



Effect of folded and crumpled morphologies of graphene oxide platelets on the mechanical performances of polymer nanocomposites



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ABSTRACT

Graphene and its chemical derivative have been taken as promising candidates in composites due to their extraordinary mechanical and physical properties. Different from conventional plate fillers, the embedded graphene fillers exhibit various morphologies (e.g. folded, crumpled, and distorted sheets) inside matrix because of its atomic thickness. In this work, we systematically investigated the influence of graphene oxide (GO) morphologies on the tensile properties of poly(vinyl alcohol)-based nanocomposites at low loading contents. Confocal laser scanning microscopy, as a characterization method, was employed to observe the morphologies of the embedded GO platelets. Tensile mechanical tests and in situ micro-Raman spectroscopy tests indicated that GO sheets with larger aspect ratios exhibited efficient interfacial load transfer and improved mechanical properties at ultra-low filler contents. However, with further increased nanofiller contents, the folded and crumpled GO sheets severely degraded the mechanical reinforcement as induced by interfacial debonding. Molecular dynamic simulation indicated obvious stress concentrations on the wrinkle throughout entire graphene platelet areas. Long-term creep tests confirmed the stress concentration eventually induced the decrease in creep resistance for nanocomposite at a high applied stress levels. All these results aided in understanding the mechanical behaviors of two-dimensional nanofiller-based nanocomposites with huge aspect ratios.

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1. Introduction

The mechanical reinforcement of conventional composites greatly depends on the load-bearing capability of embedded fillers inside the matrix. Oriented fillers with fairly high aspect ratios are crucial to substantially improving the stiffness of composites. For high aspect ratios, the fiber is sufficiently long for tensile stress to

build up until the fiber has a strain equal to that of the matrix and composites. Conversely, for low aspect ratios, stress in the fiber cannot build up to reach a plateau value; thus, the fiber cannot provide very efficient reinforcement because it carries considerably less stress than longer fibers in the same system [1]. Compared with conventional fiber materials, nanofillers such as one-dimensional carbon nanotubes (CNTs), two-dimensional (2D) silicate, and graphene platelets have at least 10^3 aspect ratios, which are conducive to efficient mechanical reinforcement in composites. Our previous works have demonstrated apparent mechanical reinforcement in the modulus, strength, and toughness of CNT-based polymer nanocomposite fibers [2–6]. Similar to the supra reinforcement of CNTs, recently, graphene becomes a highly promising material for nanocomposites [7–12]. Theoretical calculation based on micro-mechanical modeling has suggested that randomly oriented graphene platelets with $\sim 10^3$ aspect ratio may produce nanocomposites with higher stiffness and strength than randomly

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oriented nanotubes [13]. Experimental works have proven that graphene platelets have significantly outperformed CNT fillers in terms of Young's modulus, tensile strength, and fracture toughness in composites [14,15]. However, similar to CNT-filled nanocomposites, the poor dispersion in solvents of graphene and its weak interfacial interactions with polymer matrices greatly limit the widespread use of graphene in composites. Nevertheless, the chemical functionalization of graphene can improve its dispersibility and processability [16–24]. Functional groups bound onto the surface of graphene oxide (GO) sheets can improve interfacial bonding between GO and matrix, as observed for functionalized CNT-based nanocomposites [2,25–27]. Thus, various GO-incorporated water-soluble polymer nanocomposites have been prepared, and apparent mechanical reinforcement has been achieved [27–31]. For instance, Xu et al. [27] found that the Young's modulus and tensile yield strength of composites containing 3 wt.% GO could reach up to 4.8 GPa and 110 ± 7 MPa respectively, indicating 128% and 65% improvement compared with pure matrix. Zhao et al. investigated the influence of GO filler content on the tensile mechanical properties of nanocomposites, and the increasing trend was less obvious at high loading contents because of the inevitable stacking of GO sheets [28]. Coleman et al. compared the difference in reinforcement for graphene-based composites with ~ 1000 and ~ 2000 aspect ratios [29]. They predicted that reinforcement would approach theoretical limit once graphene platelets (aspect ratio $\approx 10^4$) become available. However, most works have focused on static mechanical improvement, and only a few have paid attention to the creep of graphene and its chemical derivative-based nanocomposites [30,31].

Both experimental studies and atomic simulation [32,33] have confirmed the presence of ripples, wrinkles, and corrugation in graphene sheets resulting from thermal fluctuations, structure defects, and surface functionalization [33–35]. The presence of wrinkles in sheets also greatly affects many intriguing physical properties of graphene, such as thermal conductivity, carrier mobility, and wettability [36–38]. Reports on the influence of wrinkled and crumpled morphologies of graphene platelets on the mechanical performance of nanocomposites are limited [39,40]. As expected, the wrinkled nature of graphene sheets provides less than the optimal reinforcement because of their straightening deformation mode rather than stretching between C–C bonds under in-plane tensile stress. However, the influences of crumpled, wrinkled and folded graphene sheets on mechanical behaviors and deformation modes have not yet been experimentally demonstrated. The underlying mechanism has also not been completely understood yet.

