Gel spinning of PVA composite fibers with high content of multi-walled carbon nanotubes and graphene oxide hybrids

Yizhe Wei, Dengpan Lai, Liming Zou, Xinlong Ling, Hongwei Lu and Yongjing Xu

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, 2999 North People Road, Shanghai 201620, People’s Republic of China

E-mail: lmzou@dhu.edu.cn.

Abstract. In this report, poly (vinyl alcohol) (PVA) composite fibers with high content of multi-walled carbon nanotubes and graphene oxide (MWCNTs-GO) hybrids were prepared by gel spinning, and were characterized by TGA, DSC, SEM, XL-2 yarn strength tester and electrical conductivity measurement. The total content of MWCNTs-GO hybrids in the PVA composite fibers, which is up to 25 wt%, was confirmed by TGA analysis. The DSC measurement shows that the melting and crystallization peaks decreased after the addition of nano-fillers. This is due to the reason that the motion of PVA chains is completely confined by strong hydrogen bonding interaction between PVA and nano-fillers. After the addition of GO, the dispersibility of MWCNTs in composite fibers improved slightly. And the tensile strength and Young’s modulus increased by 38% and 67%, respectively. This is caused by the increased hydrogen bonding interaction and synergistic effect through hybridization of MWCNTs and GO. More significantly, the electrical conductivity of PVA/MWCNTs/GO composite fibers enhanced by three orders of magnitude with the addition of GO.

1. Introduction

Carbon nanotubes (CNTs) have received great attention due to their unique mechanical, electrical and thermal properties since their discovery by Iijima [1]. They can find application in high performance nanocomposites [2], field-emission devices [3], hydrogen storage media [4] and sensors [5]. Incorporation of high mechanical and electrically conductive additives, carbon nanotubes, into polymer fibers can improve their mechanical properties and provide multi-functionalities needed for electrical energy storage, sensing and actuation [6]. In years past, PVA fibers containing a large fraction of carbon nanotubes were widely investigated because of their strong mechanical property, high toughness, and high electrical conductivity [7]. Vigolo proposed a new method by which fibers were spun by injecting the mixture of CNTs and SDS into a co-flowing PVA bath [8]. The fibers from this method contain large fractions of CNTs, that is, above 10 wt%. This led to fibers with large energy to failure, high electrical conductivity. However, it is particularly challenging to achieve this spinning process on large scale and in multifilament configuration. Meanwhile, much effort has been

1 Address for correspondence: Liming Zou, State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, 2999 North People Road, Shanghai 201620, People’s Republic of China. E-mail: lmzou@dhu.edu.cn.

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made to directly spin composite fibers from mixture of PVA and CNTs in static coagulating baths. However, the final content of CNTs in composite fibers was low, which is insufficient to achieve significant properties. Moreover, large fraction of CNTs may result in agglomerates [9], and bad dispersion state reduces the mechanical and conductivity properties of the fibers.

In recent years, graphene, a two-dimensional, one-atom-thick material, has attracted great attention in various practical application areas because of its extraordinary electronic, thermal, and mechanical properties. Graphene has been considered as an ideal nanofiller in polymer fibers to improve the mechanical and electrical properties. GO which bearing various oxygen functional groups is hydrophilic and can be readily dispersed in water as individual sheets to form stable colloidal suspensions. Moreover, GO can serve as a superior dispersant to disperse pristine CNTs in aqueous media or polymer matrix through supramolecular interactions [10]. More significantly, the hybridization of graphene and CNTs can lead to synergistic enhancement of the mechanical performance of their polymer composites [11]. Furthermore, the unique electrical conductive network formed by the hybridization of graphene and CNTs lead to the increasing electrical conductivity [12].

Therefore, spinning polymer composites fibers by incorporation of CNTs-GO hybrids can be an excellent route to utilize their mechanical and electrical performance of their polymer composites.

Here, we report the preparation of PVA composite fibers with high content of MWCNTs-GO hybrids by gel spinning. For comparison, PVA composite fibers with high content of MWCNTs were also spun. The composites fibers were characterized by TGA, DSC, SEM, XL-2 yarn strength tester and electrical conductivity measurement.

2. Experimental

2.1. Materials
The pristine MWCNTs (Nanocyl™ NC7000, average diameters 9.5 nm, lengths 1.5 μm, carbon purity 90% by TGA) were purchased from Sambreville Nanocyl S.A. (Belgium) and used as received. Graphite was purchased from Shanghai Yifan Graphite Co. Ltd. PVA (Mw≈114400, 99% hydrolyzed) was received from Anhui Wanwei Updated High-tech Material Industry Co., Ltd. All the other reagents were supplied from Sinopharm Chemical Reagent Co., Ltd. and used as received. All reagents are analytical grade and used as received.

