Melt-Spinning Process of a Tetrafluoroethylene–Hexafluoropropylene Copolymer

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ABSTRACT: An industrial melt-spinning process of tetrafluoroethylene–hexafluoropropylene copolymer (FEP) using an extruder was studied. The novel "spinneret," having both a large-diameter spinning nozzle and a high-temperature vessel, was used to solve the problem of filament breakage on the spinning line caused by high melting viscosity of FEP. The extruder, with its long feed zone, was newly designed to function with a geared pump. The strength of fibers increased with drawing of as-spun fiber. FEP fibers up to six denier were continuously produced through long-run production. According to this new process, FEP fibers can be supplied for textile or industrial application. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2366–2371, 2002

Key words: drawing; extrusion; fibers; fluoropolymers

INTRODUCTION

Fluorocarbon polymers have very excellent properties, such as high resistance to chemicals and thermal, electrical, and surface properties (e.g., nonstick, water-repellent, low frictional coefficient). Polytetrafluoroethylene (PTFE) is one of the representative fluorocarbon polymers. It is a crystalline and thermoplastic polymer. However, even at a temperature higher than the melting point, PTFE still shows high viscosity,[1] which makes for difficult processing. The processing method of PTFE products is quite different from that of common polymer. The typical methods are compression molding under high baking temperature and paste extrusion moldings.[2]

To improve the molding performances, various tetrafluoroethylene copolymers have been developed, for example, tetrafluoroethylene–perfluoroalkoxyvinyl ether copolymer (PFA), tetrafluoroethylene–ethylene copolymer (ETFE), and FEP, which is the copolymer of tetrafluoroethylene and hexafluoropropylene (HFP). The content of HFP in FEP affects the crystallinity, melting, and viscosity characteristics. These copolymers show high viscosity above the melting temperature. Films and electrical wire cables have already been commercialized, but to date, fibers have not been developed by the melt-spinning process.

The PTFE fibers have been prepared by three methods.[3] The first method of producing PTFE fiber is the *split peel process.* PTFE rod is made by compression molding, peeled into the film; afterward, the film is torn into filaments, which are stretched and annealed. The second method is *matrix spinning,* in which the mixture of PTFE and viscose is spun and then washed, dried, and stretched. The third method is *paste extrusion,* in which the mixture of the polymer powder and lubricating oil is extruded into a rod, calendared, dried, and stretched.

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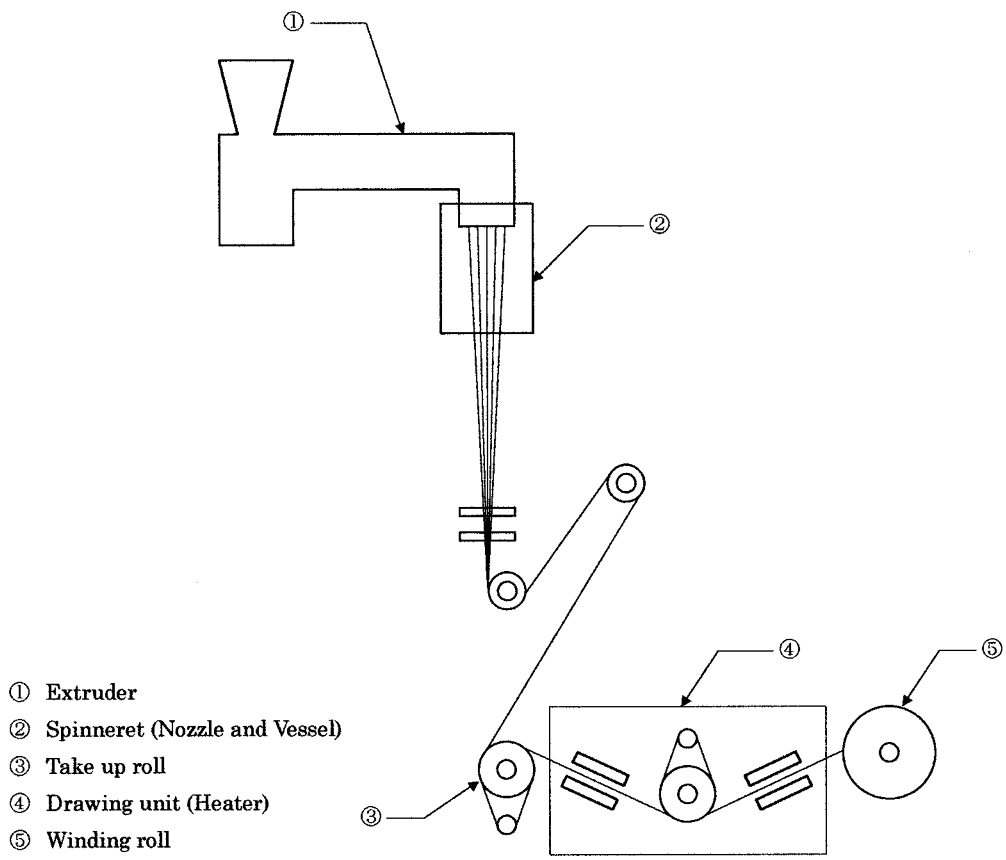

