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Structure and properties of polytetrafluoroethylene (PTFE) fibers

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Abstract: Structure and properties of polytetrafluoroethylene (PTFE) fibers were characterized thoroughly by scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analyzing (TG) and water contact angle measurement. It was found that the longitudinal surface of the fiber was not smooth and was full of grooves. The cross sections of fibers were sheet-like and irregular. The infrared spectrum of PTFE fibers was the same as that of PTFE films except the 626 cm^{-1} bands which were associated with the helix-reversal defect. The range of fineness distribution (2.09–11.50 dtex) was wide and the average strength was 1.37 cN/dtex. PTFE fibers began to be decomposed at 508.6°C and showed excellent thermal stability. The water contact angle of fibers layers was 120° indicating it to be a hydrophobic material. All these results provide a theoretical foundation for applications of PTFE fibers.

Keywords: fineness distribution; hydrophobicity; low coefficient of friction; PTFE fibers; thermal stability.

1 Introduction

As is known to all, polytetrafluoroethylene (PTFE) as engineer materials has excellent physical and chemical properties, such as outstanding thermal stability (1) and toughness at low temperature (2), low thermal conductivity, perfect insulating and dielectric properties (3), extremely low coefficient of friction (4) and chemical resistance (5). These performances could be attributed to its composition and the structure of PTFE, which is a helical linear polymer consisting of a carbon and fluorine and carbon chain tightly surrounded by fluorine atoms acting as a protective layer (4). PTFE has many exceptional properties so that it attracts many researchers (6–8) and has been used in numerous fields, such as superhydrophobic composite coatings (9), and water separation by PTFE membrane (10). Especially in textiles, protective clothing materials were produced by using PTFE membranes (11, 12) and protective undergarments were constructed employing PTFE filaments (13).

Correspondingly, PTFE fibers are thought to own the same outstanding features as that of PTFE. Thus the fibers can be used in textiles, such as in fabricating heat insulating clothes due to the low thermal conductivity, and in fabricating protective clothing because of its excellent thermal stability and chemical resistance. However, it can be difficult to manufacturer as PTFE can be neither solution processible nor melt processed by traditional techniques (14). Nowadays PTFE fibers can be obtained by extruding a mixture of viscose and aqueous dispersion containing PTFE particles into a setting medium through a shaped nozzle and subsequently sintered to get dark brown fibers (15), or by drawing a PTFE monofilament formed by paste extrusion at a temperature higher than the crystal melting point of PTFE (16, 17), or by slitting a stretched uniaxially PTFE film along the stretching direction with needle blade rolls (18). However, until now there have been few comprehensive studies on PTFE fibers and its attributes, and even fewer on the development and applications of PTFE fibers as well as its products.

In this present study, the structure and properties of PTFE fibers were investigated by some measurements, which are believed to lay a solid foundation for spinning of PTFE fibers and weaving of protective clothing.

2 Materials and methods

2.1 Materials

The PTFE fibers used in this study were provided by Changzhou XCF Polymer Materials Co., Ltd. (Jiangsu,

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PR China). The fibers were obtained by extruding a mixture of PTFE fine powder and lubricants into a rod, followed by rolling into a film and stretching uniaxially, then tearing the PTFE films into filaments and cutting the filaments into staple fibers according to the required length.

2.2 Characterization of PTFE fibers

2.2.1 Morphological structure

The morphological structures of PTFE fibers were observed using scanning electron microscopy (SEM) (TM3000, Hitachi, Japan). In order to observe its cross-section morphology, the fibers were cut into slices by a fiber slice cutter (Y172, Changzhou Textile Instrument Factory Co., Ltd., China) and set on round stainless steel holders with double-sided adhesive conductive tape and coated with gold.

2.2.2 FT-IR analysis

The infrared spectrum of PTFE fibers was recorded by an attenuated total reflection Fourier transform infrared spectrometer (ATR-FT-IR) (Nicolet 6700, Thermo Fisher, USA) in the region of 4000–600 cm^{-1} at room temperature.

