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Spherical and rodlike inorganic nanoparticle regulated the orientation of carbon nanotubes in polymer nanofibers

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ABSTRACT

PVA nanofibers containing carboxylic-modified MWCNTs were fabricated via electrospinning of PVA/MWCNTs mixed solution. The alignment of MWCNTs in PVA nanofibers was studied using transmission electron microscope and scanning electron microscope. In addition, the orientation of MWCNTs in PVA nanofibers was further investigated in the presence of rod-like nanoparticle rectorite (REC) and of spherical nanoparticle titanium dioxide (TiO_2). The images demonstrated the embedment of MWCNTs in the nanofibers and the alignment of MWCNTs along the fiber axis. Moreover, the addition of REC and TiO_2 improved the alignment of MWCNTs in PVA nanofibers.

1. Introduction

Carbon nanotubes have been discovered by Iijima back to 1991 [1]. Since then tremendous investigations have been performed due to their superb properties [2]. Multi-walled carbon nanotubes (MWCNTs) consist of multiple concentric cylindrical shells of graphene. They are arranged coaxially with an inter-lamellar space of 0.35 nm [3]. The multi-lamellar structure with a small interspace facilitates agglomeration and entanglement, thereby impacting the dispersion, orientation and alignment of MWCNTs in the carriers, which could be greatly limited for its application. Therefore, some techniques have been applied to facilitate the dispersion of MWCNTs, including precipitation of MWCNTs suspension under magnetic field, synthesis of aligned nanotubes and mechanical stretching of polymer/MWCNTs composite mats [4].

Among all these methods, the alignment of MWCNTs in composite nanofibers is promising and displays vast advantages in resistance of cross-sectional and twisting distortions, and in compression with no fracture [5,6]. All these superiorities make MWCNTs easier to disperse and orientate in nanofiber matrix.

Electrospinning has been utilized to fabricate polymer/MWCNTs composite nanofibers, which meanwhile could align the MWCNTs in polymer fibers [7–11]. Polyvinyl alcohol (PVA) is a highly biocompatible and nontoxic synthetic polymer. It is water-soluble due to the hydroxyl groups from side chain [12]. And it is also a well-established fiber-forming polymer in electrospinning.

Rectorite (REC) is a layered silicate and has wide interlayer distance. The incorporation of REC nanoplatelets into a polymer matrix improves physicochemical properties of polymer-based products in the storage modulus, the flame retardancy, the thermal stability, the gas barrier etc. [13]. Lu et al. have proved that the addition of REC was conducive to form uniform nanofibers [14], which may assist the alignment of MWCNTs in nanofibers. Recently, titanium-dioxide (TiO_2)-based composites nanofibers have been highlighted in research due to high mechanical resistance and stability. Moreover, Shahar et al. have proved that the heavy TiO_2 loading conduced to the CNTs alignment in PAN nanofibers [15]. Yang et al. have reported that MWCNTs could be coupled with TiO_2 by electrospinning [16]. Based on reports stated above, we plan to explore the impact of REC and TiO_2 on the alignment of MWCNTs in nanofibers.

In the study, PVA nanofibers containing MWCNTs were fabricated via electronspinning. The alignment of MWCNTs in the nanofibers was investigated. The impact of REC and TiO_2 on the

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alignment of MWCNTs was further studied by the supplementation into the matrix of PVA/MWCNTs. The as-spun composite nanofibers were mainly characterized by field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM) and energy dispersive X-ray spectroscopy (EDX). The tensile strength and thermo-gravimetric analysis (TGA) were performed to determine the mechanical properties and thermal stability of the nanofibrous mats.

2. Experimental procedure

Polyvinyl alcohol (PVA, $M_w = 8.5 \times 10^4$–1.24×10^5 Da) was purchased from Sigma–Aldrich Chemical Reagent Co., USA. Multi-walled carbon nanotubes (MWCNTs, Main range of diameter 60–100 nm) were supplied by Nanotech Port Co., Ltd. in Shenzhen, China. The calcium rectorite (Ca^{2+}-REC) was provided by Hubei Mingliu Co., China. The powder of TiO_2 (P-25) was supplied by Degussa AG-Germany. The aqueous solution was prepared using purified water with a resistance of 18.2 MΩ cm.

The morphologies of composite nanofibers were observed by Field Emission Scanning Electron Microscope (FE-SEM, ZEISS ∑SIGMA, Germany) and Transmission electron microscope (TEM, JEM-2100 (HR), JEOL Ltd., Japan). The mechanical properties of the membranes were tested on a tensile tester (ETM502A, Shenzhen wance Instrument Co., Ltd., China), the size of the sample was 5 cm × 1 cm. The thermal properties of the nanofibrous mats were investigated by TGA (SDT Q600, Tainstsh, USA). TGA was carried out in nitrogen atmosphere within the temperature range from 20 to 600 °C at a heating rate of 10 °C min^{-1}.

