Supplementary information to Influence of cellulose nanofibers on the behavior of Pickering emulsions

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Sample preparation

Figure SI1(a) show the pictures of most CNF emulsion after mixing of oil and water phase and homogenization. The volume of CNF aqueous dispersion (downside the bottle) and mixture oil phase (upside) have nearly height difference with the ratio of 2:1. It is obvious that the increase amount for CNF gel (white floc) would be used at higher concentration of CNF emulsion and were mainly dispersed in water. With 4.5±0.5 wt.% CNF aqueous dispersion as the raw nanofibrillated cellulose material, all the CNF dispersion of lower content can be diluted by distilled water, listing at Table SI1 for ca.2mL aqueous phase and 1mL mixture oil. For instance, assumed that 2mL aqueous phase need to be prepared for all CNF emulsion, the amount of supplying water is followed by the Eq (SI1),

$$V_{supplying\ water} = 2 - \frac{2C_{CNF}}{4.5}\ (\text{mL}), m_{CNF} = \frac{2\rho C_{CNF}}{4.5}\ (g) \tag{SI1}$$

Here, C_{CNF} is the CNF dispersion in real concentration, m_{CNF} is the obtained weight of gel-like CNF, while the density of raw CNF gel is about 1.05 g/mL. The CNF emulsion after homogenization were captured and shown at Figure SI1(b) for 0.1wt% DDAB and Figure SI1(c) for 0.5wt% DDAB with the inverted placement that observed the yield behavior. The emulsions of CNF0.5%-DDAB0.1%, CNF0.5%-DDAB0.5% and CNF1%-DDAB0.1% have too low viscosity to totally drop down for the weak yield stress, while CNF1.25&1.5%-DDAB0.1% have partly falling emulsion and there were strong and entire adhesive for emulsion of larger than 1.5 wt.% CNF content. Due to the promoted adsorption of DDAB, there are viscous gel-like emulsion and not obvious phase separation except of CNF0.5%-DDAB0.5%. Meanwhile, CNF1.5%-DDAB0.5% did not show the emulsion falling anymore and proved the stronger adsorption when introduced more DDAB content. However, an interesting discovery is the comparison of DDAB0.5% and DDAB0.1% at 0.5 wt.% CNF content that the more bubbles existed in more DDAB content.

Table SI1. The component ratio of aqueous phase including CNF gel weight and supplying water volume.

Aqueous phase (2 mL)	Raw 4.5 wt% CNF gel (g)	Water supply (mL)
CNF0.5%	0.233	1.778
CNF1%	0.467	1.556
CNF1.25%	0.583	1.444
CNF1.5%	0.700	1.333
CNF1.75%	0.817	1.222
CNF2%	0.933	1.111
CNF2.5%	1.167	0.889
CNF2.75%	1.283	0.778

CNF3%	1.400	0.667

Figure SI1. CNF emulsion pictures of (a) the mixture of oil-water before homogenization, (b) CNFX%-DDAB0.1% and (c) CNFX%-DDAB0.5%.

The intuitive morphology of emulsion could not be observed from bottles' outside, hence Figure SI2 (a-b) showed the appearance of listed CNF emulsion samples. Figure SI2(a) displays the morphology of CNF emulsion for CNFx%-DDAB0.1 & 0.5%. It is clear that gel-like emulsion would be formed at higher CNF and DDAB content, instead the liquid-like arises in low CNF content. Meanwhile, the evidence of DDAB that enhance the interfacial stability and CNF attraction could be detected due to the gel transition between 0.1% and 0.5% DDAB, among emulsion in CNF1.5% & 2% & 2.5%. On the contrary, the emulgels in low CNF content are not enough to form gel-like emulsion, even to emerge the phase separation and flocculation settling in comparison between CNF0.5%-DDAB0.1% & 0.5%. There is considerable that CNF chains in aqueous phase can assemble to become the flocks owing to the attraction of DDAB not only occurring in CNF0.5%-DDAB0.5% but in CNF3%-DDAB0.5% for the while aggregates.

