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Enhanced mechanical and thermal properties of regenerated cellulose/graphene composite fibers

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ABSTRACT

In this study, a wet spinning method was applied to fabricate regenerated cellulose fibers filled with low graphene loading which was systematically characterized by SEM, TEM, FTIR and XRD techniques. Subsequently, the mechanical and thermal properties of the resulting fibers were investigated. With only 0.2 wt% loading of graphene, a ~50% improvement of tensile strength and 25% enhancement of Young's modulus were obtained and the modified Halpin–Tsai model was built to predict the mechanical properties of composite fibers. Thermal analysis of the composite fibers showed remarkably enhanced thermal stability and dynamic heat transfer performance of graphene-filled cellulose composite fiber, also, the presence of graphene oxide can significantly enhance the thermal conductivity of the composite fiber. This work provided a facile way to improve mechanical and thermal properties of regenerated cellulose fibers. The resultant composite fibers have potential application in thermal insulation and reinforced fibrous materials.

1. Introduction

Graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice (Geim & Novoselov, 2007), possesses a number of extraordinary electronic, thermal and mechanical properties (Zhang, Li, & Pan, 2012; Balandin et al., 2008; Pandele et al., 2014), especially, it has been reported that a single-layered graphene was found to exhibit a Young's modulus of ~1100 GPa and tensile strength of 130 GPa. Similar to CNTs, graphene has demonstrated a high carrier mobility of 15,000 $cm^2 V^{-1} s^{-1}$ at room temperature and maintained current densities of six orders of magnitude higher than the copper. Graphene is thermally stable with thermal conductivities of up to 5000 $W m^{-1} K^{-1}$, higher than CNTs and metals such as gold, silver, and copper (Sun et al., 2013).

Compared with carbon nanotube (Sun et al., 2013; Rafiee et al., 2009; Martin-Gallego et al., 2013), graphene is usually recommended as a great candidate to develop multifunctional materials with enhanced properties. One-dimensional macrostructure graphene fiber is a relative novel area with attractive potential applications. The graphene fibers can be generally classified into two categories, the neat graphene fibers and the graphene composite fibers. In the neat graphene fiber issue, for instance Xu and Gao (2011) firstly manufactured pristine graphene fiber by wet-spinning, Dong et al. (2012) also reported a pristine graphene fiber prepared by the process of glass pipeline and Chen et al. (2013) achieved high performance and better understanding on the processing–structure–property relationship of graphene fibers by the wet-spinning and coagulation process. However, the yields of above obtained fibers are limited in the lab—scale level, and their procedures are usually manual, discontinuous and low efficiency. Moving to the graphene composite fibers, spinning methods used to create composite fibers containing graphene include melt-spinning, solution-spinning and electrospinning. Many kinds of polymers have been utilized to prepare the polymer/graphene composite fibers, He et al. (2012) prepared

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sodium alginate/graphene oxide (NaAlg/GO) fibers with enhanced mechanical strength via a lab-scale wet spinning method, Shin et al. (2012) obtained graphene/CNT/PVA nanocomposite fiber, and the strength of the nanocomposite fiber has been greatly improved compared with pristine PVA fiber. Xu and Gao (2010) fabricated PA6 grafted graphene composite fibers revealing an excellent reinforcement to composites by graphene. So far, however, little research has been reported on natural polymers used as the matrix for preparing graphene-containing/polymer composite fibers. Furthermore, some other potential properties of grapheme/polymer fibers, such as thermal properties, were not sufficiently carried on in the previous work.

Cellulose, the most abundant natural polymer in nature, is renewable, biodegradable and biocompatible, and its derivative, regenerated cellulose fibers, comprised of linear polysaccharide exhibited outstanding properties (Li et al., 2010; Zhang et al., 2007; Wang et al., 2013; Jiang et al., 2012), i.e. high moisture absorbency, flexibleness, dyeability, but revealed unfavorable mechanical properties. For instance, the tenacity of regenerated cellulose fibers are usually in the range of 1.8–2.5 cN/dtex which is definitely lower than cotton fiber (~4.5 cN/dtex) and some synthetic fibers, i.e. polyester fiber (~4.7 cN/dtex), polypropylene fiber (~6.5 cN/dtex) (Hearle & Morton, 2008), therefore, the modified regenerated cellulose fibers with reasonable mechanical properties could extend and escalate their potential applications. As far as we know, no studies have carried on the modified regenerated cellulose fiber with low graphene content to improve their mechanical performance and wearability. In this paper, regenerated cellulose/graphene composite fibers were fabricated by a continuous pilot-scale wet spinning procedure and their micro-structure, crystallization behavior, mechanical properties, and thermal properties were characterized and illustrated.

