

Composites Based on Poly(ethylene terephthalate) Fibers with Polyaniline. I. Effect of the Aniline Monomer in the Morphology of the PET Substrate

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ABSTRACT: Heat-treated PET fibers of different draw ratios (0X, 2.6X) were submitted to different conditions (time and temperature) of chemical treatments in the presence of aniline and aniline plus benzoic acid in order to verify the influence of these chemicals on their structure. Both crystalline structures of these fibers behaved similarly in some aspects to these applied chemical treatments, but differently in others. The major differences would be related to their original structures (control ones) due to the existence or not of previous orientation. The drawn fiber presented a more stable and more complex structure than that of the undrawn one. The crystalline structure of the drawn fibers changed from a two-form and more heterogeneous crystalline structure to a more homogeneous one, which is constituted of smaller and/or less perfect crystallites. The use of benzoic acid in combination with aniline seems to be more effective to plasticize both fibers, especially at higher temperatures and longer times of treatment. At these conditions, the fibers presented swelling and a more effective reduction of their glass transition temperatures (T_g). The swelling and the increase in the chain flexibility might be responsible for the formation of the more homogeneous crystalline structure of the drawn fibers. The swelling promoted not only disorientation of the amorphous regions, but disorientation of their crystalline regions as well. This phenomenon seems to be responsible for the observed decrease in the intensity of the X-ray diffractograms within a given treatment for both fibers. Sonic modulus analysis performed for the drawn fibers confirmed such data. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2126–2138, 2000

Key words: PET fibers; aniline; benzoic acid; plasticizing effect; morphology

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers are hydrophobic, have a very compact structure, and are highly crystalline. In addition, the stiffness imparted to the chains by the phenyl residues of the terephthalate group results in a high glass tran-

sition temperature (T_g).¹ So, the diffusion of small molecules at lower temperatures is extremely slow. Carriers have been used frequently in the textile industry to accelerate the diffusion process of the dye molecules. Carriers are low molecular weight compounds that work as a plasticizer, reducing the T_g of the fiber and increasing chain flexibility; consequently, acceleration of the dye diffusion will be achieved.^{1,2}

Benzoic acid and aniline has been referred in the literature^{1,3} as hydrophilic agents (water-soluble) that could be used as carriers in the dyeing

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process of PET fibers. Benzoic acid belongs to the class of water-soluble carriers,¹ which requires it to be used in large concentrations in order to have an effective action in the diffusion process of the dyes into the fibers.

The use of such compounds at high concentrations and for long times can induce structural changes, such as increase of crystallinity of the PET fibers.² Yet, some these compounds may induce swelling and considerable disorientation of the structure of the fibers.¹ These structural changes can affect the properties of these fibers. Therefore, knowledge of the structural changes due the action of such compounds is of great interest. Some studies^{2,4,5} have shown in great detail the influence of benzoic acid in the structure of PET fibers and, consequently, in their dyeing behavior.

On the other hand, no information about the influence of aniline in the structure of the PET fibers could be found in the literature. Aniline is a primary amine that can also be used in the production of some dyes for cotton¹ and also as monomer for the production of the polyaniline (PANi), which is a well-known conductive polymer.⁶

In recent years, the use of textile materials and films as substrates for the production of composites with conductive properties has been of much interest due to the wide possibilities for industrial applications. One of the conductive composites that has been studied⁶ is PET fiber with PANi. In the present work, PET fibers were used as substrates for PANi. Although, some description has been found in the literature,⁷ where PET films were dipped in pure aniline at room temperature for different periods of time (from 0.5 to 8 h) prior the polymerization process, neither of these works^{6,7} have shown the possible effects of aniline absorption in the structures of the PET fiber⁶ or film⁷ substrates.

As we mentioned earlier, aniline alone can work as a plasticizer for PET, and like benzoic acid, it could promote structural modifications in this polymer. Therefore, such studies would be of great importance, since morphology changes in the substrate could have consequences in the conductivity of the final composite. Some authors^{8,9} emphasized in studies with PANi films the importance of their structure (e.g., orientation) in their conductive properties.

Thus, we intend to show in this article the influence of the absorption of aniline in the structure of PET fibers in different conditions of treatment (time, temperature), in a medium contain-

ing or not containing benzoic acid. Here, benzoic acid will be used together with aniline to verify if there will be any influence in the carrier action of the aniline and later in the polymerization process of the polyaniline during the preparation of the final composite. So, we intend to use benzoic acid in the present article as a carrier and later to verify if it can act also as a doping agent in the polymerization of PANi.

Yet, to accomplish such a study, we chose PET fibers of different draw ratios (0X and 2.6X) and several structural characterization techniques: DSC, X-ray diffraction, dynamic and mechanical thermal analysis (DMTA), and sonic modulus. These techniques demonstrated to be not only essential, but also complementary to each other. Finally, we hope that this article can provide us with the necessary scientific understanding for further composites studies, which will be the subject of the next article.

EXPERIMENTAL

Sample Preparation

PET fibers from Fairway S/A (Santo André, SP, Brazil) with different draw ratios (0X, 2.6X) were submitted to a dry-heat treatment for 6 h at 130°C under an 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 in consequence of aniline absorption. The heat-treatment conditions were based upon a previous work² 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 concentration of 10 g/L. The benzoic acid was used to verify its influence in the plasticizing behavior of the aniline in the fiber substrate. Also, the absorptions were performed at two different temperatures (25 and 80°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. Since the equilibrium times were shown to be dependent on the absorption conditions, mainly temperature and the pres-

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

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

ence or not of benzoic acid in the medium, it was not possible to unify accordingly all chosen times. Therefore, 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.

