Influence of Branching on the Properties of Poly(ethylene terephthalate) Fibers

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ABSTRACT: A series of branched poly(ethylene terephthalate) samples was prepared by employing 0.07–0.42 mol % trimethylolpropane (TMP) for melt polycondensation. These polymers were characterized with respect to molar mass, intrinsic viscosity, and melt viscosity. Spinning into fibers took place at spinning speeds ranging from 2500 to 4500 m/min. The molecular orientation of the fibers as measured by birefringence and polarized fluorescence decreases with growing amounts of TMP, as does crystallinity. Thus with slightly branched polymers, higher spinning speeds than with a linear polymer can be used to achieve a certain property profile. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 728–734, 1999

Key words: poly(ethylene terephthalate); fiber spinning; branched polymers; orientation

INTRODUCTION

In the last few years, several studies were performed on linear polyesters, in particular, poly-(ethylene terephthalate) (PET), with respect to the parameters influencing structure formation during the melt-spinning process as well as to fiber properties.[1–5] Emphasis was on fibers produced with increased wind-up speeds. It is found that with rising wind-up speeds, tenacities and moduli increase and elongations decrease. These changes of the properties of the fibers are attributed to the increasing orientation of the macromolecules in the fibers due to the higher spinning stress. As a result of the higher orientation, a notable crystallization appears at wind-up speeds exceeding 4000–4500 m/min, the threshold depending somewhat on the molecular weight of the PET used.

Chemical modification can produce various advantageous features in PET as compared with the unmodified polymer. Therefore, a great number of different compounds was added to the polycondensation of PET to change the structure formation and the properties of the PET fibers. Among these chemical modifiers were branching agents like trimethylolpropane (TMP), trimesic acid (functionality of branching $f = 3$), or tetrafunctional pentaerythritol.[6–12] The incorporation of small amounts of a branching agent leads to the formation of long-chain branches. If the amount of the branching agent exceeds about 1%, crosslinked structures may be obtained. Especially in patent literature is it noted that with polyfunctional branching agents present in the polycondensation step the polycondensation time can be reduced. This may be attributed to the larger number of end groups.

If PET modified with a branching agent is spun into fibers, changes like increased dye uptake, reduced tendency to pill, or a higher degree of drawing are reported.[9–11] These effects result from the formation of long-chain branches that may cause lower orientation and crystallinity.

The existence of branched macromolecules after the addition of a polyfunctional modifier can be seen indirectly (e.g., in a broader molecular weight distribution).[7,13] However, published systematic studies on the behavior of branched PET macromolecules in melt or solution and on the effect of branching on properties of fibers spun at different wind-up speeds are scarce. In this work, we will investigate PET modified by TMP. We focus on the characterization of the long-chain branching of the polymer and the morphology as well as the mechanical properties of fibers spun from such polymers. It is an aim of this work to correlate the mechanical properties of the fibers obtained after a melt spinning process with structural data obtained from orientation and crystallinity measurements.

EXPERIMENTAL

Materials

Modified PET was obtained via the ester interchange route starting from dimethyl terephthalate (DMT, Fiber grade, Hüls AG, Marl, FRG) and a $2.5M$ excess of ethylene glycol (EG, Fiber grade, Rhône Poulenc, Freiburg, FRG). The polycondensation reactions were performed in a 5 l stainless-steel reactor with different amounts of TMP (0.07–0.43 mol % with respect to DMT) as a trifunctional modifier present in the transesterification step. TMP (97%, Aldrich-Chemie, Steinheim, FRG) had been recrystallized twice from Diethylether/Acetone (1 : 1). Transesterification catalyzed by manganese acetate (Merck, Darmstadt, FRG, 3×10^{-4} mol/mol DMT) was performed at a maximum temperature of 230°C. The subsequent polycondensation step was catalyzed by antimony acetate (Elf Atochem, Philadelphia, PA, USA, 3×10^{-4} mol/mol DMT), which was added in a slurry of EG together with triphenylphosphate (For synthesis, Merck, Darmstadt, FRG, 6×10^{-4} mol/mol DMT). Finally, polycondensation was performed at a maximum temperature of 290°C under vacuum.

