

Mechanical Properties of Polyimide/Multi-walled Carbon Nanotube Composite Fibers^{*}

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Abstract A series of polyimide (PI)/multi-walled carbon nanotube (MWCNT) composite fibers were prepared by copolymerizing a mixture of monomers and carboxylic-functionalized MWCNTs, followed by dry-jet wet spinning, thermal imidization, and hot-drawing process. The content of the carboxylic groups of MWCNTs significantly increased when treated with mixed acid, whereas their length decreased with treatment time. Both the carboxylic content and length of MWCNTs influenced the mechanical properties of the composite fibers. Fiber added with 0.1 wt% MWCNTs treated for 4 h exhibited the best mechanical properties, *i.e.*, 1.4 GPa tensile strength and 14.30% elongation at break, which were 51% and 32% higher than those of pure PI fibers, respectively. These results indicated that a suitable MWCNT content strengthened and toughened the resultant PI composite fibers, simultaneously. Moreover, raising draw ratio resulted in the increase of tensile strength and tensile modulus of the composite fibers.

Keywords: Polyimide fibers; Carbon nanotubes; *In situ* polymerization; Dry-jet wet spinning process; Mechanical properties.

INTRODUCTION

Carbon nanotubes (CNTs) are gaining considerable attention because of their extraordinary mechanical, thermal, and electrical properties since their discovery by Iijima in 1991 and reported by others^[1–4]. As a potential candidate for the reinforcement of polymer materials, interest in polymer/CNT composites has been greatly stimulated over the past few years^[5]. However, two major problems need to be overcome to obtain polymer/CNT composites with excellent properties^[6]. One is the difficulty of dispersing CNTs in the polymer matrix. The other is the weak interfacial interaction between the CNTs and the polymer matrix. Some reported works indicate that sonication could make the CNT networks untied enough, and functionalization could enhance the CNT and polymer matrix interactions^[7–10]. Therefore, the two abovementioned techniques are generally employed to solve these problems.

Polyimide (PI) is one kind of high-performance polymer that could be applied in many fields because of its outstanding properties, such as high tensile strength, high tensile modulus, and excellent temperature resistance^[11]. PI/CNT composites have definitely been widely studied in recent years. Zhu *et al.*^[12] reported that PI/multi-walled carbon nanotube (MWCNT) composite films prepared by mixing PAA solution and acid-modified MWCNT exhibited improved mechanical properties, electrical conductivity, and dielectric constant.

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Yu *et al.*^[13] prepared PI composite films by incorporating highly dispersed single-walled carbon nanotubes (SWCNTs), which were favored for their great optical, thermal, mechanical, and electrostatic charge dissipation properties. He *et al.*^[14] used the functionalized MWCNT by acylation to modify PI resin. The dynamic mechanical and dielectric properties of the resultant composites dramatically increased. However, the PI/MWCNT composite fibers are less reported in the literature. The PI fibers are considered as high-performance fibers because of their excellent thermal stability and mechanical properties, inertness to chemical solvents, and good dimensional stability, among others. These fibers have been widely used for high-temperature dust removal, flame retardation, radiation resistance, electrical insulation, and composite reinforcement^[15–17]. Yin *et al.*^[18] have recently fabricated PI fibers containing carboxylic-functionalized MWCNTs *via* wet spinning. The thermal stability and tensile strength of the PI fibers were improved, while the elongation at break was decreased. However, how to obtain PI/MWCNT composite fibers with excellent mechanical properties has remained challenging.

In the present study, a series of PI/MWCNT composite fibers with different MWCNT loadings was prepared by a dry-jet wet-spinning process. The raw MWCNTs were treated with mixed acid for different times to obtain carboxylic-functionalized samples. The mechanical properties of the resultant composite fibers were then extensively investigated.

EXPERIMENTAL

Materials

Raw MWCNTs (*p*-MWCNTs) were purchased from Shenzhen Nanotech Port Co., Ltd. They had diameters and lengths of 40–60 nm and 5–15 μm , respectively. Concentrated sulfuric acid (H_2SO_4) and concentrated nitric acid (HNO_3) were purchased from Beijing Chemical Works. Pyromellitic dianhydride (PMDA) and 4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) were purchased from Shijiazhuang Jida New Chemical Materials Co., Ltd. and Liyang Longda Chemical Co., Ltd., respectively. *N,N*-Dimethylacetamide (DMAc) was purchased from Tianjin Tiantai Fine Chemicals Co., Ltd. PMDA and BPDA were dried before use, whereas the others were used directly without further purification.

