Supplementary information of "Rheology of Graphene Oxide Stabilized Pickering Emulsions"

Shuming Cui[a,b], Saud Hashmi[c], Wenqiang Li[a], Stephan Handschuh-Wang[d], Chengtian Zhu[a], Shichang Wang[a], Yan-Fei Huang[a]*, Guangming Zhu[a]*, Florian J. Stadler[a]*

[a.] College of Materials Science and Engineering, Shenzhen Key Laboratory of Polymer Science and Technology, Guangdong Research Centre for Interfacial Engineering of Functional Materials, Nanshan District Key Laboratory for Biopolymers and Safety Evaluation, Shenzhen University, Shenzhen 518055, PR China.

[b.] South China Advanced Institute for Soft Matter Science and Technology, School of Emergent Soft Matter, South China University of Technology, Guangzhou 510640, China.

[c.] Department of Polymer & Petrochemical Engineering NED University of Engineering & Technology Karachi, Sindh 75270, Pakistan.

[d.] College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, PR China

Sample preparation

Figure SI1a showed the fabricated process of one GO emulgel (e.g., GO1%-DDAB0.1%-OW1:2) after mixing two phase and obtained solid-like emulgels that possessed adequate yield stress to resist gravitational flow after 3 min homogenization (11500 rpm). Figure SI1b show the GO-series samples, after mixing of oil and aqueous phase. It is clear to visualize GO aqueous dispersion (dark liquid, 200 μL) at bottle bottom and transparent mixture oil phase (DDAB chloroform solution, 10 μL and liquid paraffin, 90 μL) upper the GO solution, with the ratio of 2:1. Furthermore, compared with the mixture without any GO, rare GO particles diffuse to the oil phase for a long time.
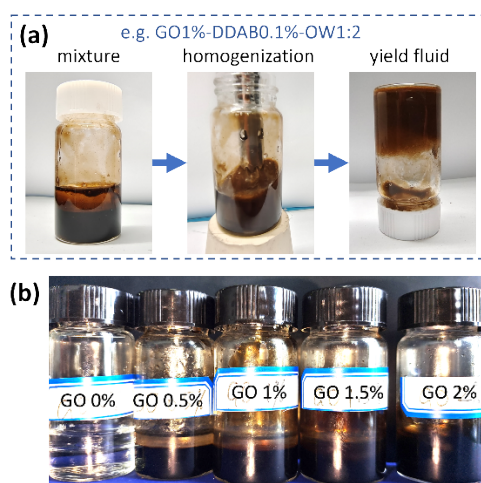

Figure SI1. (a) The common process of GO emulgels preparation based on modulated GO dispersion and DDAB additives, (b) appearance of GO-series emulgels with 0.1 wt.% DDAB.

GO stock aqueous suspension with 2.67 wt.% was obtained from Zhang et al.[1, 2] group who prepared by the modified Hummers' method. Thus, this text did not mention any process of

GO stock suspension preparation and did not conduct any chemical modification afterward. The obtained GO stock suspension diluted by distilled water and regard the diluent as one entire aqueous phase, which listed at Table SI1 for ca.2mL GO suspension being made. After dilution, at least 1 min vibration and 20 min ultrasonication was necessary to promote better GO dispersion, following by the emulsification immediately. Most of GO-emulgels could stay homogeneous that are possible to stand long-term test.

Table SI1. Diluted process of thick GO stock solution: e.g., 2 mL aqueous phase was used

Aqueous phase (2 mL)	stock 2.67 wt.% GO water solution (mL)	Water supply (mL)
GO0.5%	0.374	1.626
GO1%	0.749	1.251
GO1.25%	0.936	1.064
GO1.5%	1.124	0.876
GO1.75%	1.311	0.689
GO2%	1.498	0.502

Dielectric spectroscopy measurement

Maxwell's equations (Eq SI1) can express the definition of permittivity, defined by dielectric displacement D and electric strength E and its time dependence.

$$D = \varepsilon^* \cdot \varepsilon_0 \cdot E_{;} \ \varepsilon^* = \varepsilon' + i \cdot \varepsilon'' \tag{SI1}$$

Dipole relaxation behavior is normally represented in terms of ε^* and electric conduction behavior in terms of σ^* both of which are complex numbers. Permittivity, as a vital parameter in BDS, can characterize this polarization effectively and other relevant parameters. For instance, complex conductivity (σ^*) is defined by current density J (Eq SI2), according to Ohm's law, which can establish the relationship between ε^* and σ^* (Eq SI3). ($\varepsilon_0 = 8.854 \times 10^{-12} \, As \, V^{-1} \, m^{-1}$).

