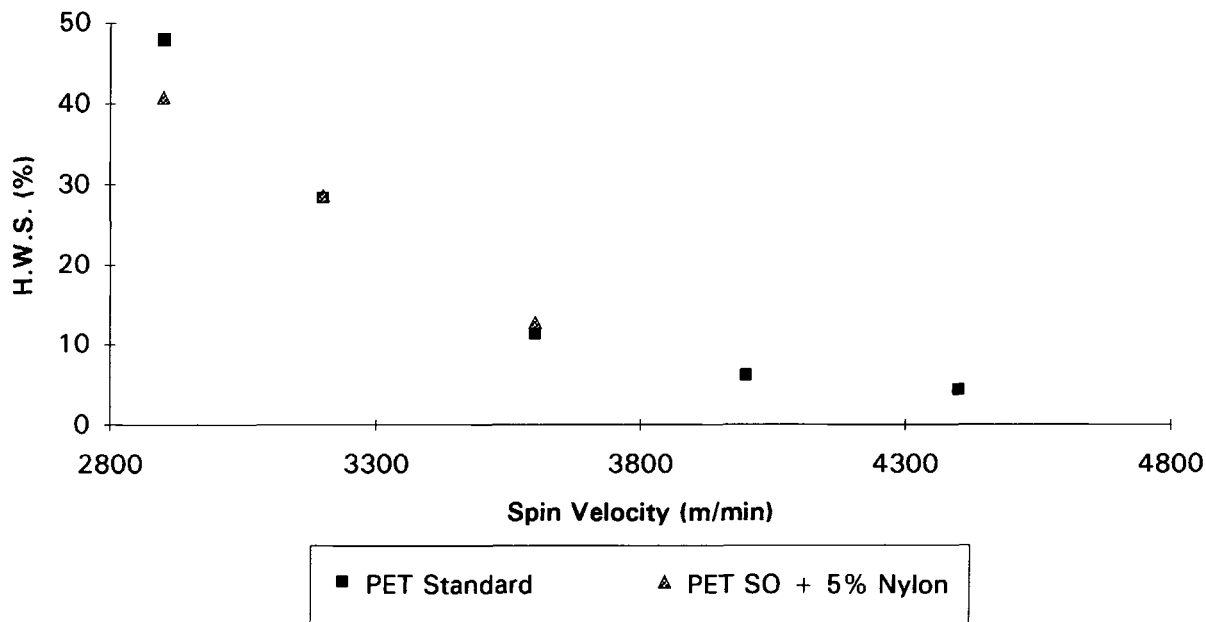


Figure 6 HWS vs. spin velocity of PET STD and PET/nylon 6 (95 : 5) blend fibers.

