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Modification of Polyacrylonitrile Nanofibers by Blending with Bacterial Cellulose

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The Polyacrylonitrile (PAN)/ bacterial cellulose (BC) blend nanofibers were prepared by electrospinning blend solutions of BC and PAN in N, N-dimethylacetamide (DMAc)-lithium chloride (LiC1). The morphology, properties and structure of electrospun PAN/BC nanofibers were characterized using Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), Thermo gravimetric analyses (TGA) and differential scanning calorimetry (DSC). The moisture absorption of the nanofibers was discussed. SEM image showed that the scope of the diameters was 480-790nm. The diameters of the blend fibers increased with the increasing of BC content. FT-IR and DSC indicated that intermolecular interactions are formed between two different polymers.

Key words: Electrospinning, Polycarylonitrile, bacterial cellulose, Nanofibers.

This Owing to its comparatively low-cost manufacturing and easy deployment even on a laboratory bench, electrospinning technology has launched polymer micro- and nano-fibers, and broadens the realms of nanotechnology and materials science[1]. Since the electrospun fiber mats have a number of characteristics such as high specific surface area, high aspect ratio, and high porosity, their applications in various fields such as optoelectronic, sensor technology, catalysis, filtration, and medicine are expected. So far, most of common single polymers have been electrospun into fibers[2–3].

Polymer blending is an effective and an economically viable way for the preparation of new materials with desired properties[4-5]. Cellulose is prepared mainly from wood pulp but can also be produced in a highly hydrated form by some bacteria (for example, Acetobacter, Rhizobium, Agrobacterium, and Sarcina), known as bacterial cellulose (BC). As opposed to plant cellulose (PC), BC does not require remedial process to remove unwanted polymers and contaminants, therefore retains a greater degree of polymerization. In a native state, BC has many excellent properties, such as high purity, high degree of polymerization, crystallizing, hydrophilicity and biocompatibility[6-7], etc.

Polyacrylonitrile (PAN) is one of the most important fiber-forming polymers and has been widely used. However, it also has some disadvantages, such as low dye affinity, low moisture regain, and high static charge due to the lack of segmental mobility resulting from intensive molecular orientation of the highly polar nitrile groups. In recent years, a lot of studies have been found in the literature concerning the combination of AN-based polymers and natural polymers. Most of the work, to our knowledge, has been focused on graft copolymerization of acrylonitrile (AN) and

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natural polymers, such as silk fibroin[8–11], casein[12–14], and wool keratin[15–19] etc. However, there is still no report about the preparation and characterization of PAN/BC composite nanofibers, which may combine both the advantages of PAN such as light weight, flexibility, and of BC such as high hydrophilic and biocompatibility.

In this work, BC was used to blend with co-polyacrylonitrile (Co-PAN) containing methylacrylate via solution mixing. The blend solution was spun into the composite fiber via wet electrospinning technique. The conductivity, property as well as morphology of the PAN/BC composite fibers were investigated.

MATERIAL AND METHODS

Solution Preparation

PAN and BC were dissolved in an 8 wt% LiCl/DMAc solution at a controlled temperature of 45! until the BC swelled to form a colloid. Then the colloid was placed at room temperature for further dissolution until completely dissolved; subsequently, it was centrifuged at the rate of 4500 rpm for 2h, debubbled and isolated, and finally a transparent blend solution was obtained. The blend ratios of PAN/BC were controlled through varying the relative weight ratios of each component as 100/0, 97/3, 95/5 and 92/8. The total polymer concentration was set to be 10 wt%.

Electrospinning

Composite solutions were fed through a capillary tip (diameter = 0.5mm) using a syringe (30 ml). The anode of the high voltage power supply was clamped to a syringe needle tip and the cathode was connected to a metal collector. During electrospinning, the applied voltage was 14 kV, the distance between the tip and collector was 17 cm, and the flow rate of the spinning solution was 1 ml/h.

Characterization and Measurement

The samples were fractured in liquid nitrogen and then coated with a thin layer of gold. The diameter and morphology of the electrospun PAN/BC composite fibers were determined by a JSM-5610 scanning electron microscope (SEM, Japan). Fourier transforms infrared absorption spectra for the blend nanofibers were taken with a Nicolet 20sx-B FT-IR spectrometer. The scanning ranged from 4000 cm^{-1} to 400 cm^{-1} with 16 times of scanning.Thermal properties of electrospun fibers were evaluated using differential scanning calorimetry (DSC) from 25 to 200 at a heating rate of 20 min^{-1} in nitrogen environment.Thermo gravimetric analyses of PAN/BC blend fibers were performed with a TA Instruments Du Pont l090 at 20°C/min in nitrogen environment.

