

Annealing Effect on Structure of Poly(trimethylene terephthalate) Undrawn Fibers

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Abstract

The undrawn monofilament of poly(trimethylene terephthalate) (PTT) was obtained by melt-spinning. After being annealed at 40 °C it was analyzed by the measurements of DSC, DMA, WAXD and ATR FT-IR. T_g of PTT fiber after annealing for more than 96 hours was 20 °C higher than that before annealing as determined by the DSC and DMA measurements. The WAXD analysis showed very weak diffraction peaks at $2\theta = 17^\circ$ and $2\theta = 24^\circ$ for the annealing time of more than 96 hours. The ATR FT-IR measurements made clear the conformational change of methylene chains of PTT glycol residue from random to gauche-gauche conformation.

Introduction

PTT is a member of thermoplastic aromatic polyesters including PET and PBT. Since Shell Chemicals established the commercial process to produce PDO in 1990s, PTT has drawn attraction. Compared to the even-numbered PET and PBT with two and four methylene units, respectively, PTT has the odd number of three methylene units and the ratio between the unit cell *c*-axis dimension and the extended chain length is only about 75 %, which indicates a zigzag chain conformation along the *c*-axis, and the conformation of the methylene segment is given as gauche-gauche.¹ The equilibrium melting temperature of PTT is reported to be 525 K and the equilibrium melting enthalpy of fusion is 28.8 kJ/mol by the study of melting behavior.² T_g of semi-crystalline polymer depends on the thermal history, such as drawing tension, temperature, and time, however, T_g of PTT is reported between 35 and 50 °C.¹

Experimental

Sample Preparation

The intrinsic viscosity of PTT was 0.92 dL/g. Fiber samples were prepared by melt-spinning at

265 °C and taken-up at 24 m/min. The fiber was cooled by the immersion in water controlled at 45 °C. The denier of the obtained monofilament was 2,280 dtex. This fiber (A) was measured as soon as possible. Also, the fiber was annealed at 40 °C for various hours. The annealing times were (B) 24, (C) 96, (D) 144 and (E) 240 hours, respectively.

Measurements

Thermal analyses were made with a Seiko Instruments DSC220 calorimetry from 20 to 260 °C at a scanning rate of 10 °C/min. Measurements of viscoelasticity were carried out by using DMS-200 of Seiko Instruments. The frequency was 10 Hz, the tension applied was 10 g and the heating rate was 1 °C/min from -100 to 200 °C. FT-IR spectra were measured with a JASCO model FT/IR-550 equipped with ATR-300/H.

Results

Fig. 1 displays thermograms obtained in DSC analysis. T_g was observed at around 35 °C in fiber A immediately measured after the sample preparation, however, T_g turned to be higher and was leveled off at 55 °C in fibers D and E by the increase of annealing time. It is clear that T_g of PTT undrawn fiber depended on the annealing time, that is, it is important to clarify the period of T_g measurements after PTT fibers were taken-up.

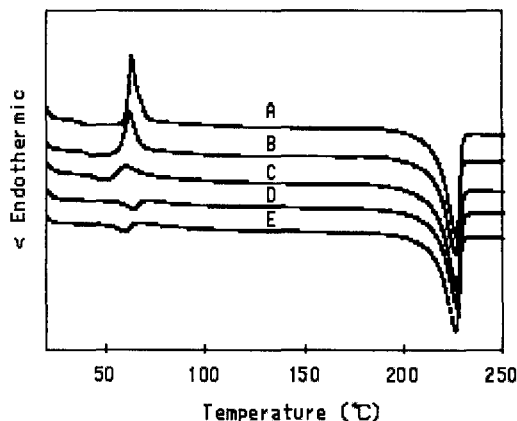


Fig. 1 DSC thermograms of the PTT fibers annealed for various time periods.