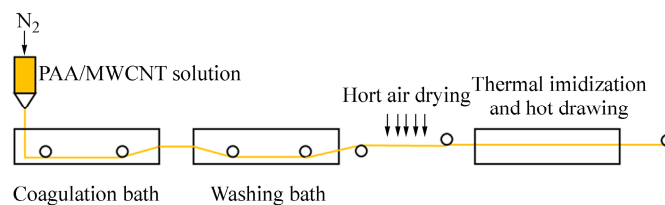
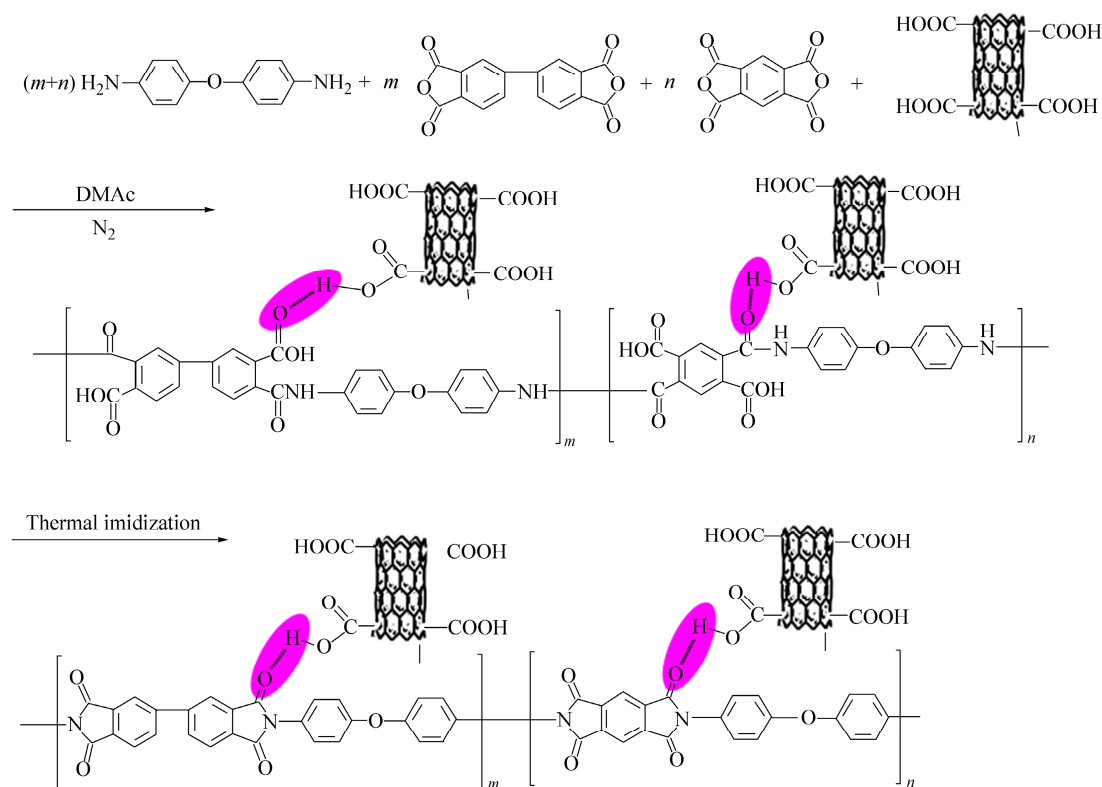
Functionalization of MWCNTs

Raw MWCNTs were added into a $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3:1, *V/V*) mixture, and sonicated at room temperature for 1 h. The suspension was then vigorously stirred at 70–80 $^\circ\text{C}$ for 2–48 h. Subsequently, carboxylic groups were introduced onto the MWCNT surface^[19–21]. The suspension was cooled and diluted with deionized water. The carboxylic groups functionalized MWCNTs (MWCNT-COOH) were obtained for further use after filtration, washing and drying.

Preparation of PI/MWCNT Composite Fibers

The polyamide acid (PAA)/MWCNT spinning solution was synthesized via in-situ polycondensation. MWCNT-COOH was first dispersed in DMAc by sonication at room temperature for 1 h. The ODA was then completely dissolved in the MWCNT-COOH suspension, followed by the addition of BPDA and PMDA (5:5 molar ratio). The mixture with 18.0 wt% solid content was stirred for 24 h at room temperature under nitrogen flow. The MWCNT treatment time was varied from 2 h to 24 h, while the MWCNT loading ranged from 0 wt% to 0.5 wt%. The polymerization process is illustrated in Scheme 1.

The as-spun PAA/MWCNT fibers were fabricated *via* dry-jet wet spinning process after filtration and degassing (Scheme 2). The homogeneous solution was extruded through a spinneret of 50 holes with 0.16 mm diameter. The solution was then entered into a coagulation bath of DMAc/ H_2O (1:1, *V/V*) at room temperature after passing through an air layer. Subsequently, the as-spun fibers were drawn, washed, and dried. The PI/MWCNT composite fibers were collected after thermal imidization at 300 $^\circ\text{C}$ and hot-drawing at 320 $^\circ\text{C}$. The draw ratio was set at 2.0, 2.35, 2.50 and 2.68, respectively.



