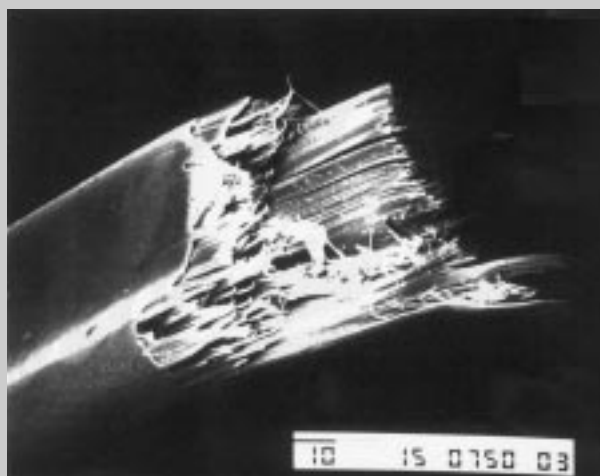


Full Paper: New liquid crystalline copolyesters have been synthesized by melt transesterification of poly(ethylene terephthalate), p(ET), with 4-acetoxybenzoic acid (H), and varying proportions of equimolar mixtures of diacetylated 4,4'-dihydroxybiphenyl (B) and terephthalic acid (T). The solidification of the polymerizing mixture due to segregation of a highly aromatic crystalline phase, which limited the available range of compositions when p(ET) was modified with H only, was shown not to take place when moderate amounts of T and B were added to H. The p(ETHB) copolyesters are shown to possess high structural homogeneity, even when the content of p(ET) in the starting mixture is as low as 10 mol-%. The thermal properties of the copolyesters can be changed in a fairly wide range by varying the chemical composition. As a result, the properties of the new LCPs can easily be optimized in view of different applications, such as the production of blends with flexible thermoplastics or of glass fiber-reinforced composites.



SEM micrograph of the fracture surface of an 85/15 fiber.

New PET-Based Liquid Crystalline Copolyesters and Their Use in Blends and Composites

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Introduction

It is well known^[1] that copolyesterifications involving monomer mixtures, blends of preformed polyesters, or even systems composed of one or more monomers and preformed polyesters, are always accompanied by transesterification reactions between the ester bonds and the free carboxyl and/or hydroxyl end groups. Such reactions normally lead to entropy-driven compositional equilibration of the copolyester chains, hence a product possessing the most probable molar mass distribution and random sequence distribution is obtained. In some cases, however, copolyesters with compositional heterogeneity can be formed, because either the transesterification reactions are not sufficiently fast with respect to polycondensation, or there may be an enthalpic gain associated with the formation of homosequences. As an example, it has been demonstrated that the liquid crystalline p(ETH) copoly-

esters synthesized by transesterification of poly(ethylene terephthalate) (p(ET)) with 4-acetoxybenzoic acid (H) according to the technique described several years ago by Jackson and coworkers^[2–4] are characterized by fairly strong compositional heterogeneity, as part of these macromolecules are particularly rich in oxybenzoate (H), whereas others are rich in ethylene terephthalate (ET). Compositional heterogeneity may sometimes be strong enough to cause phase segregation.^[5] And in fact, for the p(ETH) copolyesters with nominal H content equal to, or higher than, 80 mol-%, the aromatic-rich phase can solidify already during synthesis, thus preventing not only the occurrence of compositional equilibration, but even the formation of high molecular weight polymers. Clearly, when compositional heterogeneity results in a phase-segregated structure and the two phases possess distinctly different thermal, rheological and mechanical

characteristics, considerable difficulties may arise during processing of the material, especially when fibers are to be produced by melt spinning, and the mechanical properties of the manufactured articles may be poor. The improvement recently achieved by Suenaga et al.^[6] to Jackson's technique reported earlier led to the development of p(ETH) copolymers with enhanced homogeneity^[7,8] that were commercialized by Unitika under the trade name Rodrun®. The copolyester (Rodrun® LC5000) with the highest H content (80 mol-%) is still heterogeneous,^[9] however, and is mainly used for surface mounting technology in electronic applications as a short glass fiber composite.^[10] The product with only 60 mol-% H (Rodrun® LC3000) is practically homogeneous, but shows fairly low thermal resistance.

In a previous paper,^[9] we have shown that the partial substitution of H with equimolar amounts of diacetylated hydroquinone (Q) and terephthalic acid (T) leads to p(ETHQ) copolyesters with slightly enhanced compositional homogeneity. Although the improvement was not too significant, probably because the geometry of the Q and T units is such that the H-T-Q blocks are still able to easily organize into a crystalline lattice, it was nevertheless possible to synthesize copolyesters with room temperature morphological characteristics similar to those of Rodrun® LC5000 and Rodrun® LC3000, but with higher aromaticity, so that the thermal and mechanical properties of the products were slightly better.^[9,11,12]

It should be emphasized, on the other hand, that an attempt of using an equimolar mixture of 4,4'-diacetoxybiphenyl (B) and sebacic acid (S), instead of H as the p(ET)-modifying agents resulted in highly heterogeneous materials composed of a relatively soft copolyester matrix rich in aliphatic units and a liquid crystalline, aromatic-rich dispersed phase.^[13] Further studies on this and similar systems^[14-18] demonstrated that segregation of a mesophase within the isotropic medium, followed by compositional differentiation of the two phases, driven by the enthalpic gain due to progressive improvement of the mesophase organization, is greatly favored when a second monomer, capable of forming aliphatic polyester sequences with ethylene glycol, is present in the system. Thus, sebacic acid can combine with the ethylene glycol units of p(ET) and lead to sequences rich in S and E units, whereas the aromatic moieties concentrate in the copolyester forming the dispersed phase.

This conclusion prompted us to replace S with T and to investigate a system in which the monomer mixture consisted of H and equimolar amounts of B and T. It was expected that, compared with the p(ETHQ) copolyesters studied previously,^[9] the p(ETHB) polymers should avail from the stronger longitudinal disorder induced by the longer B units substituting the Q ones. In this paper we report on the synthesis and characterization work aimed at the optimization of the composition of the p(ETHB)

copolyesters, as well as on the preliminary characterization of the blends of some of them with p(ET) (in-situ composites) and with short glass fibers.

Wholly aromatic copolyesters based on H, T and B were studied previously by Economy and coworkers^[19] and made available commercially by Carborundum Company in developmental quantities in 1973 (Ekkcel® I-2000 and Ekkcel® C-1000).

In a recent paper by Inoue et al.,^[20] the properties of liquid crystalline copolyesters synthesized from p(ET), H, T and an unspecified "dihydroxy compound" are described in comparison with those of conventional p(ETH) LCPs. These copolyesters, probably similar to those studied in this work, are said to possess high structural homogeneity, good thermal resistance and excellent mechanical properties. They have been commercialized by Toray under the trade name Siveras®.

