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Wide Concentration Liquid Crystallinity of Graphene Oxide Aqueous Suspension with Interacting Polymers

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1. Experimental Methods

Sample Preparation Graphene Oxide (GO) was firstly suspended in water by 1 wt% after the purification step as described elsewhere[1]. The individual GO sheets have a thickness of 1 nm and an average lateral width of 1 μm. To study the dispersion of GO in a PEG solution, poly(ethylene glycol) (400 g/mol) (PEG 400) was added to various PEG concentrations of 0.01, 0.1, 1, 10, 30, 60 and 90 wt% of GO suspension and mixed using a vortex for 10 s. For high concentrations of GO suspension (ϕ>1 wt%), we added a known amount of GO suspension, water and PEG, and then evaporated the water at 20°C in a vacuum until the desired concentration was reached. The series of suspension was put in a sealed glass vial and kept at room temperature.

Phase diagram A series of samples were prepared and their phase stability has been monitored for more than 18 months. The phase diagram provided in Fig. 1a was completed after 12 months of observation. Some GO suspensions were destabilized such that initial homogeneous dispersions were phase-separated by sedimentation into solvent-rich and GO-rich phases. Optical images for confirmation of the settling are provided in SI. The liquid crystallinity of each sample is determined by polarized optical microscopy images[2-4]. Whether the sample was in a glass state or liquid state was determined by confirming whether the sample had a property of flowing when the sample bottle was turned over[5]. The glass state in Fig. 1a was not based on the rheology measurement.

Polarized Optical Microscopy (POM) The liquid crystallinity of GO suspensions at each condition was confirmed by POM images. The sample, 0.9 mm thick, was dropped on a custom-made slide glass and images were taken at 100x magnification between two crossed polarizers using *Olympus BX51M* microscope.

Small Angle X-ray Scattering (SAXS) SAXS experiments were conducted at the 9A and 6D beamline of the Pohang Accelerator Laboratory (PAL) to study the detailed structure of GO dispersions, using a sample-to-detector distance of 2 m with radiation wavelength, λ of 0.7994 Å for 9A and 3505 mm with a beam energy of 12.398 keV for 6D beamline. The scattered X-rays were analysed with a Mar charge-coupled device (CCD) area-detector. The 2-D SAXS patterns were averaged by integrating the area within 45° at the stretched direction and the relative 1-D scattering intensity was plotted as a function of the scattering vector, q (=4πsinθ/λ) where θ is the scattering angle. The two section-averaged intensities orthogonally directed, were compared in SI. . For sample preparation, 200 μl of GO suspension were slowly injected to 1.5 mm thick quartz capillary cell and relaxed for 2 min, as illustrated in Fig. 2a.

Rheometer Rheological experiments were conducted using *kinexus pro+ rheometer* with cone-and-plate geometry; the cone was 20 mm or 40 mm with an angle of 4° at 143 μm gap distance at 25 °C. After sample was loaded, it was allowed to rest on the plate of the rheometer for another 10 min. Frequency sweep experiment at a constant stress was used to measure storage (*G'*) and loss (*G"*) moduli. Shear viscosity shown in Fig. 1c was measured in the shear rate range of 0.01 to 100 s^{-1}.

Zeta-potential A *Zetasizer Nano ZS90* (Malvern Instrument) is used to measure the zeta potential (ζ) of 0.01 wt% GO suspension using a folded capillary cell. The light source power and wavelength is 4 mW and 633 nm, respectively. Every measurement was performed at a scattered angle of approximately 90° at 25°C.

Viscometer The viscosity of low concentration of PEG and GO suspension was measured using capillary viscometer (Cannon-Fenske Routine 75). The temperature was maintained at 25°C in a water bath. Samples were allowed to rest in the capillary viscometer for 30 min before the measurement.

GO film fabrication by doctor blade To evaluate the orientation of the GO sheets with shear, 2.5 wt% of GO suspension in 0 and 10 wt of PEG was blade-casted. The blade gap was ~60 μm and the casting speed was ~ 5 mm/s.

2. Total interaction energy for GO sheets

The interaction energy, *W(r)* per unit area is given by

$$W(r) = \begin{cases} \infty & 0 \le r \le (2R + \delta_a) \\ W_{EL}(r) + W_{vdW}(r) & (2R + \delta_a) \le r \le \infty \end{cases},$$

where W_{EL} and W_{vdW} are electrostatic and van der Waals energy. δ_a is the distance of closest approach. We consider δ_a is 3-5 nm from the surface roughness and polymer adsorption.

