Use of Nylon 6/Polyethylene Blends in the Preparation of Textile Yarns

Camila Alves de Rezende,[1] Ulf Friedrich Schuchardt,[1] Maria do Carmo Gonçalves[2]

[1]*Instituto de Química, Universidade Estadual de Campinas, Campinas, São Paulo, CEP 13083-970, Brazil*
[2]*Instituto de Química, Universidade Estadual de Campinas, Room I-111, P.O. Box 6154, Campinas, São Paulo, CEP 13083-970, Brazil*

ABSTRACT: Nylon 6 fibers are extensively used by the textile industry because of their excellent properties for yarn manufacturing. In this work, we show that it is possible to prepare yarns of reduced cost with blends of nylon 6 and polyethylene (PE), a lower priced polymer. Blends of nylon 6 and PE (nylon 6/PE) were tested in different compositions. Field emission scanning electron microscopy analyses and tensile tests showed better compatibilization in blends whose components had similar melt flow indices. Without adding compatibilizing agents, we incorporated up to 5 wt % PE into the nylon 6 matrix and successfully prepared yarns of nylon 6/PE blends on an industrial scale. Characterizing the yarns prepared from the blends by conventional techniques employed by the textile industry, we observed values very close to those presented by pure nylon 6 yarns, which indicated that the addition of small amounts of PE to the nylon 6 matrix could reduce the cost of the final yarns without changing significantly the properties of nylon 6. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2142–2148, 2006

Key words: blends; nylon; polyamides; polyethylene (PE)

INTRODUCTION

Nylon 6 is the most important polymer in the nylon class with respect to fiber manufacturing. This can be explained by its relatively low price because the reagent ε-caprolactam, necessary for its polymerization, can be obtained from relatively inexpensive substrates such as cyclohexane, benzene, and phenol.[1] On the other hand, in comparison with other polymer fibers, nylon 6 fibers are still expensive. This high cost can be reduced by the preparation of blends with lower cost polymers, such as polyolefins. Blend preparation is widely considered an economically viable and flexible technique for improving properties or cost–benefit relationships in common polymers without the necessity of synthesizing new polymers. However, when blended together, most polymers present an unstable two-phase morphology: the major component forms the matrix, and the minor component appears as a dispersed phase generally in the form of spheres or fibrils. In some systems, a bicontinuous network is obtained.[2,3]

The morphology of an immiscible blend depends on many factors, such as the blending history, blend ratio, interfacial tension, and differences in the viscosity and elasticity of the two components, and on the processing conditions, such as the temperature, residence time, shear rate, and shear stress.[4–7] Blends of polyamides and polyolefins are of particular interest because they can lead to materials with improved chemical and moisture resistance, dimensional stability, thermomechanical properties, impact and flexion resistance, and oxygen permeation. Besides this, the resulting materials can be processed easily and at reduced costs.[8,9]

Polypropylene (PP) is the main polyolefin used in yarn manufacturing. Besides its significantly lower cost, PP fibers present some very interesting properties, such as facility in processing, resistance to humidity and light, low retention of smog, smells, or fat, and low chemical reactivity.[10]

Through the preparation of blends with polyolefins, these properties can be incorporated into the nylon 6 matrix, improving its characteristics. Several publications have been published on fibers made from blends,[11–17] especially fibers from nylon 6 and PP.[13–17] Takahashi and coworkers[14,15] studied the physical properties of PP/nylon 6 fibers. Grof et al.[17] investigated the structure–property relationship of modified PP–polycaprolactane fibers containing modified poly (ethylene terephthalate) and PP for producing microfibers by the extraction of the continuous phase in a solvent. Microfibers obtained after the extraction of the continuous phase from an immiscible blend have

proven to be useful in making artificial leather for textile devices.

Generally, to achieve good final results for a nylon 6/polyolefin blend, some form of compatibilization is required. One successful approach has been the addition of polyolefins grafted with maleic anhydride as a third component.[5,8,9,18] The maleic anhydride units react with the amine end groups of the polyamide to form block or graft copolymers, which act as compatibilizers for the blend.[9,18] Despite the numerous publications published about yarns from nylon 6/PP blends, the scientific literature lacks information concerning nylon 6/polyethylene (PE) blends.

