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Large scale preparation of graphene oxide/cellulose paper with improved mechanical performance and gas barrier properties by conventional papermaking method

Quanbo Huang[a], Manman Xu[a], Runcang Sun[a,b], Xiaohui Wang[a,*]

[a] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China
[b] Institute of Biomass Chemistry and Technology, Beijing Forestry University, Beijing 100083, China

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ABSTRACT

Graphene oxide (GO)/cellulose paper was prepared by adding aqueous dispersion of GO into cellulose fiber pulp in a traditional papermaking procedure. Cationic polyacrylamide (CPAM) was added as a mordant to induce the self-assembly of GO layers on the fiber surfaces. The surface morphology, mechanical properties and gas permeability of GO/cellulose paper with varying GO contents were investigated by scanning electron microscopy (SEM), tensile test, burst test, tear test and densometer. It was found that CPAM could prevent the self-aggregation of GO in fiber matrix and increase the loading efficiency of GO to up to 16 wt% without sacrificing the mechanical performances of the paper. This finding permitted the large scale preparation of GO/cellulose paper with high doping amount of GO, which exhibited dense and compact geometry and low gas permeability ideal for potential packaging applications.

1. Introduction

Cellulosic paper has widely and traditionally been used in packaging for a long time. It is suitable to pack the food, glass, precious products and electronic devices and so on for its non-toxic, light, inexpensive and cushioning properties. Compared with plastic materials, cellulosic paper is sustainable, biodegradable and eco-friendly, but its low mechanical and gas barrier properties cannot meet the requirement of some perishable foods, prescription medicines or precise instruments (Hernandez et al., 2000; Lange and Wyser, 2003). Although the regenerated cellulose films prepared from some cellulose solvent systems such as ionic liquids (Wang et al., 2012), *N*-methylmorpholine-*N*-oxide hydrate (NMMO) monohydrate solvent (Kim et al., 2011), and aqueous NaOH/urea solutions (Han et al., 2011) have decreased the porosity of pristine cellulosic papers and thus enhanced the mechanical performance and barrier property. Nevertheless, the fabrications of regenerated cellulose films are complex, costly and not competitive for large-scale and continuous production.

To overcome these issues, adding filler in pulp during papermaking is a facile and common method. Impermeable layered and plate-like organic nanoclays, such as montmorillonite and rectorite, have been used to increase the barrier property of many polymeric films, including polyethylene (Durmus et al., 2007), poly(vinyl alcohol) (Strawhecker and Manias, 2000), and regenerated cellulose films (Farmahini-Farahani et al., 2015; Ho et al., 2012; Yang et al., 2014). However, when using conventional processing techniques, it is also a challenge to obtain completely exfoliated nanoclays (Huang et al., 2014).

Meanwhile, graphene oxide (GO), that can be obtained by oxidizing graphite using strong acids, has a similar layered structure to graphite and nanoclays, but the plane of carbon atoms in graphene oxide is heavily decorated by oxygen-containing groups, which not only expand the interlayer distance but also make the atomic-thick layers hydrophilic (Cai et al., 2008; Lerf et al., 1998). As a result, GO has not only excellent mechanical properties, but also excellent dispersibility in aqueous solution (Paredes et al., 2008; Zhang et al., 2010), which is appropriate as a nanofiller in papermaking.

Recent studies indicate that the composite of cellulose and GO exhibits excellent performance, especially improved mechanical property and low gas permeability. For instance, Han et al., 2011 prepared blended films of cellulose and GO using alkali aqueous solution as solvent, resulting in a 98% increase in tensile strength and a 60% enhancement in Young's modulus by addition of only

* Corresponding author at: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, China.
E-mail addresses: fewangxh@scut.edu.cn, alicewang1225@163.com (X. Wang).

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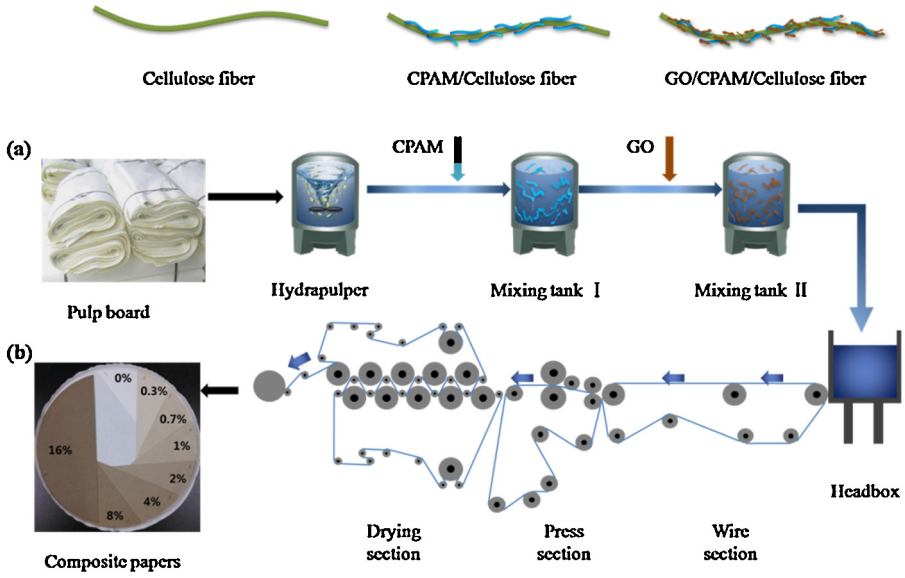

Scheme 1. Schematic illustration of the fabrication process of GO/cellulose paper with different content of GO.

