Structure and Basic Properties of Aminated PET

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SYNOPSIS

The triethylenetetramine (TETTA) surface-modification process for fibers, consisting of short-time annealing and high-temperature treating the fibers previously padded in TETTA, has been developed. The annealing (60 s, 170°C) of the fibers was performed to restrict the reaction on the surface. To characterize the structure and properties of TETTA-modified fibers, IR spectroscopy, DSC, and X-ray diffraction were applied and critical dissolution time, dye uptake, density, and basic physical–mechanical properties were determined. It was shown that after annealing and aminolysis of the fibers T_g increases to 115°C, while the crystallinity index (determined by DSC) is changed from 33 to 46% (X-ray crystallinity increased from 47 to 59%) and critical dissolution time increased from 12.9 to 58.9 min, depending on the time of aminolysis. The results obtained suggested the existence of two simultaneous processes during the aminolysis: macromolecular scission responsible for introducing the amine groups at the surface and partial crystallization of PET. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The properties of composites are often tailored by fiber hybridization. Thus, the impact resistance of C fiber-reinforced epoxy matrix composites can be increased by incorporating organic fibers, such as PET and PE, into the composite structure, without noticeably damaging the other basic mechanical properties of the composite material (CM).[1]

However, the interface fiber/matrix adhesion in hybrid composites is still among the key factors influencing the overall composite properties. Therefore, being extremely inert, PE, PET, and other organic fibers used as reinforcements in the CM usually undergo different surface modification prior use.

Among the methods of modification, fiber-surface activity, low-temperature plasma treatment, as well as chemical modification with low molecular weight compounds are often applied to increase the compatibility toward and adhesion to common polymer matrices.[2] In our previous work,[3] surface-aminated PET fibers were used in C fiber/epoxy resin com-

posites and the basic characteristics of the hybrid CM were determined. Surface amination, carried out in a triethylenetetramine (TETTA) solution, was found to affect strongly the interface properties in the composite, giving rise to the creation of chemical bonds between the fiber-surface amine groups and epoxy-end groups of the matrix, as determined by DSC and FTIR.[4] In particular, incorporation of 0.0766 mg NH_2/1 g fiber is found to be a reason for a positive hybrid effect in C fiber/epoxy resin composites.[4]

Although the method of modification with TETTA was shown to be quite efficient, it seems too difficult to be accepted for industrial scale. To simplify the surface-modification process, a two-stage procedure was developed, consisting of short-time annealing and then high-temperature treating of the fiber with TETTA, as described in detail elsewhere.[5]

It was previously established that under the proposed conditions the reaction with TETTA occurs exclusively in the thin surface layer of the fiber via a macromolecular scission mechanism. This present article deals with the basic parameters of the structure and properties of aminated PET fibers.

EXPERIMENTAL

Materials

The polyester fabric cloth used was in the form of filament woven fabric cloth made from filament yarns of dtex 140, 48 filaments, and 150 twist. Threads per cm for the fabric were 25 in ends and 24 in picks. All chemicals were of reagent grade and were used without further purification.

Reaction of PET with Amines

The sample fabrics (5 × 30 cm) were weighed, extracted with trichlorethylene using a Soxhlet apparatus to remove the softening agent, dried at room temperature, annealed 60 s at 170°C, padded with triethylenetetramine, and heated at 130°C for different periods of time (15, 30, 45, 60, and 120 s). After the reaction, the sample fabrics were washed with methanol at room temperature six times, 10 min each time, and dried in air. The weight loss of the fabrics in the aminolysis was measured after drying to a constant weight.

Characterization Techniques

IR spectra of surface-aminated PET fibers, as well as of the fibers which have undergone quaternization (to obtain detectable quaternary N groups), were recorded using KBr and MIR techniques on a Pye Unicam SP 800 spectrophotometer.

