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Preparation of bacterial cellulose/graphene nanosheets composite films with enhanced mechanical performances

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ABSTRACT

Graphene has been considered to be a promising nanofiller material for building polymeric nanocomposites because it has large specific surface area and unique mechanical property. In the study, BC/graphene composites were prepared by a simple blending method. The resulting structure and thermal stability of the composites were investigated by several techniques including TEM, SEM, XRD, TG and Raman spectrum. These results indicate graphene nanosheets were successfully impregnated and uniformly dispersed in the BC matrix. Water contact angles result showed that the addition of graphene decreased hydrophilic property since water contact angle of BC increased from 51.2° to 84.3° with 4 wt% graphene added. The mechanical performances of BC/graphene composites were highly evaluated. When compared to pristine BC, the incorporation of 4 wt% graphene improved the tensile strength from 96 MPa to 155 MPa and Young's modulus from 369 MPa to 530 MPa, respectively.

1. Introduction

Bacterial cellulose (BC) is a polysaccharide produced by several microorganisms, particularly *Acetobacter xylinus* (*A. xylinus*), which is chemically the same as plant cellulose and features a distinctive three-dimensional structure consisting of an ultrafine network of cellulose nanofibers (Kirdponpattara, Khamkeaw, Sanchavanakit, Pavasant, & Phisalaphong, 2016). This unique micromorphology determines its distinguished physical and mechanical properties, e.g. high porosity, high crystallinity, excellent mechanical strength and large surface area because its 3-D network structure enables it to have great water holding capacity, good conformability and excellent wet strength (Yang, Xie, Hong, Cao, & Yang, 2012). In the past decade, BC have been intensively studied and applied in a wide range of fields such as medicine, soft tissue engineering, paper and food industries, sewage purification and composite reinforcement (Nandgaonkar et al., 2014). Meanwhile, a promising strategy has been developed though the incorporation of nanofiller into BC matrix or the modified BC biosynthesis (Feng, Zhang, Shen, Yoshino, & Feng, 2012; Liu et al., 2015; Park, Kim, Kwon, Hong, & Jin, 2009; Ul-Islam, Khan, & Park, 2012) to obtain enhanced performances. Typical nanofillers could be other polysaccharides (Woehl et al., 2010), ceramics (Hu, Chen, Zhou, & Wang, 2010), silicates (Ul-Islam et al., 2012) and carbon nanomaterials (Kim, Khan, Kim, Cho, & Park, 2011). Among these, the addition of unique carbon nanomaterials into the BC matrix is regarded as one of ideal reinforcements for the improvement of the mechanical properties (Shi & Wang, 2014; Zhang, Liu, Zheng, & Zhu, 2012).

Graphene is a promising, novel, carbon-based nanomaterial with a two-dimensional structure consisting of sp^2-bonded carbon atoms. It exhibits many noteworthy properties, such as large specific surface area, unique mechanical, electrical, and thermal properties, fast mobility of charge carriers, remarkable antibacterial properties and good biocompatibility (Kim et al., 2011; Shao, Liu, Liu, Wang, & Zhang, 2015). Due to these properties, graphene and its derivatives are considered as ideal materials for a broad range of applications, ranging from quantum physics, nanoelectronics, catalysis and engineering of nanocomposites and biomaterials (Pinto, Goncalves, & Magalhaes, 2013; Prolongo, Moriche, Jiménez-Suárez, Sánchez, & Ureña, 2014; Sen et al., 2015; Wan, Zhao, Hu, Gogotsi, & Qiu, 2013). Graphene Oxide (GO) is an oxidized form of graphene which has been widespreadly studied as the nanofiller in various polymer matrix including BC (Han, Yan, Chen,

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& Li, 2011; Jeon, An, & Jeong, 2012; Kabiri & Namazi, 2014). One-step in situ biosynthesis of GO–BC nanocomposite hydrogels was developed (Si et al., 2014). GO/cellulose composite using N-methyl morpholine N-oxide (NMMO) monohydrate was prepared with improved electrical conductivity and mechanical properties (Kim et al., 2011). However, graphene nanosheets showed enhanced mechanical properties compared with GO (Wan et al., 2013). Hence, there could be great potentials in improved mechanical performances using graphene as reinforcements in the BC matrix. The properties of the resulting blends would expand their range of application in biomedical and pharmaceutical areas.

In this paper, BC-graphene composite films with enhanced mechanical property were developed. BC-graphene composite films were characterized by Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), X-ray diffraction (XRD), thermogravimetric analyses (TG) and Raman spectra. Water contact angles of prepared BC-graphene composite films were studied. The mechanical behaviors of BC-graphene composite films were tested and the effect of graphene nanosheets loadings were studied.

