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Effect of Solid Particles Concentration to the Size of Graphene Oxide Liquid Crystals Pickering Emulsion

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Abstract:

Graphene oxide (GO) sheets have been used as a colloidal surfactant in a Pickering emulsion system due to their amphiphilic property. They also show a liquid crystals behavior, which make them suitable to synthesize graphene oxide liquid crystals Pickering emulsion (GOLCsPE). Desired GOLCsPE sizes and stability can be obtained by controlling several parameters, especially the concentration of graphene oxide colloidal surfactant. This paper focused on the preparation of GOLCsPE with linseed oil as an internal phase. The GO concentration was varied in order to study their effect on GOLCsPE size and stability. The stability of the emulsion was observed through phase separation observation. Polarized optical microscope (POM) and particle size analyzer (PSA) were employed to characterize the size distribution of the GOLCsPE. POM analysis shows that increased in GO concentration led to the finer emulsion with the smallest droplet size around 8μm. However, the PSA analysis revealed otherwise. It was found that by increasing the amount of GO sheets, the GOLCsPE size will also increase, which could be caused by too many GO sheets laden around the oil droplets. The coefficient of variation (Cv) of the liquid crystals based on POM images showed a decreased, indicates the GO concentration improves the droplet size distribution. It also suggested that GO concentration plays a more important role in maintaining the stability of the GOLCsPE, rather than their sizes. By comparing both POM and PSA results, liquid crystals prepared with 3.7 mg/ml produced satisfied GOLCs diameter (around 8.5μm, Cv = 0.31) and stability. The shining halos around the droplets are proof that the GO acts as a colloidal surfactant and assembled themselves around the linseed oil droplets, forming a shell-like structure.

Keywords: *graphene oxide, liquid crystals, Pickering emulsion*

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I. INTRODUCTION

Liquid crystals (LCs) can be defined as highly anisotropic fluids consists of a long-range crystal-like ordering of molecules [1]. Recently, graphene oxide liquid crystals (GOLCs) has attracted enormous attention. This latest class of 2D nanomaterials possessed colloidal liquid crystallinity contributed by their intrinsic disc-like shape anisotropy [2]. Graphene oxide (GO) is a two-dimensional material that consists of partially broken sp^2-bonded carbon networks. Its basal plane is occupied by phenol, hydroxyl, and epoxide groups while carboxylic acid groups attached to the edges. These functional groups make the GO sheet possess the amphiphilic property and readily dispersed in water or any solvent [3]. Behabtu et al. [4] were the first that reported on LCs behavior of exfoliated single-layer graphene in chlorosulphonic acid. Then, Xu et al. [5] observed the nematic liquid crystallinity of GO sheets in water. As such, GOLCs can be considered as a general category

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of lyotropic colloidal LCs. [6]

Apart from behaving like a liquid crystal, GO also can act as a surfactant to stabilize the Pickering emulsion system. The high surface area of the GO sheets enables them to wrap around the linseed oil droplets. The wettability of GO also made this possible [7]. The partially hydrophilic nature of GO makes it suitable to stabilize oil-in-water Pickering emulsion. On a related note, Pickering emulsion is an emulsion stabilized by solid particles, usually in nano-sized ranges. It can be of any type, whether oil-in-water (O/W) or water-in-oil (W/O) [8]. The major advantage of Pickering emulsions compared to the classical emulsion is their superior stability and the ability to produce nanometer-sized emulsion droplets. The size of the Pickering emulsions can be controlled simply by varying the pH [9], dispersion speed [10] and concentration of solid particles [11].

Here, the effect of GO concentration to GOLCs Pickering emulsion (GOLCsPE) droplets will be reported. Linseed oil (LO) was used as the dispersed phase in this Pickering emulsion system. Linseed oil is a type of drying oil that undergoes auto-oxidation if exposed to the atmosphere [12]. In this research, GOLCsPE was produced by using only GO sheets and linseed oil with the help of high shear stirring. The ideal GO concentration was then selected to synthesize the GOLC's Pickering emulsions that will be used for future works in self-healing coating application. The effect of GO concentration on the appearance, stability and droplet size was investigated.