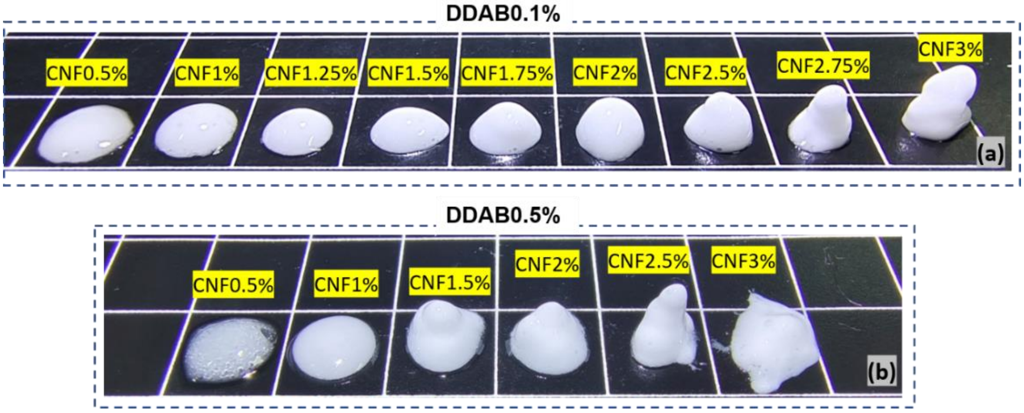

Figure SI2. The appearance of CNF emulsion of (a) CNFX%-DDAB0.1% and (b) CNFX%-DDAB0.5%.

Figure SI3 showed the sample cell and each parts' introduction for dielectric test. In general, liquid or flow -like sample can be measured by placing them between two open disposable electrodes. What's more, the diameter of sample area should be larger than electrodes and make sure the hardly influences for outside electric fields. The electrode spacing need to be adjusted by two parallel additional spacers making from 0.1mm rod-like Silica, that should have low tan δ, constant permittivity, and resistance over the used temperature and frequency range. For the conductive units, the upper electrode is pressed by a spring and the cell closing plate to the spacers. The two seal rings attached to the Teflon isolation (white color ring on the actual cell appearance) for preventing evaporation of sample.

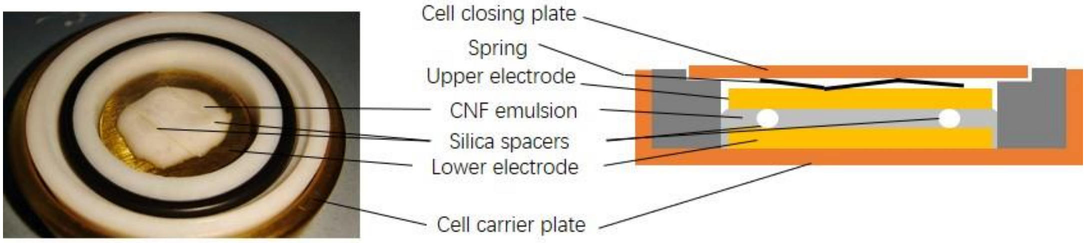

Figure SI3. The actual photo and its sectional view of liquid cell that used to load CNF emulsion.

The electric signals of input absolute AC voltage U^* and output absolute current I^* can be measured by DIS can figure out several dielectric parameters, such as complex impedance z^*, complex conductivity σ^*, complex permittivity ε^*, and complex capacity C_P^*. However, for the nature of dielectric media, there are always phase angle differences between the real and imaginary parts of U^* and I^*. In other words, AC current behave a hysteresis to AC voltage and phase angle φ can be defined as the hysteresis of them, which can show in Eq (SI1):

$$U^*(\omega t) = U'(\omega t) + iU''(\omega t), \text{ while } I^*(\omega t + \varphi) = I'(\omega t + \varphi) + iI''(\omega t + \varphi) \quad \text{(SI1)}$$

