

Effect of Solid-State Shearing of Poly(ethylene terephthalate) on Isothermal Crystallization and Fiber Structure Formation

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ABSTRACT: Solid-state shearing was applied on recycled poly(ethylene terephthalate) (PET) using twin-screw extruder. The shearing effect on isothermal crystallization was investigated by DSC. Structure formation in melt spinning was also studied by characterizing the spun fibers. It was found that the solid-state shearing imposes a great influence on its crystallization behavior. Crystallization peak temperature of the sheared PET (199°C) was much higher than that of the PET without shearing (188°C). Overall isothermal crystallization rate was found to be accelerated to

more than 50 times by the shearing. The shearing effect remained even after fiber spinning (melt processing). Differences in crystallization behavior, fiber structure formation, and tensile properties of the fibers were found. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 787–791, 2007

Key words: solid-state shearing; isothermal crystallization kinetics; fiber structure formation; recycled PET; shear memory effect

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a thermoplastic polymer that possesses high melting point, good mechanical properties, and chemical resistance. It is widely used in manufacturing of fibers, films, bottles, as well as engineering plastic parts. Among these applications, the consumption of PET bottles is great and still growing. Making good use of the PET from PET bottle waste to develop other PET products is of a great interest.

The crystallization rate of PET is known to be rather slow.¹ In engineering plastics application, enhancement in the crystallization rate of PET is essential for its manufacturing and for obtaining desirable properties. During the product processing, many factors, such as heating, drawing, and shearing, have an influence on the crystallization behavior of the polymer, then on the structure and properties of the products. It is shown that in the thermally-induced crystallization, a maximum crystallization rate appears at certain temperature, and the spherulites usually develop,^{2,3} while in the shear-induced crystallization, the number of crystallites increases and the crystallization rate markedly increases.⁴ In addition, row nucleation is characteristic to the crystallization of polymer melts under a

stress field, and an oriented crystalline structure is formed.⁵ Such shear effect on the crystallization may be caused by the decrease of entanglement density and the enhancement of molecular orientation.^{6–8} Khanna et al.⁹ found that the memory of shear in melt was not removed after 17 h of melt annealing for nylon 6 in the crystallization experiment from the melt. The strong memory is believed to be set by hydrogen-bonds between polar nylon molecules. They also found that polymers of intermediate polarity, PET, has the similar shear memory effects but to a much less extent when compared with nylon 6 and nylon 66.¹⁰ Kim and Kim¹¹ studied the shear effect on the crystallization kinetics of PET under different shear condition from 11.7 to 1168 s⁻¹ in a capillary rheometer. Their results showed that the crystallization rate of PET increased with increasing shear rate, and the shear effect was reduced when the holding time in melt state before crystallization was increased. Myung et al.¹² investigated the shear induced crystallization behavior of PET by measuring the time-dependent storage modulus and dynamic viscosity with a parallel-plate rheometer at different shear rate and temperatures, and the morphology of shear induced crystallized PET was also measured by DSC, X-ray, and polarizing optical microscopy. Souffache et al.¹³ found an increase in the crystallization rate of PET preoriented yarn with an increase in spinning rate observed by using the small-angle X-ray scattering. Thus, the effects of shearing at melt-state on the crystallization and morphology developments have been widely investigated.

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In present study, an intensive shear was applied on PET by solid-state shearing process using twin-screw extruder. Shearing effect on isothermal crystallization of PET was investigated by DSC. Shear-induced structure formation during melt spinning was also studied by characterizing the spun fibers.

EXPERIMENTAL

Materials and fiber spinning

The PET chips used in the experiments was recycled from PET bottles and supplied by Miraikasei Co. Its intrinsic viscosity measured is ~ 0.6 L/g. To study the effects of shear processing history on the crystallization behavior, two kinds of PET were prepared. One was recycled PET without shear processing (PET No. 1), the other was the recycled PET with intensive shear processing (PET No. 2). The PET No. 2 was prepared by solid-state shearing of PET No. 1 using a twin-screw extruder (37 mm diameter; TEX- α , Japan Steel Works) at 100°C.

