RESEARCH ARTICLE

The Structure and Properties of Polyethylene Oxide Reinforced Poly(Metaphenylene Isophthalamide) Fibers

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Abstract

In this paper, the efect of poly (ethylene oxide) (PEO) as an additive on the structure and properties of poly (m-phenylene dimethylene terephthalamide) (PMIA) fibers obtained by wet spinning was investigated. The tensile strength of the composite fbers was substantially enhanced compared to the pure PMIA fber. This was due to the fact that the addition of PEO weakens the hydrogen bonding between PMIA molecular chains resulting in an improved orientation of the composite fbers. It was found that the optimum PEO addition was 2% and the tensile strength of the composite fber was 4.74 cN/dtex, which was 76% higher compared to the pure PMIA fber. However, the heat resistance and fame retardancy of the composite fbers were basically unchanged compared to the pure PMIA fber. The modifcation method is simple, with low raw material cost and good stability, and has not only good academic value but also excellent industrial value.

Keywords Poly(metaphenylene isophthalamide) · Polyethylene oxide · Mechanical properties · Hydrogen bonding

Introduction

High-performance fber is a new generation of synthetic fber with high strength, high modulus and high temperature resistance. High-performance fbers have special properties that ordinary fbers do not have, and are mainly used in national defense and military industries [[1\]](#page-10-0). Aromatic polyamide fbers are high temperature resistant fbers with is a kind of early and fast development, wide application, and large production, fast development of high temperature resistant fber varieties, their total output ranked the second in the high-performance fbers. They are widely used in the felds of safety and protection, modern industry and environmental protection because of its good heat resistance, fame retardancy, chemical stability, electrical insulation and corrosion resistance $[2-12]$ $[2-12]$. Aromatic polyamide fibers mainly consist of poly(p-phenylene terephthalamide) (PPTA) fbers and poly(m-phenylene terephthalamide) (PMIA) fbers [\[13](#page-10-3)].

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However, the molecular chains of PMIA are interconnected by benzene ring and amide bond by meta-position, thus the PMIA is a polymer with fexible chain structure [[1\]](#page-10-0). Moreover, the C=O bonds and N–H bonds between PMIA molecular chains can form strong hydrogen bonding [[14\]](#page-10-4), unlike the weak force between ultra-high molecular weight polyethylene (UHMWPE) molecular chains, which makes PMIA molecular chains unable to be super-stretched and achieve highly oriented structure. Thus the mechanical properties of PMIA fbers are poor and the service life of their woven textiles is short, which limits their application in many felds. The mechanical properties of fbers are closely related to their orientation, and the fracture strength can generally be improved by increasing the orientation of fbers. Li et al. [[2](#page-10-1)] used 2,4-diamino-benzenesulfonic acid (2,4-DABSA) as the third monomer to copolymerize with m-phenylenediamine and m-phthaloyl chloride in low-temperature solution, and the results showed that the introduction of 2,4-DABSA enhanced the hydrogen bonding between the molecular chains of the modifed fbers and improved the fracture strength of the modifed fbers. However, the cost of copolymerization modifcation is high, the operation is difficult, and the modification effect is average. Many other researchers have used inorganic nanoparticles to modify PMIA, such as graphene, carbon nanotubes, boron nitride, etc. Jiang et al. [[15](#page-10-5)] prepared composite hollow