Determination of Amine Groups

The content of amine groups was determined by a titration method. One gram aminolyzed, dried fibers were treated in 20 cm^3 0.01M HCl and 20 cm^3 distilled water during 2 h at room temperature. After that, the fibers were removed and the residue titrated with 0.01M NaOH in the presence of methyl red as an indicator. The content of amine groups in aminolyzed PET fibers was determined according to the following equation:

$$(V\text{cont} - V)M = \text{mmol NH}_2/\text{g fiber}$$

with $V\text{cont} = $ cm^3 0.01M NaOH spent on titration of the control sample (without fiber); $V = $ cm^3 0.01M NaOH spent on titration of the sample with aminolyzed fiber, and $M = 0.01M$ NaOH.

The content of amine groups was also determined by a dying method. Aminolyzed fibers were dyed with 1% Nylosan Blue 26FL (acid dye) for 30 min at 100°C in the bath with a liquor ratio of 100 : 1 in an Ahiba Turbomat 6TM. After a predetermined dyeing period, the fibers were removed from the dye bath, allowed to cool, and rinsed in hot and then in cold water, the mechanical action of which helped to remove some of the free dye particles in the fiber. The dyed aminolyzed fibers were dried until a constant weight was obtained, and then the dye was extracted with pyridine and its optical transmittance measured at maximum absorbance on a Pye Unicam SP6 spectrophotometer.

Determination of Glass Transition Temperature

The glass transition temperature (T_g) of the polyester samples was determined by dyeing the untreated and aminolyzed samples in an Ahiba Turbomat 6TM with 2% Foron Marine Blue S-2GL (Disperse Blue 79, Sandoz) 60 min at 50, 60, 70, 80, 90, 100, 110, and 120°C in a bath with a liquor ratio of 50 : 1. After a predetermined dyeing period, the samples were washed under running water, the mechanical action of which helped to remove some of the free dye particles on the fiber. The remainder of the free surface-held dye was removed by rinsing five times in acetone at 20°C, each time at room temperature, which was found to dissolve all the free dye without extracting substantial quantities of absorbed dye. The dyed PET samples were dried until a constant weight was obtained and the dye extracted with chloroform and its optical transmittance were measured at maximum absorbance on the Pye Unicam SP6 spectrophotometer. The T_g of the polyester fiber was determined by the dyeing method from the intercept of the straight parts of the function of the dye uptake at different temperatures.[6]