Structural Measurements

Shrinkage Percentage

Shrinkage measurements were made by knowing the length before (S_h^0) and after (S_h^f) the treatments in aniline and aniline plus benzoic acid at different temperatures and times. Therefore, the shrinkage percentage ($\% S_h$) was calculated through the following expression:

$$\% S_h = \frac{S_h^0 - S_h^f}{S_h^0} \times 100 \quad (1)$$

Swelling Percentage

Swelling measurements were made by knowing the diameters of the fibers before (S_w^0) and after (S_w^f) the treatments in aniline and aniline plus benzoic acid at different temperatures and times. Therefore, the $\% S_w$ was calculated by the following expression:

$$\% S_w = \frac{S_w^f - S_w^0}{S_w^0} \times 100 \quad (2)$$

The diameters were calculated using an optical microscope (Olympus PME3).

Differential Scanning Calorimetry (DSC)

DSC (from Perkin–Elmer) measurements were used to evaluate the thermograms and to calcu-

late the observed areas under the heat of fusion peaks of the samples. The crystallinity percentages ($\% C$) were calculated as follows:

$$\% C = \frac{\Delta H_f}{\Delta H^0} \times 100 \quad (3)$$

where ΔH_f is the observed heat of fusion in kcal/g, and ΔH^0 = heat of fusion for the totally crystalline PET sample, or 28.1 kcal/g.² The runnings were effectuated under an inert atmosphere at heating rate of 10°C/min.

Dynamic and 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 a heating rate of 3°C/min and a 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 Ni-filtered $\text{CuK}\alpha$ 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.^{2,10–13} Our PET fibers presented a characteristic three-peak equatorial X-ray scattering pattern as described by several authors^{10,12} 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 $2\theta_1 \approx 17.5^\circ$, $2\theta_2 \approx 22.5^\circ$, and $2\theta_3 \approx 25.5^\circ$, 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,¹⁴ the method utilized by Cullerton et al.¹⁰ was chosen due to its simplicity.

The width at half-height of the three crystalline peaks after deconvolution of the curves was considered for the crystal-size calculations, through the basic Scherrer equation¹⁴ or

$$CS = \frac{K\lambda}{\beta \cos \theta} \quad (4)$$

where K is a shape factor. A value of 1.0 was considered for the calculations. λ is the wavelength of the $\text{CuK}\alpha$ radiation, or 1.5418 Å. β is the half-breath in radians and θ is the Bragg 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, since the necessary corrections for the Scherrer equation¹⁴ were not made.

The LO parameter^{12,13} can be related to several factors at the same time, such as crystallinity of the samples and the perfection, size, and distribution of the crystallites and it was calculated from the following equation:

$$\% \text{ LO} = (1 - \text{RF}) \times 100 \quad (5)$$

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

$$\text{RF} = \frac{m_1 + 2m_2}{h_1 + h_2 + h_3} \quad (6)$$

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 0 when the resolution is maximum. Thus, RF is inversely related to the LO parameter. Some authors^{12,13} used this parameter as a substitution for the crystallinity. In our study, both parameters were considered.

Sonic Modulus

The sonic modulus (E_s) was used as an indirect measurement of the orientation of the system¹⁵ through the following equation:

$$E_s = \rho c^2 \quad (7)$$

where E_s is the sonic modulus in dynes/cm²; ρ , the sample density in g/cm³; and c , the sonic velocity in centimeters/second.

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

RESULTS AND DISCUSSION

DSC Analysis

Figure 1 shows DSC thermograms of the undrawn and drawn PET fibers submitted to different conditions of aniline absorption (condition I: pure aniline; condition II: aniline plus benzoic acid). The premelting peaks that appeared after the dry-heat treatments (control fibers) are preserved for all conditions of absorption in aniline and aniline plus benzoic acid. The appearance of these middle endotherms in DSC thermograms seems to be a general phenomenon for heat-treated PET^{2,5} and nylon 6 fibers.^{16,17} Their physical meaning and correlation with the structural behavior during the heat treatment of these fibers were detailed in the literature.^{2,5,16,17}

Also, it is interesting to note that the temperatures of the premelting peaks occur in the same range of temperatures as that of the control ones. This fact indicates that the very small crystallites² (nuclei crystallites) which appear in the amorphous regions of the fibers after the annealings and which are responsible for the appearance of the premelting peaks in the DSC thermograms are probably preserving their physical characteristics, such as size and degree of perfection after the chemical treatments in aniline and aniline plus benzoic acid.

However, it seems that when the absorption in aniline and aniline plus benzoic acid are performed at 80°C, these premelting peaks become wider for both analyzed times (t_1 and t_2) and for both fibers. This fact seems to indicate the formation of a wider distribution of sizes of such nuclei crystallites at these treatment conditions.

Also, the thermograms reveal that the premelting peaks occur for the undrawn fibers at temperatures about 30–50°C above their T_g (Table II), depending on the immersion conditions. In the case of the drawn fibers, these endotherms occur at temperatures about 6–20°C above their T_g (Table II). These differences are related to the differences in their structural stability. So, the existence of a previous orientation in the fibers confer them a more stable structure which is less susceptible to the plasticizing effects of the aniline or aniline plus benzoic acid.

