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Development of High-Modulus and High-Strength Poly(tetrafluoroethylene) Fibers by Elongation at a Liquid Crystalline State

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ABSTRACT: Raw filaments of ultrahigh molecular weight poly(tetrafluoroethylene) (PTFE) (8.4×10^6) were prepared by the paste extrusion of fine powder. The raw filaments with a sag ratio of 25% were annealed at 360 °C, higher than the apparent melting point of 330 °C estimated by differential scanning calorimetry (DSC), at a heating rate of 10 °C/min. After annealing for 30 min, they were cooled to room temperature at desired rates. The resultant monofilaments were annealed for 30 min at 388 °C and were elongated up to 100 times at the same temperature. Young's modulus and the tensile strength were sensitive to the sag ratio of raw filaments under heating and cooling processes. The maximum values of Young's modulus and the tensile strength of drawn fibers reached 57.6 and 2.31 GPa, respectively, at 25−26 °C associated with the crystal transition at room temperature, when the sag ratio was 25% corresponding to the intrinsic shrinkage of the raw filaments. This indicates that a suitable level of the entanglement mesh to assure the maximum values of the tensile strength and Young's modulus was formed by the drastic shrinkage (25%) of the raw filaments, leading to molecular motion without constraints. This phenomenon is discussed in terms of the morphology of the monofilaments and drawn fibers as studied by optical microscopy (crossed-polarized), differential scanning calorimetry, and X-ray diffraction techniques. The production of high-strength PTFE fibers is attributed to the appearance of thermotropic liquid crystals at temperatures higher than the apparent melting point, reflecting the chain rigidity of PTFE.

Introduction

In the past ten years, there has been increasing interest in preparing fibers with ultrahigh modulus and high strength. Many efforts have been made to produce them with special chemical and morphological features by controlling molecular and morphological design. The molecular design is associated with the average length of the chains, the strength of the forces between polymer chains, the regularity with which the chains pack, and the stiffness of the individual chains. The morphological design is based on the intrinsic physical anisotropy of polymer molecules (e.g., mechanical and optical).

Poly(tetrafluoroethylene) (PTFE) is of special interest because of its heat resistance, low-temperature toughness, chemical resistance, characteristic electric properties, etc. Ultradrawing of PTFE was reported in 1957.[1] Young's modulus and the tensile strength, however, were much lower than those of ultradrawn polypropylene films[2,3] whose crystal lattice modulus in the chain direction is about 43 GPa. On the basis of a number of fundamental studies of PTFE,[4−11] high-modulus and high-strength PTFE fibers were reported by Okuyama et al.[12] and Uehara et al.[13] According to their reports,[12,13] PTFE powder was drawn up to 40−60 times by solid-state extrusion in the temperature range 330−340 °C. The maximum Young's modulus and tensile strength were 50 and 0.5 GPa, respectively, at 24 °C.[13] In this paper, we describe new methods to improve the tensile strength and modulus of PTFE fibers. It was found that the mechanism of ultradrawing of PTFE is quite different from that of polyethylene films prepared from solutions by gelation/crystallization.[14−17] This difference is discussed in terms of the morphological design of PTFE chains with both characteristics of rigidity and flexibility.

Experimental Section

Raw filaments of PTFE were prepared by paste extrusion of fine powder produced by emulsion polymerization by Daikin Co. Ltd. The molecular weight of PTFE powder was estimated as 8.4×10^6 from the energy $-\Delta H_c$ to crystallize by differential scanning calorimetry (DSC) and the crystallinities of the powder and raw filament estimated from the heat of fusion of crystallites of 22.2 cal/g[10] were about 73.5 and 70.9%, respectively. In the DSC measurements, specimens weighing about 5 mg were placed in a standard aluminum dish and heated at a rate of 10 °C/min. The raw filaments with the sag ratios 10, 25, and 30% were clamped in an automatic stretching device with a 2 mm distance L_0 between jaws. The sag ratio was defined as $(L - L_0)/L_0 \times 100$ (%). The raw filaments were annealed for 30 min at 360 °C, higher than the apparent melting point of 330 °C estimated by the DSC measurements, and subsequently cooled to room temperature at the indicated rates, 0.5, 1, and 10 °C/min, or quenched. A constant temperature in the stretching device was maintained by violent hot-air circulation. The annealed filaments clamped in the stretching device were heated again for 30 min at 388 °C, higher than the apparent melting point, and were elongated at a rate of 50 mm/s up to 75 or 100 times. Through trial and error, it was confirmed that 388 °C assures the most facile drawability. The possibility of elongation beyond 100 times could not be confirmed because of the limited size of the stretching device. The measurements of Young's modulus and tensile strength were carried out at 25−26 °C, associated with the crystal transition at room temperature.[18] The temperature dependence of the complex dynamic tensile modulus was measured with a viscoelastic spectrometer (VES-F) of Iwamoto Co. Ltd. The measurements were carried out over a temperature range from −150 to +350 °C at a fixed frequency of 10 Hz. The length of the fiber was about 40 mm. During measurements, the fiber was subjected to a static sinusoidal

