Rheological properties of graphene oxide liquid crystal

Pradip Kumar, Uday Narayan Maiti, Kyung Eun Lee, Sang Ouk Kim *

Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Department of Materials Science & Engineering KAIST, Daejeon 305-701, Republic of Korea

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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 ± 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,
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 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 oxygenized in 40 mL H2SO4, 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% H2O2 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 FEG-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 μm. In the steady-state measurements, shear viscosity and shear stress were monitored as function of shear rate (from 0.01 to 100 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 ~700 nm. AFM image of GO sheets with a height profile is shown in Fig. 1b, which confirms the monolayer thickness of ~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 crystalline 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, \( \phi \approx 0.08 \). 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 \( \phi \approx 0.45 \% \) 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 N2 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
law and Curreau shear thinning models. In power law shear thinning behavior ($\eta \approx \gamma^{x-1}$) with $\eta$ the viscosity, $k$ a constant, the shear rate and $x$ the power law exponent [27]. The exponent $x = 1$ is retrieved for Newtonian flow and $x < 1$ is for shear thinning fluids. In Fig. 2a, we have fitted the power law in the low shear rate regime (0.01–1 s$^{-1}$). The exponents, $x$ decrease from 0.9 to 0.29 with volume fraction (see Table 1). The exponent, $x = 0.9$ matches well with the one for isotropic dispersion at $\phi = 0.08\%$ with Newtonian behavior, while $x = 0.29$ for $\phi = 1.8\%$ corresponds the typical values of weak gels or concentrated dispersions. The shear thinning over the entire shear rate range can be also described by the simple Curreau equation [28], $\eta(\dot{\gamma}) \approx \eta(\dot{\gamma} \rightarrow 0)/[1 + (\dot{\gamma}/\gamma_c)^m]$, where $m$, and $\tau_c$ define the shear thinning exponent and orientational relaxation time in the system, respectively. We find that shear thinning exponent of $m = 0.38$ for $\phi = 0.08\%$, is close to liquid-like (isotropic) behavior. By contrast, exponent, $m = 0.61$ for $\phi = 1.8\%$ is close to highly entangled polymer melts and concentrated solutions [29]. Moreover, relaxation time, $\tau_c$ increase from 4.5 to 45 s when $\phi$ increase from 0.08\% to 1.8\%. This increase in relaxation time of GO platelets should manifest the maximization of packing and enhanced orientation of GO platelets along the shear direction.

Viscosity behavior of liquid crystalline dispersions depends not only on the GO composition but also on molecular arrangements in the dispersion. Fig. 2b shows the evolution of shear viscosity with volume fraction, $\phi$ for shear rates of 0.01, 8.5, and 92 s$^{-1}$. Interestingly, viscosity exhibits non-monotonic behavior with increasing $\phi$. At a low fraction of $\phi = 0.08\%$, GO dispersion is in isotropic phase. Afterwards, viscosity increased up to a critical fraction ($\phi_c \sim 0.33\%$) and get maxima. With the further increase in $\phi_c$, viscosity goes down and exhibits minima before increasing again. This viscosity reduction above a critical volume fraction, $\phi_c \sim 0.33\%$, is caused by the formation of low-viscosity nematic liquid crystalline phase. The viscosity minima approximately correspond to the GO composition for entire nematic phase formation. The transition from isotropic to nematic phase can be observed for the GO composition range between the maxima and minima in shear viscosity [30]. In this work, $\phi_c = 0.33\%$ is considered as the critical GO composition for isotropic–nematic phase transition, which is close to theoretical predicated value (0.25\%) for polydisperse infinitely thin platelets [31]. We note that this GO liquid crystal phase transition behavior agrees well with our previous optical characterization with polarized optical microscopy [11].