The composition of the polyester was analyzed after microwave-assisted degradation of the samples in methanol (1 g of sample plus 10 ml methanol, in addition to a small amount of Ti–butylate as a catalyst, 220°C, 20 min). The precipitated DMT formed during the methanolysis reaction was filtered off. Methanol was carefully removed from the filtrate by distillation, and the TMP was esterified with acetic anhydride for GC analysis using dodecyl acetate as an internal standard. Recoverable was 85–90% of the TMP added in polycondensation. The loss of 10–15% could be traced back to the analytical procedure, because a mixture of educts (DMT, EG, TMP, methanol) showed similar losses when an analogous treatment including the microwave irradiation was applied. This proves that the TMP is incorporated almost quantitatively into the polyester.

Solution Viscosities

Solution viscosities were measured in a phenol/tetrachloroethane mixture (1 : 1 by weight) at a temperature of 20.0°C using a Ubbelohde viscometer, capillary-type Ia. Data were taken at four concentrations between 5 to 40 g/L. Extrapolation of the reduced viscosities to zero concentration yields the intrinsic viscosities $[\eta]$.

End-Group Analysis

The amount of hydroxyl end groups was determined following the method of Zimmermann and Kolbig.[14] The samples were dissolved in nitrobenzene at 130–170°C. After reaction with o-sulfobenzoic acid anhydride, the excess of unreacted o-sulfobenzoic acid was titrated with $0.1N$ NaOH solution.

For determination of the carboxylic end-group content, the samples were dissolved in a mixture of phenol/chloroform (1 : 1 by weight) at 80–100°C followed by a conductometric titration with a $0.02N$ solution of KOH in benzyl alcohol. The number-average molecular weight of the samples is calculated from the sum of OH and COOH end groups according to eq. (1):

$$M_n = \frac{2}{E - T} \times 10^6 \quad \text{(g/mol)} \qquad (1)$$

where E is the sum of all endgroups (m equiv/kg) and T is the amount of trifunctional branching points (m equiv/kg) (= mmol TMP/kg PET).

Thermal Properties

Thermal analyses of the polymer samples were performed on a Perkin–Elmer DSC 7 differential scanning calorimeter using about 10 mg of the samples (fibers were knotted together). All DSC data were obtained from the first heating run in the temperature range of 30–300°C. The heating rate was 20 K/min.

Melt Viscosities

A dynamic stress rheometer was used with a 25-mm plate-to-plate measuring device. A measure of 1.0 g of the predried polyester sample was heated to 280°C under nitrogen purge. All measurements were performed as a dynamic frequency sweep (strain = 5%; 0.8–500 rad/s) with a plate distance of 1.50 mm, 18 min after heating. With longer heating periods, the polyester samples tend to show increased melt viscosities, especially with a high TMP content.

Static Light Scattering

Light scattering measurements using vertically polarized light of a wavelength of 633 nm were made in hexafluoroisopropanol at 20°C after removal of dust by filtration through ultrafine PTFE filters. Toluene was taken as a primary standard. The specific refractive index increment of PET was determined to 0.228 cm^3/g. Scattering intensities were measured at five concentrations between 2 and 10 g/L. Weight-average molecular weights M_w were read from Zimm plots.

Fiber Spinning

Spinning of the fibers was performed on a single screw-fed laboratory melt spinner through a 10-hole spinneret (200 μm) after drying the polymer chips in a vacuum tumble mixer. Wind-up speeds ranged between 2500 and 4500 m/min. The melt extrusion temperature was 280°C, the flow rate of the melt was adapted to keep the count of the fibers constant at dtex 33 f 10. The spinability of the polymer decreased with increasing concentrations of the branching agent. With a molar content of 0.43% TMP in PET, a maximum spinning speed of only 2500 m/min could be achieved.

Birefringence

The birefringence of the fibers was determined with the compensation method using a polarizing microscope.

Polarized Intrinsic Fluorescence

The method of polarized intrinsic fluorescence was used to determine the orientation in the amorphous regions of the polyester fibers. Details of the apparatus used are described in ref. 15.