Scheme 2 Procedure for preparation of PI/MWCNT composite fibers *via* dry-jet wet spinning process followed by thermal imidization and hot drawing

Characterization

The contents of the carboxylic groups on the MWCNT surface were characterized by thermogravimetric analysis (TGA, Perkin Elmer TGA7, under nitrogen atmosphere at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi). The MWCNT morphologies were observed using a scanning electron microscope (SEM, FEG XL30 ESEM). Wide-angle X-ray diffraction (WAXD) measurements were conducted with a Rigaku D/Max-2550 PC X-ray diffractometer using $\text{Cu K}\alpha$ radiation with 0.154 nm wavelength. The mechanical properties of the fibers were measured using the XQ-1 filament electronic drafting instrument.

RESULTS AND DISCUSSION

Contents of Carboxylic Groups on the MWCNT Surface

Figure 1 shows the content variation of carboxylic groups on the MWCNT surface with treatment time based on the TGA and XPS measurements^[22]. The calculation method of TGA is related to the following equation:

$$W = W_i - W_0 \quad (1)$$

where W is the content of carboxylic group on the MWCNT surface, W_i is the weight retention of the MWCNT with different acid treatment time at 600 °C, and W_0 is the weight retention of the MWCNT at 600 °C. The TGA calculation indicates that the contents of the carboxylic groups on the MWCNT surface significantly increase from 1.14% to 13.05%. These values correspond to the 0 h to 6 h treatment time. The treatment time extension has given rise to a further increase in the contents of the carboxylic groups from 12.80% to 19.20% until the treatment time reaches 24 h. The results of XPS measurements are calculated by taking the amount of carbon element as a reference and the content of carboxylic group on the MWCNT surface is a half of the amount of oxygen element. The XPS calculation exhibits good consistency with the previous results. The contents of the carboxylic groups on the MWCNT surface sharply increase from 6.31% to 14.67% with increasing treatment time from 0 h to 6 h respectively. The contents reach a stable state without obvious change in treatment time after a slight increase on the contents (*i.e.*, 16.53%) treated for 24 h. The results indicate that the variation of contents of the carboxylic groups on the MWCNT surface with treatment time exhibits two stages. The contents of the carboxylic groups at the initial state evidently increase with treatment time. The contents of the carboxylic groups are almost constant when the treatment time reaches 24 h.

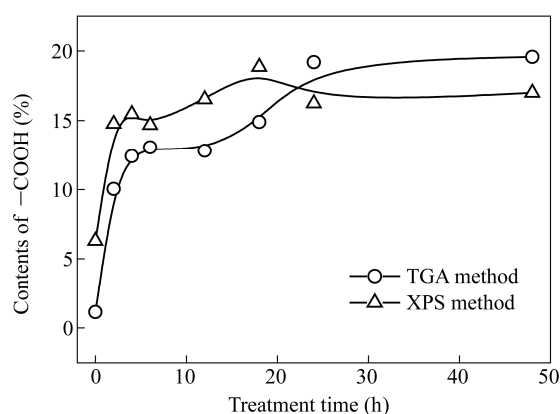


Fig. 1 Variation of contents of carboxylic groups on MWCNTs surface with treatment time by a mixed acid

Morphology of MWCNT and PI/MWCNT Composite Fibers

Figures 2 and 3 show the morphology and average size, respectively, of MWCNTs with different treatment time. The average MWCNT length significantly decreases from 10 μm to 2.3 μm with an increase in treatment time from 0 h to 2 h. A further increase in treatment time (2 h to 12 h) leads to a relatively slow decrease in the average MWCNT length from 2.3 μm to 1.1 μm . A small decrease from 1.1 μm to 0.65 μm is observed for the average MWCNT length when the treatment time continuously increases to 18 h. Then the variation of the average MWCNT length with treatment time almost remains constant. As shown in Fig. 2(a), the raw MWCNTs twist and entangle. The MWCNTs display a loose state when the treatment time increases. The length also becomes shorter (Figs. 2b–2d) possibly because of oxidation^[23, 24].

Figure 4 shows the morphologies of the pure PI and PI/MWCNT composite fibers with different MWCNT contents. All fibers have smooth surfaces with few defects. The average of diameters is about 18 μm . The MWCNTs are seen in the composite fibers, which indicates that the MWCNTs have also been well dispersed (Fig. 4c).

WAXD Results

Figure 5 shows the WAXD patterns from the crystal structure of the PI/MWCNT composite fibers. The MWCNTs display one peak at $2\theta = 26.4^\circ$ corresponding to the (002) reflection of the carbon atoms^[6]. The pure polyimide fibers exhibit three overlapped and weak peaks at $2\theta = 14.3^\circ$, 18.4° , 22.5° , which indicates a very weak fiber crystallization. The intensities of the (002) reflection from MWCNTs and crystallized PI at $2\theta = 14.3^\circ$, 18.4° , 22.5° become stronger when the MWCNT content in the composite fibers increases from 0.1 wt%