Now, considering for the analysis the main melting peaks of the fibers (Fig. 1), it is possible to verify that these peaks are wider for the as-spun fiber as compared to the drawn one. Actually, the heat of fusion of the fibers (area under the peaks)

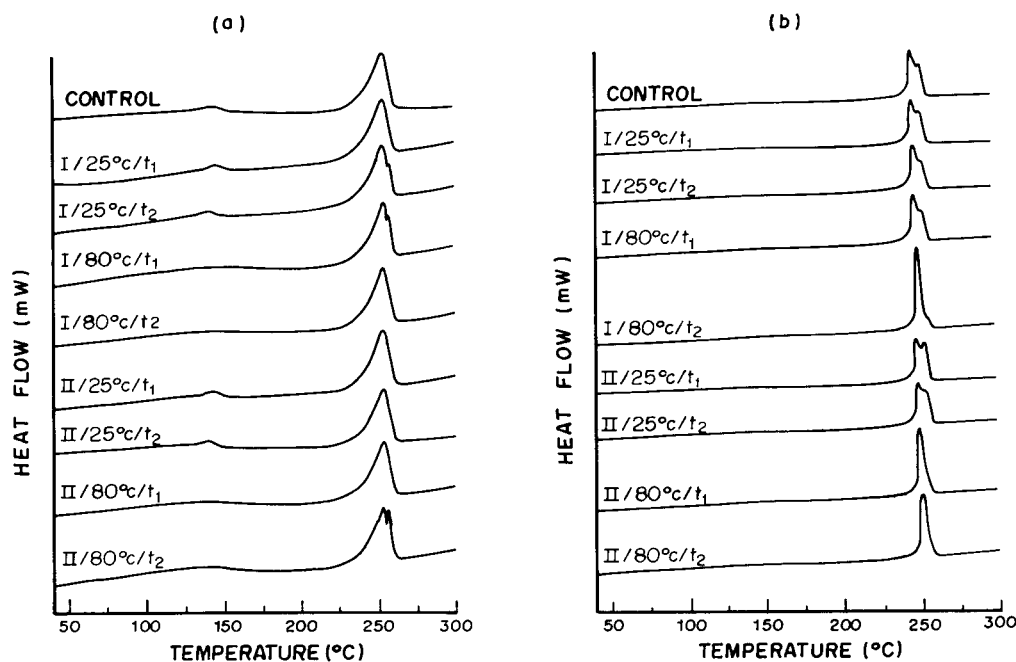


Figure 1 DSC thermograms of the (a) undrawn and (b) drawn PET fibers submitted to different conditions of treatment in (I) pure aniline and (II) aniline plus benzoic acid and comparison with the control ones (heat-treated only).

is dependent on the crystallinities and the distribution of the crystal sizes.² A large range of melting temperatures has been associated with a wide distribution of small crystals and a small range has been associated with a narrow distribution of larger crystals.¹⁸ Therefore, considering such a proposed theory, it is possible to affirm that the undrawn fiber presents a wider distribution of smaller crystals than does the 2.6X fiber. Similar results were shown by Araújo and Simal² for their PET fibers subject to benzoic acid treatments at different concentrations and times.

Another interesting observation related to the main endotherms of the drawn fibers is the occurrence of double melting peaks for most of the analyzed conditions. Such behavior was not observed for the 0X fiber. It has been suggested in the literature^{16,17,19,20} that such double melting peaks would be representative of the existence of two different crystalline forms in the fibers. Such studies were made with PET fibers²⁰ and with nylon 6.6 fibers.^{16,17}

Although there is some controversy concerning the appearance of such double melting peaks in DSC analysis, the good argument presented by Hearle¹⁹ based on the thermodynamic and structural interpretation of the differences between the two crystalline forms suggests that their oc-

currence is not only possible but also dependent on the history of the sample. More recently,¹⁷ in a publication by one of the present authors, such an argument was demonstrated to be very helpful to explain the observed morphology changes in nylon 6.6 fibers due to heat treatments at different temperatures. In addition, as in the case of this study with the nylon 6.6 fibers,¹⁷ our previously annealed drawn PET fibers (control fibers) would present a very stable structure to be influenced by the DSC running conditions, such as the heating rate.¹⁹

Therefore, considering the possibility of the existence of two crystalline forms for our control drawn fibers, the DSC thermograms [Fig. 1(b)] reveal that the areas of each peak are strongly dependent on the aniline treatment condition, that is, temperature, time, and presence or not of benzoic acid in the medium. Also, the figures show that the range of temperatures where the main melting peaks occur remains constant for all analyzed conditions of aniline treatment.

The control fiber presented a double melting peak, where the area of the lower-temperature peak is bigger (more intense) than the area of the higher temperature one. Since the lower-temperature peak would correspond to the melting of smaller and/or more imperfect crystallites,¹⁷ our

Table II Premelting Temperature (T_{pm}), Main Melting Temperatures (T_{m1} , T_{m2}), and the Respective Crystallinities (% C_1 , % C_2), Total Crystallinity (% C_t), Glass Transition Temperature (T_g), Shrinkage (S_h) and Swelling (S_w) Percentage of the 0 \times and 2.6 \times Fibers Submitted to Different Conditions of Chemical Treatments

Fiber	Conditions		T_{pm} (°C)	T_{m1} (°C)	T_{m2} (°C)	C_1 (%)	C_2 (%)	C_t (%)	T_g^a (°C)	S_h (%)	S_w (%)	
0 \times	Control ^b		141	252	—	4	37	41	110	64.0	53.6	
2.6 \times	Control ^b		142	248	254	5	48	52	132	8.3	2.2	
	System	T (°C)	Time									
0 \times	Pure aniline	25	t_1	143	252	—	4	36	40	112	64.5	56.0
			t_2	139	252	—	3	36	39	110	64.9	57.9
		80	t_1	143	253	—	6	34	40	91	65.7	62.9
			t_2	146	253	—	5	35	40	87	66.8	63.9
	Aniline + benzoic acid	25	t_1	142	252	—	5	36	41	111	64.4	62.9
			t_2	140	253	—	4	36	40	109	64.8	63.6
		80	t_1	143	253	—	7	35	42	86	65.2	63.1
			t_2	135	252	—	12	34	46	74	65.7	64.0
2.6 \times	Pure aniline	25	t_1	138	248	254	4	48	52	132	8.5	3.8
			t_2	139	249	254	4	47	51	133	8.8	4.9
		80	t_1	143	248	254	4	47	51	130	9.0	6.0
			t_2	148	250	254	5	47	52	124	17.3	7.9
	Aniline + benzoic acid	25	t_1	140	248	253	4	47	51	133	8.7	6.8
			t_2	143	249	253	4	48	52	134	9.0	7.9
		80	t_1	142	249	—	5	48	53	128	19.4	9.5
			t_2	137	251	—	12	46	58	120	20.5	9.8

^a Measured by DMTA at E'' maximum.^b Heat-treated only.

control drawn fiber would present a crystalline structure with a larger amount of small and or less perfect crystallites.