Density

The density was measured on small loops of the fiber samples with a density gradient column filled with tetrachloromethane-n-heptane at 20°C. The density gradient was calibrated with floating spheres of known density. The samples were drained with the solvent before introducing them into the column. Volume fraction crystallinity K was obtained from eq. (2),

$$K = \frac{\rho - \rho_a}{\rho_c - \rho_a} \qquad (2)$$

where ρ, ρ_a, and ρ_c are the measured density of the fibers, the density of the amorphous part (1.335 g/cm^3), and the density of the crystalline part (1.455 g/cm^3),[5] respectively.

Mechanical Properties

The strength and elongation of the fibers were measured with a Textechno Statimat M at 20°C and a relative humidity of 65%. The measuring length of the samples was 200 mm and crosshead speed was 200 mm/min. An average of at least 20 individual tensile tests was obtained for each sample.

RESULTS AND DISCUSSION

Characterization of the Polyesters

A series of PET samples containing different amounts of TMP was obtained as described in the experimental section. Table I contains a compilation of some characteristic data. M_n is obtained from end-group analysis, according to eq. (1), M_w is derived from static light scattering. The intrinsic viscosities and the melt viscosities are listed as well.

Figure 1 shows that the index of polymolecularity, M_w/M_n, rises from 2 to appreciably higher values when the amount of TMP ranges from 0 to 0.5 mol %. This is the first indication that a systematic variation in the amount of branching was achieved.

Because of the higher segment density, branched macromolecules are of a smaller mean coil size, radius of gyration, or hydrodynamic volume, respectively, as compared to linear macromolecules of the same molecular weight and composition. Data concerning the size or related properties can be derived from viscosity measurements in solution or melt as well as from size exclusion chromatography or light scattering experiments.

Table I Characteristic Data of PET Samples Modified with TMP

Sample Code	TMP Content (mol %)	M_n (g/mol)	M_w (g/mol)	$[\eta]$ (dL/g)	η_0 (Pa s)
PMT 0.05	0.071	21,900	47,000	0.636	269
PMT 0.1B	0.142	17,300	42,600	0.526	—
PMT 0.1C	0.142	20,600	50,200	0.596	235
PMT 0.15	0.212	19,900	56,400	0.588	230
PMT 0.2	0.283	21,800	55,200	0.601	252
PMT 0.25	0.354	18,800	49,200	0.584	225
PMT 0.3A	0.425	20,300	55,900	0.595	286
PMT 0.3C	0.425	19,200	49,500	0.542	195

As a quantitative measure for the characterization of branched macromolecules, the index of branching, g, has been introduced and defined as the ratio of the radii of gyration of branched and linear macromolecules of the same molecular weight and composition:

$$g = \frac{\langle s^2 \rangle_{\mathrm{br}}}{\langle s^2 \rangle_{\mathrm{lin}}} \quad (3)$$

Other more easily accessible quantities are the corresponding ratios of intrinsic viscosities,

$$g' = \frac{[\eta]_{\mathrm{br}}}{[\eta]_{\mathrm{lin}}} \quad (4)$$

or melt viscosities,

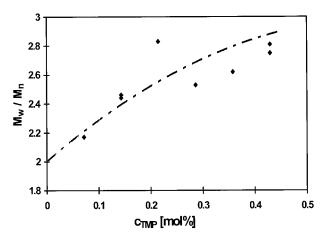$$g^* = \frac{\eta_{0,\mathrm{br}}}{\eta_{0,\mathrm{lin}}} \quad (5)$$

Figure 1 Polymolecularity M_w/M_n of the PET samples versus amount of TMP in PET.

For the calculation of the different indices of branching, it is necessary to determine experimentally the viscosities $[\eta]_{\mathrm{br}}$ or $\eta_{0,\mathrm{br}}$ for the branched samples and have the corresponding data for the unbranched samples of the same molecular weight available. As samples of identical molecular weight usually are not on hand, the corresponding viscosities of linear samples need to be calculated. For $[\eta]_{\mathrm{lin}}$ entering eq. (4) to determine g', the Mark–Houwink constants given by Koepp and Werner[16] were used; $K = 7.55 * 10^{-4}$ dL/g and $\alpha = 0.685$. For $\eta_{0,\mathrm{lin}}$ entering into eq. (5) to determine g^*, the relationship given by Gregory[17] was employed,

$$\eta_{0,\mathrm{lin}} = 1.13 \times 10^{-13} M_w^{3.5}$$
$$\exp(-11.9755 + 6802.1/T) \quad [\text{Poise}]$$

