Yield Behavior of As-Spun PET Filaments
: Activated Rate Process Approach

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1. Introduction

Among the various tensile properties of polymeric materials, the yield behavior is of great importance in terms of both manufacturing processes and service performances. The various polymer processes, such as drawing, rolling, forming, etc., are achieved through the significant plastic flow of the polymer molecules and from the viewpoint of service performances the initiation of yield implies that the product could not stand the deformation or stress any longer. These two standpoints are still more significant when the polymer products are used as the industrial products such as rope, tent, tire cord, etc.

Many researchers[1-5] have investigated the yield behavior by considering it as a thermally activated rate process, of which the basic formalism had been developed by Eyring[6] for creep at constant applied stress. Some of them[1-2] have proposed that there is normally more than one activated rate process, and could well describe the yield behavior at a wide range of strain rates and temperatures by the two activated processes. Although these approaches have successfully explained the yield behavior of many polymers, they were mainly focused on the isotropic polymers. Therefore the strain rate and temperature dependent yield behavior of anisotropic polymers including oriented and semi-crystalline polymers has rarely been investigated.

In this study, features of yield behavior of the anisotropic polymers are investigated by examining the tensile yield in PET filaments spun at different take-up velocities. The strain rate and temperature dependence of the yield stress of PET filaments is first determined as the thermally activated rate process, and its relationship with the anisotropic nature, which is the physical structure formed by the spinning process, will be discussed.

PET chips used in this study have higher intrinsic viscosity value than that of the normal ones, and they are at present in use for the commercial production of tire cord. For filaments to be used as the tire cords, it is required that the filaments should have a high dimensional stability. Therefore a study on the resistance of the filaments to a deformation is inevitable, and the analysis of the yield behavior could be an appropriate measure of it.

2. Experimental

PET chips having high intrinsic viscosity value(0.98) were used. Melt spinning was performed at the spinning conditions listed in Table 1. The take-up velocity was increased by 0.5 km/min from 2.5 up to 5.5 km/min.

Table 1. Melt spinning conditions.

Variable	Condition
Spinneret	L/D=2, 192 holes
Mass flow rate	2.4 g/min·hole
Spinning temp.	295°C
Quenching method	Air (25°C, 36 m/min)
Take-up velocity	2.5-5.5 km/min

Table 2. Strain rates used in the tensile test.

Elongation rate (mm/min)	Strain rate (s^{-1})
300.0	10^{-1}
94.9	$10^{-1.5}$
30.0	10^{-2}
9.5	$10^{-2.5}$
3.0	10^{-3}
0.9	$10^{-3.5}$
0.3	10^{-4}

Tensile tests of the as-spun PET filaments were done at different temperatures(25, 50, 75, 100 and 125°C) employing Instron tensile tester equipped with a hot chamber. The gauge length was 50 mm, and the cross-head speed was adjusted from 300.0 to 0.3 mm/min in order to give the nominal strain rates in Table 2, which were calculated as the ratio of the cross-head speed to the original gauge length.

In addition, structural characterizations were also carried out. Equatorial and azimuthal WAXS patterns were obtained, density was determined from the density gradient column, and birefringence was measured by the polarized microscope.

3. Result and Discussion

PET used for this experiment had good spinnability and could be spun up to the take-up velocity of 5.5 km/min without difficulties. The linear density of the filaments ranged from 750 to 1625 denier/192 filaments depending on the take-up velocities.

Equatorial WAXS patterns of the PET filaments spun at different take-up velocities are shown in Fig. 1. Crystallization in the spin-line begins to occur at the take-up velocity of about 3.5 km/min, and three main peaks are observed which correspond to the reflections of (010), $(\bar{1}10)$ and (100) planes of PET crystals. The crystallinity calculated from the density showed a steep increase at the take-up velocity of 3.5-4.5 km/min. Birefringence of the PET filaments shown in Fig. 2 increases to a saturated value as the take-up velocity increases. From the results of crystallinty and birefringence, it can be seen that the steep increase of the two properties starts at lower take-up velocity by about 1.0 km/min than that of the filaments spun from PET having the intrinsic viscosity of about 0.6.

Fig. 3 shows an example of the stress-strain curves of PET filaments at room temperature and the strain rate of 10^{-2}. The increase in take-up velocity leads to a decrease in natural draw ratio, and finally filament spun at the take-up velocity of 5.5 km/min exhibits a similar tensile behavior as the drawn filaments. The yield stress was calculated from the first maximum load divided by the reduced cross-sectional area, assuming the homogeneous deformation at a constant volume up to this point. When the stress-strain curves showed no maximum in stress, usually at high temperature and low strain rate or in the case of the filaments spun at 5.5 km/min having no natural drawing zone, Meredith method[7] was adopted to determine the yield point.

