Layered nanofibrillated cellulose hybrid films as flexible lateral heat spreaders: The effect of graphene defect

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ABSTRACT

The effect of graphene defects on the performance of polymer-based material was investigated to obtain thermal conductive and strong materials for various commercial portable electronics. The flexible lateral heat hybrid films based on graphene sheets (GSs) and nanofibrillated cellulose (NFC) were fabricated via a vacuum-assisted self-assembly technique. The hybrid film with low-defect density GSs exhibited high thermal conductivity (TC) of 6.75 W m^{-1} K^{-1} at 10 wt % GS loading. Compared with pure NFC film, the hybrid film showed excellent enhancement of 501.6%, which was 1.5× times higher than those with high-defect density GSs. The relationship between defect density of GSs and TC of hybrid films was consistent with the published simulation results. Meanwhile, the hybrid film with low-defect density GSs also exhibited higher toughness, tensile strength and Young's modulus than those with high-defect density GSs. NFC/GS hybrid films With high TC and mechanical properties can be used as a potential candidate for flexible lateral heat spreaders.

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1. Introduction

Lateral heat spreaders are extensively applied in various commercial portable electronics with more condensedly packed integrated circuits such as LEDs, touch panels, and smart phone [1—6]. Graphene, a monolayer of graphite, has attracted interest because of its excellent thermal properties (~2000—4000 W m^{-1} K^{-1}) [3,7,8]. This feature makes graphene a potential thermal reinforcement for multifunctional polymer composites [9—11]. Park et al. reported a thermal conductivity (TC) enhancement of 90% in polystyrene composites with 10 vol% of reduced graphene oxide (rGO) [12]. However, the TC of polymer/graphene nanocomposites only moderately increased compared with the polymer matrix, although the composite is an excellent thermal conductor with high aspect ratio [9].

The various factors, such as poor dispersion and discontinuous polymer/nanomaterial interfaces, which has caused this above phenomenon have been extensively examined [13—16]. The effect of intrinsic properties (defects, size, number of layer, etc.) of graphene on the performance of polymer-based materials has also been

attracting much attention [14,17]. This paper mainly reports on the effect of graphene defects on the performance of polymer-based material. The possible defects on graphene include topological defects, vacancies, substitutional impurities, edge defects, and sp^3-like defects, and these defects can significantly degrade the thermal performance of materials [14,15,18]. For graphene/phase change composites (PCC), the annealed graphene/PCC displays over 400% enhancement in TC compared with pristine graphene/PCC composite [15]. Annealing cause the removal of oxygen-containing functional groups and the transition of hybridized carbon atoms from sp^3 to sp^2, enabling the formation of a low heat resistant conduction path. Numerous simulations have also shown that vacancies, Stone—Wales (S—W) defect, and adatoms, such as hydrogen and various ligands, decrease the conductivity through the bulk conducting channels [19—21]. However, the mechanism and the extent by which the intrinsic properties of graphene sheets (GSs) influence the thermal conductivity and other important properties of composites remain unclear. Thus, more adequate experimental studies are necessary to establish the relationship between GS defects and properties of the composites to use graphene in the preparation of composites for specific end applications.

Nanofibrillated cellulose (NFC) exhibits high strength, high stiffness, biodegradability, lightweight, transparency, and other biobased functions. This polymer can be applied in the fabrication of high-performance material for electronic devices, batteries

electrodes, etc [22–25]. NFC can naturally form a continuous network in which the fillers are homogeneously embedded and always adjust their basal plane parallel to the surface [26]. NFC-based nanocomposites have drawn increasing attention because of their excellent properties, such as high mechanical properties and lightweight [27,28]. NFC-based nanocomposites with layered structure have been fabricated using various fillers, such as boron nitride nanosheets [27], and montmorillonite [29]. Typically, the composites present a layered structure, which provide better mechanical properties for the composites and channels for lateral heat spread [28,30]. A layered structure is beneficial for further study on the effect of intrinsic properties of graphene on the performance of composites. Moreover, NFC has a 1D nanofiber structure, contrary to other polymers, forming less thermal insulating contacts between nanosheets [27].

In this report, highly aligned NFC/GSs hybrid films have been prepared via a vacuum-assisted self-assembly (VASA) technique (Scheme 1b). The effect of the defect of the GSs on the TC and mechanical properties of the composite was explored. The results indicated that the graphene defects have substantial influences on the bulk properties of NFC/GS films, namely, TC, toughness, modulus and strength. This study provides a fundamental understanding for the design and fabrication of future high-performance materials with graphene.

2. Experimental section

2.1. Materials

Graphite powders were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Sodium cholate hydrate (NaC) was purchased from Sigma Aldrich (SigmaUltra ≥99%). Graphene nanoplatelets (G_{19} and G_{13}) were purchased from LEVSON (Shanghai, China). All other reagents and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China) and were of analytical grade. All materials were used as received.

