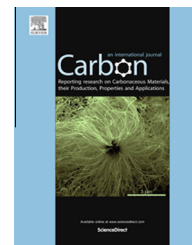


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# Rheological properties of graphene oxide liquid crystal

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## ABSTRACT

We report the rheological properties of liquid crystalline graphene oxide (GO) aqueous dispersion. GO dispersions exhibit typical shear thinning behaviors of liquid crystals, which is described by power law or simple Curreau model. Irrespective of the shear rate, shear viscosity exhibits sudden decrease with the increase of GO composition around a critical volume fraction,  $\phi_c = 0.33\%$ , demonstrating typical colloidal isotropic–nematic phase transition. Dynamic measurements reveal the liquid-like (isotropic phase,  $G' > G''$ ) behavior at a low GO composition ( $\phi \sim 0.08\%$ ) and solid-like (liquid crystalline) behavior at higher compositions ( $\phi \sim 0.45\%$ ), where  $G'$  exceeds over  $G''$ . Nematic gel-like phase is confirmed at a higher GO composition over  $\phi > 0.83\%$ , where both  $G'$  and  $G''$  moduli are nearly independent of frequency ( $\omega$ ). Simple power law scaling arguments are introduced to model the dependence of yield stress and viscoelastic moduli on the GO composition. We also observed the yield stress and rigidity percolation transition above phase transition composition  $\phi_c > 0.33\%$  with a percolation exponent of  $1.3 \pm 0.1$ . These rheological insights provide valuable information for the liquid crystalline processing of GO based materials including fibers, sheets and other complex structures for electronic/optoelectronic and energy storage/conversion applications.

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## 1. Introduction

Mesoscopic ordering of anisotropic molecules or particles in fluid states, known as liquid crystalline (LC) phase, has attracted a great deal of research attention for the significance in display devices and highly ordered materials processing [1–4]. Among various liquid crystals, carbonaceous mesophases are of particular research interest, as they offer valuable routes to functional carbon based materials [5–10]. Recently, graphene oxide (GO), an oxygenated form of graphene with spontaneous solution dispersibility, has also been reported to form discotic colloidal liquid crystalline phase in

aqueous dispersion as well as in several organic solvents [11–19]. Liquid crystalline GO dispersions have already been utilized in a number of areas including carbon based fiber spinning, alignment of one-dimensional nanomaterials, and multifunctional composites, liquid crystal displays, etc [13–19]. Manipulation of atomic thick platelet ordering by external stimuli or dynamic perturbations may provide unprecedented routes to highly ordered carbon based materials assembled from genuine two-dimensional building blocks.

Processing of liquid crystalline materials frequently encounters technological issues involved with complex multiscale structures and dynamics. For many applications,

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liquid crystalline phase formation and corresponding viscoelastic properties play significant roles to determine the material structures and properties [20–22]. In the particular case of GO liquid crystals, Gao and Xu reported the shear viscosity reduction at isotropic to nematic phase transition as an evidence for LC phase formation [23]. Yong and co-workers reported typical shear thinning and relevant shear alignment behavior of GO liquid crystals. [24]. Nonetheless, detailed rheological properties of GO liquid crystals have not been investigated thus far, despite their crucial significance for optimized processing of high-performance graphene-based materials [23–25]. The aim of this work is to investigate on the various aspects of the viscoelastic properties of GO liquid crystals. Thorough investigation over a broad GO compositional range up to  $\Phi = 1.8\%$  reveals the typical rheological behaviors involved with the isotropic-to-nematic phase transition and nematic gel formation.

## 2. Experimental

GO dispersion was prepared by the oxidative exfoliation of graphite powder (Bay Carbon, SP1 Graphite powder; lot # 060706), following modified Hummers method, as described elsewhere [11]. Briefly, 1 g of graphite powder was oxygenated in 40 mL  $\text{H}_2\text{SO}_4$ , while stirring for 15 min, which was followed by slow adding of 3.5 g potassium permanganate under an ice bath. The mixture was then continuously stirred for 2 h at 35 °C. After completion oxygenation, the excess amount of deionized water and 35%  $\text{H}_2\text{O}_2$  were added to the mixture. The obtained yellow mixture was thoroughly filter washed with 1 M HCl solution and deionized water and re-dispersed in 1 L of deionized water. The monolayer exfoliation was achieved by the sonication of the washed GO dispersion in water bath ultrasonicator. Subsequent purification was performed by dialysis and centrifugation to remove ionic impurities and unexfoliated graphite oxides. A predetermined amount of the concentrated dispersion was diluted in deionized water to prepare the GO dispersions with a desired composition.