On the dynamical view of the activated rate process[1], the yield stress denotes the point at which the internal viscosity falls to the value where the plastic strain rate equals the applied strain rate. The final formulation representing the strain rate and temperature dependence of the yield stress is given as equation (1).

$$\frac{\sigma_y}{T} = \frac{\Delta H}{VT} + \frac{R}{V}\ln\frac{2\dot{\varepsilon}}{\dot{\varepsilon}_0} \qquad (1)$$

Thus the activated rate process approach predicts the yield stress behavior as a series of parallel straight lines at various temperatures in the yield stress/temperature ~ ln(strain rate) plot. Activation enthalpy(ΔH) and activation volume(V) can be determined from the intercept and the slope of the straight lines in the plot. Fig. 4 is an example of such a plot at the tensile test temperature of 25°C. Not only for the filaments spun at lower take-up velocities, which could be regarded as an isotropic ones, but also for the filaments spun at higher take-up velocities, which are oriented semi-crystalline ones, relations of yield stress/temperature to ln(strain rate) become fairly good linearities. The level of the yield stress/temperature increases as the take-up velocity increases. This is thought to be strongly correlated with the fact that activation enthalpy, which is calculated from the intercept and has the meaning of the energy barrier that the polymer molecules should overcome in order to flow in the direction of stress, increases as the take-up velocity increases. In addition, activation volumes calculated from the slopes of the straight lines gradually decrease as the take-up velocity increases.

From the above discussion, it can be concluded that the improved orientation and enhanced crystallinity caused by the increase of the take-up velocity increase the activation enthalpy and decrease the activation volume.

4. References

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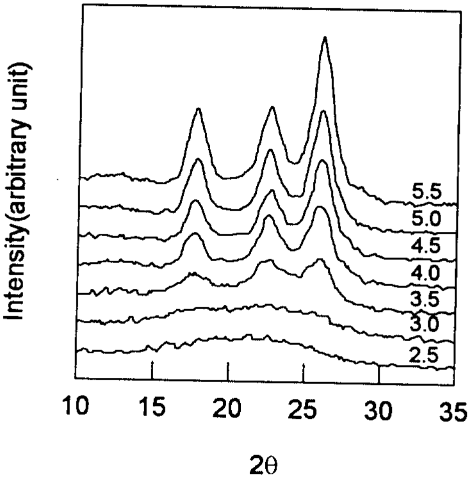

Fig. 1. Equatorial WAXS patterns of PET (I. V. : 0.98) filaments. Take-up velocities (km/min) are indicated.

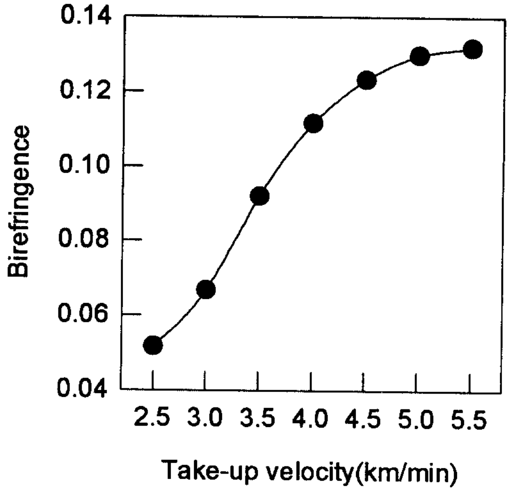

Fig. 2. Birefringence of PET(I. V. : 0.98) filaments spun at different take-up velocities.

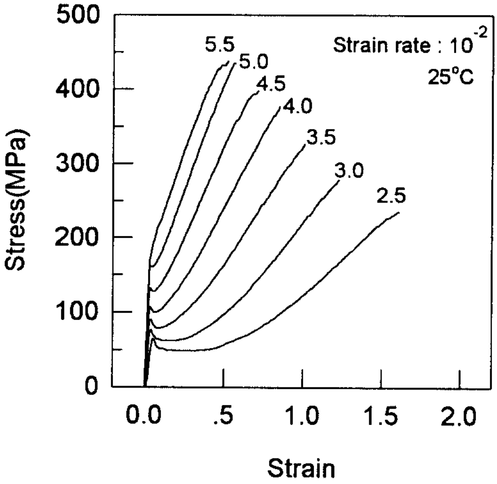

Fig. 3. Stress-strain curves of PET(I. V. : 0.98) filaments.Take-up velocities(km/min) are indicated.

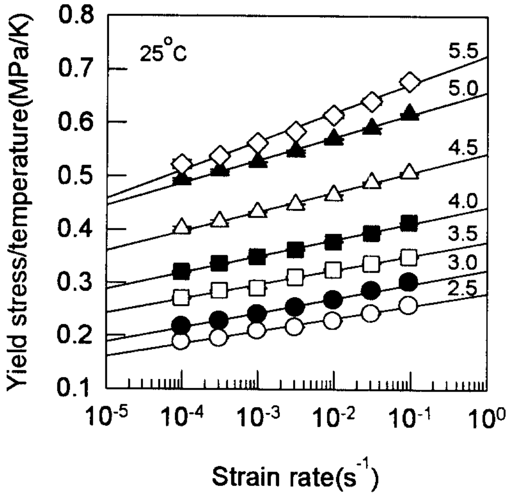

Fig. 4. The strain rate dependence of yield stress of PET filaments(I. V. : 0.98) at 25°C. Take-up velocities(km/min) are indicated.