2.2. Fiber spinning
MWCNTs were oxidized by the mixture of H₂SO₄ and HNO₃ (volume ratio: 3:1). GO was prepared using the modified Hummer’s method [13].

2.2.1. PVA/MWCNTs spinning dope preparation. 800 mg PVA was dissolved into 10 mL DMSO at around 100°C. Meanwhile, 200 mg oxidized MWCNTs was dispersed in 40 mL water and sonicated in a bath sonicator (SK2200H, 53 kHz, 100 W) for 2 hours. Then MWCNTs dispersion was gradually added into the PVA/DMSO solution. This mixture was subjected to further stirring for 12 h at around 100°C. The desired PVA/MWCNTs spinning dope was obtained by removing excess water using vacuum distillation.

2.2.2. PVA/MWCNTs/GO spinning dope preparation. 750 mg PVA was dissolved into 10 mL DMSO at around 100°C. Meanwhile, 200 mg oxidized MWCNTs was dispersed in 40 mL water and 50 mg GO which dispersed in 10 mL water was added into MWCNTs dispersion. Then the mixture was sonicated in bath sonicator for 2 hours. At last, the MWCNTs-GO hybrids aqueous dispersion was gradually added into the PVA/DMSO solution at around 100°C. This mixture was subjected to further stirring for 12 h at around 100°C. The desired PVA/MWCNTs/GO spinning dope was obtained by removing excess water using vacuum distillation.
Fiber spinning was done using syringe pump and syringe needle. The spinning dope was injected at 20 mL/h through a 0.5 mm diameter needle into methanol bath at room temperature. The as spun fibers were drawn at room temperature using a drawing machine.

For comparison, pure PVA fibers, PVA composite fibers with 20 wt% oxidized MWCNTs (PVA/MWCNTs 20 wt%), PVA composite fibers with 20 wt% oxidized MWCNTs and 5 wt% GO (PVA/MWCNTs 20 wt%/GO 5 wt%) were spun.

2.3. Characterization

SEM images were acquired on a JEOL JSM-5600 LV instrument (Japan) operating at 5 KV. Diamond DSC is at a heating rate of 10°C/min under nitrogen flow. TGA data were obtained on a TG 209 F1 Iris thermo-gravimetric analyzer (Germany), from room temperature to 800°C, at a heating rate of 20°C/min, under continuous nitrogen flow. Tensile strength was measured on XL-2 yarn strength tester. The electrical conductivity of composite fibers was measured by a two-probe method with Keithley 4200 SCS.

3. Results and discussion

3.1. TGA analysis

Based on TGA analysis (figure 1), the content of nano-fillers in composite fibers were estimated from the residual weight at 800°C, which are about 19.2%, 26.3% for PVA/MWCNTs 20wt% composite fibers and PVA/MWCNTs 20wt%/GO 5wt% composite fibers. The TGA curves of oxidized MWCNTs and GO shows multi-stage weight loss from room temperature to 800°C. The weight loss before 200°C is due to the loss of bound water which absorbed by functional groups [14]. The weight loss at the temperature between 200°C and 500°C can be attributed to the decomposition of the functional organic moieties attached to the defect sites of MWCNTs and GO during functionalization process [14, 15]. At the temperature higher than 500°C, the slight weight loss is often ascribed to the decomposition of MWCNTs [14, 16]. For PVA/MWCNTs 20 wt% composite fibers and PVA/MWCNTs 20 wt%/GO 5 wt% composite fibers, there is an obvious weight loss at the temperature between 250°C and 500°C which is due to the decomposition of functional groups and PVA molecules. The residual weight remains stable at 800°C, and the content of nano-fillers can be confirmed.

![Figure 1](image)

**Figure 1.** TGA curves of oxidized MWCNTs, GO, pure PVA fibers, PVA/MWCNTs 20 wt% composite fibers and PVA/MWCNTs 20wt%/GO 5wt% composite fibers.
3.2. DSC analysis
In order to understand the thermal properties of the composite fibers, DSC measurements were carried out on all fibers. As can be seen from figures 2(A) and (B), pure PVA fibers show obvious melting and crystallization peaks. However, for PVA/MWCNTs 20 wt%, PVA/MWCNTs 20 wt%/ GO 5 wt%, the melting and crystallization peaks decreased. This may be due to the reason that PVA chains are constrained in a tiny and fixed space by strong hydrogen bonding interaction between PVA chains and nano-fillers [17]. Compared to PVA/MWCNTs 20 wt%, the melting and crystallization peaks of PVA/MWCNTs 20 wt%/ GO 5 wt% is smaller. The major factor is that the introduction of GO enhanced the hydrogen bonding interaction between PVA chains and nano-fillers.

