

Communication

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Chemical stability of novel melt spinning FEP fibers

DOI 10.1515/epoly-2015-0252

Received November 8, 2015; accepted December 12, 2015; previously published online February 4, 2016

Abstract: Fluorinated ethylene propylene (FEP) and polytetrafluoroethylene (PTFE) are both perfluorinated polymer, thus endowing FEP fibers excellent chemical stability. Compared with the difficult processing of PTFE, FEP fibers can be fabricated by melt spinning. The FEP fibers were treated by H_2SO_4 and NaOH. After treatment, FEP fibers have a slight swelling observed by optical microscope (OM). Meanwhile, the strength of treated FEP fibers decreases slightly, while tensile modulus and elongation at break increases because of the infiltration of H_2SO_4 and NaOH. Differential scanning calorimeter (DSC) results show that the crystallinity of FEP fibers decreases, due to the regularity of macromolecules destroyed by H_2SO_4 and NaOH, which enter into crystalline region. This is consistent with WAXD results, indicating crystal size and crystal plane space decreases, owing to the infiltration of H_2SO_4 and NaOH. However, chemical bonds of FEP fibers are unaffected, which is confirmed by FTIR spectra. Therefore, FEP fibers possess excellent chemical stability.

Keywords: chemical stability; FEP fibers; melt spinning; perfluorinated polymer; PTFE.

1 Introduction

Perfluorinated polymer is the polymer in which the hydrogen atoms attached to carbon atoms in polyethylene (PE) are all replaced by fluorine atoms. At present, the

typical representatives of perfluorinated polymer are polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP), in which the former is developed earliest and its production and consumption accounts for 85% of perfluorinated polymer (1). As is known to us all, the chemical stability of polymer strongly depends on the bond energy of chemical bonds. The bond energy of C-F bonds is up to 485 kJ/mol, which is very great in single covalent bonds. The extremely stable C-F bonds endow FEP with excellent chemical stability, high and low temperature resistance, anti-aging capability and good mechanical properties (2).

The fluorine atoms surround the carbon backbone like a protective sheath, creating a chemically inert, thermal stability and relatively dense molecule with very strong carbon-fluorine bonds. Compared with PTFE, the substitution of CF_3 to F atom increases the non-regularity of the macromolecules and reduces the melting temperature, which is responsible for the stable melting point of FEP. Among other things, FEP can almost effectively resist all solvents, concentrated acid, strong alkali, oxidant and other chemicals, even concentrated nitric acid, fuming sulfuric acid and aqua regia (3). In addition to the fluorine element at high temperature, molten alkali metal and chlorine trifluoride, other chemical reagents cannot react with FEP.

Fabrication of PTFE products is difficult because the material does not flow readily even above its melting point, while FEP can be processed in melting process. As an important modification material of PTFE, FEP not only has the physical and chemical properties similar to PTFE, but also has some advantages in some aspects. Thus, FEP fibers have great values for attention. In recent years, the special fabricating methods of PTFE fibers such as carrier spinning (4), paste extrusion (5), emulsion spinning (6) and film splitting method (7) are eager to be investigated, ignoring development of FEP fibers which has the similar structure and properties to PTFE fibers. Indeed, some experts developed melt-processable PTFE which was specialized for common thermoplastic-polymer processing technologies (8). Besides, the model was proposed to

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elucidate the fundamental mechanism for the poor melt processibility of PTFE (9). However, few scientific papers on the preparation and properties of FEP fibers have been reported. Very recently, we prepared FEP fibers by melt spinning method. In the near future, FEP fibers may be partially substitute for PTFE fibers and play an important role in textile, chemical engineering, oil, paper making, food, machinery, medicine, electronics, cable wire and other fields (10). In this work, the effects of acid and alkali on the structure and properties of novel melt spinning FEP fibers were investigated, providing significant guidance for application of novel FEP fibers.

2 Materials and methods

2.1 Materials

FEP fibers, as-spun filaments with diameter of 70–80 μm , were friendly provided by Professor Shulin An from Tianjin Polytechnic University (Tianjin, China). PTFE fibers (mean diameter 73 μm) were commercially available from Shanghai Linflon Film Technology Co. Ltd. (Shanghai, China). Sulfuric acid and sodium hydroxide, analytically pure, were purchased from Tianjin Zhiyuan Chemical Plant (Tianjin, China).