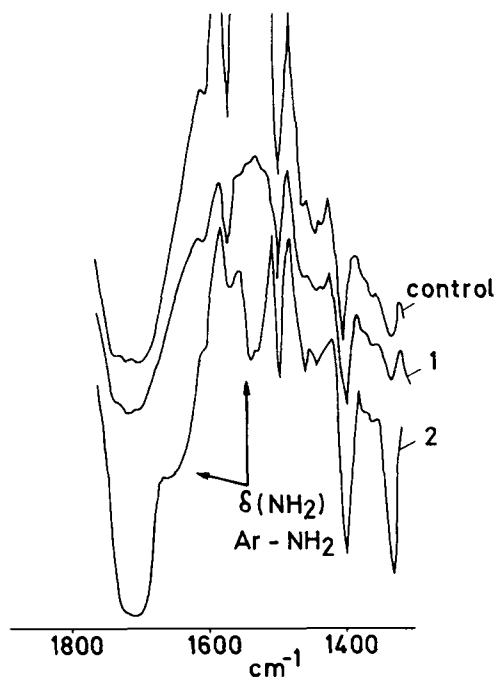### Critical Dissolution Time

The critical dissolution time (CDT) of untreated and aminolyzed fibers was measured in phenol at 60°C. Pyrex tubes 30 cm long and 4 cm in diameter containing the phenol were placed in a thermostatically controlled bath at 60°C. The yarn in the form of a single loop 1.7 cm in diameter was hung on a hooked stainless-steel rod, loaded with a 1 g copper wire weight. The yarn was submerged into the phenol. The time needed until the copper weight fell to the bottom of the glass tube was recorded. The experiment was repeated 10 times and the average value taken as the CDT.[7]
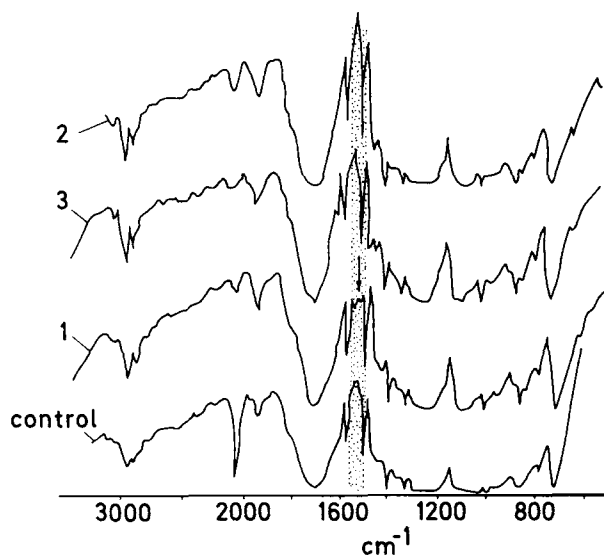
Figure 1   IR spectra (KBr technique) of aminated PET fibers at 130°C: (1) annealed, aminated 15 s; (2) annealed, aminated 60 s; (3) annealed, aminated 120 s.

Table I   Content of Amine Groups in PET Fiber Aminolyzed After Extraction of the Softening Agent and After Annealing at 60 s at 170°C
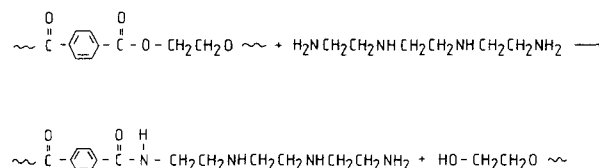
Parameters of Treatment		
Temperature (°C)	Time (s)	Content of Amine Groups (mg NH_2/g fiber)
130	15	3.941
130	30	4.729
130	60	6.305
130	120	16.550
After Annealing		
130	15	4.729
130	30	9.458
130	60	12.610
130	120	28.370

Density Measurements

The density of the samples was measured by the flotation method ASTMD1 505.[8] Mixtures of carbon tetrachloride/n-heptane solutions with different densities were prepared. A small quantity of aminolyzed fibers was inserted into the mixtures with

different densities and the positions of the fibers in the density tubes were registrated. The middle position of the fiber in the tube was taken as the density of the mixture in the tube (ρ). The density of fully crystalline and fully amorphous PET fibers were 1.455 (ρ_c) and 1.333 (ρ_a), respectively.[8] The crystallinity (X) was calculated by the following equation:

$$X = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)}$$

Mechanical Properties

The mechanical properties of the yarns (tenacity and elongation at break and initial modulus) were determined by the JUS standard.[9] The tenacity and elongation at break and the initial modulus of aminolyzed yarns were measured on an Instron tester Model 1026. A sample of 50 cm length was tested by applying the extension rate of an average breaking time of about 30 s.

Figure 2   IR spectra (KBr technique) of aminated PET fibers at 130°C after the quaternization with HCl: (1) annealed, aminated 60 s; (2) annealed, aminated 120 s.