$$J = \sigma^* \cdot E \tag{SI2}$$

The raw dielectric data of GO emulgels including 5 loops are showed in Figure SI2. For instance, "GO0.5% & GO1.25% & GO1.75% & GO2% -DDAB0.1%" for GO-series (Figure SI2 a-h) and "GO1%- DDAB0.01% & DDAB0.5%" for DDAB-series (Figure SI2 i-l) are shown below, including $\varepsilon', \varepsilon'' \sim f$ -plot (left side) and $\delta \sim f$-plot (right side). As the cycle tests progress, the curves tend to converge to the last cycle, due to the gradual stability of polarization. Thus, the last loops of all emulgels are discussed mainly in the text.
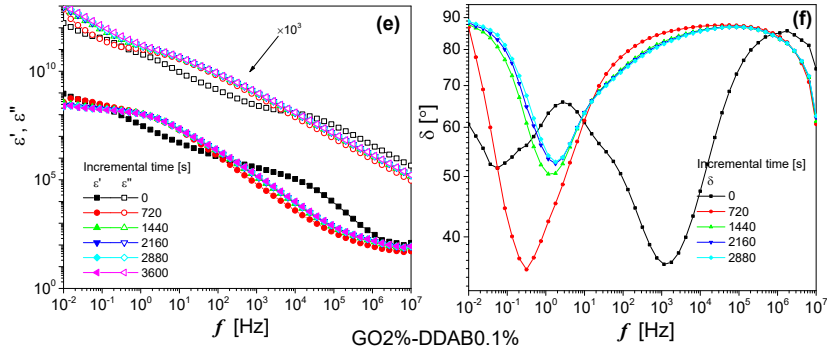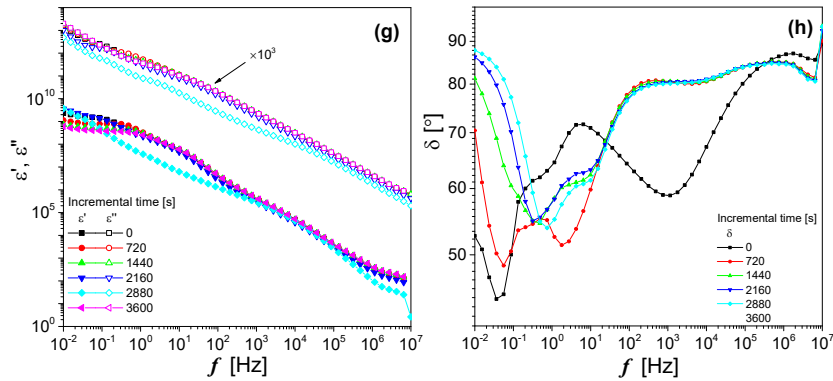
GO0.5%-DDAB0.1%

(a)

(b)

GO1.25%-DDAB0.1%

(c)

(d)

GO1.75%-DDAB0.1%

(e)
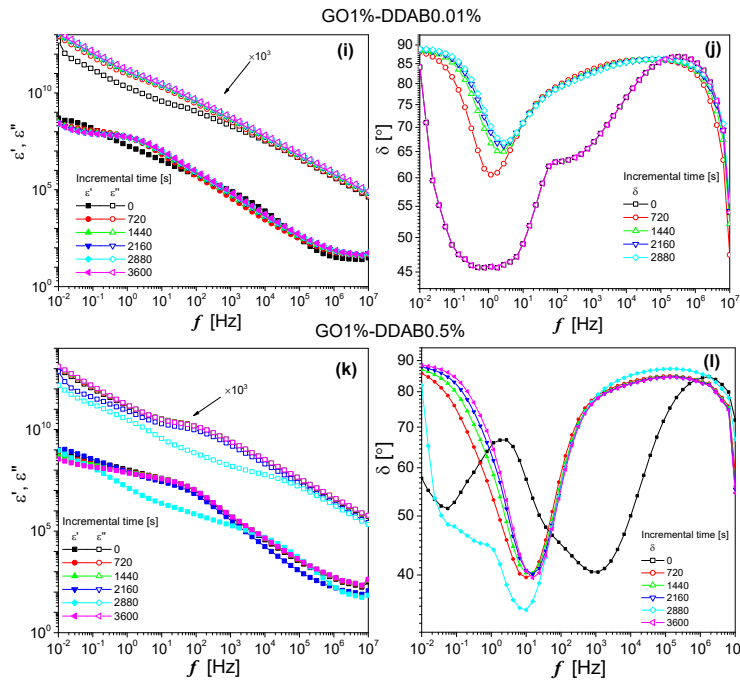

(f)

