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Regenerated cellulose/graphene nanocomposite films prepared in DMAC/LiCl solution

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ABSTRACT

Regenerated cellulose/graphene composite films had been prepared by dispersing graphene into cellulose solution in DMAC/LiCl, and then casting the solution onto glass. The thermal stability and mechanical properties of the composite materials, compared with pure regenerated cellulose film, were significantly improved. When the graphene loading was only 0.4 wt.%, the 10% weight loss temperature increased 20 °C. The Young's modulus increased from 3.4 to 7.2 GPa, while tensile strength increased from 89 to 148 MPa when 1.6 wt.% graphene was added into cellulose film. The electrical conductivity of the nanocomposite film reached 3.7×10^{-6} S/cm when 1.6 wt.% graphene was incorporated. The morphology was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The images revealed that the graphene was nano-dispersed in cellulose matrix. The effect of the graphene content in the nanocomposite material was also investigated.

1. Introduction

Cellulose, the most abundant natural polymer in nature, is renewable, biodegradable, and biocompatible. Therefore, people are increasingly paying attention to this natural polymer, considering it as an almost inexhaustible source of raw material to make petrochemicals in the future. However, the cellulose is difficult to be hydrolyzed or processed because it cannot be easily dissolved in common solvents or impossible be melted due to its strong inter- and intra-molecular hydrogen bonds, high degree of polymerization (DP) and high degrees of crystallinity.

Blending other materials with cellulose in a solvent is an efficient approach to modify cellulose (Lan, Li, & Zhong, 2009). Inorganic fillers can greatly enhance the properties of cellulose. Pierfrancesco et al. and White et al. both recently reported cellulose/clay composites with superior thermal and mechanical properties (Pierfrancesco, Veronica, & Alessandro, 2008; White, 2004). Graphene, the two nano-dimensional counterpart of carbon nanotube, consists of one atom thick layer of carbon atoms arranged in a honeycomb lattice and imposed itself as a promising alternative of carbon nanotubes in many field (Lee, Wei, Kysar, & Hone, 2008; Stoller, Park, Zhu, An, & Ruoff, 2008). It combines the lower price of the clay with the superior thermal and electrical properties of carbon nanotubes (Dreyer, Park, Bielawski, & Ruoff, 2010; Novoselov et al., 2004). In particular, its 2D flat structure should be better for the improvement of mechanical and thermal properties of composites materials. Incorporation of graphitic nanoflakes into elastomeric polymer matrix had showed enhanced mechanical and functional properties (Balandin, Ghosh, Bao, Calizo, & Teweldebrhan, 2008; Liang et al., 2009). During the past several years, many kinds of polymers had been used to prepare polymer/graphene materials. These polymers included poly (vinylalcohol) (PVA) (Zhao, Zhang, & Chen, 2010), polyethylene (PE) (Kuila, Bose, & Hong, 2011), poly (vinylidene fluoride) (PVDF) (Ansari & Giannelis, 2009), polyurethanes (PU) (Hyunwoo, Yutaka, & Christopher, 2010), polyethylene terephthalate (PET) (Zheng et al., 2010), poly (methyl methacrylate) (Potts, Lee, & Alam, 2011), polypropylene (PP). A little research had been reported on natural polymers used as the matrix material to prepare graphene composites (Kim, Khan, & Kim, 2011). It was said that it was very difficult to achieve the nano-dispersion of graphene layers in these natural polymer matrixes (Fan, Wang, & Zhao, 2010; Han, Yan, & Chen, 2011). Recently, Zhang et al. and Ang et al. both reported that the carbon nanotube could be nano-dispersed into cellulose because cellulose has very strong interaction with carbon nanotube (Ang & Zhang, 2010; Zhang, Wang, Zhang, & Zhang, 2007). This cellulose/carbon nanotube nanocomposite showed superior electronic and mechanical properties. Since graphene has similar chemical structure to carbon nanotube, the graphene should be able to be nano-dispersed into cellulose. The purpose of this article is to make the cellulose/graphene nanocomposite in the solvent of DMAC/LiCl and evaluate the mechanical properties of the regenerated films.