It is evident, however, that when these fibers are treated in the presence of pure aniline at higher temperatures (80°C) and longer times (t_2), the proportion of the area of the first melting peak increases sharply. When the treatment is realized in the presence of benzoic acid at 80°C and at the time t_1 , the second melting peak is barely distinguishable, and at the time t_2 , it disappears completely. So, it is clear that at these conditions of treatment in the presence of aniline and aniline plus benzoic acid the crystalline structure of the control fibers changes from a two-form structure to an only one-form, that is, to a more homogeneous crystalline structure constituted of smaller and or less perfect crystallites.

Thus, the aniline treatment in the presence or not of benzoic acid at higher temperatures and for longer times probably destroys the bigger and more perfect crystallites of the original structure,

which were responsible for the higher-temperature melting peak. Actually, these crystallites seem to be transformed into smaller and or less perfect ones. Also, these changes in the crystalline structure of the drawn fibers seem not to be affecting substantially their total crystallinity (% C_t).

Considering for analysis the results of Table II, it is possible to confirm the above considerations. Table II does not show significant differences in the total crystallinities (% C_t) for both fibers after the chemical treatments in most of the analyzed conditions as compared to the control ones. Actually, the only condition which presented some significant difference (an increase) was when the control fibers were treated in the presence of aniline plus benzoic acid at 80°C for long times.

But if we analyze the partial crystallinities (% C_1 , % C_2), calculated from the areas under the premelting and main melting peaks, respectively, it is possible to verify that, in general, there was a slight decrease (1–3%) in the crystallinities correspondent to the main melting peaks and a

slight increase in the same proportion for the crystallinities correspondent to the premelting peaks, which resulted in a practically constant total crystallinity (% C_t).

Therefore, in the case of the treatment in the presence of aniline plus benzoic acid at 80°C and especially for long times (t_2), it is clear that the increase in % C_t is mostly affected by a sharp increase in the crystallinity correspondent to the premelting peak. So, this treatment condition favors the generation of a larger amount of nuclei crystallites, but it does not affect substantially the crystalline percentages correspondent to the main melting peak.

Finally, considering the three-phase model²¹ to describe the structure of our PET fibers, we could say that the structure of our drawn fiber would possess microfibrillar regions (sequence of crystalline and interlamellar amorphous regions) and interfibrillar regions (extended amorphous chain molecules). Actually, this three-phase model could not be representative of our undrawn fibers. A less complex two-phase model with crystalline and amorphous regions would be more representative in this case. The original fiber was amorphous and the crystallinity was generated only after the heat treatments under a slack condition.

Thus, the nuclei crystallites generated during the annealings and which were preserved after the chemical treatments in the presence of aniline or aniline plus benzoic acid would be present in the interfibrillar regions of the drawn fibers as already suggested by other authors,² and in the case of the undrawn fiber, the generation of such nuclei crystallites would be in the interlamellar amorphous regions.

Plasticizing Effect of the Chemical Treatments in the Structure of the Fibers

Byun and Im²² suggested that since the difference between the solubility parameters of the aniline [$\delta = 10.3$ (cal/cm³)^{1/2}] and the PET [$\delta = 11$ (cal/cm³)^{1/2}] is very small the interactions between the chain molecules of the PET and the molecules of the aniline would be favored. Also, the solubility parameter of the benzoic acid [$\delta = 10.4$ (cal/cm³)^{1/2}]²³ is very close to the δ 's of aniline and the PET. So, the same kind of interactions could be expected among all these molecules.

But Table II shows that the plasticizing effect of the pure aniline (increase in the chain flexibility of both fibers) is evident only when the treatments were performed at 80°C (temperature close

to the original T_g of the fiber) and especially at long times of exposition, where a sharp reduction in the T_g value can be verified. Also, it is evident that the presence of benzoic acid in the medium accentuated this plasticizing effect at these conditions, decreasing T_g even more, and this effect is more pronounced for the case of the undrawn fiber due to its lack of orientation. So, the presence of benzoic acid in the medium is essential to improve chain flexibility or the pure aniline would be a poorer plasticizer for the fibers. These differences in the plasticizing behavior can be confirmed by the analysis of the swelling and shrinkage data.

By analyzing the swelling data (Table II), it is possible to verify that the affinity between the PET fibers and the aniline and aniline plus benzoic acid would promote swelling even when the temperature of exposition was 25°C. It is possible to verify an additional increase in diameter of about 2.4–10.4% for the undrawn fibers and of 1.6–7.6% for the drawn ones depending on the treatment condition. The highest values were reached for the treatments in the presence of aniline plus benzoic acid independently of the temperature (room temperature or 80°C) and for the treatments in the presence of pure aniline at a temperature of 80°C. Therefore, the presence of benzoic acid in the medium increases the swelling of the fibers even when the treatment is performed at room temperature. At 80°C, the swelling effect is accompanied by a decrease in T_g . Thus, these results suggest sharp changes in the amorphous regions due to swelling of both fibers such as voids formation and disorientation. It has been shown in the literature^{1,2,4,5} that many plasticizers can induce crystallization but others would not affect the crystalline regions, but would promote increased disorientation.¹ So, our system seems to be compatible, at least in part, with this last behavior, once, in the DSC results, sharp changes were not observed in the total crystallinities (% C_t) of the fibers for most the applied chemical treatments. Also, it is interesting to note that since the 0X fiber has shrunk almost completely during the thermal annealing (control fiber) it did not present significant shrinkage (maximum of 2.8%) after the chemical treatments. Again, the absence of previous orientation in this fiber is the reason for such behavior.