To discuss the shearing effect on the structure formation, PET fibers were spun by melt spinning. The fiber spinning conditions were as follows: spinning at temperature of 290°C, spinneret with 28 holes, and take-up at a rate of 400 m/min. The spinning machine used in the experiment is FUJI filter MST C-400. The as-spun fiber from PET No. 1 was marked as "F1," the as-spun fiber from PET No. 2 was marked as "F2," respectively. Then the as-spun fibers F1 and F2 were annealed at 155°C for 30 min without tension to stabilize the fiber structure. The annealed fibers from F1 and F2 were marked as F1_a and F2_a, respectively.

DSC measurements

A Perkin-Elmer Pyris DSC system was used in the study. All the DSC experiments were carried out in a nitrogen atmosphere, and the mass of sample was about 5 mg. All samples were dried in the vacuum oven at 80°C for 24 h before DSC measurement to remove moisture.

PET Nos. 1 and 2 were heated up to 290°C at a programmed rate of 20°C/min, held at 290°C for 10 min, and then cooled down at the rate of 20°C/min to obtain nonisothermal crystallization thermogram in the cooling run.

PET Nos. 1 and 2 were heated up to 290°C at a programmed rate of 20°C/min, hold at 290°C for 10 min, and then quenched at the rate of 100°C/min to a preprogrammed temperature T_c for isothermal crystallization. The preprogrammed isothermal crystallization temperatures (T_c) were 3, 6, 9, and 12°C higher than the crystallization peak temperature (T_{cc}), which was measured at the above cooling run. The isothermal crystallization exotherm was recorded at T_c .

To discuss the effect of shearing on the isothermal crystallization kinetics, holding temperature and holding time at melt-state before crystallization were varied for PET No. 2 as follows: (1) PET No. 2 was heated up to 290°C at a programmed rate of 20°C/min, hold at the temperature for 5, 10, and 15 min, and then quenched at the rate of 100°C/min to a preprogrammed temperature of 202°C for isothermal crystallization. (2) PET No. 2 was heated up to 280°C and 290°C at a programmed rate of 20°C/min respectively, hold at the temperatures for 10 min, then quenched at the rate of 100°C/min to a preprogrammed temperature of 202°C for isothermal crystallization.

As-spun fibers, F1 and F2, were heated at a programmed rate of 20°C/min to 290°C, and the crystallization thermogram in heating run were recorded.

Measurement of structure and properties of PET fibers

The measurement of birefringence of the as-spun fibers, F1 and F2, and annealed fibers, F1_a and F2_a, were carried out on the polarizing microscopy, lighted by Na-ray with the wavelength of 589 nm. The birefringence of the fibers was calculated by

$$\Delta n = (\theta/180^\circ)(\lambda/d)$$

where Δn is the birefringence of the fiber, θ is the compensation angle (degree), λ is the wavelength of the Na-ray (nm), and d is the diameter of fiber (mm).

The wide-angle X-ray diffraction (WAXD) scans were carried out on a Rigaku Dmax- γ B X-ray diffractometer to determine the crystallite structure of fibers. The samples were measured in the form of powder.

The tensile properties of fibers were measured by the XQ-1 fiber tensile tester, using a gauge length of 20 mm and a crosshead speed of 50 mm/min.