Experimental Part

Materials

The p(ET) sample used in this work was a bottle-grade material produced by Cobarr S.p.A., Anagni (Rome), Italy, with an intrinsic viscosity (*IV*), measured at 25 °C in phenol/tetrachloroethane (50/50 by volume) of *IV* = 0.74 dL/g. For the synthesis of the copolyesters, the p(ET) was used as a coarse powder obtained by grinding the pellets in a laboratory mill. Terephthalic acid, 98% (Aldrich, Milan, Italy) was used as received. 4,4'-Dihydroxybiphenyl (Aldrich) and 4-hydroxybenzoic acid (Aldrich) were acetylated with excess acetic anhydride in a sodium hydroxide solution at 0 °C. 4,4'-Diacetoxybiphenyl (B) was purified by repeated crystallization from ethanol. The purity was checked by ¹H NMR spectroscopy and differential scanning calorimetry (DSC, m.p. 167.4 °C). 4-Acetoxybenzoic acid (H) was recrystallized three times from chloroform (m.p. 194.3 °C). Sodium acetate, 99+%, (Aldrich) was employed as a catalyst for the polymerizations. Rodrun® LC3000 and Rodrun® LC5000 were purchased from Unitika, Tokyo, Japan. The type E glass fibers used for the preparation of the composite specimens were provided by Vetrotex (France); the diameter was 10 μm and the length-to-diameter ratio *L/D* was 450. All materials were thoroughly dried in vacuo at 50 °C (monomers) or 120 °C (polymers and glass fibers) for at least 24 h, before use.

Copolyester Synthesis

The calculated amounts of monomers and ground p(ET) were dry-blended, a small amount (≈0.3 g/Kg) of sodium acetate was added and the mixture charged into the Pyrex round-bottomed cylindrical reactor fitted with a helicoidal stainless-steel stirrer, the speed of which could be adjusted between 40 and 100 rpm, nitrogen inlet and vacuum outlet. Two types of reactors were used. The smaller one, of ≈200 mL capacity, was employed for the production of most copolyester samples (40–60 g). The larger one, of ≈1500 mL capacity, was used for the synthesis of a few larger-volume

(about 200 g) samples. The flask was closed and purged with pure nitrogen by repeated evacuation and nitrogen admission cycles. A salt bath preheated to about 295 °C was then placed around the flask in order to heat the charge rapidly to about 290 °C. This temperature was kept constant during the early stage (about 30 min) of the polymerization process by means of the thermostated bath and was then risen gradually to 300–315 °C, the higher temperatures being used to form copolyesters with higher aromaticity. During the heating period, the inner pressure was kept slightly lower than atmospheric by adjusting the vacuum tap. After immersing the reactor in the salt bath, monomers B and H melted rapidly to give a clear colorless liquid, whereas T remained as a white suspended powder for a few minutes before dissolving completely. The p(ET) particles also melted rapidly and dissolved within about 5 min so that the reaction mixture became homogeneous. Concomitantly, a lively development of acetic acid vapors was observed. The vapors were condensed into a side trap cooled with liquid nitrogen. Thereafter, the viscosity increased gradually and the reaction mixture became hazy and then opaque, as a result of mesophase formation. When the evolution of acetic acid ran to completion, the temperature was gradually brought to the final value, and the pressure was slowly reduced. The reaction was completed under a residual pressure of about 0.1 mmHg. The application of vacuum caused further release of volatile by-products and resulted in increased mass viscosity. The reaction was stopped when even at lower stirring speed the viscous polymer could not be kept any more from coming off from the reactor walls. At the end of the reaction, nitrogen was admitted and the reactor was opened under nitrogen flush. The produced copolyesters were collected with a stainless steel spoon while hot, and were then cooled and ground.

p(ET)/LCP Blends and Short Glass Fiber Composites

The blends of some of the p(ETHB) copolyesters with p(ET) were prepared in a Brabender Plasticorder apparatus at 35 rpm and 280 °C (the copolyesters with a melting point lower than 280 °C were used). Blending was carried out while purging with nitrogen and was continued until constant torque was recorded (about 4 min). Extruded blend samples were obtained, with and without drawing, using a capillary viscometer (Rheoscope 1000, CEAST) provided with a melt spinning unit; a die of 0.5 mm diameter, an *L/D* ratio of 20, and a temperature of 265 °C were employed.

The copolyesters with higher aromatic content were filled with short glass fibers (GF, 25 or 30 wt.-%) in the Brabender mixer. The temperature was about 20 ° higher than the calorimetric melting point of the polymers. The properties of a 30% GF composite were preliminarily studied.

Characterizations

Solubility tests were carried out on the copolyesters with the procedure used by Suenaga and coworkers^[6] and by us^[9] for the p(ETH) and the p(ETHQ) copolyesters, respectively. A 1 g sample of powdered copolyester was added to 75 mL of a 50/50 v/v mixture of phenol and tetrachloroethane, and the suspension was immersed in an oil bath thermostated at

150 °C and shaken occasionally. After 24 h the solid was separated from the solution by centrifugation, washed with two portions of preheated solvent mixture and then twice with acetone and dried in vacuo at 130 °C for 24 h. The combined solutions were precipitated in excess methanol (500 mL) under vigorous stirring. The precipitate was separated by centrifugation, washed with fresh methanol and dried in vacuo at 100 °C for 24 h. Both fractions were weighed.

The copolyesters and their fractions, and the blends with p(ET) were analyzed by DSC with a Perkin Elmer DSC4 and with a Mettler DSC30 apparatus. The morphology of the polymer samples and of their blends with p(ET) was studied by scanning electron microscopy (SEM) with a Jeol T300 apparatus. Wide-angle X-ray diffraction was used to investigate the crystalline structure of powder polymer samples. A D500 Siemens diffractometer was employed, using Ni-filtered CuK_α radiation. The X-ray diffraction analysis of fibers of the p(ET)-p(ETHB) blends was carried out with a PW 1050 Philips diffractometer (CuK_α Ni-filtered radiation). The patterns were recorded using an imaging plate Fujix BAS-1800 system. Mechanical properties were determined at room temperature with an Instron testing machine (Mod. 4301) operating with a cross-head velocity of 10 mm/min on extruded and drawn samples. Dynamic-mechanical thermal analysis (DMTA) of some of the copolyesters, and of their glass fiber composites was conducted with a Polymer Laboratories apparatus, using samples of 20 × 8 × 2 mm, compression-molded in a Carver laboratory press. The measurements were carried out in flexural mode, with a 1 Hz frequency and a heating speed of 10 °C/min in the 25–300 °C range.

