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Fiber making directly from poly(tetrafluoroethylene) emulsion

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ABSTRACT

Poly(tetrafluoroethylene) (PTFE) fiber with a superior mechanical property was prepared directly from its emulsion by the novel manufacturing process. The PTFE emulsion turned into a paste when a high shear flow was applied and the paste was extruded through a nozzle into a strand consisting of fine PTFE particles. The diameter of the strand was reduced stepwise by applying the die-drawing process through a conical die at a low temperature. The strand was further die-drawn down at elevated temperatures into fine PTFE fibers with a highly oriented crystalline structure. The crystalline orientation factor of the PTFE fiber reached very close to unity. Although the fibers obtained have a very high tensile modulus, the tensile strength was not as high as that expected from the crystalline orientation, suggesting that the presence of some defects in the PTFE fiber formed in the instantaneous deformation.

1. Introduction

Poly(tetrafluoroethylene)(PTFE) has a chemical structure, $-(CF_2-CF_2)_n-$. The fluorine atoms surround the carbon backbone like a protective sheath, creating a chemically inert and relatively dense molecule with very strong carbon–fluorine bonds. The polymer does not melt below 327 °C and has a low coefficient of friction. These properties allow it to be used for bushings and bearings that require no lubricant, as liners for equipment used in the storage and transportation of strong acids and organic solvents, as electrical insulation under high-temperature conditions, and in its familiar application as a cooking surface that does not require the use of fats or oils.

Fabrication of PTFE products is difficult because the material does not flow readily even above its melting point [1]. Although the PTFE with a very low Mw tends to flow above its melting temperature, the melt processed parts are usually very brittle. Tervoort et al. [2] reported that the blend of PTFEs with a moderate and a low Mw can be melt compression molded into sheets and extruded to be strands. The sheet and the strand obtained are ductile and tough. Unfortunately they did not perform further structure development and improvement of the mechanical property at all.

Usually molded parts have been prepared by compressing and heating fine powders mixed with volatile lubricants. Metallic surfaces can be sprayed or dipped with aqueous dispersions of PTFE particles to form a permanent coating. The fibers of PTFE have been produced by utilizing complex processes. One of them is called “the emulsion spinning” [3]. The PTFE emulsion and the viscose are mixed and wet-spun into fine fibers of PTFE/Cellulose blend. After sintering at an elevated temperature to fuse the PTFE particles and to eliminate the cellulose component, the fiber is drawn and annealed to be fine PTFE fibers. Another process is to make slit yarns from PTFE film [4–6]. Some auxiliary is added to the PTFE fine particles and the paste is extruded through a slit die into film. After sintering at an elevated temperature to fuse the PTFE particles and to eliminate the auxiliary, the film is slit into flat yarns.

Here we have developed a novel fiber manufacturing processes directly from the PTFE emulsion much simpler than those complicated processes described above. PTFE thick strand was directly prepared from the emulsion in water and the thinning of the strand was carried out by the tensile die-drawing process at a low temperature (~90 °C). No auxiliary was necessary. Then the structure development of the strand was performed by the similar tensile die-drawing process at an elevated temperature (~380 °C). This paper shows the mechanism of the fiber formation and changes in various fiber properties during each stage of the manufacturing process.

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2. Experimental

2.1. Materials

PTFE emulsion was supplied by Asahi Grass Co. Ltd. This contains 60 wt% of PTFE fine particles with about 0.3 μm in average diameter dispersing in water. The dispersion state is stabilized with the addition of 3 wt% non-ionic surfactant, poly(oxyethylene) alkylether, C_xH_y–O–$(CH_2CH_2O)_{10}$–H, where $x = 12–13$ and $y = 25–27$, respectively. The cloud point of this surfactant is about 60 °C.

2.2. Preparation of the PTFE strand

PTFE emulsion was injected from a nozzle into a vessel at an apparent shear rate of 2×10^4 s^{-1}. Because of the viscous dissipation, the temperature of the emulsion went up to about 90 °C. The emulsion injected turned to a soft and more or less elastic paste containing 40 wt% of water. The paste was then extruded through a die with 1.6 mm in inner diameter to be a strand with 2 mm in diameter. The strand obtained is shown in Fig. 1(a).

2.3. Die-drawing

The PTFE strand was pulled stepwise through plastic conical dies with 0.75, 0.98, 1.2, 1.4 and 1.7 mm in inner diameters of the outlet and the half angle of the dies 6.5°. The die-drawing was carried out in water at 90 °C and the drawing velocity was set at 4.7 m/min.