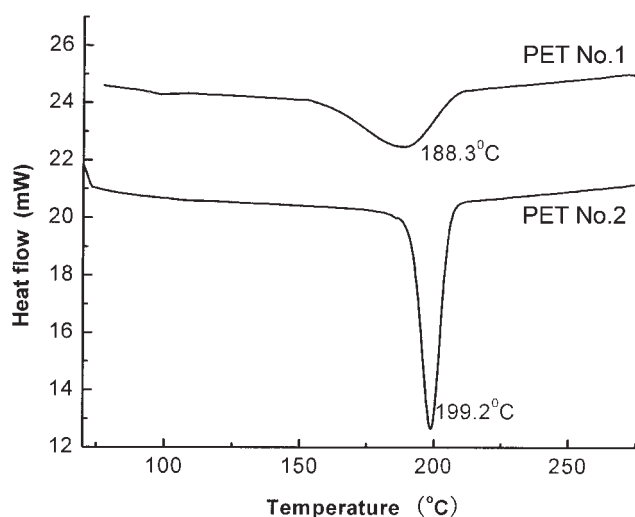


Figure 1 DSC crystallization thermograms of PET Nos. 1 and 2 on the cooling run.

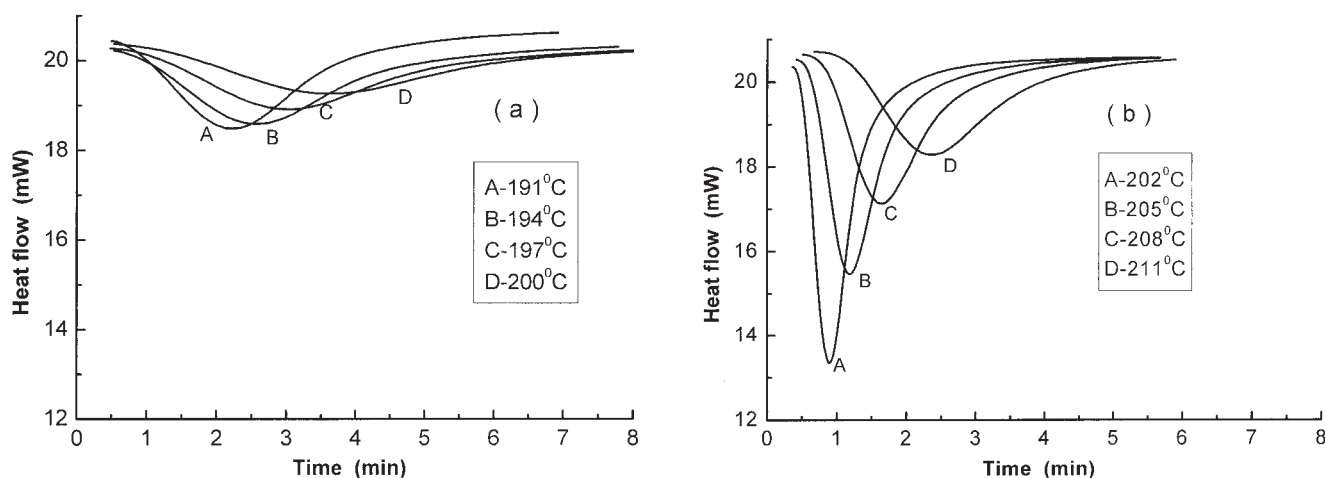


Figure 2 Isothermal crystallization exotherms at different T_c 's after holding at 290°C for 10 min: (a) PET No. 1; and (b) PET No. 2.

RESULTS AND DISCUSSION

Nonisothermal crystallization from melt during cooling run

Figure 1 shows the DSC crystallization thermograms of PET Nos. 1 and 2 from the melt-state during cooling run.

For the crystallization of polymer from melt-state, the crystallization temperature of polymer is in between its melting point T_m and its glass transition temperature T_g , and a maximum of crystallization rate appears at a certain temperature, which is usually called T_{cc} . Figure 1 shows that the T_{cc} of PET No. 2 (199°C) is much higher than that of PET No. 1 (188°C), and the endotherm peak of PET No. 2 is much bigger than that of PET No. 1. The results imply that by the solid-state shearing the crystallization on-set at the higher temperature and the higher degree of crystallization is achieved. The shearing effect on the crystallization is really amazing.