7.5 wt.% GO. Huang et al., 2014 used a simple and environmentally friendly method to fabricate GO/regenerated cellulose films that the permeability coefficient of O_2 (Po_2) was reduced by over three orders of magnitude at a low GO loading of 1.64 vol%. However, the self-aggregation of GO sheets usually appears when the GO content was high, probably due to the van der Waals interactions between the layers of GO nanosheets. As a result, the mechanical properties would be reduced and the homogeneity of films/papers would be disrupted (Wang et al., 2012). As we know, cellulose pulp (Rojas and Neuman, 1999) and GO nanosheets (Li et al., 2008) are both negative charged in aqueous suspensions, which prevents the adsorption of GO nanosheets on cellulose fibers. Therefore, there is a strong need to find an effective way to prevent the self-aggregation of GO nanosheets in the composites, and also improve the adsorption of GO onto the cellulose fibers to form stable composites.

Cationic polyacrylamide (CPAM), a water-soluble cationic polymer decorated with carbamoyl group, is a commonly used retention and drainage agent in papermaking industry (Asselman and Garnier, 2000; Raj et al., 2015). So, CPAM is very suitable to use in the fabrication of graphene oxide/cellulose paper. Herein, we used a simple, efficient, low cost and large-scale method to fabricate a novel GO/cellulose paper through modern papermaking machine. The as-prepared paper has potential of reaching high loading ratio and uniform distribution of GO nanosheets in cellulose fiber matrix and thus obtain improved mechanical performance and low gas permeability. The current study provides an easy, versatile and applicable way to produce functional inorganic paper in large scale for potential applications in value-added fields, such as active packaging, energy, etc.

2. Material and methods

2.1. Materials

Cellulose fibers were obtained by defibering the dissolved wood pulp (Pinus radiata, α-cellulose content: 93.2%), which was provided by Shan Dong Sun Paper Industry Joint Stock Co., Ltd. The graphite flakes (particle size < 45 μm) used in experiments were purchased from Nanjing XF NANO Materials Tech Co., Ltd. Cationic polyacrylamide (CPAM), $KMnO_4$, concentrated H_2SO_4, concentrated HCl, and H_2O_2 aqueous solutions were all of analytical reagent grade and used directly without further purification.

2.2. Preparation of graphene oxide dispersion

The GO was prepared from natural graphite by a modified Hummers method (Marcano et al., 2010). In brief, 1.0 g of the graphite flakes were added to cold concentrated H_2SO_4 (46 ml). Then 3.0 g of $KMnO_4$ was added slowly with an ice bath under stirring to keep the reaction temperature. After even agitation, the ice-bath was removed and the mixture was heated at 35 °C for 1.5 h, and then 46 ml water was added slowly and continuously. Next, the reaction temperature was maintained at 98 °C for 30 min before 140 ml cool water was added to stop the reaction. 10 ml 30 wt% H_2O_2 solution, 1000 ml HCl solution (1:10) and deionized water was used successively to reduce the residual $KMnO_4$ and MnO_2 to colorless $MnSO_4$ salts, remove the sulfate ion and control the pH of the washed solution to around 6.0, respectively. Finally, brown powder was obtained after freeze-dried the suspension. As-prepared powder was dispersed in water and the aqueous dispersion (5 mg/ml) of GO was obtained by an ultrasonic treatment of dispersion for 1 h to yield a stable brown solution.

2.3. Fabrication of GO/cellulose paper

GO/cellulose paper with different content of GO ranging from 1 wt% to 16 wt% was prepared using a handsheet former in laboratory. Same procedure can be performed on fourdrinier paper machine in paper mill as well. The basis weight of the GO/cellulose paper was around 120 g/m^2. The ratio of CPAM and GO was kept 0.04:1 in weight. Before being used, CPAM was processed as polymer solution (0.001 g/ml) with stirring velocity below 100 rpm. As illustrated in Scheme 1: first, the pulp board was dispersed in water (2.0% wt/vol) with vigorous stirring in hydrapulper. And then in the mixing tank I, CPAM was coated on the cellulose fiber through electrostatic interaction to form the CPAM-coated cellulose slurry with stirring velocity around 150 rpm in one minute. Next in the mixing tank II, GO was absorbed onto the CPAM through electrostatic interaction with stirring velocity around 300 rpm in two minute. Consequently, CPAM acts as an intermediate that induces the self-assembly of cellulose fibers and GO nanosheets. In addition, CPAM enhances the retention of GO during the filtration process in the following step. Finally, the slurry (0.5% wt/vol) was send to the headbox and GO/cellulose paper was obtained through three sections of the papermaking machine.