

# Composites Based on Poly(ethylene Terephthalate) Fibers with Polyaniline. II. The Effect of the Growth of the Polyaniline Molecules during the Polymerization in the Morphology of the PET Substrate

ABIGAIL LISBÃO SIMAL, ADRIANA MARTINELLI CATELLI DE SOUZA

Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, Via Washington Luiz, Km 235, Cx. Postal 676, 13565-905, São Carlos, SP, Brazil

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**ABSTRACT:** PET fibers of different drawn ratios were used as substrates to produce composites with PANi. The influence of the growth of the polyaniline molecules in the structure of the fibers previously pretreated in the presence of aniline at different conditions were studied by different characterization techniques (differential scanning calorimetry, X-ray scattering, dynamic and mechanical thermal analysis, sonic modulus, and scanning electron microscopy). The polymerization of the aniline inside the fiber substrates modified the structure of the fibers. In the case of the drawn fiber substrates the growth of the PANi molecules occurred mainly in the interfibrillar regions, which promoted reorganization of the preexisting crystals such as defect elimination (mainly in the interface of these regions with the lamellar regions) and at same time reorientation of their amorphous and crystalline regions. Also, due to this reorientation process the crystals became not only bigger and more perfect, but also they became more homogeneous. In the case of the undrawn fiber substrates, due to the lack of previous orientation, the growth of the PANi molecules would be occurring in the amorphous interlamellar regions only. Finally, the use of fibers with different drawn ratios as substrates for the composites was essential to reach such conclusions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2346–2362, 2000

**Key words:** composites; polyaniline; PET fibers; morphology; conductive polymers

## INTRODUCTION

In recent years, conductive polymers have received a lot of attention due to their great potential for technological applications.

Within the class of conducting polymers, polyaniline (PANi) occupies an important place.<sup>1</sup> PANi is unique in that it is soluble and, hence, processible in the conducting form. It is thermally stable

and stable in air.<sup>1</sup> Others properties of interest are: the monomer (aniline) is inexpensive; the conversion to monomer to polymer is straightforward; the polymerization reaction proceeds with high yield, and the resulting polymer is quite stable and shows a high level of conductivity.<sup>1</sup>

The use of textile materials as substrates and reinforcing materials for many polymers has wide industrial applications.<sup>2</sup> The use of textile materials as substrates to impart conductivity into these structures has been known for some time.<sup>2</sup>

Among the textiles fibers mentioned in the literature,<sup>2</sup> which has been used as substrates for conductive polymers, we can find the nylons 6 and

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Correspondence to: A. L. Simal.

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6.6 and the poly(ethylene terephthalate) (PET) fibers.

It is well known that the PET fibers have good fiber-forming properties, good mechanical properties, and low moisture absorption.<sup>3</sup> These properties arise from the stiff polymer chain and resulting high modulus, and the fact that the interchain bonds are not susceptible to moisture.<sup>3</sup> These outstanding properties made this fiber commercially successful.

So, the preparation of composites based on PET fibers with PANi has the objective to unify the good mechanical properties of the PET fibers with the conductive properties of the PANi.

In most of the studies<sup>2,4-7</sup> that have been made on this subject the films and fibers used as substrates were immersed directly in the reactional medium of the polymerization of the conductive polymer without any previous pretreatment (thermal or chemical) of the substrates. In the case<sup>4</sup> where some previous chemical treatment was applied to the PET films, no studies were carried out on the effect of this chemical treatment on the morphology of this polymer.

The thermal and chemical treatments would be very important tools to stabilize the structure of the substrate against possible changes due to the effect of the chemicals involved in the polymerization process. It is clear that such knowledge would help us to make a better correlation between the structure of the composites and their conductive properties. Because order and crystallinity have a significant influence on the conductivity and structural stability of the conductive polymers,<sup>2</sup> the understanding of the morphological changes of the substrate due to the action of the monomer (aniline) and the growth of the PANi molecules in the polymerization, can give us a better insight of the final conductive properties of the composite.

In the first part of this series of articles,<sup>8</sup> the influence of aniline diffusion into the fiber substrate after several conditions of treatment was examined (time, temperature, and presence or absence of benzoic acid in the medium).

In this article, we are interested in evaluating the influence of the chain growth of the PANi during its polymerization reaction on the structure of the fibers substrates. The final correlation between the structure and the conductive properties would be a matter for further work.

To accomplish this objective, PET fibers of different drawn ratios were submitted to the polymerization process as described elsewhere,<sup>9</sup> and

the resultant morphology of the composite was studied by several characterization techniques: Differential Scanning Calorimetry (DSC), Dynamic Mechanical Thermal Analysis (DMTA), X-ray Scattering, Sonic Modulus, and Scanning Electron Microscopy (SEM). All these techniques have been shown to be of fundamental importance, and are complementary among each other.

## EXPERIMENTAL

### The Substrate Preparation

PET fibers from Fairway S/A, Santo André, SP, Brazil, with different draw ratios ( $0\times$ ,  $2.6\times$ ) were submitted to a dry heat treatment for 6 h at  $130^\circ\text{C}$  under inert atmosphere in an evacuated oven. Following this dry treatment, the fibers were submitted to a treatment for 1 h in distilled boiling water. In both treatments, the fibers were allowed to shrink freely. These heat treatments were performed to promote structural stability in the fibers. So, any additional change in the structure of the fibers would be the consequence of aniline absorption. The heat treatment conditions were based on a previous work<sup>10</sup> of one of the present authors with PET fibers.

The heat-treated fibers were submitted to two different absorption conditions in the presence of distilled aniline: pure aniline and aniline plus benzoic acid at a concentration of 10 g/L. The benzoic acid was used to verify if there is any influence in the plasticizing behavior of the aniline in the fiber substrate. Indeed, in the previous work,<sup>8</sup> it was verified that the  $T_g$ s of the fiber substrates have decreased more effectively for the treatments performed in presence of aniline plus benzoic acid and at higher temperatures. Also, the absorptions were performed at two different temperatures ( $25$  and  $80^\circ\text{C}$ ) and times ( $t_1$  and  $t_2$ ) in a bath with controlled temperature and agitation. The times  $t_1$  and  $t_2$  were chosen based upon the obtained absorption curves at the equilibrium region. Because the equilibrium times showed to be dependent on the absorption conditions, mainly temperature and presence or not of benzoic acid in the medium, it was not possible to unify accordingly all chosen times. So, Table I illustrates the chosen times, where the times  $t_1$  and  $t_2$  will correspond, for simplicity in the discussion section, to the shorter and longer times, at equilibrium regions of the absorption curves respectively.

**Table I** Experimental Times  $t_1$  and  $t_2$  at Equilibrium Region of the Absorption Curves

Absorption Condition		Times (Minutes)	
Medium	Temperature (°C)	$t_1$	$t_2$
Pure aniline	25	40	240
	80	5	40
Aniline + benzoic acid	25	15	240
	80	5	40

### The Composite Preparation

The composites were prepared by immersing the substrates that were previously pretreated as described in the sample preparation section in the reactional medium of the PANi synthesis under constant agitation for 1 h and half at room temperature (25°C). The polymerization reaction that was utilized in this experiment is the same as that described elsewhere.<sup>9</sup> First, a solution A was prepared, containing 4.0 mL of distilled aniline in 300 mL of aqueous solution of HCl (1M). Then, a solution B was prepared containing 2.3 g of ammonium persulfate in 200 mL of aqueous solution of HCl (1 M). Then solution B was added to solution A to initiate the synthesis reaction.

After the polymerization, the composites that were formed were washed with aqueous solution of HCl (1M) and placed in a desiccator to control humidity, for about a week before the structural measurements. The final composites presented a smooth layer of a very dark greenish color (Esmeraldine), which was verified by the analysis of their cross-section areas by optical microscope.