2.2 Preparation of FEP fibers

A special twin screw extruder (Research Group of Professor Shulin An, Tianjin Polytechnic University) was employed to carry out the experiment. Melt spinning was performed at the extrusion temperature of 295°C using a spinneret plate with 36 holes and each having a diameter of 0.3 mm. The extruded fine streams were air-cooled, and they were spun into fibers (as-spun filaments) at the spinning speed of 300 m/min.

2.3 Acid and alkali treatment of FEP fibers

The treatment of FEP fibers was carried out in a computer type thermostatic-humidistat cultivating box at 40°C. A certain amount of the fibers were located in H_2SO_4 (volume concentration, 30%, 60% and 90%) and NaOH (volume concentration, 10%, 20% and 30%) solutions. After 10 h, the treated fibers were washed by distilled water, and then dried at room temperature naturally for testing.

2.4 Characterization

2.4.1 Optical microscope (OM)

A bunch of fibers with length of 1 cm was placed on the slides, which were separated into many single fibers with the aid of glycerin, and then the surface morphologies were observed on an optical microscope (Laborlux 12). Besides, the diameter of the fibers can be measured by the software of fiber fineness analyzer (HD002C, China Textile Academy).

2.4.2 Mechanical properties/shrinkage

Tensile testing was performed on a universal testing machine (Model 2343, Instron, USA). The filaments were tested using a gage length of 200 mm and a constant crosshead speed of 200 mm/min. Besides, the elastic recovery ratio was conducted by means of constant elongation cycle.

2.4.3 Differential scanning calorimeter (DSC)

A differential scanning calorimeter thermal analyzer (Pyris 1, Perkin Elmer, USA) was used for DSC analysis. Each sample of 5–10 mg was weighed before being placed in DSC span. Under nitrogen atmosphere, it was heated from room temperature to 290°C with a heating rate of 20 K/min. The sample was kept for 5 min at this temperature to eliminate the heat history before cooling at 20 K/min. Then the melt was cooled to room temperature at 20 K/min. Subsequently, the samples were undergone the second heating course at 20 K/min. The crystallinity (X_c) of the fibers was determined with the following commonly used relation (11–13):

$$X_c = \frac{\Delta H_c}{\Delta H_c^0} \times 100\% \quad [1]$$

Where ΔH_c is the crystallization enthalpy, ΔH_c^0 refers to enthalpy of 100% crystalline FEP, considered as 87.9 J/g (10).

2.4.4 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra of R-PET fibers were recorded on a Nicolet 5700 spectrometer (Nicolet, USA) over a frequency range from 400 to 4000 cm^{-1} . Thin film specimens were pressed with KBr powders.

2.4.5 Wide-angle X-ray diffraction (WAXD) measurement

WAXD measurements were used to observe the structure of FEP fibers, and were performed in a diffractometer (X'Pert, PANalytical, The Netherlands) with Cu source ($\lambda=1.54 \text{ \AA}$), scanning 2θ from 6° to 36° , at a 0.05° step. The generator tension was 50 kV at 20 mA. All the specimens were compression molded. According to Scherrer's equation, the crystal size of FEP fibers (L) and crystal plane space (d) can be calculated as follows (14, 15):

$$L = \frac{0.89\lambda}{B \cdot \cos\theta} \quad [2]$$

$$d = \frac{2\lambda}{\sin\theta} \quad [3]$$

where λ is the wavelength of X-ray, B the full width at half maximum (FWHM) intensity of the peak and θ the diffraction angle.

3 Results and Discussion

3.1 Observation surface morphologies

The OM images of cross-section and longitudinal morphologies for treated FEP fibers are shown in Figure 1. From cross-sections, after treated by H_2SO_4 and NaOH, FEP fibers underwent a slight swelling, leading to more round cross-sections and clearer images. Besides, some tiny cracks occur near the surfaces of the treated fibers,

especially treated by 90% H_2SO_4 . In longitudinal direction of treated fibers, the surface are still smooth and flat, and no obvious damage is found caused by H_2SO_4 and NaOH.

3.2 Mechanical properties

The mechanical properties of treated FEP fibers are listed in Table 1. After treated by H_2SO_4 and NaOH, the strength and initial modulus of FEP fibers slightly decreases, while the elongation at break obviously increases. This is similar to mercerization of cotton fibers. In the process, the small molecules of acid and alkali penetrate into the gaps among macromolecule chains, and they plays an important role as a plasticizer. This increases the distance between the adjacent macromolecule chains, and they are easy to slide. Therefore, the tensile modulus of the

Table 1: The mechanical properties indexes of treated FEP fibers.

