폴리에틸렌테레프탈레이트의 고속 In-Line 연신공정내에서의 섬유형성 메커니즘에 대한 연구 (II)

-구조물성분석에 의한 섬유내 고유 고차구조형성기구 해석 -

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Mechanism of Fiber Structure Development in High-Speed In-Line Drawing Process of Poly(ethylene Terephthalate) (II)

-Studies on Structure Evolution and Property of Obtained Fibers-

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1. Introduction

Recently, several research groups have investigated the structure evolution of poly(ethylene terephthalate) with off-line drawing and annealing processes paying particular attention to the properties of mesophase, i.e. the non-crystalline phase with high chain extension, and its role for the formation of crystalline structure. Despite of these intensive investigations, studies on the structural development of PET under the industrial drawing conditions are rarely found. In the present work, we conducted the high-speed in-line drawing of PET filament at the final take-up velocity of 5 or 6 km/min. Dependence of the structures and thermo-mechanical properties of the obtained fibers on drawing conditions was discussed in detail considering the variation of the amount of three phases, i.e. amorphous phase, oriented mesophase and crystalline phase.

2. Experimental

PET with intrinsic viscosity of 1.0 dl/g was supplied by Toyobo Co. Ltd. Melt spinning of the polymer was executed using a single-hole spinneret of 1 mm diameter. Throughput rate and spinning temperature were controlled at 6.0 g/min and 300 ℃, respectively. High speed in-line drawing (Fig. 1) was carried out using a pair of heated godet rolls (GR-1 & GR-2) at take-up velocities of 5 and 6 km/min. Draw ratio was varied by changing the velocity of GR-1. On-line measurements of filament diameter and velocity were performed in both the melt spinning and drawing regions. Structure and property of obtained fibers were analyzed by measurements of wide-angle X-ray diffraction (WAXD), birefringence, modulated differential scanning calorimetry (MDSC), and thermo-mechanical analysis (TMA).

3. Results and discussion

3.1 Overall diameter and velocity profiles

The measured velocity profiles of the melt spinning line of PET indicated that neck-like deformation started to occur at the GR-1 velocity of 4 km/min (Fig. 2). The neck-like deformation became steeper and its position shifted to upstream with an increase in the velocity of GR-1. The maximum strain rate analyzed from the overall velocity profile of the spinning line at the GR-1 speed of 5 km/min was 250 s^{-1}. On the other hand, deformation of filament in the drawing line finished within 30 cm from the GR-1, and the maximum strain rate reached a high value of around 890 s^{-1} when the velocities of GR-1 and GR-2 were set to 2 and 5 km/min, respectively.

3.2 X-ray Scattering Analysis

Mass fractions of crystalline-, oriented meso- and amorphous-phases in the resultant fibers were analyzed from 2D WAXD patterns. In the PET fibers prepared without applying the in-line drawing by setting the same velocity to GR-1 and GR-2, the amount of crystalline phase increased with increasing velocity after the starting of neck-like deformation (Fig. 3). On the other hand, at the GR-2 speed of 5 km/min, the amount of oriented mesophase increased significantly with an increase in the draw ratio, i.e. with a decrease of GR-1 speed. A sharp meridional reflection, which is known to correspond to (001′) of well-ordered smectic-C phase, was clearly observed in the WAXD patterns of fibers prepared at high draw ratios (Fig. 4). The intensity of (001′) reflection increased with increasing draw ratio. Birefringence, tensile modulus and strength of drawn fibers also increased with increasing draw ratio. These results indicate that at a fixed final take-up velocity, the improvement of the mechanical performance of in-line drawn PET fibers can be achieved by the control of drawing conditions rather than that of spinning conditions.

