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Colloidal and rheological behavior of aqueous graphene oxide dispersions in the presence of poly(ethylene glycol)

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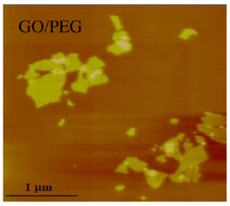
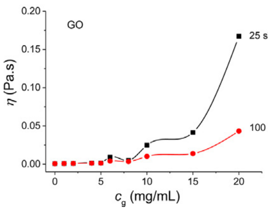
HIGHLIGHTS

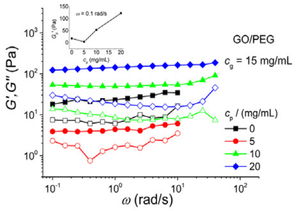
- The critical concentration of isotropic-nematic phase transition for aqueous GO dispersions was determined by shear rheology.
- Effect of PEG concentration on the linear and non-linear rheological behavior of aqueous GO/PEG dispersions was firstly studied.
- PEG chains adsorbing effects were studied by Atomic force microscopy images and zeta-potential measurements.

GRAPHICAL ABSTRACT

The effects of the concentration of graphene oxide (GO) and poly(ethylene glycol) (PEG) on the colloidal and rheological behavior of GO aqueous dispersions were investigated. The critical concentration of isotropic-nematic phase transition of GO aqueous dispersions was about 6 mg/mL. Significantly, the aqueous GO/PEG dispersions presented a lowest viscosity and minimum linear storage modulus linear G' at the saturation adsorbing concentration $cp_{,s}$. Therefore, the PEG concentration had a significant effect on the linear and non-linear rheological behavior of GO/PEG dispersions.







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ABSTRACT

In this work, the effects of the concentration of graphene oxide (GO) and poly(ethylene glycol) (PEG) on the colloidal and rheological behavior of aqueous GO dispersions were investigated. The concentration of GO and PEG was varied from 0 to 20 mg/mL, respectively. Atomic force microscopy (AFM) images and zeta-potential measurements demonstrated that PEG chains were adsorbed on the colloidal GO sheets. The red-shift of D and G bands in the Raman spectra of GO/PEG compared with pure GO suggested that there was hydrogen bond interaction between GO and PEG. Steady state shear results indicated that GO aqueous dispersions changed from Newton fluids to pseudoplastic fluids as the concentration of GO increased. The critical concentration of isotropic–nematic phase transition of aqueous GO dispersions was about 6 mg/mL. Significantly, the aqueous GO/PEG dispersions presented a lowest viscosity and minimum linear storage modulus linear G' at the saturation adsorbing concentration $cp_{,s}$, which were determined by steady state shear and small amplitude oscillatory frequency sweep, respectively. Therefore, the

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PEG concentration had a significant effect on the linear and non-linear rheological behavior of GO/PEG dispersions. In addition, the concentrated aqueous GO dispersions showed typical yield flow behavior and the yield stress σ_y firstly decreased and then increased with the increasing of GO concentration. These results could contribute to understand the interplay between microstructure and mechanical behavior of GO/polymer in aqueous dispersions, and also provide some guidance for the processing of GO-based polymer nanocomposites.

1. Introduction

Graphene is a two-dimension sheet of single atomic thick layer of hexagonally arranged carbon atom [1,2]. Graphene has attracted significant interests due to its extraordinary physical properties which make it an ideal candidate for a wide range of applications, such as actuators [3,4], supercapacitors [5], hydrogen storage [6], nanocomposites [7].

In particular, graphene/polymer nanocomposites have become a hot topic in the field of polymer-based nanocomposites due to their excellent electrical, mechanical properties and thermal stability [8–11]. However, graphene/polymer nanocomposites still face several challenges during processing, such as homogenous dispersion of graphene in polymer matrix, interfacial interactions and the effect of graphene fillers on the viscoelasticity of nanocomposites [9,11]. It is well-known that rheological characterization can provide much valuable information on the processing property of polymer-based nanocomposites. Therefore, it is necessary to explore the rheological performance of graphene/polymer nanocomposites. Up to now, there have been many reports on the rheological behavior of graphene/polymer nanocomposites, while which mainly focused their attention on graphene/polymer melts [12–15]. However, the graphene are usually processed from graphene oxide (GO) dispersed in some common solvents, like water, *N*,*N*′-dimethyl formamide (DMF), and *N*-methyl pyrrolidone (NMP) [16]. Moreover, aqueous GO dispersions have been widely used as precursor to produce chemically converted graphene in large-scale [17,18]. Thus, it is fundamentally important to investigate the rheological behavior of aqueous dispersions of GO/polymer. However, to the best of our knowledge, there are few reports on the rheological behavior of aqueous dispersions of GO/polymer so far [19].