Reagents	Breaking strength (cN/tex)	Elongation at break (%)	Breaking work (mj)	Initial modulus (cN/tex)
H_2SO_4 (%)				
0	4.9	122.1	7.4	4.8
30	4.5	160.1	9.0	4.4
60	4.2	133.6	6.8	4.0
90	3.9	129.3	6.4	3.6
NaOH (%)				
0	4.9	122.1	7.4	4.8
10	4.7	132.3	6.9	3.6
20	4.5	132.6	7.3	4.5
30	4.6	143.4	7.9	4.5

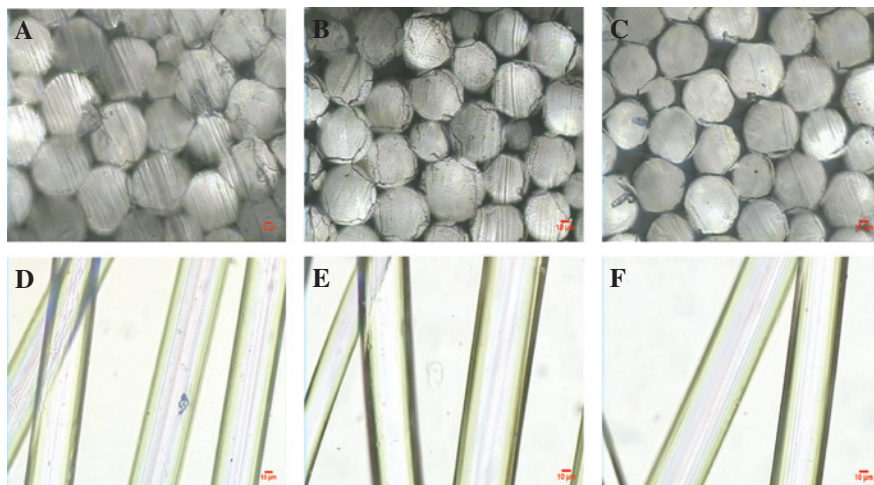


Figure 1: The OM images of cross-section and longitudinal morphologies for treated FEP fibers (400 \times). (A) Untreated, cross-section (B) 90% H_2SO_4 , cross-section (C) 30% NaOH, cross-section (D) untreated, longitudinal direction (E) 90% H_2SO_4 , longitudinal direction (F) 20% NaOH, longitudinal direction.

fibers decreases and the elongation at break increases. Meanwhile, the infiltration of H_2SO_4 and NaOH increases the distance between molecules and reduces entanglement points of molecule chains. In addition, the surfaces of FEP fibers in OM images are slightly affected by H_2SO_4 and NaOH. Based on these two reasons, the strength of FEP fibers decreases, even though the strength is still relatively high. Therefore, FEP fibers have excellent resistance to chemical corrosion.

As an ideal modification material of PTFE fibers, a comparative study of mechanical properties for FEP and PTFE fibers was carried out deeply. Figure 2 illustrates the strength-elongation curves of PTFE fibers treated by H_2SO_4 and NaOH. It shows that the strength of PTFE fibers becomes smaller and the elongation at break turns to be greater, which presents the same tendency as FEP fibers. It is indicated that the chemical resistance of FEP fibers is similar to that of PTFE fibers.

The strength results show that the molecular structure of the FEP molecules is not damaged by the infiltration of the acid and sodium hydroxide, but it is likely to have an

effect on the elasticity of the fibers due to being widen the distance between molecule chains. It is necessary to test the elastic recovery properties of FEP fibers after treatment by H_2SO_4 and NaOH. The results are summarized in Table 2. It demonstrates that the elastic recovery ratio of treated FEP fibers decreases, while the plastic deformation ratio and stress relaxation ratio increases, which attributes to the increasing distance between between molecular chains.