The shear effect on GO liquid crystal dispersion is further described by shear stress-shear rate flow curve (Fig. 3). The flow curves were measured for a wide range of GO composition from 0.08\% to 1.8\%. The representative shear stress-shear rate plots for $\phi = 0.08\%$ and 0.83\% are presented. At $\phi = 0.08\%$, shear stress varies almost linearly up to the shear rate of 1 s$^{-1}$ with a constant viscosity (see Fig. 2a), which confirm the typical Newtonian behavior in isotropic phase. As shear rate increases, horizontal stress plateau are observed for both samples, where the constant shear stress values are...
measured from 1 to 18 s\(^{-1}\) for \(\phi = 0.08\)\% and from 0.1 to 5.9 s\(^{-1}\) for \(\phi = 0.83\)\%, respectively. For \(\phi = 0.83\)\% we performed measurements decreasing the shear rate, as shown in inset of Fig. 3. As arrows indicate shear rate change direction, hysteresis is clearly observed. The observed stress plateaux and hysteresis loops in steady state flow curves are often associated to the typical bistability of various soft materials, including aqueous surfactant solutions, emulsions, and liquid crystals to concentrated colloidal suspensions [32–36]. In liquid crystalline materials, such bistability can be linked to the phenomenon of shear banding; separation of the flow in high and low shear regions. Under a shear flow, many complex fluids have been reported to form macroscopic bands, perpendicular to the flow direction at different shear rate levels. In liquid crystalline systems, an ordered phase co-exists with a disordered one in the shear-banding regime. Our observation of such a bistability can be associated to the different orientational states of GO platelets in the direction of shear flow as well as banded structure formation. In addition to shear banding GO liquid crystal also exhibits yield stress (\(\sigma_y\)) behavior. This steady shear yield stress can be estimated from the observed stress plateau (Fig. 3), where shear stress starts again increase as shear rate further increases. The observed yield stress is plotted as a function of GO composition along with dynamic yield stress in the inset of Fig. 4b.

![Graph showing shear viscosity vs shear rate for different GO compositions.](image)

**Fig. 2** – (a) Evolution of shear viscosity with shear rate at different GO composition. (b) Non-monotonic constitutive relation between shear viscosity vs GO composition demonstrating isotropic to nematic phase transition.

**Table 1** – Power law \((\eta \propto \gamma^x)\), and Carreau equation \((\eta(\gamma) \approx \eta(\gamma \to 0)/[1 + (\gamma \tau)^2])\) fitted parameters.

<table>
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<tr>
<th>(\phi) (vol%)</th>
<th>(x)</th>
<th>(\tau/s)</th>
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<tr>
<td>0.08</td>
<td>0.9</td>
<td>4.4</td>
<td>0.38</td>
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<td>0.16</td>
<td>0.77</td>
<td>15</td>
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<td>0.28</td>
<td>45</td>
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<tr>
<td>1.80</td>
<td>0.29</td>
<td>42</td>
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3.2.2. Dynamic characteristics

To establish the limits of the linear viscoelastic regime (LVR), where dynamic moduli are independent on the applied stress, oscillatory stress sweep measurements are performed. We note that non-Newtonian systems such as polymer solution, concentrated colloidal suspensions, and liquid crystalline dispersion do not show true LVR. For practical measurement, linear viscoelastic regime can be defined as the region in which both \( G' \) and \( G'' \) are nearly constant up to a critical stress of 1.27 Pa. Above the critical value, both moduli become stress dependent. The yield stress with \( \phi_r = 0.83\% \), where both \( G' \) (solid) and \( G'' \) (open) moduli are nearly constant up to a critical stress of 1.27 Pa. Above the critical value, both moduli become stress dependent, \( G' \) begin to decrease due to rupture of the GO network and eventually cross \( G'' \). The crossover of \( G' \) and \( G'' \) can be employed to estimate the yield stress \( \sigma_y \) of GO dispersions [37]. Fig. 4b shows the strong dependency of yield stress on GO composition. Along with the increase of \( \phi \), \( \sigma_y \) first moves to high values \( (\phi_\text{c} = 0.33) \) and then decreases at single nematic phase fraction \( (\phi_N = 0.45) \) and finally increases again to higher values. This intermittent decrease in yield stress at single nematic phase composition is caused by the alignment or orientation of GO platelets that reduces the entanglements among platelets. The yield stress values are plotted against GO composition up to \( \phi \geq 0.45 \) in the inset of Fig. 4b. Simple scaling argument; \( \sigma_y \sim \phi^n \) is used to quantitatively link the \( \phi \) dependence of the yield stress with \( n = 2.86 \) and 3.14 for dynamic and steady yield stresses, respectively. Similar scaling exponents have been reported for discotic laponite gels and concentrated yield stress fluids [38].