Figure 1 Schematic of FEP melt-spinning apparatus.

To prepare fluorocarbon fibers, the melt-spinning process should be suitable because conventional synthetic fibers are produced generally by this process.

In this study, FEP was selected because it can be extruded in a molten state, even though its viscosity is very high.[4] In view of this, however, there arose the need to develop new equipment for its production.

The purpose of this study is to establish the melt-spinning process of FEP multifilaments with fine and uniform diameter.

EXPERIMENTAL

Melt-Spinning Apparatus

A schematic of the equipment for the melt-spinning of FEP is shown in Figure 1. FEP pellets were supplied to the extruder in a molten state. The fixed weight of the polymer was extruded and the multifilaments were taken out through the spinneret. When fluorocarbon polymer is molten at 300–400°C, corrosive gas generates by decomposition of FEP. Therefore, the screw and cylinder in the extruder, the die, and the spinneret should resist both high temperature and corrosive gas. To avoid the corrosion, high-content nickel alloy, Hastelloy C-276 (Mitsubishi Kinzoku Co., Japan) was used. No trouble caused by corrosion and heat was encountered throughout this investigation.

The diameter of the extruder was 30 mm ϕ and the ratio of screw length and cylinder diameter (L/D) was 26. Two types of nozzle, with 48 and 200 holes, were used.

The as-spun filaments were drawn and wound.

Materials

Tetrafluoroethylene–hexafluoropropylene copolymer [Daikin Co., Japan; NEOFRON FEP NP-100 (MFR = 24 g/10 min at 380°C, 5 kg weight)] was used in this investigation. The content of hexafluoropropylene was 9.1%, which was determined by infrared spectroscopy[5] using a Japan Spectroscope FT/IR-550.

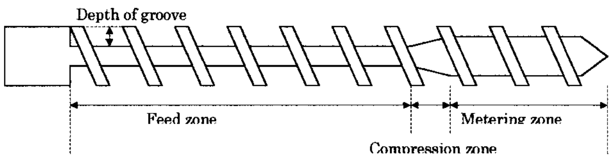

Figure 2 Schematic of our designed view.

RESULTS AND DISCUSSION

Extruding Process

In general, by the melt-spinning process of synthetic fiber, such as polyester, nylon, acrylic fiber, and so forth, the extruding machine consists of the extruder and the geared pump.[6] The extruder usually does not exert enough control over the fixed extruding weight, so the geared pump is usually equipped at the same time, which is very important in melt-spinning process.

In long-time running of FEP extrusion molding, a contamination is observed in the extruded polymer, which is caused by decomposition of polymer that is generated in the dead space. In this investigation, we could run for 10 days; after that time, the contamination appeared and the fibers were broken, so we had to stop running and clean up the equipment every 10 days. Although the cleaning the extruder did not take much time, cleaning the geared pump was difficult because of its complicated structure; in fact, we had to replace the geared pump.