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Table 1. Young's Modulus and Tensile Strength of PTFE Drawn at the Indicated Conditions

cooling rate (°C/min)		draw ratio (λ)					
		75			100		
		10% sag ratio	25% sag ratio	30% sag ratio	10% sag ratio	25% sag ratio	30% sag ratio
0.5	Young's modulus (GPa)	22.4	41.6	13.0	9.80	12.4	16.2
	tensile strength (GPa)	1.15	1.65	0.95	0.96	1.03	1.22
1	Young's modulus (GPa)	20.0	45.6	18.5	40.2	46.2	31.9
	tensile strength (GPa)	1.09	1.76	0.87	1.53	1.62	1.28
10	Young's modulus (GPa)	14.0	32.4	10.7	32.0	57.6	42.3
	tensile strength (GPa)	1.21	1.91	0.93	1.12	2.31	1.35

oscillation with a peak deformation of 0.025%. The complex dynamic modulus was measured by imposing a small dynamic strain to assure linear viscoelastic behavior of the fiber. Optical micrographs were obtained with a Nikon polarizing microscope (Labophot 2-Pol). To achieve isothermal conditions in the measurements, the sample was thermostated to ±0.2 deg by a temperature controller (Linkam TH-600PH) of Japan High-Tech Co. Ltd. Observations were made after 30 min to ensure the attainment of a thermal equilibrium. Scanning electron microscopy (SEM) and wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS) patterns were obtained using methods described elsewhere.[14,15]

Results and Discussion

Table 1 shows Young's modulus and the tensile strength of drawn PTFE fibers. As described before, the raw filaments clamped with the indicated sag ratios were annealed for 30 min at 360 °C and cooled to room temperature at the indicated rates. The annealed filaments were heated again for 30 min at 388 °C and were elongated at a rate of 50 mm/s up to 75 or 100 times. For most of the specimens, the tensile strength and Young's modulus are higher than 20 and 1 GPa, respectively, at 25−26 °C associated with the crystal transition relating to a drastic decrease in Young's modulus. The maximum values of Young's modulus and tensile strength of the drawn fiber with a draw ratio of $\lambda = 100$ reached 57.6 and 2.31 GPa, respectively, when the monofilament, which was prepared by heat treatment with a sag ratio of 25% and subsequently cooled to room temperature at a rate of 10 °C/min, was employed as a test specimen. In comparison with the reports by Okuyama et al.[12] and Uehara et al.,[13] a drastic improvement could be realized for tensile strength in the present method. The raw filament with a 25% sag ratio was straight between the jaws during its shrinkage under the heating and cooling processes, but the inner tension within the raw filament detected by the stretching device was almost zero, indicating that the intrinsic shrinkage of the unconstrained raw filament is about 25%. Incidentally, the inner tension increased with a decreasing sag ratio and, at sag ratios <7%, the raw filaments were torn by the drastic inner tension during the cooling process. This suggests that the shrinkage creates an intermolecular entanglement mesh sufficient to assure the formation of a high modulus and high strength within the raw filaments, leading to a free molecular motion. It may be questioned why Young's modulus and the tensile strength of the fiber due to elongation of the monofilament prepared by heat-treating with a 30% sag ratio are lower than those of the monofilament prepared with a 25% sag ratio. This remains unknown but may be due to a nonuniform shape with some crimps and a nonuniform fiber diameter.

