Industrial Crops & Products 124 (2018) 519–529

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

The use of cellulose nanofibrils to enhance the mechanical properties of graphene nanoplatelets papers with high electrical conductivity

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ARTICLE INFO

Keywords:
Cellulose nanofibrils
Graphene nanoplatelets
Mechanical properties
Electrical conductivity
Paper

ABSTRACT

Mechanically flexible and high electrically conductive multilayered graphene nanoplatelets (GnP)/cellulose nanofibrils (CNF) composite papers were successfully fabricated through a vacuum-assisted self-assembly technique. The morphology observation showed that highly disassembled CNF were achieved by high-pressure homogenization of water-based cellulose slurry, and the homogenized CNF uniformly interpenetrated within the microporous GnP paper network. The analyses of mechanical properties and morphology suggest that the CNF effectively bridged the adjacent GnP sheets and efficiently strengthened the GnP papers by producing strong GnP/CNF interfacial interactions resulting from mechanical interlocking, van der Waals forces and hydrogen bonds between the GnP and the CNF. Moreover, it was noticed that hot-pressing pressure is necessary to be applied on samples to produce stronger papers with higher electrical conductivity. As the CNF loading reached 60 wt%, the Young's modulus and tensile strength of the hot-pressed GnP/CNF hybrid paper were significantly increased to 9.1 GPa and 57.7 MPa, respectively. In addition, a high electrical conductivity of 26.8 S/cm was retained for the paper with 30 wt% CNF. Our approach provides a facial and eco-friendly fabrication route to produce strong and highly conductive GnP/CNF papers which are of great practical appeal as a new type of nanomaterials in various fields.

1. Introduction

Natural biomass have draw a considerable attention because of their renewability and biodegradability (Han et al., 2011; Ragauskas et al., 2006). Natural fibers, such as carboxymethyl cellulose, chitosan, bacterial and algal cellulose etc., have been extensively investigated due to their huge potential applications in various fields (Eichhorn et al., 2010; Fernandes et al., 2009; Rajinipriya et al., 2018; Velásquez-Cock et al., 2016). The natural fibers have superior paper-forming properties, but the fiber papers are generally electrically non-conductive and low in gas barrier property which restrict their applications. Graphene, a two-dimensional structure consisting of sp^2-bonded carbon atoms, has been regarded as one of the most effective nanofillers for the modification of other materials. It has been reported that a single-layered graphene exhibits a Young's modulus of ~1100 GPa and tensile strength of 130 GPa, demonstrates amazing electrical conductivity, up to 6000 S/cm (Du et al., 2008; Lee et al., 2008). As such, to meet the high demand for the development of mechanically flexible and eco-friendly paper materials with multifunctional properties, more and more researchers are devoting their efforts to develop hybrid papers with desirable properties by strategically integrating graphene with natural fibers (Chen et al., 2018; Gan et al., 2017; Hou et al., 2018; Sen et al., 2015; Yenier et al., 2016).

Among different bio-natural fibers, cellulose is one of the world's most plentiful, natural and renewable bioresources which is readily accessible from plants, wood or even invertebrate animals like tunicates (Chun et al., 2012). It was reported that the cellulose was widely used in many areas such as sensor, actuators and flexible electronics due to its exceptional benefits including good mechanical properties, low cost, biodegradability and ease of chemical modification (Czaja et al., 2007; Gan et al., 2014; Kim et al., 2006; Pacheco et al., 2017). Generally, raw cellulose fibers (regular pulp fibers) are noticeably long, and often branched or forked with diameter and length both in the micrometer-scale range. Recently, many researchers have been attempting to incorporate graphene or graphene oxide (GO) into the cellulose fiber papers to enhance the mechanical properties or endow the papers with desired electrical and barrier properties (Huang et al., 2016; Kang et al., 2012).

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https://doi.org/10.1016/j.indcrop.2018.08.019
Received 16 May 2018; Received in revised form 4 August 2018; Accepted 7 August 2018

More recently, nanocellulose with diameters at the nanoscale has attracted a great deal of scientific interest due to its large specific surface area, outstanding elastic modulus and tensile strength (Yousefi et al., 2018). Yousefi et al. (2013) reported that the tensile properties of nanopapers prepared from nanocellulose fibers outperform the micropaper that fabricated with raw cellulose fibers due to the high specific surface area of nanocellulose fibers. Typically, two main categories of nanocellulose are distinctive: (i) the one obtained by acid treatment, called cellulose nanocrystals (CNC), and (ii) the one produced mainly with mechanical disassembly method, named cellulose nanofibrils (CNF) (Nechyporchuk et al., 2016). In general, the CNC are tiny nanomaterials having a diameter and length of 5–35 nm and 150–500 nm, respectively, while the CNF possess a length in the micrometer range and a diameter of 5–50 nm. The CNF generally exhibit a few interesting properties, such as high theoretical strength and modulus (3 GPa and 160 GPa, respectively), highly expanded surface area and very high aspect ratio (L/D) (Andersen et al., 2006; Lee et al., 2014). Many researchers have tried to combine CNF with graphene to create novel nanocomposites with improved properties. For instance, Beeran et al. (2016) successfully improved the Young's modulus and tensile strength of the CNF paper by introducing 3 wt% modified graphene oxide into CNF suspension. Luong et al. (2011) fabricated reduced graphene oxide (RGO)/CNF hybrid paper, and the conductivity was increased to 0.718 S/cm at 10 wt% RGO. The reported CNF/graphene hybrid papers showed encouraging results. However, to achieve good electrical conductivity, the reported fabrication procedures usually involve in complex reduction process of GO. Besides, the electrical conductivity of the cellulose-dominated papers is still not high enough for certain applications, such as electric heating elements and devices (Lee and Jeong, 2015).