We designed a new extruder without a geared pump. The extruder with $L/D = 26$ was slightly larger than the conventional extruder ($L/D = 24$).[2] The screw type was full-flight and the depth of the groove was slightly large. This screw had a long feed zone, with 70% of the screw length. Thus the compression zone was steep, whereas the length of the metering zone was short. A schematic of the screw used for the extruder is shown in Figure 2. The extruded polymer weight was controlled within $\pm 1\%$.

The weight of fiber depends on the number of filaments (number of holes in the spinneret). When the number of holes was 200, the extruded weight was 10 kg/h, and the denier of filament was 6 (the diameter is 20 μm). This was fit for industrial scale.

Spinning Process

The capability of spinning depends on filament breakage caused by either cohesion break[7] or melt fracture, both of which phenomena we have to avoid during spinning. The cohesion break is observed quite often for high-viscosity polymers such as FEP.

When the polymer is extruded from a narrow opening, the shear velocity of the polymer increases.[8] Then the surface of the extruded polymer becomes rough, thus leading to filament breakage. The shear velocity at the melt fracture point is called the *limiting shear velocity*. It is lower for FEP than for conventional polymers.[9] The limiting shear velocity of FEP for extrusion is about 20 s^{-1} and for injection is about 2 s^{-1} at 372°C, respectively.[2] Each value is lower than that of conventional polymers, for example, poly(hexamethylene adipamide) (Nylon 66) is about 10^5 s^{-1} at 275°C.[7] We measured the limiting shear velocity using the equipment shown in Figure 3. The limiting shear velocity of FEP NP-100 was 9.8 s^{-1} at 375°C.

Photographs of filament surface with different values of shear velocity are shown in Figure 4. Photographs (a) and (b) in Figure 4 were the fibers prepared by the equipment shown in Figure 3. The shear velocity of photograph (a) was at 5.0 s^{-1} and the filament surface was smooth. Photograph (b) was at 11.0 s^{-1}. The melt fracture occurred because this value was over the limiting shear velocity. Photograph (c), prepared from the spinning nozzle (no high-temperature vessel) at 15.0 s^{-1}, shows that the surface was rough and was easily broken by taking up.

To avoid the melt fracture, the orifice diameter of the spinning nozzle must be large. When the large diameter is applied, the diameter of the filament decreases rapidly. At this condition the cohesion break readily occurs.

To avoid the melt fracture and the cohesion break, we designed the "spinneret" to have both the nozzle and the high-temperature vessel, as shown in Figure 5. The nozzle has a large diameter with 0.8 mm ϕ and short length to prevent

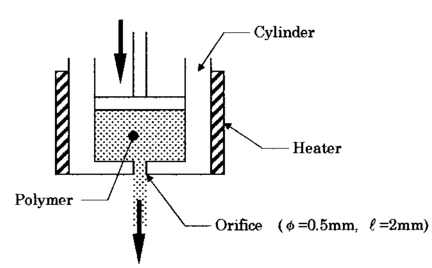

Figure 3 Schematic of measuring the limiting shear velocity.