In this work, no compatibilizing agent was employed. To minimize the problems caused by the immiscibility between nylon 6 and the polyolefin, blends were prepared with small amounts of the dispersed phase. As the final properties of the textile did not depend only on the yarn manufacturing process, there was a possibility of getting around the possible incompatibility. Nylon 6/PE blends were prepared with different compositions and analyzed with field emission scanning electron microscopy (FESEM) and tensile tests. Nylon 6/PE yarns produced from the best system were then characterized with FESEM, denier value determination, and tensile tests.

EXPERIMENTAL

Blend preparation

The raw materials were fiber-grade nylon 6, supplied by Invista (Americana, Brazil), and two PEs of different melt flow indices (MFIs), PE-A (MFI = 0.2 ± 0.1 g/10 min, density = 0.918 g/cm^3) and PE-B (MFI = 18.8 ± 0.6 g/10 min, density = 0.923 g/cm^3), both supplied by Braskem (Camaçari, Brazil). Pellets of the blend components were mixed in the desired weight ratios for obtaining final proportions of nylon 6/PE in the blends of 99/1, 97/3, 95/5, 93/7, 90/10, and 85/15. The polymers were extensively dried in vacuo for 24 h at 100°C before and after extrusion and were kept inside a desiccator until characterization. The polymer blends were prepared via melt mixing in a single-screw extruder [WE X30, Wortex (Campinas, Brazil); screw diameter = 30 mm, length/diameter = 30] at a screw rotation speed of 100 rpm with temperatures ranging from 235 to 255°C in each region of the extruder barrel. After extrusion, the blends were cut into pellets with a Wortex granulator.

Blend characterization

The blends were characterized with FESEM and tensile tests. For FESEM, transversal sections of the samples were obtained by cryogenic fracture in liquid nitrogen and coated with a thin layer of carbon and gold. The equipment used to obtain the micrographs was a JEOL JSM-6340F field emission scanning electron microscope (Tokyo, Japan). Image Pro-Plus 3.0 (Media Cybernetics Inc., Silver Spring, MD) was used to analyze domain sizes in the images, and Origin 6.0 (OriginLab Corporation, Northampton, MA) was used for statistical data treatment. Tensile testing specimens (ASTM D 638, type I)[19] were obtained in an Arburg All Rounder 221 K injection machine (Lossburg, Germany) under the following conditions: the injection speed and pressure were 8 cm^3/s and 900 bar, respectively, and the mold temperature was 35°C. Tensile testing was carried out in an EMIC DL 2000 machine tester (São José dos Pinhais, Brazil) at 23 ± 2°C and 50 ± 5% relative humidity, with a crosshead speed of 30 mm/min. The mechanical properties (the tensile strength and Young's modulus, which was measured as the tangent modulus at zero strain) were determined from the force–displacement curves. Twelve specimens were tested to obtain each reported value.

Yarn processing

Yarns of blended polymers were processed on an industrial scale by the textile industry. Before processing, 4000 kg of fiber-grade, bright nylon 6 in chip form was dried for 12 h at room temperature. Melt spinning was performed in a single-screw extruder with spinnerets containing 18 orifices each. The extruder was set with five different temperature zones ranging from 260 to 290°C along the extruder barrel. Yarns were manufactured in a trilobal shape. Multifilament nylon 6 yarns of 55 denier/12 filaments were prepared with PE concentrations of 1, 2, 3, 4, and 5%. The samples were stored between the two stretching steps for 12 h under controlled humidity and temperature. Other parameters were the screw speed (50 rpm), cooling air temperature (35°C), cooling air rate (0.58 m/s), and bobbinning temperature (20°C).