## STRUCTURAL MEASUREMENTS

### Differential Scanning Calorimetry (DSC)

DSC (from Perkin-Elmer) measurements were used to evaluate the thermograms and to calculate the observed areas under the heat of fusion peaks of the samples. The Crystallinities Percentages (%C) were calculated as follows:

$$\%C = \frac{\Delta H_f}{\Delta H^0} \times 100 \quad (1)$$

where  $\Delta H_f$  is the observed heat of fusion in kcal/g, and  $\Delta H^0$  is the heat of fusion for the totally crystalline PET sample, or 28.1 kcal/g.<sup>10</sup>

The runnings were effuetuated under inert atmosphere at a heating rate of 10°C/min.

### Dynamic Mechanical Thermal Analysis (DMTA)

DMTA (from Polymer Laboratories) runnings were used to evaluate the dynamic and mechanical properties of the samples through  $E'$ ,  $E''$ , and  $\tan \delta$  measurements, as well as their glass transition temperature ( $T_g$ ) taken, where  $E''$  is maximum. The running conditions were: heating rate of 3°C/min and frequency of 10 Hz, utilizing a tensile head system.

### X-ray Analysis

Wide-angle X-ray scattering was performed in a Rigaku Rotaflex diffractometer, model R1-200B, utilizing a Ni-filtered Cu K $\alpha$  radiation. The obtained diffractograms were used to calculate the Crystallinity Index (CI), Crystal Size (CS), and Lateral Order (LO) as described in detail in the literature.<sup>10-14</sup> Our PET fibers presented a characteristic three peaks equatorial X-ray scattering pattern as described by several authors<sup>11,13</sup> for all analyzed treatment conditions in the presence of pure aniline and aniline plus benzoic acid.

The observed peaks maxima for the PET fibers were:  $2\theta_1 \cong 17.5^\circ$ ,  $2\theta_2 \cong 22.5^\circ$ , and  $2\theta_3 \cong 25.5^\circ$ , which correspond to the reflection planes (010), (110), and (100), respectively. Although much more precise methods for crystallinity determinations can be found in the literature,<sup>15</sup> the method utilized by Curleton and colleagues<sup>10</sup> was chosen due to its simplicity.

The width at half height of the three crystalline peaks after deconvolution of the curves were considered for the crystal size calculations, through the basic Scherrer equation<sup>15</sup> or:

$$CS = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where  $K$  is a shape factor (a value of 1.0 has been considered for the calculations);  $\lambda$  is the wavelength of the Cu K $\alpha$  radiation, or 1.5418 Å;  $\beta$  is the half breath in radians; and  $\theta$  is the Bragg's angle.

The crystalline sizes correspond to the direction perpendicular to the respective observed planes. The calculated values of the CS should be

considered as relative values only, because the necessary corrections for the Scherrer equation<sup>15</sup> were not made.

The LO parameter<sup>13,14</sup> can be related to several factors at the same time, such as crystallinity of the samples, perfection, size, and distribution of the crystallites, and it was calculated from the following equation:

$$\%LO = (1 - RF) \times 100 \quad (3)$$

where RF is the resolution factor, which for the PET case, is given by the following expression:

$$RF = \frac{m_1 + 2m_2}{h_1 + h_2 + h_3} \quad (4)$$

where  $m_1$  and  $m_2$  correspond to the minima between the planes (010) and (110) and between the planes (110) and (100), respectively. The variables  $h_1$ ,  $h_2$ , and  $h_3$  are the observed maxima diffraction peaks correspondent to the planes (010), (110), and (100). When the resolution is absent, RF tends to be 1, and RF tends to be zero when the resolution is maximum. Thus, RF is inversely related to the LO parameter. Some authors<sup>13,14</sup> have used this parameter as a substitution for the crystallinity. In our study, it was considered by both parameters.

### Sonic Modulus

The Sonic Modulus ( $E_s$ ) has been used as an indirect measurement of the orientation of the system<sup>16</sup> through the following equation:

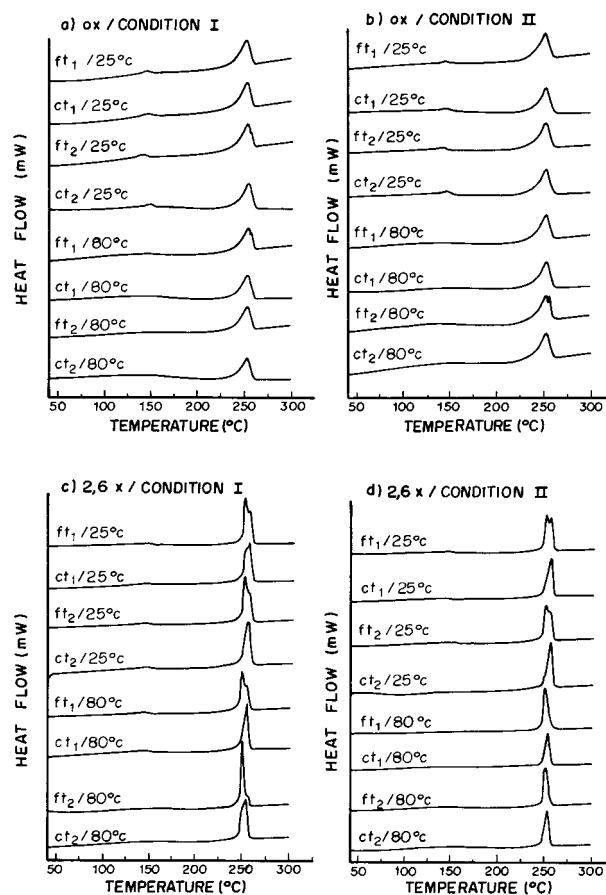
$$E_s = \rho c^2 \quad (5)$$

where  $E_s$  is the sonic modulus in dynes/cm<sup>2</sup>;  $\rho$  is the sample density in g/cm<sup>3</sup>; and  $c$  is the sonic velocity in cm/s.

The equipment utilized for the sonic modulus determination was the PPM-5, which belongs to the Fairway S/A. The densities determinations were made by the flotation method (ASTM-D792-79) using a mixture of *n*-heptane and carbon tetrachloride.

### Scanning Electron Microscopy (SEM)

In this technique was used the electron microscope model DSM-940-A from Zeiss to analyze the surface of the cross section area of the fiber PET-PANi composite.



**Figure 1** DSC thermograms for the undrawn (a,b) and drawn (c,d) fiber substrates and their correspondent composites with PANi for several conditions of aniline pretreatment: Condition I: pure aniline; Condition II: aniline plus benzoic acid.

The samples were prepared by the ultramicrotoming process, using Reichert Ultracut-S equipment from Leica. Then, they were covered by evaporation with a thin layer of conducting material (gold).

## RESULTS AND DISCUSSION

### The DSC Analysis

Figures 1(a) and (b) reveal the DSC thermograms of the composites based on the undrawn fibers. For comparison, the figures also show the thermograms of their correspondent fiber substrates for all studied conditions of aniline absorption (condition I: pure aniline, and condition II: aniline plus benzoic acid).



It is possible to observe in these figures that there are no significant changes in the resulting endotherms correspondent to the premelting and main melting peaks, and also in the temperature of occurrence of these peaks.

Also, the partial crystallinities calculated from the areas (heat of fusion) of the premelting and main melting peaks did not show any significant changes, resulting in a constant total crystallinity (see Table I). These results seem to indicate that the polymerization of the aniline in the undrawn fiber used as a substrate is not affecting its crystalline structure.

But, when the drawn fibers are used as the substrate for the polymerization of the aniline, the DSC thermograms show a different picture.

Although the DSC thermograms [Fig. 1(c) and (d)] are not showing changes in the format and in the temperature of occurrence of the premelting peaks, it is possible to visualize clearly changes in the format and in the temperature of occurrence of the main melting peaks of these fibers.

