Original Research

Fabrication and characterization of poly(vinyl alcohol)/carbon nanotube melt-spinning composites fiber

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Abstract

A composite fiber based on carbon nanotube (CNT) and poly(vinyl alcohol) (PVA) was prepared by melt-spinning. Structural features and the mechanical performances of the PVA/CNT composite fiber were investigated as a function of draw condition. Initial moduli and tensile strengths of the drawn composite fibers are much higher than those of undrawn composite fiber. It is identified from XRD and 2D XRD that the composite fiber exhibits enhanced crystallinity and orientation degree with increasing the draw ratio. Accordingly, finger-like pores distributed along the axial direction homogeneous on the melt-spinning PVA fiber surface. After dry and hot-drawn, the hydrophobicity of PVA/CNT composites fiber decreased gradually.

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1. Introduction

Carbon nanotube (CNT), which is an ideal one-dimensional carbon nanomaterial, has been extensively studied with a number of objectives since it have been under investigation as a potential additive for composites. Many potential applications of CNT include multi-functional composites or fibers, hydrogen storage, nanometer-sized electronic device, and sensor\textsuperscript{[1–4]}. CNT itself has remarkable mechanical, thermal properties and outstanding electrical conductivity. These unique properties of CNT provide the potential to make much stronger and more functional fibers than current traditional industrial fibers.

In the recent years, several studies have focused on composites made of polyvinyl alcohol (PVA) loaded with carbon nanotubes. Most of research focused on functional membrane\textsuperscript{[5–12]} and films\textsuperscript{[13–19]}. As for CNT reinforced PVA fiber, the wet-spinning is a very common technique to prepare various types of CNTs reinforced poly(vinyl alcohol) composite fiber\textsuperscript{[20–28]}. In addition, the methods of Gel-spinning\textsuperscript{[29–31]} and electrospinning\textsuperscript{[32–40]} also have been applied to prepare PVA/CNT composites fiber. In general, achieving CNT reinforced PVA fiber mainly through wet or gel spinning, they are less effective and more complicated process accompany with difficult to disperse the CNT particle(low CNT content). Although a number of studies have focused on production of composite fibers by melt processing. But due to the melt and decomposition temperature of PVA is too close, melt spinning PVA/CNT fiber nearly no reported.

Apart from the traditional wet spinning methods, PVA/CNT composite fibers can also be produced by melt processing. In this study the effects of CNT content, surface groups and disperse agent on the dispersibility of CNT in the compound plasticizer, PVA fiber produced by melt extrusion followed by cold and hot stretching, were investigated. Various tests were carried out to describe the melt rheology behavior and spinability of swollen PVA raw materials, and the micromorphology, structure and mechanical property of melt-spinning PVA/CNT fiber were characterized. Furthermore, the formation mechanism of microporous surface
after stretching and annealing was investigated. The current work would provide an optimization method for preparation the melt-spinning PVA/CNT composites fiber.

2. Experimental

2.1. Materials and preparation

Poly(vinyl alcohol) (PVA) with a polymerization degree of 1700 and an alcoholysis degree of 99% was purchased from the Sinopec Sichuan Vinylon Works Group (China). Multi-walled carbon nanotubes (MWCNTs) were obtained from the Institute of Organic Chemistry, Chinese Academy of Sciences (Chengdu, China). Both industrial MWCNTs-OH, which -OH content is 2.48 wt% and Industrial MWCNTs-COOH, which COOH content is 1.55 wt%. The average outer diameter is 10–30 nm, and average length 10–30 μm of CNT. MWCNTs were used directly without further purification or treatment. Two kinds surfactants such as polyoxyethylene sorbitan monooleate (Tween 80) and polyvinylpyrrolidone (K30) were used to disperse CNTs in compound plasticizer.

Plasticizer was the key material to realize melt-spinning of PVA. Carbon nanotube was dispersed in plasticizer with different concentrations, and Tween 80 and K30 were used as the dispersant (100 wt% of CNTs). The dispersion was homogenized applying strong sonication treatment (30 min at 20 W, 15 kHz).

The commercial raw PVA particles were mixed with a range of compound plasticizer, and then the mixtures were stored in air tight container, which was placed at room temperature until entirely swollen. Finally, the swollen PVA particles were extruded and spun in a melt spinning system. The original melt-spinning PVA fibers were drawn following special process.

