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Facile and simple fabrication of strong, transparent and flexible aramid nanofibers/bacterial cellulose nanocomposite membranes

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ABSTRACT

Mechanical strength, transparency and flexibility are the leading bottlenecks for the application of a membrane. Thus, the development of co-effectively strong, transparent and flexible membranes is significant for various industries. Here, we fabricated the ANFs (aramid nanofibers)/BC (bacterial cellulose) nanocomposite membranes with different ANFs loadings (up to 8.0 wt%) via a facile and simple vacuum-assisted flocculation route. FT-IR, XRD and SEM were applied to characterize the pure BC membrane and ANFs/BC nanocomposite membranes. The resultant membranes maintained excellent transparency and flexibility at relatively low ANFs concentrations ($\leq$4.0 wt%). The mechanical properties of ANFs/BC nanocomposite membranes could be altered by changing the ANFs content, in which the ANFs served as an enforcement agent, and the nanocomposite membrane exhibited the highest tensile strength at ANFs content of 4.0 wt%. Besides the excellent tensile strength, transparency and flexibility, the surface wettability of the ANFs/BC decreased compared to that of pristine BC, indicating a relative stability in humidity. These results showed that the ANFs/BC nanocomposite membrane is strong, transparent and flexible, thus making it an excellent candidate for electronic substrates and optical materials.

1. Introduction

The development patterns of composite materials science have been dramatically affected by nanomaterials and nanotechnology. The ever-growing library of nanoscale building blocks with variable shapes, sizes and compositions has provided great opportunities for designing the materials based on multi-features fusion [1,2]. Nanomaterials scientists predict that composite made with nanoscale building blocks such as nanotubes, platelets, and nanofibers will combine two or more desirable properties, as exhibiting exceptional mechanical performance [3], or provide thermal stability for otherwise highly labile materials [4]. In particularly, the effective use of nanoscale building blocks as reinforcement may not only result in superior properties to other systems [1,5,6] but also retain the original performance such as excellent transparency [7] and good flexibility [8]. In addition, the significance of mechanical reinforcement for optically functional materials has been witnessed by the rapid development of electronic industries which, in turn, have created a great demand for transparent and strong materials [9]. Meanwhile, flexibility is necessary for high-strength materials to be employed in various applications [10]. Encouragingly, the availability of nanofibers offers a potential way to avoid this limitation of opaqueness [7].

One of the most versatile polymer matrixes may be BC, which is a homopolymer made up of β-D-glucopyranose units linked by (1–4)-glycosidic bonds [11], regarding as promising biodegradable fiber-reinforcement for polymeric composites [12–14]. Additionally, as the efficiency of reinforcement depends on the especial characteristics of nanofillers such as aspect ratios and intrinsic mechanical properties, nanoscale building blocks including graphene [15] and CNTs [16,17], and metal nanoparticles [18] have been widely used in the preparation of BC nanocomposites. BC nanocomposites with high mechanical strength have potential applications in a variety of industries. Addition of some nanomaterials to BC producing media or direct blend with BC could result in such nanocomposites, which subsequently leads to enhancement of the mechanical properties and the widen applications [19]. However, the incorporation of nanomaterials into BC for imparting increased properties or special characteristics sometimes deteriorates its intrinsic performance such as

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transparency [18,20,21], which may restrict its application to a certain extent. Therefore, it is important to open to the wide vision on the exploration of strong, transparent and flexible BC composite, which may serve as a basis for further application in various fields.

To address the challenge, it is quite useful to have a suitable nanoscale building block which in nature can realize these aspects. Nanoscale fibers have the extremely high surface-to-volume ratio and is expected to exhibit superior mechanical performance, unique optical properties and other amazing characteristics [22,23]. Recently, the nanoscale form of aramid fiber has emerged with maintaining the excellent mechanical performance [1,23,24] similar its original macro-fiber (Kevlar™) [25], and the ANFs can be easily obtained via deprotonation in KOH/DMSO [23,26,27]. ANFs have been incorporated into some polymers as nanoscale fillers to achieve the attractive properties [1,6], and its hybrids with CNTs and graphene have been synthesized and exhibited high performance [5,28,29], in spite of its unsatisfactory biocompatibility compared to other biologically derived nanofibers such as phage nanofibers and bacterial flagella [30–32]. These previous studies show that ANFs are promising nanoscale building block in nanocomposites with multiple intriguing properties.

Here we describe the ANFs/BC nanocomposite membranes based on BC and ANFs by a vacuum-assisted filtration method. The obtained membranes exhibit excellent mechanical properties at suitable ANFs concentration, which is required for high-performance nanocomposite membranes. Beyond that, the use of ANFs also could retain the good transparency and flexibility, which are essential for some special applications.

2. Experimental section

2.1. Materials

Bacterial cellulose was purchased from Hainan Yeguo Foods Co., Ltd., Hainan, China. Kevlar-29 brand yarns (136 dtex) were obtained from DuPont, USA. DMSO, NaOH and KOH were supplied by Shuang Shuang Chemical Co., Ltd, Yantai, China. Nylon filtration membranes (0.1 μm pore size) were obtained Filtration Equipment Factory Co., Ltd., Haining, China.

