KNITTABILITY AND OXYGEN PLASMA TREATMENT ON POLYIMIDE FIBERS

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ABSTRACT

The knittability of Polyimide (PI) fibers with high strength and high modulus were investigated. The tensile strength and Young’s modulus of single fiber were 3.41GPa and 92.94GPa, respectively. As seen from a home-made simulative knitting device analysis results, the PI fibers were difficult to form flexible loops to a fabric. To analyze this phenomenon, the composition, structure, mechanical property of PI fibers were detailedly characterized using the infrared spectroscopy (FTIR), X-ray scattering (XRD), a tensile testing machine and scanning electron microscopy (SEM). As a result of analysis, the knittability of PI fibers was mostly related to the mechanical properties, especially its low strain, low toughness, fewer failure fractions and low residual strength after 300 knitting cycles. In order to improve its knittability, it was used oxygen plasma to treat the fiber surface to enhance the interfacial compatibility between the fiber and resin and a traditional method of coating PI resin on the fiber. Furthermore, the fibers with better knittability and the fabric with good appearance characteristics were obtained.

1 INTRODUCTION

As an important member of the family of high-tech polymeric fibers, polyimide (PI) fibers are attracting people’s interests for their promising use in a variety of industrial applications because of their excellent mechanical properties, outstanding thermal-oxidative stabilities, superior chemical and irradiation resistance as well as good electric and dielectric performances [1, 2]. Since initially proposed by Irwin in 1960s, the typical two-step technique is commercially adopted in the preparation of PI fibers. It involves the copolymerization of dianhydrides and diamines in a dipolar aprotic solvent to yield the corresponding poly(amic acid) (PAA) solution, which is then extruded into a coagulation bath to get as-spun PAA fibers and subsequently being converted into the final PI fibers through thermal or chemical imidization process [3-5]. Over the past decades, a number of advances have been made in the field of PI fibers. For instance, D Wu’s group [4-5] prepared a series of aromatic co-PI fibers via a typical two-step wet-spinning method. The Qh. Zhang group [6] reported a Kapton-type PI fiber synthesized by the dry-spinning process. Qiu’s group [7] synthesized a series of PI fibers containing phosphorous groups in the main chain with excellent tensile strength. Until recent years, commercial PI fibers include not only P84 fibers (Evonik Co., Ltd.) and Kermel fibers (Kermel Co., Ltd.), but also Yilun, ASPI and Upilex fibers produced by Hipolyking, Aoshen and Shino in China. The interfacial properties of the fiber and matrix play an important role in the overall performance of the final product [8, 9]. Good interfacial adhesion facilitates the efficient load transfer from matrix to fibers, which can reduce internal stress concentration and improve overall composite mechanical properties [10, 11]. However, the surface of the PI fibers is relatively smooth, which leads to very poor interfacial adhesion between fiber and matrix. To overcome this limitation, many efficient approaches included grafting modification, surface etching, and the incorporation of metal layers are applied [8-11]. Compares with those methods, plasma modification [9] is cleaner and more efficient, and only the uppermost layers of the substrates can be treated by plasma, while the bulk properties are retained. The reinforcing fibers of the composite component are in the form of a textile structure owing to their
attractive properties in intra- and inter-laminar strength, damage tolerance, and near-net-shape fabrication capability, which can be based on woven, braided and knitted fabrics. Fabric-reinforced composites are widely used in the aerospace industry, boat manufacture, architectural engineering, etc [12, 13]. Unfortunately, high-strength-high-modulus PI fibers have not been successfully used as fabric-reinforced material because of the difficulties of obtaining PI fabrics with high count and high density. Up to this point, the study of the relationship of the knittability and structural properties to PI fibers is very insufficient. In this study, we investigate the structures, tensile properties of PI fibers to explore the potential ability of knitting PI fibers into fabrics. Then, use oxygen plasma to treat the surface of the fiber to enhance the interfacial adhesion between fiber and resin and obtain a good-looking fabric.