In part 1 of these series of articles<sup>8</sup> changes were observed in the main melting peaks when the drawn fibers were treated chemically in presence of aniline and aniline plus benzoic acid in the more aggressive conditions of temperature and time (80°C, time  $t_2$ ). In these conditions, the characteristic double main melting peak of the control fiber was transformed in a single peak by the disappearance of the less intense but higher temperature one. It was suggested in that article<sup>8</sup> that the original and heterogeneous crystalline structure was transformed in a more homogeneous one after these chemical treatment conditions. These new crystalline structure would be formed by smaller and or less perfect crystallites. It has been suggested in the literature<sup>17-20</sup> that such double melting peaks would be representative of the existence of two different crystalline forms in the fibers. So, changes in the format and position of the double melting peaks would correspond to changes in their crystalline structure.

Now, in the present work, when these PET fibers (used as substrates for the composites formation) are submitted to the polymerization reaction medium in the presence of an aniline monomer, the growth of the PANi chains seems to be generating a new crystalline structure in these fibers. It is clear in the thermograms, that even for the less aggressive chemical pretreatment conditions (lower temperatures and shorter times) where the characteristic double melting peak was still present, the more intense peak that

originally occurred at lower temperatures is now occurring at higher temperatures. In those cases already described, where the more aggressive conditions of chemical pretreatments had transformed the double melting peaks of the drawn fibers into a single and lower temperature one, they are after the polymerization being transformed into a higher temperature and more intense single peak.

Also, the thermograms show that these more intense single peaks of the composites are occurring at the same temperature of the originally less intense second main melting peak of their respective substrate PET fibers.

Now, Table II shows that like the undrawn fiber, the partial crystallinity ( $\%C_1$ ) calculated from the area under the premelting peak is not presenting any significant changes. But, the partial crystallinities calculated from the areas under the main melting peaks are showing a small decrease, especially for the composites whose substrates were pretreated in the presence of aniline plus benzoic acid. So, the total crystallinities ( $\%C_t = \%C_1 + \%C_2$ ) are also presenting a slight decrease at the same conditions, mainly due to these observed decreases in the partial crystallinities ( $\%C_2$ ) correspondent to the main melting peaks.

These main melting peaks indicate that the polymerization of the aniline monomer inside these drawn and chemically modified PET fibers is promoting some changes in their crystalline structure.

To better explain the phenomenological aspects concerning the observed changes in the DSC thermograms of the composites based on the drawn PET fibers, it is worthwhile to formulate three hypothesis that could be responsible for such changes: (1) influence of the chemical components involved in the synthesis medium of the polyaniline (chlorine hydroxide and ammonium persulfate); (2) existence of possible transitions of polyaniline; and (3) influence of the chain growth of the polyaniline molecules during the polymerization reaction.

Thus, to analyze the first hypothesis, the drawn fibers used as substrate for the composite were submitted to a chemical treatment with the same components and in the same conditions used in the PANi synthesis, but in the absence of the monomer for obvious reasons. The resulting DSC thermogram (Fig. 2) of this fiber shows that the applied chemical treatment did not affect the characteristics of the endotherms, i.e., the format

**Table II Partial Crystallinities Percentages ( $\%C_1$ ,  $\%C_2$ ) of the Premelting and Main Melting Peaks; Total Crystallinity Percentage ( $\%C_t$ ) and the Glass Transition Temperatures ( $T_g$ ) of the Fiber Substrates ( $F$ ) and Their Respective Composites ( $C$ ) for the 0 $\times$  and 2.6 $\times$  Fiber**

Fiber	Conditions	$C_1$ (%)		$C_2$ (%)		$C_t$ (%)		$T_g$ (°C)	
		$F$	$C$	$F$	$C$	$F$	$C$	$F$	$C$
0 $\times$	Control <sup>a</sup>	5	5	37	36	42	41	110	109
2.6 $\times$	Control <sup>a</sup>	5	5	48	47	53	52	132	133

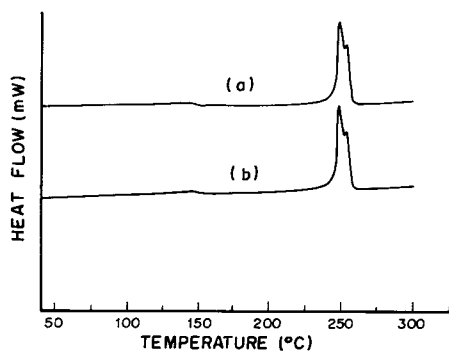
  

	System	$T$ (°C)	Time	$C_1$ (%)	$C_2$ (%)	$C_t$ (%)	$T_g$ (°C)	
0 $\times$	Pure Aniline	25	$t_1$	4	3	36	37	
			$t_2$	3	3	36	37	
		80	$t_1$	6	6	34	35	40
			$t_2$	5	6	35	35	40
	Aniline + Benz. Acid	25	$t_1$	5	5	36	36	41
			$t_2$	4	4	36	36	40
		80	$t_1$	7	7	35	36	42
			$t_2$	12	12	34	34	46
2.6 $\times$	Pure Aniline	25	$t_1$	4	4	48	47	
			$t_2$	4	4	47	46	
		80	$t_1$	4	5	47	45	
			$t_2$	5	4	47	46	
	Aniline + Benz. Acid	25	$t_1$	4	3	47	45	
			$t_2$	4	3	48	45	
		80	$t_1$	5	5	48	45	
			$t_2$	12	12	46	44	

<sup>a</sup> Heat treated only.

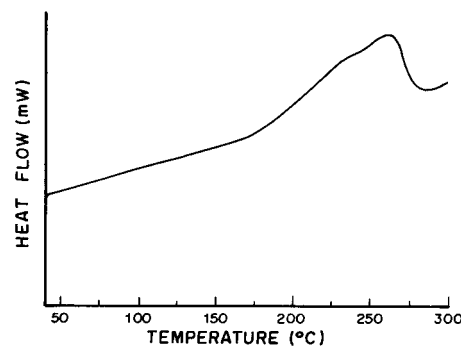
and the temperature of occurrence of the premelting and main melting peaks were preserved.

To analyze the second hypothesis, DSC thermograms were obtained (Fig. 3) of the pure PANi, which was in the form of a very dark greenish powder, i.e., of the polymer product resulting from the direct synthesis of the pure aniline.



**Figure 2** DSC thermograms of the drawn fiber: (a) pretreated at 25°C in pure aniline and short time ( $t_1$ ); (b) same of (a), but submitted to the reational medium condition of PANi synthesis without aniline.

The thermograms of the pure polyaniline shows a wide endotherm ranging from 175 to 275°C.  $T_g$  usually manifests in the DSC thermogram as a change in the baseline (curve shift),<sup>21</sup> but Wei and colleagues<sup>22</sup> have shown for their PANi samples that the  $T_g$  could also appear as an endotherm peak. In our case, we also believe that this observed endotherm would correspond to the manifestation of the  $T_g$  of our PANi sample. Others transitions, such as the melting temperature



**Figure 3** DSC thermograms of the pure polyaniline.

(if possible to reach) would occur at temperatures much above 275°C, and reactions such as degradation by reticulation or oxidation, would appear as an exotherm peak.<sup>21</sup>

Thus, it is possible to affirm that what we are really observing for our samples in their DSC thermograms (Fig. 1) are the main melting peaks of the PET fibers used as substrates for the composites. However, it is clear that the range of temperatures of occurrence of these main melting peaks (from 230 to 265°C) are within the range of temperatures of the occurrence of the glass transition temperature of the PANi.

So, someone could propose a fourth hypothesis that is: the mobility of the PANi molecules would be contributing somehow to the observed changes in the crystalline structure of the PET substrates, during the DSC runs, which involves heat. But as we know, these drawn PET fibers presented a very compact and highly crystalline structure. For this reason, it is expected not only a very low amount of PANi inside these fibers, but also a final structure stable enough to be changed during the DSC runs. So, this hypothesis would be of very least probability. Even so, the X-ray analysis that does not involve heat can be very helpful to clarify this subject. In the same way, the analysis of the cross-section areas of the fibers by the electron microscopy experiments will be very useful to clarify this hypothesis. The analysis by X-rays scattering and by electron microscopy will be discussed in the next sections of this article.