GO2%-DDAB0.1%

(g)

(h)
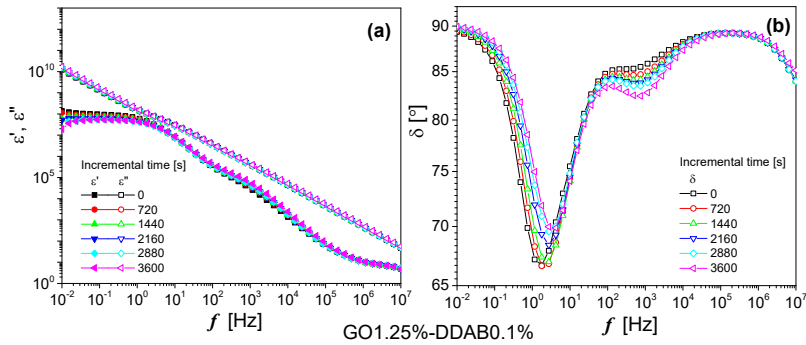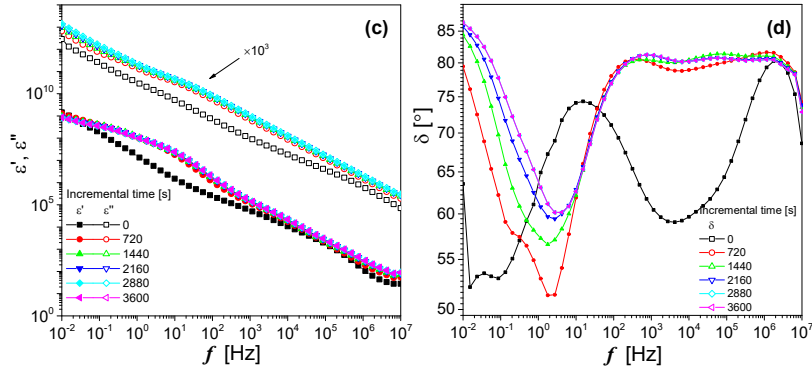
Figure SI2. (a-b) GO0.5%, (c-d) GO1.25%, (e-f) GO1.75%, (g-h) GO2% for 0.1 wt.% DDAB in chloroform and (i-j) DDAB0.01%, (k-l) DDAB0.5% for 1 wt.% GO in water phase are shown including permittivity (left) and loss angle (right) dependence on frequency. All GO emulgels possess identical oil and water phase ratio with 1:2.

Startup flow test

Figure SI3a, b show the droplets' arrangement by FM including before and after steady shear, respectively. Obviously, the morphology of motion state displays the uniform direction of most droplets along the flowing (approximately bottom right to top left) and remarkable aggregation of flowing droplets that merely stuck to each other but did not rupture. The droplets' adhesion is a reason that the interfacial resilience occurs after the droplets' movements because of the presence of remaining pressure to hinder droplets' recovery affected by the disorder GO sheets, for which can maintain structural stability after ink extrusion and possibly improve the 3D-printing product's reliability.
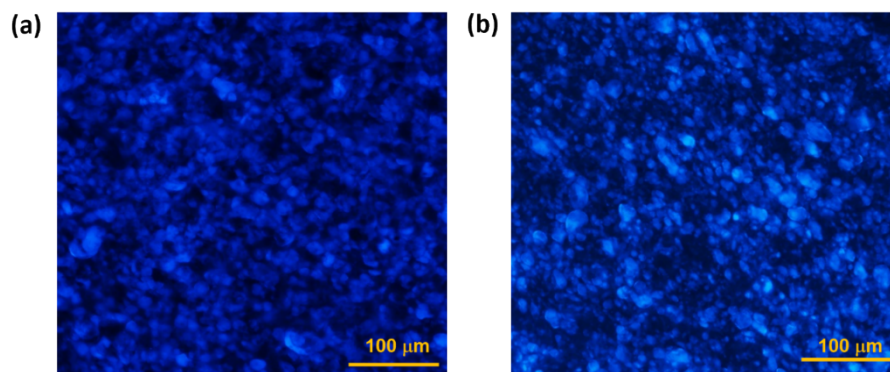

Figure SI3. The FM images of e.g., GO1%-DDAB0.1%-OW1:2 show the droplets' arrangement for (a) before and (b) after 1 times cycle (0.01 s^{-1} to 1000 s^{-1}) of startup flow test.

