Preparation of organically dispersible graphene nanosheet powders through a lyophilization method and their poly(lactic acid) composites

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ABSTRACT

Solvent-free graphene nanosheets (GNSs), which are in the form of chemically reduced graphite oxide nanosheets, were prepared using an environmentally friendly freeze drying process. Compared with those produced through the vacuum filtration method, the lyophilized GNS powders were extremely light, loosely packed and could be readily redispersed in appropriate organic media like N,N-dimethylformamide as individual sheets with the aid of sonication. The ability of the as-lyophilized GNS powders to be redispersed in organic solvents facilitates their incorporation into polymers like poly(lactic acid) through a solution-based processing method. In the resulting composite, GNSs were uniformly dispersed in the matrix and enhanced the mechanical and thermal properties of the host polymer, suggesting the great potential of the lyophilized GNS powders in the field of polymer composites.

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1. Introduction

Graphene nanosheets (GNSs), one-atom-thick two-dimensional (2D) layers of sp²-bonded carbon [1], are fascinating carbon nanostructures that are not only of interest as model materials [2] but also hold great promise in many potential applications such as composites [1,3–6], transparent conductive films [7], field effect transistors [8] and ultrasensitive sensors [9]. Especially, the high aspect ratio combined with the extraordinary properties make GNSs ideal fillers in polymer composites. Several methods have been developed to produce these 2D carbon materials [10–19]. Compared with other fabrication strategies such as exfoliation of graphite [10] and epitaxial growth on silicon carbide [11], the deoxygenation (including thermal [12,13], chemical [14–18] and electrochemical [19] approaches) of graphite oxide (GO) nanosheets appears to be more feasible in that it enables mass production of GNSs at low cost. Moreover, the GNSs produced from GO nanosheets are decorated with some reactive groups, which facilitate their further functionalizations for various specific purposes [3,20].

The chemical reduction method, which has been frequently used to produce high-quality GNSs [14], is generally composed of two steps. Firstly, GO powders are exfoliated into single-layer GO nanosheets in water with the aid of sonication. Subsequently, a reduction process is carried out on these GO nanosheets in the liquid phase, yielding aqueous GNS suspensions. Although the as-reduced GNSs are hydrophobic, their aggregation tendency in the resulting aqueous dispersions could be inhibited by using polymeric or surfactant stabilizers [15,16]. Moreover, the generation of stable aqueous dispersions of GNSs without stabilizers has also been realized by Wallace and co-workers through electrostatic stabilization [17]. Nevertheless, in the polymer composite realm, the aqueous dispersions are of much less interest than their organic counterparts because many engineering polymers are mostly...
soluble in organic solvents. Recently, Villar-Rodil et al. have prepared GNS dispersions in N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) through in situ reduction of GO nanosheets in these solvents [4]. Using these dispersions, they successfully fabricated homogeneous GNS-based poly(methyl methacrylate) composites, and found noticeable improvements in the thermal stability of the as-fabricated composites. In order to prepare GNS dispersions in a wider variety of organic media, several strategies have been developed for the functionalization of GNSs [3,20–22], which could also make GNSs uniformly incorporated into various polymer matrices. Compared with unmodified GNSs, the functionalized ones are much more effective in enhancing the ultimate properties of the resulting composites [20], because of their largely improved compatibility with polymer hosts.

However, as potential commercial products for industrial applications, the GNS suspensions are less attractive than their powder counterparts because of the following reasons. Firstly, the GNS suspensions can only be used to fabricate specific composites whose matrices can be dissolved in them, while the GNS powders can be incorporated into different polymers by choosing different solvents to disperse them. Secondly, the purification of powder samples is simpler and faster than that of suspension samples. Lastly but most importantly, compared with the solid products, the liquid products have to face the inconveniences and risks in the transportation, which greatly hamper their commercialization. In fact, considerable efforts have already been devoted to the preparation of GNS powders from their dispersions. For example, Yang et al. and Srinivas et al. acquired GNS powders from their suspensions through centrifugation [23] and vacuum filtration [24], respectively. Unfortunately, these powders were found to be in a highly agglomerated state, and could not be redispersed in solvents. These irreversible agglomerates form due to the high aspect ratio and strong van de Waals interactions of GNSs, which then makes their dispersion within polymer matrices at the individual sheet level impossible [1]. Therefore, the development of effective approaches to prepare organically dispersible GNSs from their dispersions is an essential topic in the GNS research field.