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fber membranes by combining molybdenum disulfde oxide nanosheets and PMIA. The carbon nano tube and molybdenum disulfde nanosheets could efectively enhance the PMIA hollow fber membranes. However, most inorganic nanoparticles are difficult to be well dispersed in the matrix [\[16](#page-10-6), [17](#page-10-7)], which makes the effect of using inorganic nanopar-ticle modification method not very effective. Wang et al. [\[18\]](#page-10-8) coated the PMIA surface with dopamine and then coated the fber surface with a layer of silver, and the results showed that the conductivity of modifed PMIA fbers was greatly improved. However, the mechanical properties of the fbers were hardly improved. The substances used for surface modification are generally easy to fall off, which makes the efect of surface modifcation short-lived. A common modifcation method that is simple, easy to operate and can be produced industrially is blend modifcation [[8,](#page-10-9) [19,](#page-10-10) [20](#page-10-11)]. Many researchers strengthened the fbers by weakening the hydrogen bonds between molecular chains. Chen et al. [[21\]](#page-10-12) prepared composite fbers by adding Antarctic krill protein to chitosan solution during wet spinning process. The results showed that the Antarctic krill protein weakened the hydrogen bonding between the chitosan molecular chains, which led to the improvement of the fber orientation and thus the mechanical properties. Lei et al. [\[22](#page-10-13)] stretched the chitosan hydrogel in water to make its molecular chains arranged regularly. Therefore, this research enhanced PMIA fbers by adding a certain amount functional components to PMIA solution through blend modifcation method. Poly (ethylene oxide) (PEO) is a very crystalline substance that is used as a solid electrolyte and forms hydrogen bonds with other substances easily [[23\]](#page-10-14). Liu et al. [[4\]](#page-10-15) prepared PMIA/PEO solid electrolytes and found that PMIA could form good hydrogen bonding with PEO.

The strong hydrogen bonding between PMIA molecular chains makes it difficult to achieve a high degree of orientation. The drawability of PMIA fbers may be enhanced by adding substances that weaken the hydrogen bonding between PMIA molecular chains. Thus PEO can be added to PMIA as a functional component to improve the orientation of the fber and thus the mechanical properties of the fber.

In the present study, PEO was added to PMIA solution and prepared PEO/PMIA composite fbers by wet spinning. The structure and properties of the composite fbers were characterized in details.

Experiments

Materials

PMIA solution with a solid content of 18.5% was supported by X-Fiper New Material Co., Ltd. PEO powder with different weight average molecular weight (Mw) of 8000, 600,000, 4,000,000, and 5,000,000 were purchased from BASF Co., Ltd. *N*, *N*-Dimethylacetamide (DMAc) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd.

Preparation of PEO/PMIA Blend Solution

The PMIA solution with a PMIA content of 18.5% was diluted with DMAc into PMIA concentration of 15% in a three-neck fask, then a corresponding mass of PEO was added into the solution and stirred at 70 °C for 8 h. The PEO additions were 0, 1%, 1.5%, 2%, 2.5% relative to PMIA, and such blend solutions and the prepared fbers were named PMIA, 1% PEO/PMIA, 1.5% PEO/PMIA, 2% PEO/PMIA and 2.5% PEO/PMIA, respectively.

Preparation of PEO/PMIA Composite Fibers via Wet‑Spinning

PEO/PMIA composite fbers were prepared by a laboratorymade wet spinning device. The PEO/PMIA/DMAc solution was extruded from a spinneret with 50 spinnerets of 0.08 mm diameter at 40 °C and subsequently entered into a Coagulation water bath containing 50% DMAc and solidifed into fbers under the draw ratio of 0.5. Then the fbers entered into a water bath and stretched with diferent ratios under 80 °C, fnally washed in a water bath at 60 °C. The collected fbers were soaked in a 60 °C water bath for 24 h with several water changes to remove residual solvent. After dried, the fbers were stretched 1.1 times in a heat pipe at 300 °C. The technological diagram of fbers preparation is shown in Fig. [1](#page-2-0).

Characterization

The steady-state and dynamic rheological behavior of the solutions were characterized by means of a rotational rheometer (Physica MCR 301, Anton Paar). The diameter of the plate used was 25 mm, the distance between two fat plates was 1 mm, the shear rate range for steady-state rheology was from 0.1 to 100 s^{-1} , and the temperatures chosen were 40 °C, 50 °C, and 60 °C. The viscoelastic range was determined by dynamic tensile scans using a frequency of 6.3 rad/s. The strain 10% was in the linear viscoelastic range and the dynamic rheological strain was 10% with a frequency scan range of 100–0.1 rad/s.

Fourier transform infrared spectra (FTIR) of the composite fbers were characterized by Nicolet Nexus 670 spectrometer at wavenumber of 600–4000 cm−1 with an attenuated total refection (ATR) accessory.