2.2. Properties testing and structure characterization

The melt behavior of PVA at high shear rate during the spinning process was observed by capillary rheometer (Malvern Instruments Ltd. Rosand RH7). The experiments were carried out using the barrel having diameter and length of 15 mm and 250 mm, respectively and a capillary die having the L/D ratio of 16/1 mm/mm in right barrel and a zero die as a reference in left barrel. The obtained data were corrected according to the Bagley correction. The temperature of testing condition was 130-150°C, equivalent to die temperature in the spinning.

Fiber mechanical properties were determined using VIBRO-DYN 400 (Lenzing Instruments GmbH & Co. KG). The gauge length and crosshead speed for the tensile tests were 10 mm and 10 mm/min, respectively. For tensile tests, at least 20 filaments were tested in each case. Dynamic Mechanical Analysis (DMA) were conducted at 10 Hz at a heating rate of 2 °C/min from −90 to 100 °C, and on bundles of 10 filaments at 25 mm gauge length.

A D2 Phaser diffractometer (Bruker), equipped with a lynxeye detector was used to record the X-ray diffractograms. All the X-ray curves have 2θ ranging from 5° to 60°. The degree of crystallinity Xc for each specimen was obtained from the ratio between the area under the crystalline peaks and the total area under the diffraction curve, with different contributions of the crystalline and amorphous regions considered. The orientation degree of PVA was measured by Bruker D8 Discover with 2D detector Vantec 500, the distance between the sample and the area detector was 183 mm and the scan time was 2 min. A FEI Quanta 250 scanning electron microscope (SEM) was used to examine the surface and cross-sectional morphology of melt-spinning PVA/CNT fiber.

To investigate the surface hydrophobicity of fibers, the water contact angle (θ) of melt-spinning PVA fibers was measured by an optical contact angle instrument (Dataphysics, OCA 40). The surface contact angle was measured when the water dropped on the fiber surface stably. Each θ value used for the calculations was the average of five determinations.

3. Results and discussion

3.1. Dispersion of CNTs in plasticizer and swollen PVA preparation

CNTs have a tendency to cluster via secondary (van der Waals) interactions between their high specific surface areas. The surfactant and method play an important role in dispersion of CNTs. The general protocol for all solution processing methods includes the dispersion of CNT powder in a liquid medium by vigorous stirring and/or sonication, then mixing the CNT dispersion with a polymer solution. Thorough dispersion of CNTs within the mixing plasticizer homogeneously is the key first step toward achieving uniform dispersion of nanomaterials within the swollen PVA matrix.

Fig. 1 shows the whole preparation and melt-spinning process of PVA fiber. Table 1 lists the effect of different surfactant on CNT dispersion condition with different concentration. It can be seen from Fig. 2(a), all CNT in the each system can exist
stably, no visual settlement even 360 days later. The probable reason is the CNTs with hydroxyl and carboxyl groups bonded covalently at their interfaces, these hydrophilic groups allow the stabilization of CNTs in compound plasticizer.

After dispersion, mixing the plasticizer containing CNT with PVA particles was carried out, and keeping swelling was continued until all plasticizer absorbed by PVA resin for spinning (Fig. 2(b)). The higher CNT content (up to 1%) will lead to the more dispersing agent needed, and hence affecting the swelling process and deteriorate spinnability. So the CNT proper content should be less than 1%, and Tween 80 be the better choice. Fig. 2(c) shows the finished common and CNT reinforced melt PVA fibers.

3.2. Melt-spinning PVA in lab scale

The Fig. 3 shows the strength of as-spun fiber. The results in Fig. 3 indicate that adding CNT has less impact on the fiber strength, all samples’ strength were about 17.5 MPa, and the elongation at break nearly 400%. The authors observed that the strength of composite fiber was improved dramatically by increasing the draw ratio. After the cold (at room temperature) drawing 3 times, the fiber’s strength significantly increased (over 60 MPa), especially the strength of sample B and C as high as 80 MPa, while samples of D, E, F was slightly lower, but still higher than the control sample. In addition, the elongation at break of samples containing CNT decreased compared with the control sample. But when the CNT content increased to 5‰, the mechanical properties of fiber decreased. Further increased to 1‰, the spinning process become not stable because the CNT aggregated in the fiber matrix and forming mechanical defect, and reduced the strength of the fiber. Therefore, PVA optimal content should be in the range of 0.1–0.5% of enhancing CNT.

Based on the aforementioned research result, the scalable spinning of melt PVA fiber will apply the following system: 1‰ CNT disperse in compound plasticizer using Tween 80.