Here, ω is the value related to the frequency: $\omega = 2\pi f$ and U', U'', I' and I'' are the real and imaginary parts of AC voltage and current, respectively. The complex impedance z^* can be defined as the ratio of U^* and I^* and deduce to the complex conductivity σ^*, defined in Eq (SI2):

$$z^* = z' + iz'' = \frac{U^*}{I^*} = \frac{\sigma^*}{i\omega C_0 \varepsilon_0} \quad \text{(SI2)}$$

$$C_0 = \frac{\pi}{4}\frac{D^2}{d}\varepsilon_0 \quad \text{(SI3)}$$

Here, ε_0 =8.859 pFm^{-1} is the vacuum permittivity, which is lower than any material permittivity. C_0 is the empty cell capacity calculated by the area of the parallel electrode and the thickness of loaded samples. z^* is subjected to the intrinsic properties of CNF emulsion rather than the AC voltage and current. Moreover, other dielectric parameters have their relation in these equations:

$$\sigma^* = \sigma' + i\sigma'' = i\omega\varepsilon_0\varepsilon^* \quad \text{(SI4)}$$

$$\varepsilon^* = \varepsilon' + i\varepsilon'' = \frac{C^*}{C_0} \quad \text{(SI5)}$$

Here, C^* is the complex sample capacity and is usually affected by external capacity, which can be solved by adjusting the electrodes to minimum *d*/*D*. From these equations, there is a significant proportionality among σ^*, ε^*, z^*, and C*. Furthermore, the real part ε' of permittivity is used to figure out the polarization *P* in the case of known electric current density *D* and field intensity *E*, shown in Eq (6):

$$D = \varepsilon'(\omega)\varepsilon_0 E = (1+\chi)\varepsilon_0 E = \varepsilon_0 E + P \tag{SI6}$$

Here, χ is the susceptibility. The polarization process of CNF emulsion can be divided into three kinds: electron and ion displacement and the orientation of dipole moment. In CNF emulsion systems, the time scale of the interfacial polarization is dominated by orientational molecular mobility as the main process, which affects by the behavior of CNF film at the AC field, while the process of the first two polarization is transient. Therefore, orientation polarization is mainly discussed in this paper.

The frequency and concentration dependence of ε' and ε'' for CNF emulsion is shown in Figure 4(a-c). In general, the ε' and ε'' show typical decrease trends in accordance with the Debye's classical equations:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1+\omega^2\tau^2} \;\&\; \varepsilon'' = \frac{(\varepsilon_S - \varepsilon_\infty)\omega\tau}{1+\omega^2\tau^2} \tag{SI7}$$

When $f = \omega = 0$, the permittivity of emulsion is $\varepsilon_s = \varepsilon'$ in the case of DC field and $f \to \infty$ show the $\varepsilon' = \varepsilon_\infty$ in the case of optical frequency, while $\varepsilon'' = 0$ at the two limitations and would arise a maximum value on the condition of $\partial\varepsilon/\partial\omega = 0$ at the same time $\omega = \tau^{-1}$. Very large values of ε'' at low frequency are due to ionic conduction loss. There are not remarkable contrasts and closest overlap of ε' and ε'' among curves of all CNF emulsion at whole frequency range except of CNF0.5%-DDAB0.5% that presents phase separation easier at long time placement (Figure SI1). That is means the unique dielectric properties of CNF emulsion but hardly dependence on CNF and DDAB content, which could be compared with another emulsifiers, e.g., GO Pickering emulsion (Figure SI4). The relations between loss angle and frequency are made, in order to show their differences further and compare the influence of CNF and DDAB concentration in precise that shows in Figure 4(d-f), and the phase angle δ is the hysteresis for the response of dielectric media during the electric frequency range, which can calculate by this Eq (SI8):

$$\delta = \arctan\left[\frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}\right] = \frac{\varepsilon_S - \varepsilon_\infty}{\varepsilon_S + \varepsilon_\infty} \tag{SI8}$$