However, the third hypothesis considered earlier seems to be the most probable factor that would be responsible for the observed changes in the crystalline structure of the drawn PET fibers.

Therefore, it seems that the growth of the PANi molecules during the synthesis are responsible for the following phenomena: (1) the shifting of the single peaks of the substrate fibers to higher temperatures for those cases where the previous chemical treatment had changed the format of the main melting peaks of these fibers (controls) from double to single; and (2) the changing of the format of the original double melting peaks of the substrates, by increasing the intensity of the peak that occurs at higher temperature or by transforming this double peak into a higher temperature single peak.

The tendency of the curves for all cases are toward the transformation and or shifting to a higher temperature single peak. So, it is possible to assume that in all cases the growth of the PANi molecules might be somehow affecting the crys-

talline structure of the substrate, i.e., it seems that the crystals are becoming not only bigger and/or more perfect, but also they are becoming more homogeneous with only one crystalline form. The small decrease in the % $C_t$  (total crystallinity) observed for these composites might be related to the reorganization of the crystalline structure responsible for the main endotherm due to the presence of the PANi molecules inside the substrate. During the growth of the PANi molecules, some defect elimination of the preexisting crystals might be occurring, probably in the interface between the crystalline and the amorphous regions. In the case of the drawn fiber, that would be mainly in the interface with the interfibrillar regions.

When the as-spun fibers were used as the substrate, the DSC technique was not sensitive enough to detect the effect of the presence of the PANi molecules in their crystalline structure. A possible explanation for this fact would be the absence of previous orientation in this fiber, which showed a more homogeneous crystalline structure. As revealed by the DSC runs, all the composites based on these fibers present only one main melting peak. Thus, any possible transformation in the crystalline structure of the substrate due to the presence of the PANi molecules would be revealed by the X-ray analysis.

Therefore, to better understand all these phenomenological aspects just described, we will present in the following sections, a discussion based on the DMTA and X-ray scattering results.

### Dynamic and Mechanical Properties

Table III compares the results of the Dynamic Mechanical Properties, i.e., the glass transition temperature ( $T_g$ ) at the maximum of the  $E''$  and the intensity where  $\tan \delta$  is also maximum for all the fibers substrates ( $F$ ) submitted to different conditions of treatment in presence of aniline and aniline plus benzoic acid and their respective composites ( $C$ ).

Comparing the data of the chemically untreated substrate fibers (controls) and their respective composites, is possible to verify that after the polymerization process, both  $T_g$  and the intensity at  $\tan \delta$  maximum did not change. Because these control fibers (0 $\times$ , 2.6 $\times$ ) were not submitted to any previous chemical treatment in presence of aniline monomer and at any condition, we believe that this result is indicating that the PANi might not be occupying the core of the

**Table III Glass Transition Temperature at  $E''_{\max}$  and the Intensity of the  $\tan \delta_{\max}$  for All the Substrate Fibers ( $F$ ) ( $0\times$ ,  $2.6\times$ ) and Their Respective Composites ( $C$ )**

Fiber	Conditions	$T_g$ ( $^{\circ}\text{C}$ )		$\tan \delta_{\max}$			
		$F$	$C$	$F$	$C$		
$0\times$	Control <sup>a</sup>	110	109	0.21	0.21		
$2.6\times$	Control <sup>a</sup>	132	133	0.17	0.17		
	System	$T$ ( $^{\circ}\text{C}$ )	Time				
$0\times$	Pure Aniline	25	$t_1$	112	111	0.21	0.24
			$t_2$	110	111	0.24	0.22
	80	$t_1$	91	90	0.23	0.21	
		$t_2$	87	87	0.22	0.21	
	Aniline + Benz. Acid	25	$t_1$	111	110	0.22	0.22
			$t_2$	109	108	0.22	0.21
80	$t_1$	86	83	0.24	0.22		
	$t_2$	74	71	0.21	—		
$2.6\times$	Pure Aniline	25	$t_1$	132	133	0.19	0.21
			$t_2$	133	134	0.22	0.21
	80	$t_1$	130	130	0.19	0.22	
		$t_2$	124	123	0.18	0.21	
	Aniline + Benz. Acid	25	$t_1$	133	134	0.18	0.20
			$t_2$	134	135	0.20	0.19
	80	$t_1$	128	127	0.20	0.18	
		$t_2$	120	121	0.19	0.17	

<sup>a</sup> Heat treated only.

control fibers, or the extent of penetration would be very little, i.e., it would resume only in the skin of these fibers. These results are in agreement with the DSC data as already discussed in the last section (see results for the control fibers in Table II).

Analyzing now the  $T_g$  data for the undrawn fibers that were previously pretreated chemically, we can verify some slight decrease (about  $3^{\circ}\text{C}$ ) only for the composites correspondent to those substrates that were pretreated in the presence of aniline plus benzoic acid at  $80^{\circ}\text{C}$ . In the first part<sup>8</sup> of these series of articles, we have shown that this condition of treatment is the one that promotes the most accentuate disorientation and swelling of the fibers. So it is possible that an additional swelling could be occurring when this fiber substrate is exposed to the reactional medium during the polymerization, resulting in an additional decrease of the  $T_g$ .

Considering now the data of the  $\tan \delta$  maxima for the composites based on the as-spun fiber substrates, we can see that their intensity values are, in general, slightly smaller than their respective substrates for most of the analyzed conditions of

chemical treatment. It is interesting to note that the  $\tan \delta$  intensities values are not in agreement with the  $T_g$  results, which did not shown any significant changes for most of the analyzed conditions. It is well known from the literature<sup>23</sup> that changes in the height and width of the  $\tan \delta$  peak can be related to changes in the structure of the polymer such as changes in the crystallinity, orientation, and crystal size. In general, when crystallinity and/or orientation increase, the intensity of the  $\tan \delta$  peak decreases, and its width increases. On the other hand,  $T_g$ , which is a property of the amorphous regions<sup>23</sup> of the polymer, can also depend on the size and distribution of the crystallites.

However, it seems that the  $\tan \delta$  values are basely reflecting for most of these samples, the compactness of the structure of the fibers due to the presence of the PANi molecules in their amorphous regions, but this compactness is not affecting the  $T_g$  values. This fact is indicating that the previous treatment in the presence of the aniline monomer is essential to promote chain growth inside the fiber substrates. This increase of compactness decreases the internal friction of the

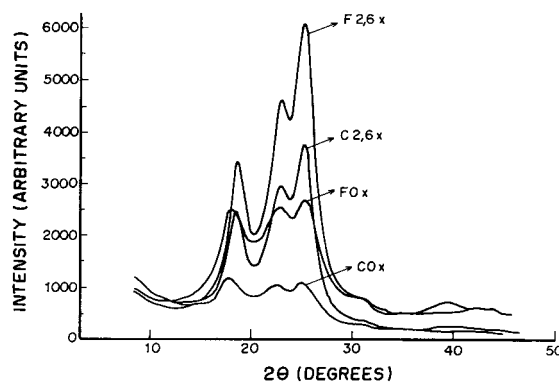


chain molecules, causing a slight but detectable decrease in the  $\tan \delta$  maxima values. Therefore, the extent of the penetration of the PANi molecules in the core of these fibers seems to be deeper than the observed for the control ones, as discussed earlier. But it was not deep enough to promote significant changes in  $T_g$ .

As in the case of the composites based on the as spun fiber substrates, the composites based on the drawn fibers did not show any significant changes in their  $T_g$ s for all the analyzed conditions of chemical treatments of their substrates. Actually, the major differences are again in the intensities of their  $\tan \delta$  maxima. But now, two different behaviors could be detected: a general increase for the composites based on the fibers that were previously pretreated in presence of pure aniline, and a decrease for the composites whose substrates were pretreated in presence of the aniline plus benzoic acid, especially when the treatments were performed for long times and higher temperatures.