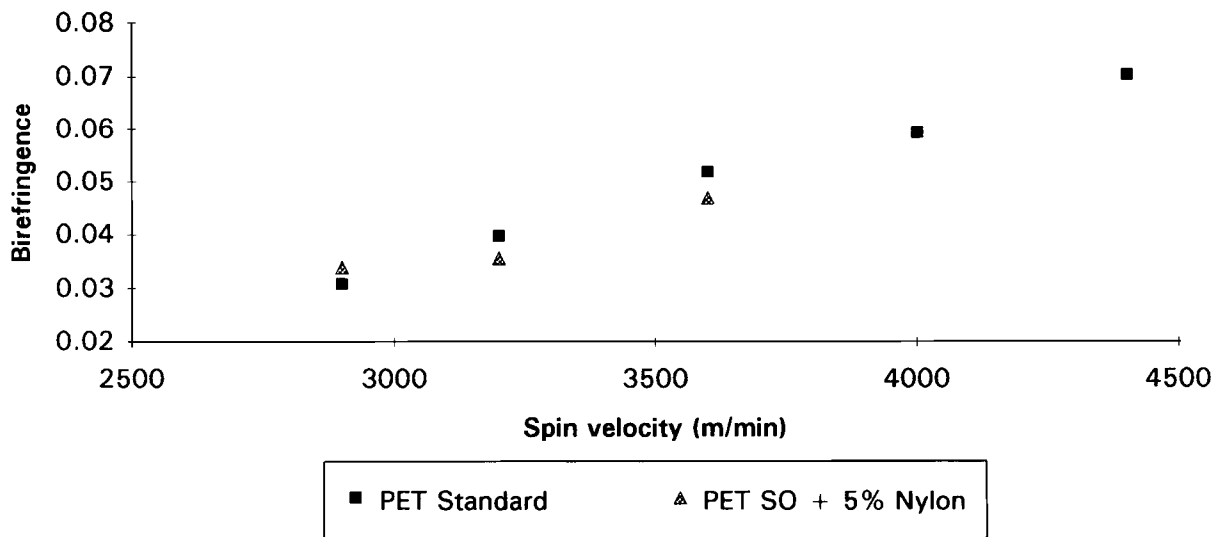


Figure 7 Birefringence vs. spin velocity of PET STD and PET/nylon 6 (95 : 5) blend fibers.

cording to this, the prepared blend was subjected to several spinning velocities ranging from 2,900 to 4,000 m/min. At each spin velocity, the feed was adjusted to obtain a preoriented yarn (POY) always in the same size range (133 dtex/36 filaments). To always obtain filaments at the same size range, it was necessary to decrease the processing temperature by 9°C with respect to PET STD (from 288°C to 279°C). It was also recorded a pack pressure drop by 63 bar with respect to that of PET STD (from 204 to 141 bar). Such effect may be related to two factors: (1) increase in the MFI of blend with respect to PET STD, and/or (2) decrease in the η of PET in the blend.

To understand the origin of the above findings, another spinning process was performed by using a

PET STD with $\eta = 0.572$ dL/g. This test has shown that the spinning conditions necessary to obtain a POY 133/36 require a reduction of 70 bar in pack pressure compared to PET STD, but at a processing temperature still of 288°C. This seems to indicate that the origin of the drop in the processing temperature must be, at least partly, attributed to a modification in the rheological behavior of blend compared to neat PET.

Relevant properties of spun fibers are collected in Table I and are graphically reported in Figures 2-7. It can be seen that mechanical performances are slightly inferior in blend compared to PET homopolymer (Figs. 2-4). Dynafil at fixed draw ratio,

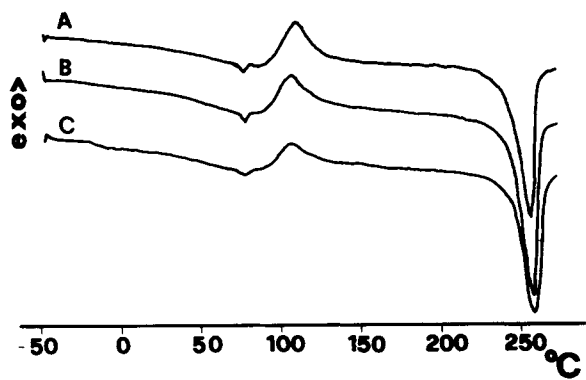


Figure 8 DSC thermograms of PET STD. (A) spin velocity 2,900 m/min; (B) 3,200 m/min; (C) 3,600 m/min.

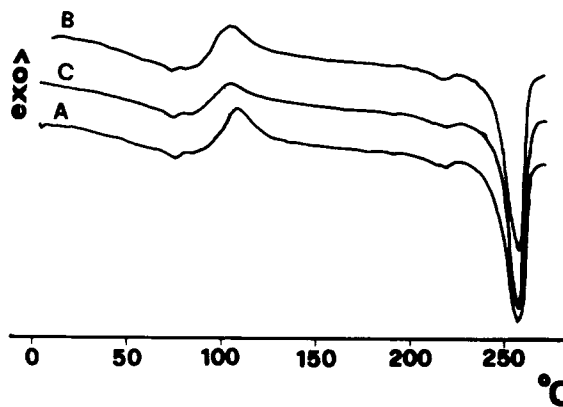


Figure 9 DSC thermograms of PET/nylon 6 blend fibers (95 : 5). (A) spin velocity 2,900 m/min; (B) 3,200 m/min; (C) 3,600 m/min.