The AC electric field stimulates the sample for several periods of 720s time increment and every intervals data for CNF 1-2.5 %-DDAB0.1% are displayed in Figure SI4 with permittivity and loss angle on dependence of frequency. In general, the first two intervals show the different curves shape in comparison with other intervals and the last two intervals maintain similar curve regulation. After three times of frequency sweep, the lowest δ move upside and ε'' increase totally, then they would concentrate to the equilibrium response at same time the overlapping curves arise. CNF2.5%-DDAB0.1% have nearly overlapped curves at the last two intervals, but such situation cannot be searched with the emulsion at lower CNF content, which means it needs to take a longer test time. Another investigation that also can be found between the curves of Figure SI4 (a, c, e, g) and (b, d, f, h) is the closer overlapping curve at real and imaginary parts of permittivity than δ-plot. Thus, the plotting of δ on dependence of frequency can illustrate obviously the contrast about the dielectric properties by varying CNF or DDAB content. In case of better comparison of any samples, the data of last intervals would tend to balance and get more precise results.

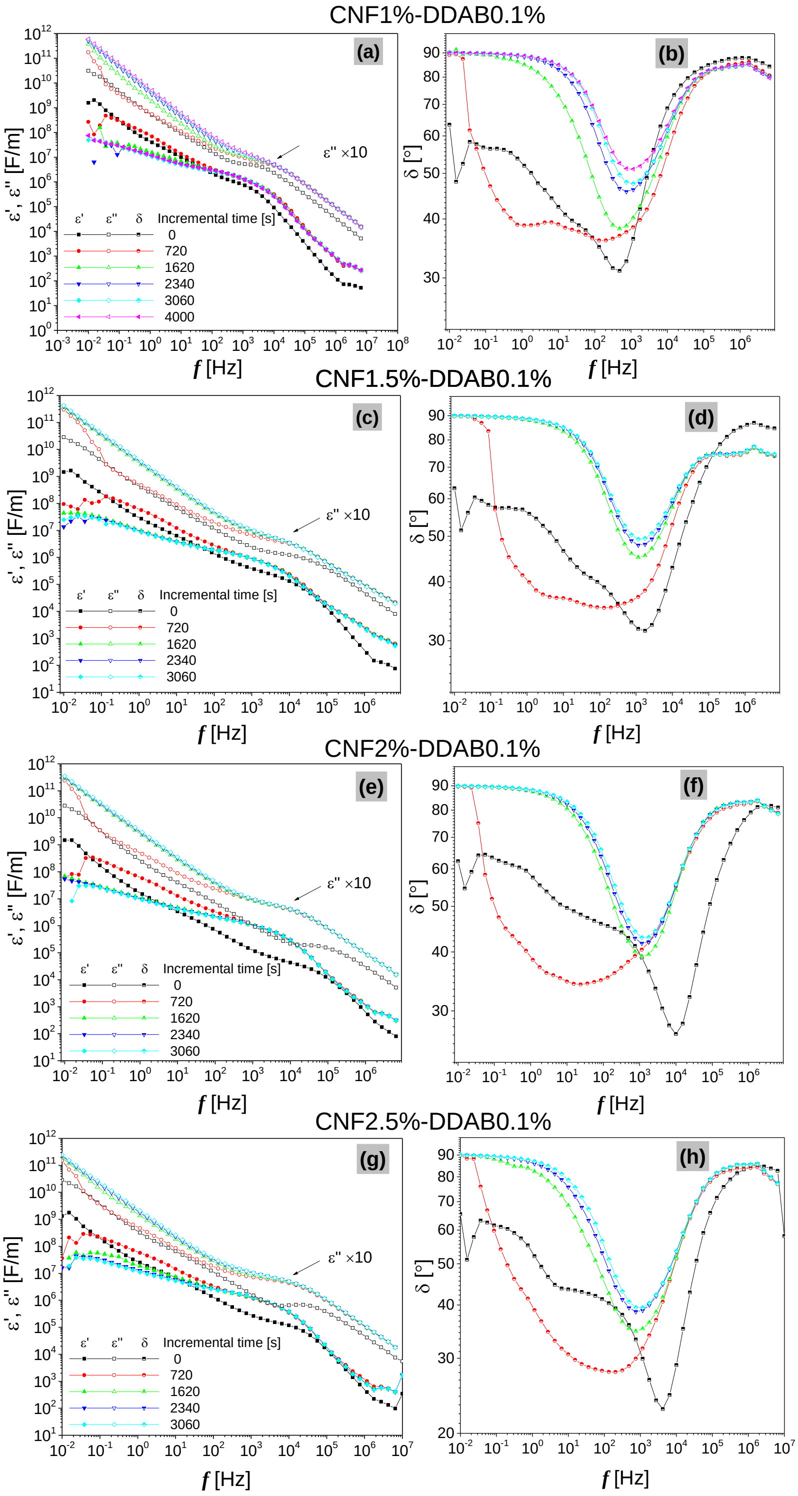

Figure SI4. The dielectric raw data of 0.1wt% DDAB emulsion of (a, b) CNF1%, (c, d) CNF1.5%, (e, f) CNF2% and (g, h) CNF2.5% at all time intervals with the real and imaginary parts of permittivity and loss angle on dependence of dielectric frequency.

Figure SI5 show the emulsion systems stabilized by Graphite Oxide for the different interfacial structure but same other components. There are the similar properties of the permittivity dependence on frequency for GO emulgel compared with CNF emulgel, like the negative slopes at both of them (Figure SI5(a, c)). However, ε'' of GO emulsion do not behave the slight plateau at around $f=10^3$ Hz, but at $f=10$ Hz. What can be seen more remarkably, the δ of GO emulsion possess the lowest values for lower AC frequency, which can significantly prove the unique dielectric properties about CNF emulsion. Different interfacial stabilizers affect the relation between ε′ and ε′′ resulting to the contrast on conductivity, impedance, phase angle and so on, but rarely influence the general variation range of ε′ and ε′′ from 10^2 to 10^9 approximately.