2.2. Pretreatment of BC and preparation of BC/water suspension

BC sheets were rinsed with deionized water and then immersed in a solution of 0.1 mol/L NaOH at 80 °C for 3 h to remove the impurities such as medium, microbial cells at al, followed by washing with deionized water to pH = 7. In order to prepare a uniform suspension of BC nanofibers, the resulting BC sheets were cut into small pieces and pulped with a mechanical homogenizer at a speed of 20000 rpm. Then the slurry of BC was diluted with deionized water to obtain a suspension of BC at a concentration of 3.281 mg/mL.

2.3. Preparation of ANFs/DMSO dispersion

ANFs/DMSO dispersions were synthesized by following the method described previously with some small modifications [23,26]. Firstly, the extraction of Kevlar-29 yarns was realized by using acetone as solvent for 72 h followed with oven-drying at 60 °C overnight. Next, accurately weighting of 0.5 g above Kevlar-29 yarns was dispersed into a 500 mL round-bottom flask which containing 250 mL of DMSO in the presence of 1.0 g of KOH. Then the flask was sealed, and the Kevlar/KOH/DMSO mixture was vigorously stirred for 7 days at room temperature to generate a homogenous, viscous and crimson solution of ANFs at a concentration of 2 mg/mL.

2.4. Fabrication of ANFs/BC nanocomposites membranes

BC suspension and ANFs dispersion were mechanically mixed in various proportions, giving a mixture ready for filtration. Specifically, ANFs dispersion of different volumes (0.837, 1.709, 2.618 and 3.566 mL) were added dropwise into 25 mL BC suspension with vigorously stirring at room temperature, which were corresponding to ANFs/BC mixtures containing 2.0, 4.0, 6.0 and 8.0 wt % of ANFs, respectively. Subsequently, the mixtures were further vigorously stirred for an additional 1.0 h to achieve a uniform dispersion, and after then the obtained dispersions were vacuum filtrated using the nylon membranes. Finally, the ANFs/BC nanocomposite membranes were dried in N_2 atmosphere and peeled off from the nylon membranes.

2.5. Characterization and testing

FT-IR spectra were collected on a Perkin Elmer Spectrum One spectrometer, on which the membrane was immobilized for measurement directly. SEM observations were obtained in a Hitachi S-4700 SEM. XPS measurements were performed on a Probe ESCA with the Al Kα radiation. XRD measurement was carried out on a D/man-rBX X-ray generator operated at 30 mA and 40 kV. Tensile strength of the materials was measured by a Cmt8102 Electric Universal Testing Machine with a test speed of 10 mm/min. The wettability of the membranes was examined by static water contact angle SL200KB measurement at room temperature. Static contact angle measurements were performed by depositing 5 μL droplets of deionized water onto the surfaces of the membranes, and images were collected using an 87-340FPS Cam.

3. Results and discussion

3.1. Chemical structure

The FTIR spectra of pristine BC, pure ANFs and ANFs/BC nanocomposites containing varying amounts of ANFs are shown in Fig. 1. The spectrum for BC (Fig. 1a) reveals the presence of all fundamental peaks for various chemical groups, and Fig. 1b presents the typical characteristic absorptions of aramid [5,23,28]. For the ANFs/

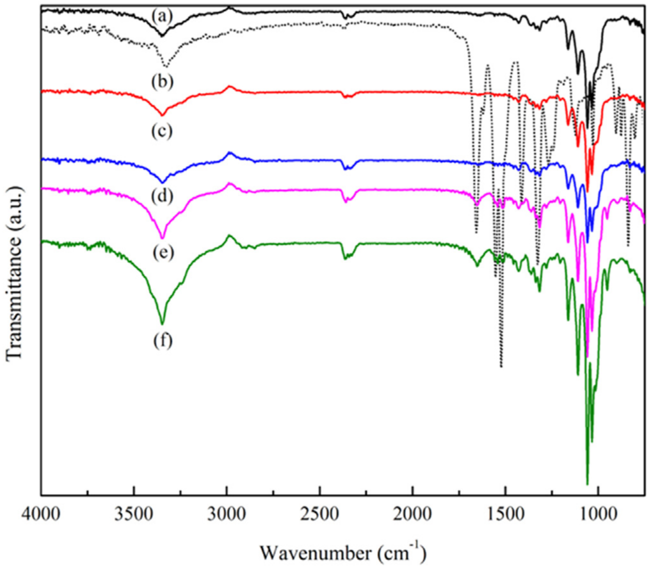

Fig. 1. FTIR spectra of (a) BC, (b) ANFs and ANFs/BC nanocomposite membranes with different amounts of ANFs: (c) 2.0 wt%, (d) 4.0 wt%, (e) 6.0 wt%, and (f) 8.0 wt%.