3.3 Thermo-Mechanical Properties

MDSC thermograms and TMA curves for fibers prepared at GR-1 & GR-2 speeds of 5 & 5 km/min (S5) and 2 & 5 km/min (D25) are compared in Fig. 5. From the total heat flow, high-speed spun fibers (S5) were found to show higher crystallinity, cold crystallization temperature (T_c) and melting temperature (T_m) than those of highly drawn fibers (D25). On the other hand, glass transition of D25, which was clearly observed in the reverse heat flow, started at a relatively lower temperature, and additional broad and weak transition was observed around 100-140 ℃. Contractive stress and thermal shrinkage of D25 were higher than those of S5, and the peaks in contractive stress curves correspond to the transitions in reverse heat flow. Starting of cold crystallization and thermal shrinkage also corresponds to the onset of the first glass transition. It was worth noting that contractive stress increased steeply below the glass transition temperature (T_g). It was also confirmed from in-situ measurement of WAXD pattern of D25 (Fig. 6) that the intensity of (001′) peak started to increase at a temperature lower than T_g. With the starting of the increase in the amount of crystalline phase, amounts of amorphous phase, oriented mesophase and Smectic-C mesophase started to decrease. (001′) peak disappeared around 100 ℃. Above this temperature, the reduction rate of the amount of amorphous phase decreased, and mesophase with relatively low order mainly contributed to the additional crystallization.

4. Conclusion

High-speed in-line drawing of poly(ethylene terephthalate) (PET) filament was conducted at various draw ratios. The take-up velocity was fixed at 5 or 6 km/min and the draw ratio was controlled by varying the velocity of the first godet roll. Although the PET filament was drawn above the glass transition temperature, significant development of oriented mesophase was confirmed and also a sharp meridional (001′) peak, which is reported to be originated from well-ordered smectic-C phase, was clearly observed. Birefringence, tensile modulus and tensile strength of the drawn fibers increased with an increase in the amount of oriented mesophase. To analyze the temperature-dependent behavior of the mesophase, in-situ measurement on the change of WAXD pattern during the heating process of highly drawn non-crystalline filament was carried out, and the result was compared with the results of modulated differential scanning calorimetry and thermo-mechanical analyses.

5. References

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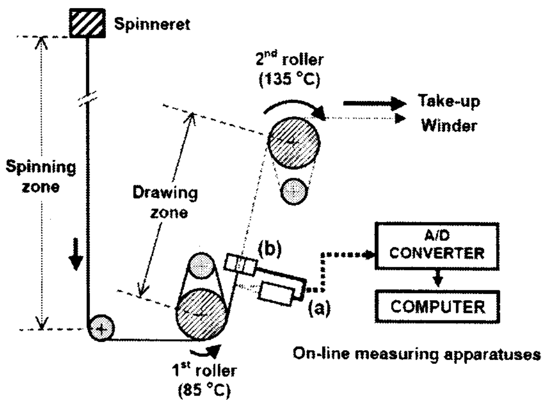

Fig. 1 Schematics of high speed in-line drawing process and on-line measuring apparatuses

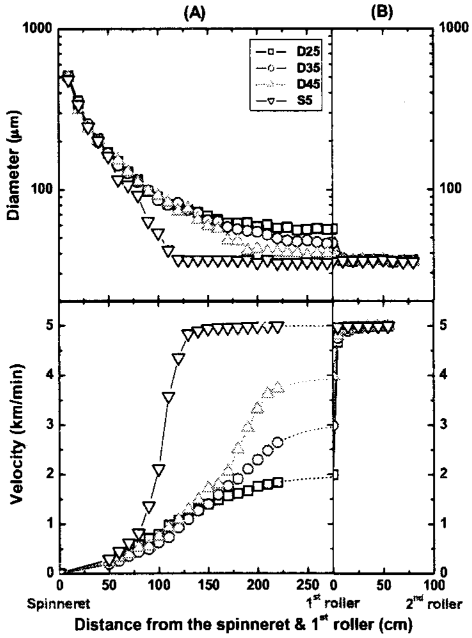

Fig. 2 Overall diameter and velocity profiles of PET filaments at various GR-1 speeds in high speed in-line drawing process, where (A) and (B) are spinning and drawing zones. The final take-up velocity was fixed at 5 km/min.

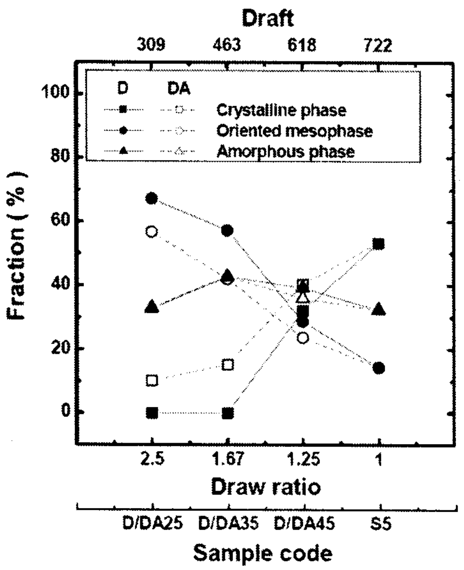

Fig. 3 Variations of fraction of crystalline phase, oriented mesophase, and amorphous phase in PET filament at various GR-1 speeds in high speed in-line drawing process. The take-up velocity was same and fixed at 5 km/min.