The cross-section and surface morphology of the fbers were measured by a scanning electron microscope (SEM) (SU8010, Hitachi, Japan). Stick the broken fber

after mechanical performance test on conductive glue and spray gold to observe its morphology.

The thermal properties of the composite fbers were tested by a thermogravimetric analysis (TG209F1, Netzsch, Germany). The measurements were carried out under high purity nitrogen atmosphere with a temperature range from 50 to 800 ºC at a heating rate of 20 ºC/min.

Fiber tensile tester (XQ-1, China) was used to test the mechanical properties of fbers. The tensile rate chosen for the test was 30 mm/min, the clamping distance was 20 mm. Each sample was measured 30 times and the averaged value was got.

According to GB-T5454 use the limit oxygen index tester to test the limit oxygen index of the fber (JF-3, China). Take 1 m fber separately. Fix one end of the fber, pinch the other end by hand, twist the fber with a twist number of 60, then fold it into a strand along the middle, twist the strand 30 times again by the same method, fold it into a strand, then twist it 10 times again, then fold it, and tie the head of the strand to prevent the strand from falling apart, the strand was the test sample.

The thermodynamic mechanical behavior of fbers was recorded on the dynamic mechanical analysis (DMA) system (Q800, America) at temperatures ranging from 30 to 370 °C. The frequency was 1.0 Hz and the heating rate was 4 ºC/min.

The SCY-3 type sound velocity orientation meter was used to measure the sonic orientation of fber (fs). The experiment was repeated 5 times to get the average value. fiber orientation factor was calculated according to Eq. (1) (1) (1) .

$$
f_s = 1 - \frac{Cu^2}{C^2} \tag{1}
$$

where C and Cu are the sound velocity of fiber sample and Polypropylene amorphous fbers, respectively.

X-ray difraction (XRD) patterns were recorded on an X-ray difractometer (D2 Phaser), by using Cu Ka radiation at 40 kV and 30 mA with a difraction angle ranged from 5 to 60º.

Wide-angle X-ray difraction (WAXD) patterns of the composite fbers were collected using this XRD machine with an imaging plate. The Herman orientation factor (*f*c) is acquired by Eq. ([2\)](#page-2-2). The orientation function of fbers is usually gained using Eq. ([3\)](#page-2-3).

$$
fc = \frac{3(\cos\varphi)^2 - 1}{2} \tag{2}
$$

$$
(\cos \varphi)^2 = \frac{\int_0^{\frac{\pi}{2}} I(\varphi) \sin \varphi (\cos \varphi)^2 d\varphi}{\int_0^{\frac{\pi}{2}} I(\varphi) \sin \varphi d\varphi}
$$
(3)

where, $(cos \varphi)^2$ is orientation function, *I* is diffraction peak intensity, $φ$ is azimuth angle.

Fiber thermal shrinkage test process was as follows: take 30 cm long fber, place them in high temperature oven under loose state for 30 min, and accurately measure the fber length (L, cm), the temperature used were 280, 300 and 320 ºC, respectively (Fig. [2](#page-3-0)). The fber thermal shrinkage (s) was calculated according to the Eq. ([4\)](#page-2-4).

$$
s = \frac{30 - L}{30} \times 100\%
$$
 (4)

Results and Discussion

Figure [3](#page-3-1) shows the shear rheology curves of diferent blend solutions at diferent temperatures. From Fig. [3a](#page-3-1), it could be seen that the viscosity of the blend solution tends

Fig. 2 Photos of 2% PEO solutions (**a**, **b**) and 2% PEO/PMIA blend solutions (**c**, **d**) under diferent temperatures (PMIA concentration=15%, PEO Mw=600,000)