Isothermal crystallization kinetics

The isothermal crystallization exotherms of PET Nos. 1 and 2 at different crystallization temperatures T_c after holding at 290°C for 10 min are shown in Figure 2. It can be easily seen from Figure 2 that the isothermal crystallization of PET No. 2 is much faster than that of PET No. 1. From the isothermal DSC thermogram, one can obtain the crystallization kinetics. The difference of isothermal crystallization can be discussed more quantitatively in terms of the kinetic parameters on the basis of the Avrami equation:

$$1 - X_t = \exp(-Kt^n)$$

where X_t is the weight fraction of crystallized material at time t , K is the over-all crystallization rate con-

stant, and n is the Avrami exponent, which varies from 1 to 4 depending on the nature of the nucleation and crystallite growth processes. X_t is given by the ratio of total ($t = 0 - \infty$) exotherm peak area (A_∞) and that by a time t (A_t); and $X_t = A_t/A_\infty$. Then plotting $\log[1 - \ln(1 - X_t)]$ vs. $\log t$, the values of n and K are obtained by the slope and intercept. The crystallization kinetic parameters thus obtained are plotted as a function of T_c in Figure 3. Comparing the K value of PET Nos. 1 and 2 at the same temperature level, the K value of PET No. 2 seems to be much bigger than that of PET No. 1. If one extrapolates the value of K for PET No. 1 to 202°C, it would be around 1. The K value of PET No. 2 at that T_c (202°C) is more than 50 times. It is well known that the overall crystallization rate above T_{cc} (see Fig. 1) is mostly governed by the nucleation process. Then the results in Figure 3 may imply that the solid-state shearing memory still remained even after annealing above T_m for long time (for 10 min at 290°C).

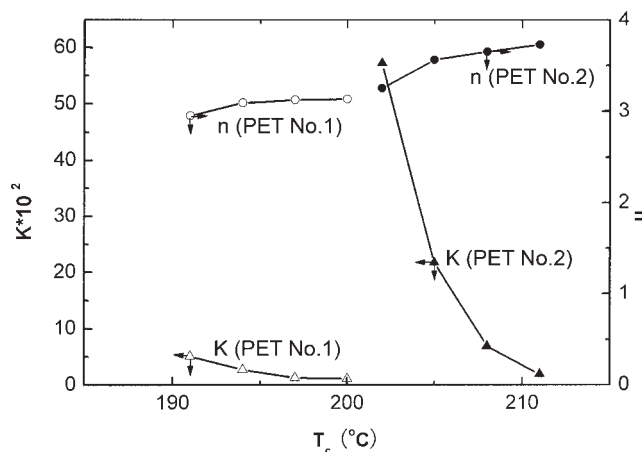


Figure 3 Crystallization kinetics parameters as a function of T_c (isothermal crystallization after holding at 290°C for 10 min).

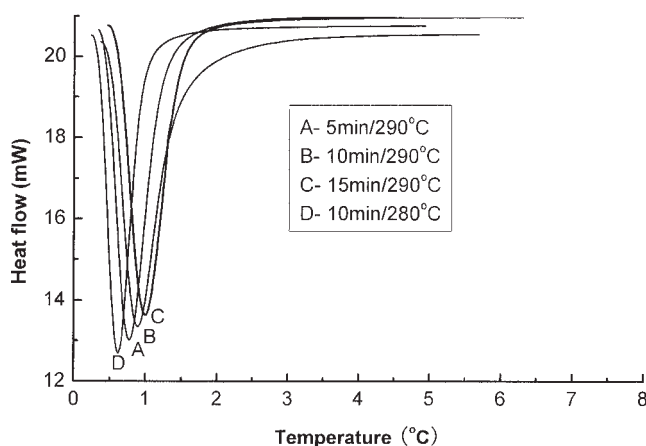


Figure 4 Isothermal crystallization exotherms of PET No. 2: crystallization at 202°C after holding various temperatures and times at melt-state.