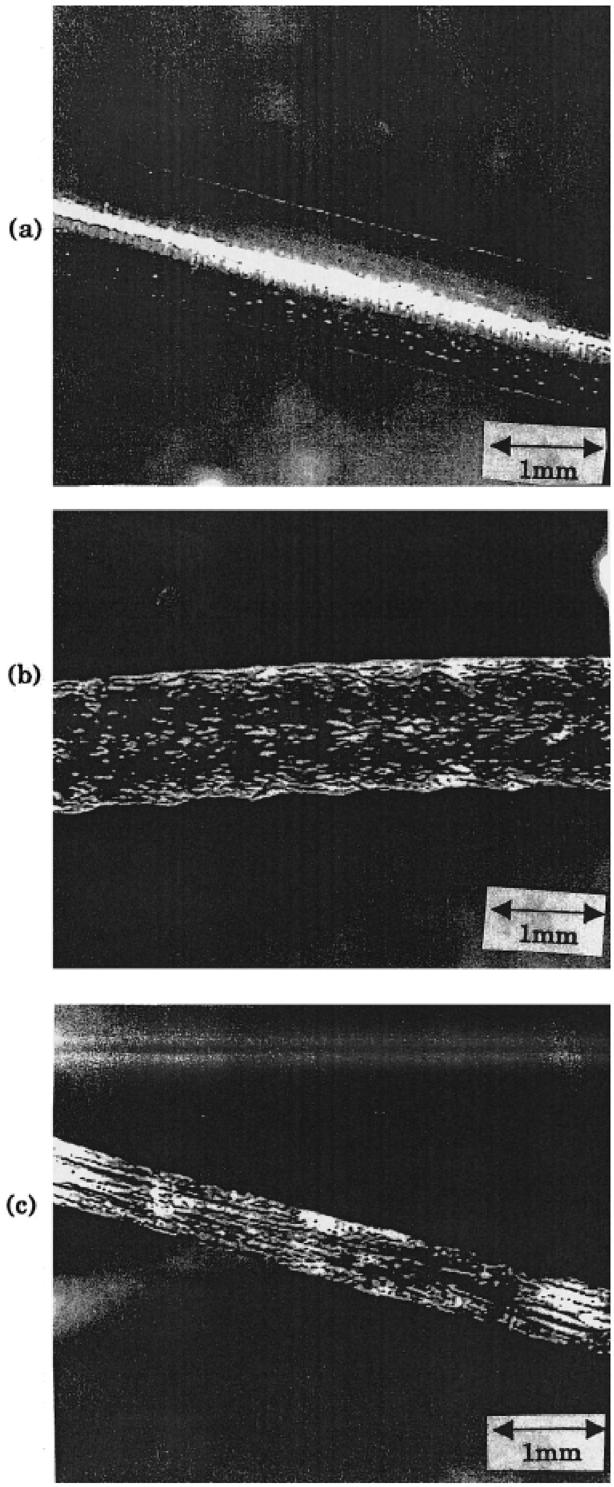

Figure 4 Melt-fracture phenomena of FEP. (a) Shear velocity = 5.0 s^{-1}, prepared by the equipment shown in Figure 3; (b) shear velocity = 11.0 s^{-1}, prepared by the equipment shown in Figure 3; (c) shear velocity = 15.0 s^{-1}, prepared by spinning nozzle (no high-temperature vessel).

the melt fracture. This orifice diameter was more than 10 times larger than that of the conventional spinneret of synthetic fibers. The high-temperature vessel length was 50 cm and it was kept higher than the spinneret temperature. The vessel was heated by band heater because blowing hot air broke the filaments.

The temperature of spun fibers was as high as over 350°C, after which they were cooled at ambient temperature. The take-up speed was up to 800 m/min, but at higher than 900 m/min, the fibers broke. In this way, we succeeded to produce the as-spun multifilaments of FEP.

Drawing Process

The fibers were drawn by a two-step stage with heating. The heater length was 2 m at each step. Fibers stayed in the heater for 0.2–0.4 s. The first heater temperature was 150°C and the second heater was at 160°C. When the heater temperature was higher than 180°C or lower than 100°C, the fibers were broken. The temperature of drawing is between the glass-transition temperature and the melting temperature, the same as that of synthetic fiber.[7] The proper condition of draw ratio was 1.5–2.0 in the first step and total draw ratio was 2.0–2.5. When the total draw ratio was higher than 3.0, the fibers were broken. The draw ratio of polyester fiber by heat is usually more than 4 times; then, the draw ratio of this study was lower than that of polyester.[7] In this condition we were able to obtain the fiber strength with 0.14 GPa.