Yarn characterization

Yarns were characterized with FESEM, denier determination, and tensile tests. For FESEM, transversal sections of the yarns were obtained by inclusion in a resin, microtoming, and coated with carbon and gold. Denier analysis (the determination of the fiber mass by the unit of length) was undertaken with an American Sod Producers Association Marte apparatus (Santa Rita do Sapucai, Brazil). Diameter regularity analysis (the determination of the ratio of the medium thickness of the fiber to the unit of length) was carried out with a KET 80 II/C regularimeter (Keisokki Kogyo Co. Ltd., Hyogo, Japan). The dynamometric characteristics of the fibers (tenacity and elongation) were determined
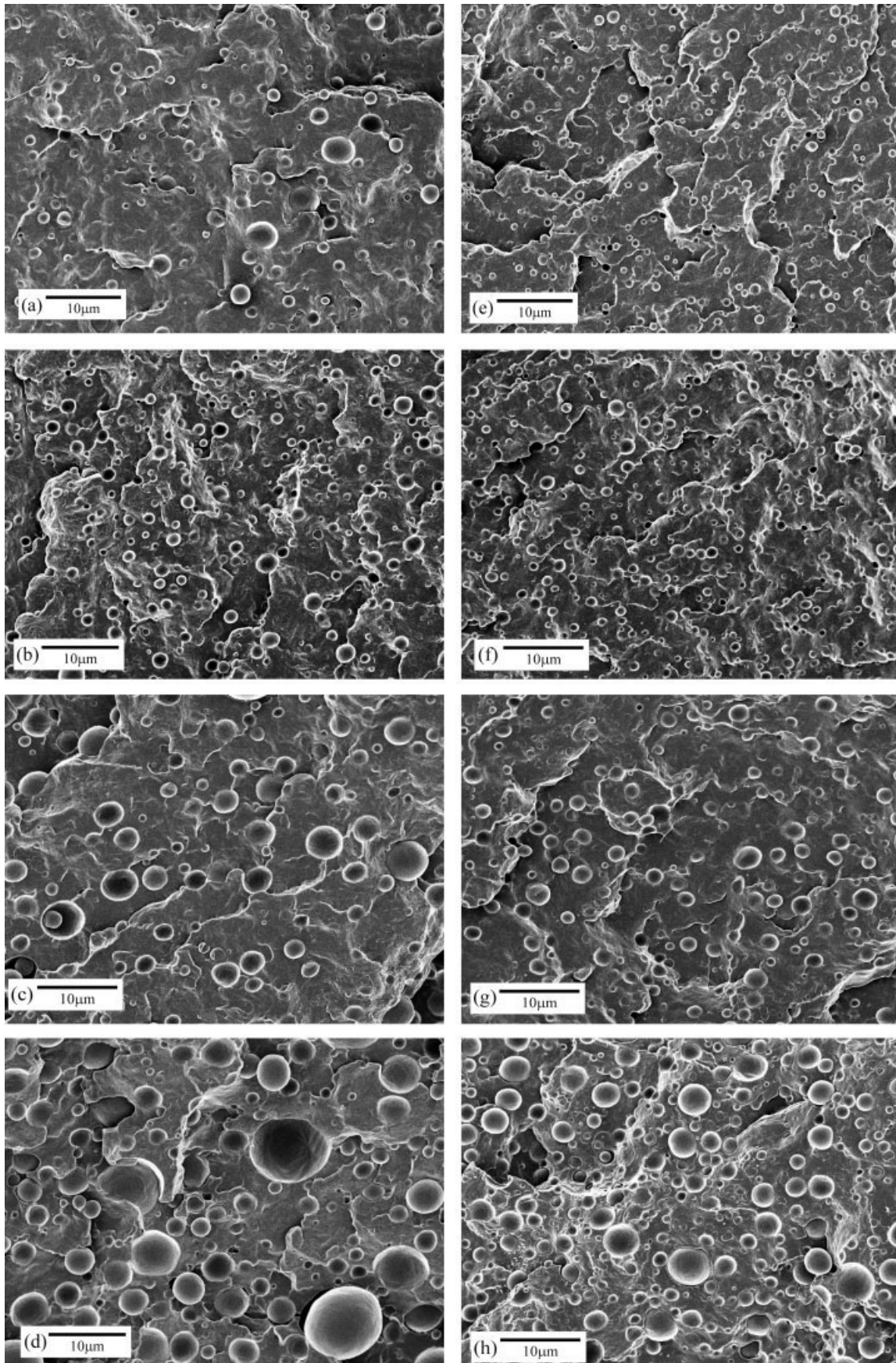
Figure 1 Scanning electron micrographs of (a) 97/3, (b) 95/5, (c) 93/7, and (d) 85/15 nylon 6/PE-A blends and (e) 97/3, (f) 95/5, (g) 85/15, and (h) 85/15 nylon 6/PE-B blends.