But contrarily to the 0X fiber, the 2.6X fiber permitted increased (additional) shrinkage after these treatments, especially in the more severe ones, that is, at 80°C in medium containing ben-

zoic acid. At this condition, this fiber presented an additional shrinkage of 12.2%. Usually, the shrinkage mechanism can be associated to several factors, such as release of tension due processing and recrystallization.¹⁵ It has been shown^{2,17} that the recrystallization process can involve the generation of new crystallites and growth of the preexisting ones. All these phenomena can occur during the preheat treatment of the fibers (controls), including the generation of the nuclei crystallites in the amorphous regions as already discussed in the DSC section. But after the chemical treatments, the shrinkage behavior associated to the swelling and the intense chain motion would be responsible also for the increase in the partial crystallinity correspondent to the premelting peaks that occurred at 80°C and for long time of exposition in aniline plus benzoic acid for both fibers. In the case of the 2.6X fiber, this plasticizing effect at more severe conditions of chemical treatments could be responsible also for the disorientation process and for the changes in size and perfection of their crystallites as demonstrated in the DSC section.

So, the diffusion mechanisms of the aniline and aniline plus benzoic acid into the fiber substrates would be different depending on the temperature and exposition time. At lower temperatures, the swelling effect by the generation of voids would be the governing mechanism, but at 80°C, the intense mobility of the chain molecules due to the presence of these lower molecular weight molecules in addition to the swelling effect would be the other main governing mechanism, and it is the intense chain flexibility at this treatment condition for long times that is favoring the formation of a larger amount of new nuclei crystallites in the amorphous regions of both fibers. In the case of the 2.6X fiber, this phenomenon allowed additional shrinkage at these conditions of treatment and was also responsible for the destruction of the original crystalline structure, which promoted the formation of a more homogeneous one constituted of smaller and or less perfect crystals.

Thus, it is possible to suggest that the crystalline structure of the undrawn and drawn fibers respond in some aspects similarly to the chemical treatments in aniline and in aniline plus benzoic acid, but differently in others. The major differences would be related to their original structures (control fibers) due to the existence of a previous orientation or not. The existence of a previous orientation in the fibers will confer not only a more stable structure to the fibers, but also a

more complex one. To confirm these plasticizing effects on the structure of the two fibers, DMTA and wide-angle X-ray scattering will be considered for discussion in sequence.

Dynamic Mechanical Properties and X-ray Scattering Analysis

Table III shows the dynamic mechanical properties data for the studied fibers before and after the chemical treatments in aniline and aniline plus benzoic acid in all analyzed conditions. It is well known²⁴ that both the height and width of the $\tan \delta$ peaks can be associated to changes in the structure of the polymers. An increase in the crystallinity, for example, can induce a decrease in the height of the α -peak and an increase in the width of the E''_{\max} peak at $E''_{\max}/\sqrt{2}$. Similar considerations can be made for the changes in the $\tan \delta$ peak. For convenience, the intensity where the $\tan \delta$ peak is maximum and its width at $\tan \delta/\sqrt{2}$ will be considered for our analysis.

Thus, Table III shows that the values of the $\tan \delta$ maxima obtained for the undrawn fibers after the chemical treatments are about the same or of superior intensity when compared to the value obtained for the correspondent control fiber. Also, the width of the $\tan \delta$ peaks decreased for most of the aniline treatment conditions. The only exception was when the treatment was performed in the presence of benzoic acid at 80°C for longer times of treatment (t_2), where the measured width increased deeply. Similar behavior was also observed for the drawn fiber.

The increase in width of the $\tan \delta$ maximum for the treatment at 80°C for longer times in the presence of aniline plus benzoic acid might be related somehow to the observed increase in the partial crystallinity as a consequence of the nuclei crystallites responsible for the premelting peak, as already discussed in the previous sections of this article. It was considered that these small crystallites would be located in the amorphous regions of the fibers. So, it seems that their presence in the amorphous regions would restrain somehow the chain motion at these regions. It is well known²⁴ that at constant crystallinity many small crystallites are more effective in restraining chain motion than are a few larger crystallites. Therefore, someone could expect that this effect should also promote an increase in the T_g of the fibers, contrarily to the observed results presented in Table II. Thus, other factors might be taken in account for the analysis of the observed

Table III Intensity Where $\tan \delta$ is Maximum, Width of $\tan \delta$ Peak at $\tan \delta \text{ Max}/\sqrt{2}$, % CI and % LO, and CS Perpendicular to the Planes (010), (110), and (100) for the Undrawn (0 \times) and Drawn (2.6 \times) Fibers

Fiber	Condition	Tan δ Intensity	Width at Tan $\delta/\sqrt{2}$	CI (%)	LO (%)	CS(A)				
						(010)	(110)	(100)		
0 \times	Control ^a	0.21	43	49	21	31	30	23		
2.6 \times	Control ^a	0.17	44	70	32	41	34	28		
	System	<i>T</i> (°C)	Time							
0 \times	Pure aniline	25	<i>t</i> ₁	0.21	31	47	21	32	28	25
			<i>t</i> ₂	0.24	—	46	19	32	29	22
		80	<i>t</i> ₁	0.23	41	54	26	32	28	24
			<i>t</i> ₂	0.22	33	50	22	32	27	24
	Aniline +	25	<i>t</i> ₁	0.22	30	50	22	33	29	23
			<i>t</i> ₂	0.22	—	52	28	30	32	24
benzoic acid	80	<i>t</i> ₁	0.24	28	52	24	31	28	23	
		<i>t</i> ₂	0.21	58	52	24	32	29	24	
2.6 \times	Pure aniline	25	<i>t</i> ₁	0.19	25	66	30	36	33	26
			<i>t</i> ₂	0.22	31	62	26	44	34	25
		80	<i>t</i> ₁	0.19	32	60	23	43	34	23
			<i>t</i> ₂	0.18	44	64	33	40	32	28
	Aniline +	25	<i>t</i> ₁	0.18	29	60	22	42	32	23
			<i>t</i> ₂	0.20	27	64	28	42	34	26
	benzoic acid	80	<i>t</i> ₁	0.20	32	64	33	41	33	27
			<i>t</i> ₂	0.19	48	55	23	37	31	21

^a Heat-treated only.