Fig. 3 Rheological properties of **a** PEO/PMIA blend solutions with diferent contents of PEO at 40 ºC, **b** PMIA solution at diferent temperatures, **c** 2% PEO/PMIA blend solution at diferent temperatures (PMIA concentration=15%, PEO Mw=600,000)

to increase with the addition of PEO, which was because the solid content of the whole solution increases with the addition of PEO, and the higher molecular weight of the added PEO resulted the viscosity of the whole solution increase. With the increase of PEO addition in the blend solution, the phenomenon of shear thinning of the blend solution with the increase of shear rate was more obvious. This was because the addition of PEO weakens the hydrogen bonding between the molecular chains of PMIA, which resulted in the decrease in the entanglement of the molecular chains in the solution, and then reduced the intermolecular forces in the whole solution, thus the solution viscosity decrease faster as the shear rate increases [\[24\]](#page-10-16). From Fig. [3b](#page-3-1) and c, it could be seen that the viscosity of both pure PMIA solution and 2% PEO/PMIA solution tended to decrease as the temperature increases, which was due to the increase in the molecular chain movement ability with the increase of temperature, thus the whole molecular chain interaction became weaker and solution viscosity decreased. However, the viscosity of the 2% PEO/PMIA blend solution decreased more obviously with the increase of temperature. Because the addition of PEO weakened the intermolecular force between the PMIA molecular chains, which made it easier to destroy the intermolecular force with the increase of temperature.

Figure [4](#page-4-0) shows the dynamic rheological results of the blend solutions with different amounts of PEO. From Fig. [4](#page-4-0)a, and b, it could be seen that the storage modulus and the loss modulus of the blend solution increased as the amount of PEO in the blend solution increased. This was because the addition of PEO increased the solid content of the whole solution. The energy storage modulus and loss modulus of the solution were closely related to its concentration, and since the concentration of the whole solution increased after the addition of PEO, the energy storage modulus and loss modulus both increased. From Fig. [4](#page-4-0)c, it could be seen that the loss factor of the blend solution decreased, and the more the loss factor decreased with the increase of PEO addition. The loss factor of the solution was closely related to its structure, and the loss factor can refect the ratio of solution viscosity and elasticity. Because the addition of PEO weakened the hydrogen bonding between the molecular chains of PMIA, the intermolecular forces in the solution reduced and the entanglement between the molecular chains reduced, which resulted the viscosity of the whole solution decrease and the elasticity ratio increase.

Fig. 4 Angular frequency dependence of shear storage modulus and loss modulus and loss factor Tanθ at 40 ºC of PEO/PMIA blend solutions with different contents of PEO (PMIA concentration = 15% , PEO Mw = $600,000$)

Figure [5](#page-5-0) shows the FTIR spectra of the composite fbers with diferent PEO additions. The FTIR spectra of the composite fbers were similar to that of pure PMIA fber, and no new absorption peaks appeared. The infrared spectrum of PEO showed a distinctive absorption peak at 1280 cm−1 for carbon oxide–carbon, which indicated that there was no new chemical bonding between the two. However, there was no PEO characteristic absorption peak inside the composite fber. This was because the added amount of PEO was too small or because PEO was removed during the washing pro.

To investigate the reinforcing efect of diferent molecular weight of PEO, 1% PEO/PMIA composite fbers were

Fig. 5 Fourier transform infrared spectrum of composite fbers (PEO $Mw = 600,000$

prepared by adding diferent Mw of PEO to PMIA solution. Figure [6](#page-5-1) shows the efect of PEO Mw on the mechanical properties of the composite fbers. PEO was soluble in water $[25]$ $[25]$ $[25]$, and the lower the molecular weight, the better its solubility in water. As the added PEO molecular weight was 8000, the added PEO would be washed away during water bath stretching and washing process, their reinforcement efect would become weak. Besides, as the PEO Mw is low, too much PEO chain ends would become the defects of the fbers and the mechanical properties of the fbers would be worse. When the molecular weight of PEO added was 5,000,000, they have fewer chain ends and basically no PEO would be washed away, so its reinforcing effect was the best. However, the added PEO had a negative efect on the heat resistance and fame retardancy of the fber. When the molecular weight of PEO added was 600,000, the mechanical properties of the composite fber can be greatly improved, so PEO with a Mw of 600,000 was chosen as the additive in this study.