These results seems to be indicating two different situations, and both related to the original structure of the substrates. Recalling the DSC results for the 2.6 $\times$  fibers discussed in detail in the first part<sup>8</sup> of this series of articles, we have shown the formation of two different structures, depending on the applied chemical treatment: a more heterogeneous one, which was represented by the preservation of the double main melting peak, and another one, which was more homogeneous and represented by a single and low-temperature main melting peak. These two different structures are shown in the thermograms of Figure 1(b) together with the thermograms of their respective composites.

It seems that a substrate with a more heterogeneous structure would result in a less homogeneous distribution of the PANi molecules in the core of the PET fiber substrate. So, the general increase in the intensities of the  $\tan \delta$  maxima for the composites based on these PET substrates would be a result of a poorer distribution of the PANi molecules in the amorphous region of these fibers. Consequently, this more heterogeneous distribution of the PANi molecules in the amorphous regions of these fibers would result in a less compact structure. However, this fact is not avoiding the transformation of the original crystalline structure of the substrate in a more homogeneous one after the polymerization of the PANi, due to the influence of the chain growth as already discussed in the DSC section of this article.



**Figure 4** X-ray diffractograms of the composites (*C*) based on the control fibers with different drawn ratios (0 $\times$ , 2.6 $\times$ ) and of their respective control fiber (*F*) substrates (heat treated only) for comparison.

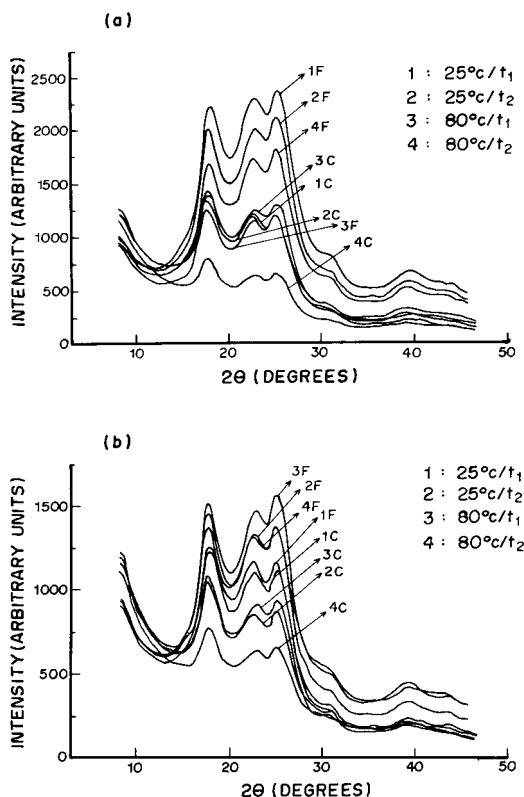
In the second situation, where the original substrate structure was already more homogeneous, as represented by the single main melting peak in the DSC thermograms, the distribution of the PANi inside the PET fibers core would be a more homogeneous one, resulting, therefore, in a composite with a more compact structure. Again, an increase in the compactness of the structure would decrease the internal friction of the chain molecules, resulting in a decrease in the intensity of the  $\tan \delta$  maximum peak. This would be a similar situation observed for the case of the composites based on the as-spun fibers and already discussed.

Here, the major difference between the two fibers used as substrates (0 $\times$ , 2.6 $\times$ ) is that to obtain a better distribution of the PANi molecules into the 2.6 $\times$  fiber, which is oriented, it is necessary to use its previous treatment in the presence of aniline plus benzoic acid.

Again, the previous chemical treatment of the drawn fiber is essential to increase the extent of penetration of the PANi molecules into the core of these fibers, and a better performance would be reached with a pretreatment in the presence of aniline plus benzoic acid. Also, for this same condition of pretreatment, the longer the time of exposition and the higher the temperature, the deeper would be the penetration of the PANi molecules.

#### The X-ray Scattering Analysis

Figures 4, 5, and 6 and Table IV show the X-ray data for all analyzed fibers and their respective composites. Also, it is presented in Fig. 7 for com-



**Figure 5** X-ray diffractograms of the undrawn ( $0\times$ ) PET fibers ( $F$ ) submitted to different conditions of pretreatment and their respective composites ( $C$ ) with PANi: (a) pure aniline; (b) aniline plus benzoic acid.

parison, the X-ray diffractograms of the pure polyaniline powder.

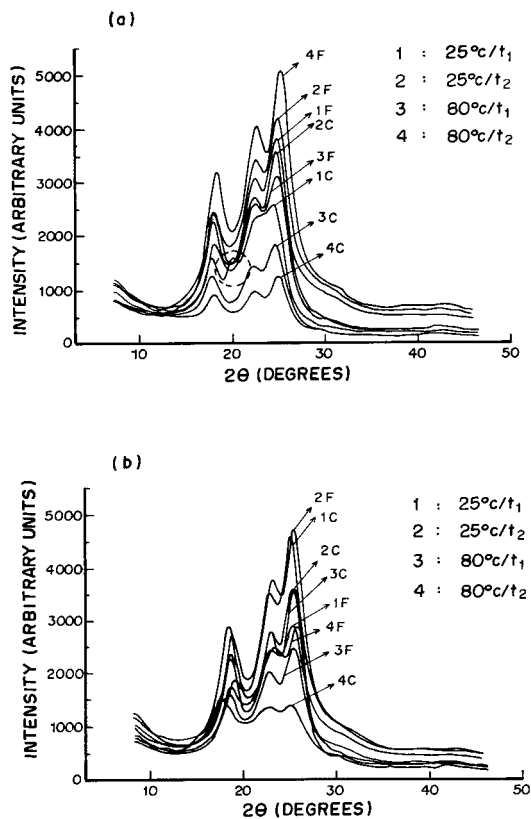
The figures show that the diffractogram of the pure polyaniline is quite different from the diffractogram of the PET substrate and also of the final composite. The composites are preserving the same characteristic three peaks of the PET substrates for all analyzed samples.

The diffractogram of the pure polyaniline is presenting two major characteristic peaks at  $2\theta \cong 20^\circ$  and  $24^\circ$ , revealing the presence of crystallinity in this sample (esmeraldine powder). But when the polymerization is carried out in presence of the PET substrate, the two characteristic peaks of the pure aniline disappear. The only observed exception was for the composite based on the  $2.6\times$  fiber substrate, which suffered a previous chemical treatment in the presence of pure aniline at  $25^\circ\text{C}$  and for short time ( $t_1$ ). The PANi peak at  $2\theta \cong 20^\circ$  is clearly visible, and is marked with a circle in Figure 6(a). The absence of any of these characteristic PANi peaks in the diffractograms of the other analyzed composites might be

indicating that the PANi has not the tendency to crystallize when polymerized inside of the PET substrates, at least not in the form presented by the pure PANi powder diffractogram (Fig. 7). So the presence of the PANi peak in that particular sample seems to be an exception for reasons not clearly determined.

Another interesting observation concerning the diffractograms of the composites are the deep changes in the observed intensities. As can be observed in Figures 4 to 6, the intensities of the composites diffractograms are decreasing when compared to the diffractograms of their correspondent substrates for the majority of the applied chemical pretreatments and for both fibers. The only exceptions were for the composites based on the 2.6 fibers, which suffered a previous chemical treatment in presence of aniline plus benzoic acid at temperatures of 25 and  $80^\circ\text{C}$  (time  $t_1$ ). In these cases, the intensities of the X-ray diffractograms increased.

This apparent discrepancy concerning these substrates seems not to be related to the observed



**Figure 6** X-ray diffractograms of the drawn ( $2.6\times$ ) PET fibers ( $F$ ) submitted to different conditions of pretreatment and their respective composites ( $C$ ) with PANi: (a) pure aniline; (b) aniline plus benzoic acid.