3.3. Melt behavior and rheology of Swollen PVA

Fig. 4 shows the rheological properties of different content of CNT modified PVA. It can be seen from the figure that pure PVA and CNT reinforced PVA system are pseudo-plastic fluid, with increasing the shear rate, the viscosity of the system decreases gradually. This may be due to the presence of physical crosslinking points between PVA molecules destroyed in the high shear stress and improve the activity of the molecular chain. At the same temperature of 130 °C, it was found that adding a small amount of CNT increased the viscosity of PVA/CNT composites, but when the CNT content reached 5‰, instead of the viscosity of the system reduced. When keep the shear rate 100–2000 S⁻¹ range at 130 °C, the viscosity of CNT reinforced PVA was about 100–400 Pa s, which is equivalent to the melt viscosity of polypropylene and polyamine suitable for melt spinning.

3.4. Mechanical of CNT reinforced PVA fiber

The properties of melt-spun PVA/CNT fibers were strongly affected by the quality of CNT dispersion and the post-treatment process. Fig. 5 shows the CNT enhancement of mechanical property curves of as-spun and final PVA fiber. As can be seen from the graph, the tensile strength of PVA/CNT(OH) fiber has certainly enhanced, and the CNT(COOH) did not significantly increase the tensile strength of PVA fiber. As for PVA/CNT(OH) fiber, they are about 27.59 MPa for the

Table 1

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
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<tr>
<td>CNT</td>
<td>-OH</td>
<td>-OH</td>
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<td>(1‰)</td>
<td>(1‰)</td>
<td>(1‰)</td>
<td>(1‰)</td>
<td>(3‰)</td>
<td>(5‰)</td>
<td>(10‰)</td>
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Note: K30 in the system of A and B, others using Tween 80 as surfactant.

![Fig. 2. Raw materials and melt-spinning PVA fiber. (a) Different dispersants on the dispersion of CNT effect (b) The swollen PVA containing CNT. (c) Picture of long PVA composite filaments on bobbin. (left: normal PVA fiber, right: CNT(OH)-1‰ reinforced).](image)
raw fiber and 565 MPa for the stretched fiber, respectively. Mechanical measurements also reveal a significant improvement of the tensile strength with a value near 20 times stronger for the stretched fiber. Mechanical drawing was the dominant factor in enhancement of physical properties, and it is believed to be the effect for further orienting and ordering of both the nanotubes and polymer chains in the fiber.

The storage modulus–temperature curves of different fibers are shown in Fig. 6. With increasing the draw ratio, the crystallinity enhanced, which improved the storage modulus of the fibers. The difference between the storage modulus of the composite (5) and that of the control (1) sample represents the contribution of the drawing to the overall modulus. For CNT(OH) containing samples, the difference between E5 and E1 decreased from 35.14 GPa at −50 °C to 21.1 GPa at 0 °C. These observations depict the variation of composite fiber modulus as a function of temperature. Changing in crystallinity, orientation degree and interaction between PVA and CNT under stretching may be related to the varying extent of storage modulus in PVA/CNT composite fibers.

Fig. 7 shows tan δ as a function of temperature for PVA/CNT(OH) composite fibers at a fixed frequency of 10 Hz. It can be observed that all PVA composites fiber did not show a clear peak corresponding to its glass temperature (Tg). But after post-treating, broadening of tan δ peak in the vicinity of γ-relaxation also indicates the stronger interaction between PVA and CNT as compared to as-spun PVA/CNT(OH) composite fiber. Due to the fact that PVA fiber crystallinity increased with draw ratio increased, the amorphous region of the molecular chain segment movement was restricted, PVA fiber mechanical loss was reduced.

3.5. Crystallization and Orientation Studies of melt PVA fiber

These characterization results suggest that the mechanical properties of these PVA/CNT composites are closely related to the polymer crystallinity and orientation degree. PVA was a partially crystalline polymer, six obvious crystallization peak appeared in the 2θ values from 10° to 45° range [41]. From Table 2 it can be found that the crystallization of as-spun PVA fiber is 27.3%, with low crystallinity and large amorphous area proportion, which is advantageous for the fiber to be stretched at room temperature. With the increase of stretching ratio, its crystallinity increased gradually. The crystallinity reached 46.2% after 3 times cold drawing. Based on the XRD diffraction curve it can be found that with the increase of drawing ratio, the diffraction peak of 22.7° was gradually strengthening, and a new diffraction peak appeared at 40.5°. After post-treatment, the crystallinity further increased by factors of 24.3%. The crystallization of PVA fiber was as high as 67.7% after drawing at 170 °C, but when the temperature was continued to increase to 210 °C, the crystallinity decreased to 57.6%. This may be attributed to the disorientation of PVA molecular chain while stretching at higher temperature. It is believed that this stretch-treatment improves the nanotube and PVA alignment and increases the PVA crystallinity. The latter has been shown to be critical to enhancing stress transfer between nanotubes and PVA in composite materials. The carbon nanotubes can enhance the crystallization of the PVA also has been reported in some references [42–48].
Orientation degree is an important parameter to indicate the internal super-molecular structure of fiber, and is also an important parameter to characterize the mechanical properties of fiber. The XRD method can be used to determine the fibrous crystal and amorphous region of the average degree of orientation. The degree of orientation is listed in Table 2, and Fig. 8 shown symmetrical diffraction ring of the PVA raw fiber. It had no obvious orientation at any angle and indicate that the as-spun PVA fiber with random orientation. Increasing the draw ratio, the X ray diffraction arc of PVA fiber became strong and very concentrated alone the equatorial line, indicating that the PVA molecular chain can be stretched along the axial orientation rapidly and formed axial orderly structure under tension. Increasing the tensile temperature, the orientation of the fiber was further increased. But when the temperature reached to 210°C, the orientation degree became lower than 170°C due to the polymer chain disorientation at high temperature, which has the same trend of the fibers crystallinity.