Table [1](#page-5-2) shows the maximum water bath draw ratio of the composite fbers with diferent PEO additions. It could be

Table 1 The maximum water bath draw ratio, sonic orientation factor (fs), crystal orientation factor (fc) and crystallinity of diferent fbers

| Sample | Maximum draw ratio | fs | fc | Crystallinity $(\%)$ |
|---------------|-----------------------|-------|-------|----------------------|
| PMIA | 4 | 0.656 | 0.832 | 25.44 |
| 1% PEO/PMIA | 4.5 | 0.699 | 0.826 | 26.42 |
| 1.5% PEO/PMIA | 4.7 | 0.726 | 0.844 | 32.75 |
| 2% PEO/PMIA | 5 | 0.735 | 0.851 | 34.89 |
| 2.5% PEO/PMIA | 4.7 | 0.720 | 0.851 | 34.22 |

Fig. 6 Fiber mechanical properties of 1% PEO/PMIA fibers with different molecular weight of PEO(Mw = 600,000), F1-8000, F2-600,000, F3-4,000,000, F4-5,000,000

seen that the maximum water bath draw ratios of PEO/PMIA composite fbers were higher than that of pure PMIA solution, and the water bath draw ratio of 2% PEO/PMIA could reach up to 5 times. Before the addition of 2%, as the addition of PEO increased, the maximum water bath draw ratio increased. This was because the increase in PEO content caused more hydrogen bonding between PMIA molecular chains to be destroyed, thus the drawability of PMIA fbers in water bath became better and higher draw ratio was obtained. However, when the added amount of PEO was 2.5%, too many hydrogen bonding between PMIA molecular chains were destroyed, which resulted in the slippage of fber chains in water bath drawing process and the drawability of fbers became decreased.

Figure [7](#page-6-0) shows the mechanical properties of the composite fbers before hot stretching and after hot stretching. From Fig. [7](#page-6-0)a, it could be seen that the tensile strength of the composite fbers after water bath stretching were increased compared with that of pure PMIA fber, and the tensile strength of 2% PEO/PMIA fbers could reach 3.61 cN/dtex. However, the fber strength decreased a little as the amount of added PEO continued to increase. This was because the water bath draw ratio of the composite fbers increased after added PEO, the higher the water bath drawing ratio, the higher the orientation of fbers and the better the mechanical properties. 2% PEO/PMIA had the highest maximum water bath draw ratio, so its tensile strength was the highest. As the added PEO content increased to 2.5%, the maximum water bath draw ratio decreased to 4.7, and the fiber strength decreased a little.

Figure [7b](#page-6-0) shows the mechanical properties of the fbers after hot stretching at 300 °C. Comparing with Fig. [7](#page-6-0)a, it could be found that the mechanical properties of the fbers were substantially improved after the hot stretching. This was because the water or solvent molecules acted as the plasticizer for the water bath stretching of fbers, which made the structure of the fbers not very compact, and larger defects would be generated inside the fber after solvent was washed away and the water was removed after dried. During hot stretching process at 300 °C, which was much higher than the glass transition temperature of PMIA, PMIA molecular chains segment could move under the stretching force and the structure of the composite fbers became more compact at certain stretching multipliers. The tensile strength of 2% PEO/PMIA fbers reached 4.71 cN/dtex, which was 76% higher than that of pure PMIA fber. In short, the addition of PEO weakened the hydrogen bonding between the PMIA molecular chains so that the PMIA molecules can be arranged in a more regular manner during the stretching process, as illustrated in Fig. [8.](#page-7-0) The regular molecular chain arrangement made the tensile strength of the fber be improved.

From the X-ray difraction pattern in Fig. [9](#page-7-1), it could be seen that PEO was a very crystalline substance, and the PMIA fbers without hot stretching were less crystalline. Although PEO is highly crystalline, the crystalline characteristic absorption peak of PEO did not appear inside the composite fber. This was partly due to the fact that the amount of PEO added was too small, and PEO was soluble in water, and part of PEO would be removed during water bath stretching and washing.

The crystallinity of diferent fbers are listed in Table [1.](#page-5-2) It could be seen that the crystallinity of the composite fbers increased compared with that of pure PMIA fber, and the highest crystallinity of 2% PEO/PMIA reached 34.89%. This was probably due to the increase in the water bath drawing ratio of the composite fbers, and the larger drawing ratio was beneficial to the crystallization of molecular chains. Higher crystallinity of the fbers contributed to their higher mechanical properties.

