

The Surface Composition of Biconstituent Fibers

INTRODUCTION

Biconstituent fibers can be prepared by extruding blends of poly(ethylene terephthalate) and nylon 6.^{1,2} The properties of the drawn fibers are dependent on the axial and radial homogeneity of the blend. Proper mixing of the two components should give uniformity along the length. However, preferential migration of one of the components to the surface of the fiber can result in a radial concentration gradient. Since the fibers under consideration are of the order of 25 microns in diameter, conventional microscopic examinations of the surface are not feasible. Scanning electron microscopy has been used,¹ but quantitative data are difficult to obtain by this technique.

An infrared method based on a reflectance technique was chosen in order to obtain a quantitative estimate of the composition of the fiber surface.

EXPERIMENTAL

The polymers under investigation were prepared from blends of nylon 6 and poly(ethylene terephthalate). These blends, when extruded in fiber form, consist of fine diameter fibrils of the minor phase dispersed in a matrix of the major phase. The fibrils, whose diameters are of the order of 0.06 μ , align themselves along the fiber axis whose diameter is of the order of 25 μ . Details of the preparation and microscopic examination of these bicomponent nylon 6 and PET fibers can be found elsewhere.^{1,2} In the present work, multifilament yarns and cords prepared from three plies of such yarns were examined.

The objective of the present work was to examine the fiber surfaces by means of infrared attenuated reflectance techniques to determine if there was any preferential concentration of one phase at or near the surface.

The method of analysis was based on the measurement of the 1725 cm^{-1} (5.8 μ) and 1643 cm^{-1} (6.1 μ) bands of the blend. These corresponded respectively to the carbonyl of the ester group in PET and the carbonyl of the amide group in nylon 6.

A value of 1.45 was obtained for the ratio of the absorbances (A_{PE}/A_N) of the ester to the amide carbonyl determined from transmission spectra. The nylon 6 spectra were obtained in trifluoroethanol solution and the PET, in solutions of orthochlorophenol. The value of A_{PE}/A_N would be expected to be about 1.38 under ATR conditions since the effective thickness would be about 5% greater for nylon 6 due to the deeper penetration at the longer wavelengths (5.8 μ vs. 6.1 μ).

The apparatus used in determining the surface composition of the fibers under study was a Wilks Model 12 FMIR unit.

Principals of the ATR technique have been covered in detail by several authors.^{3,4} A number of other authors have applied this technique to the surface study of fibers.^{5,6,7}

In the present work, FMIR spectra were obtained on fibers which were wound around a 2-mm-thick KRS-5 prism. A ratio of weight-% polyester to weight-% nylon 6 was calculated from the following expression:

$$\%PE/\%N = A_{PE}/A_N \times 1/1.38.$$

Since $\%PE + \%N = 100$, the per cent nylon could be calculated from

$$\%N = \frac{100}{1 + \frac{A_{PE}}{1.38A_N}}$$

The depth of penetration of the infrared radiation into the sample is related to the effective thickness. The effective thickness, defined as the thickness of film required to obtain the same absorption in a transmission measurement as that obtained in a

reflection measurement on a relatively thick sample,⁴ was estimated as several microns.⁸

The effective thickness was reduced further in another set of experiments. In these experiments, a thin solid copolymer film (transparent at an infrared wavelength of $6\ \mu$) of chlorotrifluoroethylene (96%) and vinylidene fluoride (4%) was placed between the KRS-5 prism and the material to be examined. The effective thickness was therefore reduced, at least approximately, by the thickness of the film. Therefore, by using different thicknesses of the copolymer film, the surface layer of the fibers being examined could be varied.

The copolymer films were prepared by casting a solution of the copolymer in hexafluorobenzene directly on the KRS-5 prism to be used in the FMIR apparatus.

Film thickness was calculated from the absorption of the $967\ \text{cm}^{-1}$ band in a transmission spectrum. Since the KRS-5 is transparent through this infrared region, the transmission spectrum of the film could be obtained without removing the film from the prism. The $967\ \text{cm}^{-1}$ band is one of the strongest absorptions in the copolymer spectrum. Therefore, an extremely thin film was needed in order to be able to read the optical density accurately and to calculate an absorption coefficient for the band. The thickness was calculated for such a film by the interference fringe method. A value of 0.13 was calculated for the absorbance of the $967\ \text{cm}^{-1}$ band for a film $1\ \mu$ thick. This value was then used to calculate the thickness of the copolymer films cast on the prism from the absorption obtained at $967\ \text{cm}^{-1}$ in their transmission spectrum.