In the present work, GO sheets with aspect ratios of $\sim 1.5 \times 10^3$ and $\sim 7.4 \times 10^4$ were used to prepare GO/poly(vinyl alcohol) (PVA) nanocomposites through solution-casting method. We systematically compare the mechanical properties of nanocomposites with different aspect ratios at relatively low contents (< 1 wt.%). Confocal laser scanning microscopy characterization indicated the crumpled and irregularly folded microstructural features of GO sheets inside the matrix. Both static tensile and in situ micro-Raman spectroscopy tests were used to evaluate the reinforcement of GO platelets at macroscopic and microscopic levels. The influences of crumpled and folded GO sheets on the mechanical performance of composites were determined by experiment and molecular dynamic (MD) simulation. The influence of wrinkled, folded, and distorted morphologies of GO sheets on the mechanical performances of nanocomposites were examined through long-term tensile creep tests based on the time–temperature superposition principle (TTSP). Our work can help elucidate the mechanical behaviors of 2D filler-reinforced polymer nanocomposites, particularly those with huge aspect ratios.

2. Experimental

2.1. Material

Preparation of small-size GO sheets (*s*-GO): *s*-GO was prepared from purified natural graphite (obtained from Qingdao Yingshida graphite Co., Ltd., with an average size of 20 μm) by a modified Hummers method [41]. Under agitation, graphite powder (4 g) and NaNO_3 (3 g) were mixed with H_2SO_4 (250 ml, 98 wt. %) in an ice bath, and KMnO_4 (25 g) was slowly added to prevent the temperature from exceeding 20 °C. The reaction was kept at 20–30 °C for 2 h with gas release, and then deionized water was gradually added. The resultant bright-yellow suspension was diluted and further treated with a H_2O_2 solution (30%), followed by centrifugation and careful washing to clean out remnant salt. Colloidal dispersions of individual GO sheets in water (5 mg/ml) were prepared with the aid of an ultrasonic bath.

Preparation of large-size GO sheets (*l*-GO): The detailed experimental procedure for the preparation of *l*-GO sheets is described as follows [42]. Natural flake graphite (2 g) with an average size of 500–600 μm , NaNO_3 (2 g), and concentrated H_2SO_4 (96 ml) were mixed at 0 °C. Then, KMnO_4 (12 g) was gradually added to the mixed solution while keeping the temperature at 0 °C. The mixture obtained was stirred at 0 °C for 90 min, and then at 35 °C for 2 h. Deionized water was slowly dropped into the resulting solution, over a period of around 30 min, to dilute the mixture. Then deionized water (200 ml) was added followed by H_2O_2 (10 ml, 30%), and the stirring continued for 10 min to obtain a graphite oxide suspension. The graphite oxide deposit was collected from the graphite oxide suspension by high-speed centrifugation at 12,000 rpm for 40 min, and repeatedly washed with deionized water until pH = 7. Then a mild sonication (40 W, 15 min) was used to exfoliate the graphite oxide to obtain a GO suspension. To obtain uniform *l*-GO sheets, a low-speed centrifugation at 3000 rpm was first used to remove thick multilayer sheets until all the visible particles were removed (3–5 min). Then the supernatant was further centrifuged at 5000 rpm for 5 min to separate large sheets (precipitate) and small sheets (supernatant). Finally, the obtained precipitates containing large sheets were re-dispersed in water to get *l*-GO sheet suspension (5 mg/ml).

The average aspect ratio of individual GO sheets was obtained by $A_f = \ell/t$, where ℓ presents half of the perimeter of individual GO sheets, t is average thickness of individual GO sheet referred Ruoff's work [43]. More than 100 individual GO sheets based on SEM images were analyzed for *s*-GO and *l*-GO sheets respectively.

Preparation of GO/PVA composites: PVA with $M_w \approx 120\,000$ was purchased from Beijing Chem. Reagents Co. (Beijing, China) and used as received. The procedures for preparing PVA/GO composite films are described as following: PVA (8 g) was dissolved in 392 ml deionized water at 90 °C to give a 2 wt. % solution. Then, PVA (25 ml) solution was added to 0.1, 0.5, and 1 ml GO dispersion (5 mg/ml), and the mixtures were well stirred immediately to obtain uniform dispersions. The solution was further cast on the Petri dish dried overnight under vacuum at 60 °C. The weight contents of GO in the three films described above were calculated to be about 0.1, 0.5 and 1 wt. %, respectively. The filler concentration was transformed from mass fraction (wt. %) to volume fraction (vol. %) by the following Equation (1):

$$v = \frac{w\rho_p}{w\rho_p + (1-w)\rho_g} \quad (1)$$

where, v and w are the volume fraction and mass fraction of GO sheets. ρ_p and ρ_g represent the density of PVA matrix and GO sheets, which can be taken as 1.3 g/cm³ and 2.2 g/cm³ [44,45], respectively.

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