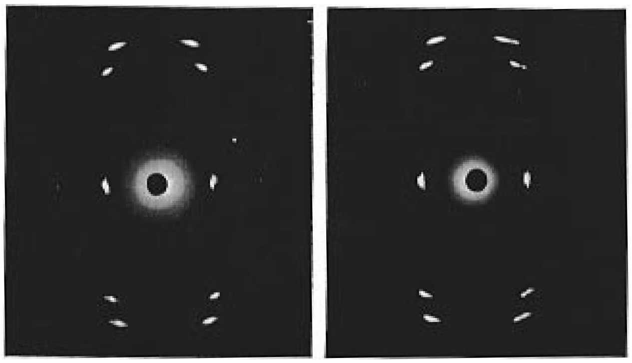
(a) (b)

Figure 1. WAXD patterns from the drawn fibers ($\lambda = 100$) prepared from monofilaments: (a) fibers prepared by drawing the monofilaments heat-treated with 25% sag ratio and cooled to room temperature at the rate of 10 °C/min; (b) fibers prepared by drawing the monofilaments heat-treated with fixed dimensions without the following cooling process.

Among the monofilaments prepared by heat treatment with a 25% sag ratio, the crystallinity depended on the cooling rate. The crystallinities at a cooling rate of 10, 1, and 0.5 °C/min were 25.5%, 31.6%, and 34.0%, respectively. Judging from the results in Table 1, it is evident that high-modulus and high-strength PTFE fibers could be realized by elongation of monofilaments with the lowest crystallinity, although the corresponding drawn fibers had the highest strength and modulus. This means that the number of entanglements increases as the crystallinity decreases. Incidentally, the crystallinity of the drawn fibers cooled at 10°C/min was about 45% but the crystallinities of the other two fibers were 40% or less.

Parts a and b of Figure 1 show WAXD patterns from the fibers obtained by ultradrawing ($\lambda = 100$) of the monofilaments prepared by the heat treatment of the raw filaments with a 25% sag ratio and with fixed dimensions, respectively. The latter fiber was prepared without a following cooling process. The raw filaments were annealed for 30 min at 388 °C and elongated immediately up to 100 times. Both patterns display very sharp diffraction spots for the (100), (106), and (107) reflections,[4] indicating an extremely high orientation of PTFE molecules in the stretching direction, which is quite similar to the orientational mode of ultradrawn polyethylene.[14−18] The preferential orientation of PTFE crystallites within the monofilaments with respect to the extrusion direction was also confirmed by the WAXD patterns (not shown in this paper). Incidentally, the reflections from the monofilaments exhibited more effective molecular orientation as the sag ratio became lower. This is due to an increase in the inner tension due to the restriction on the shrinkage of the monofilaments under the cooling process.

Figure 2 shows SAXS patterns (through view), in which patterns a and b show scattering from the raw filament and the monofilament prepared by the heat treatment with a 25% sag ratio, respectively, while

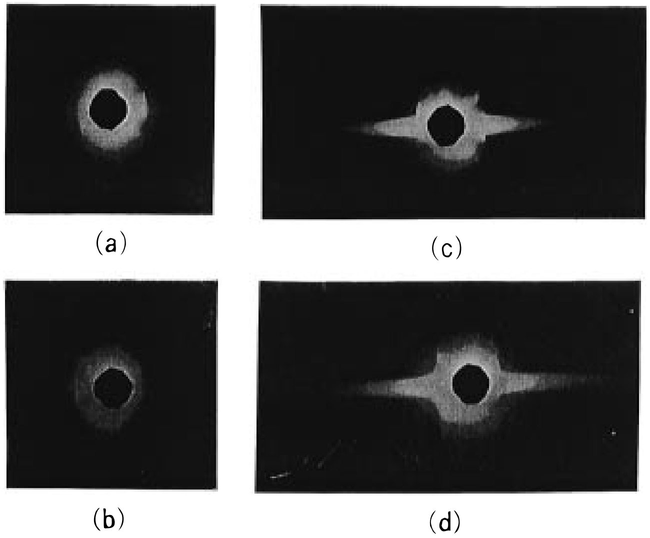

Figure 2. SAXS patterns from four kinds of specimens: (a) raw filament; (b) monofilament heat-treated with a 25% sag ratio and cooled to room temperature at the rate of 10 °C/min; (c) drawn fiber prepared from the monofilament corresponding to (b); (d) fiber prepared by drawing the monofilament heat-treated at fixed dimensions without the following cooling process.