Table II Enthalpy of Crystallization, Measured on the Exothermic Peak at about 110°C

PET STD Spin Velocity (m/min)	Enthalpy of Residual Crystallization (J/g)	PET + 5% Nylon 6 Spin Velocity (m/min)	Enthalpy of Residual Crystallization (J/g)	Percent Change in Residual Crystallization (%)
2,900	19.9	2,900	20.7	5
3,200	16.5	3,200	18.2	9
3,600	11.2	3,600	14.2	26

i.e., 1.7 (Fig. 5), and hot water shrinkage (Fig. 6), parameters closely related to the residual free volume of fibers, are equivalent in blend and in PET, indicating that nylon 6 does not adversely affect the development of equilibrium structure in PET, at least at the investigated composition.

DSC calorimetric analysis of PET and blends are shown in Figures 8 and 9, respectively, where the I runs traces are reported. The enthalpy of crystallization, measured on the exothermic peak at about 110°C, are reported in Table II. The values for blends are normalized on the PET content. A small,

but regular increase of the enthalpy of crystallization in blends compared to PET homopolymer seems to indicate a slight negative influence of nylon 6 on the crystallization of PET during spinning. Moreover, such negative influence increases with the spinning rate, as it is shown in Table II as a percent change in residual crystallization. The meaning of such a finding is still unclear. This is also confirmed by the qualitative analysis of WAXS powder spectra reported in Figures 10 and 11 of PET and PET/nylon 6 blend, respectively, where it can be seen a more ordered structure in PET compared to blend (quan-

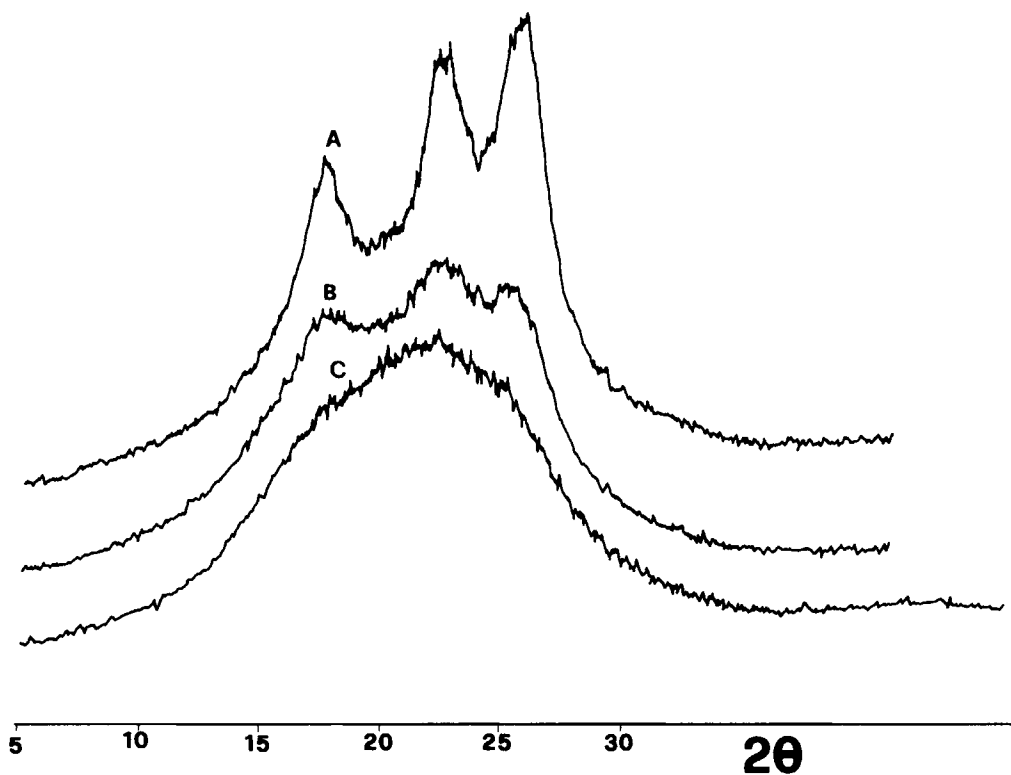


Figure 10 WAXS spectra of PET STD. (A) spin velocity 3,600 m/min; (B) 3,200 m/min; (C) 2,900 m/min.