2. Materials and methods

2.1. Preparation of graphene oxide nanoflakes

Graphite powder was expanded to exfoliated graphene based on the modified Brodie's method (Wang et al., 2009). 20 g of graphene powder (nature flake graphite, sized at 30 μm), 260 mL of fuming nitric acid and 160 g of sodium chlorate were mixed and stirred for 24 h using a magnetic stirrer at room temperature. Then the resultant solution was washed 5 times with 200 mL of 5% hydrochloric acid and 7 times with 1 L of distilled water to remove all acidic and saline impurities. Graphite oxide was collected through a precipitation method and evaporation of the solution at 60 °C. 8 mg/mL graphene oxide dispersion (GO) was fabricated with ultrasonication for 30 min and stabilized with assistance of ammonia.

2.2. Preparation of regenerated cellulose/graphene composite fibers

The pilot-scale production route and the apparatus of the spinning process (Speakman & Chamberlain, 1944) are shown in Fig. 1. Regenerated cellulose aqueous solution (α-cellulose 8.2 wt%, NaOH 5.5 wt%) was kindly provided by Shandong Helon Group Co. Ltd., graphene oxide solution 8 mg/mL with different amount (0, 300 mL, 600 mL) were injected into 300 L regenerated cellulose solution, respectively, forming hybrid spinning solutions with different graphene loading: 0%, 0.1 wt% and 0.2 wt%. The resultant spinning solutions were vigorously stirred at room temperature for 6 h to form homogenous solutions in 500 L dissolution tank (a). After filtered by filter papers (b), and degassed in storage tank (c) under diminished pressure and vacuum condition, spinning solutions were quantitatively transferred with flow control pump (d). A

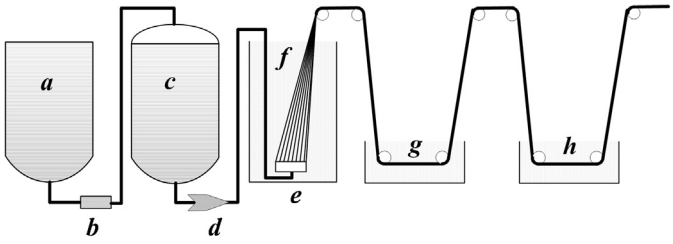

Fig. 1. The pilot-scale production route and the apparatus of the spinning process.

30-hole (0.08 mm diameter) spinneret (e) was employed to extrude the solutions into coagulating bath solution (f) of H_2SO_4 100 g/L, Na_2SO_4 300 g/L, $ZnSO_4$ 15 g/L at 35 °C. The spun fibers were washed and stretched (stretching ratio is 20%) in washing bath (g) with further dehydration in the alcohol leaching bath (h). According to Fan et al. (2008), under strong alkaline solution (NaOH or KOH), exfoliated graphite oxide can be directly reduced and deoxygenated into graphene. Since in our route the hybrid spinning solution was strong alkaline solution (NaOH 5.5 wt%), stable regenerated cellulose/graphene spinning solutions can be facilely prepared in the absence of reducing agents.

Then, a series of composite fibers were prepared as pristine regenerated cellulose fiber, regenerated cellulose/graphene fiber (0.1 wt%), regenerated cellulose/graphene fiber (0.2 wt%) and labeled as RC, RC/G 0.1 and RC/G 0.2, respectively.

2.3. Characterization and measurement

The morphology of the resulting graphene and composite fibers were investigated through SEM (JEOL JSM-840 SEM) and transmission electron microscopy (TEM, JEOL-JEM 2100). Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet 5700 FT-IR Spectrometer (Thermo Nicolet Corporation, USA) with the wave number range of 500–4000 cm^{-1} (KBr disk). X-ray diffraction (XRD) measurements were performed on a D8 ADVANCE X-ray diffract meter equipped with a Cu *K*a radiation source (λ = 1.5406 Å) operating at 40 kV and 40 mA in the range of 2θ = 5–60°.

Mechanical properties of composite fibers were conducted with FAVIMAT Single Fiber Electronic Tensile Strength Tester (Textechno, USA) according to ASTM D3822, and the work condition was at 20 °C and relative humidity of 65%. The initial gage length was set at 15 mm and the crosshead speed at 10 mm/min and a pretension of 0.02 cN/dtex. All fibers were tested 50 times and their average value was reported.

Thermal behaviors of samples were characterized with a NETZSCH STA 409 PC/PG, using a heating rate of 10 K/min from 25 to 800 °C in a nitrogen atmosphere. Furthermore, the thermophysical properties (thermal conductivity, thermal diffusivity and specific heat capacity) of our fiber assemblies were simultaneously obtained by the transient approach proposed from Tian, Zhu, and Pan (2012a).

2.4. Dynamic heat transfer of composite fiber assemblies

In order to elucidate the enhanced heat transfer of the margin graphene filler in the resulting fibers, we utilized a setup apparatus in our lab to simulate the dynamic thermal response of fiber assemblies under unsteady-state conditions. As shown in Fig. 2, 10 g fiber assemblies were homogeneously laid in a flask and a thermometer was placed at the center of the flask. For each case, the filled flask was moved into a 100 °C water bath from the initial temperature 30 °C, meanwhile, the fixed thermometer measured the temperature curve and then recorded by a computer system at 1 s interval.