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2. Experimental

2.1. Materials

The cotton linter was used as a cellulose source. It was obtained from Dezhou Tianma Fiber Company, Dezhou, China. It contains over 97.6% cellulose. Its viscosity-average molecular weight was determined in DMAC/LiCl solution to be 1.05×10^5 g/mol (DP = 640) by a multi-angle light scattering (DAWN DSP, Wyatt Technolog Co., Santa Barbara, USA). Graphene was prepared as literature (Zheng, Zhang, & Yan, 2010). *N*,*N*-dimethylacetamide DMAC (Anhydrous, 99.8%, CP) was obtained from a Guoyao group. LiCl (AP, 97%), were purchased from Shanghai Jufeng Chemical Company. Fuming nitric acid (63%), sulfuric acid (98%), potassium chlorate (98%) and hydrochloric acid (37%) were all obtained from Sinopharm Chemical Reagents (China).

2.2. Preparation of graphene

The graphene was prepared according to the method from previous report (Zheng et al., 2010). First of all, the reaction flask was purged with nitrogen and immersed in an ice bath; 40 g graphite was then added to the homogeneous mixture of concentrated nitric acid (270 ml) and sulfuric acid (525 ml) under vigorous stirring. After uniform dispersion of the graphite powder, 330 g potassium chlorate was added slowly to minimize the risk of explosion. The reaction was then allowed to last for 120 h at room temperature. After reaction, the slurry resultants were filtered and washed with excess deionized water and 5% HCl solution to remove the sulfuric ions, then GO aqueous solution was neutralized with potassium hydroxide solution. GO powder was extracted from the solution by using GQ75 high-speed centrifuge, and dried in an air-circulating oven at 135 °C for 24 h followed by another 24 h at 135 °C in a vacuum oven. The dried GO powder was quickly inserted into a muffle furnace preheated to 1050 °C and held in the furnace for 30 s. The detail characterization of the graphene can be found in the literature (Zheng et al., 2010).

2.3. Preparation of cellulose/graphene blend films

Prior to dissolution, the cellulose sample was firstly activated by heating and stirring at 160 °C for 30 min in DMAC, then removed and squeezed at 180 °C. The activated sample was put into DMAC/LiCl (91/9, weight ratio) solution. The solution was heated to 100 °C and kept for about 3 h until it formed the gel. Transparent solution was obtained after 24 h. Colloid of graphene in DMAc/LiCl was prepared by adding10 mg graphene into 20 ml DMAC/LiCl solution with mild ultrasound sonication. The concentration of the colloid of graphene in DMAc/LiCl obtained was 0.5 mg/ml. The cellulose/graphene composites were prepared by putting the obtained two solutions together according to mass ratios of cellulose to graphene: 100/0 (RC), 99.8/0.2 (RC0.2), 99.6/0.4 (RC0.4), 99.2/0.8 (RC0.8), and 98.4/1.6 (RC1.6). The mixed solutions were stirred vigorously at 85 °C for 0.5 h, and then spread over a glass plate to give a 0.25 mm layer of solution by glass rod with copper wire, whose diameter is 0.25 mm. The glass plate covered with the mixed solution was coagulated in the air and then the film was detached in distilled water. The detached film was immersed in running water for over 12 h. The blend film was finally dried and stored for characterization.

2.4. Apparatus and measurements

The films were frozen in liquid nitrogen, snapped immediately, and then vacuum dried. Cross-section of the fractured films was coated with a thin layer of gold (about 2 nm) to observe their microstructures by using a Field Emission Scanning Electron Microscope (SEM) instrument (S-4800, JEOL, Japan). The microstructures of cellulose/graphene nanocomposites were characterized using a tecnai G2F20 TEM at an accelerating voltage of 100 KV. The film was embedded in epoxy resin, and cured at 80 °C for 8 h, and then ultra thin sections with thickness less than 100 nm were cut with a diamond knife using a microtome and collected on 300-mesh copper grids. The tensile properties were measured on Instron 5567 tester at a crosshead speed of 5 mm/min at room temperature. The specimen gauge lengths were 50 mm and the specimen widths were 10 mm. Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer Diamond TG/DTA instrument at a heating rate of 20 °C/min under nitrogen (flow rate of 50 ml/min). The transmittance was also measured by standard test method for haze and luminous transmittance by WGT-S haze and luminous transmittance instruments. Electrical conductivity of the samples was measured by a four-point probe method from Jandel Engineering Ltd. connected to a Keithley 4200 source meter using a standard four-probe technique with a threshold detection limit of 100 MΩ.