Results and Discussion

Synthesis and Characterization of the p(ETHB) Copolyesters

The chemical structure of the p(ETHB) copolyesters is identified herein by the R_1/R_2 label, with R_1 and R_2 defined as follows:

$$R_1 = (\text{T} + \text{B} + \text{H})/(\text{ET} + \text{T} + \text{B} + \text{H})\%$$

$$R_2 = (\text{T} + \text{B})/(\text{T} + \text{B} + \text{H})\%$$

where T, B, H, and ET are the molar concentrations of the relevant monomer units in the copolyester chains. The R_1 ratio is a measure of the degree of chemical modification of the initial p(ET), whereas R_2 indicates the extent to which H has been substituted by the two other aromatic monomers T and B. The R_1 ratio was first used by Jackson and Kuhfuss^[3] to identify their p(ETH) copolyesters. The polymer containing 40 mol-% p(ET) and 60 mol-% H, which corresponds to Rodrun® LC3000, is indicated here as 60/00, and that with 20 mol-% p(ET) and 80 mol-% H, corresponding to Rodrun® LC5000, is indicated as 80/00. As a general example, the molar composition of the copolyester 80/15, that is that having $R_1 = 80$ and $R_2 = 15$, can be calculated as shown in Table 1.

The degree of aromaticity of the copolyesters, defined according to Calundann and Jaffe^[21] as the percent ratio

Table 1. Molar composition of the 80/15 copolyester.

$(T + B + H)/(ET + T + B + H) = 0.8$	ET	T + B + H		
$R_1 = 80$	20	80		
$(T + B)/(T + B + H) = 0.15$		T + B	H	
$R_2 = 15$		12	72	
Copolyester composition	E	T	B	H
	20	26	6	72
	16.13%	20.97%	4.84%	58.06%

of the number of aromatic carbons to the total number of atoms in the backbone, which is commonly used as an index of anisotropy of the LCP macromolecules, increases monotonously with R_1 , and, contrary to the case of the p(ETHQ) copolyesters described earlier,^[9] also increases slightly with R_2 .

The copolyesters synthesized in this work are presented in Table 2, together with their molar compositions and degrees of aromaticity. The solubility in the phenol/tetrachloroethane mixture at 150 °C, measured as described in the experimental part, is given in the last column of Table 2.

Compared to the copolyester synthesis described in the previous paper,^[9] the behavior of the reaction mixture during polymerization was greatly improved by replacing Q by B. In fact, whereas segregation of a highly aromatic phase did take place quite often during the preparation of the p(ETHQ) copolyesters and led to solidification of the reaction mixture,^[9] especially when R_1 was close to, or higher than, 80, no such problem was ever met with the p(ETHB) copolyesters studied here. The investigated compositions are shown graphically in Figure 1. The range of R_2 was limited to 10–20 in order to keep the production cost of the polymers low. The copolyesters 60/00 and 80/00, indicated by square symbols in Figure 1, correspond to the commercial p(ETH) products (Rodrun® LC3000 and LC5000). The copolyesters 100/50 and 100/80, also identified by squares, correspond to the products

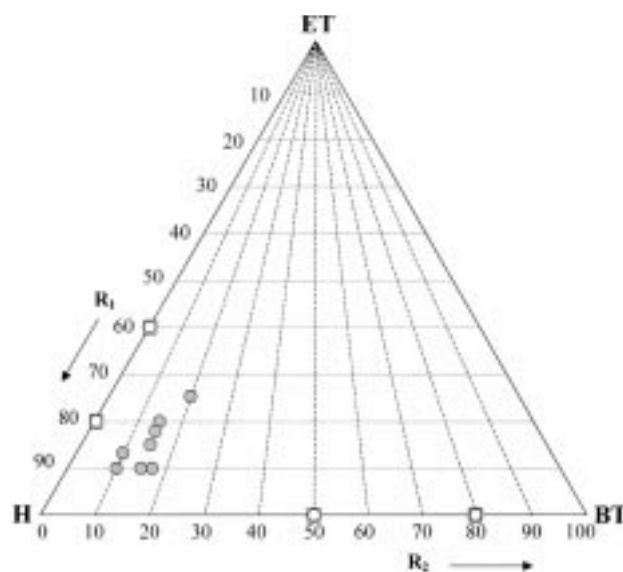


Figure 1. Triangular composition plot of the copolyesters. Square symbols on the ET-H side indicate commercially available p(ETH) copolyesters (Rodrun® LC3000 and LC5000, by Unitika). The square symbols on the H-BT side correspond to compositions described in the literature.^[19]

developed by Economy and coworkers.^[19] The latter copolyesters have melting points above 400 °C^[19] and could not be synthesized with the technique used in this work. Among the other copolyesters shown in Figure 1, the only one, of which the reaction mixture solidified during the synthesis, was 80/00.^[9] In contrast, with R_2 ranging between 10 and 20, it was possible to increase the degree of aromaticity considerably (R_1 up to 90) without observing solidification.

The results of solubility tests are also collected in Table 2. As already found for the p(ETHQ) copolyesters,^[9] the solubility drops to very low values when the degree of aromaticity increases beyond a certain limit. R_2

Table 2. Composition, degree of aromaticity and solubility of the p(ETHB) copolyesters.

Copolyester R_1/R_2	E %	T %	B %	H %	Degree of aromaticity	Solubility %
60/00 ^{a)}	28.6	28.6	0.0	42.8	52.62	100
75/20	20.0	26.0	6.0	48.0	58.90	100
80/00 ^{a)}	16.7	16.7	0.0	66.6	58.81	86.5
80/15	16.7	21.7	5.0	56.6	60.21	100
80/15 ^{b)}	16.7	21.7	5.0	56.6	60.21	100
82/15	15.2	20.5	5.2	59.1	60.95	92
85/15	13.0	18.6	5.5	62.8	62.08	17.3
85/15 ^{b)}	13.0	18.6	5.5	62.8	62.08	20.2
87/10	11.5	15.4	3.8	69.3	62.34	11.3
90/10	9.1	13.2	4.1	73.6	63.52	9.2
90/15	9.1	15.2	6.2	69.5	64.03	6.1
90/15*	9.1	15.2	6.2	69.5	64.03	6.6
90/17	9.1	16.0	7.0	67.9	64.22	6.8

^{a)} Compositions corresponding to those of Rodrun® LC3000 and LC5000.

^{b)} Preparations carried out in the 1.5 L reactor.