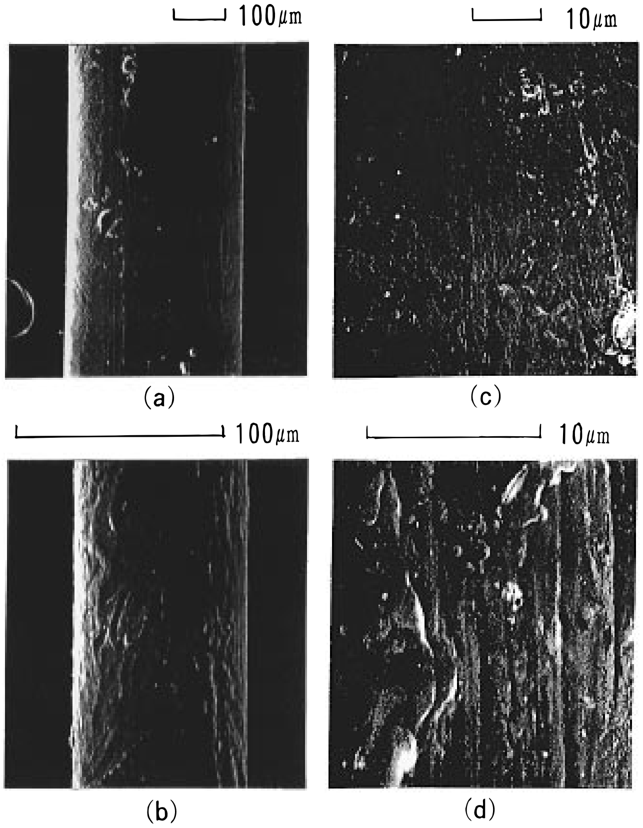

Figure 3. Scanning electron micrographs: (a) monofilament heat-treated with a 25% sag ratio and cooled to room temperature at the rate of 10 °C/min; (b) drawn fibers prepared from the corresponding monofilament; (c) enlargement of (a); (d) enlargement of (b).

patterns c and d show scattering from the fiber prepared by ultradrawing of monofilaments heat treated at fixed dimensions and with a 25% sag ratio, respectively. In (d), the monofilaments were drawn without the following cooling process, as described before. The draw ratio is 100 times. The SAXS patterns a and b show circular-type diffuse scattering, while patterns c and d show an equatorial streak that originates in scattering from elongated voids. These patterns indicate either an absence of crystal lamellae or a difference of electron densities between crystal and amorphous phases which is too small to give a distinct scattering maximum of SAXS intensity distribution in the meridional direction. If the former is the case, the mechanism of ultradrawing of PTFE is quite different from that of polyethylene. This shall be discussed later.

The change in the appearance by elongation of the monofilaments heat-treated with a 25% sag ratio was clarified by SEM. Parts a and b of Figure 3 display the micrographs of the monofilament and the drawn fiber ($\lambda = 100$), respectively and (c) and (d) are enlargements. As illustrated in the four micrographs, the surface of the monofilament has a smooth but fibrillar texture within the drawn fiber oriented in the stretching direction. The enlarged micrograph (d) illustrates oriented fibrillar textures having some projections within the drawn fiber ($\lambda = 100$). Such projections have been observed for initial elongation of ultrahigh molecular weight polyethylene (UHMWPE) dry gel films,[19] but they were disruptively deformed into fine filaments with further elongation up to 300 times. The morphology of ultradrawn UHMWPE films indicates the possibility of a more than 100 times elongation of PTFE fibers, but the elongation could not be realized because of the physical restriction of the size of the oven.