Since the work reported in Nature demonstrated that the GO can be used to construct building blocks for novel applications in paper-like materials (Dikin et al., 2007), many studies describing good mechanical and electrical properties of graphene papers derived from non-conductive GO have been published (Park et al., 2012; Ranjbartoreh et al., 2011; Sun et al., 2018). However, reduction of GO is still required to produce graphene papers with high electrical conductivity. More importantly, the limited production capacity and high manufacturing cost of GO cannot meet the rapidly rising market demand for graphene-based papers (Liu et al., 2016). As an alternative approach, we attempt to directly fabricate graphene-based papers using cost-effective graphene nanoplatelets (GnP) which can avoid the reduction process. The GnP with multilayered structures could be commercially produced in large quantity at low cost with the treatments of combined microwave and mechanical exfoliation of acid pre-treated graphite (Drzal and Fukushima, 2006; Fukushima, 2003; Kalaitzidou et al., 2007; Li et al., 2017). It has been reported that the pure GnP papers usually display high electrical conductivity, and composites that embedded with the GnP paper demonstrate outstanding barrier properties (Wu and Drzal, 2012; Xiang and Drzal, 2011). However, the pristine GnP papers directly prepared from the GnP are very fragile and suffer from the lack of mechanical performance due to deficiency of functional groups on GnP, which has restricted the further industrial applications.

Previously, improved mechanical properties of the GnP paper were achieved by introducing the CNC into the GnP paper with the assistant of polyethyleneimine (PEI) (Wang et al., 2015). The PEI is a type of viscous water-soluble polymer, which was retained in the paper to assist the paper formation (Wang et al., 2015; Xiang and Drzal, 2011). However, the PEI and numerous tiny CNC coated on GnP significantly decreased the electrical conductivity of the resulting papers due to the high interfacial electrical contact resistance between GnP sheets. Moreover, the CNC are much shorter than the size of GnP and not long enough to connect the isolated micro-sized GnP, and they would deliver very limited mechanical reinforcing effect for the GnP paper if there is no PEI in the paper.

In the present work, we aim to enhance the mechanical properties of the GnP paper by employing continuous CNF which are long enough to connect and bridge the adjacent GnP sheets, and meanwhile preserve a relatively high electrical conductivity. To the best of authors' knowledge, the research on the combination of commercially available GnP with CNF based on a simple water-based method has not been reported yet. In this article, triton-X100, a non-ionic surfactant, was selected as a dispersing agent for GnP because it offers good compatibility with CNF. The influence of CNF on the mechanical properties and electrical conductivity of the prepared papers were thoroughly investigated and evaluated. The mechanisms of mechanical enhancements and the interactions between the CNF and GnP were also carefully studied by examining the morphology with scanning electron microscope.

2. Experimental

2.1. Materials

Water-based cellulose slurry without any chemical treatment was purchased from the University of Maine (Orono, American). Bleached wood pulp was used as the raw material, and the solid content of the cellulose slurry is 3 wt% according to the supplier. GnP with an average lateral dimension of 5 μm and a thickness of ~5 nm was kindly supplied by XG Sciences, Inc. (Lansing MI, American). Triton-X100 used as surfactant was ordered from Sigma-Aldrich. Filter membranes with a pore diameter of 0.22 μm were obtained from Merck Millipore (Massachusetts, American).

2.2. Disassembly process of CNF

The homogenization of cellulose bundles is necessary to be performed to achieve individual cellulose nanofibrils (CNF) which are high in specific surface area and long enough to connect the adjacent GnP. The as-received cellulose slurry was dispersed in deionized water to prepare cellulose solution with a concentration of around 5 wt%, and then the prepared solution was vigorously stirred overnight. After that, isolation of cellulose bundles was performed on a high-pressure mini DeBee homogenizer (Fig. 1a, BEE International, Inc, American). Specifically, the cellulose solution was first processed with a D5 nozzle (400 μm in diameter) under intensive pressure in batch mode for 50 cycles, followed by processing for 30 cycles with a Z8 nozzle (195 μm in diameter) at the same pressure. During the continuous homogenization process, the cellulose bundles were repeatedly isolated and exfoliated due to the high shear force. As a result, a homogeneous disassembled cellulose nanofibrils (CNF) suspension with individual nanofibers was obtained. In order to prepare a CNF solution with desired concentration, the homogenized CNF solution was diluted with deionized water and further subjected to high shear forces using a high shear digital homogenizer (Fig. 1b, IKA T25, Germany) for a few minutes. Finally, a stable CNF suspension with a concentration of approximately 1 mg/ml was produced.

2.3. Fabrication process of GnP/CNF hybrid papers

Measured quantities of GnP and triton-X100 were added to deionized water, and the concentration of GnP and triton-X100 were both produced at 1 mg/ml. The GnP solution was then ultrasonicated for a few minutes followed by vigorously stirring for 12 h. After that, the CNF suspension was dropwisely added to the prepared GnP suspension (25 ml) until desired CNF ratio (0–60 wt%) was obtained. Subsequently, the obtained solution was sonicated at a high power for 5 min, after which a stable and uniform GnP/CNF suspension was produced. This was followed by the filtration of the resultant suspension through a filter paper (0.22 μm). After filtration, the paper was thoroughly washed with deionized water for 3 times to remove the excessive triton-X100. The obtained wet cake along with the filter were then dried at ambient temperature overnight. Finally, the paper was peeled off from