T_g values (reduction). Again, it seems that the plasticizing effect for this particular case is being governed not only by the improvement of the chain motion due to the presence of the benzoic acid in the medium, but also by the swelling effect as mentioned earlier. For this particular case, the swelling effect might surmount some chain-motion restriction imposed by the generation of these new nuclei crystallites in the amorphous regions. Thus, the presence of these nuclei crystallites in the amorphous regions did not avoid the T_g reduction of these fibers.

Finally, it was shown in the literature²⁴ that not only the crystallinity percentage but also the orientation can promote changes in the $\tan \delta$ height and width of the PET fibers. Since orientation can induce an increase of crystallinity in the fibers, it is the combined effect of crystallinity and orientation that might be taken in account in the dynamic and mechanical analyses of the fibers. So, as the fibers became more crystalline and or oriented, the value of the $\tan \delta$ maximum decreases and the width of the peak increases.

Certainly, this is the reason for the observed differences in the height and width of the $\tan \delta$ peak of the analyzed fibers. As can be seen in Table III, the values observed for the drawn fibers are lower than for the undrawn ones.

Now, considering for discussion the X-ray data (Table III), it is possible to see that the undrawn fibers did not show any significant changes in their crystalline parameters (CI, LO, and CS) after the chemical treatments for all the studied conditions. Actually, a slight increase is observed in the CI (1–5%) and in the LO parameters, especially for the treatments at higher temperatures in the presence of pure aniline and for all conditions of time and temperature, when the benzoic acid was present in the medium of treatment. So, these results indicate that there were not significant changes in the crystalline regions of these fibers, which is in agreement with the DSC data, as already discussed.

Now, if we analyze the X-ray diffractograms of the undrawn fibers [Fig. 2(a,b)], it is possible to see a decrease in the intensities of the curves for

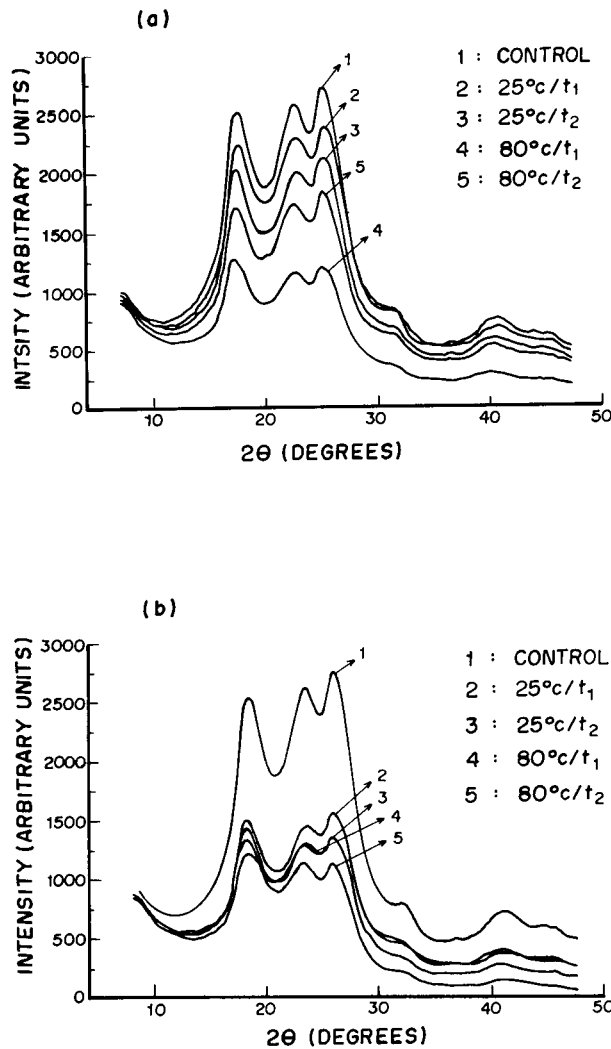


Figure 2 X-ray diffractograms for the undrawn fibers (0X) submitted to different conditions of treatments: (a) pure aniline; (b) aniline plus benzoic acid.

all analyzed conditions of treatments of aniline and aniline plus benzoic acid when compared to the correspondent control fiber. Also, it is interesting to note that the decrease in the intensity of the diffractograms depends on the severity of the treatment, that is, the lower intensities were obtained for the treatments at 80°C in the presence of aniline (a) and aniline plus benzoic acid (b).

Therefore, the following hypothesis can be traced: The swelling as a consequence of the aniline or aniline plus benzoic acid penetration in the amorphous regions is promoting not only disorientation and formation of voids in these regions, but, also, these structural modifications would be promoting disorientation of their crystalline regions as well. Thus, this phenomenon would be

responsible for the observed decrease in the intensity of the X-ray diffractograms.

Also, this disorientation process of the amorphous and crystalline regions seems to be responsible for the observed increase in the intensity of the $\tan \delta$ maximum and a decrease in their width for most the analyzed conditions, as already discussed. So, this disorientation process might be accompanied by some looseness of the structure or loss of compactness of the structure, especially for the treatments at room temperature. At 80°C, this loss of compactness would be accompanied by intense chain motion, as detected by the reduction in their T_g . The intense mobility of the molecules segments at this treatment condition might be responsible for the slight increase in the CI and LO parameters.