Figure [10](#page-7-2) shows the cross-sectional view of the thermally stretched fbers after pulling of. It could be seen that the

Fig. 7 Mechanical properties of composite fbers: **a** before hot stretching, **b** after hot stretching, F0-PMIA, F1-1% PEO/PMIA, F2-1.5% PEO/ PMIA, F3-2% PEO/PMIA, F4-2.5% PEO/PMIA (PEO Mw=600,000)

Intermolecular hydrogen bond reorganization

Fig. 9 XRD patterns of PEO/PMIA composite fbers after water stretching: **a** 5–60°, **b** 10–30°

Fig. 10 The photos of tensile fractured surface of hot-drawn fbers: **a** PMIA, **b** 1% PEO/PMIA, **c** 1.5% PEO/PMIA, **d** 2% PEO/PMIA, **e** 2.5% PEO/PMIA

cross sections of the PEO/PMIA composite fbers with different content of PEO exhibited much tough structures after stretching. Pure PMIA fber and 1% PEO/PMIA fber had a relatively regular cross-sectional structure with no obvious hairline structure. However, 2% PEO/PMIA and 2.5% PEO/PMIA fbers had more hairy flaments in their fractured surface. The higher the orientation of the fibers, the more regular the arrangement of their molecular chains, which lead to a fbrious structure during the stretching process. It was the higher orientation of the composite fber that led to a higher tensile strength and resulted in a more hairy structure in its fractured surface.

The fiber orientation of different fibers are measured by sonic velocity and XRD method, the orientation factors are listed in Table [1](#page-5-2). The mechanical properties of the fbers were closely related to their orientation, and the greater the orientation of the fber, the higher its tensile strength. From Table [1](#page-5-2), it can be seen that the orientation factors of composite fbers changed with the same trend as that of pure PMIA fber. Composite fbers had higher orientation factor than that of pure PMIA fber, which was due to their increased water bath draw ratio. So the fracture strength of composite fbers was increased compared with that of PMIA fber. 2% PEO/PMIA composite fber have the maximum orientation factor, which resulted in the highest tensile strength for 2% PEO/PMIA composite fber.

Figure [11](#page-8-0) shows the thermal properties of PMIA fber and PEO/PMIA composite fbers, Table [2](#page-8-1) shows temperature at maximum decomposition rate (Tmd) of PMIA fber and PEO/PMIA composite fbers. It could be seen that the heat resistance of the composite fiber and PMIA fiber were almost the same, and the temperature of starting decomposition and the temperature of maximum decomposition rate of the composite fbers were very close to that of PMIA. This was probably because the PEO content added was too small and part of the PEO would be removed during water bath drawing and washing process, so the amount of PEO contained in the composite fber was too small. The Tmd of 1% PEO/PMIA and 1.5% PEO/PMIA composite fbers was increased compared with that of pure PMIA fiber, while 2% PEO/PMIA and 2.5% PEO/PMIA composite fbers had a lower Tmd. This was because 1% PEO/PMIA and 1.5% PEO/PMIA fbers had increased molecular chain orientation than pure PMIA fber, while 2% PEO/PMIA and 2.5% PEO/ PMIA fbers had increased molecular chain orientation and contained more PEO than pure PMIA fber. Overall, the heat resistance of the composite fber did not deteriorate signifcantly, indicating that the composite fbers could still meet the basic requirements of protective clothing applications.

Table 2 Temperature at maximum decomposition rate (Tmd), glass transition temperature (Tg) and Limiting oxygen index (LOI) of PMIA fber and PEO/PMIA composite fbers

Figure [12](#page-9-0) shows the DMA curves of the composite fbers, the glass transition temperature (Tg) of diferent fbers are listed in Table [2](#page-8-1). As can be seen from Fig. [12b](#page-9-0), the temperature at which the energy storage modulus of the composite fber began to drop was relatively close to that of pure PMIA fiber, which indicated that the heat resistance of the composite fber remains essentially unchanged. The Tg of the composite fbers increased compared with that of pure PMIA fber, and the Tg of 2% PEO/PMIA was the highest. The Tg was closely related to the orientation and crystallinity of fbers, and the higher the orientation and crystallinity of fbers, the higher the glass transition temperature. It may be because that higher orientation and higher crystallinity resulted in much compact structure of the composite fbers, thus the glass transition temperature of the fbers became higher. 2% PEO/PMIA fiber had the highest orientation and highest crystallinity (see Table [1](#page-5-2)), and its Tg was also the highest. The Tg of the material determines its service temperature range, and it could be seen that the increase in the glass transition temperature of the composite fber makes the application range of the composite fber larger.