Lyophilization, an environmentally friendly process, has been frequently used to prepare aerogels of nanomaterials, such as cellulose nanowhiskers [25]. These aerogels are extremely light, loosely packed and thus gifted with some peculiar properties. For example, van den Berg et al. found that the lyophilized tunicate cellulose nanowhisker powders could be redispersed in organic media [26]. It is to be expected because the loosely stacked structure of these powders would lead to decreased van de Waals interactions. Recently, some pioneering works have used the lyophilization method to prepare GNS powders, which were showed to be extremely light and macroporous [20,27–30]. In our previous work, we found that the as-lyophilized GNS powders could be readily redispersed in DMF with the aid of sonication, facilitating their functionalization and incorporation into polymer hosts [20]. A control experiment on vacuum-filtered GNS powders revealed that they couldn’t be redispersed in DMF. Obviously, the preparation process of GNS powders has great influence on their redispersibility: compared with the vacuum filtration method, the lyophilization method is more feasible in producing organically dispersible GNS powders. Although the organic dispersibility of lyophilized GNS powders has been illustrated in some previously reported works, it lacks a specific and systematic study to reveal the superiority of the lyophilization method in producing organically dispersible GNS powders. Considering the tremendous interest of the organically dispersible GNS powders in many applications and their potential importance in promoting the development of GNSs as commercial products, such study is urgently required. Therefore, we took a comparative study on the lyophilized and vacuum-filtered GNS powders to definitely clarify the important role of the lyophilization method in the production of organically dispersible GNS powders. Moreover, the possible application of as-lyophilized GNS powders in the field of polymer composites was also illustrated.

2. Experimental

2.1. Materials

The starting material in the production of GO and GNS powders is expandable graphite (Yingtai Co., China). PLA (Dow Chem. Co.) employed to fabricate GNS-based composites has a number average molecular weight of about 150,000. Other reagents were purchased from commercial suppliers (Aldrich and Sinopharm) and used without further purification.

2.2. Preparation of GNS powders

Synthesized from expandable graphite by a modified Hummers method [31], GO powders were homogeneously dispersed in water with the aid of sonication. The aqueous GO nanosheet dispersion was chemically reduced with hydrazine to generate a GNS suspension, as described elsewhere [17]. Subsequently, the aqueous GNS suspension was frozen into an ice cube in a refrigerator (–4 °C) and then freezes dried using a FD-1A-50 lyophilizer (Boyikang Co. Ltd., China) with a condenser temperature of –50 °C and inside pressure less than 20 Pa. After 7-day lyophilization process, low-density, loosely packed GNS powders were finally obtained (Fig. 1b). In a control experiment, 25 ml of GNS aqueous suspension (containing about 6 mg of GNSs) was vacuum-filtered through a 220 nm PTFE membrane and dried under vacuum, yielding paper-like GNS powders.

2.3. Fabrication of neat PLA and PLA/GNS composite

The composite was fabricated using a solution-based processing method. Briefly, 8 mg of lyophilized GNS powders were redispersed in 80 ml of DMF with the assistance of stirring and sonication at room temperature. Then, 4 g of PLA was added to the suspension. After agitation at 85 °C for 2 h, and sonication at 70 °C for another 2 h, the mixture was coagulated with methanol (800 ml). The flocculent was filtered under vacuum, and then vacuum dried at 80 °C for 10 h. The obtained composite, which has GNS loading of 0.2 wt.%, is denoted as 0.2G-PLA. The neat PLA control sample was fabricated in the same manner for the sake of comparison.
2.4. Measurements