Since the crystal sizes in all analyzed directions did not change, the slight increase in the CI and LO might be due mainly to crystalline reorganization, such as defect elimination, which would result in more perfect crystals and also to the generation of the new nuclei crystallites, especially for the chemical treatments performed at 80°C. Again, the DSC data are compatible with these observations.

In the case of the drawn fibers, Table III shows that the chemical treatments affect more effectively the crystalline structure of these fibers. It is possible to verify a decrease in the CI from 6 to 15% depending on the treatment condition. The major decrease was observed for the fibers treated at 80°C for longer times in the presence of aniline plus benzoic acid. Similarly, the LO parameter decreases for most the applied treatments and the intensity of such a decrease will depend on the severity of the treatment (time, temperature, and presence of benzoic acid in the medium).

So, the X-ray data show that the additional shrinkage presented by this fiber after the chemical treatments does not promote an increase in the CI or even crystal growth when compared to the control ones. Actually, the crystal size seems to be presenting some decrease (if we consider the average sizes of the three directions), especially for the case of the more severe treatment (80°C, t_2 , and in presence of benzoic acid), where a clear decrease in the three directions can be visualized.

Since the DSC data did not detect also any additional increase in the total crystallinity percentage for most of the applied chemical treatments, it is possible to consider that the decrease in the CI measured by X-ray analysis might be reflecting mainly the loss of order due to loss of

orientation of the crystalline region rather than the loss of crystallinity by itself, as a consequence of the disorientation of the amorphous region due to the swelling effect. The LO parameter is in agreement with such a hypothesis. This parameter reflects the total order of the system, that is, it is related to several factors at same time, such as crystallinity, perfection, size, and distribution of the crystallites.^{2,13,16} So, changes in any of these factors can cause changes in the LO parameter. Thus, in addition to the loss in the orientation of the system, the slight decrease in the crystal size described above might influence also the reduction in the LO parameter. Also, contrarily to the as-spun fiber, the generation of the nuclei crystallites in the drawn fibers as detected by the DSC data, especially after the more severe conditions of chemical treatments, does not affect the CI and LO parameters. Again, the disorientation process just described is the commanding factor.

Again, the observed loss in the intensity in the X-ray diffractograms of these drawn fibers as compared to the control ones [Fig. 3(a,b)] reflects, basically, the same phenomenological aspects as already described for the undrawn ones. Also, this phenomenon is responsible in the same manner to the observed changes in the intensity and width of their $\tan \delta$ peaks.

Figure 3(a,b) reveals, also, an interesting behavior concerning the intensities of the X-ray diffractograms of the drawn fibers. In comparing the curves for the same chemical treatments, it is possible to observe that, when they were performed at longer times, the intensities of the diffractograms are higher than are the intensities of the diffractograms of the fibers treated at short times. This fact was observed for all the analyzed chemical treatments.

But a clear relationship between the measured crystalline parameters and these changes in the X-ray intensities within a certain chemical treatment was not possible to establish. Such apparent discrepancies were not observed in the same way for the undrawn fiber. Actually, it was observed for only one condition of chemical treatment, that is, for the sample treated in the presence of pure aniline at 80°C. Thus, we believe that this increase in the diffractogram intensities for the chemical treatments performed at long times would be related more to the structural differences observed between the fibers, due mainly to the presence or not of a previous orientation.

In previous sections of this article, it was presented that the oriented fiber responded somehow

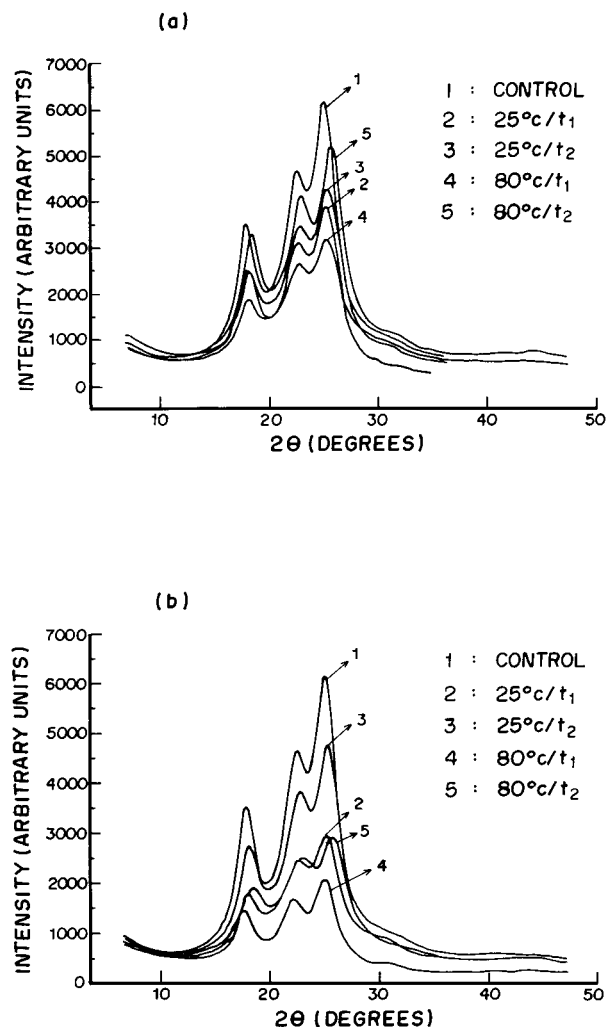


Figure 3 X-ray diffractograms for the drawn fibers (2.6X) submitted to different conditions of treatments: (a) pure aniline; (b) aniline plus benzoic acid.

differently to the chemical treatments. The drawn fibers presented, after the prolonged chemical treatments, a more homogeneous structure, which was constituted mainly of smaller and or less perfect crystallites, as detected by the changes in the format of the DSC main melting peaks (from a double melting peak to a single and low-melting temperature one).