2.2.3 Orientation and crystallinity

The orientation and degree of crystallinity of PTFE fibers were examined with X-ray diffractometer (XRD) (D/max 2550 PC, Rigaku, Japan). The scanning speed was 20°/min with a range of 5°–60° using CuKα radiation (λ=1.54 Å), the orientation and crystallinity were calculated by full width at half maximum (FWHM) with an integral method and peak separation program of Jade 9.0 [Materials Data, Inc. (MDI), CA, USA] which is an XRD analysis software, respectively.

2.2.4 Fiber fineness

Two hundred pieces of PTFE fibers sampled at randomly were used to measure the fineness with a fiber fineness tester (XD-1, Shanghai New Fiber Instrument Co., Ltd., China), the principle of which is based on string vibration. Experimental methods were made in accordance with the standard GB/T 14335-2008 (testing method for linear density of man-made staple fibers).

2.2.5 Tensile properties

One hundred pieces of PTFE fibers randomly selected were tested for tensile properties by a modified fiber tensile tester (XQ-2, Shanghai New Fiber Instrument Co., Ltd., China), the holder of which was replaced by a metal one in order to prevent the fibers slipping during stretching. Tests were carried out according to the standard GB/T 14337-2008 (testing method for tensile properties of man-made staple fibers), in which the gage length was 20 mm, the cross-head speed of the tester was 10 mm/min, and the pre-tension was 0.05 cN/dtex.

2.2.6 Thermal properties

The thermal analysis of PTFE fibers was conducted by a thermal gravimetric analyzer (TG 209 F1 Libra, Netzsch, Germany) and a differential scanning calorimeter (DSC Q20, TA, USA). For TG, the sample in the form of powder (4.9 mg) was charged in an aluminum oxide crucible and heated from 30°C to 600°C at a heating rate of 10°C/min in a nitrogen atmosphere. For DSC, PTFE fibers (6.6 mg) were charged in an aluminum crucible with lids of the DSC, and heated from 30°C to 380°C at a heating rate of 30°C/min in a nitrogen atmosphere to eliminate the effect of thermal history, and then cooled to 30°C at 10°C/min to obtain the recrystallization curve. After that, the sample was reheated to 380°C at 10°C/min to get the melting curve. The crystallization temperature (T_c) and melting temperature (T_m) were defined as the onset temperature of the recrystallization peak and melting peak, respectively.

2.2.7 Surface properties

Wetting properties: water contact angles of PTFE fibers were measured by using an optical contact angle meter (OCA15EC, Dataphysics, Germany). Before measuring, the fibers were combed tidily along the axial direction and paved on glass slides with double-side tape. Three samples were prepared and each sample was measured five times at different points.

Coefficient of friction: the static friction coefficient μ_s and the dynamic or kinetic friction coefficient μ_k of PTFE fibers with a stainless steel roller were tested by a fiber friction coefficient tester (XCF-1A, Shanghai New Fiber Instrument Co., Ltd., China) under the following conditions: the speed of friction roller was 30 rpm, and pre-tension was set to 100 cN.

3 Results and discussion

3.1 Morphological structure

Longitudinal and transverse cross section SEM images of PTFE fibers are presented in Figure 1. The longitudinal surface of the fiber was full of grooves, which would largely increase the specific area of the fiber. The cross sectional figures of the fibers were sheet-like, irregular with rough edges due to the method of tearing stretched uniaxially films into fibers. The rough surface could increase cohesion among the fibers in the yarns.