### 3.6. Surface morphology and its form mechanics

Fig. 9 are the SEM pictures of PVA/CNT composite fiber surface and section. With the draw ratio increases, the fiber diameter decreased gradually. It has been found that CNT was well-distributed without obvious aggregation, even for the case that the content of CNT was as high as 5%.

The analysis of the cross-section morphology showed that the raw PVA fiber shape was round and with dense sections. After cold and hot stretching, the shape of PVA fiber were kept round, the porous belt region appeared in the cross sections, and the distance between the belt no-dense regions was not the

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**Table 2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>1#</th>
<th>2#</th>
<th>3#</th>
<th>4#</th>
<th>5#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity</td>
<td>27.3%</td>
<td>46.2%</td>
<td>51.6%</td>
<td>67.7%</td>
<td>57.6%</td>
</tr>
<tr>
<td>Orientation degree</td>
<td>–</td>
<td>88.6%</td>
<td>89.4%</td>
<td>93.2%</td>
<td>92.25%</td>
</tr>
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</table>

Note: 1#-As-spun PVA fiber; 2#-3 times drawn at room temperature; 3#-3 times drawn at room temp and dry; 4#- hot drawn at 170°C; 5#- hot drawn at 210°C.
same. But the finished fiber’s cross section became compact and relatively less pores.

In addition, the finger-like pores distributed along the axial direction relatively homogeneous on the melt-spinning PVA fiber surface, the length of pores was about 20–40 μm, and the distance between the adjacent pores was only several micrometers by visual inspection. It is speculated that these finger-like pores were formed for evaporating plasticizer during dry and heat drawn, which may
Using Tween 80 as dispersing agent, the CNT can disperse in compound plasticizer stably, and achieved melt-spinning of PVA/CNT composites fiber in lab scale. CNT reinforced PVA system are pseudo-plastic melt fluid, this is due to the presence of physical crosslinking points between PVA molecules and CNT.

Mechanical properties of PVA composites fiber can be improved by cold and hot-drawing. This treatment improves the nanotube alignment along the fiber axis and increases the PVA crystallinity and orientation degree.

3.7. Contact angle (hydrophilic characteristics)

PVA is a hydrophilic polymer with polar hydroxyl groups on the molecular chain. The hydrophilicity can be tested by the contact angle. The more hydrophilic, the smaller contact angle is. The optical contact angle of PVA/CNT(OH)-1% composite fibers with different tensile conditions are depicted in Fig.10. The hydrophilicity of PVA fiber decreased gradually after stretching and drying (Table 3). This may be due to that the most of plasticizer was removed in the dry and tensile process, and the hydrophilicity of the plasticizer containing multi hydroxymethyl compounds greater than hydrophilic PVA itself. And therefore the contact angle became bigger and bigger, and the hydrophilicity was weakened.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1#</th>
<th>2#</th>
<th>3#</th>
<th>4#</th>
<th>5#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle(°)</td>
<td>23.3</td>
<td>28.3</td>
<td>38.3</td>
<td>39.1</td>
<td>45.2</td>
</tr>
</tbody>
</table>

Table 3 Contact angle value of PVA/CNT(OH)-1% single fiber.

The CNT is well-distributed without obvious aggregation in composites fiber, even when the content of CNT is as high as 5%. The finger-like pores were observed on the melt-spinning PVA fiber surface to be relatively homogeneous. At the same time, the hydrophilicity weakening due to the hydrophilic plasticizer has been removed during dry and hot-draw.

Acknowledgments

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References