To characterize the GO sheet size and thickness, extremely diluted GO dispersion was dried at Si substrate surface. Atomic force microscopy (SPA400) image was recorded in the non-tapping mode under ambient conditions. Orientational arrangement of GO sheets was characterized by FE-SEM (Hitachi S-4800 SEM). Optical birefringence of GO liquid crystal dispersion was observed with light microscopy between crossed polarizers. Rheological characterization of GO dispersions was performed on a stress controlled Advanced Rheometer (Bohlin Instrument) in both steady and dynamic mode. All measurements were performed with cone-plate configuration (radius: 44 mm, cone angle: 4°) with truncated gap of 150  $\mu\text{m}$ . In the steady-state measurements, shear viscosity and shear stress were monitored as function of shear rate (from 0.01 to 100  $\text{s}^{-1}$ ). The shear rate was increased continuously with the 30 s integration time for each shear rate. Dynamic frequency sweep tests were performed from 0.1 to 100 rad/s. All samples are compressed slowly to the set gap and allowed to equilibrate for 10 min prior to each measurement. All measurements were performed at room temperature (20 °C).

## 3. Results and discussion

### 3.1. Characterization of GO liquid crystal dispersion

Fig. 1a shows the SEM image of as-synthesized GO platelets with the mean lateral size of  $\sim 700$  nm. AFM image of GO sheets with a height profile is shown in Fig. 1b, which confirms the monolayer thickness of  $\sim 1$  nm. The structure and properties of GO dispersions are strongly dependent on the interactions between the platelets. The steric hindrance from overlapping of GO platelets arises at high composition, results in configurational entropy driven excluded-volume effects [12]. Well-known Onsager's model accounts for the formation of nematic liquid crystals based on purely entropy-driven mechanism [26]. The thermodynamic equilibrium liquid crystal phase originates from the competition between orientational and positional entropies. In dilute dispersion, the orientational entropy is maximized due to random orientation of GO platelets. By contrast, above critical GO concentration, the GO platelets orientate parallel to each other in order to minimize the excluded volume of the approaching platelets. Thus, the parallel arrangement of anisotropic GO platelets maximizes the packing or positional entropy that governs the formation of nematic liquid crystalline GO dispersions. The liquid crystalline phase can be easily identified from polarized optical microscopy. GO dispersions does not show any optical birefringence at low volume fraction,  $\phi \sim 0.08\%$ . Biphasic dispersion is observed between 0.15% and 0.45%. Entire nematic phase is confirmed above a volume fraction of 0.45%. Typical optical birefringent texture of single nematic LC phase for  $\phi \sim 0.45\%$  is shown in Fig. 1c. This birefringence texture indicates the characteristic of anisotropic phases originates from the alignment of anisotropic platelets. The liquid crystalline GO dispersions are further confirmed from freeze-dried sample. Aqueous dispersion of  $\phi = 0.45\%$  quenched in liquid  $\text{N}_2$  and subsequently freeze-dried. The freeze-dried sample was subjected to SEM observation. Fig. 1d clearly demonstrates the ordered GO platelets in the nematic phase.

### 3.2. Rheological study

#### 3.2.1. Steady shear flow

Molecular ordering is particularly significant in the systems of anisotropic colloidal particles, polymers or worm-like micelles, where external shear can readily induce alignment and orientational order. To understand the orientational behavior of GO dispersions under shear, steady state shear flow curves were measured. Fig. 2a shows the evolution of shear viscosity against shear rate for various GO compositions. GO dispersion exhibits Newtonian and non-Newtonian (shear thinning) behavior strongly depend on the  $\phi$ . At low  $\phi = 0.08\%$ , shear viscosity shows Newtonian behavior at low and high shear rate with a shear thinning region at intermediate range. At a high GO composition, GO dispersion exhibits typical shear thinning behaviors. Moreover, the viscosity is found to show non-monotonic behavior with composition, which will be discussed later. Observed shear thinning is associated to the orientation of GO platelets in nematic dispersion. The flow behavior can be approximated by power

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