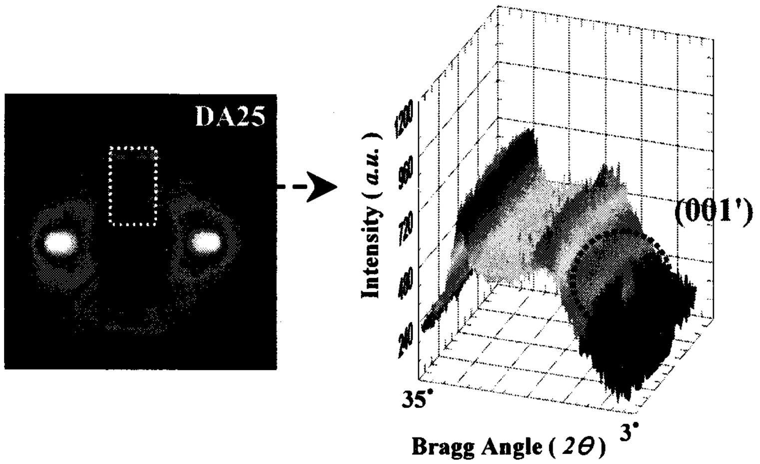

Fig. 4 2D WAXD pattern and (001') peak of highly drawn non-crystalline filament (D25).

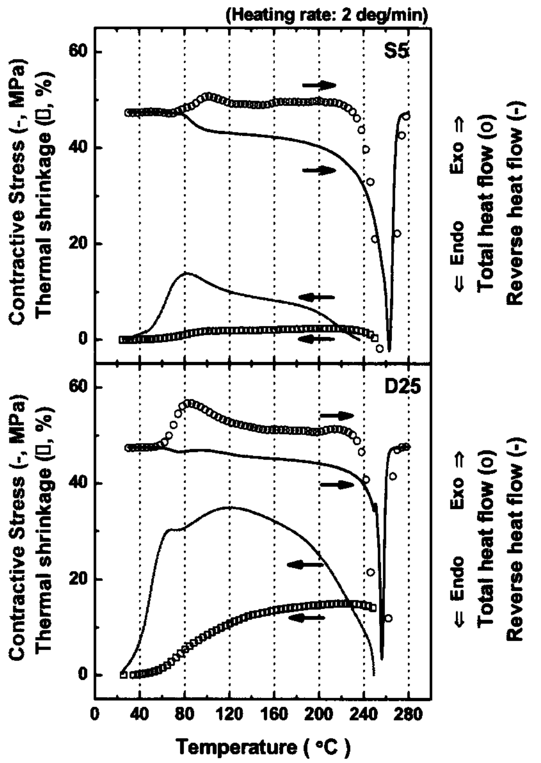

Fig. 5 MDSC thermograms compared with the curves of TMA for S5 and D25 samples.

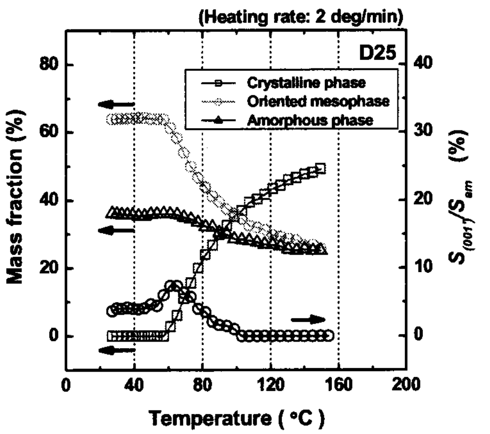

Fig. 6 Variations of the mass fractions of crystalline-, meso- and amorphous-phases and the relative intensity of (001') peak analyzed from 2D WAXD during the heating process of highly drawn non-crystalline filament (D25).