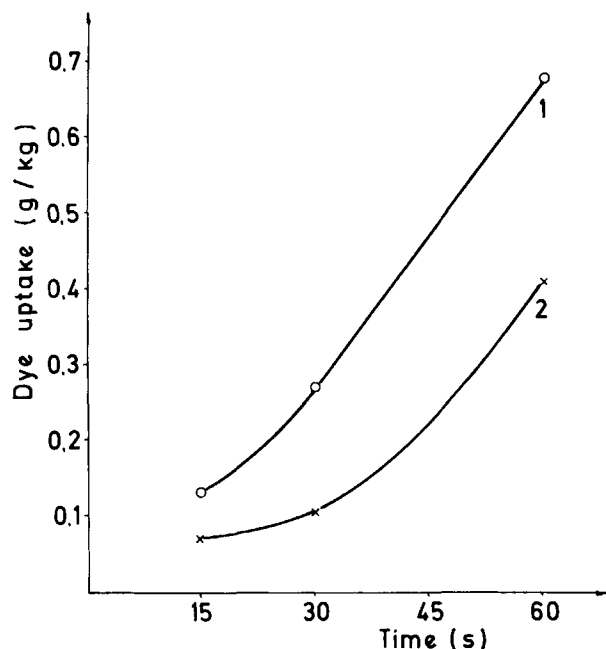**Figure 3**   Reaction of aminolysis (amination) of PET with TETTA.

Figure 4   Effect of time of amination on dye uptake (Nylosan Blue 26 FL at 100°C for 30 min) on PET fiber: (1) aminated; (2) annealed and aminated.

DSC Analysis

DSC measurements were performed with a Perkin-Elmer DSC 7 instrument in the temperature range from 10 to 280°C under nitrogen. The instrument
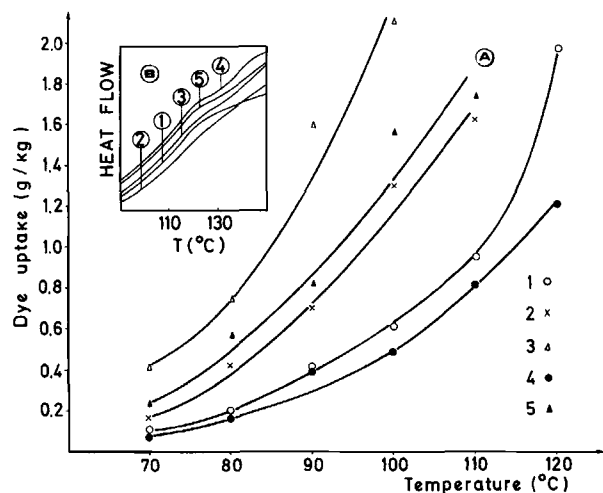

Figure 5   (a) Effect of temperature of dyeing on dye uptake (Foron Marine Blue S-2GL) on PET fibers aminated at 130°C for different periods of time: (1) control; (2) aminated 30 s; (3) aminated 120 s; (4) annealed and aminated 30 s; (5) annealed and aminated 120 s. (b) (1) control; (2) annealed 60 s at 170°C; (3) annealed and aminated 15 s; (4) annealed and aminated 60 s; (5) annealed and aminated 120 s.

Table II   Density and the Degree of Crystallinity of Aminolyzed PET Fibers

| Treatment Parameters | | Density | Crystallinity |
Temperature	Time	(g/cm³)	(%)
130	15	1.415	69.9
130	30	1.406	62.0
130	60	1.406	62.9
130	120	1.421	74.5
After Annealing			
130	15	1.412	67.6
130	30	1.411	66.8
130	60	1.413	69.1
130	120	1.414	69.1
Control		1.380	42.1
Annealed			
170	60	1.395	53.0

was calibrated with indium. Fibers were very finely cut and compressed into a soft pellet at 10,000 psi, and approximately 7 mg of the fibers was used per sample. Specimens were investigated with a heating rate of 20 K/min with five measuring cycles (first heating from 10 to 120°C, rapid cooling; second heating from 10 to 190°C, cooling; third heating from

Table III   Effect of Pretreatment and Time of Amination on CDT of PET

| Treatment Parameters | | |
Temperature (°C)	Time (s)	CDT (s)
130	15	27.5
130	30	36.7
130	60	37.1
130	120	30.7
After Annealing		
130	15	58.9
130	30	56.3
130	60	47.4
130	120	52.6
Control		12.9
Annealed		
170	60	45

Table IV   Mechanical Properties of PET Fibers

Treatment Parameters				
Temperature (°C)	Time (s)	Tenacity at Break (cN)	Extension at Break (%)	Initial Modulus (cN)
130	15	1170	17.3	228
130	30	895	15.3	222
130	60	791	13.0	241
130	120	412	3.5	163
After Annealing				
130	15	1726	30.0	300
130	30	1366	22.0	196
130	60	575	5.7	294
130	120	693	10.0	113
Control		1883	32.0	320
Annealed				
170	60	1977	42.2	215

10 to 280°C and fourth cooling to 10°C; and fifth heating from 10 to 280°C.