2. Materials and methods

2.1. Preparation of BC/graphene composite films

BC was prepared in a static culture medium by *A. xylinum* GIM1.327, which was purchased from BNBio Tech Co., Ltd, China. The method of preparing BC was well-established and described in literature (Wu et al., 2004). Briefly, in a static culture system enriched with polysaccharides, bacterial strain was incubated and was able to produce a thin film layer of BC in the interface of liquid/air (Wan et al., 2009). This layer was washed by de-ionized water and then boiled in a 0.1 M NaOH solution at 80 °C for 60 min to eliminate impurities such as medium components and attached cells. BC films were further washed thoroughly with de-ionized water until pH became neutral. The as-obtained wet BC membranes (5 g) were cut into small pieces and crushed by high speed homogenizer (XHF-D, Ningbo Xingzhi Biotechnology, China) in 50 mL de-ionized water at 15,000 rpm for 30 min to achieve BC fiber slurry. A graphene dispersion with a concentration of 1 mg/mL was purchased from XFNANO Materials Tech Co., Ltd. (Nanjing, China). Graphene aqueous solution was added into the BC homogenate and treated by ultrasonication at supersonic power of 500 W (YQ-1003A, Ningbo Power Ultrasonic Equipment Co., Ltd., China) for 30 min in ice-water bath. The weight ratio of graphene to BC was controlled to be 0.5 wt%, 1 wt%, 2 wt%, 4 wt%, 8 wt%, and 12 wt% (marked as $BC_{0.5}$, BC_1, BC_2, BC_4, BC_8 and BC_{12}, respectively). The homogeneous dispersions were filtered through cellulose acetate membrane filter (0.22 μm pore size, 47 mm in diameter) by filtration under negative pressure at −0.1 MPa. Finally, BC/graphene composite films were freeze-dried under −40 °C for 10 h. Then the prepared films were used directly for analysis.

2.2. Structural characterization

TEM images were taken by a JEOL JEM-1400 model instrument (Japan) operated at an accelerating voltage of 100 kV. A JEOL JSM-7600F Scanning Electron Microscope (Japan) operating at an accelerating voltage of 10–15 kV was used to investigate the surface morphologies of BC and its composites with magnification 20,000×. The samples were coated with a thin layer of gold under high vacuum conditions (20 mA, 100 s). XRD patterns of the samples were recorded using a Rigaku Ultima III X-ray powder diffractometer, using a Cu Kα X-ray tube with a wavelength of 1.5406 Å, running at 40 kV and 30 mA. The diffraction angle (2θ) ranged from 5° to 60° with a step size of 0.02°. Thermogravimetric analysis (TG) was carried out by using a TA Instruments model Q5000 TGA. The samples were heated from 20 to 600 °C with a heating rate of 10 °C/min under nitrogen atmosphere. Raman spectra were recorded on a DXR Smart Raman spectrometer (Thermo Fisher) with 532 nm laser excitation. Water contact angles were measured using the sessile drop method with a JC2000D contact angle analyser (Powereach, China). Five contact angle measurements were made on each sample.

2.3. Mechanical properties

The tensile properties of BC and its composite films were measured by a dynamic mechanical analyzer (CMT4204, Shenzhen SANS Testing Machine Co., Ltd., China). Samples were cut manually by a razor blade into strips 30 mm × 3 mm × ∼45 μm). The static tensile tests were conducted in a ramp displacement mode at a cross-head speed of 1 mm/min. Each sample was measured for at least five times. The average value was calculated and the error bars were calculated.

3. Results and discussion

3.1. Surface morphology

The morphology of graphene nanosheets and graphene nanosheets in the BC matrix was observed by TEM (Fig. 1). TEM image of graphene nanosheets was shown in Fig. 1A. Graphene nanosheet displays a typical almost-transparent large leaf-like

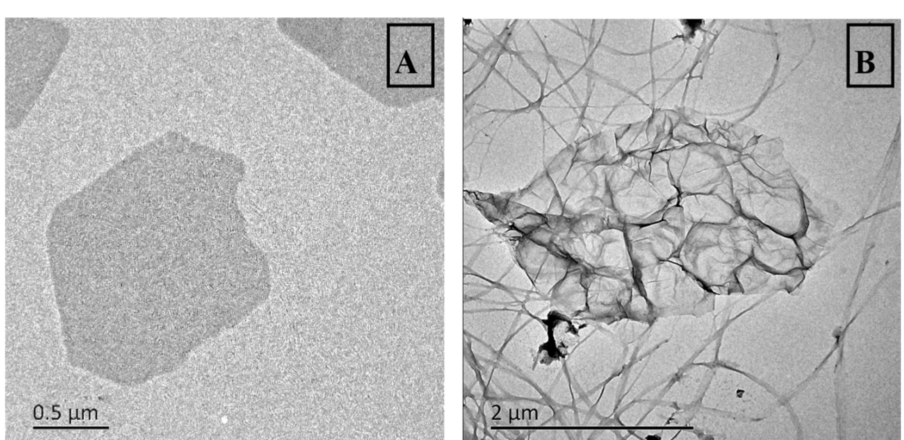

Fig. 1. TEM pictures of graphene nanosheets (A) and BC/graphene composite (B).