Fig. 11 TGA curves (**a**) and DTG curves (**b**) of PMIA fber and PEO/PMIA composite fbers

Fig. 12 DMA curves of PEO/PMIA composite fbers. **a** Tanθ-Temperature curves, **b** Storage modulus-Temperature curves

Table 3 Thermal shrinkage of composite fbers at diferent temperature $(\%)$

| Sample | 280 °C | 300 °C | 320 °C | |
|--------------|--------|--------|--------|--|
| PMIA | 0.17 | 0.33 | 0.67 | |
| 1%PEO/PMIA | 0.16 | 0.33 | 1.16 | |
| 1.5%PEO/PMIA | 0.18 | 0.35 | 1.33 | |
| 2%PEO/PMIA | 0.18 | 0.33 | 1.67 | |
| 2.5%PEO/PMIA | 0.20 | 0.46 | 1.83 | |

The limit oxygen index (LOI) of the composite fbers was also tested and listed in Table [2](#page-8-1). The LOI of the material determines whether it could be used for fame retardant protection, and the higher the LOI value, the better the fame retardant performance. From Table [2,](#page-8-1) it can be seen that the LOI of the composite fber decreased a little bit, but it was still a fame retardant fber, and the LOI decreased as the PEO content in the composite fber increased. This was because PEO was a fammable polymer, with the increase of PEO content inside the composite fber, the fber became more fammable. PEO was a water-soluble polymer, part of PEO would be removed during water bath stretching and washing process, which resulted in the decrease in the PEO content inside the composite fber, so that the LOI of the composite fber would not change signifcantly. Overall, the composite fbers were still fame-retardant fbers and can still meet the application needs in the feld of fame retardant protection.

Table [3](#page-9-1) shows the thermal shrinkage results for diferent fbers at temperatures between 280 and 320 °C. One of the main reference factors for the application of fbers in the feld of fame retardant protection is their high temperature thermal shrinkage. From Table [3](#page-9-1), it can be seen that the thermal shrinkage of the composite fbers was about the same as that of pure PMIA fiber at 280 °C and 300 °C. The thermal shrinkage of 1% PEO/PMIA fber at 280 °C had a little decrease, and at other temperatures the thermal shrinkage of the fber showed a tendency to become larger as the PEO content inside the composite fber increases. This was because the PEO content in the 1% PEO/PMIA composite fber was little, but its structure was denser than PMIA fber, which induced its thermal shrinkage rate decreased. When the surrounding temperature was higher as 320 °C, the thermal shrinkage of the composite fbers became obviously higher than that of pure PMIA fiber. This was because that PEO was a kind of polymer which was not resistant to high temperature and it was easy to shrink at high temperature, as the PEO content in the composite fber increased, the thermal shrinkage rate of the composite fbers also increased. Overall, the heat shrinkage of the composite fbers does not change signifcantly compared with that of pure PMIA fber, and it can still meet the application requirements in the feld of fame retardant protection.

Conclusions

A novel technique for PEO reinforced PMIA fbers was proposed in the present study. The efects of PEO addition on structure and properties of PMIA fbers were investigated in details. The optimum PEO addition was 2%, which increased the tensile strength from 2.68 cN/dtex of pure PMIA fber to 4.74 cN/dtex of the composite fber, with increased Tg. Meanwhile, the heat resistance, fame retardancy and thermal stability of composite fbers did not change signifcantly.

The higher degree of fber orientation greatly enhanced the fber strength. This modifcation technology will provide a highly oriented, high-strength PMIA composite fber that retains its excellent heat and fame resistance.

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Declarations

Conflict of interest The authors state that there are no conficts of interest to disclose.

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