Figure 4 shows differential scanning calorimetry (DSC) curves and optical micrographs (crossed polarization) at temperatures beyond the apparent melting point, in which the results in the upper graph correspond to the monofilament heat-treated with a 25% sag ratio and cooled to room temperature at 10 °C/min, while the results in the lower graph correspond to the fiber drawn by the monofilament. Among the seven micrographs in the upper graph, two micrographs belong to the monofilament (FEA) heat-treated in a ceramic box under unconstrained dimensions and cooled to room temperature at 10 °C/min. Interestingly, the birefringent phase of all the specimens spontaneously exhibited an irregular or regular patchwork of predominantly blue, yellow, and pink regions at temperatures slightly higher than their apparent melting point estimated by the DSC curve, indicating a phase transition from a solid to a liquid crystal. Such a phase transition could not be observed for the raw filaments at elevated temperatures. The brightness disappeared and reappeared on the rotation of the sample stage, indicating the preferential orientation of PTFE molecules with respect to the stretching direction. The appearance of the thermotropic liquid crystal at temperatures above the apparent melting point is thought to be reflected in the rigidity of PTFE chain molecules. On heating beyond 450 °C, the micrograph showed a decreasing brightness and finally a dark field, indicating a random orientation of PTFE chain molecules. The orientation of the specimens persisting beyond the apparent melting point could be confirmed for ultradrawn polyethylene prepared from dilute solutions by crystallization/gelation[14,15] according to the method of Smith and Lemstra.[16,17] For ultradrawn polyethylene films drawn up to 300 times, the apparent melting point was 155 °C, which is higher than the theoretical value of 145.5 °C.[20] This may be explained by assuming that the polyethylene chains in the melt retained the extended chain arrangement so that the entropy of fusion would be smaller than the value calculated for random coils in