The van der Waals interaction energy between GO sheets is given by[6-7]

$$W_{vdW} = -\frac{H}{12\pi}\left(\frac{1}{d^2} + \frac{1}{(d+2t)^2} - \frac{1}{(d+t)^2} - \frac{1}{(d+t)^2}\right)$$

where *H* is Hamaker constant and t is the thickness of interacting slabs.

For van der Waals attraction, the Hamaker constant is varied for different PEG concentrations as the refractive index and dielectric constant of the solvent are varied. The Hamaker constant between GO sheets (1) interacting across a medium (2) can be estimated as follows:[8]

$$H = \frac{3}{4}k_B T\left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^2 + \frac{3hv_e}{8\sqrt{2}} \frac{\left(n_1^{\ 2} - n_2^{\ 2}\right)^2}{\left(n_1^{\ 2} + n_2^{\ 2}\right)\left(2\sqrt{n_1^{\ 2} + n_2^{\ 2}}\right)}$$

where k_B is the Boltzmann constant, *T* is the absolute temperature, *ε* is the dielectric constant of solvent, *n* is the refractive index, *h* is the Planck constant, and v_e ($\approx 3 \times 10^{15}\ s^{-1}$) is the main absorption frequency. As adding polymer changes *ε* and *n* of the solvent, *ε* and *n* are accordingly adjusted with polymer concentration.

Materials	ε	n
Water	78	1.33
PEG400	17.3	1.75
GO	3	1.467

Table S1. Optical properties used in estimation of Hamaker constants.

The electrostatic interaction between two identical interfaces is modeled using linearized Poisson-Boltzmann approximation for two planar surfaces as follows:[6-7]

$$W_{EL} = \frac{2\sigma^2}{\varepsilon\varepsilon_0\kappa}e^{(-\kappa d)}$$

where σ is the surface charge density, ε_0 is the permittivity of vacuum and κ is the inverse of the Debye length, which is given by[6]

$$\kappa^{-1} = \sqrt{\frac{\varepsilon\varepsilon_0 k_B T}{2N_A e^2 I}}$$

where N_A is the Avogadro number, e is the elementary charge, and I is the ionic strength of medium. We calculated the Debye length at each PEG concentration based on the adjusted ε and measured ionic strength. The ionic strength of PEG solution is estimated based on the Ref. 9 and conductivity of the solution. The measured conductivity of PEG solution was 13.70, 55.23 and 69.97 µS/cm at c_p =1, 10 and 20 wt%, respectively.

The surface charge density, σ, is correlated with zeta potential, ζ by the Gouy-Chapman equation[10]

$$\sigma = \frac{2\varepsilon\varepsilon_0 k_B T}{ze}\sinh\left(\frac{ze\zeta}{2k_B T}\right)$$

where z is the valency of the conterions and $e=1.6\times 10^{-19}$ Coulombs. Zeta potential, ζ of GO suspensions were experimentally measured at each PEG concentration as shown in Fig. S3.