3.3 Melting and crystallization

The DSC curves of FEP fibers in heating and cooling process are shown in Figure 3. From the curves, the melting temperature and crystallization temperature of FEP fibers have no obvious changes before and after treatment. Besides, the peak patterns are almost the same (16). The thermal transformation parameters of treated FEP fibers are summarized in Table 3. The sulfuric acid

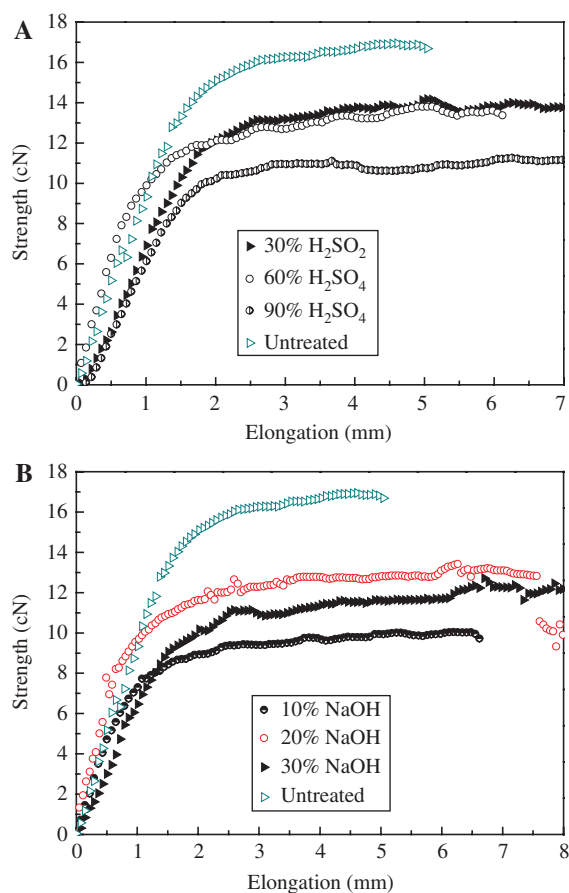


Figure 2: The strength-elongation curves of PTFE fibers treated by H_2SO_4 and NaOH. (A) H_2SO_4 , (B) NaOH.

Table 2: The elastic recovery properties of FEP fibers.

Reagents	Elastic recovery ratio (%)	Plastic deformation ratio (%)	Stress relaxation ratio (%)
H_2SO_4 (%)			
0	86.3	0.8	20.7
30	78.8	1.2	24.7
60	75.8	1.4	26.9
90	68.1	1.9	27.3
NaOH (%)			
0	86.3	0.8	20.7
10	76.0	1.4	26.8
20	75.5	1.4	27.9
30	75.3	1.5	28.0

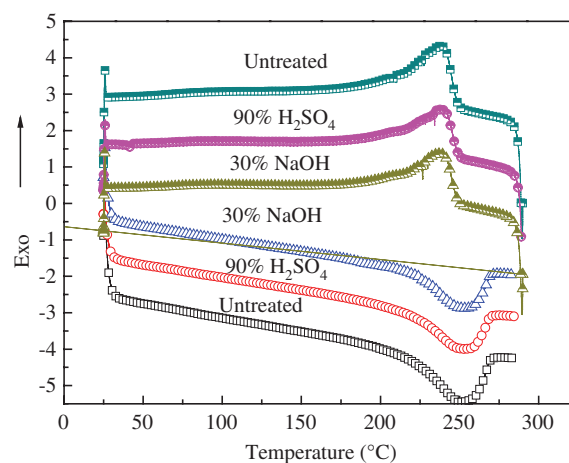


Figure 3: The DSC curves of FEP fibers in heating and cooling process.

Table 3: The thermal transformation parameters of treated FEP fibers.

Samples	Crystallization temperature (°C)	Crystallization enthalpy (J/g)	Melting temperature (°C)	Melting enthalpy (J/g)	Crystallinity (%)
Untreated	239.5	17.0	250.2	19.0	19.3
90% H ₂ SO ₄	240.0	15.5	250.2	18.2	17.6
30% NaOH	239.8	16.6	251.1	17.9	18.9

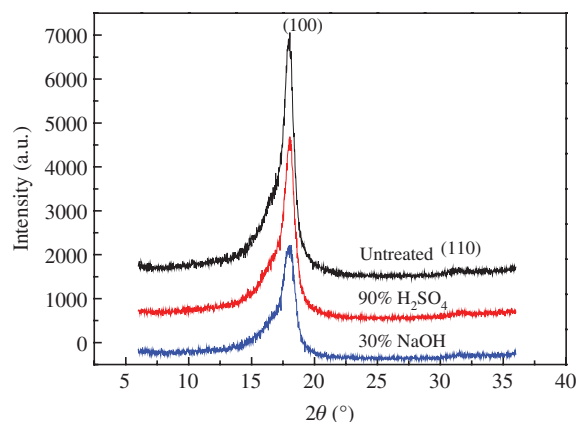
and sodium hydroxide penetrate into crystalline region of FEP fibers, and this destroys the ordered structure of macromolecules. The original crystalline region partially transforms into amorphous region. Thus, the crystallinity of FEP fibers decreases.