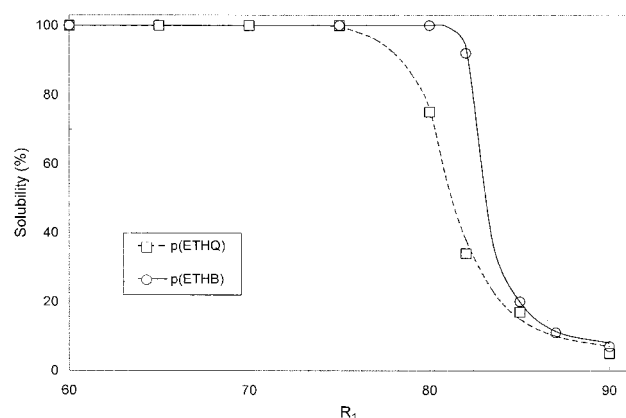


Figure 2. Solubility of the p(ETHQ) and p(ETHB) copolyesters in a 50/50 v/v mixture of phenol and tetrachloroethane at 150 °C, as a function of R_1 .

also has an effect on the solubility, which is higher when R_2 is in the range between 10 and 20.^[9] It is interesting to note, however, that the solubility of the p(ETHB) copolyesters with $R_2 = 10$ –20 decreases much more steeply (when R_1 exceeds 82) than does the solubility of the corresponding p(ETHQ) polymers (Figure 2). This is another piece of evidence confirming the conclusion that the copolyesters studied in this work possess considerably higher homogeneity than those synthesized by transesterification of p(ET) either with H, or with mixtures of H, T, and Q.

The thermal properties of the copolyesters and of their soluble and insoluble fractions have been studied by DSC. The main calorimetric data are collected in Table 3. A comparison with the thermal properties of the p(ETHQ) copolyesters described elsewhere^[9] shows that the fusion enthalpies measured for the copolyesters containing B in place of Q, for comparable values of R_1 and R_2 , are generally higher (up to 4.9 J/g). They are even higher than those (up to 2.5 J/g) reported^[20] for the Siveras® copolyesters.

As expected, the data in Table 3 show that the fusion temperatures increase appreciably with an increase of R_1 (degree of aromaticity). It can also be observed that, for copolyester 82/15, whose solubility is 92%, the melting points of the fractions and of the whole copolyester are in the range of 258–264 °C and therefore quite close to each other. For all the copolyesters with $R_1 \geq 85$, but 90/10, the soluble fractions show melting points close to 255 °C, which is the temperature typical for a copolyester with $R_1 \approx 80$ –82. It should be pointed out, however, that their amount decreases rapidly down to 6%, as R_1 exceeds 85. The melting temperatures of the corresponding insoluble fractions increase monotonously with R_1 and remain close to the melting temperature values of the whole polymers. All these findings provide further evidence supporting the conclusion that the investigated copolyesters possess appreciable homogeneity.

Table 3. Calorimetric data of the copolyesters and their soluble and insoluble fractions.

Copolyester R_1/R_2	T_m °C	T_c °C	ΔH_m J/g	ΔH_c J/g
60/00 ^{a)}	196	155	2.1	-2.2
75/20	214	180	1.8	-1.8
80/00 ^{a)}	287	265	2.2	-2.4
80/15 ^{b)}	248	203	3.5	-3.3
82/15	261	232	4.0	-3.7
82/15 soluble	258	239	3.9	-3.7
82/15 insoluble	264	240	3.3	-3.2
85/15 ^{b)}	274	234	4.4	-4.1
85/15 soluble	244	218	3.8	-3.4
85/15 insoluble	277	245	4.6	-4.2
87/10	268	237	2.2	-1.8
87/10 soluble	254	206	1.9	-1.2
87/10 insoluble	269	243	2.8	-2.5
90/10	270	258	2.6	-2.5
90/10 soluble	252	231	2.4	-0.9
90/10 insoluble	283	266	3.3	-3.2
90/15 ^{b)}	308	273	4.9	-4.6
90/15 soluble	288	261	2.9	-2.7
90/15 insoluble	309	279	4.8	-4.7
90/17	304	280	4.8	-4.4
90/17 soluble	258	221	1.7	-1.0
90/17 insoluble	305	283	4.9	-4.7

a) Compositions corresponding to those of Rodrun® LC3000 and LC5000.

b) Preparations carried out in the 1.5 L reactor.

The wide-angle X-ray diffraction patterns of the investigated p(ETHB) copolyesters consist of a strong, broad reflection peaking at $2\theta \approx 20^\circ$, plus a more or less pronounced shoulder, or diffuse peak, at $2\theta \approx 28^\circ$. These spectra are qualitatively similar to those of the p(ETHQ) copolyesters with $R_1 > 75$, discussed earlier.^[9] Here also the intensity of the broad reflection at $2\theta \approx 28^\circ$ increases slightly with an increase of R_1 , as shown in Figure 3. However, a comparison with the X-ray diffractograms reported previously^[9] for the p(ETHQ) copolyesters of similar composition shows very clearly that the prominence of this reflection is always much lower for the polymers based on B, despite of their slightly higher degree of aromaticity. Moreover, contrary to what it was found for the p(ETHQ) polymers,^[9] the spectra of the insoluble fractions of the p(ETHB) copolyesters do not differ too much from those of the unfractionated polymers. The soluble fractions, on the other hand, show very often X-ray patterns with more intense secondary reflections. An example illustrating the two above observations is presented in Figure 4 for the case of copolyester 85/15 and its fractions. As the insoluble fraction of this material represents about 80% of the whole polymer, the absence of strong reflections in addition to that at $2\theta = 20^\circ$ is an indication that the material does not contain a separate crystalline phase rich in aromatic units, as do the parent copolyesters of the p(ETH) and p(ETHQ) types. The

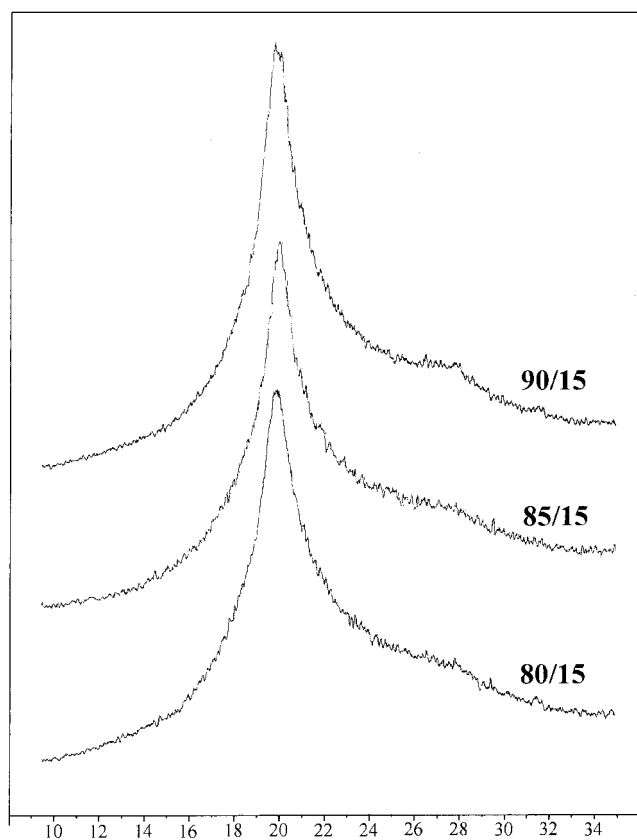


Figure 3. Powder X-ray diffractograms of copolyesters 80/15, 85/15, and 90/15.

soluble fraction of this particular copolyester displays an X-ray pattern implying a structural organization, which is considerably more ordered (Figure 4). This observation may be rationalized assuming that the relatively small amount of soluble material is characterized by lower molar mass and higher crystallizability. In general, especially for the case of copolyesters showing higher solubility, another mechanism, that is solvent-assisted crystallization caused by the extraction/precipitation and final drying treatment, may contribute to the observably higher organization of the soluble phases.