3.2 FT-IR analysis

Figure 2 showed the infrared spectrum of PTFE fibers, three apparent peaks can be seen at 1207, 1151 and 636 cm^{-1}, respectively. The 1207 and 1151 cm^{-1} bands, which were considered to be insensitive to crystallinity (19), were assigned as the symmetric and asymmetric CF_2 and CC stretching vibrations (20, 21). The doublet at 638–626 cm^{-1} appeared in the spectrum of PTFE film (22) was not found in that of PTFE fibers except a peak at 636 cm^{-1}. From previous research, we learned that the band at 636 cm^{-1} was assigned to a regular helix and the band at 626 cm^{-1} was associated with the helix-reversal defect accompanying the conformations transition (23). Biswas and Vijayan stated in a review that the molecular conformations of the PTFE chain involved 13_6 helix, 15_7 helix, disordered 15_7 helix, etc, i.e. 15_7 helix meant that 15 -CF2- units were present in seven turns of the chain, and the thermally activated structural transformations of PTFE chain (from 13_6 helix to 15_7 helix) would happen when the temperature was increased to 19°C (4). Therefore we speculated that there were no helix-reversal defects in the fibers and the conformations transition of the fibers did not happen, however, whether it was 13_6 helix or not was still an intriguing issue.

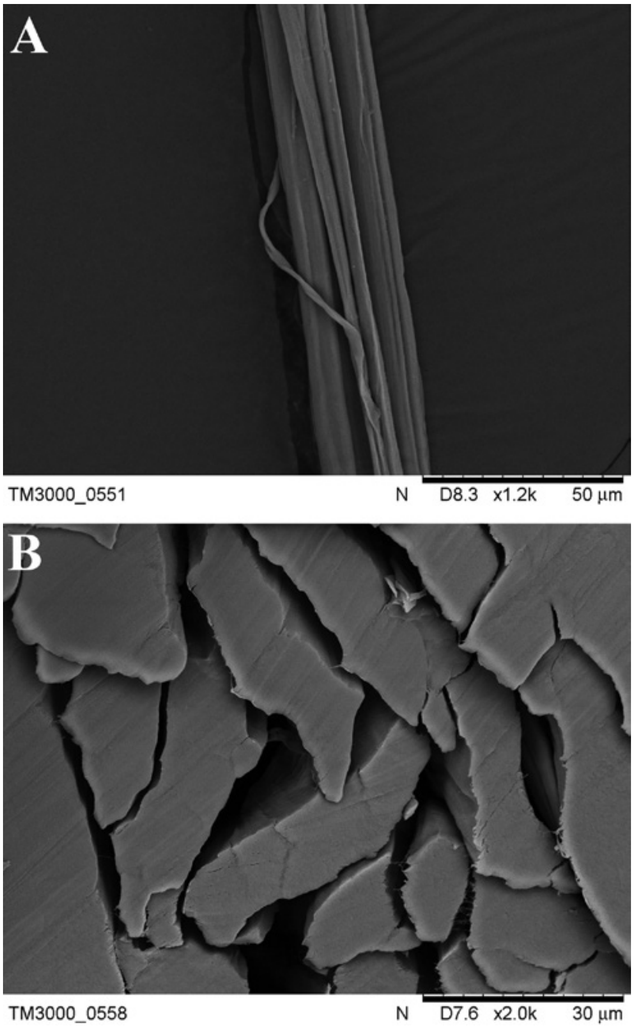

Figure 1: SEM images of PTFE fiber, indicating (A) longitudinal surface morphology and (B) cross sectional morphology.

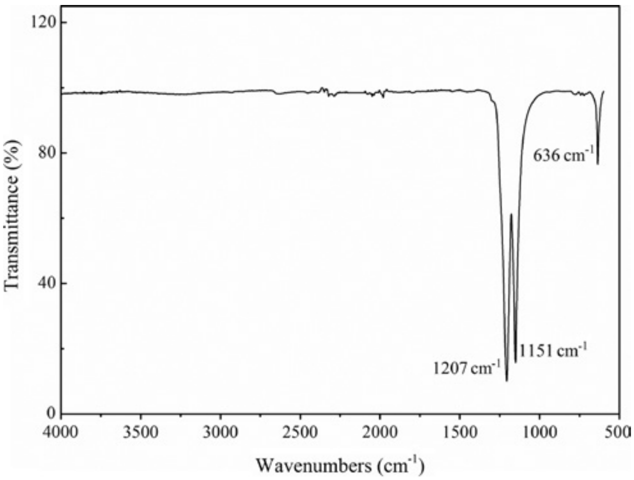

Figure 2: FT-IR spectrum of PTFE fibers.