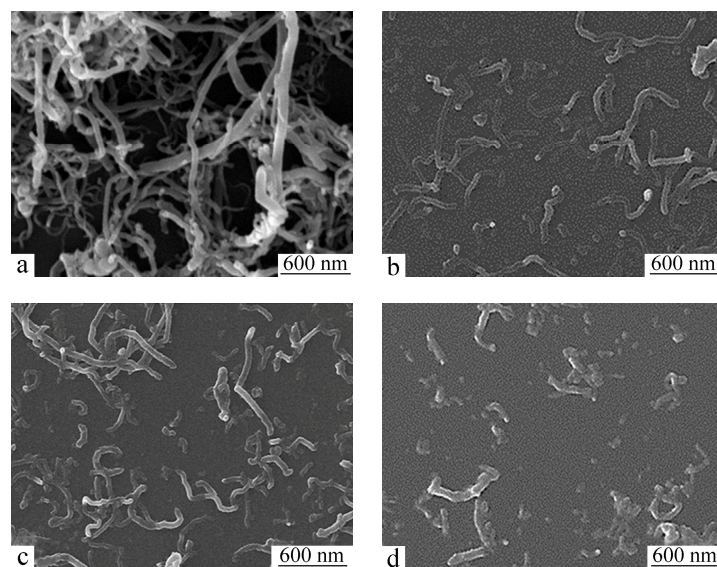


Fig. 2 SEM images of MWCNTs treated for (a) 0 h, (b) 4 h, (c) 18 h and (d) 24 h

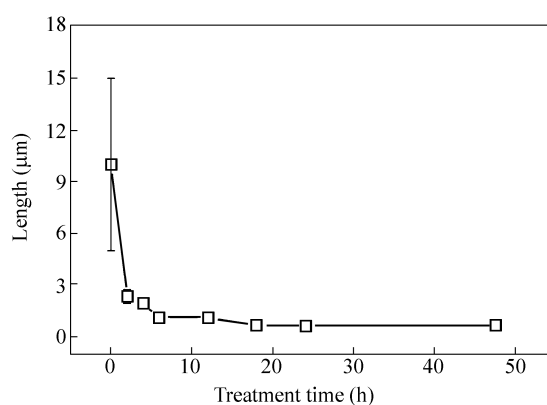


Fig. 3 Variation of lengths of MWCNTs with treatment time

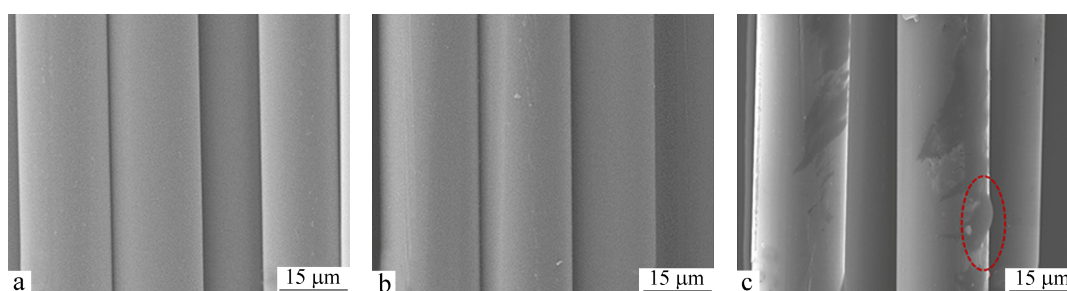


Fig. 4 SEM images of PI/MWCNT composite fibers with MWCNT content of (a) 0 wt%, (b) 0.2 wt%, and (c) 0.5 wt%

to 0.5 wt%. Adding MWCNTs seems to induce or facilitate the PI fiber crystallization to some extent. According to Di *et al.*, the CNT alignment can be improved by post drawing processing, and most of the CNTs are well aligned along the drawing direction^[25]. In the present work, the composite fibers are stretched at a drawing ratio of 2.5. In this process, the MWCNTs are arranged regularly, which will benefit to crystallization for the PI fibers. Based on the WAXD curves, the crystallization and amorphous contributions are separated by the Peak-fit

Software. The composite fibers with MWCNT content of 0.5 wt% show the crystallinity of 14%, and 10% crystallinity is calculated for the PI fibers, as seen in Fig. 6. It may later improve the mechanical properties.

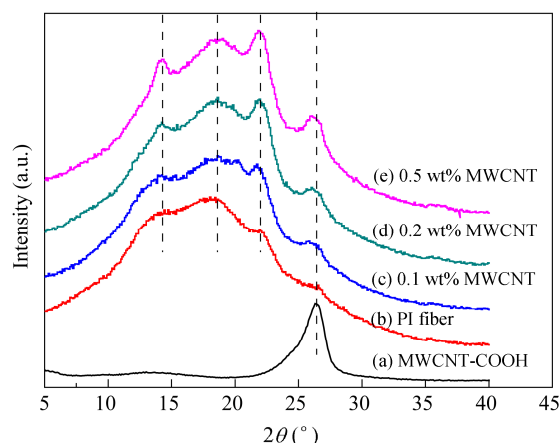


Fig. 5 Wide-angle X-ray diffraction patterns of (a) MWCNT-COOH, (b) PI fibers and PI/MWCNT composite fibers with MWCNT content of (c) 0.1 wt%, (d) 0.2 wt%, and (e) 0.5 wt%

