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Characterization for Melt-Spun Fiber of Fluorocarbon Polymer

1. Copolymer of Tetrafluoroethylene and Hexafluoropropylene

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Abstract: Melt spinning of a fluorocarbon copolymer of tetrafluoroethylene and hexafluoropropylene was performed for the first time under various conditions with the take-up velocity up to 800 m min⁻¹ and the draw ratio up to 2.5. The fine long filaments with diameters of 20 – 60 µm were obtained. The molecular orientation in the fiber developed and the melting peak in the DSC thermogram sharpened with an increase in take-up velocity as well as in draw ratio. The mechanical properties of the fiber varied from 0.271 to 1.26 GPa in Young's modulus, from 0.0285 to 0.137 GPa in the break stress and from 300 to 25 % in the break strain under the spinning condition, respectively.

1. Introduction

Fluorocarbon polymers have grown steadily in technological and marketplace importance since the serendipitous discovery Teflon® at the Dupont Jackson Laboratory in 1938.¹ They are a class of plastics with great promise because of their superlative properties advantageous to applications, such as outstanding resistance to chemicals and heat, extraordinary non-stick and water repellent characteristics, low coefficients of friction, and electrical superior properties. On the other hand, they are difficult to be spun as well as formed, molded or shaped due to high melt viscosity. Fluorocarbon polymer fibers have been prepared by the following three methods.² The first is *split peel process* where the polymer film is torn up into filament, stretched and annealed. The second is *matrix spinning* where the mixture of fluorocarbon polymer and viscose is spun, washed, dried and stretched. The third is *paste extrusion* where a

mixture of the polymer powder and lubricating oil is extruded into a rod, calendared and dried. The fibers obtained there are used in hot gas filtration, sewing yarn, but not useful for textile. Recently, one of the authors (T. U.) succeeded in melt spinning of fluorocarbon polymers and production of fine fibers and filaments useful to textile for the first time.³ In this study, we prepared the melt-spun fiber of FEP (poly(tetrafluoroethylene-co-hexafluoropropylene)) prepared under various conditions and investigated structure and properties of the fiber by optical microscopy, wide-angle X-ray diffraction, differential calorimetry and stress-strain measurement.

2. Experimental

FEP pellet (Daikin Co. Ltd. NEOFロン FEP N-100) was used for melt spinning. The hexafluoropropylene content of 9.1 wt% was determined by the infrared spectroscopy method.¹

Melt spinning of multi-filament fibers was carried out with a productive equipment in Toyo Polymer Co. Ltd. Diameters of the fibers were measured with an Olympus BX-P50 optical microscope. Birefringences of the fibers were determined for the fiber mounted between crossed polars in the microscope using a U-CBE compensator at 530 nm. Wide-angle X-ray diffraction measurements were performed using a Rigaku-Denki RU-200A X-ray generator with Ni-filtered $\text{CuK}\alpha$ radiation. Differential scanning calorimetry measurements were carried out with a Perkin-Elmer Pyris 1 DSC at a rate of 5°C min^{-1} . Stress-strain curves for the fibers were obtained by using a Toyo Seiki STROGRATH-R2 tensile testing machine. Samples with a gauge length of 50 mm were tested at 23°C with a strain speed of 25 mm min^{-1} .

3. Results and discussion

3.1 Melt spinning of FEP

The screw extruder has 48 nozzles of 0.3 mm in diameter. The polymer pellets were melted in the cylinder at 345°C , extruded through the spinneret at 370°C and melt-drawn at a constant mass flow rate of $0.67\text{ g min}^{-1}\text{ hole}^{-1}$. The as-spun fiber was wound up on a godet roll. The rotation frequency of the godet roll could be varied stepwise resulting in take-up velocities between 100 and 900 m min^{-1} . Drawing of filaments was carried out continuously at 140, 150 and 160°C with four rolls rotating with speeds of 400, 430, 720 and 1030 m min^{-1} . The imposed draw-ratios of the fibers wound up on the second, third and fourth rolls were thus 1.08, 1.80 and 2.58, respectively. The spinning conditions are summarized in Table. 1.

Table 1 Preparation condition of FEP fibers.

Sample	Take-up Velocity ($\text{m}\cdot\text{min}^{-1}$)	Draw Ratio
A	100	not drawn
B	200	not drawn
C	400	not drawn
D	600	not drawn
E	800	not drawn
F	400	1.08
G	400	1.80
H	400	2.58

3.2 Characterization of melt-spun fibers

The diameter of the as-spun fibers obtained at various take-up velocities is plotted in Fig. 1. The fiber diameter R can be calculated as

$$R = 2 \sqrt{\frac{Q}{\pi \rho v}} \quad (1)$$

where Q , ρ and v are mass flow rate, density of the polymer melt and take-up velocity, respectively. The data show good agreement with the calculated diameter shown with a solid line. This fact suggests that the spinline is stable under the spinning conditions and that homogeneous fibers are obtained at a take-up velocity less than 900 m min^{-1} at which the fiber was cut off.

Fig. 1 Variation of diameter of melt-spun FEP fibers upon take-up velocity. The solid line represents the value calculated with Eq. 1 ($Q = 0.67\text{ g min}^{-1}$, $\rho = 2.15\text{ g cm}^{-3}$).