**Table IV** Crystallinity Index Percentage (%CI), Lateral Order Percentage (%LO), and Crystal Sizes (CS) Perpendicular to the Planes (010), (110), and (100) for the Composites (C) and Their Respective Fiber Substrates (F) (0×, 2.6×) Submitted to Different Chemical Treatments

Fiber	Conditions	CS (Å)									
		IC (%)		OL (%)		(101)		(110)		(100)	
		F	C	F	C	F	C	F	C	F	C
0×	Control <sup>a</sup>	49	58	21	30	31	40	30	36	23	29
2.6×	Control <sup>a</sup>	70	70	32	32	41	44	34	38	28	31

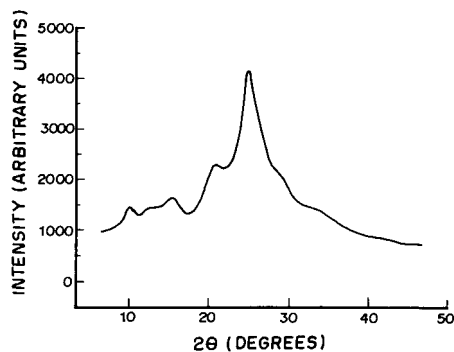
  

System		T (°C)	Time	CS (Å)									
0×	Pure Aniline	25	<i>t</i> <sub>1</sub>	47	54	21	27	32	35	28	33	25	27
			<i>t</i> <sub>2</sub>	46	55	19	26	32	39	29	36	22	30
		80	<i>t</i> <sub>1</sub>	54	56	26	23	32	36	28	32	24	29
			<i>t</i> <sub>2</sub>	50	66	22	35	32	39	27	33	24	30
	Aniline + Benz. Acid	25	<i>t</i> <sub>1</sub>	50	55	22	27	33	38	29	34	23	29
			<i>t</i> <sub>2</sub>	52	60	28	31	30	36	32	34	24	26
80		<i>t</i> <sub>1</sub>	52	59	24	27	31	40	28	36	23	29	
		<i>t</i> <sub>2</sub>	52	66	24	35	32	34	29	28	24	26	
2.6×	Pure Aniline	25	<i>t</i> <sub>1</sub>	66	59	30	37	36	38	33	35	26	29
			<i>t</i> <sub>2</sub>	62	70	26	30	44	44	34	38	25	31
		80	<i>t</i> <sub>1</sub>	60	74	23	32	43	41	34	37	23	30
			<i>t</i> <sub>2</sub>	64	77	33	44	40	42	32	33	28	30
	Aniline + Benz Acid	25	<i>t</i> <sub>1</sub>	60	69	22	29	42	42	32	38	23	30
			<i>t</i> <sub>2</sub>	64	70	28	31	42	43	34	37	26	30
80		<i>t</i> <sub>1</sub>	64	73	33	40	41	45	33	38	27	33	
		<i>t</i> <sub>2</sub>	55	86	23	57	37	44	31	35	21	31	

<sup>a</sup> Heat treated only.

changes in their crystalline structure during the formation of the composites, as revealed by the DSC data.

As detected in the first part<sup>8</sup> of these series of articles, someone could suggest that this additional decrease in the intensities of the diffracto-

**Figure 7** X-ray diffractograms of the polyaniline powder (Esmeraldine).

grams of the composites could be due to an additional disorientation promoted by another additional swelling or plasticizing effect of the aniline monomer during the immersion of these fibers substrates in the reactional medium of synthesis of the polyaniline. But, it was detected in the first part of this series of articles<sup>8</sup> that the pure aniline was less effective to plasticize these fibers, especially when the treatments were performed at room temperature. Here, the polymerization reaction was performed at room temperature, 25°C.

Also, as the dynamic and mechanical data revealed, if such effect is occurring, it would be a minor one. The  $T_g$ s have not shown any significant changes for all analyzed samples. Yet, it would be more logical to think that this effect would be more prone to occur with the control fibers, which did not suffer any previous chemical treatment. In other words, these control fibers would be more susceptible to the chemicals presented in the medium of the polymerization, be-

cause they were not previously treated in presence of the aniline (its structure would be more unstable to the action of these chemicals). But, recalling the dynamic and mechanical data for the composites based on these control fibers (Table III), it is possible to verify that the immersion of these substrates in the reactional medium of synthesis of the PANi did not cause any change in their  $T_g$ s or even in the intensity of their  $\tan \delta$  peak maxima. This fact might be indicating that the polymerization reaction of the polyaniline in the surface of these substrates is occurring too fast, and as a consequence of that, it would be forming a barrier against any further diffusion of the aniline molecules into the core of these fibers.

Yet, Figure 4 reveals that the decrease in the X-ray diffractogram intensity is also being observed for the composites based on these same control fibers with no previous chemical treatment, and as was discussed before, these are the substrates with a poorer extent of penetration of the PANi molecules into their cores. So, it is strongly believed that these observed depressions in the intensities of the X-ray diffractograms for the great majority of the composites are more directly related to a special effect of the PANi layer that smoothly covers the entire surface of the fiber substrates. This coherent layer of PANi, with a dark greenish color (esmeraldine), that also seems not to be prone to crystallize in the surface of the substrate, could be working like a "filter" for the incident X-ray beams during the X-ray experiments. In addition, the possible discrepancies in the intensities results described earlier for the two composites based on the  $2.6\times$  fibers substrates could be more related to a less homogeneous outer layer of the PANi in their surfaces rather than to changes in their structures. Now, the results presented in Table IV seems to reinforce this hypothesis.

As can be seen in the Table IV, the IC and the OL parameters are increasing for the great majority of the composites when compared to their respective substrates. Now the only exception was for the IC parameter of the composite based on the  $2.6\times$  fiber substrate, which suffered a previous chemical treatment in presence of pure aniline at  $25^\circ\text{C}$  and time  $t_1$ , where a decrease was observed. This fact can be related somehow to the presence of the PANi peak in the X-ray diffractogram of the composite at  $2\theta \cong 20^\circ$  as described earlier [see Fig. 6(a)]. The presence of this peak might be interfering somehow in the crystallinity index calculation for this particular sample. Also,

its presence might be indicating some crystallization of the PANi in this particular sample with consequences in the crystalline structure of the PET substrate. These consequences could be some kind of partial destruction of the preexisting crystals. As was said before, this phenomenon might be an isolated one (an exception). The rule seems to be the absence of the crystallization of the PANi molecules inside and outside the fiber substrates, at least in the original form observed in the diffractogram of the PANi powder (see Fig. 7).

Thus, the observed increase in the IC parameters might be reflecting the increase of the Lateral Order (LO) of the crystalline structure due probably to a reorientation process of the crystalline and amorphous regions. The LO parameter represents the total order of the system rather than the absolute crystallinity.<sup>14</sup> It is related to several parameters at same time,<sup>13,14</sup> such as crystallinity, perfection, size, and distribution of the crystallites. So, changes in any of these structural parameters can promote changes in the LO values. Therefore, the growth of the polyaniline molecules inside the fiber substrates could be responsible for such X-ray results. This effect was not observed by the DSC data. Actually, the DSC data showed a slight decrease in the crystallinity percentage. Contrarily to the X-ray experiments, the DSC technique do not visualize the crystalline organization in the system as a whole. So, any changes in the order of the entire system would be observed only by the X-ray analysis. Actually, these are complementary techniques.

Another interesting result is the observed increase in the crystal size for all the analyzed composites based on the drawn and undrawn fibers substrates. So, this fact is confirming the earlier conclusions concerning the DSC data, where it was observed changes in the format and the position of the melting peak, especially in the case of the drawn fibers. Thus, the growth of the PANi molecules inside the PET substrates is really affecting their crystalline structure, i.e., their crystals are becoming not only bigger and or more perfects, but also becoming more homogeneous and reoriented in the direction of growth of the PANi molecules. The presence of previous orientation in the drawn fibers enhance such structural changes and the comparative study between the different fibers was very helpful to enlighten these conclusions.