Two biconstituent yarn samples (A and B) and two biconstituent cord samples (C and D) were characterized by the infrared reflectance technique. The materials differed in their nylon 6-poly(ethylene terephthalate) content. The fibers were extracted with cyclohexane before examination in order to remove surface finishes which might interfere with reflection measurements.

The samples were then wrapped around the prism holder such that good contact was made between the prism surface and the fibers. The fibers were examined at two different penetration levels. They were first examined at the natural effective thickness depth of the apparatus. This value is estimated at about several microns in the region where the measurements were made ($1725\ \text{cm}^{-1}$ or $5.8\ \mu$ to $1640\ \text{cm}^{-1}$ or $6.1\ \mu$). A thinner surface layer was then examined by use of a film of fluorocopolymer of about $0.5\ \mu$ which was placed between the prism and the sample. Quantitative measurements on the carbonyl absorption were made after expanding the transmission scale with the $5\times$ and $10\times$ instrument settings. Spectra were obtained on a Perkin Elmer Model 21 instrument using a $1000\ (2\times)$ slit program. The region between $1820\ \text{cm}^{-1}$ ($5.5\ \mu$) and $1540\ \text{cm}^{-1}$ ($6.5\ \mu$) was scanned at about $3\ \text{min}/\mu$. Absorbance measurements were made on the peak heights of the $1725\ \text{cm}^{-1}$ band due to the ester carbonyl and $1640\ \text{cm}^{-1}$ due to the amide carbonyl. Per cent nylon was calculated from the previous expression.

DISCUSSION OF RESULTS

In Table I are listed the surface compositions at two levels of penetration for the four samples. Also listed are the values for the nylon content calculated by a nitrogen determination (Micro Dumas).

Several conclusions can be drawn from the data in Table I. In all the samples there is a greater amount of nylon on the surface than in the materials as a whole. Sample B showed a considerable excess of nylon on the surface relative to the total nylon concentration.

The data further indicate that a gradient in the concentration is observed in approximately the first several microns of surface layer of the cord samples. An increase in the nylon concentration is observed as thinner surface layers are examined. This change in composition in the first several microns of surface was not observed in the yarns. The cord-forming process and subsequent treatment may be changing the surface composition of the fibers.

It was also noticed that the surface composition could be varied by remolding. All the yarn and cord samples were molded into thin films about 2 mils thick. They were molded by heating at 250°C for 3 min under 20 tons of pressure and then cooled in the press. In Table II are listed the results obtained on the film specimens at an effective thickness of about several microns. They are compared with the results on the fibers and cords. An increase in the nylon on the surface has occurred for three out of four of the materials. A decrease in nylon concentration may have occurred in the case of the material which initially contained about 75% polyester (sample B). However, the change was small and there was still an overall excess of nylon on the surface as

TABLE I
Nylon 6 Weight Per Cent on the Surface of Biconstituent Fibers
of Nylon 6 and PET

Sample	Nylon 6 content, wt-%		
	Surface ^a		Whole sample ^b
	(a)	(b)	
A	91	91	86
B	45	45	27
C	77	85	66
D	63	69	48

^a (a) Effective thickness estimated at several microns; (b) effective thickness reduced by about 0.5 microns.

^b Based on nitrogen analysis of whole samples.

TABLE II
Comparison of Surface Compositions of Biconstituent Fibers and Films
of Nylon 6 and PET

Sample	Nylon 6 Content, wt-%		
	Film	Fiber	Whole sample ^a
A	97	91	86
B	42	45	27
C	81	77	66
D	69	63	48

^a Based on nitrogen analysis of whole sample.

compared to the amount given for the whole material. Overall, the data indicate that there is a preferential migration of nylon to the surface in melt processed nylon 6-PET bicomponent fibers.

It is further evident that surface compositions can be altered by heating the mixture of polyester and nylon above the melt. The effect is probably diffusion controlled which in turn indicates that temperatures along with time and pressure (shear) are the important variables involved.

In general, the infrared reflectance technique appears to be a valuable tool for the study of biconstituent fiber surfaces.

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