Molecular orientation in the fiber occurred both under elongation and under spinning. Variation of birefringence of the fiber upon take-up velocity and elongation ratio are shown in parts (a) and (b) of Fig. 2, respectively. Here the initial fiber for elongated ones (fibers F, G, H) is identical with the fiber taken up at a rate of 400 m min^{-1} (fiber C). The birefringence is in proportion to the take-up velocity less than 900 m min^{-1} and reaches the comparable value with that for the fiber hot-drawn with a ratio of 2. The molecular orientation of the fibers can be recognized directly with the X-ray diffraction patterns of the fibers shown in Fig. 3. The patterns include an inner sharp strong reflection and an outer

Fig. 2 Variation of birefringence of melt-spun FEP fibers upon take-up velocity (a) and drawing ratio (b). Drawing of filaments was carried out continuously at 140, 150 and 160°C with four rolls rotating with speeds of 400, 430, 720 and 1030 $\text{m}\cdot\text{min}^{-1}$.

weak broad halo. With an increase in take-up velocity or in elongation ratio, the inner ring reflection concentrates on the equator and the outer ring concentrates into four spots on each side of the meridian. Thus molecules oriented under the spinning process as much as under the hot drawn process. The diffraction pattern for the fiber exhibits less order than homopolymer of tetrafluoroethylene (PTFE).^{4,5} The sharp spots on the equator results from the lateral hexagonal packing of molecules. The broadening of the reflections on the layer lines is attributed to longitudinal disorder induced thermally and by perfluoromethyl group in the copolymer.⁶

The DSC curves for crystal melting of the fibers are shown in Fig. 4. With an increase in take-up velocity, the melting peak temperature shifts to high temperature, but the width of the peak and the fusion enthalpy keep almost constant (see curves A, B, C

Fig. 3 X-ray diffraction patterns of melt-spun FEP fibers; (a) fiber A, (b) fiber C, (c) fiber E and (d) fiber H. The arrows indicate the reflections on the equator attributed to the lateral hexagonal packing of molecules.

Fig. 4 DSC heating curves of melt-spun FEP fibers. (a) as-spun fibers taken up at rates indicated in Table 1 (fibers A, B, C and E) and (b) hot-drawn fibers with ratios indicated also in the same table (fibers C and F ~ H).

and E in Fig. 4). On the other hand, for hot-drawn fibers, the broad melting peak shifts to higher temperature and changes drastically into a sharp one. The fusion enthalpy increases slightly with increasing draw-ratio (see curves C and F ~ H in Fig. 4). The DSC endotherms give a distribution of melting temperatures that in principle can be converted to a distribution of crystalline thickness by means of the relation

$$T_m = T_m^\circ \left(1 - \frac{2\sigma_e}{\Delta H_u L} \right) \quad (2)$$

where T_m is the observed melting temperature of a lamellar crystal of thickness L , T_m° is the equilibrium melting temperature of the infinitely thick crystal, σ_e is the interfacial free energy associated with a basal plane, and ΔH_u is the enthalpy of fusion per unit volume. Equation 2 is a variant of the Thomson-Gibbs equation that was derived for a lamellar crystal of great lateral dimensions and small thickness. It

can be assumed that the rate of the heat flow at a given temperature is proportional to the fraction of lamellae that have a thickness L . Thus these data can be interpreted as that thickening of crystalline lamella proceeds with reducing the thickness distribution by the drawing.

Stress-strain curves of the melt-spun fibers are shown in Fig. 5. This figure indicates that the mechanical properties of the fiber depend significantly on the spinning condition. Stress and strain at the breaking point are plotted against the birefringence of the original fiber in Fig. 6. It can be assumed that molecular orientations in the fibers with the same birefringence are identical if the crystallinity and crystal form do not change significantly between the fibers. This assumption is supported by the X-ray diffraction patterns of fibers E and G with almost the same birefringence. The

Fig. 5 Stress-strain curves of melt-spun FEP fibers.

Fig. 6 Stress (squares) and strain (circles) at the breaking point for melt-spun FEP fibers as a function of birefringence. The open symbols are for as-spun fibers and the closed ones are for hot-drawn fibers.

X-ray diffraction patterns are indistinguishable, and thus the molecular orientation and the crystal form is identical between the fibers. Though the molecular orientations are same between the as-spun fiber (E) and the elongated fiber (G or H), their tensile strengths and break strains are remarkably different. The elongated fiber shows larger strength and smaller strain than the as-spun one. The increment in tensile strength and the decrease in break strain can be attributed to orientation of the molecules for the as-spun fibers, on the other hand, to thickening of lamellar crystal in the elongated fibers. Thus, elongation is effective to increment of the elastic constant and the tensile strength of the FEP fibers.

4. Conclusions

In this study, FEP fibers were prepared with the melt-spinning method and characterized. Significant

increment in orientation was achieved by melt-spinning at a low take-up velocity of $800 \text{ m} \cdot \text{min}^{-1}$ as well as by hot drawing to a low ratio of 2.5. The mechanical properties depend significantly on the take-up velocity and the draw ratio attributable to molecular orientation and thickening of crystalline lamellae in the fiber.

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