**Table V Sonic Modulus ( $E_s$ ) of the Composites (C) Based on the Drawn Fibers and Their Respective Fibers (F) Substrates Submitted to Different Chemical Treatments**

Fiber	Conditions		$E_s$ (dynes/cm <sup>2</sup> ) $\times 10^{-10}$		% $\Delta^a$	
			F	C		
2.6 $\times$	Control <sup>b</sup>		6.80	6.87		
	System	T (°C)	Time			
2.6 $\times$	Pure Aniline	25	$t_1$	6.12	6.33	3.4
			$t_2$	5.55	5.80	4.5
		80	$t_1$	6.07	6.29	3.6
			$t_2$	5.20	5.45	4.8
	Aniline + Benzoic Acid	25	$t_1$	6.10	6.30	3.3
			$t_2$	5.32	5.57	4.7
		80	$t_1$	6.04	6.26	3.6
			$t_2$	5.18	5.40	4.3

<sup>a</sup> % $\Delta$  = increase percentage in the sonic modulus.

<sup>b</sup> Heat treated only.

### The Sonic Modulus Analysis

The sonic modulus analysis were performed to certify that the growth of the PANi chains are, in fact, promoting the reorientation of the crystalline regions of the PET substrates as indicated by the X-ray analysis. These analysis were realized only with the drawn fibers due to technical difficulties in performing these experiments with the undrawn fibers. But because both fibers presented similar X-ray results, one could expect they could present also similar results by the sonic modulus. Therefore, the conclusions reached for the composites on the drawn fibers could be extended in some degree for the undrawn ones.

Thus, Table V is showing that the sonic moduli of the composites based on the drawn fibers are indeed slightly higher than their correspondent fibers substrates. The percent of increase was about 3.3 to 3.6% for the fibers substrates, which were previously treated for short period of times ( $t_1$ ) in presence of pure aniline and aniline plus benzoic acid independently of the temperature of pretreatment. But the percent of increase was about 4.3 to 4.7% when the same treatments were performed for long times ( $t_2$ ).

Also, it is clear from Table V that when the fiber substrates presented a more disoriented structure due to the conditions of the pretreatments (higher temperatures and times), which

would correspond to the fibers with lower sonic modulus, their composites would correspondingly present the same tendency, i.e., their sonic moduli were also lower.

Therefore, the fibers substrates that presented originally higher disorientation produced less oriented composites. But, it is evident that the less oriented substrates produced higher percent of increase in the sonic moduli of their composites. However, it seems that the longer times of pretreatments are indeed more efficient to promote the aniline monomer penetration and, consequently, a more efficient polymerization of the PANi molecules into the fibers substrates.

Recalling the X-ray data (Table IV), it is possible to see that the IC and the LO parameters seem to be following the same behavior pattern, with higher values for the composites based on the fiber substrates that were pretreated for longer times in the presence of aniline and aniline plus benzoic acid. So, these more severe conditions of pretreatments favors a more effective chain growth of the PANi inside the amorphous regions of the fiber substrates and, consequently, a more effective change in their structures.

Within these structural modifications, the reorientation process of the amorphous and crystalline regions are evident for all cases, because the sonic moduli are higher for all the analyzed composites. The reorientation process of the drawn



fibers substrates is caused by the chain growth of the PANi molecules mainly into their amorphous but originally more oriented interfibrillar regions.<sup>24</sup> The chain growth of the PANi molecules would be realigning these regions and, consequently, the crystalline regions.

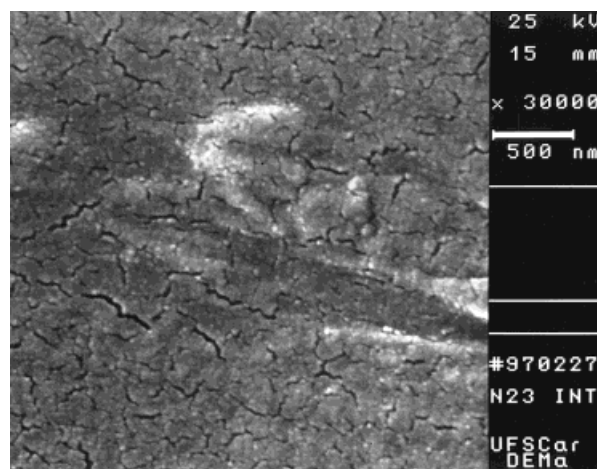
In the case of the undrawn fibers substrates, these phenomena would be occurring in their interlamellar amorphous regions because, as we suggested earlier,<sup>8</sup> we expect that these fibers would not present interfibrillar regions due to the lack of previous orientation during their spinning process. But, even so, the PANi molecules would promote a more compact structure with some reorientation of their crystalline regions as detected by the X-ray analysis. So, in all cases, the PANi molecules are promoting reorientation and compactness of the fibers structure.

### Scanning Electron Microscopy

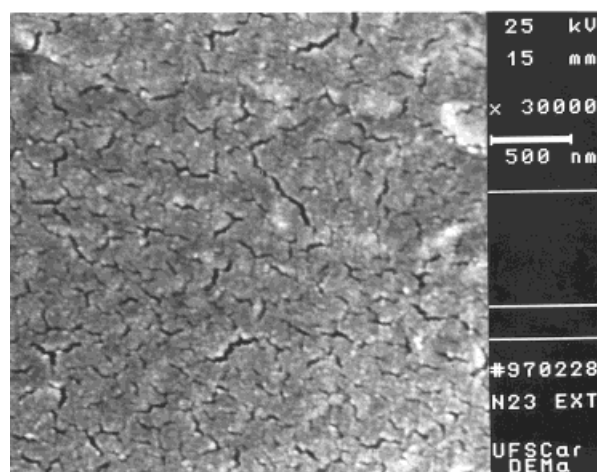
Based upon the earlier discussion we selected some samples for the analysis of their cross-section areas. The selected samples were those where the pretreatments conditions more efficiently favored the chain growth of the PANi molecules inside the PET substrates, i.e., the substrates that were pretreated in presence of aniline plus benzoic acid at 80°C and time  $t_2$ .

The micrographies of the composites based on the undrawn and drawn fibers are shown in the Figures 8(a) and (b) and 9(a) and (b), respectively. Figures 8(a) and 9(a) reveal the inner layers, and 8(b) and 9(b), the outer layers of the cross-section areas of the samples. In all cases, is possible to see fissures in consequence of the swelling suffered by the substrates due to the applied pretreatments as demonstrated earlier.<sup>8</sup> Also, it is possible to see that the fissures of the undrawn fibers are bigger than the ones presented by the drawn fibers. The absence of previous orientation during the spinning process of this fiber favored a less stable structure.

In addition to the fissures, Figure 8(a) and (b) reveals a granulated texture in the inner and outer layers of the cross-section area that seem to be strongly indicative of presence of titanium dioxide, which is commonly present in the spinning process of these fibers. Also, it is possible to see that some of these granules are bigger in size (clearer spots) and are more scarcely distributed in surface of the cross section area of this fiber. These granules could be indicative of presence of polyaniline molecules. Another interesting obser-



(a)

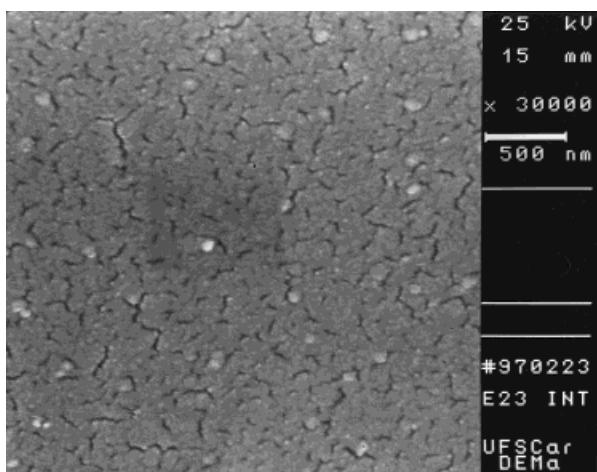


(b)