Frequency sweep of rheology

Figure SI4a shows the G' and G'' of emulgels with varying GO content and 0.1 wt.% DDAB for 1% constant strain. Remarkably, the emulgels of GO1%-DDAB 0.25% & 0.5% show the entirely liquid-like properties ($G'' > G'$) at γ_0=10%, indicating that a GO-network destruction resulting from the excessive DDAB, which reduces the jamming and elastic limitation of GO emulgels. Figure SI4b show the GO1%-DDAB0.1%-OW 1:2 is an optimal recipe with lowest loss angle and the most proper GO-network.
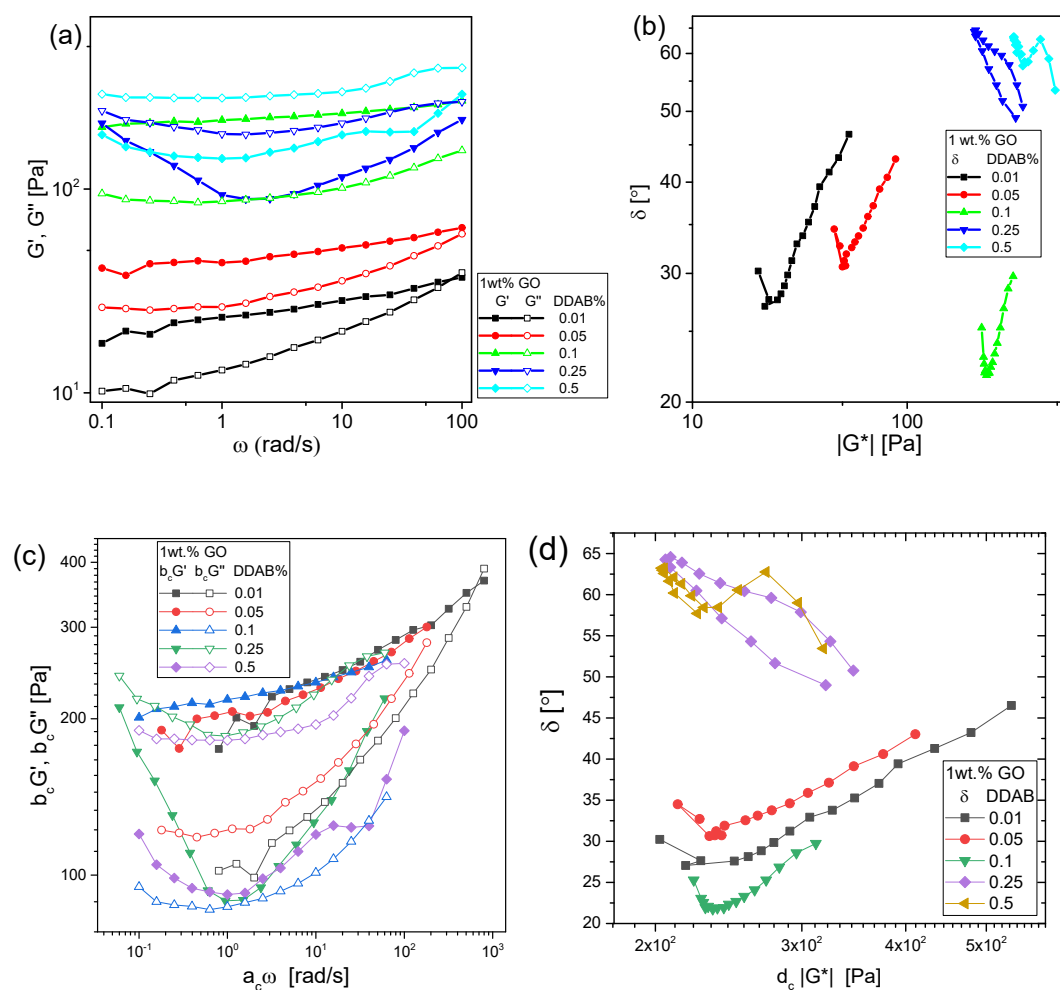

Figure SI4. Raw data of frequency sweep with varying DDAB content at γ_0=10% for (a) G', G''(ω) and (b) δ($|G^*|$)-plot. Evaluation data after concentration-dependent shift for (c) b_cG', b_cG''($a_c\omega$) and (d) δ($|G^*|$)-plot. corresponding to data in (a) and (b).

1. Y. Y. Zhang, G. Zhu, B. Dong, F. Wang, J. Tang, F. J. Stadler, G. Yang, S. Hong and F. Xing, *Nature communications*, 2021, **12**, 111.
2. Y. Y. Zhang, P. Pan, W. Q. Li, B. Q. Dong, J. N. Tang, F. Xing and G. M. Zhu, *Additive Manufacturing*, 2022, **59**. 103140