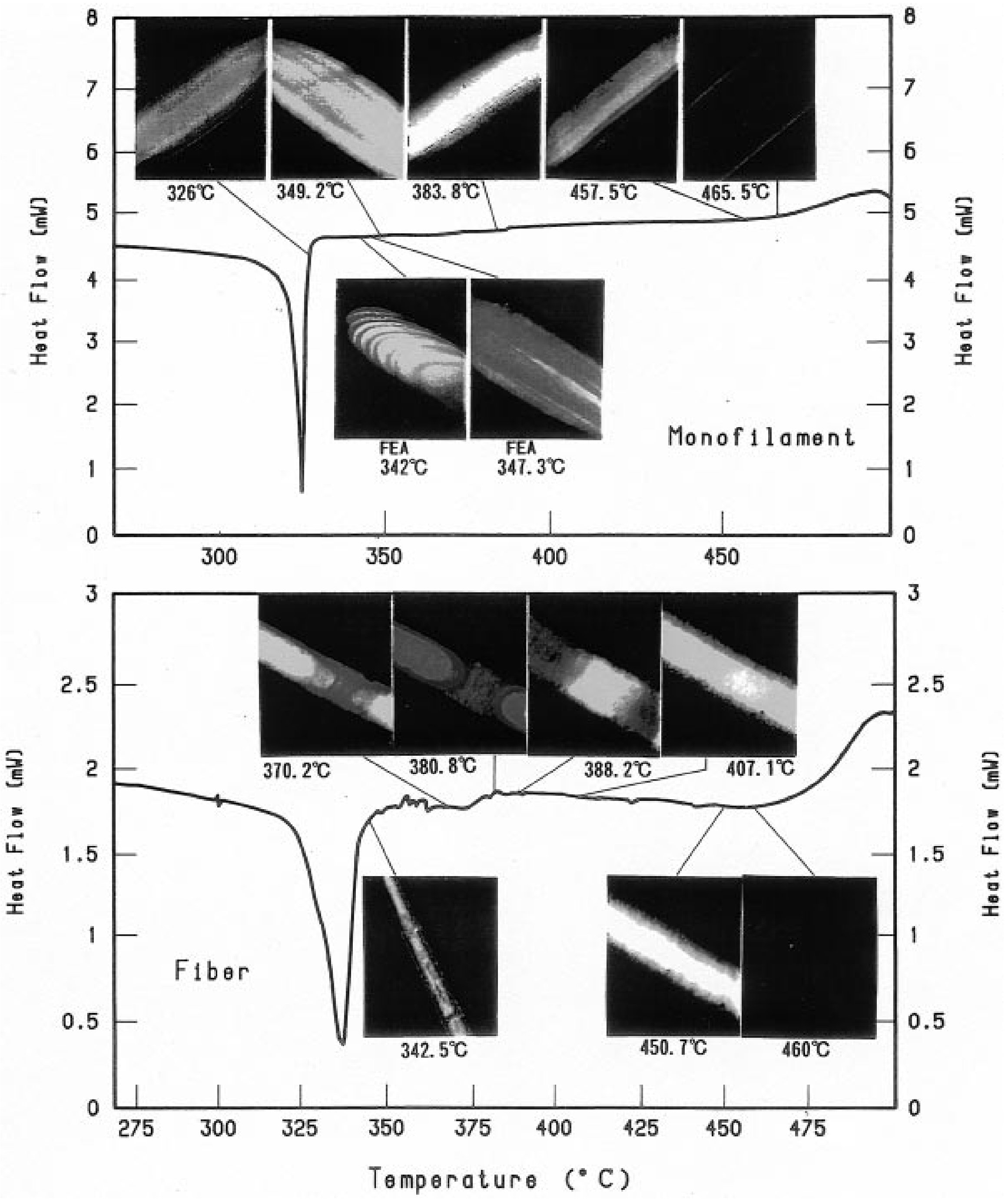

Figure 4. Differential scanning calorimetry (DSC) curves and optical (crossed polarized) micrographs at the indicated temperatures. Upper: heat-treated with 25% sag ratio and cooled to room temperature at the rate of 10 °C/min. Lower: the drawn fiber ($\lambda = 100$) of the above monofilament. Incidentally, among the top seven micrographs, two micrographs belong to the monofilament (FEA) heat-retated in a ceramic box under unconstrained dimensions and cooled to room temperature at 10 °C/min.

the melt. However, it may be expected that because of the chain rigidity of PTFE, the chain restriction for the present PTFE above the apparent melting point is still considerable and allows the formation of liquid crystals. The reversibility of the liquid crystal transition in the temperature range 300−370 °C could be confirmed under optical micrographs (cross-polarized). The appearance of liquid crystals was also observed with optical micrographs (crossed-polarized) for an anisotropic suspension of PTFE whiskers produced by emulsion polymerization with 1% w/v of ammonium perfluorodecanoate as surfactant.[11] This liquid crystal is lyotropic, different from the present case, but the formation of liquid crystals demonstrates the chain rigidity of PTFE.

Figure 5 shows the temperature dependence of the storage modulus E' and the loss modulus E'' at a frequency of 10 Hz for the fiber ($\lambda = 100$) prepared by elongation of the monofilament heat-treated with a 25% sag ratio. The measurements could be carried out in the range −150 to +330 °C. The storage modulus tends to decrease gradually with temperature except for a drastic decrease around 20 °C. The loss modulus E'' shows a peak around 20 °C. This peak corresponds to the β dispersion associated with the crystal transition, which is known to be very sensitive to the decrease in the storage modulus.[18] Even so, the storage modulus was about 70 GPa at 20 °C. The value is higher than the ultimate values (41 GPa) corresponding to the

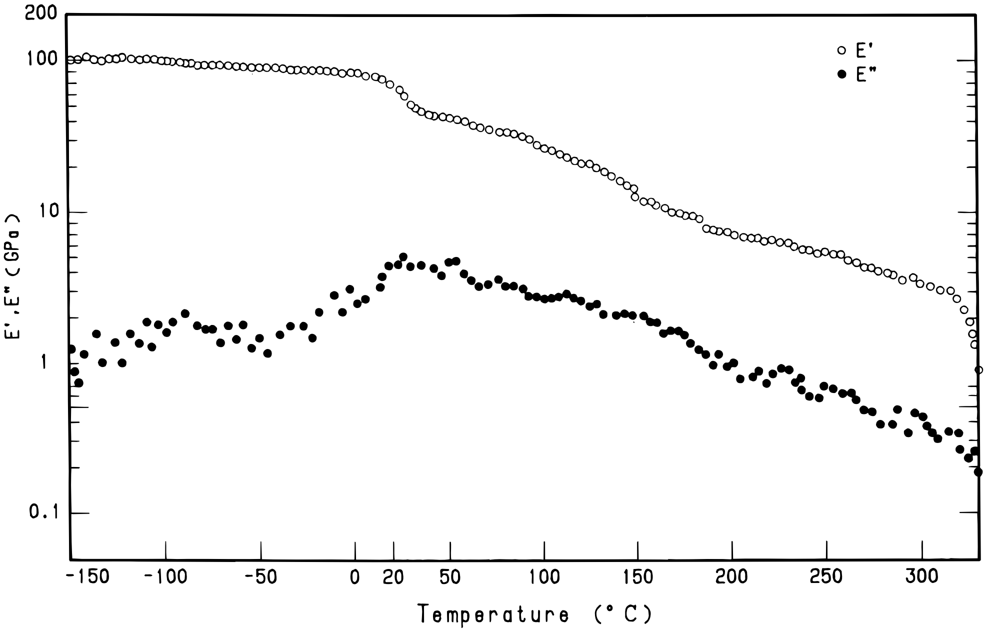

Figure 5. Temperature dependence of the storage and loss moduli of the drawn fiber of the monofilament heat-treated with 25% sag ratio and cooled to room temperature at the rate of 10 °C/min.

crystal lattice modulus of polypropylene in the chain direction[3] and is equal to the modulus of aluminum.