The dynamic-mechanical behavior of the p(ETHB) copolyesters is in line with the results of similar DMTA investigations carried out on the p(ETHQ) polymers.^[9] The DMTA curves of the 80/15, 85/15, and 90/15 polymers are compared with those recorded for Rodrun® LC5000 (80/00) in Figure 5. The curves of the two polymers with similar aromaticity (80/15 and LC5000) follow similar trends. However, the low-temperature transition that is observed in the 130–150 °C range for LC5000 is displaced toward higher temperatures (150–170 °C) for 80/15 and is appreciably less intense. As a result of this, the p(ETHB) copolyester has a slightly higher modulus at temperatures above ≈150 °C. On the other hand, the modulus drop associated with the melting transition of this

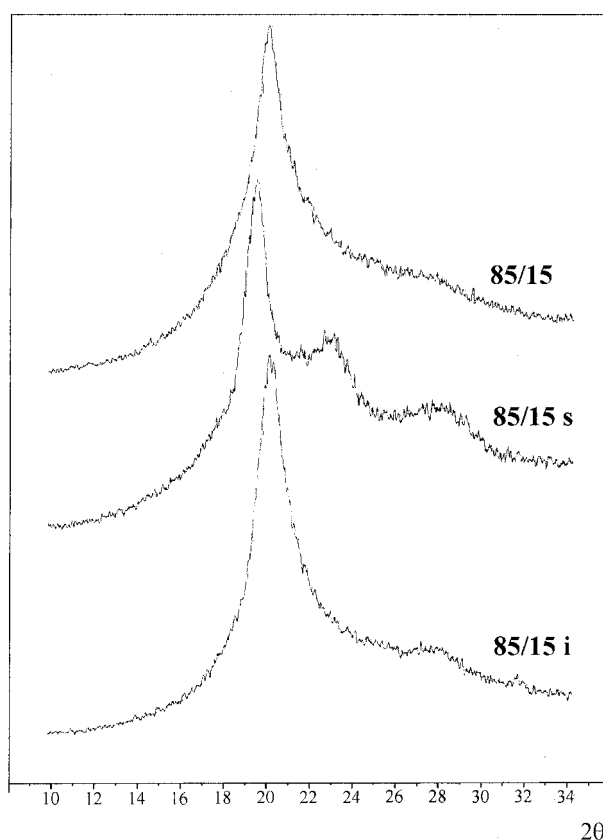


Figure 4. Powder X-ray diffractograms of copolyester 85/15 and of its soluble (s) and insoluble (i) fractions.

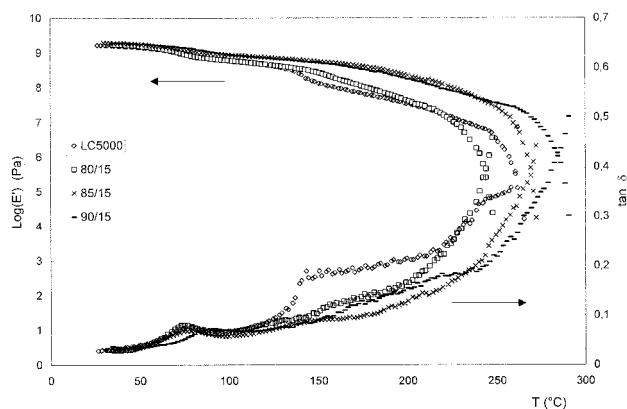


Figure 5. DMTA curves of copolyesters 80/00 (Rodrun® LC5000), 80/15, 85/15, and 90/15.

material is observed at temperatures lower than that found for LC5000, which is in agreement with the DSC data shown in Table 3. An increase of R_1 from 80 to 90 (that is impossible to achieve for the p(ETH) copolyesters due to solidification during the synthesis) brings about a considerable increase of the temperature of fusion, as already found from DSC studies. Moreover, the transition in the 150–200 °C range becomes even less intense, thus minimizing the corresponding modulus drop, and moves