X-ray photoelectron spectroscopy (XPS, PHI-5000C ESCA, Al Kα) and X-ray diffraction (XRD, PANalytical X’pert diffractometer with Cu Kα radiation) were used to characterize the chemical components and structure of GO and lyophilized GNS powders. For atomic force microscopy (AFM, Multimode Nano 4 in tapping-mode) observation, the aqueous GO nanosheet suspension and DMF suspension of lyophilized GNSs (both of the suspensions had a sheet concentration of 0.2 mg/ml) were spin-coated onto freshly cleaved mica surfaces. XRD, thermogravimetric analysis (TGA, Perkin–Elmer, heating from 50 to 600 °C at a rate of 20 °C/min in air), tensile test (CMT4102 tester, Sans Co., China. The data reported here represent the average of three tests) and dynamic mechanical analysis (DMA 242, Netzsch in the tensile mode) were conducted to identify the properties of PLA/GNS composite, as well as those of neat PLA. Before these examinations, the samples were compress molded into 0.4–0.45 mm thick sheets at 185 °C under 10 MPa. The specimens for tensile tests were prepared by cutting these sheets into dog-bone type with dimensions of 50 mm (length) × 9 mm (width) × 17 mm (narrow portion width) × 0.4 mm (thickness). The tensile-fractured surfaces of two samples were observed with field emission scanning electron microscopy (FESEM, Hitachi, S-4800). The 0.2G-PLA fractured surface was observed directly, while that of neat PLA was aurum sputter coated before FESEM observation due to its poor electrical conductivity.

3. Result and discussion

3.1. Characterization of GNSs and GO powders

The appearances of vacuum-filtered and lyophilized GNS powders are showed in Fig. 1b and c. The vacuum-filtered GNS powders are paper-like materials which have been reported to be closely stacked in a layered structure [27]. The attempt to sonically disperse them in DMF failed (Fig. 1b), which might be due to the strong van de Waals forces between GNSs [18]. Compared with vacuum-filtered ones, lyophilized GNS powders are rather light and fluffy. According to van den Berg et al., lyophilization of aqueous tunicate cellulose whisker dispersions could generate dry tunicate cellulose whiskers with similar morphology characteristics, and these samples could be redispersed in organic solvents because of their decreased van de Waals forces [26]. Analogously, our as-lyophilized GNS powders should also be able to be redispersed in appropriate solvents, such as DMF and NMP [14]. Indeed, after dispersing them in DMF with the aid of sonication, a homogeneous suspension was generated (Fig. 1c). Compared with GO nanosheet dispersion (Fig. 1a), the GNS suspension is much darker in color (Fig. 1c). This increased absorption in the
visible region is to be expected if reduction succeeds and the conjugated \( sp^2 \) network within the carbon structure restores [19]. The successful reduction is confirmed by C1s XPS spectrum of GO and lyophilized GNS powders (Fig. 1): Upon reduction, the higher binding energy side of the C1s envelope, which constitutes the main feature for the unreduced material and stems from the most electropositive, oxidized carbons [4], decreases to yield just a tail.

Obviously, the enhanced dispersibility of as-lyophilized GNS samples should be ascribed to their weak van de Waals interactions. The weak interactions could be recognized from the disordered stacking structure of lyophilized GNS powders, as we can deduce from their XRD pattern (Fig. 2). Compared with the XRD trace of GO powders, which exhibits a strong diffraction peak at 12° (corresponding to interlayer spacing of about 0.74 nm), that of lyophilized GNS powders presents no visible peak. Although this does not necessarily require that all stacking is lost, it does indicate that any remaining stacking is disordered [13]. The weak van de Waals interactions of as-lyophilized GNS powders should not only facilitate their uniform dispersion in appropriate organic media, but also make their exfoliation into individual sheets available.

In order to illustrate the complete exfoliation of lyophilized GNS powders in DMF, AFM observations were conducted. The tapping-mode AFM image of lyophilized GNSs redispersed in DMF is illustrated in Fig. 3b. From the cross-section analysis, we could find that lyophilized GNSs have a height of around 0.6 nm, matching well with the reported thickness of single-layer GNSs [4]. It should be noted that the thickness of lyophilized GNSs is much lower than that of GO nanosheets dispersed in water (1.4 nm, Fig. 3a), which has been suggested to be due to the removal of oxide groups [23]. Moreover, compared to GO nanosheets whose lateral dimensions are several hundred nanometers, lyophilized GNSs are less than 50 nm in size. Since the van de Waals interparticle adhesion energy decreases with the particle size [32], this thorough exfoliation may also be partly attributed to the small size of lyophilized GNSs.