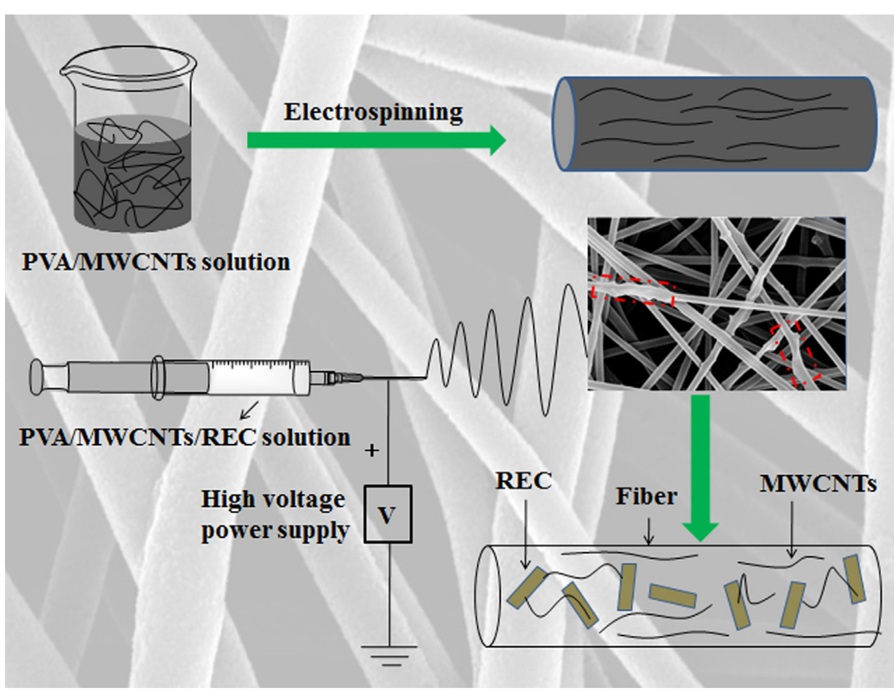
In the study, MWCNTs were carboxylic-modified to promote their interaction with the hydroxyl group of PVA, thereby facilitating their embedment into nanofibers. The mixture of sulfuric acid and nitric acid at a ratio of 3/1 (v/v) were utilized to oxidize MWCNTs at 70 °C for 3 h [17]. The product was collected by the filtration with nylon membrane filter (d = 0.45 μm), and washed to a neutral pH value with purified water. Afterwards the product was dried at 65 °C in vacuum for 6 h.

To obtain homogenous PVA/MWCNTs solutions for electrospinning, firstly carboxylic-modified MWCNTs were ultrasonic-treated in water solution for 1 h at room temperature. Secondly PVA aqueous solution was added into homogenous MWCNTs solution under continuous stirring for 6 h. The concentration of PVA and MWCNTs in the solution was maintained at 8% (w/w) and 1% (w/w), respectively. In the investigation of the impacts from REC or TiO_2, the concentration of REC or TiO_2 was maintained at 1% (w/w) as well.

To fabricate PVA nanofibers containing MWCNTs, the as-prepared MWCNTs/PVA solutions were fed into a 10 mL plastic syringe equipped with a blunt metal needle with internal diameter of 1.2 mm. The syringe was driven by a syringe pump (LSP02-1B, Baoding Longer Precision Pump Co., Ltd., China). The positive electrode of the high voltage DC power supply (DW-P303-1ACD8, Tianjin Dongwen Co., China) was clamped to the metal needle tip of the syringe. The applied voltage, distance of tip to collector and the delivery speed of solutions were 15 kV, 15 cm and 1 mL/h, respectively. The as-spun fibers were collected by a grounded cylindrical collector covered by aluminum foil. The ranges of ambient temperature and relative humidity were kept at 20–25 °C and 45%, respectively. The prepared nanofibers were dried under vacuum at room temperature to remove the trace solvent.

3. Results and discussion

The schematic diagram illustrates the fiber formation during electrospinning. PVA/MWCNTs solution prepared as stated above is stretched, elongated and thinned under a high voltage to the formation of uniform fibers with nanometer scale diameters. Initially MWCNTs were added randomly in the solutions, but they gradually oriented along the streamlines when the electrospun flow jet produced on a rotating disk with a tapered edge. Then MWCNTs are sucked into the jet and get oriented along the direction of fiber stretched. The polymer/MWCNTs composite nanofibers were motivated to align MWCNTs along the axis of polymer fibers due to the rapid fiber-draw from the process of electrospinning [18]. Meanwhile the shape and alignment of MWCNTs has impact on the morphology of nanofibers. The nanofibers containing the regular-shaped and well-aligned MWCNTs tend to be smoother than those containing bending or unaligned MWCNTs (Scheme 1).



Scheme 1. Schematic diagram illustrating the fabrication of PVA/MWCNTs and PVA/MWCNTs/REC nanofibers.