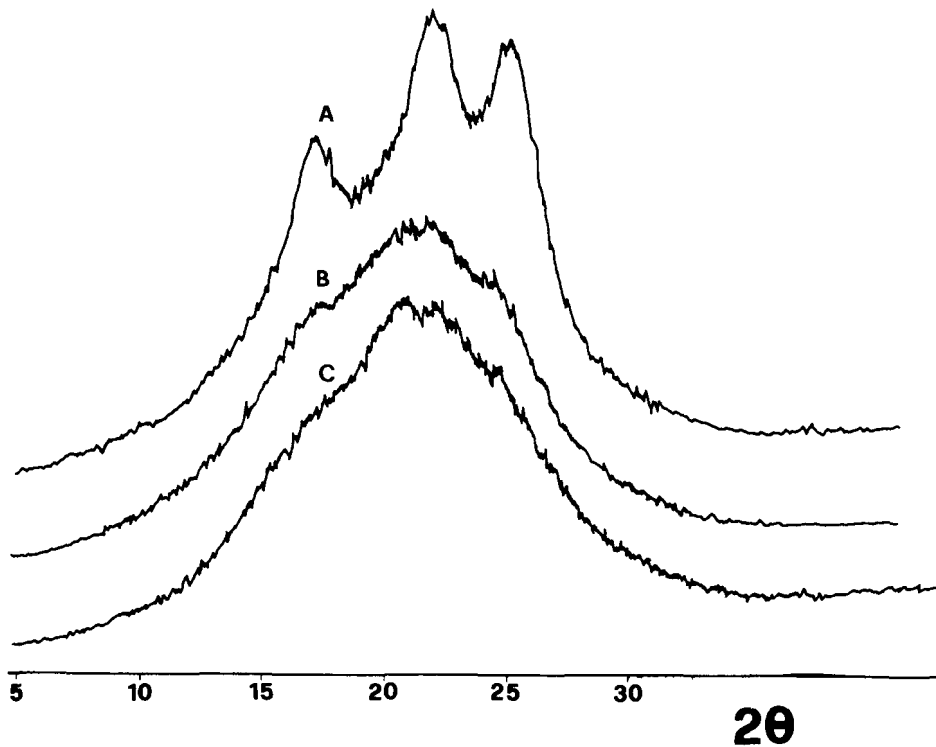


Figure 11 WAXS spectra of PET/nylon 6 blend fibers (95 : 5). (A) spin velocity 3,600 m/min; (B) 3,200 m/min; (C) 2,900 m/min.

titative analysis is obstructed by the overlapping of nylon 6 reflections).

The overall increase in crystallinity when increasing the spinning velocity is expected, and it is related to a preorientation effect of yarns at high velocity of spinning. Nevertheless, there is no significant change at the final enthalpy of fusion of PET in the blend compared to PET STD as the velocities of spinning change (T_m of PET = 256.8°C).

Besides, the yarn obtained from 2,900 m/min (spin velocity) has been drawn to various drawn ratios. Resulting properties at the stated draw ratios are shown in Table III, while the curves are reported in Figures 12 and 13. Once again, the mechanical properties of blends are comparable to those of PET.

After spinning, the strong elongation of fibers makes the detection of nylon 6 particles very difficult. Nevertheless, at least for a single spinning velocity (i.e., 2,900 m/min), fibers broken in liquid N₂ have shown evidence of a heterophase (Fig. 14), whose dimensions are highly reduced compared to the starting material. This finding indicates that nylon 6 particles are probably elongated during spinning. The length of resulting rods can be esti-

mated, assuming that each spheres of the original blend [Fig. 1 (a and b)] turn into a cylinder of identical volume. The original average diameter of the spheres is 2 μ where the final diameter of the cylinders is 0.5 μ on the average. According to this estimation, it has been found that the spheres of nylon 6 are elongated to microfibrils of 21 μ.