To express the degree of branching, we use the number-average branching density, B_n (i.e., the number of branches per macromolecule), evaluated according to the following formula[8,18]:

$$B_n = \frac{2r}{3 - r - 3p} \quad (6)$$

with r being a parameter indicating the initial composition

$$r = \frac{3n_{\mathrm{trif}}}{3n_{\mathrm{trif}} + 2n_{\mathrm{bif}}} \quad (7)$$

where n_{trif} is the number of initial trifunctional molecules, n_{bif} is the number of initial bifunctional molecules, and p is the extent of reaction, which can be evaluated from the end-group analysis of the final polymer:
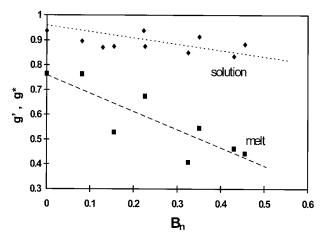
Figure 2 Indices of branching, g' ($\blacklozenge$) and g^* ($\blacksquare$), for PET modified with TMP as a function of the average number of branches per molecule B_n.

Figure 4 Amorphous orientation factor P_2^a of yarns spun at different wind-up speeds versus amount of TMP in PET.

$$p = \frac{E}{10^6}\left[\frac{M_b}{2} - r\left(\frac{M_b}{2} - \frac{M_t}{3}\right)\right] \qquad (8)$$

where M_b = 192.17 g/mol for PET and M_t = 134.18 g/mol for TMP.

Figure 2 shows that the indices of branching, g' and g^*, both decrease with an increase in the average number of branches per molecule. This clearly indicates the presence of long-chain branches in the PET samples examined. As expected, the effect of branching is more significant in the melt than in the dilute solution. The structural modification, although only a modest change, clearly influences the properties of the polymer.
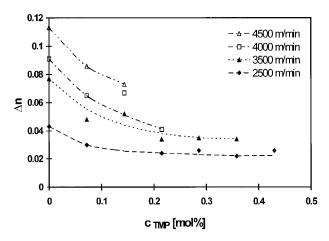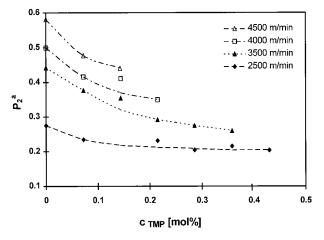
Fiber Properties

It is well known that increased wind-up speed leads to a higher molecular orientation in the fibers.[1,3] This can be seen, for example, in an increased birefringence. The rise of orientation finally leads to partial crystallization, the formation of a two-phase morphology of highly oriented crystalline areas dispersed in an amorphous, usually less oriented phase. The measured density of the samples can serve to evaluate the composition of this two-phase system. As a result of the increased orientation and crystallinity, fibers with higher strength and less elongation to break are obtained.

For economic reasons, it is desirable to use high spinning speeds and yet obtain fibers with comparably low orientation and crystallinity (e.g., for the draw–texturizing process). Such a reduction of orientation can be achieved by blending PET with other polymers[19] or, more often, by changing the molecular architecture of the polymer by the addition of a small amount of polyfunctional agent.[9–12,20]

Molecular Orientation of the Fibers

The molecular orientation was determined by measuring birefringence and polarized fluorescence. Figure 3 shows Δn as a function of the TMP content of the polymer for fibers obtained at several spinning speeds. The corresponding relationships for the second moment of the orientation distribution function of the amorphous part, P_2^a, is depicted in Figure 4. Both quantities exhibit
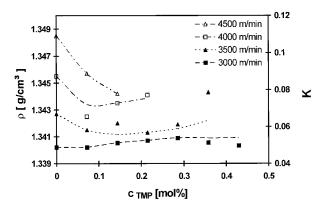

Figure 3 Birefringence Δn of yarns spun at different wind-up speeds versus amount of TMP in PET.

Figure 5 Density ρ and calculated crystallinity K of yarns spun at different wind-up speeds versus amount of TMP in PET.