The take-up roll speed was varied stepwise from 100 to 800 m/min. Drawing of the fibers was carried out continuously at 150 and 160°C. The

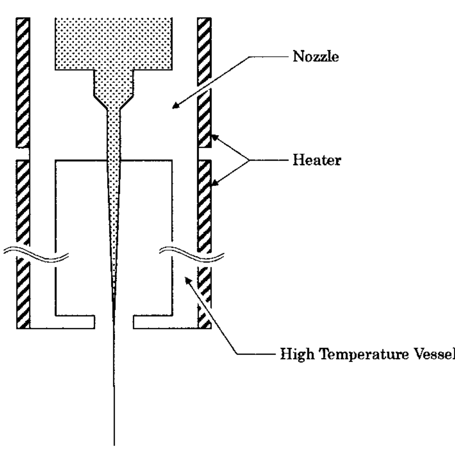

Figure 5 Schematic of our designed "Spinneret."

Table I Preparation Conditions of FEP Fibers

Sample	Take-up Velocity (m/min)	Draw Ratio	Capability of Spinning
1	100	Not drawn	Good
2	400	Not drawn	Good
3	800	Not drawn	Good
4	900	Not drawn	Filament break
5	400	1.80	Good
6	400	2.58	Good
7	400	3.00	Filament break

draw ratios of the fibers were 1.80 and 2.58, respectively. The spinning conditions are summarized in Table I. Stress and strain curves of the filaments are shown in Figure 6. The mechanical properties of the fiber depend significantly on the spinning conditions. By increasing the take-up velocity (samples 1–3), the strain decreased and stress slightly increased. When the draw ratio was 1.80 and 2.58 (samples 5 and 6), the stress increased remarkably. Drawing effectively increases the modulus and the tensile strength. The drawing process was necessary to strengthen the fiber similar to that of the usual melt-spinning polymer.

Total Process and Operating Conditions

Total operating conditions and properties of FEP to produce multifilaments are shown in Table II. When the temperature of the spinneret vessel was lower than that of the nozzle and when the second drawing temperature was 180°C, the filaments were broken (runs a-2, a-3, b-2, b-3).

Multifilaments of 1200 denier were produced for long-time running of 10 days. The number of filaments was 200 and the filament diameter was 20 μm (6 denier). The operating condition was run a-1. Also, 144 denier with 24 filaments and 20 μm diameter were produced for 10 days. The operating condition was run b-1. In this case, 288 denier multifilaments were spun and drawn, then separated into two winding rolls. No production difficulties and no breakage were encountered during these runs.

When the number of holes was 48, the strength was 0.14 GPa; in the case of 200, the strength was 0.12 GPa. The filament diameter was uniform with 20 μm, as shown in Figure 7. Then, the FEP filaments were characterized by properties that were useful for textile or industrial uses.

CONCLUSIONS

In conclusion, the process using melt-spinning of tetrafluoroethylene–hexafluoropropylene copolymer was studied and developed.

The "spinneret," consisting of the nozzle and the high-temperature vessel, was newly designed.

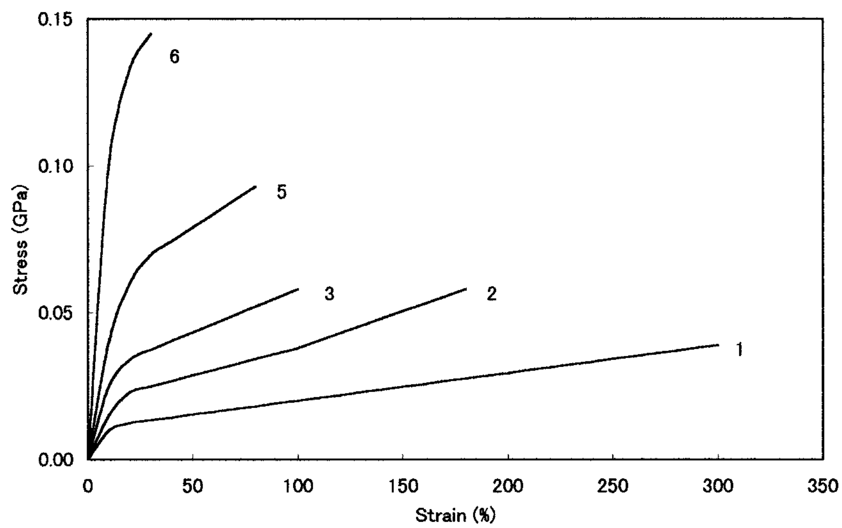

Figure 6 Stress–strain curves of as-spun fibers and elongated fibers. (1) As-spun fiber, take-up velocity = 100 m/min; (2) as-spun fiber, take-up velocity = 400 m/min; (3) as-spun fiber, take-up velocity = 800 m/min; (5) elongated fiber of 2, draw ratio = 1.80; (6) elongated fiber of 2, draw ratio = 2.58.