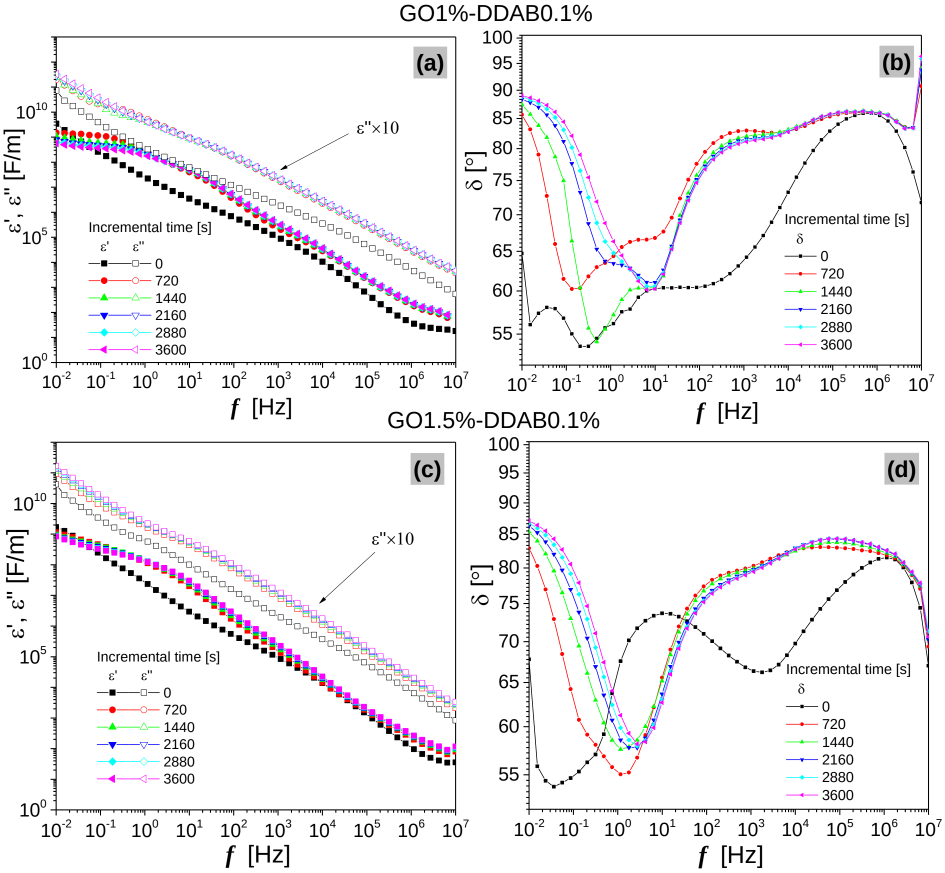

Figure SI5. The dielectric raw data of 0.1wt% DDAB emulsion of (a, b) GO1% and (c, d) GO1.5% at all time intervals with the real and imaginary parts of permittivity and loss angle on dependence of dielectric frequency so as to compare the common properties of CNF emulsion.

Figure SI6 show the $\tau(\dot{\gamma})$ and $F_N(\dot{\gamma})$ raw data of startup-flow test for two different emulsions. The typical original flow behavior is shown for the first ramp that is obvious unstable data of stress and normal force because the bulk movement of droplets need to be drove. That means the data of first ramp can be ignore and the last ramp data need to be selected due to obtain the more stable curves. Moreover, the similar data for 2-4 ramps represent the continuous deformation of droplets, which illustrates the constant flow