Wide-angle X-ray Diffraction (WAXS)

The WAXS measurements were performed on parallel fiber bunches normal to the fiber axis in transmission. A horizontal scanning diffractometer HZG 4 (PC version) with a Si(Li) semiconductor detector probe was used. Scanning of the fiber samples was done in the reflectance mode from (10 to 32°/2θ angle) at a rate of $\Delta(2\theta) = 0.1°$ and a measuring time $t = 20$ s.

RESULTS AND DISCUSSION

The IR spectra of control and aminolyzed PET samples are shown in Figure 1. A comparison of the spectra of control and aminolyzed PET samples show some difference in the region of 1540 cm^{-1} assigned to amine groups. To overcome the difficulties of registration of — NH$_2$ groups, assigned to their low content in the aminolyzed fibers, the reaction of quaternization of these groups with HCl was performed. Aminolyzed PET fibers were treated in the HCl solution (pH 2) 30 min at room temperature and then IR spectra were recorded. As can be seen from Figure 2, the differences near 1500–1670 cm^{-1} are noticed, and intensities of 1540 and 1650 cm^{-1} bands assigned to the — NH$_2$ group appeared. These changes indicate that the amide bond was newly

formed as a result of the reaction of the ester bond of PET with TETTA. The content of amine groups in aminolyzed PET fibers, determined by the titration method, is given in Table I.

To examine whether the annealing of PET fibers (60 s at 170°C) before the aminolysis restricted the reaction mainly on its surface, treatment of the fibers with TETTA immediately after extraction of the softening agent, as well as after annealing, was done and the content of amine groups determined. The results in Table I confirmed our expectations.

Thermal treatment of PET fibers for 60 s at 170°C leads toward the formation of a larger number (higher degree of crystallinity) of small crystallites,[10] thus reducing the accessible space between the crystalline units and the formation of the more compact structure and restricting the reaction of TETTA to the thin surface layer of the fiber via a macromolecular scission mechanism (Fig. 3).

Since the content of — NH$_2$ groups examined by the titration method was determined at room temperature, far below the T_g of the fiber, the increase of the content of amine groups on the aminolyzed annealed PET fiber, compared with the aminolyzed, is obviously due to the increase of the content of amine groups on its surface. The content of amine groups in PET fibers is also examined by dyeing the aminolyzed fibers with acid dye Nylosan Blue 26FL (Fig. 4). As can be seen from Figure 4, the content of acid dye on the fiber increased with increase of the time of aminolysis, but is always lower on the

Table V T_g Data, Melting Points (T_m), Heats of Fusion (ΔH_f), Heats of Crystallization (ΔH_c), Cold Crystallization Peaks, and Degree of Crystallinity of Annealed Aminolyzed PET Fibers ($X\%$)

| Parameters of Treatment	2-Run T_g (°C)	3-Run		4-Run		X (%)
		T_m (°C)	ΔH_f (J/g)	T_c (°C)	ΔH_c (J/g)	
Control	115	254.2	39.07	201.9	−41.9	33.9
Annealed	—	254.7	39.04	199.4	−42.1	34.3
Aminolyzed 130°C, 15 s	—	255.3	41.49	201.5	−43.7	36.4
Aminolyzed 130°C, 60 s	—	255.4	51.09	210.2	−48.8	44.3
Aminolyzed 130°C, 120 s	—	254.0	52.94	213.2	−49.5	46.0