2.2. Preparation of GSs

Low-defect GSs (G_{24}) were manufactured using a previously reported method [31]. NaC was dissolved in deionized (DI) water at the concentration of 0.1 mg mL^{-1}. Graphene dispersion was prepared by adding 2 g of graphite powders to 400 mL of NaC solution in a 500 mL capped beaker, and then the beaker was placed in a low-power (80 W) sonic bath for 24 h. Samples were left overnight and then centrifuged for 90 min at 1500 rpm. Then, the top two-thirds of the dispersion was extracted and retained for use. The rGO (G_{131}) was synthesized by reduction of graphene oxide (GO) with hydrazine (Fig. S1) [32,33]. GO was prepared from natural graphite powers using a modified Hummer's method [34]. The sizes of G_{131} and G_{24} were controlled by polytetrafluoroethylene micro-filtration membrane (50 mm in diameter, 1.2 μm pore size). The commercially available G_{19} and G_{13} are 10 μm in size with 6 and 8 layers (Fig. S2), respectively. These characteristics are according to manufacturer's specifications.

2.3. Preparation of hybrid films

NFC dispersion (Fig. S3) was prepared according to Saito (see Supplementary material) [35–37]. All GSs and NFC were dispersed in DI water and were used directly after preparation. In this study, the NFC/GS hybrid films were fabricated via the VASA process (Scheme 1b). The detailed mechanism and methodology of VASA have been reported by Liimatainen and in our previous study [26,38]. Various GS dispersions were controllably added to the NFC suspensions at room temperature. Then resulting suspension was vigorously stirred for approximately 1 h to yield a homogeneous dispersion with graphene content from 0 to 10 wt % relative to NFC.
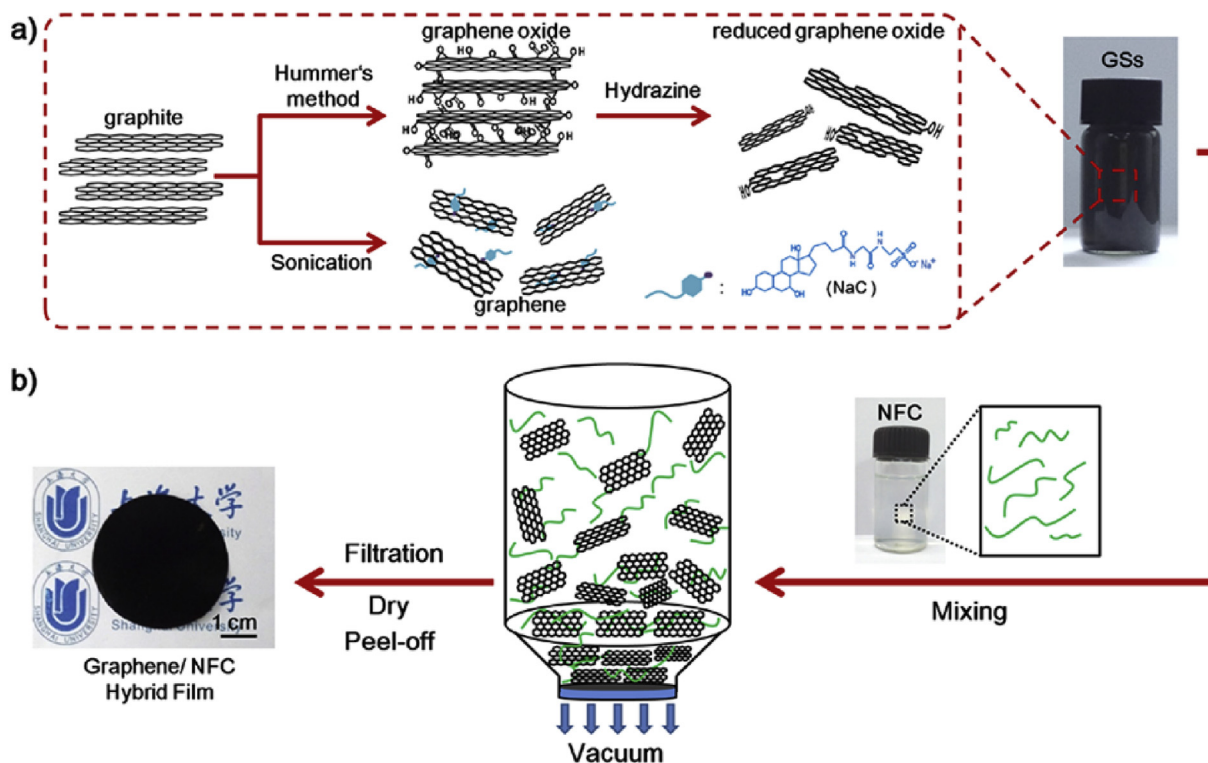
Scheme 1. Preparation of a) graphene sheets (GSs) and b) hybrid films consisting of GSs and nanofibrillated cellulose (NFC).