TABLE I
PE Domain Diameters in Nylon 6/PE-A Blends

Nylon/ PE-A blends	Minimum diameter (µm)	Maximum diameter (µm)	Medium diameter (µm)	Standard deviation	Number of measured domains
99/1	0.2	2.7	1.1	0.5	254
97/3	0.2	4.5	1.3	0.6	500
95/5	0.2	4.8	1.3	0.6	707
93/7	0.2	5.7	1.1	0.8	898
90/10	0.2	12.3	1.4	1.1	699
85/15	0.3	11.8	2.8	2.1	434

by tensile tests in a Statimat dynamometer (Textechno, Mönchengladback, Germany).

RESULTS AND DISCUSSION

FESEM micrographs have been used to analyze the morphology of the blends and the sizes and distributions of the domains because the morphological characteristics have fundamental importance with respect to the final properties. Figure 1(a–d) shows micrographs of the cryogenic fractures of nylon 6/PE-A blends prepared from PE of low MFI at different concentrations. It is possible to observe the presence of small PE domains, which characterize the blend as a phase-segregated system. When the PE content increases, larger domains appear together with small domains whose presence can be observed in all the samples. The effect of increasing domain size as the PE concentration increases was previously observed by Afshari et al.[2] and Willis et at.,[20] who also studied blends of nylon 6 and PE. It is also possible to verify the presence of spaces between the dispersed domains and the matrix caused by lower interfacial adhesion. In fact, some domains even detach from the matrix during the fracturing process, leading to spherical voids. This effect can be especially noted around bigger domains. Thus, to minimize this effect, it is necessary to obtain systems with small PE domains, which can be obtained only with lower PE concentrations. To improve phase compatibility in the blend, a compatibilizing agent can be used. The compatibilizer acts by reducing the interfacial tension and the coalescence of the phases, improving both the morphological and mechanical

properties, as shown by many studies published in the literature.[4,8,9,18] However, the aim of this work is to obtain a low-price material with optimized properties, without the addition of other components to the system. The addition of such components would require modifications in the industrial-scale processing of the yarns, which would be very expensive. The addition of small amounts of neat PE can be done without changes in any processing parameters.

In Figure 1(e–h), nylon 6/PE-B blends, prepared from PE with a higher MFI, are shown. Domain sizes seem to be smaller in nylon 6/PE-B blends than in nylon 6/PE-A blends of the same compositions. To verify this observation, domain size distributions have been obtained through the measurement of all the domains present in a series of micrographs acquired for each blend concentration. Information about the PE domain diameter for nylon 6/PE-A and nylon 6/PE-B blends is shown in Tables I and II, respectively, and in the histograms shown in Figure 2.

Observing the data presented in Tables I and II, we can note that a high number of domains has been measured for each blend concentration to guarantee the statistical reliability of the results. The presence of small domains is verified for all the concentrations in both blend types, and the minimum diameter does not change significantly when the PE content increases. On the other hand, the maximum diameter increases with higher PE concentrations, indicating the formation of larger domains due to the coalescence of smaller ones and the coexistence of different domain diameters. Comparing the maximum diameter values in blends prepared from PE-A and from PE-B, we can observe larger values in ny-