The die-drawn strand was dried and further pulled through a metal conical die with an outlet diameter 0.5 mm and the half angle 30° heated at temperatures ranging from 250 to 380°. The drawing velocity was set at 0.8 m/min. The tension applied to the strand was measured with a tension meter (HS-4000, Eiko Sokki Co. Ltd).

2.4. Measurements and observation

Steady state shear viscosity and the dynamic viscosity of the emulsion were measured with a double cone type rheometer (RheoStress 600, HAAKE). The diameter of the cone was 60 mm and the cone angle was 2°. Dynamic viscoelasticity measurements of the PTFE paste was carried out by using a parallel plate rheometer (MR-300, Reoroji) at a 1% strain. Both Double cones and parallel plates were covered with a shield to prevent the water evaporation.

Mechanical property of the PTFE strand and the fibers was measured with a tensile tester (CATYT500BH, Yonekura Manufacturing Co. Ltd). The diameter of the strand was measured with a micrometer at each stage of the processing. Although some of the PTFE strands in the thinning process consists of the aggregation the particles, the apparent cross-section area calculated from the diameter was used to determine the mechanical property. Water content of the PTFE strand was determined by the weights of the wet and dry strands.

Thermal property was evaluated by using a DSC (DSC3100SA, Bruker axs) under N_2 atmosphere at a heating rate of 10 °C/min. The degree of crystal χ_c was determined from the melting peak area using Eq. (1).

$$\chi_c(\%) = \left(\frac{\Delta H_f}{\Delta H_f^{100\%}}\right) \times 100 \quad (1)$$

Where ΔH_f and $\Delta H_f^{100\%}$ are the melting enthalpies of the sample and the completely crystallized PTFE, 22.2 cal/g as reported by Starkweather et al. [7], respectively.

Wide-angle X-ray diffraction (WAXD) patterns were obtained at 19 and 24 °C on a flat imaging plate using a nickel-filtered CuKα radiation of the wave-length 0.1542 nm from a Rigaku RAD2C sealed beam X-ray generator operating at 40 kV and 18 mA. WAXD scans were recorded on a Rigaku RINT 2100 FSL system using nickel-filtered CuKα radiation operated at 40 kV and 30 mA from a Rigaku RINT 2000 X-ray generator.

Morphological study was carried out by using a SEM (VE-7800, KEYENCE) for the gold-coated surface. The sample was fractured in liquid nitrogen.

3. Results and discussion

3.1. Rheology of the PTFE emulsion

Because of the high injection rate applied to the PTFE emulsion, the temperature of the emulsion rose up to about 90 °C. As already mentioned, PTFE emulsion is stabilized with the addition of non-ionic surfactant. It has been known that the non-ionic surfactants lose their surface activation function above their cloud points and the particles tend to aggregate.

Fig. 2 shows the shear rate dependences of the steady shear viscosity of the PTFE emulsion measured at 25 and 60 °C. It showed nearly Newtonian behavior with a low viscosity at 25 °C indicating that the particles were well dispersed and did not form any 3-dimensional structure. On the other hand, it showed a strong shear thinning behavior at 60 °C suggesting that the particles form a strong 3-dimensional structure especially at a low shear stress level.

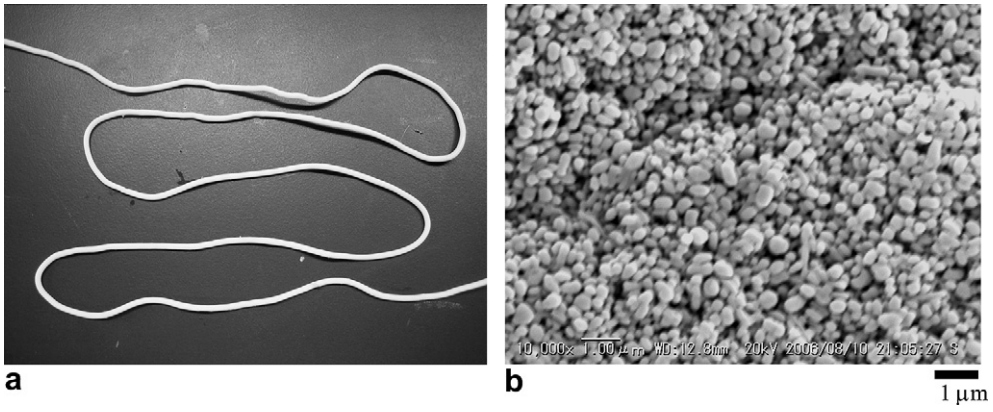

Fig. 1. PTFE strand (a) and its inner structure (b).