EFFECT OF ALKALI TREATMENT ON BASIC PROPERTIES AND INTERFACIAL BONDING PROPERTIES OF POLYIMIDE FIBERS

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ABSTRACT

Polyimide(PI) fiber as a popular material with considerable development potential is widely used in the preparation of advanced composite materials. However, low surface energy and smooth surface of PI fiber lead to poor interfacial adhesion between the fiber and matrix, which seriously affects the performance of the composites. To overcome the above problems, alkali treatment was often used for surface modification of PI fiber. In this paper, PI fiber was modified by aqueous sodium hydroxide(NaOH) solutions. PI fibers were treated at temperature (30 ±1°C) with four different concentrations of NaOH solutions: 5, 10, 15, and 20% w/w for 2 min. The treated PI fibers were repeatedly washed with deionized water, dried in an oven at 60 °C for 12 hours, and placed in a sealed bag for use. The effects of alkali treatment on the mechanical properties, linear density, and thermal properties of PI fiber were analyzed. At the same time, the influence of modification on the interfacial shear strength of PI fiber was investigated by the single fiber fragmentation test(SFFT). After the alkali treatment, the mechanical properties and fineness of the PI fiber decreased slightly, but the thermal stability was almost unchanged. SEM observation showed that the impurities on the surface of PI fibers were removed after NaOH treatment, and there were corrosion spots or even pits on the surface of PI fibers with different degrees and random distribution. The best treatment effect was 10% concentration. The chemical structure of PI fibers before and after NaOH modification was analyzed by FT-IR. It was found that the modification only occurred on the surface of the fibers due to the small degree of hydrolysis of the imide ring. And the interfacial shear strength of the PI fiber treated with 10% NaOH solution increased from 20.14 MPa to 23.74 MPa. Excessive concentration will decrease the interfacial adhesion performance of PI fiber, so attention should be paid to the control of treatment conditions.

Key Words: polyimide fibers; alkali treatment; basic performance; single fiber fragmentation test; interfacial shear strength

1. INTRODUCTION

Polyimide fiber has broad application prospects in aerospace, defense military, electronic machinery, space environment and other fields due to its excellent radiation resistance, thermal stability, flame retardant self-extinguishing and excellent mechanical properties. Most of the above applications involve the recombination of polyimide fibers with other materials, the composite effect is closely related to the surface properties of the fibers, including surface chemical composition, roughness, electrical conductivity, crystallinity, hydrophilicity and so on[1]. However, low surface energy and smooth surface of PI fiber lead to poor interfacial adhesion between the fiber and matrix, which seriously affects the performance of the composites. Therefore, it is necessary to modify the surface of the polyimide fiber, which can enhance the interfacial adhesion property and improve the surface activity without damaging the excellent properties of the fiber itself.

To overcome the above problems, alkali treatment was often used for surface modification of polyimide fiber[2]. The polyimide fiber is hydrolyzed under alkali conditions to form a polyamic acid， and further reaction to form a carboxylate. At the same time, the reaction is accompanied by etching of the surface of the alkali, so that the surface roughness and hydrophilicity of the polyimide fiber are improved.

In this paper, we report a facile and effective way to improve the surface of polyimide fibers. polyimide fiber was modified by aqueous sodium hydroxide(NaOH) solutions at temperature (30 ±1°C) with four different concentrations of NaOH solutions: 5, 10, 15, and 20% w/w for 2 min. The treated PI fibers were repeatedly washed with deionized water, then dried in an oven at 60 °C for 12 hours, and placed in a sealed bag for use. And the effects of alkali treatment on the mechanical properties, thermal properties of PI fiber were analyzed. At the same time, the influence of modification on the interfacial shear strength of PI fiber was also investigated by the single fiber fragmentation test(SFFT).

2. EXPERIMENTAL

2.1 Materials and Alkali treatment

Suplon® PI fibers were provided by Jiangsu AoShen Hi-Tech Materials Co., Ltd., China. The diameter of single fiber is 13 μm. Sodium hydroxide (NaOH, AR) were produced by Sinopharm Chemical Reagent Co., Ltd. PI fibers were treated at temperature (30 ±1°C) with four different concentrations of NaOH solutions: 5, 10, 15, and 20% w/w for 2 min. The treated PI fibers were repeatedly washed with deionized water, dried in an oven at 60 °C for 12 hours, and placed in a sealed bag for use.