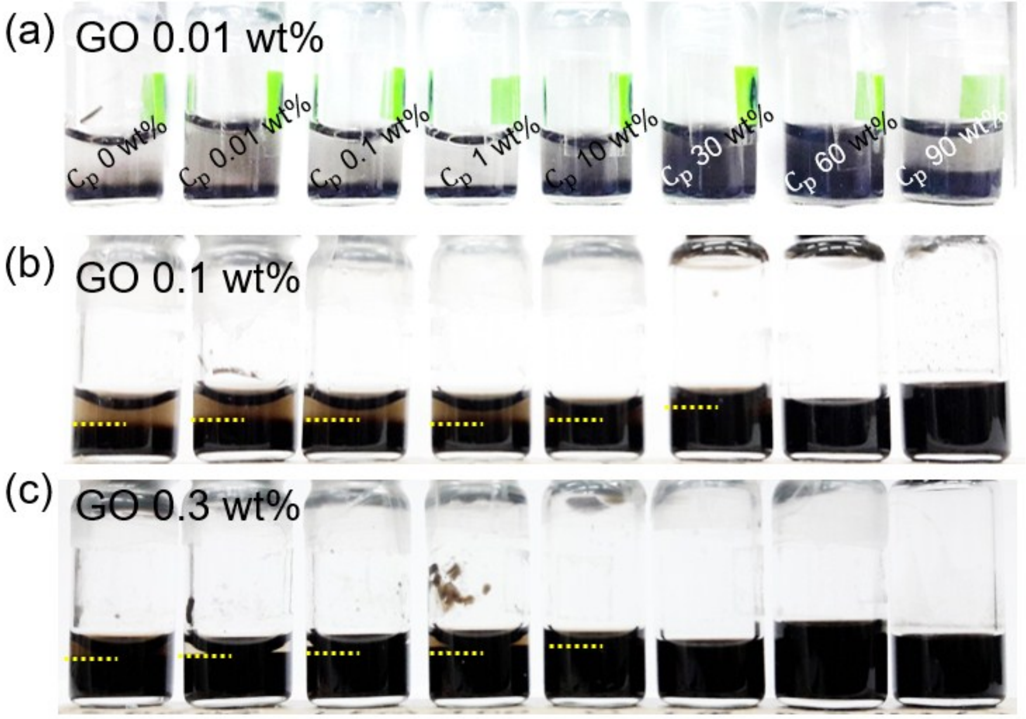
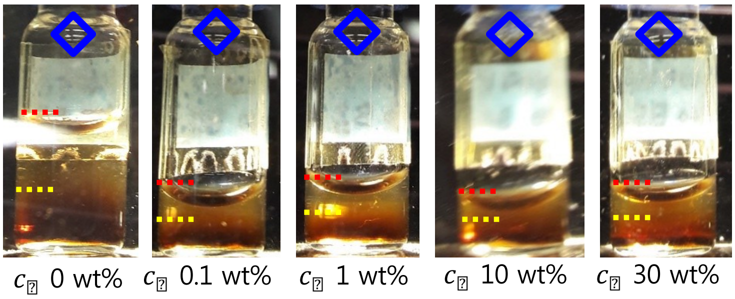


Fig. S1. Optical images of samples for GO 0.01, 0.1, and 0.3 wt%. PEG concentrations are 0, 0.01, 0.1, 1, 10, 30, 60 and 90 wt% from left to right. Phase separation is found with sedimentation of GO suspensions. While sedimentation occurs at all PEG concentration in (a), a few samples remain stable at 0.1 and 0.3 wt% of GO. Due to the low contrast of images, we marked the phase separation lines in (b) and (c) in case of sedimentation.

(a) GO 0.1 wt%



(b) GO 0.2 wt%

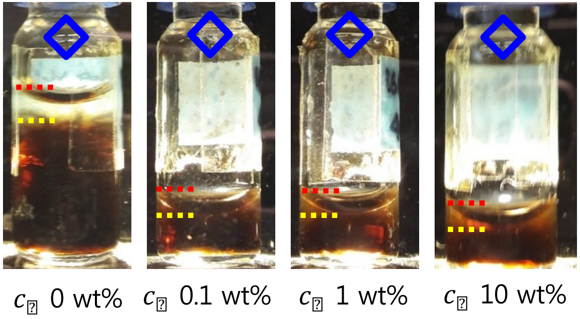


Fig. S2. Optical images of biphasic samples given in Fig. 1a in the main text. These images were obtained putting vials between two crossed polarizers.