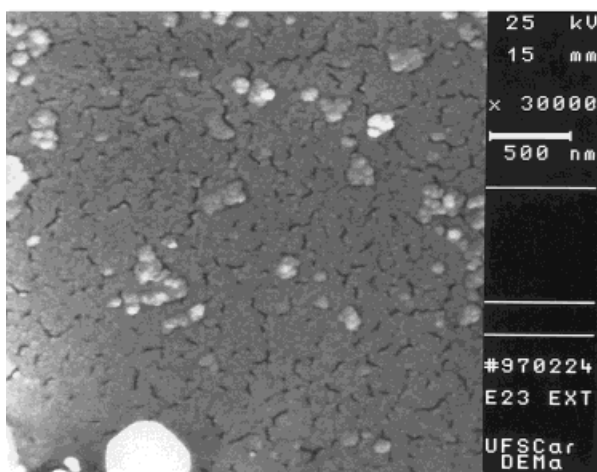
**Figure 8** Scanning electron micrographies of the composites based on the undrawn fibers pretreated in the presence of aniline plus benzoic acid at 80°C, time  $t_2$ : (a) inner layer; (b) outer layer.

vation concerning this particular sample is that the fissures seem to be homogeneous in size in the entire cross-section area of this fiber.

In the case of the drawn fibers, in addition to the fissures and the granulated texture, it is possible to see very clearly agglomerates, which are spread all over the surface of the transversal area. These agglomerates are strongly indicative of presence of polyaniline molecules. Also, Figure 9(a) and 9(b) reveals that these agglomerates are smaller in size and less concentrated in the inner part of the cross-section area of the sample, which



(a)



(b)

**Figure 9** Scanning electron micrographies of the composites based on the drawn fibers pretreated in the presence of aniline plus benzoic acid at 80°C, time  $t_2$ : (a) inner layer; (b) outer layer.

would correspond to the presence of a less amount of PANi.

Another interesting observation related to these micrographies is that these agglomerates seem to be flourishing in the surface of the cross section area, as they had grown in the direction of the fiber axis. This observation seems to be in agreement with the earlier discussion, where we expected that the PANi molecules would be growing mainly in the amorphous interfibrillar regions of the drawn fibers. Considering the three phases model described in the literature<sup>24</sup> for PET fibers, these interfibrillar regions would be in the direc-

tion parallel to the fiber axis. So, the PANi molecules are really growing in the direction of the fiber axis, and these results are in agreement with the X-ray and sonic modulus data, already discussed.

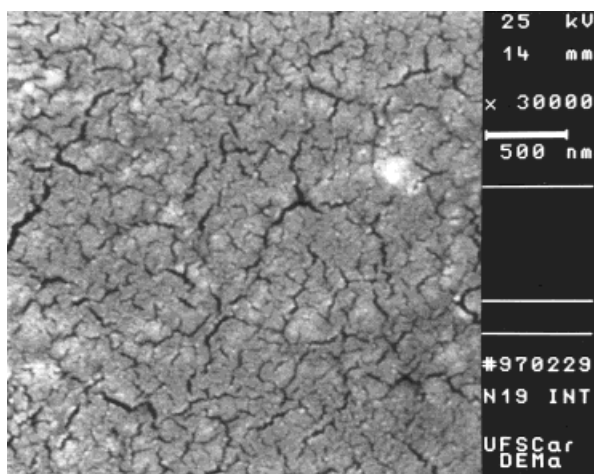
Yet, in the case of the undrawn fibers, the absence of such agglomerates in the surface of their cross-section area would be a consequence of a more homogeneous distribution of the PANi molecules into these fibers, due to their simpler structure. As we proposed earlier,<sup>8</sup> that would be a two phase structure due to absence of previous orientation. The micrographies presented in Figure 10(a) and (b) for the composites based on the undrawn fibers previously treated with pure aniline at 80°C and time  $t_2$  seem to be in agreement with the above discussion. The granules (clearer spots) observed in Figure 8 are not as evident in this particular sample. So, the pretreatment in presence of benzoic acid seems to improve not only the plasticizing effect of the aniline in the fiber but also its polymerization. As can be seen in the outer layer [Fig. 10(b)] of this composite based on the undrawn fiber, the fissures are more closely packed, indicating a less homogeneous distribution of the polyaniline molecules when the pretreatment of the fibers were performed in presence of pure aniline. So, the polyaniline molecules would be concentrated more in the outer layer of this particular sample.

## CONCLUSIONS

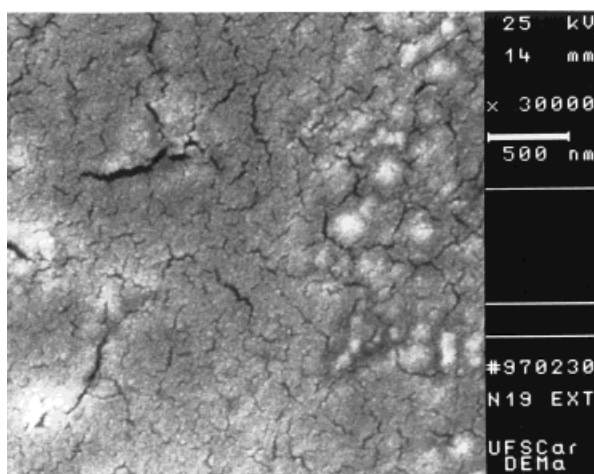
The polymerization of the aniline inside the PET fiber substrate has transformed the structure of the fibers.

Based on the analysis of the DSC thermograms of the drawn fibers, it seems that the crystals responsible for the main melting peaks are becoming not only bigger and or more perfect, but also they are becoming more homogeneous with only one crystalline form. Also, during the growth of the PANi molecules, some defect elimination of the preexisting crystals might be occurring, probably in the interface between the crystalline and the amorphous regions (mainly in the interface with the interfibrillar regions).

The previous treatment in the presence of an aniline monomer is essential to promote chain growth inside the fiber substrates. The  $\tan \delta$  values are reflecting for most of the undrawn fibers the compactness of their structure, due to the



(a)



(b)

**Figure 10** Scanning electron micrographies of the composites based on the undrawn fibers pretreated in the presence of pure aniline at 80°C, time  $t_2$ : (a) inner layer; (b) outer layer.

presence of the PANi molecules in their amorphous regions.

In the case of the drawn fibers, the composites based on the substrates with a less homogeneous crystalline structure would present a less compact structure than the composites based on the substrates with a more homogeneous one (represented by a single main melting peak in the DSC thermograms).

Also, a better distribution of the PANi molecules would be for the fiber substrates pretreated in the presence of aniline plus benzoic acid for longer times.

The decrease in the intensity of the X-ray diffractograms for the majority of the composites are directly related to the special effect of the PANi layer that smoothly covers the entire surface of the fiber substrates.

The observed increase in the IC parameters might be reflecting the increase of the lateral order (LO) of the crystalline structure due to a reorientation process of the crystalline and amorphous regions, which was confirmed by the sonic modulus analysis. Again, the X-ray data are confirming the DSC results, where an increase of the crystal sizes for all analyzed composites based on the undrawn and drawn fibers are being observed. The growth of the PANi molecules inside the PET substrates is transforming their crystals in bigger and or more perfect ones.

The reorientation process of the drawn fibers is caused by the chain growth of the PANi molecules mainly in their amorphous but originally more oriented interfibrillar regions. Because these regions are oriented in the direction of the fiber axis, the PANi molecules are also growing in this direction. Consequently, the PANi molecules are realigning the crystalline regions during their growing process.

In the case of the undrawn fiber substrates, these phenomena would be occurring mainly in their interlamellar amorphous regions, as a result of their simpler structure based on the proposed two phases model structure. The absence of previous orientation would be responsible for such simpler proposed model.

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