Table III Change in Fiber Fineness, Tenacity, and Elongation with Respect to Draw Ratio

Type	Draw Ratio	Fiber Fineness (dtex)	Tenacity (cN/tex)	Elong. (%)
PET + 5% NYLON	1.6	82.2	33.48	31.30
PET + 5% NYLON	1.7	77.0	39.54	29.24
PET + 5% NYLON	1.8	73.5	40.60	17.86
PET STD	1.6	85.5	31.18	33.70
PET STD	1.7	79.0	37.45	31.70
PET STD	1.8	76.0	40.79	24.48

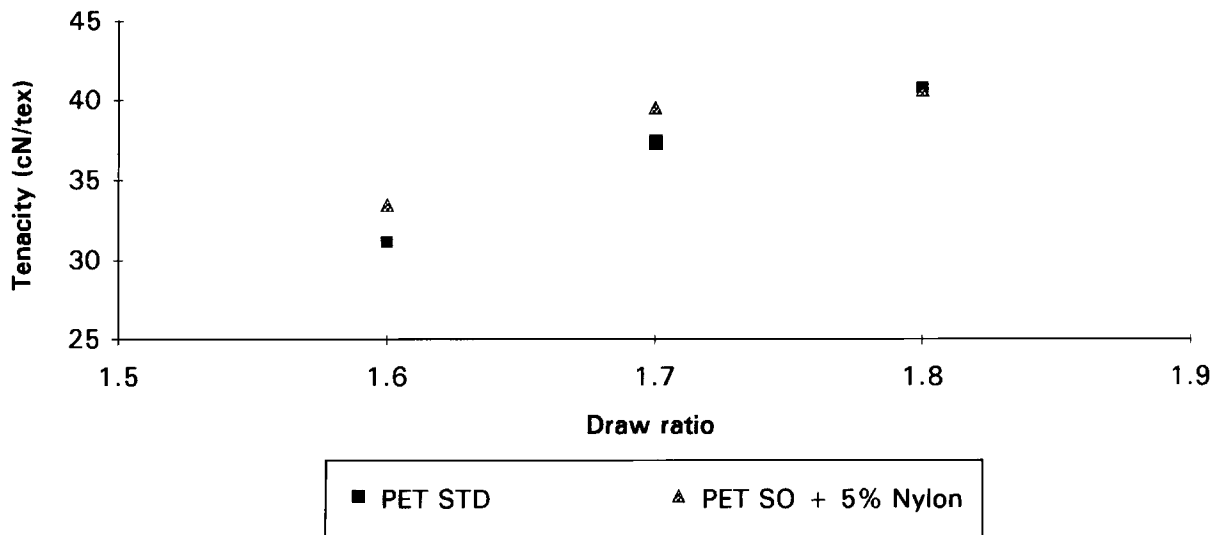


Figure 12 Tenacity vs. draw ratio.

CONCLUSION

From the above, we can conclude that the addition of nylon 6 to PET fibers can, in small amounts, have a beneficial effect on the rheological properties of the polyester, without significantly depressing the mechanical properties. To assure a homogeneous distribution of nylon 6 particles in PET, a pre-homogenization step is needed, as the extruders normally employed to feed the spinning apparatus are not designed to mix together molten polymers.

This finding might be a good technological input for designing innovative extruders for spinning plants. The addition of 5% nylon 6 into PET matrix led to a decrease in the processing temperature and pressure of the polymer by 9°C and 63 bar, respectively. These effects resulted in an interesting technological improvement of the spinning process of PET together with a saving on energetical requirements.