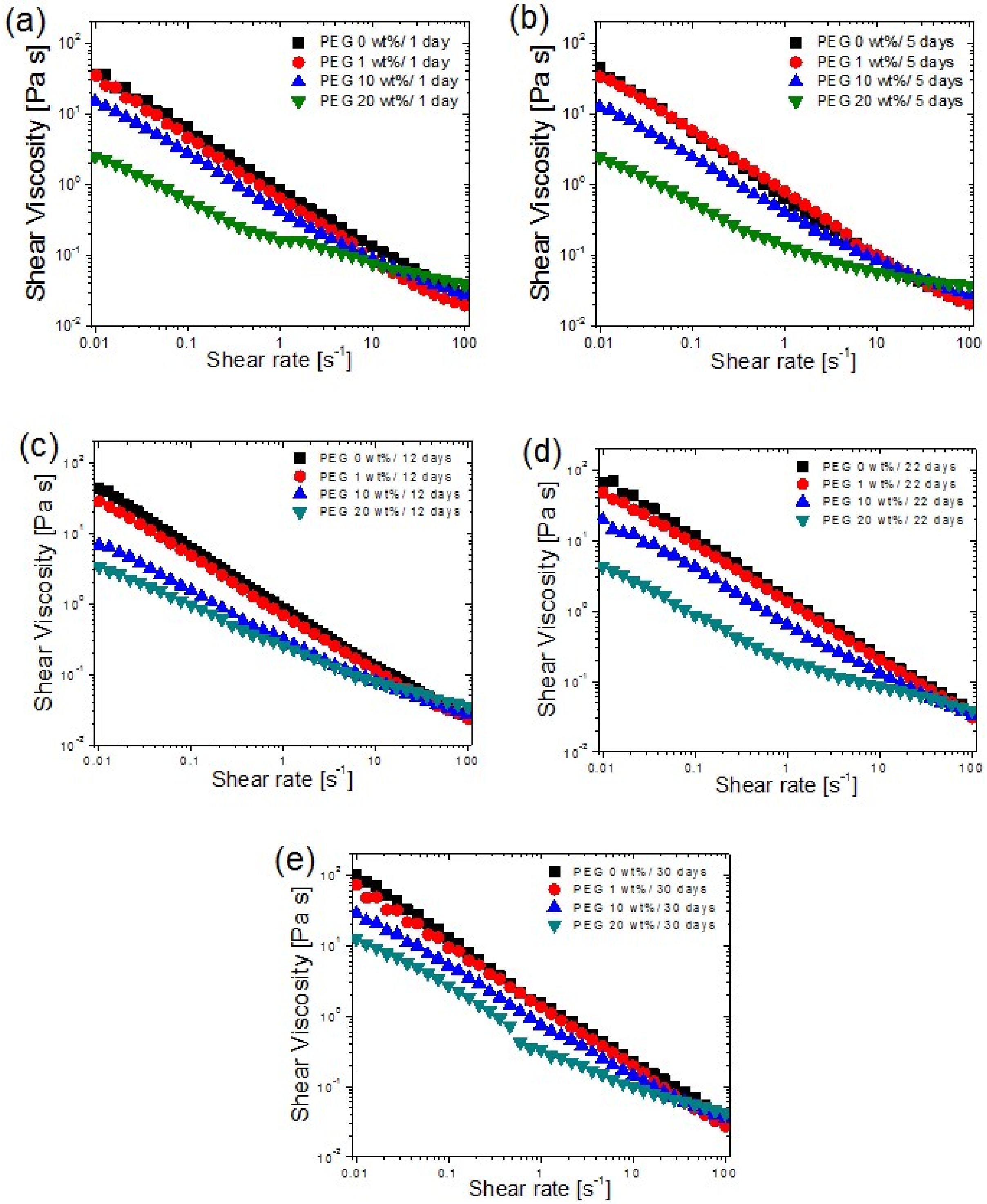


Fig. S3. Time-dependent shear viscosity of GO dispersions as a function of shear rate at different PEG concentrations as indicated in legends. Data in (a), (b), (c), (d), and (e) is obtained after 1, 5, 12, 22 and 30 days from the sample preparation, respectively. Shear viscosity in Fig. 2a in the main text was based on the viscosity at 0.01 s^{-1}.