Fig. 2 shows the temperature dependence of storage and loss moduli, E' and E'' , of PTT fibers annealed for various hours by dynamic viscoelastic measurement. E' increased with the increase of annealing time, and there were two groups, the one was fibers A, B, and C, and the other was fibers D and E. This suggested that the rigidity of the fiber annealed less than 96 hours were different from that annealed more than 96 hours. The temperature dependences of E' were quite different between 30 and 80 C, that is, E' s of fibers A, B and C abruptly decreased at around 35 C, passed through a minimum at 57 C, increased, and then gradually decreased at higher than 65 C. Why E' passed the minimum was that E' decreased by the transition from glassy state to rubbery state, and at the same time, PTT might be crystallized during the measurement, and then the chain was stiffened. On the contrary, in another group consisting of fibers D and E, there were only two inflection points without E' increase.

The peak temperature of E'' of fiber A was lowest and it increased with increasing the annealing time. Concerning the results of temperature dependence of E' , the peak temperature at 50 C of E'' -temperature curve of fiber A is caused by from glassy state to the rubbery state, and another peak at around 65 C is by the crystallization of PTT fiber. On the other hand, the peak temperatures of fibers D and E were at 60 and 70 C, respectively. Tg increased with the increase of annealing time.

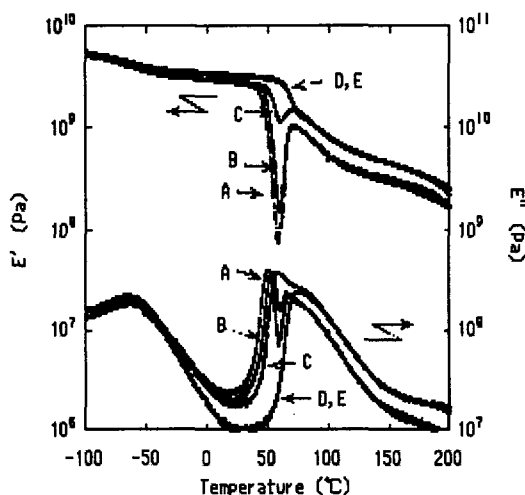


Fig. 2 Temperature dependence of the storage (E') and loss (E'') moduli of the PTT fibers annealed for various time periods.

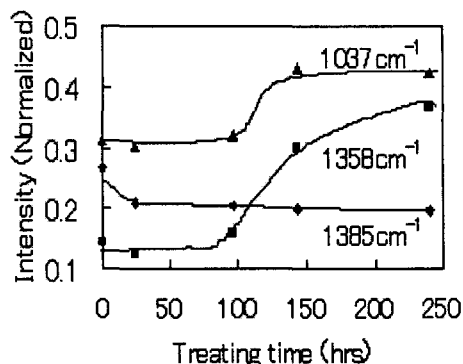


Fig. 3 Absorption intensities of 1037 cm^{-1} (gauche in the crystalline), 1358 cm^{-1} (gauche in the crystalline) and 1385 cm^{-1} (trans in the amorphous) bands as a function of treating time

The ATR FT-IR measurements were carried out to make the conformation of PTT fibers clear. The absorption bands of 1358 and 1385 cm^{-1} are assigned to CH_2 wagging, and the former is associated with trans conformation in the amorphous phase and the latter with gauche conformers in the crystalline phase.^{3,4} The absorption band of 1037 cm^{-1} is from gauche C-C stretch of glycol residue. The annealing time dependence on the absorption intensities of 1358, 1385, and 1037 cm^{-1} , used as internal reference band of 1410 cm^{-1} , is shown in Fig. 3. The intensities of 1037 and 1358 cm^{-1} increased between 96 and 144 hours, respectively, however, that of 1385 cm^{-1} did not change.

Conclusions

The glass transition temperature of PTT undrawn fiber depended on the annealing time at 40 C, which was caused by the conformational change of methylene chains of PTT glycol residue from random to gauche-gauche conformation.⁵

References

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