RESULTS AND DISCUSSIONS

Morphology of Nanofibers

In this paper, we mainly focus on investigating the effects of BC content on electrospinning of blend fiber. The morphology of the electrospun nanofibers was observed using a scanning electron microscope (SEM). SEM images of PAN/BC nanofibers electrospun in LiCl/DMAc solvent system with different BC are shown in Figure 1 (the concentration of solution is 10 wt %). Straight individual nanofibers are observed.

The diameter distribution of the nanofiber mats is shown in Fig.2. The mean diameter of nanofiber lies between 480 and 790 nm and gradually increases with increasing BC content. All electrospinning experimentations in this paper were carried out under the same condition.

Viscosity and conductivity

The morphology of electrospun fibers is influenced by various parameters. In fact, one of the most significant parameters influencing fiber morphology is the solution viscosity [20]. When the solution viscosity is low, the jets from the needle are unstable and likely to break up and form beads on fiber surface, and it will be difficult to get a continuous nanofiber on the collector. For high viscosity solutions, the jets would not break up but rather travel and split into filaments and form fibers with increased diameter. To understand the relationship between nanofiber diameter and BC content, the viscosity and conductivity were measure for all electrospinning solution and are shown in figure 3. Increased BC content is associated with increased viscosity of the spinning solution (i.e., form about 997 mP for neat PAN solution to about 1451 mP for spinning solution containing 8 wt% BC), which in turn is associated with increased electrospun fiber diameter.

FT-IR spectra

FT-IR spectra of the pure PAN and PAN/BC nanofibers were recorded in the range 4000-

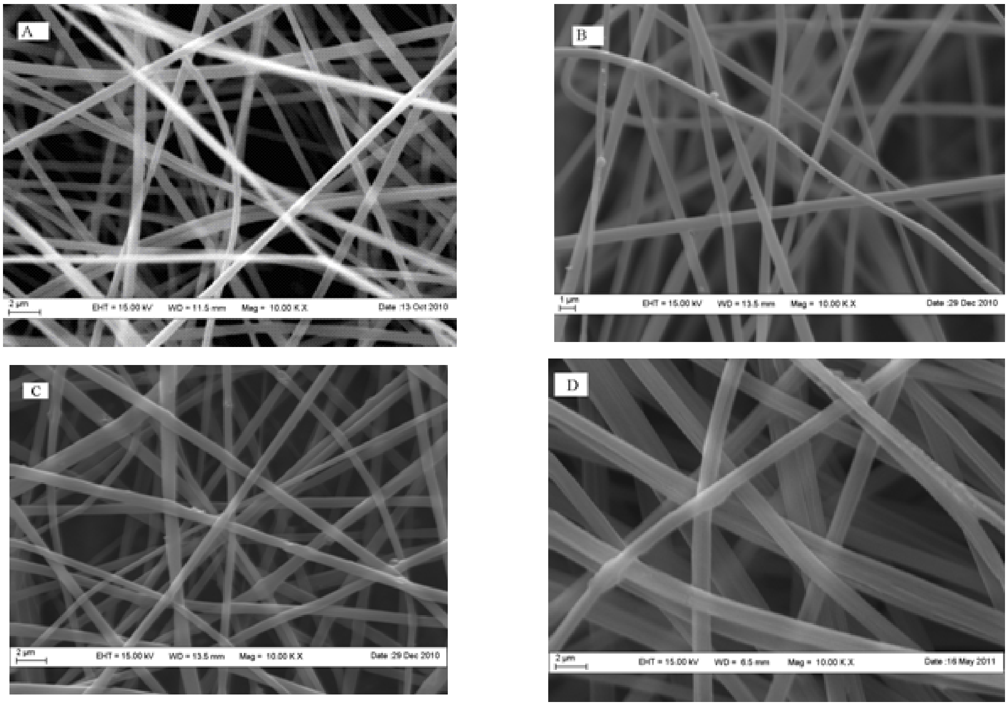

Fig. 1: SEM images of PAN/BC nanofibers with different BC contents, (A)0 wt %, (B) 3 wt %, (C) 5 wt % and (D) 8 wt %