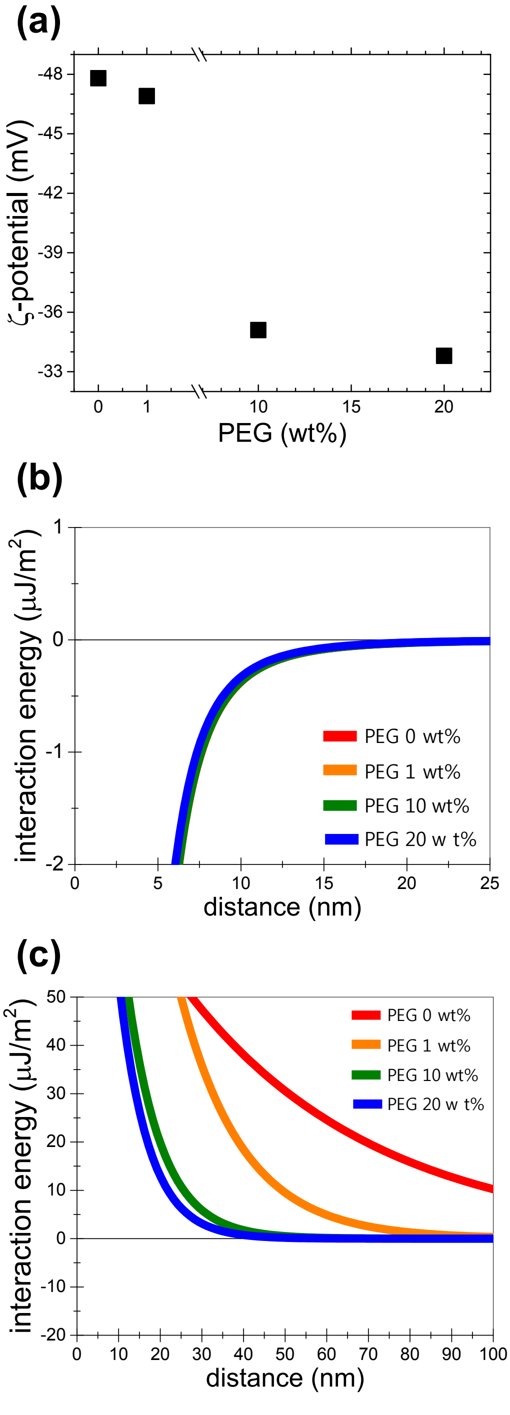


Fig. S4. (a) Experimentally measured zeta-potential of GO at 0, 1, 10 and 20 wt% PEG solution. (b) van der Waals attraction energy of GO and (c) electrostatic energy of GO based on the DLVO theory.

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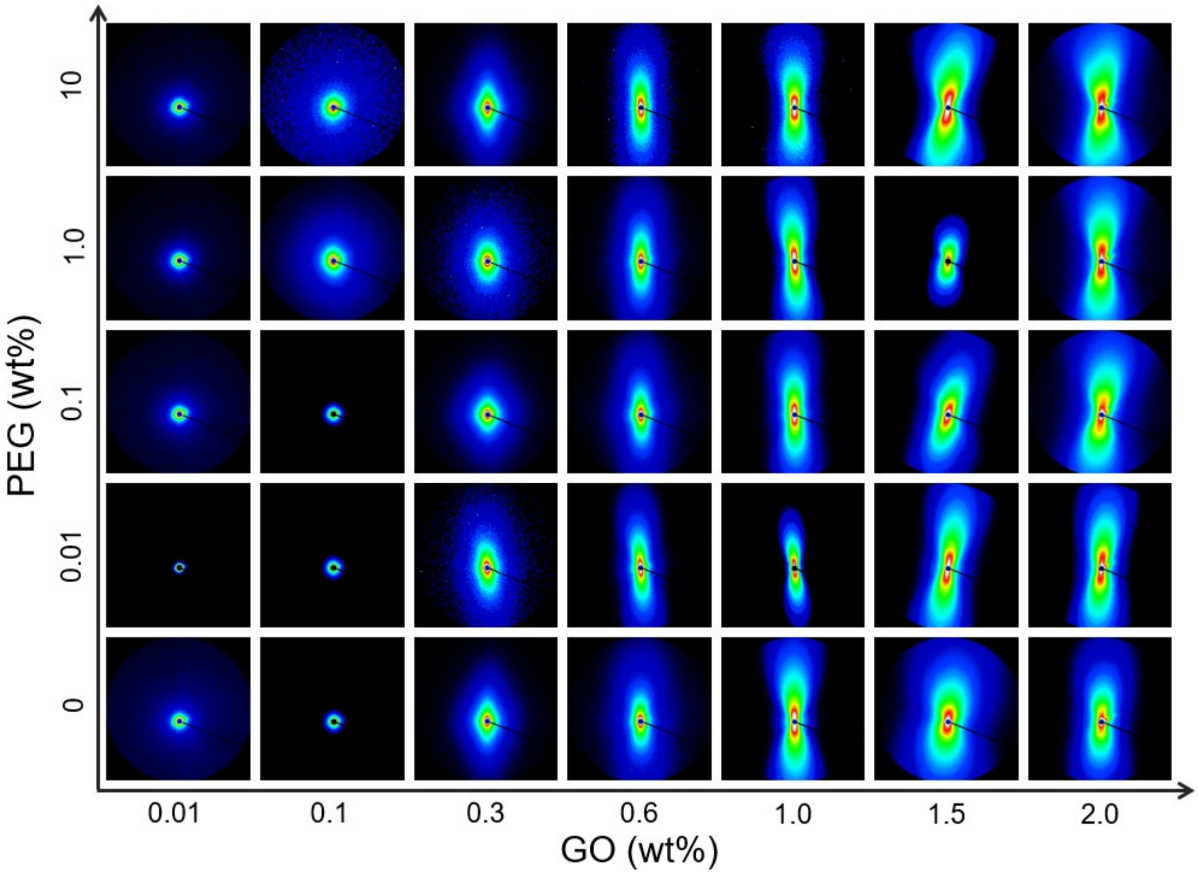

Fig. S5. SAXS 2D patterns of GO dispersion at various GO and PEG concentration. All images were taken within a few minutes after sample loading. The exact concentration of GO and PEG is found from axis label.