Frequency-dependent measurements for the storage \( G'(\omega) \) and loss \( G''(\omega) \) moduli, exhibit typical liquid- or solid-like behavior for volume fraction ranged from \( \phi = 0.08\% \) to 1.8% in the linear viscoelastic regime at constant stress of 0.1 Pa. Fig. 5a shows the typical frequency sweep measurements for the GO dispersion with \( \phi = 0.08, \) 0.45, and 1.8%. For \( \phi = 0.08\% \), both moduli, \( G' \) (solid symbol) and \( G'' \) (open symbol) have very low amplitudes and fluctuate continuously with frequency. By contrast, for \( \phi > 0.08\% \), \( G' \) and \( G'' \) increase monotonically up to a critical frequency and exhibits a sharp minima before fluidization. This observation of minima (dynamic instability) will be discussed later. We further observed that \( G' \) and \( G'' \) become independent of frequency as \( \phi \geq 0.83\% \). Low-frequency \( G' \) and \( G'' \) moduli can be described by the power-law relationship, \( G(\omega) \sim \omega^n \), where the exponent \( n \) is the magnitude of slope in the double logarithmic plot and \( k \) is the intercept which defines the degree of network connectivity [39,40]. The linear viscoelasticity model proposed by Winter [41] predicts that the stress relaxation follows the power-law frequency dependence \( G' \sim \omega^n \) with \( 0 < n < 1 \). Stoichiometric balanced and imbalanced cross-linked networks showed \( n < 0.5 \) in the presence of excess cross-linker, and \( n > 0.5 \) in the short of cross-linker, respectively. This description strictly applies to chemically cross-linked gels. It has been known that \( n > 0 \) for a physical (weak) gel, whereas \( n = 0 \) for a chemical (strong) gel [42,43]. The exponent \( n \) can therefore be used as a quantitative measure of the resemblance of an elastic network system. In viscoelastic measurements, the liquid-like behavior is governed by \( G' \sim \omega^2 \) and \( G'' \sim \omega \). The data in Fig. 5a are fitted with the aforementioned power law and the obtained exponent values are plotted as a function of \( \phi \) (Fig. 5b). At low \( \phi \), both \( G' \) and \( G'' \) are of the same order of magnitude and exhibits frequency dependence, \( G' \sim \omega^{1.65} \) and \( G'' \sim \omega^{0.79} \), confirms the isothermal phase. At \( \phi \geq 0.33 \), \( G' \) exceeds over \( G'' \) across the low frequency range and indicates that GO sheets relaxation time is longer than experimentally accessible value, exhibiting nematic phase (solid-like) behavior, whereas \( n = 0.28 \) for \( \phi = 0.45\% \). For even higher volume fraction of \( \phi = 1.8\% \), \( G' \) and \( G'' \) are independent of frequency with very low exponent of \( n \geq 0.05 \), confirming the gel-like phase formation. It is noteworthy that our finding is qualitatively similar to previous...
observations of aqueous CNT dispersions [44–46]. Taken together, we may conclude that the elasticity arises from GO platelet network and nematic ordering of GO platelets. Our results are consistent with the recent observations of gel-like phase formation of aqueous GO dispersion at high composition [47,48]. The formation of GO liquid crystalline gel or three-dimensional network is attributed to the large and flexible two-dimensional structure of GO platelets and the force balance between their static repulsion and bonding interaction. Increasing the bonding force or decreasing the repulsion force between GO sheets in dispersion will reinforce the gel network. In GO liquid crystalline dispersions, two sorts of inter-sheets forces work together; repulsive forces due to the negatively charged functional groups (oxygenated functional group) and attractive forces arising from $\pi-\pi$ interaction among the graphitic patches and vander Walls interaction. At a high GO composition, the strength of attractive forces may dominant due to the small inter-sheets separation. This resulted in strong sheets interlinked GO gel-like phase formation.