Probably, small crystallites and/or local chain orientation survived even after annealing at melt state and they could act as the embryos of nuclei to accelerate the crystallization. The Avrami exponent n is believed to consist of the growth-mode factor (λ) and the nucleation factor (r): $n = r + \lambda$, where λ is 1 for linear (1D) crystal development, 2 for disc (2D) development, and 3 for sphere (3D) development. All n values for PET No. 1 are close to 3 and the temperature dependence is weak. The n values for PET No. 2 is slightly bigger and shows slightly stronger temperature dependence, suggesting the bigger nucleation contribution than the un-sheared PET.

Figure 4 shows the isothermal crystallization exotherms of PET No. 2 after holding various times and temperatures at melt-state. The corresponding isothermal crystallization kinetics parameters are summarized in Table I. Note that the crystallization was carried out at a fixed temperature ($T_c = 202^\circ\text{C}$). However, the crystallization rate constant K clearly varied with the holding time and temperature before the crystallization. The longer holding time and the higher temperature result in the slower crystallization. The results may suggest that the nucleus embryos set up by the solid-state shearing does not disappears immediately by holding at melt temperature. They can survive for rather long time; however,

TABLE I
Crystallization Kinetics Parameters of PET No. 2
(isothermal crystallization at 202°C after holding various temperatures and time periods at melt-state)

Holding temperature (°C)	Holding time (min)	K (10^2)	n
290	5	62	3.12
290	10	57	3.25
290	15	52	3.32
280	10	78	3.31

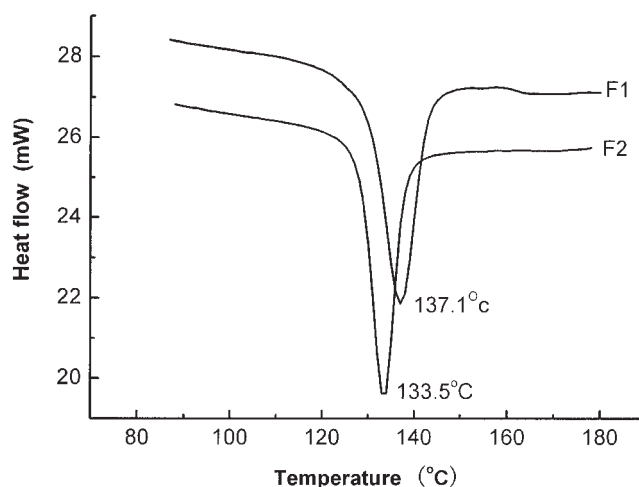


Figure 5 DSC curves of as-spun fibers during heating run.

some tend to disappear by the longer annealing at the higher temperature. Note also that the K values are still larger than 50 times of that for un-sheared PET (PET No. 1), suggesting that the average life of shearing effect is surprisingly long. As shown in Table I, Avrami exponent n hardly changes with holding time and temperature. This may suggest that the annealing does not affect the crystallization mechanism.

Structure and properties of spun fibers

The DSC curves of as-spun PET fiber during heating run are shown in Figure 5. The crystallization of F2 (as-spun fiber from PET No. 2) takes place at lower temperature than F1 (as-spun fiber from PET No. 1). The solid-state shearing history seems to be kept even after the fiber spinning.

The results of birefringence measurement of the fibers are listed in Table II. The birefringence of F2 is slightly higher than that of F1, suggesting a better molecular chain orientation. After annealing, the birefringence decreases. It should be caused by chain relaxation during annealing at a temperature above glass transition T_g without intension.