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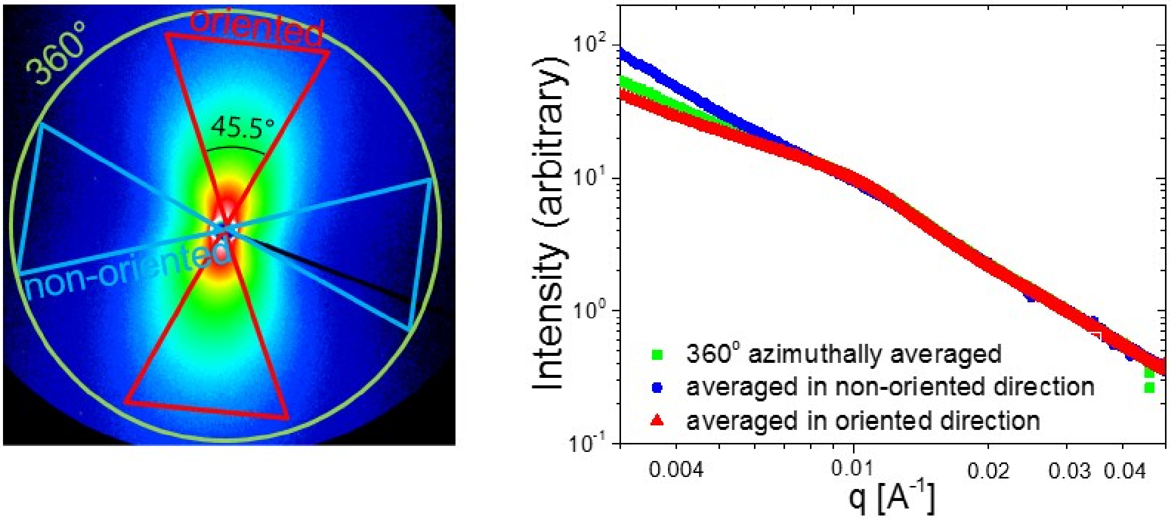

Fig. S6. 1D scattering intensity extraction from 2D SAXS data. (left) The original 2D SAXS pattern with different area masks. Three different masks are used indicated by different colors. Each 2D intensity in the mask is averaged to obtain 1D-intensity vs. q data. (Right) Depending on the masks, different intensity profiles are obtained. All 1D data used in the main manuscript is extracted based on the mask in intensity stretched direction (red).

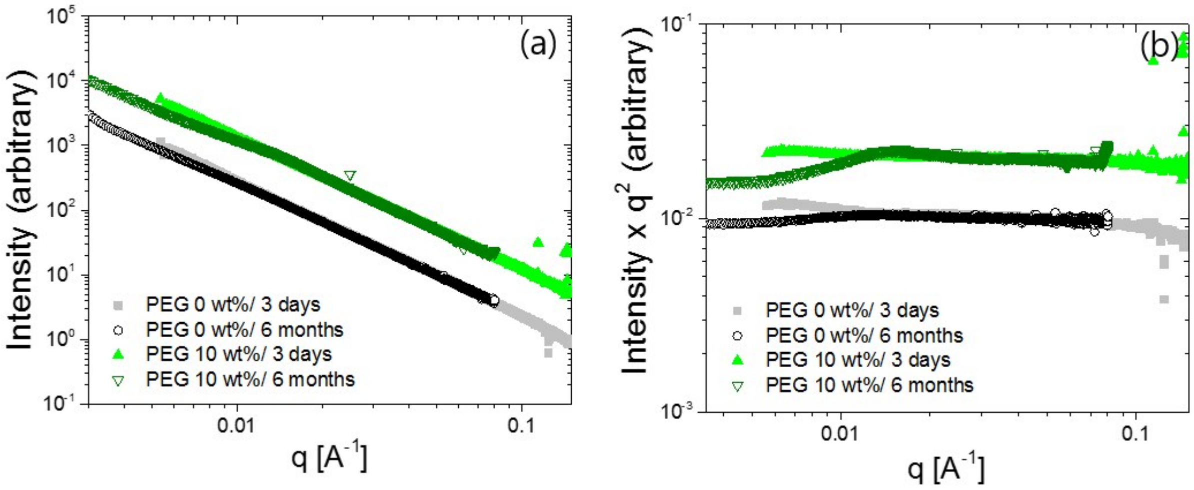

Fig. S7. Time-dependent scattering change in 0 and 10 wt% PEG solutions for 0.8wt% GO dispersions. (a) Scattering intensity and (b) normalized intensity by q^2 vs. q-vector.