TABLE II
PE Domain Diameters in Nylon 6/PE-B Blends

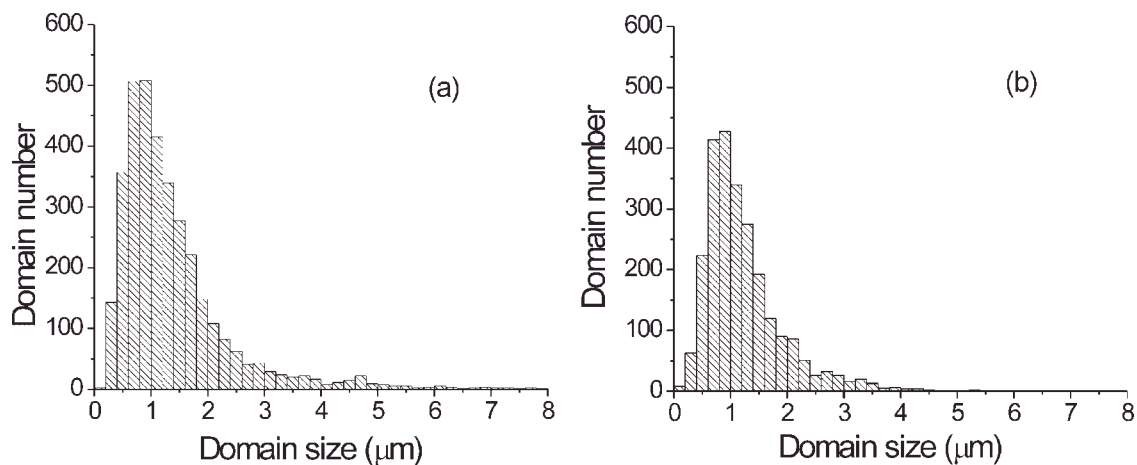| Nylon/ PE-B blends	Minimum diameter (µm)	Maximum diameter (µm)	Medium diameter (µm)	Standard deviation	Number of measured domains
99/1	0.1	2.3	0.8	0.3	415
97/3	0.1	2.5	0.8	0.3	499
95/5	0.1	2.6	1.0	0.4	528
93/7	0.2	3.7	1.4	0.6	324
90/10	0.3	4.6	1.4	0.7	461
85/15	0.4	5.2	1.8	0.9	432

Figure 2 Size distributions of PE domains in (a) nylon 6/PE-A and (b) nylon 6/PE-B blends.

lon/PE-A blends. This can also be visualized in the histograms in Figure 2 and confirm what has been already noted in the micrographs: blends prepared with PE with MFI values closer to that of the matrix show smaller domain sizes (MFI for nylon 6 = 23.5 ± 0.4 g/10 min).

This result indicates the importance of the component viscosity in the blend morphology and is in agreement with results obtained by other authors for similar systems.[4–7] Kudva et al.[4] investigated the

effects of the concentration, melt viscosity, and functionality of maleated PEs on the properties of their blends with nylon 6. These authors showed that the size and distribution of the domains in their blends changed with the composition and viscosity of the components and the presence of compatibilizing agents, influencing the final morphology and the mechanical properties. Therefore, to reduce the viscosity difference between the phases and to obtain better results, the yarn should be prepared with PE-B,
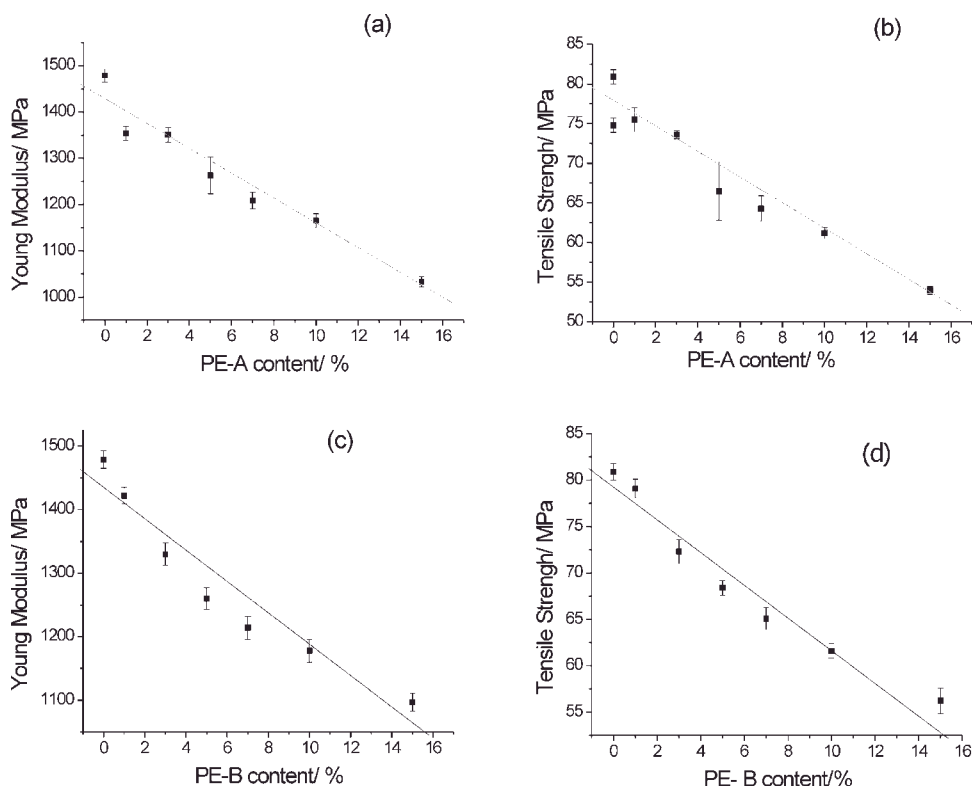