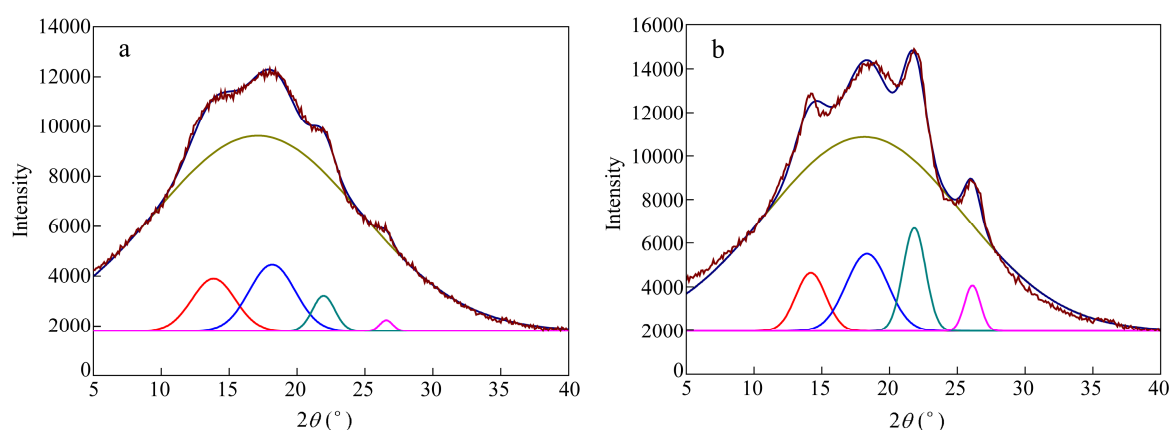


Fig. 6 Wide-angle X-ray diffraction peak fitting results for the (a) PI fibers, and (b) PI/MWCNT composite fibers with MWCNT content of 0.5 wt%

Mechanical Properties

Figure 7 shows the influence of MWCNT treatment time on the mechanical properties of the PI/MWCNT composite fibers containing 0.1 wt% MWCNTs. The tensile strength and elongation at break of the composite fibers increase from 0.93 GPa to 1.4 GPa and 10.81% to 14.30%, respectively, when the treatment time is increased from 0 h to 4 h (Figs. 7a and 7c). The tensile strength and elongation at break decrease to 1.08 GPa and 12.2%, respectively, when the treatment time is extended to 6 h. The tensile strength and elongation at break eventually show a slight fluctuation with the extension of treatment time to 24 h. However, a different result can be obtained in the tensile modulus shown in Fig. 7(b). Increasing the treatment time from 0 h to 2 h decreases the tensile modulus from 10.06 GPa to 8.07 GPa. The tensile modulus shows an increase to 9.96 GPa when the treatment time increases to 4 h. Extending the treatment time to 6 h decreases the tensile modulus to 8.45 GPa. The tensile modulus finally changes from 8.45 GPa to 10.09 GPa in a treatment time from 6 h to 24 h. Overall, a slight fluctuation in the tensile modulus of the composite fibers with addition of MWCNT treated at different time is observed. Definitely, the composite fiber with 0.1 wt% MWCNT content exhibits excellent mechanical properties (*i.e.*, tensile strength, tensile modulus, and elongation at break) when the MWCNTs are treated for 4 h with mixed acid.