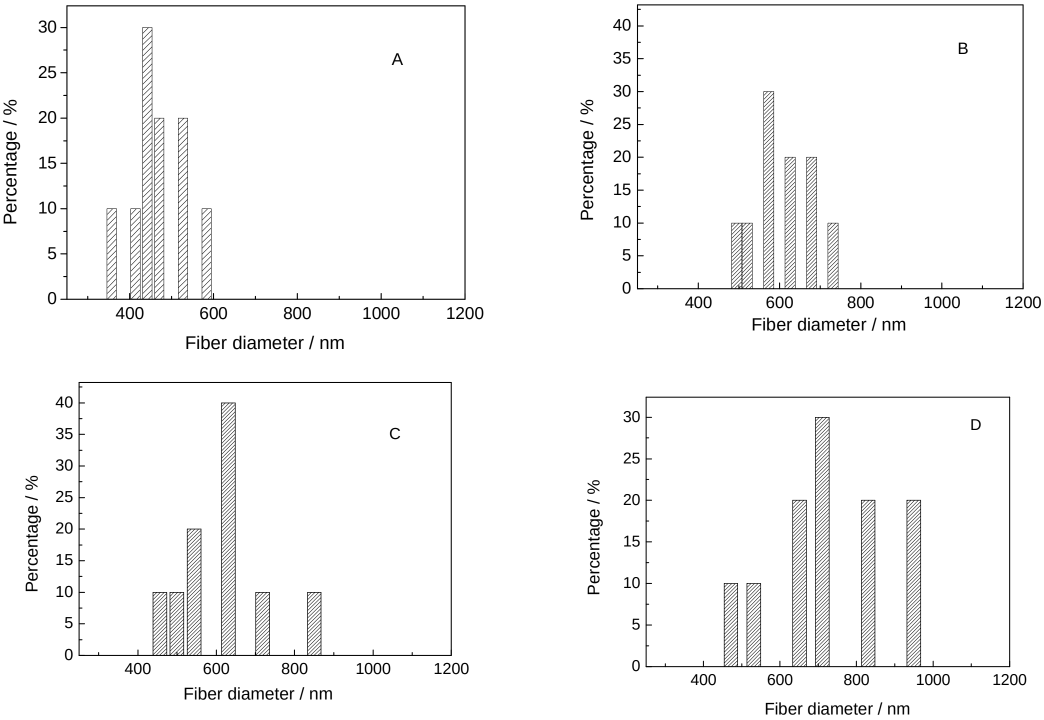

Fig. 2: Diameter of PAN/BC nanofibers with different BC contents, (A) 0 wt %, (B) 3 wt %, (C) 5 wt % and (D) 8 wt %

600 cm^{-1} are shown in Fig. 5. In the case of pure BC, a band at 3358 cm^{-1} is attributed to O-H stretching vibration. Fort PAN fibers,the peak is observed in the range of 2243cm^{-1} which is related to presence nitrile (Ca"N) bonds and indicates the nitrile group exists in polyacrylonitrile chain.

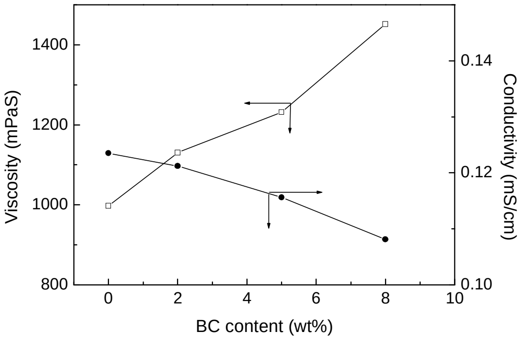

Fig. 3. The conductivity and viscosity of electrospinning solution as a function of BC content

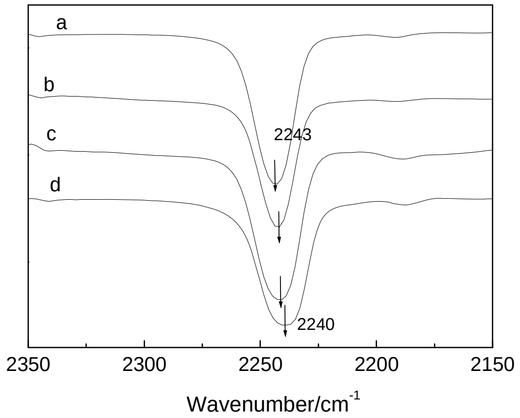

Fig. 4. FTIR spectra of the nitrile (Ca"N) band in (a) PAN; PAN/BC blends nanofibers with BC content (b) 3 wt %, (c) 5 wt % (d) 8 wt %