Figure 3 Young's modulus and tensile strength for nylon 6/PE blends as a function of the PE content: (a,b) nylon 6/PE-A and (c,d) nylon 6/PE-B. The angular and linear correlation coefficients of the fitted lines are (a) −26.84 and −0.98, (b) −1.61 and −0.99, (c) −24.70 and −0.97, and (d) −1.76 and −0.98, respectively.

whose MFI value does not differ too much from the MFI matrix value. Moreover, a low concentration of PE should be used to minimize domain sizes. On the basis of the micrographs and the tables of the domain sizes, it seems that the maximum useful concentration of PE for preparing the yarns is 5% because the domain sizes increase significantly at higher concentrations.

Figure 3(a,b) shows graphs of the Young's modulus and tensile strength for nylon 6/PE-A blends versus the PE-A content, and Figure 3(c,d) show the same graphs for nylon 6/PE-B blends.

Before testing, specimens were maintained under controlled temperatures and closed inside a desiccator, as recommended by the ASTM 638 standard. This is fundamental for the final results because all polyamides absorb moisture to various degrees, depending on the polymeric structure, the environment, and the temperature. Moisture mainly affects the amorphous phase of the polyamide and acts as a plasticizer: increasing moisture content will reduce the tensile strength, modulus, and stiffness.[21]

Observing the curves, we can verify that both the Young's modulus and tensile strength for the blends are always smaller than the values obtained for the pure nylon 6 (1479 $\pm$ 14 MPa and 80.9 $\pm$ 0.9 MPa, respectively) and decrease linearly when the PE proportion increases. The decrease in both properties occurs in a similar way for both blends, notwithstanding the PE used. The addition of 5% PE-A leads to a decrease of 15% in Young's modulus and 18% in the tensile strength, and the addition of 5% PE-B to the nylon 6 matrix reduces both mechanical properties by 15%. The results show that it is possible to control the mechanical properties of nylon 6/

PE blends through changes in the PE amount added to the matrix.

Considering the results obtained, we prepared yarns from nylon 6/PE-B blends with concentrations ranging from 1 to 5% PE-B. The spinning process was carried out under the same conditions used for the nylon 6 fibers, and the yarns were successfully produced. The fibers produced from nylon 6/PE-B blends were robust and presented an appearance that was very similar to that of pure nylon 6 fibers.