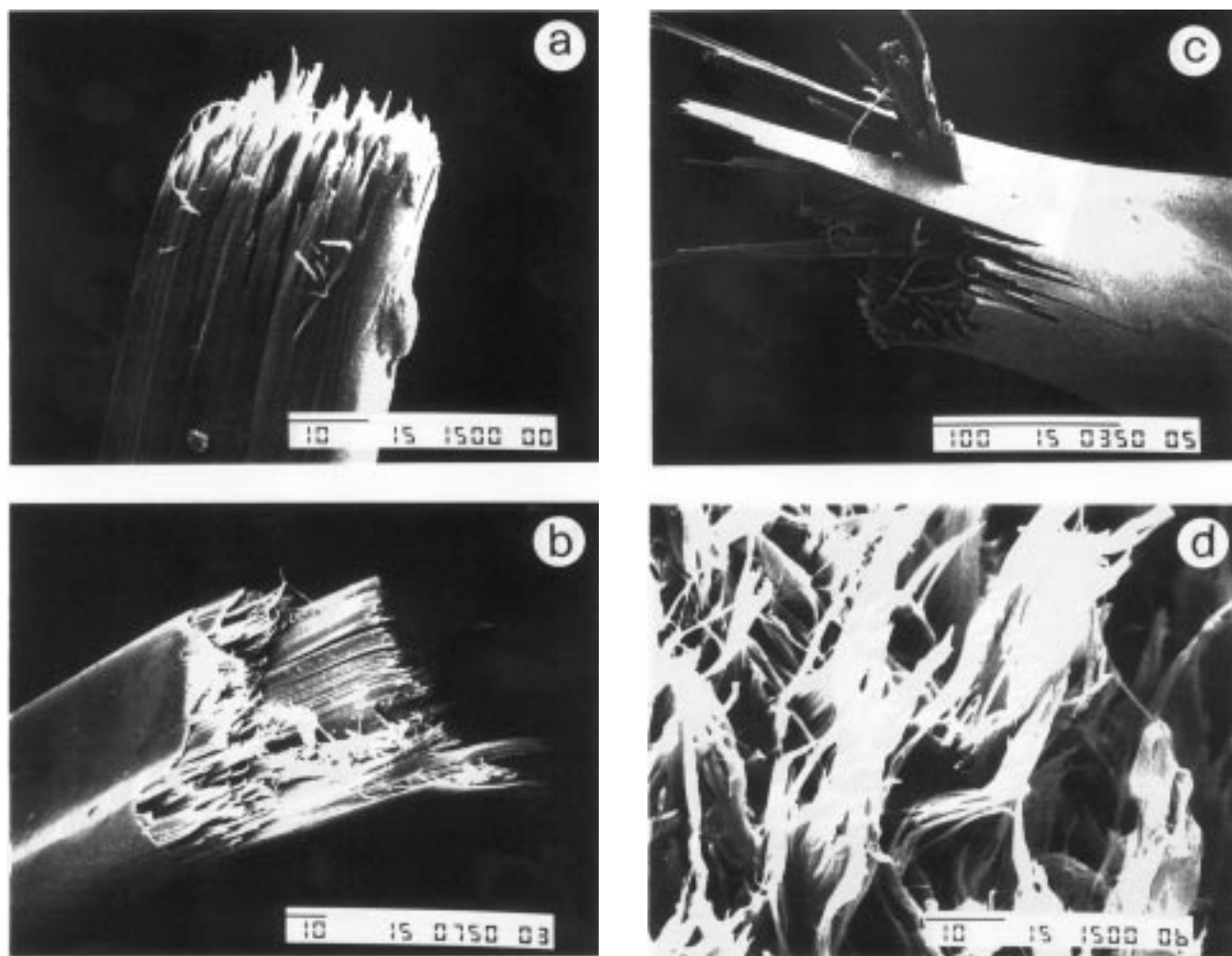


Figure 6. SEM micrographs of the fracture surfaces of (a) 80/15 fiber, (b) 85/15 fiber, (c) 90/15 fiber, and (d) 90/15 bulk material.

toward higher temperatures. The low-temperature transition corresponding to the maximum of $\tan \delta$ at 70–90 °C, also moves toward higher temperatures and causes a less marked modulus decrease. All these effects are clearly due to the higher degree of aromaticity that is achieved by the use of B as one of the modifying monomers.

The morphological investigation of the p(ETHB) copolyesters, carried out by SEM, confirms that these materials possess much higher structural homogeneity than those synthesized using H, or H, T, and Q mixtures as the p(ET) modifying monomers. Contrary to the p(ETH) copolyesters, such as Rodrun® LC5000, and the p(ETHQ) polymers described earlier,^[9] the polymers studied in this work show no evidence of the presence of a segregated phase, when viewed by SEM either in the form of fibers (Figures 6a–c) or bulk materials (Figure 6d), even when R_1 is higher than 80. This is another confirmation that these materials possess high structural homogeneity. On the other hand, the fact that the polymers can be easily spun to give highly oriented fibers^[22] demonstrates that these materials are either homogeneous or composed of

phases possessing very similar thermal and rheological characteristics.^[23,24]

The above results demonstrate that the transesterification of p(ET) with appropriate mixtures of H, T, and B takes place without solidification of the polymerizing mass even when the molar concentration of the modifying aromatic monomers is as high as 90% ($R_1 = 90$). The products appear to be quite homogeneous when characterized with a number of techniques, and can be processed easily and spun to highly oriented fibers. This could be achieved neither with H only ($R_2 = 0$) nor with H, T, and Q mixtures.^[9] Solidification was in fact observed during the synthesis of both the p(ETH) (for $R_1 \geq 80$) and the p(ETHQ) (for $R_1 \geq 85$) copolyesters.

When $R_2 = 10$ –20, the thermal properties of the p(ETHB) copolymers strongly depend on R_1 . Thus, for example, the melting points of the 80/15, 82/15, 85/15, and 90/15 copolyesters are, in the order, 248, 261, 274, and 308 °C. Concurrently, the high-temperature mechanical properties are improved, as the transition associated with polymer softening under load (for Rodrun® LC5000

Table 4. Calorimetric data of p(ET)-LCP blends (ΔH values are normalized to the p(ET) content).

p(ET)-LCP	Composition (w/w)	First heating		Cooling		Second heating	
		T_m °C	$\frac{\Delta H_m}{J/g}$	T_c °C	$\frac{\Delta H_c}{J/g}$	T_m °C	$\frac{\Delta H_m}{J/g}$
p(ET)	100–0	250.0	39.8	194.1	41.2	249.7	38.5
p(ET)-80/15	90–10	249.9	40.5	184.1	38.9	246.7	37.1
p(ET)-80/15	85–15	250.3	41.2	184.4	41.4	247.2	40.6
p(ET)-80/15	80–20	249.7	41.9	181.8	40.6	246.9	37.6
p(ET)-85/15	90–10	249.2	39.4	187.1	41.2	244.0	41.7
p(ET)-85/15	80–20	248.9	42.4	179.4	41.6	238.1	37.9
p(ET)-VA	90–10	249.1	38.9	195.4	43.5	249.2	39.4
p(ET)-VA	80–20	249.2	38.3	193.3	42.7	248.1	39.4

the transition determined by DMTA is found at $\approx 140^\circ\text{C}$, as shown in Figure 5, and the heat deflection temperature at 1.8 MPa is reported^[25] as 170°C becomes less intense and moves toward higher temperatures. As a consequence, the properties of the copolyesters can be accurately tailored in view of their targeted applications by simply changing their composition and, in particular the R_1 ratio.

Blends of p(ET) with p(ETHB) and Glass Fiber Composites Based on p(ETHB)

For a preliminary investigation of the in situ composites obtainable by blending moderate amounts of the p(ETHB) copolyesters with commercial flexible polymers, it was decided to use p(ET) as the matrix and two p(ETHB) polymers, with appropriate thermal properties, namely, the 80/15 and 85/15 copolyesters, as reinforcing agents. The blends were characterized by DSC and SEM. Some of them were also extruded with or without drawing, as described in the experimental section. Further characterizations were then conducted with the blends containing the 80/15 LCP, which proved to be more suitable as an in-situ reinforcing agent for p(ET).

The calorimetric data obtained under dynamic conditions (scanning rate of $10^\circ\text{C}/\text{min}$) are collected in Table 4. The same measurements were also carried out with blends of p(ET) with Vectra®-A950 (VA) prepared by the same technique. These results are also shown in Table 4. Vectra®-A950 is a copolyester of H with 2-hydroxy-6-naphthoic acid, manufactured by Hoechst-Celanese. It should be pointed out that the thermal transitions associated with the LCPs could not be identified in the DSC traces of the blends. In fact, the relevant peaks that would be extremely weak in any case because of the small LCP content and the intrinsic low intensity are completely masked by the peaks associated with the p(ET) phase. Nevertheless, an insight into the phase behavior of the blends can equally be gained by considering the changes of the p(ET) transitions induced by the presence of the LCP minor phase.