![Figure 2. DSC curves of PVA composite fibers. (A) cooling curves and (B) melting curves.](image)

3.3. Morphology characterizations
To investigate dispersion of MWCNTs and GO in PVA composite fibers, SEM was used to observe the cross-section morphology of as-spun fibers. As can be seen from figure 3(B), there are no obvious aggregates in PVA/MWCNTs 20 wt% composite fibers. This can be attributed to strong hydrogen bonding interaction between oxidized MWCNTs and PVA chains which damages the strong van der Walls interaction among MWCNTs. Compared to PVA/MWCNTs 20 wt% composite fibers, the dispersibility of MWCNTs in PVA/MWCNTs 20 wt%/ GO 5 wt% composite fibers improved slightly. The main reason is that GO serves as a superior dispersant to disperse MWCNTs in PVA composite fibers through supramolecular interactions [10]. The cross-section shape of the PVA/MWCNTs 20 wt% composite fibers is circle. However, that of PVA/MWCNTs 20 wt%/GO 5 wt% composite fibers turned into irregular circle after the introduction of GO. This may be due to the untight stack of GO and oxidized MWCNTs in composite fibers.
Figure 3. SEM images of the cross-section of (A), (B) PVA/MWCNTs 20wt% composite fibers, (C) and (D) PVA/MWCNTs 20wt%/GO 5wt% composite fibers.

3.4. Tensile strength

The mechanical properties of PVA composite fibers were shown in table 1. The tensile strength and Young’s modulus are 0.21 GPa and 10.98 GPa, respectively, for PVA/MWCNTs 20 wt% composite fibers. The value for PVA/MWCNTs 20 wt% / GO 5 wt% composite fibers spun in similar conditions increased by 38% and 67%, respectively, after the addition of GO. They are 0.29 GPa, 18.31 GPa, respectively. And the elongation for PVA/MWCNTs 20 wt% composite fibers is 20.52%, while that of PVA/MWCNTs 20 wt%/GO 5 wt% composite fibers is 2.74%. The major factor responsible for these differences is the interfacial interactions between the nano-fillers and PVA molecules and synergistic effect through hybridization of MWCNTs and GO [18]. There are a lot of carboxyl and hydroxyl groups on GO sheets, which formed hydrogen bonds with PVA molecules. The hydrogen bonding greatly enhances interfacial interactions and hinders the slippage of nano-fillers and PVA molecules, which leads to high tensile strength and low strain to break.

Table 1. Mechanical properties of gel-spun fibers.

| Sample          | Tensile strength (GPa) | Young’s modulus (GPa) | Elongation (%) |
|-----------------|------------------------|-----------------------|----------------|
| PVA/MWCNTs 20wt%| 0.21                   | 10.98                 | 20.52          |
| PVA/MWCNTs 20wt%/GO 5wt% | 0.29     | 18.31                 | 2.74           |

3.5. Electrical property of the composite fibers

PVA/MWCNTs 20 wt% composite fibers were found to be poorly conductive despite the high content of MWCNTs they contains. Oxidation treatment which can bring in large damages to the MWCNTs must be the main reason. Moreover, the agglomerates also can reduce the electrical conductivity [18]. The electrical conductivity of PVA/MWCNTs 20 wt% composite fibers at room temperature is about $7.3 \times 10^{-5}$ S/m. That of PVA/MWCNTs 20 wt%/ GO 5 wt% composite fibers increased to $5.3 \times 10^{-2}$ S/m. The obvious improvement, by three orders of magnitude, is ascribed to the better dispersion of MWCNTs in PVA/MWCNTs 20 wt%/ GO 5 wt% composite fibers and synergistic effect through hybridization of MWCNTs and GO. GO can serve as a superior dispersant to disperse CNTs in
polymer matrix through supramolecular interactions. And the introduction of GO allows better intertube contacts. These all contribute to the increasing electrical conductivity.

4. Conclusion

In summary, PVA composite fibers with high content of MWCNTs-GO hybrids were prepared by gel spinning. The total content of MWCNTs-GO hybrids in the PVA composite fibers is up to 25 wt%. The DSC measurement shows that the melting and crystallization peaks decreased due to strong hydrogen bonding interaction between PVA and nano-fillers which constrain the motion of PVA chains. After the introduction of GO, the dispersibility of MWCNTs in composite fibers improved slightly. The tensile strength and Young’s modulus increase by 38% and 67%, respectively, due to the increased hydrogen bonding interaction and synergistic effect through hybridization of MWCNTs and GO. More significantly, the electrical conductivity of PVA/MWCNTs/GO composite fibers enhanced by three orders of magnitude with the addition of GO.

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