Table II Operating Conditions for FEP Fibers and Characteristics of the Filaments

		Spinneret			Drawing				Properties of Filaments		
		Nozzle									
Run	Extruder Cylinder Temp. (°C)	Number	Temp. (°C)	Vessel Temp. (°C)	First Temp. (°C)	Second Temp. (°C)	Total Draw Ratio	Capability of Spinning	Filament Diameter (μm)	Tensile Strength (GPa)	Elongation (%)
a-1	345	48	375	380	150	160	2.5	Good	20	0.14	20
a-2	345	48	375	340	—	—	—	Filament Break	—	—	—
a-3	345	48	375	380	160	180	2.5	Filament Break	—	—	—
b-1	340	200	375	390	150	160	2.0	Good	20	0.12	28
b-2	340	200	375	350	—	—	—	Filament Break	—	—	—
b-3	340	200	375	390	160	180	2.0	Filament Break	—	—	—

The orifice diameter had large and the vessel temperature was kept upper than that of the nozzle. The large-diameter orifice prevented melt fracture. The slow transformation of fiber diameter in the vessel obstructs cohesion breakage. This "spinneret" solved the problem of filament breakage. There is no need for a cooling unit because cooling was sufficient at room temperature.

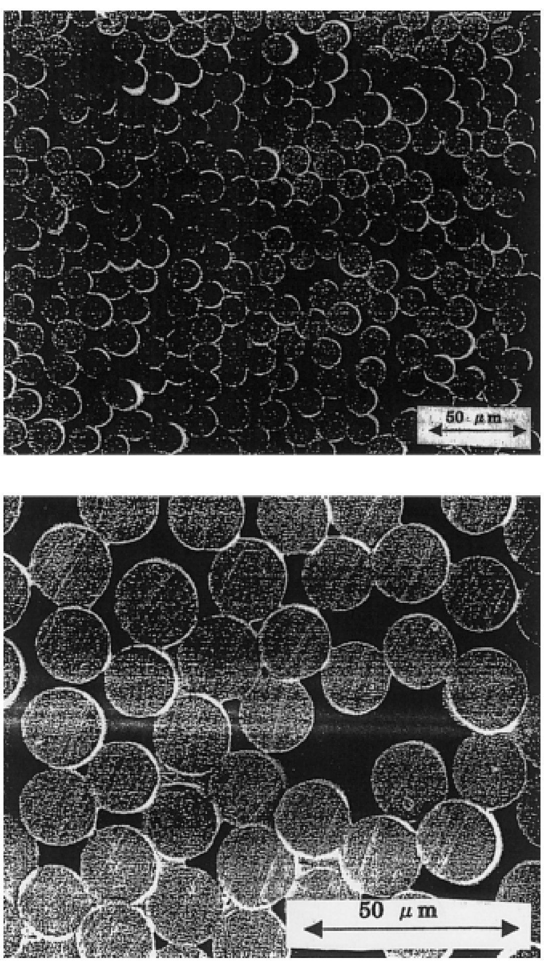

Figure 7 Cross section of FEP filaments.

The extruding process was established by the newly designed screw and cylinder. The good performance of the extruder controlled the weight of polymers, so the geared pump was omitted.

The drawing of as-spun FEP fiber was effective to increase the modulus and the tensile strength. The drawing process was necessary to strengthen the fiber.

The total process of producing FEP fine denier filaments was confirmed through long-run production. The filaments were characterized by properties that make them sufficiently useful for textile or industrial uses.

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