We have above discussed that GO dispersion exhibits liquid crystalline and thixotropic fluid like features. This thixotropic behavior may arise from the breakup of interconnected network and the enhanced orientational ordering of

Fig. 4 – (a) Dynamic oscillatory stress sweep measurements for $\phi = 0.16\%$ (sphere), and $\phi = 0.83\%$ (triangle) GO dispersions. Solid symbol for storage ($G'$) and open symbol for loss ($G''$) moduli. (b) Double logarithmic plot of estimated yield stress as a function of GO composition. Inset shows the double logarithmic plot of dynamic yield stress (solid sphere) and steady shear yield stress (open sphere) for fully nematic GO dispersions.
GO platelets. In frequency sweep measurements elastic storage modulus at low frequencies defined as plateau modulus $G_0$ is plotted as a function of $\phi$ as shown in Fig. 5c. The noticeable increase of $G_0$ more than five orders of magnitude between $\phi = 0.16\%$ and $0.33\%$ is due to rigidity percolation. Near the percolation threshold, $G_0$ can be correlated to the volume fraction $\phi$ through a power law relationship as $G_0 \propto (\phi - \phi^*)^p$, where $\phi^*$ is the percolation volume fraction, and $p$ is the percolation exponent. We obtain percolation volume fraction of $\phi^* = 0.30$ and exponent of $p = 1.32 \pm 0.08$ by varying $\phi^*$ to minimize the error in the slope of a double logarithmic plot of $G_0$ vs $(\phi - \phi^*)$ (see inset of Fig. 5c). This power law increase in the elastic modulus is possible due to the nematic ordering of GO platelets. The percolation exponent of 1.32 obtained in current work is comparable to single-walled, multi-walled nanotube dispersions and their polymer nanocomposites [46,49–51].

Lastly, we found the interesting dynamic instabilities in GO liquid crystalline dispersion at a critical frequency, which strongly depends on the GO composition. The dynamic instabilities in a fluid mechanics are responsible for a variety of important common phenomena, such as waves on the sea surface or Taylor vortices in Couette flow [52]. Observation of distinct minima in the frequency sweep test ($G', G''$) displayed in Fig. 5a signifies existence of dynamic instability. As obvious from the Fig. 5a, the critical instability frequency shifts to the higher values with the increase of GO composition (Fig 5d). The mechanism for such kind of instability has not been clearly understood, however, there are few reports on the oscillatory flow induced instabilities for other colloidal systems. Torralba et al. [53] have reported that oscillatory flow of the Maxwell fluid is unstable at high driving frequencies. In other report, the binary mixture under horizontal vibrations have revealed the existence of a new dynamical instability due to size segregation under oscillatory shear and its connections to pattern formation in granular flows [52]. Our finding of dynamic instability should be significantly considered in the processing of GO based materials.

4. Conclusions

We have reported that aqueous GO dispersion exhibit the well-defined LC phases and gel-like behavior based on rheological measurements. The GO dispersion exhibit shear
thinning behavior, which is well described by power law and Carreau models. Concentration dependent shear viscosity confirms the typical colloidal isotropic–nematic phase transition at \( \phi_c = 0.33\% \). Viscoelastic measurements revealed that liquid crystals and gel-like phase exhibit well-defined elastic shear modulus and yield stress, which increase with GO composition following a power law. Moreover, GO liquid crystalline dispersion shows the rigidity percolation transition with an onset of solid-like elasticity at \( \phi^* = 0.3\% \) and the percolation exponent of 1.32 ± 0.08. Our observations of strongly nonlinear rheology under flow (shear thinning, banding and dynamic instabilities) demonstrate that precise rheological characterization of GO liquid crystalline dispersion is required for their processing into desired structures and properties.

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**References**