Figure 4 shows micrographs of surfaces and cross sections of nylon 6/PE-B yarns with 3% PE. Figure 4(a) shows the transversal section of a nylon 6/PE yarn, pointing out the trilobal form. Figure 4(b,c) also shows transversal sections of the same blend, and it is possible to verify the presence of small PE domains dispersed in the yarn structure. Figure 4(d) shows a set of aligned nylon 6/PE yarns. These yarns have a very smooth surface, which can also be noted in the amplified image presented in Figure 4(e). The surface of the nylon 6/PE yarns is very similar to the surface of pure nylon 6 yarns [Fig. 4(f)]. The presence of dispersed PE domains in the matrix can be clearly observed in the images taken from the yarn cross section but do not appear on the surface. Measuring the diameters of the domains dispersed in the yarn structure, we obtained a mean diameter of 0.23 $\pm$ 0.07 μm for the PE domains. The minimum diameter is 0.02 μm and the maximum diameter is 0.42 μm for a total of 398 domains measured. From this analysis, it is possible to verify that the PE domains in the yarns are 4 to 5 times smaller than the domains in the blends. As the same materials were used for preparing both the blends and the yarns made from the blends, this difference in domain size can be attributed to differences in the processing of the blends
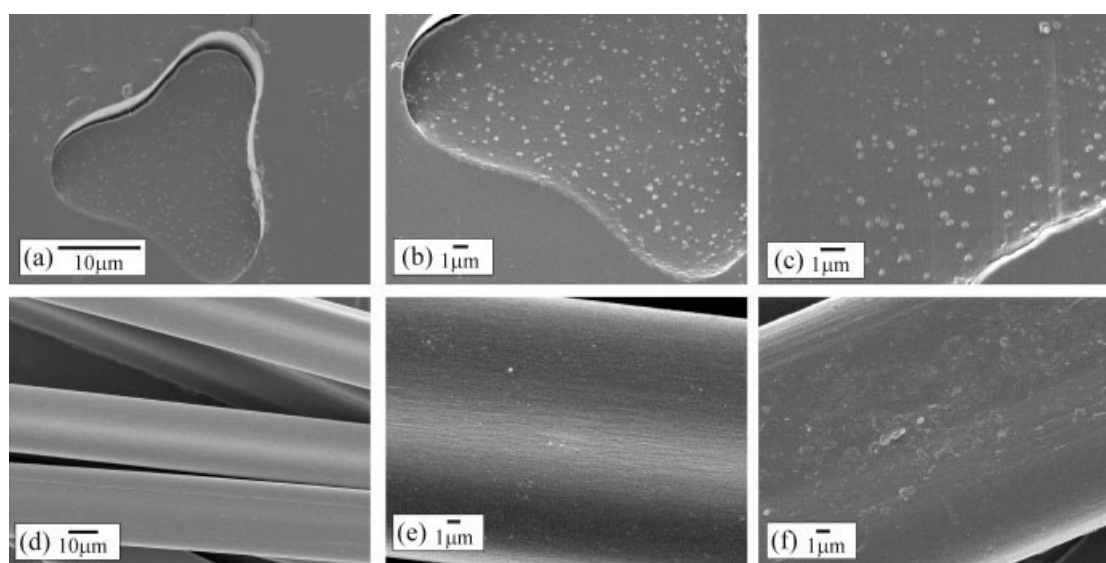

Figure 4 Field emission scanning electron micrographs: (a–c) transversal cross sections of a 97/3 nylon 6/PE-B blend, (d,e) surface of a 97/3 nylon 6/PE-B blend yarn, and (f) surface of pure nylon 6 yarn.

TABLE III
Denier, Tenacity, and Elongation for Nylon
6/PE-B Blend Yarns

PE-B (%)	Denier (dtex)	Tenacity (cN/dtex)	Elongation (%)
0	55.3 ± 0.5	4.09 ± 0.10	32.9 ± 1.9
1	55.0 ± 0.7	4.22 ± 0.27	33.2 ± 7.5
2	54.0 ± 0.6	4.35 ± 0.21	31.4 ± 3.6
3	52.8 ± 0.3	4.39 ± 0.51	31.7 ± 3.2
5	54.1 ± 0.5	4.35 ± 0.22	32.3 ± 3.5

and yarns. In the melt-spinning process, the melt material is submitted to a different shear stress, and the spinnerets direct them to a more elongated form. Perhaps the differences in the dispersed domain size represents a modification not only of the size of the phase but also of its format. Because they become more elongated, the domain diameters are smaller even if the overall volume of the domains does not change.