3.3 Fiber fineness

The linear density of PTFE fibers ranged from 2.09 dtex to 11.50 dtex and the average value was 5.07 dtex. The fineness distribution of PTFE fibers are shown in Figure 3(A). The distribution was approximately partial normal distribution and the linear density under 5 dtex accounted for 60%. This would bring difficulties for spinning and weaving of PTFE fibers, so most of PTFE fibers have been used in non-woven in the past years. During the fineness test, some fibers had branches or were not completely separated, which may make the test complicated.

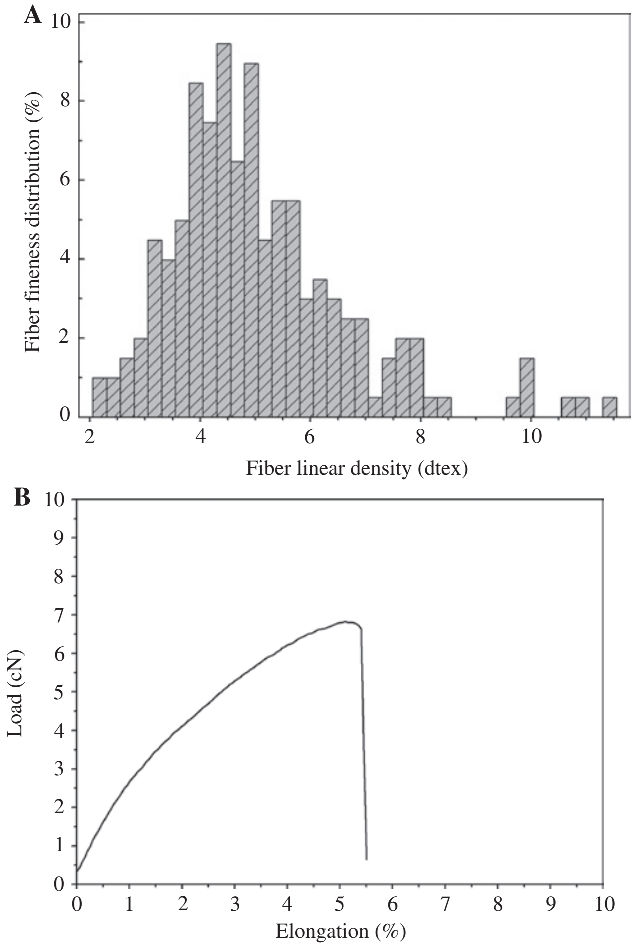

Figure 3: (A) Fineness distribution of PTFE fibers, (B) Typical tensile curve of PTFE fiber.

3.4 Tensile properties

As shown in Table 1, the average strength of PTFE fibers (1.37 cN/dtex) was calculated. Both orientation and degree of crystallinity of fibers were high, but the strength of fibers was low. As shown in Figure 3(B), there were no jitter at the end of load-elongation curve, so we considered that low strength may be not ascribed to non-simultaneous breaking of fibril bundles, but due to weak links between crystal networks.

3.5 Thermal properties

TG and DSC curve of PTFE fibers are depicted in Figure 4. The melting point (T_m), crystallization temperature (T_c) and the decomposition temperature (T_d) were noted on the DSC and TG curves. The T_d was defined as the point at which the mass loss was 5%. As shown in Figure 4, the T_m of PTFE fiber was 329.1°C, which was consistent with that of PTFE film (329°C). The T_d of PTFE fiber was 508.6°C, which was a little lower than that of PTFE film (525°C) (24). These data indicated that PTFE fibers still possessed the excellent thermal stability although the degree of crystallinity of fibers (shown in Table 1) was reduced compared with that of PTFE films. No glass transition temperature can be detected on the DSC curve due to the still high degree of crystallinity.