$X(\%) = (\Delta H_f / \Delta H^*)$. ΔH_f = heat of fusion of the examined sample; ΔH^* = heat* of fusion of 100% crystal PET; ΔH^* = 115 J/g.

annealed aminolyzed fibers compared to aminolyzed PET, due to the deeper diffusion of TETTA inside the fiber. Annealed aminolyzed PET fibers have a higher T_g compared with only aminolyzed ones (Fig. 5) due to the recrystallization processes taking place during the heat settling.[11-13] The density measurements and the degree of crystallinity of aminolyzed fibers are given in Table II. Obviously, the density and the degree of crystallinity of aminolyzed fibers increased with the increase of the time of aminolysis,

and both are always higher when compared to untreated fibers.
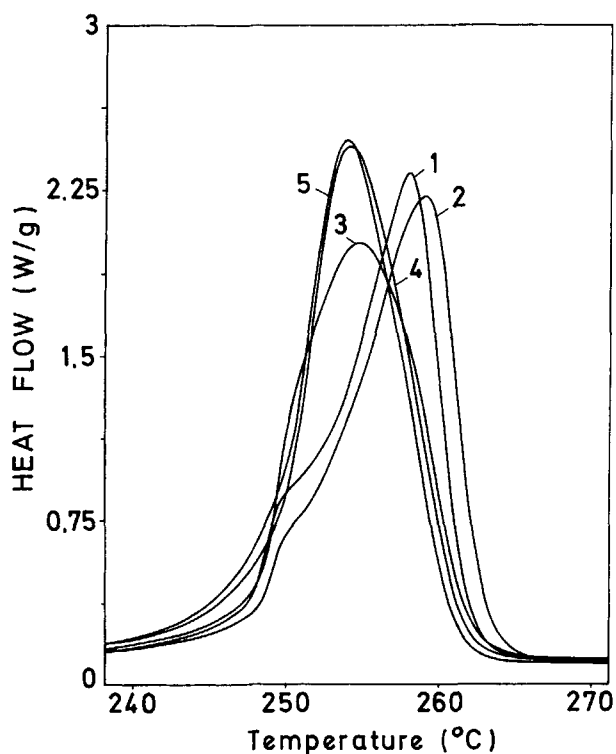
Figure 6   DSC thermograms of aminated PET fibers at 130°C (dT/dt = 20 K/min): (1) control; (2) annealed 60 s at 170°C; (3) annealed and aminated 15 s; (4) annealed and aminated 60 s; (5) annealed and aminated 120 s.
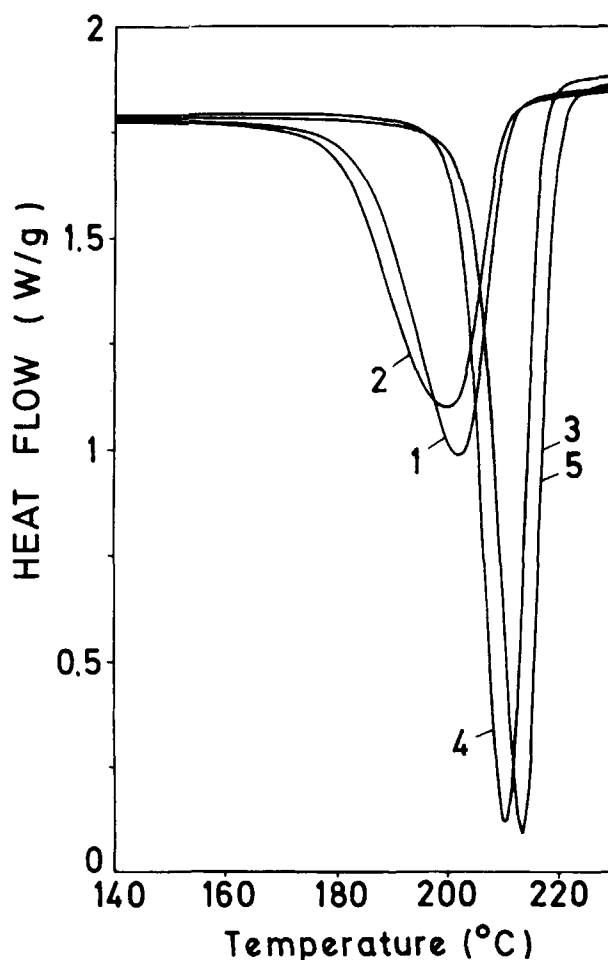
Figure 7   DSC thermograms of crystallization of aminated PET fibers at 130°C (dT/dt = −20 K/min): (1) control; (2) annealed 60 s at 170°C; (3) annealed and aminated 15 s; (4) annealed and aminated 60 s; (5) annealed and aminated 120 s.