The calorimetric study showed that the dynamic crystallization temperature (T_c) of p(ET), blended with 80/15 or 85/15, is lowered by $7\text{--}14^\circ\text{C}$, whereas no such reduction is found with VA. Moreover, a slight decrease of the fusion temperature T_m measured during the second heating run is determined for the p(ET)-p(ETHB) blends, but not for those with VA. On the contrary, no appreciable effect of the presence of any of the LCPs on the enthalpy changes associated with the fusion/crystallization transitions could be observed. In a previous work,^[26] some of us investigated the phase behavior of blends of p(ET) with various LCPs, namely VA and other p(ET)-based copolyesters including Rodrun® LC3000 and Rodrun® LC5000 and found that none of the LCPs is miscible with p(ET), although slight interphase interactions could be shown to occur between the p(ET) matrix and all the semi-flexible LCPs. Similar conclusions can be drawn from the DSC investigation of the polymer blends presented in Table 4. In fact, the effect of the p(ETHB) copolyesters on the thermal properties of the p(ET) matrix is very similar to that of the other p(ET)-based copolyesters studied earlier.

The effect of the thermomechanical history on the thermal properties of the 80-20 p(ET)-80/15 blend was studied by recording the heating DSC traces of extruded and spun samples. In both cases a cold crystallization was observed at $\approx 124^\circ\text{C}$, with an enthalpy of $\Delta H \approx 24\text{ J/g}$, whereas the subsequent fusion was found at $\approx 247^\circ\text{C}$, with a $\Delta H \approx 45\text{ J/g}$. The thermal characteristics of similarly prepared samples of pure p(ET) did not differ appreciably from those of the blends. This confirms that the interactions between the two phases coexisting in the blends are rather weak.

It is known that in order to obtain a reinforcing effect by the in-situ addition of an LCP to a flexible matrix the droplets of the dispersed phase should be easily deformed into fibrils while processing the blend. To this end, the viscosity of the LCP should be comparable or, preferably, slightly lower than that of the matrix under the conditions employed for processing.^[27, 28] Thus, a preliminary investigation of the melt viscosity of the p(ETHB) copoly-

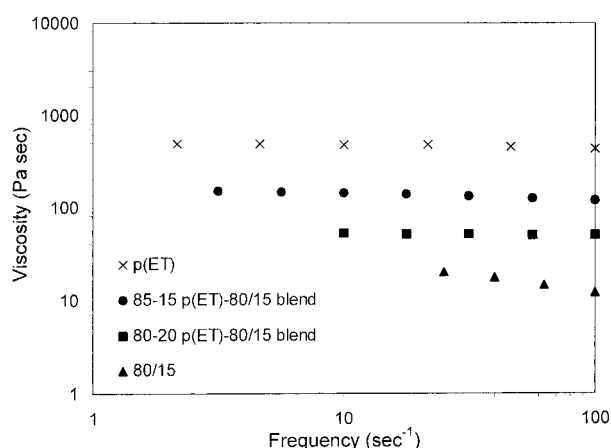


Figure 7. Viscosity vs frequency curves measured at 280 °C for p(ET), the 80/15 p(ETHB) copolyester, and their 85-15 and 80-20 blends.

esters and of their blends with p(ET) was carried out to identify the optimum composition of the copolyester to be used as a reinforcing agent. The viscosity curves of the p(ET)-80/15 blends with 0, 15, 20 and 100% LCP, measured at 280 °C in a frequency range between 1 and 100 s⁻¹, are shown in Figure 7. As it can be seen, the p(ET) viscosity is higher than that of the LCP in the whole frequency range investigated. The addition of 80/15 to p(ET) brings about a strong reduction of the matrix viscosity. In particular, at a frequency of 40 s⁻¹, the viscosity drops from ≈460 Pa · s for pure p(ET) to ≈50 Pa · s for the 20% blend. This blend is expected, therefore, to behave as an in-situ composite when processed under extensional flow conditions.

The morphological investigation of the p(ET)-p(ETHB) blends, carried out by SEM, confirmed the conclusions drawn from the previous characterizations. The LCP phase of samples obtained by cooling from the melt in the absence of flow consists of uniformly dispersed droplets showing poor adhesion to the p(ET) matrix. The fracture surface of the as-prepared blend of p(ET) with 20% 85/15 is shown as an example in Figure 8a. The spherical LCP droplets have an average diameter of 1–2 μm and fairly smooth surfaces. The Figure shows that

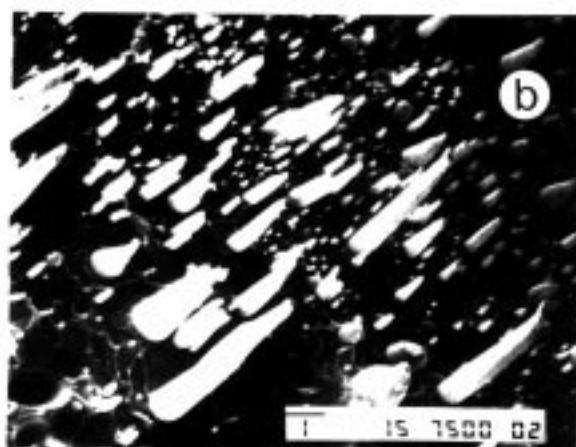
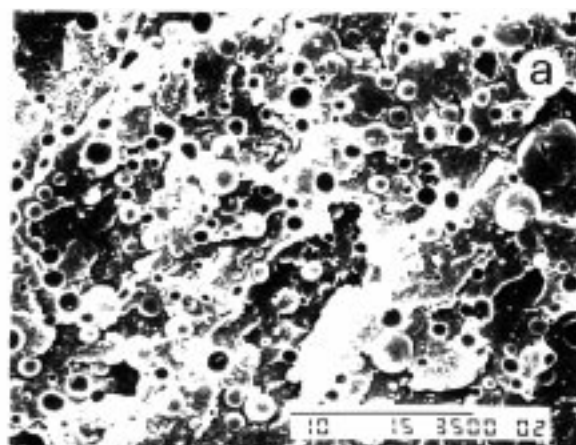


Figure 8. SEM micrographs of the fracture surfaces of (a) 20 p(ET)-85/15 blend, (b) 80-20 p(ET)-80/15 fiber.

the fracture line propagates freely along the interface between matrix and droplets. The micrograph taken of a spun sample of the same blend (not shown) does not differ appreciably from that displayed in Figure 8a, thus showing that the droplets of 85/15 are not easily deformed when this blend is extruded at 265 °C and drawn with a draw ratio (*DR*) of about 150. In contrast, as was argued from the rheological study, fairly good deformation of the dispersed LCP droplets into fibrils was achieved under similar conditions for the 80-20 p(ET)-