So, the increase in the intensities of the diffracted X-rays for these particular cases would probably be the result of this improvement in the homogeneity of the preexistent crystalline structure, rather than to a gain in crystallinity or even to some reorientation mechanism of the crystalline structure. The generation of this more homogeneous structure for these particular samples

would be facilitated by the intense chain flexibility as detected by the T_g reduction (see Table II).

Actually, some enhancement in the intensities of the equatorial reflections could be expected due to an apparent improvement in the order of the system. A particular X-ray diffraction pattern is a result of the superposition of the diffraction from each crystallite individually and, thus, is a function of the number of crystallites present in the X-ray beam and the position of each crystallite relative to the X-ray beam.¹⁴ Also, it is well known¹⁴ that among the factors that govern the intensities of the diffracted X-rays by a crystalline structure, for some fixed origin in the structure, the positions of the atoms relative to a given set of planes is the most significant factor determining the intensity of the X-ray reflected by those planes. So, we expect that a more uniform crystalline structure would improve the array of the crystallites and the positions of the molecules within these crystallites. Consequently, their positions relative to the studied reflections would also be improved, increasing, therefore, the intensities of the diffracted X-rays. That would be like finding some order into a not-so-ordered structure.

Finally, the X-ray data confirm, also, some of the other structural differences between the studied fibers and already pointed out by the DSC analysis. It was mentioned earlier that the 0X fiber would be constituted by a wider distribution of smaller crystals than would the 2.6X fiber, and Table III indicates that the as-spun fiber has, indeed, smaller crystals than has the drawn ones, independently of the applied chemical treatment.

In addition to the disorientation process detected by the DMTA and X-ray analysis for both fibers, the treatment in the presence of aniline and aniline plus benzoic acid transforms the crystalline structure of the 2.6X fiber into a more homogeneous one with smaller and/or less perfect crystals, especially when treated at 80°C for long times. The DSC data are, again, in concordance with the X-ray results, where the smallest crystal sizes were detected for this condition of treatment.

Sonic Modulus Analysis

To confirm the disorientation process observed for the PET fibers after the chemical treatments, the samples were submitted to an analysis by the sonic modulus. Unfortunately, it was not possible to perform these analysis for the undrawn fibers,

Table IV Sonic Modulus E_s for the Drawn Fibers Submitted to Different Chemical Treatments

Conditions			E_s (dynes/cm ²) $\times 10^{-10}$
Control Fiber ^a			6.80
System	Temperature (°C)	Time	
Pure aniline	25	t_1	6.12
		t_2	5.55
	80	t_1	6.07
		t_2	5.20
Aniline + benzoic acid	25	t_1	6.10
		t_2	5.32
	80	t_1	6.04
		t_2	5.18

^a Heat-treated only.

since the lengths of the resulting samples after all the applied treatments were not adequate for this system of measurement. But since both fibers behaved similarly concerning to the disorientation of their structures after the applied chemical treatments, the sonic modulus data obtained for the drawn fiber were considered enough for the analysis.

The sonic modulus as presented in Table IV represents the total orientation of the system. It is a function of the orientation of the crystalline and amorphous regions, as well as of the amount of the each phase present in the sample.¹⁵

Therefore, Table IV shows that the sonic modulus of the control fiber (heat-treated only) was indeed higher than was the sonic moduli of the fibers submitted to the different chemical treatments. Also, it is possible to observe that the more severe treatment (80°C, t_2) conditions were more effective in reducing the total orientation of the system. Again, these data are in agreement with the swelling behavior presented by this fiber after the chemical treatments and, therefore, with the discussion presented in the previous section.

CONCLUSIONS

The crystalline structure of the PET fibers with different draw ratios (0X, 2.6X) behaved similarly in some aspects concerning the applied chemical treatments but differently in others. The major

differences would be related to their original structures due to the existence of previous orientation or not. The drawn fibers presented a more stable and complex structure than that of the undrawn ones.

The diffusion mechanisms of the pure aniline and aniline plus benzoic acid into the fiber substrates would be different depending on the temperature and exposition time. At lower temperatures, the swelling effect by generation of voids would be the governing mechanism, but at 80°C, the improved flexibility of the chain molecules due to the plasticizing effect of these lower molecular weight molecules in addition to the swelling effect would be the other main governing mechanism. At higher temperatures of treatment, the presence of benzoic acid in the medium improved the flexibility of the chains, reducing more effectively the T_g of the fibers. At this condition of treatment, the swelling effect together with the intense chain flexibility might be the major factors responsible for the formation of a more homogeneous crystalline structure of the drawn fibers, which is constituted of smaller and or less perfect crystals. This fact was evident through the DSC data, where the format of the main melting peaks changed from a double peak to a single and lower temperature one for these conditions of chemical treatments.

DMTA and X-ray analysis are also indications for both fibers that the swelling of the amorphous regions is promoting not only disorientation and formation of voids in these regions, but that these structural modifications would also be promoting disorientation of their crystalline regions as well. This phenomenon would be responsible for the observed decrease in the intensities of the X-ray diffractograms. Since the crystal sizes did not change in all directions for the undrawn fibers, the slight increase observed in their CI and LO parameters might be due mainly to reorganization of the crystalline regions by defect elimination, which would result in more perfect crystals and also to the generation of the nuclei crystallites as detected by the DSC thermograms.

In the case of the drawn fiber, it was observed that a decrease in the CI and LO parameters, which seemed to be reflecting mainly the loss of order due to the loss of orientation of the crystalline regions rather than to the loss of crystallinity by itself, that would be a consequence of the disorientation of the amorphous regions due to the swelling effect. In addition to the loss of orientation of the system, the slight decrease in the crys-

tal sizes for these fibers might have some contribution to the observed decrease in their LO parameter. But, contrarily to the as-spun fiber, the generation of the nuclei crystallites did not affect the CI and LO parameters. Again, in this case, the disorientation process is the commanding factor.

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