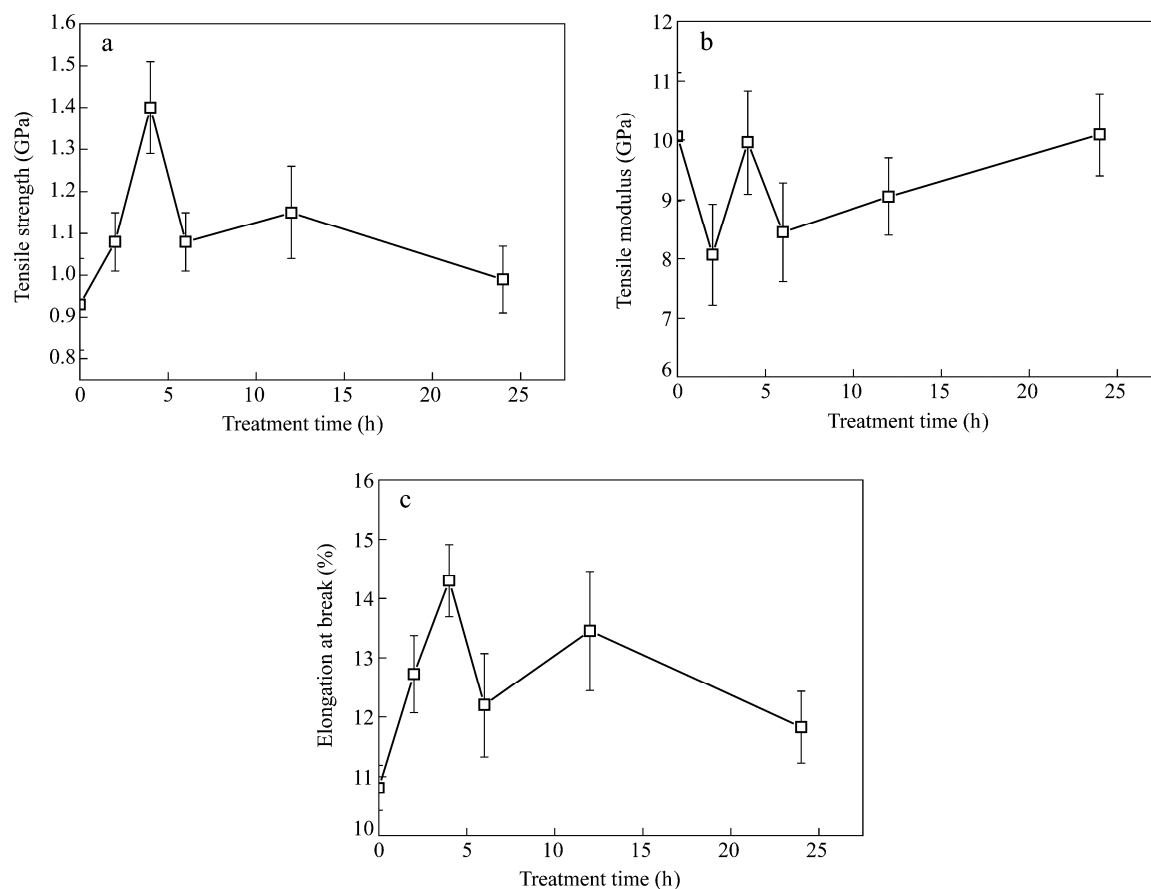


Fig. 7 Influence of treatment time of MWCNTs on the mechanical properties of PI/MWCNT composite fibers: (a) tensile strength, (b) tensile modulus and (c) elongation at break

The results indicate that the tensile strength and ductility of the PI/MWCNT composite fibers are simultaneously improved when the carboxylic-modified MWCNTs are added. The intermolecular hydrogen bonding is readily formed between the carboxylic groups on the MWCNT surface and the carbonyl groups of the PI molecular chains as shown in Scheme 1. Consequently, these MWCNTs could evenly disperse in the PI matrix. The interfacial interaction between the MWCNTs and the matrix is also well built, which triggers the composite fibers to show higher tensile strength and elongation at break. The above results have already been proved by Jiang *et al.*^[8] and Yin *et al.*^[18]. However, further increase in the treatment time causes the MWCNTs to shorten. Furthermore, fewer link points between the MWCNTs and the PI molecular chains are formed. Therefore, the binding force between the MWCNTs and the PI chains is reduced, which also reduces the tensile strength and elongation at break for resultant composite fibers. A significant improvement in the mechanical properties of the composite fibers is observed when the MWCNTs are treated with mixed acid at a suitable treatment time.

The MWCNTs with a treatment time of 4 h and 12.41% content of the carboxylic groups are used to prepare the PI/MWCNT composite fibers and investigate the influence of MWCNT loading on the mechanical properties of the composite fibers. The tensile strength of the composite fibers increases from 0.93 GPa to 1.4 GPa with the MWCNT loading from 0 wt% to 0.1 wt% (Fig. 8a). The tensile strength of the composite fibers decreases to 1.13 GPa when the MWCNT loading increases to 0.2 wt%. The tensile strength remains stable at about 1.13 GPa when the MWCNT loading is further increased from 0.2 wt% to 0.5 wt%. A similar trend is observed for the elongation at break as shown in Fig. 8(c). The elongation at break exhibits an increase from

10.81% to 14.30% when the MWCNT loading increases from 0 wt% to 0.1 wt%. The continuous increase in loading of MWCNTs to 0.5 wt% causes the decrease of the elongation at break to 11.57%. Notably, the MWCNT loading seems to have no influence on the tensile modulus of the composite fibers, which remains at 10.0 GPa (Fig. 8b). However, Yin *et al.*^[18] have stated that the tensile strength and modulus of the MWCNT/PI composite fibers showed an increase with the MWCNT loading increase from 0 wt% to 1 wt% and reached peak values of 1.52 GPa and 58.5 GPa at 1 wt% MWCNT loading. The tensile strength and modulus of the composite fibers decrease when the MWCNT loading increases to 2.0 wt%. The elongation at break reduces from 3.8% to 2.3% when the MWCNT loading increases from 0 wt% to 2 wt%. Different results are obtained in the present work. Both reinforcement and toughening are simultaneously observed when only a small amount (*i.e.*, 0.1 wt%) of MWCNT is added in the polyimide fibers.