To produce high-strength and high-modulus PTFE fibers, the results in Table 1 and Figure 4 together lead to two conclusions: (1) the raw filaments clamped between jaws of a stretcher must be heat-treated with a sag ratio of 25% corresponding to their intrinsic shrinkage under unconstrained dimensions and cooled to room temperature at a rate of 10 °C/min, and (2) the monofilaments must be elongated at 388 °C, higher than the apparent melting point. It is of interest to consider the difference of facile drawability between PTFE and polyethylene. For polyethylene, the effective drawability is attributed to the existence of a network in the wet or dry gel in which crystalline regions act as the junction points. The maximum draw ratio depends principally on the concentration of the solution from which the gel was prepared, because of a sufficiently high molecular weight ($M_w = 6 \times 10^6$).[21,22] This phenomenon was attributed to a greatly reduced number of entanglements per molecule in solution cast/spun polymers in comparison with those obtained from the melt.[23] In contrast, for ultrahigh molecular PTFE with $M_w = 8.4 \times 10^6$, the heat treatment with a 25% sag ratio corresponding to the intrinsic shrinkage of the filament is an essential condition to produce high-strength and high-modulus PTFE materials. In the heating and cooling processes, a suitable number of entanglements may be formed and they play an important role in transmitting the inner stress uniformly at the junctions of PTFE chains. We propose that because of the molecular chain rigidity of PTFE, a number of entanglements to hamper the facile drawability cannot be formed even in the temperature range 260–388 °C, higher than the apparent melting point, in spite of ultrahigh molecular weight PTFE ($M_w = 8.4 \times 10^6$). If this were not so, PTFE chains would be random coils and the liquid crystalline phase in Figure 4 could not be observed. Actually, when the raw filaments with a 0% sag ratio were maintained for 30 min at 388 °C and were drawn at that temperature without the following cooling processes, the drawn fibers with high molecular orientation provided only a Young's modulus higher than 40 GPa but the corresponding tensile modulus was less than 0.5 GPa, although the X-ray pattern from this fiber showed the same profile as the pattern from the fiber with tensile strength 2.31 GPa (see Figure 1). This is probably due to a too small number of entanglements per molecule to assure the high tensile strength. Accordingly, it is evident that the shrinkage of the raw filaments under the cooling process plays an important role in increasing the number of entanglements. Finally, we must emphasize that when the raw filaments were heated under unconstrained dimensions for 30 min at 360 °C in a ceramic box and cooled at 10 °C/min to room temperature, the maximum Young's modulus and tensile strength of the fiber drawn up to 100 times reached 82 and 2.65 GPa, respectively. These values are much higher than the maximum listed in Table 1. This must be taken into account in further studies.

Conclusion

Raw filaments of PTFE were prepared by paste extrusion of fine powder ($M_w = 8.4 \times 10^6$) produced by emulsion polymerization. The raw filaments with the sag ratios 10, 25, and 30% were clamped in an automatic stretching device. They were annealed for 30 min at 360 °C and cooled to room temperature. The cooling rates chosen were 0.5, 1, and 10 °C/min. The annealed monofilaments were heat-treated again for 30 min at 388 °C and then elongated up to 100 times at the same temperature. The maximum values of Young's modulus and tensile strength reached 57.6 and 2.31 GPa, respectively, at about 25 °C. These values could be realized when the raw filaments used in the present work were heat-treated at 388 °C with a sag ratio of 25% corresponding to the intrinsic shrinkage of the filaments. At 388 °C, higher than the apparent melting point of PTFE, thermotropic liquid crystals could be observed under optical microscopy (crossed-polarized). It is thought that molecular chains of PTFE are stiffer than those of polyethylene and the 25% shrinkage of raw filaments under annealing and cooling processes assures a suitable level of entanglement mesh that effectively transmits the drawing force and prepares high-strength PTFE fibers.

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