2 MATERIALS AND METHODS
2.1 Materials

Commercially available PI fibers by two-step techniques with high strength and high modulus were used as received from Jiangsu Shino new materials technology co., LTD.

2.2 Characterizations

A home-made device was applied to evaluate the knittability of PI fibers. The diameter was measured by a polarized light microscope (ECLIPSE LV100 POL, Nikon) with a digital image capturing system. The tensile properties were measured using an XQ-1C tensile testing machine (Xinxian Instrument Co., China) at 20°C and 65% relative humidity, with a gauge length of 20 mm, crosshead speed of 20 mm/min and a load cell of 0.2 cN. At least 20 specimens were tested for each sample and the means were reported. The morphological features were investigated using a Scanning Electron Microscope (SEM, Hitachi TM3000, and 5 kV). Fourier transform infrared spectroscopy (FTIR) was performed on the Nicolet Nexus 670 using an ATR accessory with a resolution of 2 cm⁻¹. Molecular structural characterizations of the PI fibers were investigated using X-Ray Diffraction (XRD, D/Max-2550PC, Japan RIGAKU) technique. The plasma treatment was conducted in an HD-300 plasma apparatus (Changzhou Zhongkechangtai Plasma Technology, China) with oxygen pressure value of 20Pa, a treatment time of 180s and power values of 100W.

3 RESULTS AND DISCUSSIONS

3.1 Knittability of PI fiber

![Figure 1: Typical tensile stress-strain curves after 300 knitting cycles compared with its original tensile strength.](image)

The knittability of PI yarns (consisted of 20 continuous fibers or filaments) is evaluated by measuring the residual strength of the fiber after abrasion on simulative knitting process. After knitting simulation abrasion at the same position for 400 cycles, the PI yarns were broken, demonstrating the
bad knittability. Furthermore, the strength could only retain 70% and drop to 2.38 GPa after knitting processing simulation 300 cycles, demonstrating the bad knittability again (see Fig. 1). To analyze this phenomenon, the composition, structure, mechanical properties of PI fibers were detailedly characterized.

3.2 Compositions and structures of PI fiber

The chemical structure of PI fibers is confirmed by FTIR as revealed in Fig. 2. The PI fibers exhibit four characteristic absorption bands at 1785, 1714, 1354 and 720 cm⁻¹, ascribing to the C=O asymmetrical stretching of imide groups, C=O symmetrical stretching of imide groups, C–N stretching and C=O bending of imide ring, respectively. Meanwhile, there is no evidence of the characteristic absorption bands of PAA fibers (1660 cm⁻¹ for the amide-I band and 1550 cm⁻¹ for the amide-II band), suggesting that the PI fibers have completed imidization, which ensured the high strength and high modulus of the PI fibers. In addition, in Fig. 3, an XRD patterns in the range of 15-30 can be observed and the shape of XRD pattern of the PI fibers implying its orientation and crystallinity. It has been calculated that PI fiber has an excellent orientation of 92.4%, which ultimately contribute to the high tensile strength and high Young’s modulus. But the low crystallinity of 19.27% implying amorphous polymer chains. The amorphous polymer chains are the main reason of the tensile properties are not deserve a higher strength.
3.3 Tensile properties of PI fiber

![Tensile stress-strain curve of PI fiber](image)

Figure 4: Typical stress–strain curves of PI fiber.

![Tensile fracture of PI fiber](image)

Figure 5: Tensile fractures of PI fiber.

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<thead>
<tr>
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<th>PI-fiber</th>
<th>Error bar</th>
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<tr>
<td>Diameter [um]</td>
<td>13.93</td>
<td>0.21</td>
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<tr>
<td>Tensile strength [GPa]</td>
<td>3.41</td>
<td>0.06</td>
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<tr>
<td>Young’s modulus [GPa]</td>
<td>92.94</td>
<td>2.17</td>
</tr>
<tr>
<td>Strain [%]</td>
<td>3.96</td>
<td>0.07</td>
</tr>
<tr>
<td>Toughness [MJ/m³]</td>
<td>67.88</td>
<td>–</td>
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</table>

Table 1: The main parameters of the PI fiber.