Poly(ethylene glycol) (PEG) is a common water-soluble non-ionic polymer which has been widely used as a kind of model polymers to tailor the interaction between colloidal particles in aqueous dispersions [20,21]. The colloidal and rheological behavior of aqueous dispersions of inorganic nanoparticles, such as silica sphere [22], montmorillonoid [23], and Laponite® [24–26] in the presence of PEG have been widely reported. Therefore, PEG could be an ideal polymeric additive to explore the colloidal and rheological behavior of aqueous dispersions of GO/polymer.

In the present study, we investigated the effects of the concentration of GO and PEG on the colloidal and rheological behavior of GO aqueous dispersions through atomic force microscopy (AFM), zeta-potential and rheological measurements. It was found that the GO sheets with a single atomic layer thickness were successfully prepared by ultrasonic exfoliation with an aspect ratio of ∼570. The concentrated aqueous dispersions of GO showed characteristic shear-thinning behavior, and thus could be classified as a kind of yield stress fluids. The adsorbing behavior of PEG on GO sheets in aqueous dispersions were probed by AFM and zeta-potential measurements. The critical concentration of isotropic–nematic liquid crystal transition in aqueous GO dispersions was approximate 6 mg/mL. Furthermore, the effect of the concentration of PEG on the rheological properties of aqueous dispersions of GO was probed by small amplitude oscillatory frequency sweep and steady state shear tests. Significantly, a lowest viscosity and minimum linear storage modulus G' at the saturation adsorbing concentration $c_{p,s}$ were observed in the aqueous GO/PEG dispersions with the increasing of PEG concentration. Therefore, the study of colloidal and rheological behavior of aqueous dispersions of GO/PEG could contribute to understand the phase transition of a class of two-dimensional anisotropic colloid sheets with large aspect ratio and also maybe provide some guidance for the processing of GO/polymer nanocomposites.

2. Experimental

2.1. Materials

Natural graphite flakes (purity degree >99%, Qingdao Huatai Lubricant Sealing S&T Co. Ltd., Qingdao, China) were used after dried at 60 °C in vacuum for 12 h. Poly(ethylene glycol) (PEG, analytical grade) with molecular weight M_w of 20,000 g/mol was used after dried at 50 °C in vacuum for 12 h. All other reagents were analytical grade and used as received without further purification. Water was purified by deionization and filtration with a Millipore purification apparatus (18.2 MΩ·cm).

2.2. Sample preparation

Graphite oxide was prepared by the improved Hummers' method [27]. Typically, a mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was first added to a mixture of graphite flakes (3.0 g) and $KMnO_4$ (18.0 g). Then, the reaction mixture was heated to 50 °C and stirred for 12 h. Next, the reaction was cooled to room temperature and poured onto ice (400 mL). Lastly, H_2O_2 (30%) was added drop-wise into the reaction mixture until the color of the solution became bright yellow. In order to remove the excess metal salts, the mixture was filtered and washed with 1:10HCl aqueous solution. The product was firstly purified by centrifugation at 12,000 rpm for 20 min, decantation and re-dispersed in de-ionized water repeatedly for several times until the pH of the dispersion became neutral (pH ≈ 7). Then, the product was subjected to dialysis of two weeks to completely remove residual salts and acids. The as-prepared graphite oxide was freeze dried under a vacuum for 48 h.

The aqueous stock dispersion of GO (20 mg/mL) was achieved by dispersing 0.2 g of graphite oxide into 10 mL of de-ionized water using an ultrasonicator (180 W) for 1.5 h at room temperature. A series of aqueous dispersions of GO with desired concentration were acquired by diluting the GO stock dispersion with de-ionized water.

An aqueous stock solution of PEG (50 mg/mL) was prepared by dissolving dried PEG in de-ionized water and occasional shaking until a homogeneous solution was obtained (ca. 24 h). The aqueous dispersions of GO/PEG were prepared by mixing stock solutions of GO and PEG according to the required volume ratio. The mixed dispersions were further ultrasonicated for 15 min. The concentration of GO (*cg*, in mg/mL) in all GO/PEG dispersions was fixed