Figure 6 $(\Delta H_m + \Delta H_c)$ of yarns spun at different wind-up speeds versus amount of TMP in PET.

similar features. The orientation increases with rising wind-up speeds. On the other hand, a growing TMP content gives rise to a significant drop of orientation, especially at wind-up speeds > 3500 m/min.

Crystallinity

Due to modest spinning speeds, crystallinity is generally low, and wide-angle X-ray diffractograms show an amorphous halo with little or sometimes no indication of crystal reflections. The crystallinity was therefore estimated by density measurements and calorimetry.

As seen in Figure 5, the density of the samples increases with rising wind-up speed and decreases with a growing amount of the branching agent. Equation (2) was used to convert the measured densities into the degree of crystallinity. Such values are given on the right-hand coordinate in Figure 5. It should be kept in mind, however, that this calculation implies that the calibration data, ρ_a and ρ_c, are exact and do not change with orientation or degree of modification. The dependence of density on the amount of TMP is similar to the corresponding change of the orientation, as seen in Figures 3 and 4. Hence it cannot be ruled out that the slight density change only reflects orientation effects.

Another access to the crystallinity of a polymer sample is possible via the determination of the enthalpy of fusion. In the first heating cycle of a DSC experiment, the polyester fibers exhibit a crystallization peak around 95–115°C and then a fusion peak at 255–258°C. The enthalpy corresponding to the crystallinity of the as-spun fibers is therefore the sum of the heat of crystallization
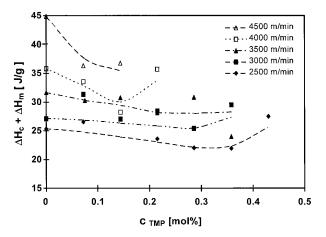
(ΔH_c) and melting (ΔH_m). As can be seen from Figure 6, this value increases with rising wind-up speed and decreases or remains constant on a low level with growing amounts of TMP. The general trend is the same as with the density data, although the scatter is somewhat larger. This trend supports the view that there is in fact a slight crystallinity in the fibers and that by the incorporation of TMP it is possible to lower not only the orientation, but also the crystallinity of the fibers in a broad range.

Mechanical Properties of the Fibers

Typically, the tenacity of undrawn polyester fibers rises with increasing wind-up speed, whereas the break elongation decreases. This is due to the increasing molecular orientation. Be-
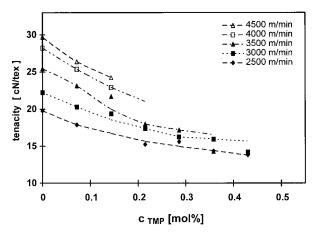

Figure 7 Tenacity of yarns spun at different wind-up speeds versus amount of TMP in PET.
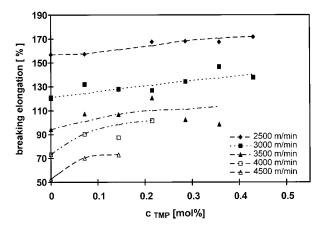
Figure 8 Breaking elongation of yarns spun at different wind-up speeds versus amount of TMP in PET.

cause it has been shown in the preceding section that the orientation can be impaired by introducing branches, an effect on the mechanical properties is expected.

Figure 7 shows the dependence of the tenacity on the amount of TMP in the polymer. It parallels nicely the course of orientation (Figs. 3 and 4) and proves that by introducing branch points, certain mechanical and structural properties can be achieved at a higher spinning speed than required to obtain such properties with linear polyesters. The dependence of the break elongation (Fig. 8) shows the opposite trend.

CONCLUSIONS

The experiments and measurements performed clearly show that the branching of the macromolecules impedes structure formation during spinning in a very consistent way. The primary effect is on molecular orientation. At the same spinning speed, with branched polyester, less oriented fibers are developed than with linear polyester. To obtain identical orientation factors, branched polyesters can be processed at higher spinning speeds. The crystallinity is a function of orientation and thus shows the same dependence. Orientation and crystallinity together determine the mechanical properties of the fibers.

In essence, the addition of a branching agent like TMP has the same effect as a reduction of spinning speed. Thus higher spinning speeds can be used with slightly branched polymers to achieve the same property profile, and this may turn out to be an economical advantage. Other benefits of branching, like increased dye uptake and reduced tendency to pill, have also been mentioned.

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