3. Results and discussion

The mixed solution of cellulose and graphene was very stable. Fig. 1(a) showed the photographs of the mixture of graphene and cellulose (RC0.8) in DMAc/LiCl solution. Fig. 1(b) showed the photographs of the mixture of graphene and cellulose (RC0.8) solution after standing over 30 days. The as-prepared homogeneous suspension of cellulose and graphene made it possible to prepare the composite film. The graphene can be dispersed in DMAc/LiCl solution with the low LiCl and graphene concentration at ultrasonic power of 250 W. The ultrasonic time is more than 24 h. It should be noted that the graphene liked to form aggregates in the DMAc/LiCl solution when the ultrasonic power was removed. So the dispersed graphene solution of DMAc/LiCl was taken out, and then put into the cellulose solution very quickly. The reason is that the mixture of graphene is colloid. The high concentration of graphene and LiCl will lead to the effect of salting out.

The optical photographs of the cellulose/graphene films were shown in Fig. 2. The thicknesses of these films are 26 ± 6 μm. The

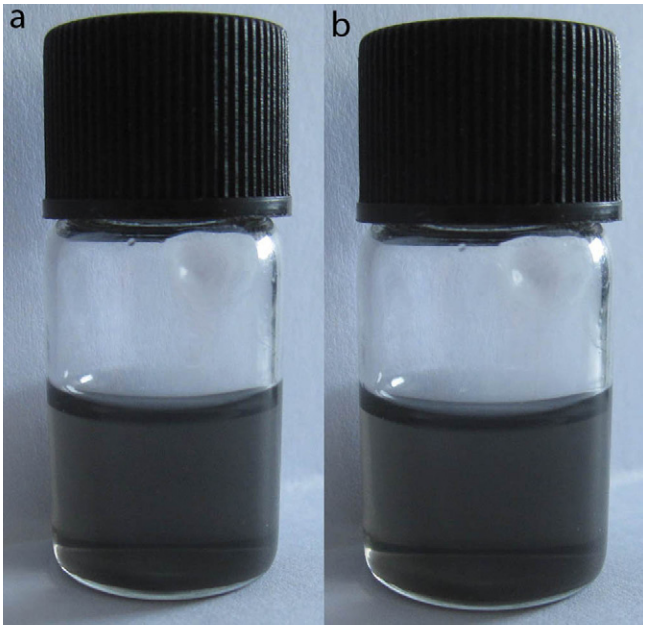

Fig. 1. The photographs of the cellulose solution with 0.8 wt.% graphene (a) and the solution after 30 days (b).

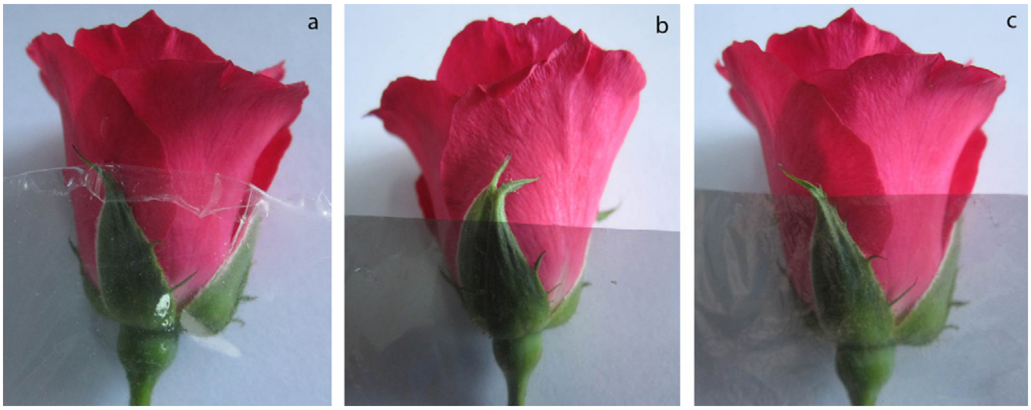

Fig. 2. The photographs of regenerated cellulose and its composites: cellulose (a), 0.4 wt.% graphene (b) and 1.6 wt.% graphene (c).

Table 1
The transmittance of the regenerated cellulose/graphene composite films.