Table VI   X-ray Data for Annealed (170°C, 30 s) and Annealed Aminated PET Fibers

Parameters of Treatment	$Lhkl^a$ (A)			KF^b (%)
	(010)	(110)	(100)	
Control	66	50	49	47
Annealed	64	49	49	52
Annealed, aminolyzed 130°C, 15 s	65	49	48	52
Annealed, aminolyzed 130°C, 60 s	65	52	55	49
Annealed, aminolyzed 130°C, 120 s	64	49	48	59

a Index of crystallinity.

b Average crystallite size.

During the two-step procedure of modification consisting of short time annealing, padding with TETTA, and high-temperature treatment, a neglectable weight loss occurred (0–0.01% wt), again suggesting that aminolysis takes place in the outer surface layer of the fiber.

The density and crystallinity of aminolyzed PET fibers for 120 s at 130°C without annealing are insignificantly higher, probably due to a higher degree of decomposition of more accessible amorphous regions and the simultaneous solvent-induced crystallization during aminolysis. CDT values of aminolyzed PET fibers are given in Table III. The CDTs of annealed aminolyzed PET fibers are almost twice higher compared with the CDTs of the only aminolyzed fibers, which is attributed to the additional thermal-induced crystallization (during the heat settling) prior aminolysis.

A remarkable difference in the mechanical properties (Table IV) occurred in aminated when compared with untreated fibers. Tenacity at break and the initial modulus of the fibers are actually decreased by aminolysis, especially for the only aminolyzed fibers. Dramatic changes in the mechanical

properties of PET fibers occur in the samples aminolyzed 60 and 120 s at 130°C.

The three-phase model of Prevorsek et al.[14] is frequently used for describing the structural constitution of polyester fibers. This model postulates the existence, alongside the crystalline zones of the intrafibrillar amorphous phase (located between the crystallites within the microfibrils) and the interfibrillar amorphous phase (located between adjacent microfibrils). During the aminolysis, the macromolecular scission probably occurs in these two regions proceeded by solvent-induced recrystallization. The content of interconnecting tie molecules which determines the fiber elastic properties is decreased, attributed to the decay of crystal network structures
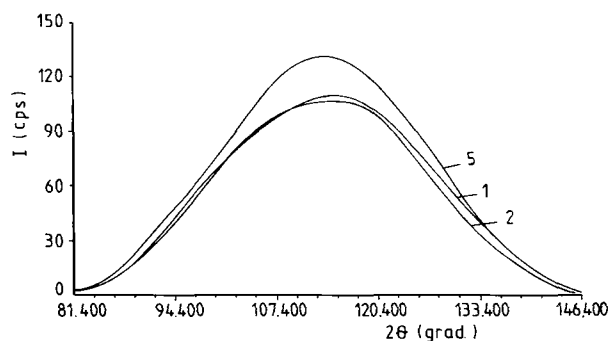
Figure 8   X-ray diffractograms of (a) aminated PET fibers by bath method and (b) aminated PET fibers by high-temperature treatment method at 130°C.
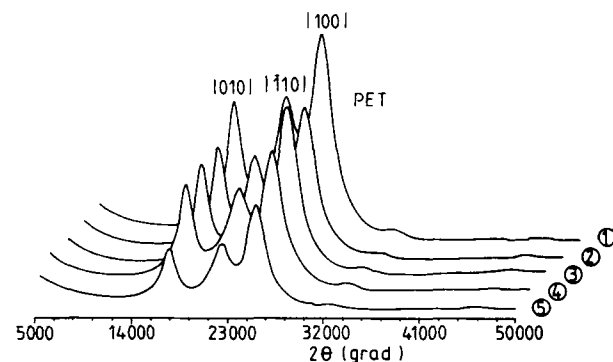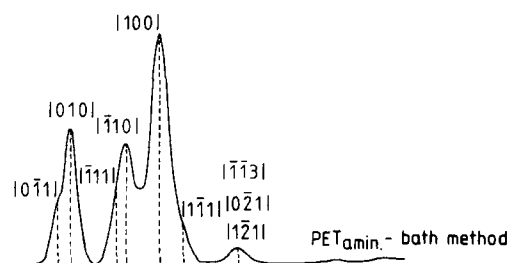
Figure 9   X-ray diffractograms of (1) control, (2) annealed 60 s at 170°C, and (3) annealed and aminated 120 s at 130°C.