behavior for these CNF emulgels. More importantly, the effects associating with DDAB absorption is critically strong owing to the “stress step” appearing among 2-4 ramps.

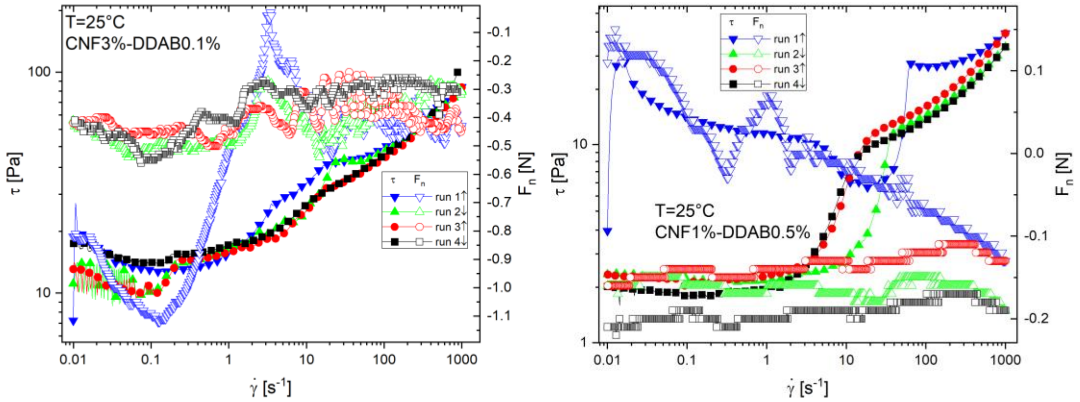

Figure SI6. The original data of startup-flow for 2 typical CNF emulgels. 1-4 ramps of shear rate were plotted with stress and normal force but the first ramp did not behave well because previous large deformations do not largely change the structure.

The initial appearance of one CNF2.5%-DDAB0.1% emulgel is shown for comparison with the appearance after dielectric test for totally 5 frequency ramps. The remarkable carbonization illustrates the formation of stable conduction matrix and proper gap.

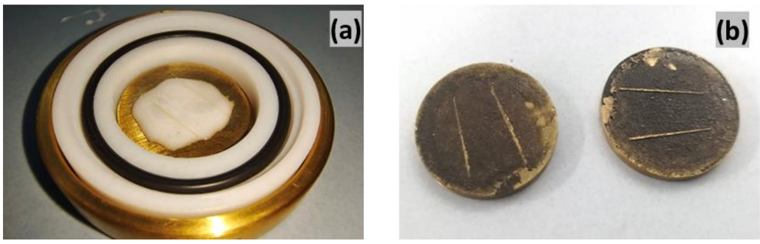

Figure SI7. The pictures of (a) before and (b) after dielectric tests of CNF emulgel relating to carbonization.