Samples	RC	RC0.2	RC0.4	RC0.8	RC1.6
Transmittance (%)	91.5	81.4	78.2	72.3	67.6

background can be seen very clearly, indicating that the graphene was well dispersed in cellulose matrix. The transmittance of the blend films were measured by the light transmission detector. The results were shown in Table 1. It can be seen that the transmittance of the blend films were kept above 60%.

To reveal the dispersion of graphene in cellulose matrix, TEM was used to watch the microstructure of the nanocomposite films. Fig. 3 showed the TEM image of cellulose nanocomposite with 1.6 wt.% graphene. It can be seen that the graphene nanosheets were homogeneously dispersed in cellulose matrix. The exfoliation of graphene was achieved in cellulose matrix. SEM was also used to investigate microstructure of the blend films. Fig. 4 showed SEM image of cross-sections of RC1.6 and RC. The SEM image also confirmed the nano-dispersion of graphene in the cellulose matrix. This indicated that cellulose had very strong interaction with graphene, similar to the strong interaction between cellulose and carbon nanotube reported by Zhang et al. (2007). The abundant thin stacks of a few sheets of monolayer graphene in cellulose had significant effect on the improvement of thermal and mechanical properties of cellulose. The addition of graphene significantly increased the Young's modulus and tensile strength as shown in Fig. 5. For example, the Young's modulus of the nanocomposite film with 1.6 wt.% of graphene was 7.2 GPa, corresponding to an increase of 110% compared to 3.4 GPa of pure cellulose film. The tensile strength was increased to 148 MPa, corresponding to an increase of 66% compared to 89 MPa of pure cellulose film. The elongation at break did not change much with addition of graphene. It is obvious that the addition of graphene has significant improvement on the mechanical behavior of the pure cellulose film. This can be attributed to the strong interaction between graphene and the polymer matrix, which restricts the movement of polymer chains.

The thermal stability of the nanocomposites was measured by TGA. The TGA data in Table 2 and TGA curves in Fig. 6 clearly showed that the cellulose/graphene nanocomposite exhibited enhanced

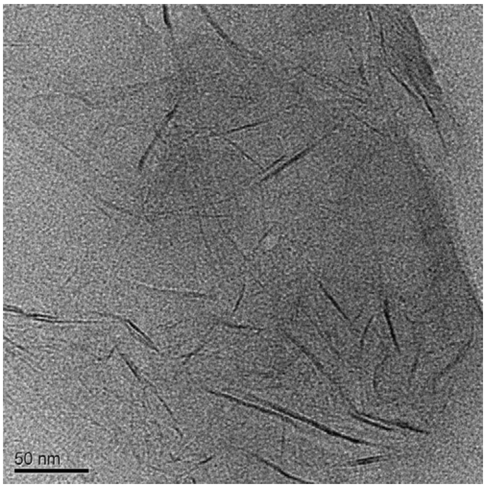

Fig. 3. TEM image of the cellulose composite with 1.6 wt.% graphene.

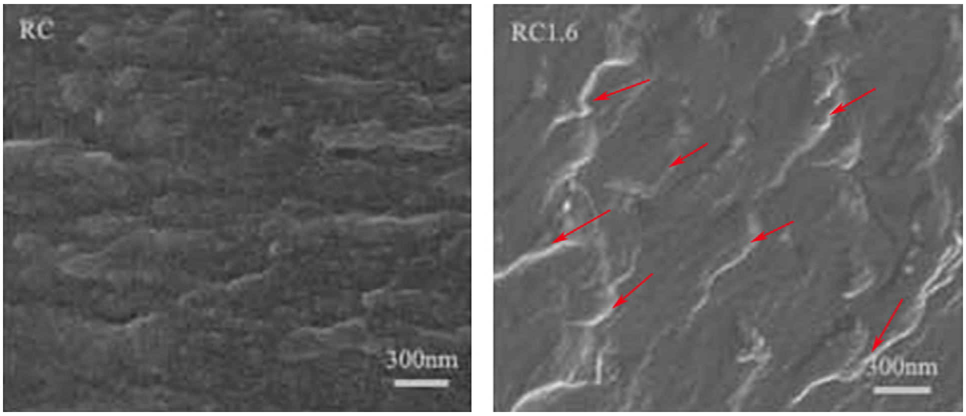

Fig. 4. SEM images of regenerated cellulose and composite with 1.6 wt.% graphene.