The WAXD profiles of as-spun fibers are shown in Figure 6. Figure 6(a) shows that the as-spun fiber from

TABLE II
Birefringence and Tensile Properties of Fibers

Sample	F1	F2	F1 _a	F2 _a
Birefringence	0.0129	0.0135	0.0017	0.0015
Tensile strength (cN/dtex)	0.98	1.29	0.63	0.84
Elongation at break (%)	501.5	457.2	263.1	22.2
Young's modulus (cN/dtex)	9.1	13.9	10.0	18.3

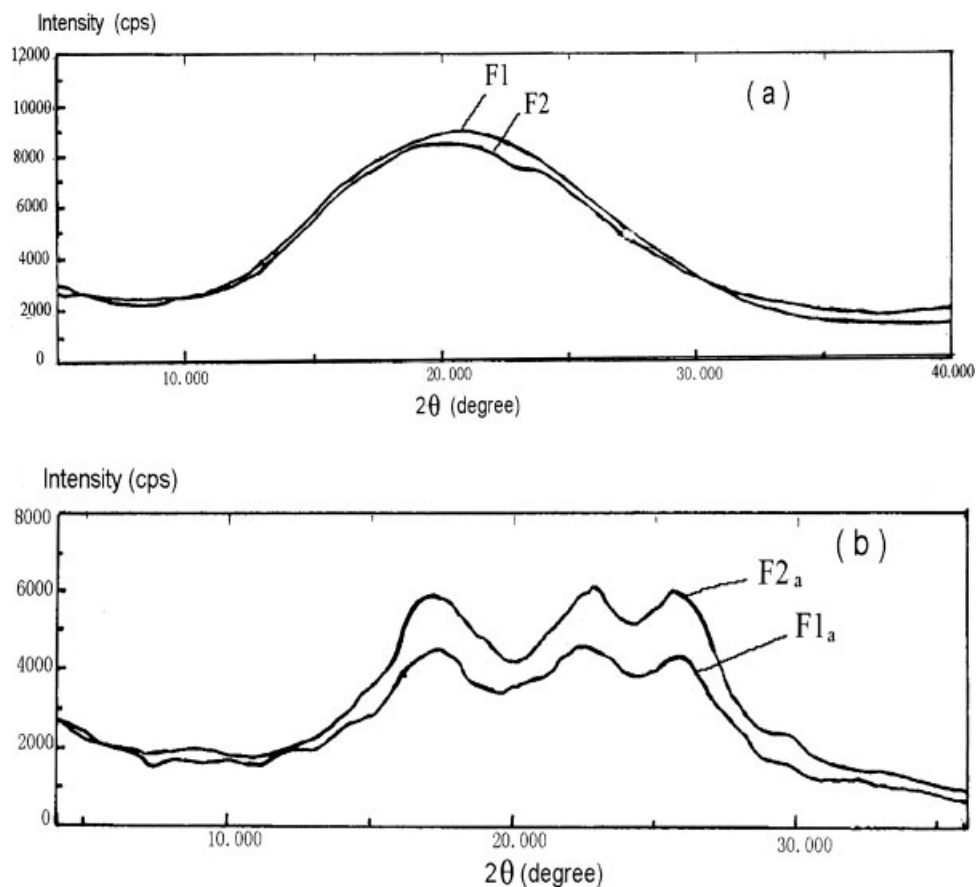


Figure 6 WAXD profiles of PET fibers: (a) as spun; (b) after annealing at 155°C for 30 min.

unsheared PET (F1) is almost amorphous. By contrast, the fiber from sheared PET (F2) shows a weak but definite crystalline peak at $2\theta = 22.5^\circ$. Figure 6(b) shows that by annealing at 155°C, many WAXD peaks appear ($2\theta = 17.5^\circ$, 22.5° , and 26.5°). All peaks are characteristic to PET crystal. WAXD profiles of F2_a shows much stronger intensity than that of F1_a. It suggests that the solid-state shearing has provided the better molecular alignments for the crystallization.

The results of tensile tests of the fibers are shown in Table II. F2 shows higher tensile strength and Young's modulus than F1, while lower elongation at break than F1. This situation is same for the fibers after annealing. However, for the fibers from sheared PET, the elongation at break markedly decreases by annealing. The serious deterioration may be caused by a terrible loss of tie chains with annealing.

CONCLUSIONS

Thus, we have shown that the memory of solid-state shearing can remain even after annealing above the

melting point of PET and it imposes remarkable effect on the crystallization and the fiber structure formation.

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