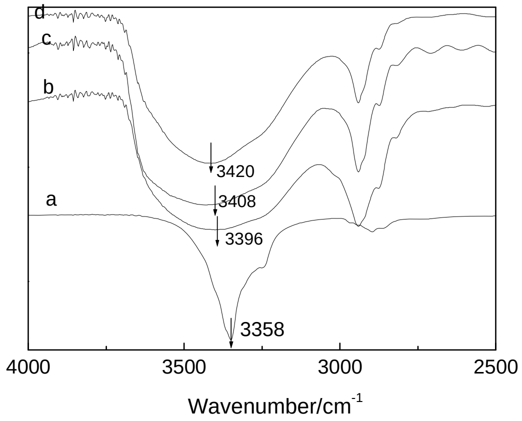

Fig. 5. FTIR spectra of the hydroxyl (0-H) group in (a) BC; PAN/BC blends with BC content (b) 8 wt %, (c) 5 wt % (d) 3 wt %

Figure 6 shows the corresponding hydroxyl groups of BC and PAN/BC blends. The peak around 3358 cm^{-1} comes from hydroxyl groups of BC, the band is observed to shift to high wavenumbers. The more the PAN content, the higher the wavenumbers. This is should be attributed to the hydrogen-bonding between imine and carbonyl group.

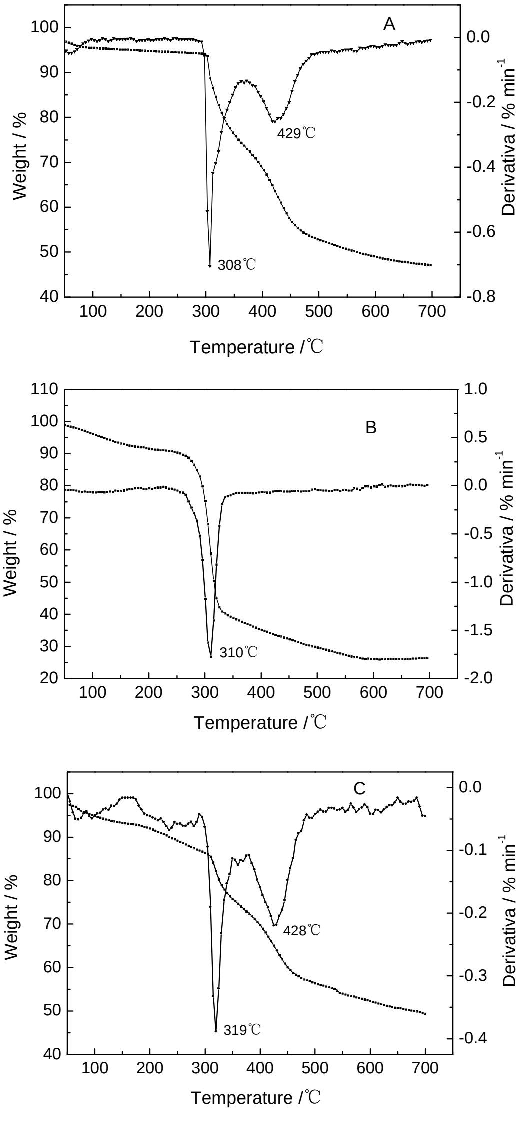

Fig. 6. TGA and DTG thermograms of (A) PAN, (B) BC and (C) PAN/BC blend nanofiber with 8 wt% BC

TGA Analysis

TGA and DTG curves in figure 7 show the thermal stabilities of pure PAN,pure BC and PAN/BC blend fiber with 8 wt % BC. There are two obvious weight loss peaks at 308 ºC and 429ºC in the TGA curve of pure PAN (Fig. 7A). The DTG minimum at 308 ºC is attributed to cyclization and the DTG minimum at 429ºC is attributed to carbonization I. The TGA tracing of the BC exhibits a typical single weight-loss step, with a maximum decomposition rate at308 ºC (Fig. 7B). For PAN/BC blend fiber, the temperature of the first weight loss peak becomes higher when with BC, while the temperature of the second weight loss peak remained almost unchanged with addition of BC (Fig.7C). The better thermal stability of the blend than either of pure BC and pure PAN could be considered as additional evidence of interactions between BC and PAN.

CONCLUSION

The PAN/BC composite nanofibers containing different amounts of BC were prepared by electrospinning composite solutions containing BC and PAN in N, N-dimethylacetamide -lithium chloride. SEM images showed that the scope of the diameters was 480-790nm, and the spun fibers became thick with the ratio of BC to PAN increasing. DSC and FT-IR indicated that there may be interactions between BC and PAN. The addition of BC could greatly improve the antistatic property of PAN fibers.

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