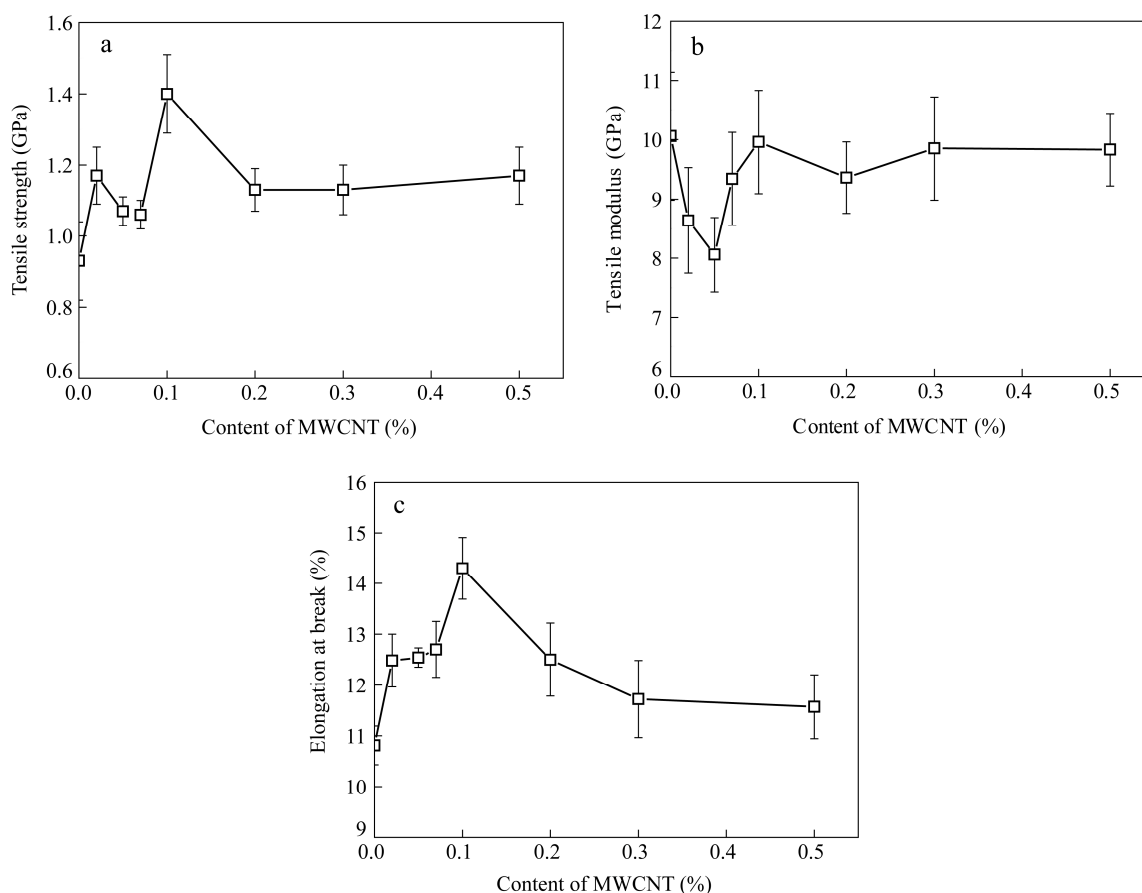


Fig. 8 Influence of MWCNTs content on the mechanical properties of PI/MWCNT composite fibers: (a) tensile strength, (b) tensile modulus and (c) elongation at break

The intermolecular hydrogen bonding between the MWCNTs and the PI matrix is strengthened with more carboxyl-modified MWCNTs. Furthermore, long MWCNTs can serve as link points between PI chains and CNTs and improve the toughness of the composite fibers. Adding MWCNTs possibly induces the crystallization of polyimide chains to some extent, which will contribute to fiber reinforcement. However, *in situ* PI polymerization is interfered when the MWCNT contents increase to a certain extent, which leads to relatively lower polymer molecular weight^[6, 18, 26]. Therefore, a slight decrease in the mechanical properties of the composite fibers is experienced.

As well known, the mechanical properties of PI fibers could be improved by increasing the draw ratio

during heating process. The effect of draw ratio on the mechanical properties of the PI/MWCNT composite fibers containing 0.1 wt% MWCNTs is further investigated and the results are illustrated in Fig. 9. When the draw ratio is increased from 0 to 2.5, the tensile strength and tensile modulus of the composite fibers show an increase from 0.38 GPa to 1.40 GPa and 3.59 GPa to 9.96 GPa, respectively. When the draw ratio is raised to 2.68 continuously, both the tensile strength and the tensile modulus of fibers reach a constant level. However, the elongation at break of fibers decreases from 42.9% to 14.03% with raising the draw ratio from 0 to 2.5. A constant of elongation at break is observed with an increase of draw ratio from 2.35 to 2.68. Actually, the macromolecular orientation of composite fibers is improved by raising the draw ratio, which give rise to the increase of tensile strength and tensile modulus of fibers.