### 3.2. Morphology and properties of PLA and PLA/GNS composite

The FESEM images of the fractured sections of neat PLA and 0.2G-PLA are presented in Fig. 4. Obviously, GNSs are homoge-

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**Fig. 2** – XRD patterns of GO and GNS powders.

**Fig. 3** – AFM images of (a) GO nanosheets dispersed in water and (b) GNSs redispersed in DMF.

**Fig. 4** – FESEM images showing the fractured sections of (a) PLA and (b) 0.2G-PLA. Inset in (b): enlarged morphology of indicated region (by white arrow).
neously dispersed in PLA with no large-size aggregates observed. These FESEM micrographs also suggest intimate adhesion between GNSs and matrix, which would be discussed below. In order to confirm the absence of GNS aggregation in the polymer host from macroscopic view, XRD measurements of neat PLA and GNS-containing PLA were carried out with results presented in Fig. 5. The XRD pattern of 0.2G-PLA is almost the same as that of pure PLA, with no graphite layer structure peak at 26° or graphite oxide peak at 12° detected. As suggested by Ramanathan et al., this result indicates that the dispersion of GNSs in PLA matrix is close to single-sheet level [5].

Fig. 6 illustrates the TGA traces of neat PLA and 0.2G-PLA. Recent researches have demonstrated that the incorporation of GNSs could largely enhance the thermal stability of polymers [4,5]. In our PLA/GNS system, the GNS addition induces thermal stabilization of the matrix: with the filling of only 0.2 wt.% GNSs, the temperature for 5% weight loss of PLA increases by more than 10 °C. This improvement in thermal stability could be attributed to the so-called “tortuous path” effect of GNSs, which delays the permeation of oxygen and the escape of volatile degradation products and also char formation [33]. Because of the enormous surface area of GNSs [1], their significant effects on composite properties are often seen at low loadings [1,5]. As simplified calculated by Ramanathan et al., the GNS fraction required for rheological percolation in polymers is extraordinarily small (0.05 wt.%), and their results are consistent with this calculation [5].

According to mechanical properties of PLA and 0.2G-PLA, which could be seen in Fig. 7, the reinforcing effect of GNSs is rather significant: the 0.2 wt.% GNS incorporation leads to a 26% increase in tensile strength and a 18% raise in Young’s modulus. In this study, Young’s modulus is determined from DMA traces as storage modulus at 35 °C, at which PLA and 0.2G-PLA are both in the glassy state. Given the excellent modulus (~1100 GPa) and intrinsic strength (125 GPa) of GNSs [3], these improvements are to be expected. In addition, these enhancements should also be ascribed to the strong interaction between GNSs and PLA because it ensures the efficient load transfer between these two components. As shown in Fig. 4b, although no obvious GNSs can be observed to be pulled out, the vicinity of GNSs is rather rough. It is in vivid contrast to the smooth fracture surface of PLA (Fig. 4a), indicating that GNSs intimately interact with matrix. From the high magnification FESEM image of 0.2G-PLA (inset in Fig. 4b), we can see that GNSs are embedded into host polymer with their flake-like morphology well remaining, another evidence of the strong adhesion between GNSs and PLA.

4. Conclusions

In conclusion, through a comparative study on the redispersibility of lyophilized GNS powders and vacuum-filtered GNS powders, we have definitely revealed the superiority of the lyophilization method in producing organically dispersible GNS powders. AFM observations confirmed the single layer nature of the lyophilized GNS powders in organic media. The possible application of the lyophilized, organically dispersible GNS powders in the field of polymer composites...
was illustrated through their homogenous incorporation into PLA. In the resulting composite, GNSs were uniformly dispersed in the matrix and enhanced the mechanical and thermal properties of the host polymer. Therefore, our results could provide a general pathway to utilize the lyophilization method in preparing organically dispersible GNS powders, which would greatly promote the development of GNS-based polymer composites.

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