Typical stress-strain curves of the PI fibers are shown in Fig. 4. The tensile test results are tabulated in Table 1. As we can see, PI fiber is a typical brittle material, with high strength of 3.41 GPa and high Young’s modulus of 92.94 GPa, while short failure strain of 3.96%. Images are shown in Fig. 5 is the typical tensile failure modes captured from the tensile fractures of PI fiber, which are coincided well with the tensile properties. The PI fiber exhibits homogeneous surfaces and dense, round, uniform morphologies. The tensile failure is due to a brittle fracture, and some chain scission and breakage of the chain bundle can be found in the tensile fracture. These highly fibrillated structures were beneficial for the high tensile strength and high modulus. Therefore, the failure mechanism of the PI fiber is mostly due to defects and breakage of the polymer chain. However, PI fiber has a low failure strain of 3.96%. The failure strain of fibers or yarns plays important roles in knittability. In addition, we...
calculated the toughness of the PI fibers is 67.88 MJ/m³, which means the fabric was not liable to obtain.

4 OXYGEN PLASMA TREATMENT OF PI FIBER

![SEM micrographs of the PI fiber for oxygen plasma treatment process: (a) untreated; (b) treated.](image)

The surface morphologies of the PI fiber untreated and treated were examined by SEM. As shown in Fig. 6, the pristine PI fiber displays a relatively smooth surface. By the contrast, after plasma treatment, many spots, protuberances, and concave points are observed on the surface of PI fiber (see red arrows). As we can see, the surface roughness also considerably increased. Furthermore, the single fiber tensile strength decreases from 3.41 to 3.35 GPa, retaining more than 98% of its original tensile strength. Due to relatively slight plasma treatment powers and short treatment time, the damages to the fiber was only in the uppermost layers. The mechanical interlock and adhesion between PI fibers and PI resin can be improved with the increasing surface roughness.

5 IMPROVED FIBER COHESION AND GOOD FABRIC

![SEM micrographs of the PI fabric for different magnification times (a) 50 times; (b) 200 times.](image)

Fig. 7 shows the surface characteristics of the final product of the PI fibers. The surface morphologies of the fabric show that there is a relatively even surface. For the treated PI yarns sample, plenty of resin is covered evenly and it can be found that the resin is present among the fiber filaments as well (see blue arrows). The results indicate that the PI resin could show a better wetting behavior on
PI fiber surface with the oxygen plasma treatment, which agrees with the literature [9]. We all know that good wetting behavior of resin on fiber surface plays an important role in the formation of interface with excellent performance. The modification of oxygen plasma on PI fiber surface is to make the treated fiber have a good adhesion behavior with the resin matrix, and then to successfully fabric a good textile. As the results shown, oxygen treatment of the plasma can increase the surface roughness of PI fibers, enhancing the fiber interfacial adhesion and leading to good knittability to a textile.

6 CONCLUSIONS

The knittability of PI fibers is a complicated process, it is determined by several fiber parameters. In this study, it seems that the knittability of PI fibers is mostly related to the tensile properties and the fracture mode. As for PI fiber, it consists of stiff polymer chains, thus it can keep high strength and high modulus, but it also make the fiber is hard to form a fabric. So we use the oxygen plasma treatment to make the fiber surface more roughness and coating PI resin on the fiber. The results show that after an 180s, 100W, 20Pa plasma treatment, the PI fiber surface roughness is evidently improved and the interfacial adhesion between the fiber and resin is clearly enhanced as illustrated by SEM. All these are indicating a good knittability of the PI fibers.

ACKNOWLEDGEMENTS

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