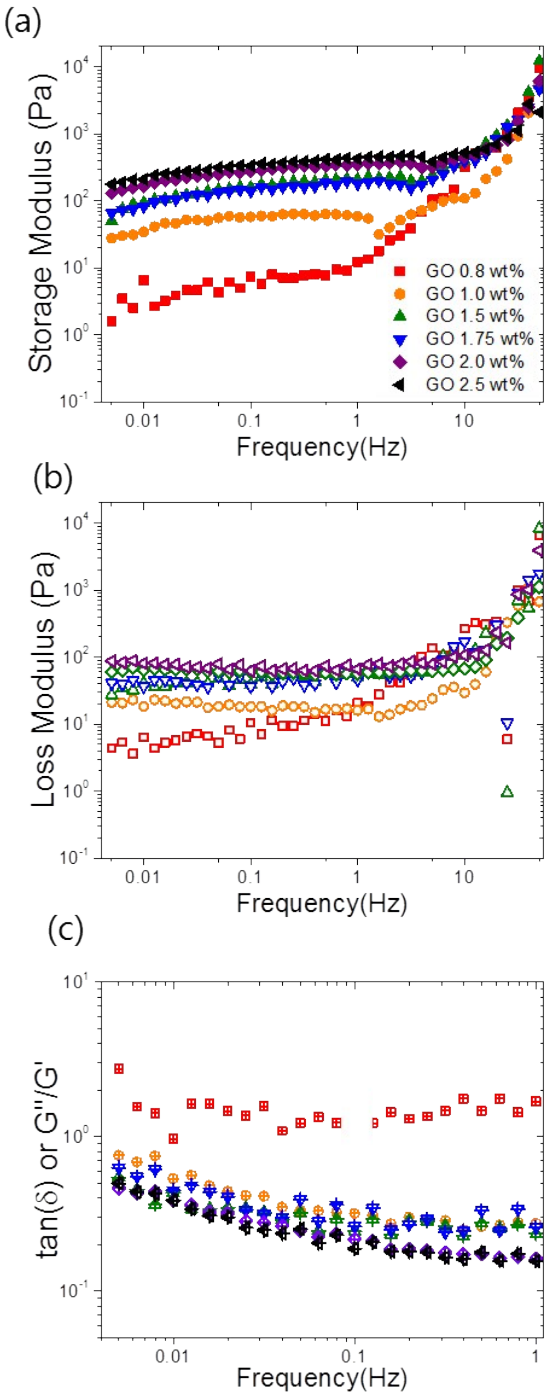

Fig. S8. Frequency-dependent (a) storage modulus, (b) loss modulus and (c) tan(δ) at constant shear stress of 1 Pa for varying GO concentrations in water. GO concentration is shown in the legend. tan(δ) is defined as G″/G′. Fig. S8 shows the elastic (G′) and loss (G″) modulus of GO suspensions in pure water as GO concentration varied from 0.8 to 1.5 wt%. While both moduli increase with GO concentration, tanδ is lower than unity (<1) at all concentrations except for 0.8 wt%, signifying that PEG-free suspensions possess a solid-like elastic property in the given frequency ranges.