caused by the degradation of amorphous regions. PET fibers became brittle after aminolysis.

The DSC results are reported in Table V. The heat of fusion and crystallization increase with the time of amination. It was expected that the heat-capacity values of the aminolyzed PET fibers would decrease, as the ΔC_p of a polymer indicates the chain mobility in the noncrystalline regions, but no large differences in heat-capacity values were found.[15]

Moreover, it was impossible to determine exact values of the T_g, except for the control PET (see Table V) (2-run), although some differences in the curves can be seen [Fig. 5(b)]. Similar behavior was observed on determining the T_g by the dyeing method [Fig. 5(a)]. The melting behavior of some samples is shown in Figure 6. The melting temperature (T_m) was determined as the peak temperature (Table V). A significant difference exists between the melting behavior of unaminated and aminated samples, due to the reorganization processes in the melting range induced by aminolyses. An increase in the heats of fusion and in the crystallinity are also found, once more confirming the results previously discussed.

The aminated samples have a higher crystallization temperature (Table V) and higher crystallization rate (Fig. 7). Apparently, the products of the aminolysis act as nucleating species of the PET crystallization and the structure received after the aminolysis is more homogeneous due to the partly extracted amorphous phase of PET.

The WAXS data of PET fibers are presented on Table VI and Figure 8. During heat treatment as the first stage of modification, the changes of lateral dimensions of crystallites are induced and, consequently, the total crystallinity of PET is increased.[16] Despite the differences in thermal behavior of the aminated fibers, treated with TETTA for 15–120 s, observed by DSC measurements, significant effects on PET crystallinity were found by WAXS, although the apparent crystallite size in the (010), (110), and (100) planes varies with the time of aminolysis. The (100) plane data suggest that after 60 s amination time the recrystallization around the existing crystallites is likely to be the dominant mechanism of structural changes in PET. The degree of orientation, determined from (105) azimmuthal scans (see Fig. 9), is practically unchanged during aminolysis. On the other hand, on inspection of Figure 8, where the WAXS patterns of annealed aminolyzed PET and aminolyzed under the previously proposed bath method are presented, the same conclusions could be derived concerning the two-step procedure of TETTA modification recently developed. The appearance of

a new quadrant reflexes in an equatorial scan of TETTA bath-treated PET is evidence of a strongly damaged overall fiber structure as a result of TETTA action across the fiber volume.

It was shown[4] that for the successful processing of hybrid CM, based on epoxy resin (C and PET aminated fibers) the contribution of $- NH_2$ groups may affect the cure kinetics and the interfacial adhesion between the fibers and the matrix. It is thus clear that the proposed procedure for modification of PET fibers in its first step protects the interior fiber structure and enables the reaction with TETTA to be localized in the thin surface layer.

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