2.2 Mechanical Properties of PI fiber

The mechanical properties were tested at temperature of 20 (±1) °C and relative humidity of 65 (±1)%. Refer to GB/T 14337-2008, PI fiber was stretched with pre-tensioning tension of 2cN, tensile gauge of 20mm, 10mm/min tensile rate. Each sample was tested by 40 times. The strength data of PI fibers were very dispersive. Therefore, the Weibull statistical distribution model after taking logarithm could be obtained as follows.

$$\boldsymbol{ln\{ln[1/(1-F(\sigma))]\} = lnL + \lambda ln\sigma - \lambda ln\sigma_0} \tag{1}$$

Where σ is tensile stress of PI fiber; L is interval length;σ0 and λ are the scale parameter and the shape parameter respectively obtained by the Weibull distribution fitting, where λ is the intrinsic characterization parameter of the fiber;and F(σ) is refers to the cumulative distribution function of the fracture probability of the polyimide fiber when the fracture stress is less than or equal to σ when the tensile gauge is L.

2.3 Thermal Stability Performance of PI Fiber

The thermal stability of PI fibers were measured by thermogravimetric analyzer, and the corresponding thermogravimetric curve was obtained. The samples were heated from room temperature to 900 °C in a N2 atmosphere. The heating rate was 10 °C/min, and the flow rate was 19.8 m L/min.

2.4 SFFT

According to the standard JIS K6251, dumbbell type specimens were prepared and then tested in the universal testing machine (INSTRON 5967, Instron Engineering Corporation Co., Ltd., America). Then critical fracture length of fiber was observed by the polarizing microscope (ECLIPESLV 100N POL, Nikon Co., Ltd., Japan). According to Kelly-Tyson[3] theory, the formulas for calculating interfacial shear strength are as follows.

$$\boldsymbol{\tau = \frac{d\sigma_c}{2L_c}} \quad (2)$$

$$\boldsymbol{L_c = \frac{4\bar{L}}{3}} \quad (3)$$

$$\boldsymbol{\sigma_c = (L/L_c)^{\frac{1}{\lambda}}} \quad (4)$$

Where τ is interfacial shear strength, d is the fiber diameter. L_c is the critical length, $\bar{L}$ is average fragment length, $\bar{\sigma}$is the fiber tensile strength at length L, and σ_c is the fiber strength at the critical length.

3 RESULTS AND DISCUSSION

3.1 Effect of Alkali Treatment on the Mechanical Properties of PI Fiber

The strength and elongation at break of PI fiber before and after modification are shown in Figure 1. After alkali treatment, the breaking strength of PI fiber decreases with the increase of NaOH solution concentration. The modified PI fiber exhibts the minimum breaking strength of 763 Mpa at NaOH solution concentration of 20%, which is a 17% decrease from the breaking strength of untreated PI fibers. This may be due to the hydrolysis of PI macromolecules in an alkaline environment resulting in a decrease in mechanical properties.