3.4 Crystal structure of treated FEP fibers

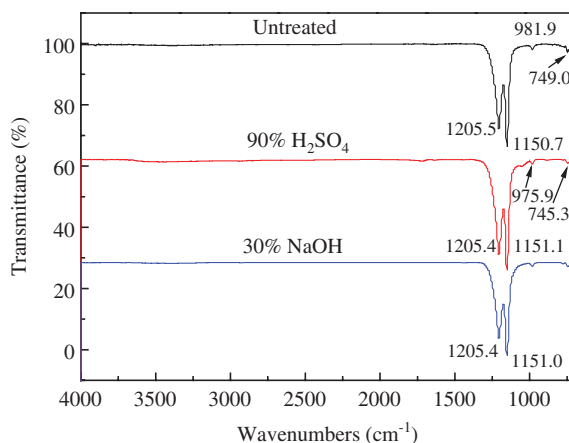
Figure 4 presents the WAXD patterns of FEP fibers. In all curves, almost the same diffraction peaks appear, corresponding to the (100) and (110) crystal plane. After treatment by H₂SO₄ and NaOH, the intensity of diffraction peak corresponding to (100) significantly weakens. The obtained structure parameters of crystals are summarized in Table 4. The results confirm that H₂SO₄ and NaOH penetrating into crystalline region reduces crystal size and crystal plane space, which indicates that the aggregation structure of FEP fibers are more or less affected after treatment.

3.5 FTIR spectra of treated FEP fibers

Figure 5 shows the FTIR spectra of FEP fibers, in which the absorption peaks of FEP fibers have hardly changed before and after treatment. Based on the results from DSC and

**Figure 4:** WAXD patterns of FEP fibers.**Table 4:** The thermal transformation parameters of treated FEP fibers.

Samples	Crystal planes (hkl)	2θ (°)	Crystal size (nm)	Crystal plane space (nm)
Untreated	(100)	16.48	7.96	5.37
90% H ₂ SO ₄	(100)	18.01	7.92	4.92
30% NaOH	(100)	17.98	5.86	4.93

**Figure 5:** FTIR spectra of FEP fibers.

WAXD, the aggregation structure of FEP fibers is slightly affected. Seen from Figure 5, the chemical structure of FEP fibers is not destroyed by H₂SO₄ or NaOH, because the C-F bond in FEP molecules displays supreme bond energy in chemical bonds. Even so, compared with other organic fibers, FEP fibers have incomparable chemical stability.

4 Conclusions

FEP fiber is another novel perfluorinated polymer fiber, which can be considered as modified PTFE fibers with a series of outstanding properties, especially chemical corrosion resistance. The investigation on chemical stability of FEP fibers was comprehensively conducted. After treated by H₂SO₄ and NaOH, FEP fibers have a slight

swelling, showing in OM images of the cross-sections. The strength of treated FEP fibers decreases slightly, while tensile modulus and elongation at break increases because of the infiltration of H_2SO_4 and NaOH. The melting temperature and crystallization temperature of FEP fibers have no obvious changes before and after treatment. However, the crystallinity presents a decreasing trend, because H_2SO_4 and NaOH have penetrated into crystalline region and destroyed the regularity of macromolecules. This is also demonstrated by WAXD, which indicates that crystal size and crystal plane space decreases. FTIR spectra confirms that the chemical bonds of FEP fibers have hardly changed before and after treatment. FEP fibers have excellent chemical stability.

Acknowledgments: The authors gratefully acknowledge the financial support of doctoral scientific research funds of Shandong university of technology (4041-413047), the open project program of key laboratory of eco-textiles, ministry of education, Jiangnan university (No. KLET1401), Shandong province higher educational science and technology program (J14LA56) and Shandong provincial natural science foundation, China (ZR2014EMP004).

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