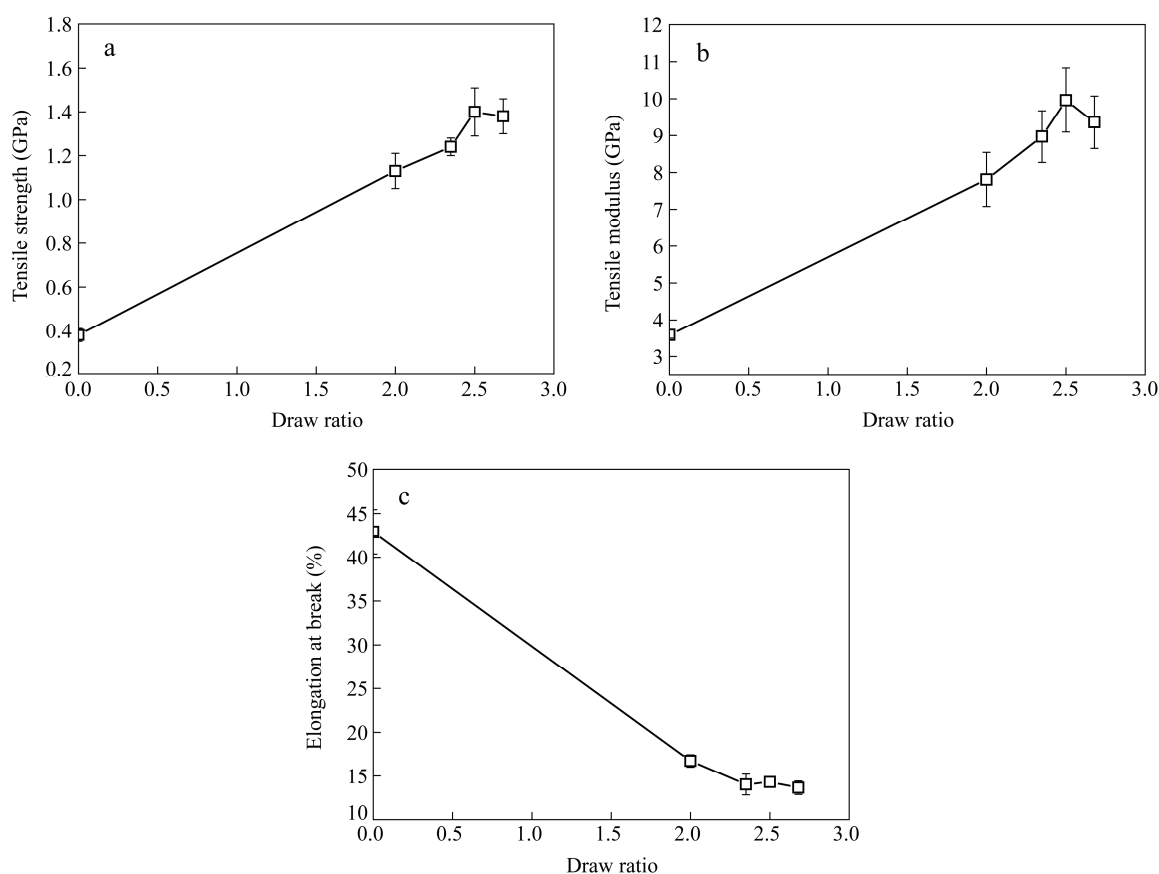


Fig. 9 Influence of draw ratio on the mechanical properties of PI/MWCNT composite fibers: (a) tensile strength, (b) tensile modulus and (c) elongation at break

CONCLUSIONS

A series of PI/MWCNT composite fibers were prepared through the dry-jet-wet spinning process, wherein the MWCNTs are treated with mixed acid of concentrated H_2SO_4 and HNO_3 . The content of the carboxylic groups on the MWCNT surface increases with treatment time while the length of the MWCNTs gradually shortens. The mechanical properties of the as-prepared composite fibers are significantly influenced by the content of the carboxylic groups and the length of the MWCNTs. Higher contents of carboxylic groups facilitate stronger interfacial binding between the MWCNTs and PI matrix. Therefore, better mechanical properties of the composite fibers are available. The shorter length of the MWCNTs introduces lower number of link points with PI chains, which leads to a decrease in the mechanical properties of the composite fibers. Adding MWCNTs possibly induces the crystallization of PI chains to some extent, which will contribute to fiber reinforcement.

Both tensile strength and elongation of break increase when the MWCNT loading (with 12.41% carboxylic groups) in the composite fibers is less than 0.1%. This result implies that a suitable MWCNT content can strengthen and toughen resultant polyimide composite fibers. Furthermore, with increasing the draw ratio, the tensile strength and tensile modulus of fibers are enhanced by 268% and 177% respectively when compared to the composite fiber without drawing.

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