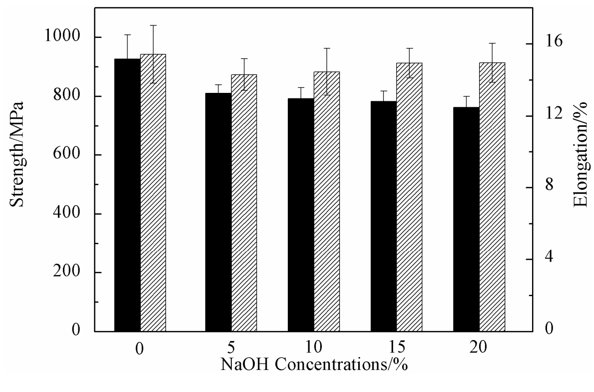

Figure 1. Tensile strength and elongation of PI fiber by NaOH treatment

3.2 Effect of Alkali Treatment on the Thermal Stability Performance of PI Fiber

In order to investigate the effect of NaOH solution on the thermal stability of PI fiber, TGA test was carried out on untreated PI fiber and PI fiber modified with 20% NaOH solution for 2 min respectively, as shown in Figure 2. The initial decomposition temperature of PI fiber decreased from 546.1 °C to 540.8 °C after alkali treatment, which just proves that the excellent performance of PI fiber is high temperature resistance. Figure 3 is a differential analysis of the TGA curve, which represents the rate of decomposition of the PI fiber as a function of temperature. The maximum rate of decomposition of the PI fiber after alkali modification was reduced from 614.3 °C to 610.1 °C compared to the untreated fiber. The above results show that even the modification of the PI fiber with the highest concentration (20%) of NaOH solution causes only weak mechanical and thermal stability damage to the fiber.

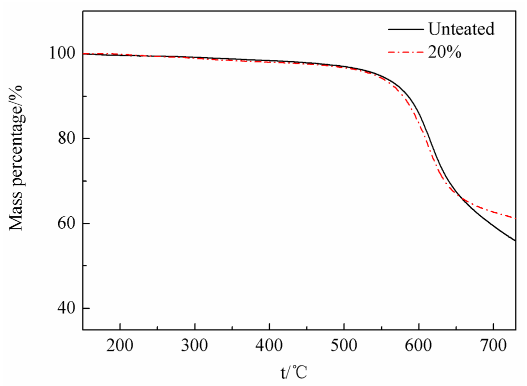

Figure 2. TGA curves of PI fibers

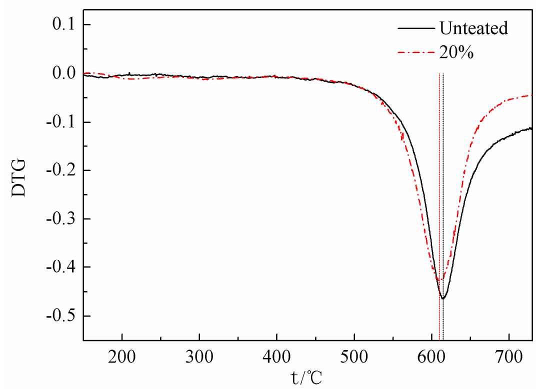

Figure 3. DTG curves of PI fibers

3.3 Effect of Alkali Treatment on the Interfacial Shear Strength of PI Fiber

With the increase of NaOH concentration, the interfacial shear strength between PI fiber and matrix show a wavy trend, as shown in Table 1. After 10% NaOH solution modification, the interfacial shear strength of the PI fiber reached the highest value of 23.74 Mpa and increased by 18% compared with the unmodified PI fiber. The reason is the appearance of corrosion spots on the fiber surface, the increase of roughness and the introduction of more oxygen-containing groups. With the continuous increase of alkali concentration, the interfacial shear strength between PI fiber and matrix exhibit greatly reduced. Although active groups were introduced into the fiber surface, the surface structure of the fiber was seriously damaged due to the exfoliation of oxygen-containing functional groups due to severe surface etching.

Table 1. Comparison of interfacial shear strength of PI fiber by NaOH treatment

Concentrations/%	λ	L_c/μm	τ/MPa
0	13.07	401.35	20.14
5	31.99	327.82	18.22
10	25.00	255.68	23.74
15	26.35	376.30	15.52
20	24.20	715.81	7.91

4. CONCLUSIONS

In this paper, polyimide fibers were modified with different concentrations of NaOH solution, and the basic properties and surface properties of the fibers after alkali treatment were analyzed. Under the condition of modification time of 2 min and temperature of 30 °C, the effects of different concentrations on polyimide fiber were studied by changing the concentration of NaOH solution. The mechanical properties and thermal stability of the fiber before and after modification were also analyzed. After the alkali treatment, the mechanical properties and fineness of the PI fiber decreased slightly, but the thermal stability was almost unchanged. And the interfacial shear strength of the PI fiber treated with 10% NaOH solution increased from 20.14 MPa to 23.74 MPa. Excessive concentration will decrease the interfacial adhesion performance of PI fiber, so attention should be paid to the control of treatment conditions.

5. REFERENCES

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