Table 5. Mechanical properties of extruded and drawn samples of p(ET)-p(ETHB) blends.

p(ET)-LCP	Composition (w/w)	Status	E GPa	σ_y MPa	ε_y %	σ_b MPa	ε_b %
p(ET)	100–0	extruded	1.6	52	3	54	810
p(ET)	100–0	drawn	1.7	43	3	52	610
p(ET)-80/15	90–10	extruded	2.0	44	3	54	690
p(ET)-80/15	90–10	drawn	2.5	38	2	56	580
p(ET)-80/15	80–20	extruded	2.1	55	4	51	580
p(ET)-80/15	80–20	drawn	5.6	–	–	70	2
p(ET)-85/15	80–20	extruded	1.8	–	–	48	4
p(ET)-85/15	80–20	drawn	2.4	–	–	40	2

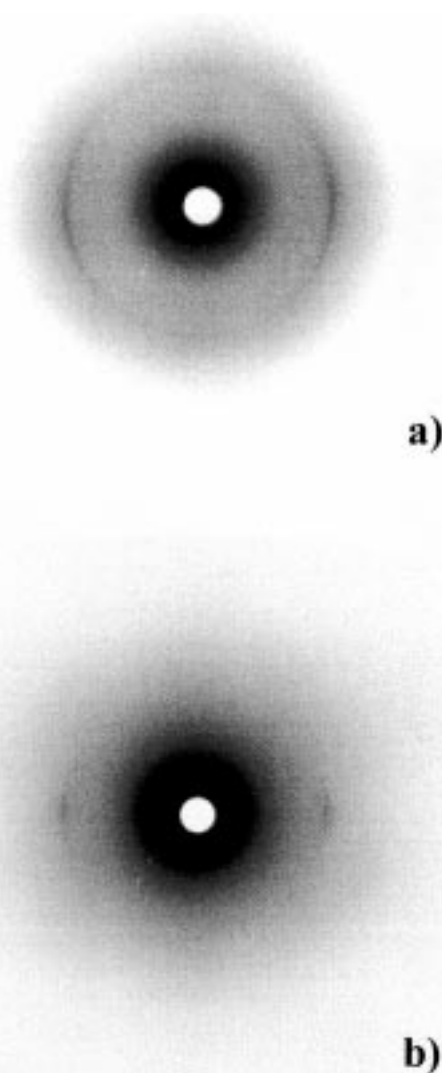


Figure 9. X-ray diffraction patterns of (a) unstretched and (b) stretched filaments of an 80-20 p(ET)-80/15 blend.

80/15 blend, as is demonstrated by the micrograph in Figure 8b. When the content of 80/15 was reduced to 10%, fibrillation was much less pronounced, probably because the average dimensions of the LCP particles were too small in this case. Figure 8b confirms that the adhesion between the p(ET) matrix and the LCP is poor. In fact, the fracture line is shown to slip out the fibrils rather than break them.

The mechanical properties of undrawn and drawn ($DR = 166$) filaments of the blends of p(ET) with 20% of either 80/15 and 85/15 are collected in Table 5 and confirm above conclusions. The 80-20 p(ET)-85/15 blends, in fact, show brittle behavior, whereas the modulus is only slightly improved with respect to pure p(ET). The blends with 80/15, in contrast, show ductile behavior and a modest modulus improvement unless good fibril formation occurs. Upon stretching, however, the fiber with 20% 80/15 shows more than a doubled modulus and very

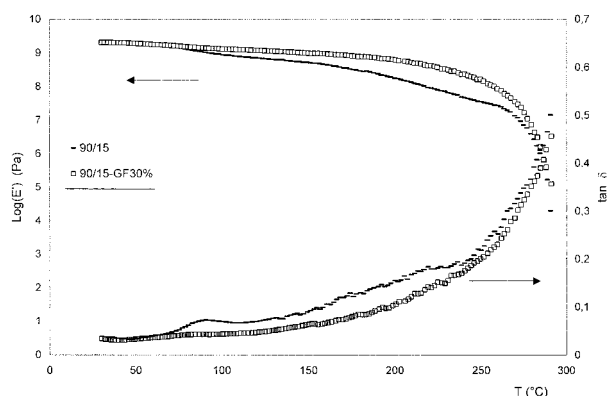


Figure 10. DMTA curves of copolyester 90/15 and its 30% GF composite.

small elongation at break, thus demonstrating the reinforcing effect of this copolyester.

The deformation of the 80/15 droplets caused by stretching a filament of the 80-20 blend, and the consequent orientation of the LCP macromolecules in draw direction are also clearly demonstrated by the X-ray diffraction patterns shown in Figure 9. The wide angle reflection due to the lateral packing of the longitudinally disordered copolyester chains is shown by equatorial arcs for the extruded specimen (Figure 9a), whereas these become spots for the drawn fiber (Figure 9b).

The p(ETHB) copolyester with higher aromaticity and consequently higher melting point (90/15) was used as a matrix for the preparation of GF composites. A sample of this composite containing 30 wt.-% GF was prepared by blending in a Brabender mixer and compression molding in a Carver press as described in the experimental section. The blend was then preliminarily characterized by DMTA. The modulus and the $\tan \delta$ curves of the composite are compared in Figure 10 with those of the pure LCP. The addition of GF leads to a considerable intensity reduction of the two low-temperature ($\approx 80^\circ\text{C}$ and $\approx 170^\circ\text{C}$) transitions of the LCP, and therefore to a strong increase of the high-temperature modulus. GF composites similar to that studied here can therefore be used for applications requiring high thermal resistance.

Conclusions

The liquid crystalline polymers synthesized by transesterification of p(ET) with blends of H and small, equimolar amounts of T and B have been shown to consist of p(ETHB) copolyesters with considerable structural homogeneity. As a result, copolyesters with a p(ET) content as low as 10 mol-% could be prepared without incurring the drawbacks of phase segregation experienced when modifying p(ET) either with H only or, to a lesser extent, with a blend of H, T and Q.^[9] The properties of the p(ETHB) copolyesters, in particular their thermal behavior, can be

easily changed over a wide range by varying the composition of the starting mixture. The preliminary investigation of blends of these copolyesters with flexible polymers and with short glass fibers has shown, in particular, that the copolyesters with an R_1 ratio equal to about 80 can be usefully employed for the preparation of in-situ composites with thermoplastics, such as p(ET), that are normally processed at temperatures in the range between 260 and 290 °C, whereas those with R_1 equal to about 90, having melting points higher than 300 °C, lend themselves to the preparation of GF composites for high-temperature applications.

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