



Clarification of GO acted as a barrier against the crack propagation of the cellulose composite films



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ABSTRACT

Graphene oxide, flat carbon nanosheets, has generated extensive interests in many areas of science and engineering due to its unprecedented physical and chemical properties. With the development of wide-scale applicability including facile synthesis and high yield, this exciting material is ready for practical applications. In this work, fully exfoliated graphene oxide nanosheets were introduced into cellulose matrix through a facial pathway. A significant increase in the elongation at break of the composites was observed; that was, a 120% improvement in the tensile strength and a nearly 3 times increase in elongation at break were achieved for the composite films with GO content of 0.27 vol%. The microstructures of the regenerated cellulose films before and after loading of GO nanosheets were characterized by using SEM and TEM. Furthermore, the theoretical simulation from Young's modulus of the composite films indicated that the GO nanosheets had unidirectional arrangement tendency rather than random dispersion in cellulose matrix, which contributed to the improvement in the elongation of the composites, which was supported by the SEM results of the cross-section of the broken composite.

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1. Introduction

Cellulose, the most abundant renewable resource, can be converted into derivatives, regenerated fibers and films, as well as various functional materials [1]. However, cellulose is not soluble in common solvents because of the inter- and intra-molecular hydrogen bonds interactions. There are some organic solvents including N-methylmorpholine-N-oxide [2], lithium chloride/N, N-dimethylacetamide [3], and 1-butyl-3-methylimidazolium chloride [4], can dissolve cellulose at high temperature. However, the development of aqueous solvent for cellulose dissolving has obvious advantages. In our previous works, aqueous solvents containing alkali/urea have been developed for cellulose dissolving [5–7]. Novel fibers have been spun from the cellulose dopes, and many functional materials have also been created [8–13]. The aqueous solvent systems have great potential to prepare functional cellulose composites. In our previous research results, regenerated cellulose films prepared from alkali/urea solvents have good mechanical strength, while the elongation at break was low (less than 10%) compared with some ordinarily used cellophane or some plastics, and there

is great significance to improve the toughness of the cellulose films.

Graphene oxide (GO), a precursor of graphene, has attracted extensive interests due to its unique structure and outstanding physical and chemical properties [14]. GO behaves like an amphiphilic macromolecule with hydrophilic edges and a more hydrophobic basal plane, which makes it an attractive building block for the construction of various supramolecular architectures. Moreover, it is possible to achieve a truly molecular-level dispersion of GO when aqueous system is used for GO dispersion, and the functional groups allow GO to be easily dispersed in the composites. Some polymers, including poly(vinyl alcohol) (PVA) [15,16], chitosan [17], poly-(bibenzimidazole) [18], cellulose [19–21], etc., have been used to prepare GO/polymer composites, and their properties, especially mechanical properties, were improved obviously. However, little attention has been put on the clarification of the effects of the distribution state of GO in polymer matrix on the mechanical performance of the composites. In the current work, we found that GO could be dispersed into aqueous LiOH/urea solution and form stable dispersion. Interestingly, the mixed solution could also be used for cellulose dissolving directly, and the obtained composites had improved mechanical properties, especially the toughness of the composite films with a small amount

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of GO was about 2–3 times than that of pristine cellulose films. In order to clarify this interesting phenomenon, the comparison between the experimental and theoretical simulation results of the composite films have been performed, and it indicated that the GO nanosheets in cellulose matrix had unidirectionally arrangement tendency rather than dispersed randomly, and SEM images of the fractured surfaces of the RC and composite films supported the conclusions. We hope to provide useful information for the fabrication of cellulose based materials with improved properties and extend its applications.

2. Experimental section

2.1. Materials

Native cellulose (Cotton linter, α -cellulose $\geq 95\%$, viscosity-average molecular weight (M_η) was determined to be 1.07×10^5 in cadoxen at 25 °C) was supplied by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China). Other chemicals with analytical grade were used without further purification. Deionized water was used in the experiments.

2.2. Preparation of graphene oxide (GO)

Graphene oxide was prepared according to the reported method with minor modifications [15]. Graphite powder (2 g), P_2O_5 (3 g), and $KMnO_4$ (3 g) were mixed with 98 wt% H_2SO_4 (12 mL). The mixtures were treated at 80 °C overnight. The preoxidized graphite was collected by centrifugation, and then washed with water and dried at vacuum. The obtained preoxidized graphite was added into 98 wt% H_2SO_4 (120 mL). $KMnO_4$ (15 g) was gradually added into it within 1 h. The mixture was kept at 35 °C for 2 h and gradually diluted with 200 mL cooled water. After the dilution, the mixture was magnetically stirred at room temperature for 2 h, and then deionized water (400 mL) and 30% H_2O_2 were added into the mixture, respectively. Lightly yellow suspension was filtered and washed with aqueous HCl solution and subsequently washed with water, and then freeze-dried, sponge-like GO were obtained.