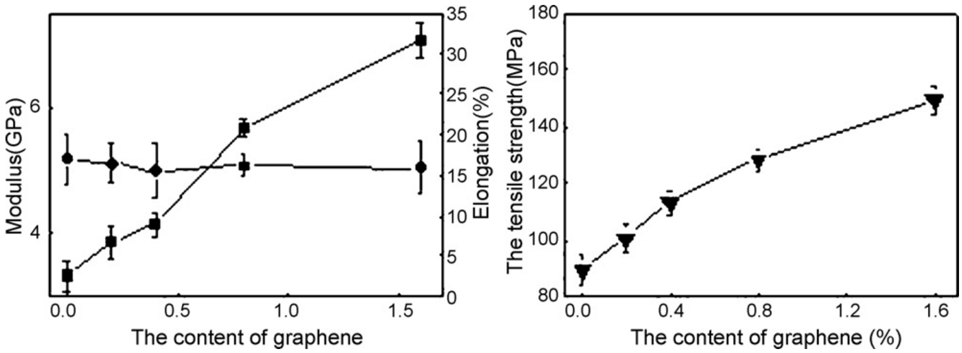

Fig. 5. The dependence of elongation at break (●), modulus (■) and tensile strength (▼) of the nanocomposite films with different contents of graphene.

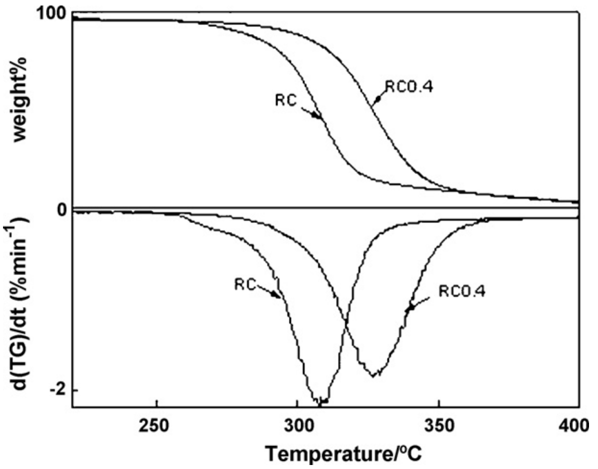

Fig. 6. The TGA and DTG curves of regenerated cellulose and its nanocomposite with 0.4 wt.% graphene.

thermal stability compared to pure cellulose. The initial decomposition temperature ($T_{10\%}$) of RC0.4 was about 307 °C, which increased nearly 21 °C compared to that of pure cellulose. And the temperature of RC0.4 with maximum decomposition rate was 327 °C, which also increased 20 °C compared to that of RC. Even the amount of graphene was only 0.2 wt.%, the 50% weight loss temperature was increased up to 18 °C. The significant improvement at such low loading showed the strong nano-effect of graphene on cellulose, which was similar to the effect of nanoclay on thermal property of polystyrene (Zhu et al., 2000).

Electrical conductivity of cellulose film was measured by a four-point probe method. The conductivity of the nanocomposite film reached 3.7×10^{-6} S/cm when 1.6 wt.% graphene was incorporated. The conductivity of the nanocomposite film was not good as the graphene/cellulose nanocomposite papers made by combining reduced graphene oxide sheets and amine-modified nanofibrillated cellulose (Luong, Pahimanolis, & Hippi, 2011). The possible reason could be due to incomplete reduction of graphene oxide. The further study will be done in the future.

Table 2
The degradation temperatures of the regenerated cellulose/graphene.

Samples	RC	RC0.2	RC0.4	RC0.8	RC1.6
$T_{10\%}$ (°C)	286	302	307	308	307
$T_{50\%}$ (°C)	315	330	325	336	334
DTG (°C)	307	325	328	326	325

4. Conclusions

The graphene-based cellulose nanocomposite films were successfully prepared by incorporating graphene into cellulose matrix in the solvent of DMAC/LiCl. The cellulose has very strong interaction with graphene, and this made graphene well dispersed into cellulose matrix. The graphene/cellulose nanocomposite films exhibited a significant improvement on the mechanical and thermal properties. The thermal property was also improved with addition of graphene. The electrical conductivity of cellulose/graphene film was also improved. With these enhancements, the cellulose/graphene nanocomposite films may find applications in the future.

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