Table III shows the denier, tenacity, and elongation at break values for the yarns prepared from nylon 6/PE blends. The denier value is the mass of 10,000-m-long yarn, and the tenacity is the relation between the tensile strength at break and the dernier value. The elongation is the increase in the fiber length produced by a tensile load and can be expressed in units of length or as the percentage of elongation with respect to the initial length. The denier value depends on the polymer density, but as the PE content is small, these values do not change significantly. The tenacity values after the addition of PE are better than the tenacity of nylon 6 yarns, and the elongation values are very close to the matrix elongation values. For all the properties that were measured (denier, tenacity, and elongation values), small changes in the values obtained for the yarns made from blends, compared with those of nylon 6, were observed. This means that the addition of small amounts of PE does not modify nylon 6 properties significantly.

CONCLUSIONS

By characterizing nylon 6/PE blends, we can point out that these blends form a biphasic system with dispersed PE domains. Domains of small diameter appeared in all the samples, whereas domains with larger diameters appeared only in the samples with high PE contents. Because of the small difference in the MFIs of PE-B and nylon 6, this blend presents smaller diameter domains than blends prepared

with PE-A. Considering the mechanical properties of the blends, we can also verify that the Young's modulus and tensile strength are always smaller than those of nylon 6 and decrease linearly when the PE proportion increases, indicating that these properties can be controlled by changes in the PE proportion. Yarns of nylon 6/PE with low contents of PE with an MFI value close to that of nylon 6 can be prepared without processing problems and present good properties with respect to the denier value, elongation, and tenacity. Domains measured in the yarns are much smaller than domains in the blends, and this can be explained by differences in the melting process. Because of the low price of PE in comparison with nylon 6, textile products prepared with these yarns will be cheaper and could be used in many applications.

References

1. Herlinger, K. H.; Gebhardt, F. S. In Ullmann's Encyclopedia of Industrial Chemistry, 5th ed.; VCH: New York, 1987; p 10.
2. Afshari, M.; Kotek, R.; Kish, M. H.; Dast, H. N.; Gupta, B. S. Polymer 2002, 43, 1331.
3. Vainio, T. P.; Seppala, J. V. Polym Polym Compos 1993, 1, 427.
4. Kudva, R. A.; Keskkula, H.; Paul, D. R. Polymer 1999, 40, 6003.
5. Utracki, L. A.; Dumoulin, M. M.; Toma, P. Polym Eng Sci 1986, 26, 34.
6. Favis, B. D.; Chalifoux, J. P. Polymer 1988, 29, 1761.
7. Plochocki, A. P.; Dagli, S. S.; Andrews, R. D. Polym Eng Sci 1990, 30, 741.
8. Gonzáles-Montiel, A.; Keskkula, H.; Paul, D. R. J Polym Sci Part B: Polym Phys 1995, 33, 1751.
9. Ide, F.; Hasegawa, A. J Appl Polym Sci 1974, 18, 963.
10. Alfieri, P. Textília 1998, 27, 50.
11. Varma, D. S.; Dhar, V. K. Text Res J 1998, 58, 274.
12. Tsebrenko, I. A.; Pakharenko, V. A. Fibre Chem 1999, 31, 23.
13. Lyoo, W. S.; Choi, Y. G.; Ha, W. S.; Kim, B. C. Int Polym Proc 2000, 15, 369.
14. Takahashi, T. Sen I Gakkaishi 2002, 58, 238.
15. Takahashi, T.; Konda, A.; Shimizu, Y. Sen I Gakkaishi 1996, 52, 396.
16. Li, X.; Chen, M.; Huang, Y. Polym J 1997, 29, 975.
17. Grof, I.; Durcova, O.; Jamlich, M. Colloid Polym Sci 1992, 270, 22.
18. Chow, W. S.; Mohd Ishak, Z. A.; Karger-Kocsis, J.; Apostolov, A. A.; Ishiaku, U. S. Polymer 2003, 44, 7427.
19. Standard Test Method for Tensile Properties of Plastics; ASTM D 638-95; American Society for Testing and Materials: West Conshohocken, PA, 1995.
20. Willis, J. M.; Caldas, V.; Favis, B. D. J Mater Sci 1991, 26, 4742.
21. Seldén, R.; Dartman, T. Text Res J 1998, 68, 264.