2.3. Preparation of GO/cellulose composites

The freezing–thawing method was used for cellulose dissolving. Briefly, GO was dispersed into 100 g aqueous LiOH/urea (7 wt%/12 wt%) solution, then, native cellulose (5.3 g) was dispersed into it and put in a refrigerator, after it had been frozen, took it out and thawed at room temperature to obtain GO/cellulose solution. The viscous solution was subjected to centrifuge at 7500 rpm and 15 °C for 10 min to eliminate some bubbles. The bubble-free solution was cast on a glass plate and the thickness was controlled to be about 1 mm, and then immersed it into ethanol (98%) to coagulate and regenerate for 10 min. The composite films were washed with deionized water thoroughly and then dried at ambient conditions. For Scanning electron microscopy (SEM) tests, the pure cellulose and composite films after being washed with water were treated with ethanol to replace the water in the matrix, and then dried with supercritical CO_2 . The composites containing 0.02, 0.04, 0.05, and 0.06 g GO nanosheets were coded as CG-02, CG-04, CG-05 and CG-06, respectively. Pure cellulose film without adding GO was coded as RC. As a matter of convenience, the filler concentration was transformed from mass fraction w (wt%) to volume fraction v (vol%) by the following equation [22]:

$$v(\%) = \frac{w\rho_C}{w\rho_C + (1-w)\rho_G} \cdot 100\%$$

where v and w are the volume fraction and mass fraction of GO nanosheets. ρ_C and ρ_G represent the density of cellulose and GO nanosheets, which can be taken as 1.52 g/cm^3 and 2.25 g/cm^3 , respectively. Then, the volume fractions of GO nanosheets filled into the cellulose matrix was 0.27, 0.54, 0.68, and 0.82 vol% accordingly.

2.4. Characterization

Typical tapping-mode atomic force microscopy (AFM) measurements were taken by using Multimode SPM from Digital Instruments with a Nanoscope IV controller made by Veeco Instruments Inc. Samples for AFM observation were prepared by depositing GO solution (0.1 mg mL^{-1}) onto the surface of a freshly cleaved mica and dried in air. X-ray diffractometry (XRD) test was performed by using a reflection mode (Rigaku RINT 2000, Japan) with Ni-filtered $CuK\alpha$ radiation. The static shear viscosity of the solutions was characterized with a digital viscometer (NDJ-8S, China) with a shear rate of 4000 rpm at 25 °C. The viscosity of the RC, CG-02, CG-04, CG-05 and CG-06 was about 10.39 ± 0.13 , 13.51 ± 0.17 , 14.16 ± 0.11 , 17.76 ± 0.15 and $19.41 \pm 0.22 \text{ Pa s}$, respectively. Thermal gravimetric analysis (TGA) was carried out on the thermogravimetric analysis (Ulvac TGD 9600). The samples were cut into powders and about 30 mg was used, the temperature was increased from 20 to 700 °C at a rate of 10 k min^{-1} in N_2 atmosphere. Scanning electron microscopy (SEM) test was carried out with a HitachiS-4800 microscope. Transmission electron microscopy (TEM) test was carried out on a JEOL-1010 apparatus. The mechanical properties of the films were characterized with a tensile tester (CMT 6503, Shenzhen SANS Test machine Co. Ltd, China) according to ASTM/D638-91 with a speed of 1 mm min^{-1} .

3. Results and discussion

Fig. 1a shows the photos of GO and graphite dispersed in aqueous LiOH/urea solution. The obtained GO could be dispersed into aqueous LiOH/urea solution and formed stable dispersion, furthermore, the solution could be kept for more than 2 months without aggregation, while the graphite was ready to form irreversible aggregates in the same condition. The difference was ascribed to the different surface properties of GO and graphite. Fig. 1b shows the AFM image of GO nanosheets that dispersed in H_2O . GO had a lateral dimension of several hundreds nanometers with a thickness about 0.76 nm. The thickness of the GO was larger than that of the theoretical thickness of a perfect graphene sheet. In theory, the thickness of the graphene sheet is about 0.34 nm [23]. The variation in the thickness was due to the presence of oxygen-containing functional groups, and also the GO nanosheet was not generally lying perfectly flat on the mica surface [24,25]. Fig. 1c shows the morphology of the GO sheets, it exhibited a folded feature and verified the formation of single GO sheets.

Fig. 2 shows the SEM and TEM images of the cellulose film after being freeze-dried. The freeze-dried cellulose film had porous structure, composing of fibrils that entangled to each other and formed interconnected networks. Fig. 2b shows the ultrathin section of the cellulose film after being freeze-dried, porous structure had been formed in the film, which agreed well with the results from SEM. While for the composite films after being freeze-dried, the morphology was totally different, as it was shown in Fig. 3. GO conferred an obvious influence on the microstructure of the composite films, leading to the formation of compact morphologies in the surface of the composite films. It would be ascribed to the strong interaction between GO and cellulose, which was supported by the fact that the viscosity of cellulose solution containing GO was higher than that of pure cellulose solution. Fig. 4 shows the TEM images of the composite films. The surroundings of the pores

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