Further work is being carried out to investigate the influence of nylon 6 on the dyeability of PET fibers. Moreover, the analysis will be extended to

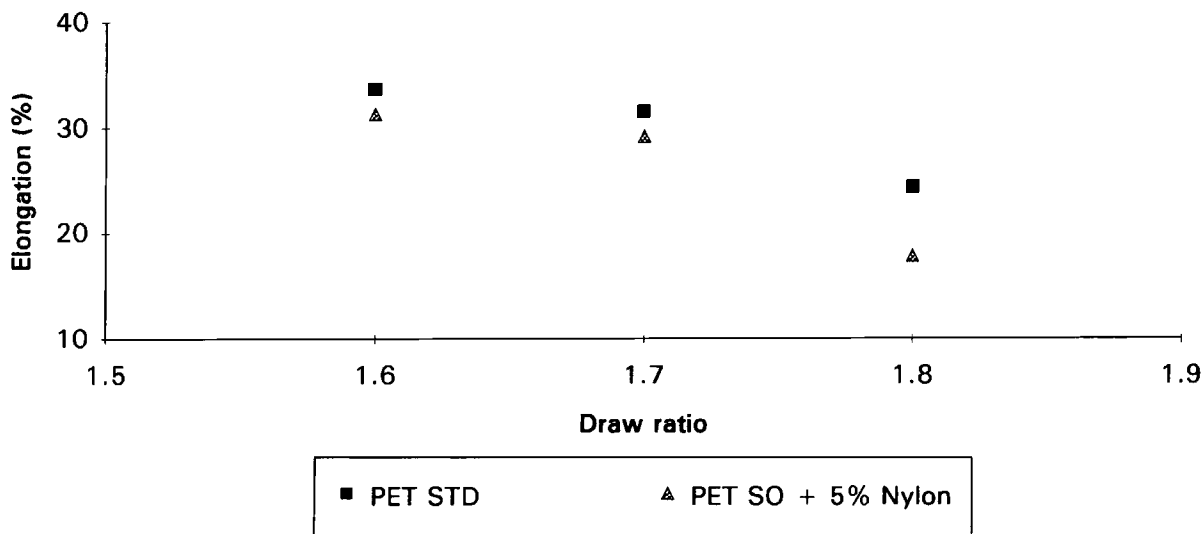


Figure 13 Elongation (%) vs. draw ratio.

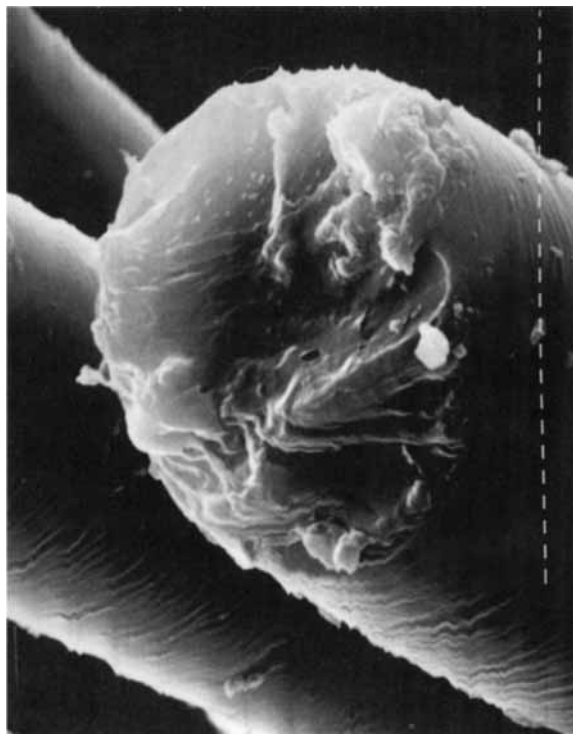


Figure 14 SEM micrograph of PET/nylon 6 fibers, $\times 3,000$.

use (i) different ratios of PET/nylon 6 molecular weight, (ii) different composition of the blend, and (iii) different spinning parameters. Each of these will influence the dimension of dispersed particles as well as the inter-particle distance distribution which will also be analyzed.

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