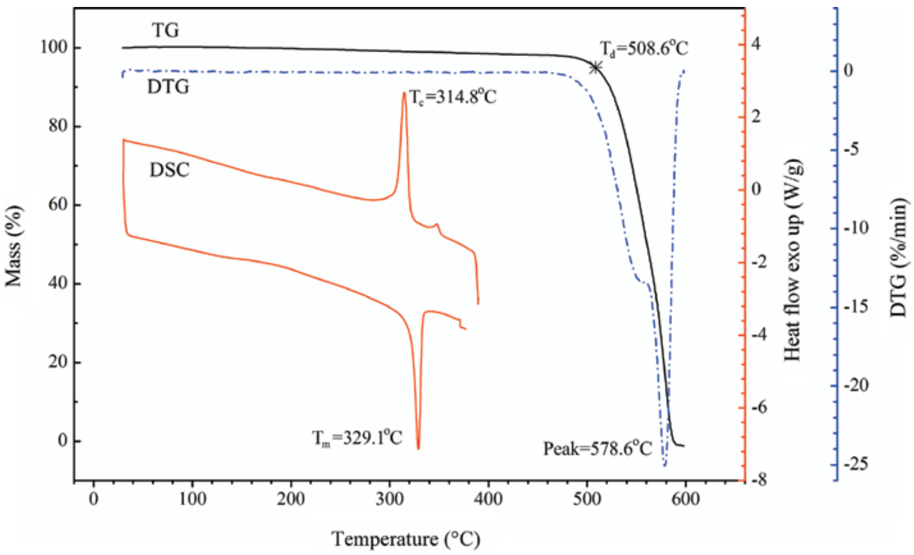

Figure 4: TG analysis and DSC curve of PTFE fibers.

Table 1: Partial physical properties parameters of PTFE fibers.

Sample	Orientation (%)	Crystallinity (%)	Tensile strength (cN)	Elongation at break (%)	Water contact angle (°)	Friction coefficient	
						μ_s	μ_k
PTFE fibers	88.30	74.85	6.92	6.38	119.93	0.19	0.17

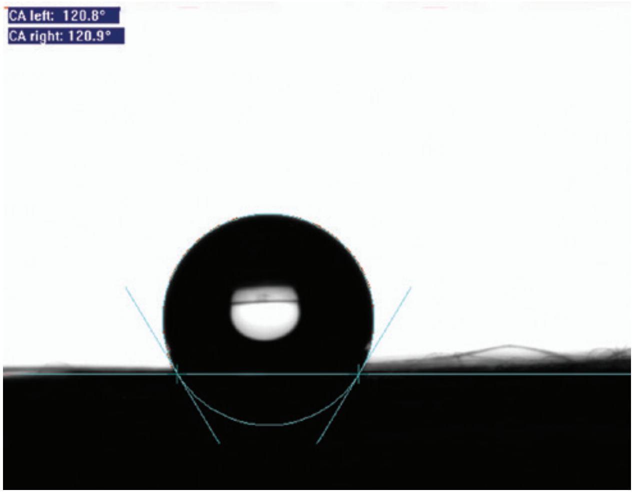

Figure 5: Water contact angles of PTFE fibers.

3.6 Surface properties

Table 1 summarizes the results of surface properties. The water contact angle and the shape of the water droplets on the surface of the fibers layer are shown in Table 1 and Figure 5, respectively. The water contact angle was around 120°, which indicated that it was a hydrophobic surface, and could be used as a self-cleaning surface with some treatments. Friction coefficient of fibers (0.17–0.19) was lower than that of hydrocarbon polymers, but a little higher than that of PTFE films (0.14) (20) because of the rough surface full of grooves.

4 Conclusions

The structure and properties of PTFE fibers were studied by several experiments in this paper. We found that the longitudinal surface of the fiber was full of grooves and the cross sections of fibers were sheet-like, irregular and with rough edges. The infrared spectrum of PTFE fibers was the same as that of films except bands at 626 cm^{-1} which occurred due to the helix-reversal defect. The range of linear density distribution of fibers was wide. PTFE fibers showed excellent thermal stability and a low friction coefficient. The high contact angle showed that the fibers were hydrophobic.

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