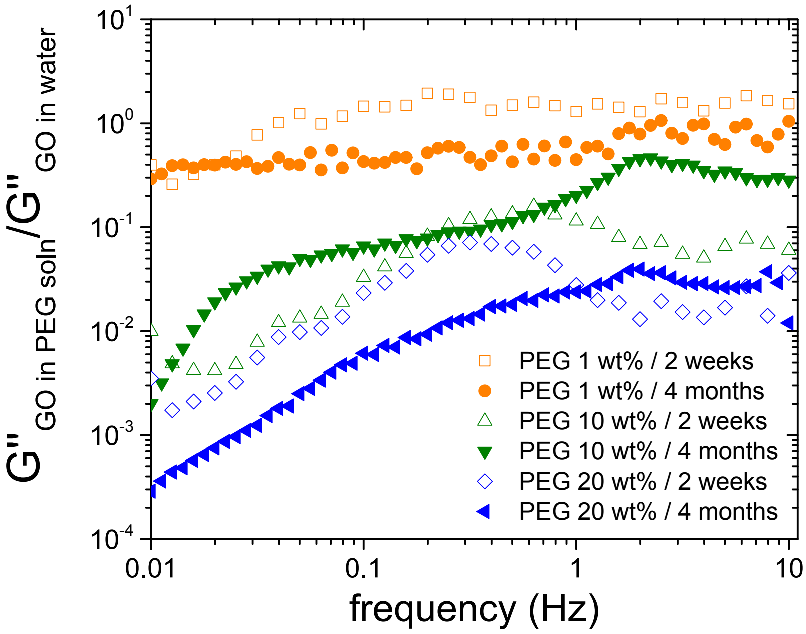

Fig. S9. Viscosity reduction by adding PEG. Note that reduced viscosity effect with adding PEG is scaled as $G''_{\text{GO in PEG soln}}$/ $G''_{\text{GO in water}}$. $G''_{\text{GO in PEG soln}}$/ $G''_{\text{GO in in water}}$ at each polymer concentration is plotted based on the Fig. 4 in the main text.

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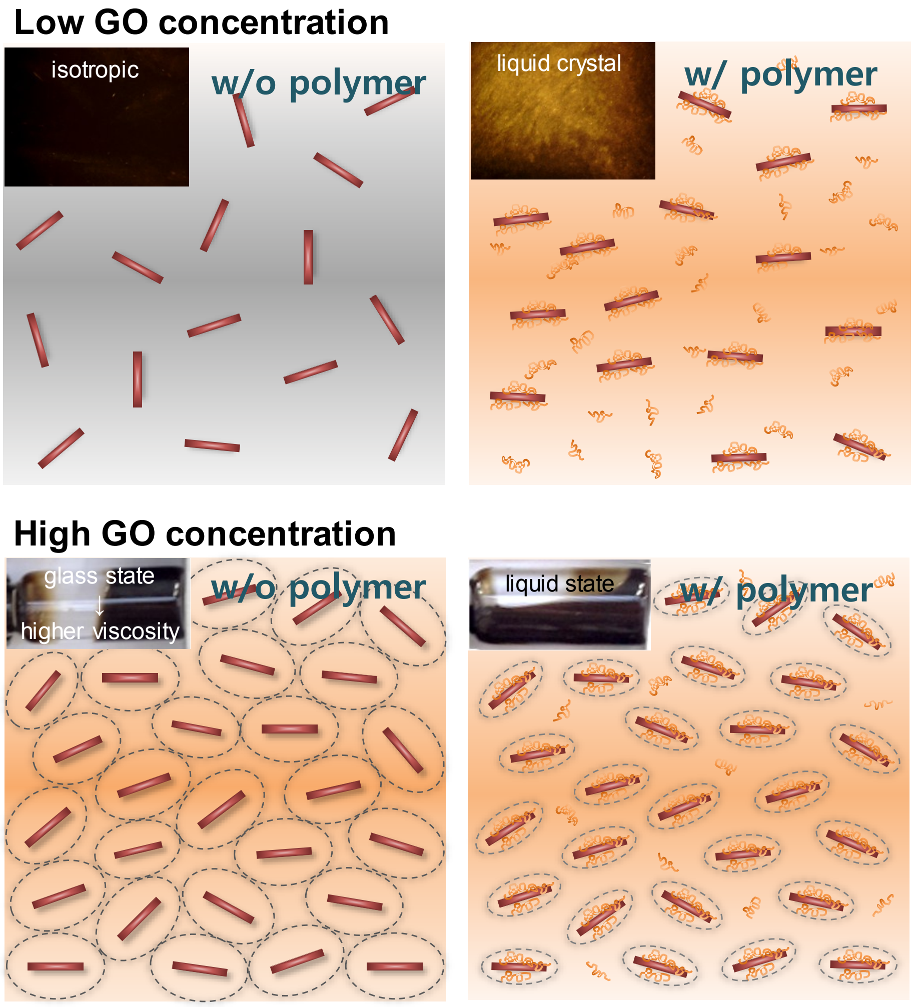

Fig. S10. Schematic diagram showing GO dispersions at different GO and polymer concentration. Insets of low GO concentration are POM images.

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