II. EXPERIMENTAL PROCEDURES

Table- I: GOLCsPE prepared with varied GO concentration

Sample	GO Concentration (mg/ml)	Mass of LO (g)	Disperse Speed (rpm)
$GOLCsPE_{1.0}$	1.0	0.37	1200
$GOLCsPE_{3.7}$	3.7	0.37	1200
$GOLCsPE_{5.0}$	5.0	0.37	1200
$GOLCsPE_{7.0}$	7.0	0.37	1200

GOLCsPE was prepared according to Li et al. [13] by adding the linseed oil into the 5ml graphene oxide solution and followed by mixing it with an overhead stirrer for 10 minutes. 4 different samples was prepared with varied GO concentration while maintaining the disperse speed. The emulsion formed was then transferred to 7ml polyethylene vial. The samples prepared are summarized in Table- I.

The resultant emulsions were characterized through a polarized optical microscope (POM) (model: LEXT OLS4100). The emulsions formed are viscous and not suitable for optical microscope characterization. To capture the image clearly, the emulsions were first diluted with deionized water and dropped onto the surface of a glass slide. The average droplet size is recorded based on the POM images. The coefficient of variation, C_v is also calculated from the POM images by using the formula C_v = standard deviation/mean size. Droplets size distribution for oil-in-water emulsions were analyzed by Particle size analyzer (PSA) (model: Malvern Zetasizer Nano).

III. RESULT AND DISCUSSION

A. Phase Separation Observation

Solid particles concentration is a vital factor that has a remarkable influence on the emulsion stability and size. The GO concentrations used to prepare the emulsion were varied to 1.0, 3.7, 5.0 and 7.0 mg/ml. Higher than that led to high-viscosity gel-like slurry which was not suitable for the formation of an emulsion. It will contribute to the quasi-solid consistency once mixed with the discontinuous oil phase. This observation is in a good agreement with Wan et al. [14].

Fig. 1 shows the digital image of the emulsions prepared under various GO concentration. The dark color intensity of the emulsions increased with the increasing concentration of GO sheets due to the excess solid particles in the aqueous phase. Besides, the increasing concentration of GO sheets contributed to the thickening of the emulsion. This phenomenon is important because high viscosity slows down the destabilization process by lower down the movement speed of the dispersed phase and eventually led to excellent long-term storage [15].

According to Kang et al. [16], thickening contributes to the stabilization of the emulsion. The destabilization phenomenon that happened to emulsions can be proven by the emulsion prepared with low GO sheets concentration. Based on Fig. 1, all samples do not show any phase separation right after the high shear mixing. But after a few minutes,

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creaming occurs on emulsion with low solid particles concentration

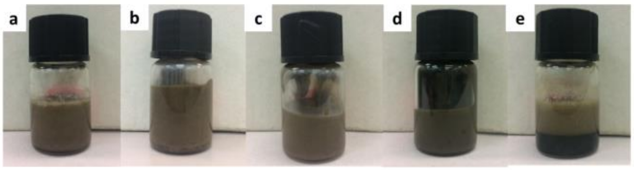

Fig. 1.Digital image of the emulsions formed with different GO concentration a) $GOLCsPE_{1.0}$, b) $GOLCsPE_{3.7}$, c) $GOLCsPE_{5.0}$, d) $GOLCsPE_{7.0}$ and e) $GOLCsPE_{1.0}$ after few minutes.

(GOLCsPE1.0). The emulsion separates into two distinct phases, one of which (the cream) is richer in the disperse phase than the other.

Creaming, which is also the precursor to coalescence occurred to $GOLCsPE_{1.0}$. Based on the Stokes equation of the creaming rate [17];

$$\upsilon = 2\, r^2 (\rho - \rho o)\, g / 9\eta \quad (1)$$

where υ is the creaming (settling) rate, r is the droplet radius, ρ is the density of the droplet, ρo is the density of the dispersion medium, η is the viscosity of the dispersion medium (continuous phase) and g is the local acceleration due to gravity. The Stokes' equation shows that a small droplet radius, low-density difference between the oil and water phases, and a highly viscous continuous phase could inhibit creaming.

B. Polarized Optical Microscope (POM)

Fig. 2 shows the presence of shining halos around the oil droplets for all emulsions, suggesting the GO sheets self-organized themselves at the oil-water interface. The distinct shining halos observed indicate the emulsion was isotropic except for the bright GO shells. The birefringence has a cross-shape originates from the presence of oil droplets in the anisotropic colloidal structure [18]. It should be noted that the birefringence is a typical fingerprint of liquid crystals [19]. The same pattern also can be observed in spherical inclusion in nematic liquid crystals [20].

The destabilization of $GOLCsPE_{1.0}$ is proven by the POM images in Fig. 2(a). The uneven shape of the shining halos is due to the low amount of GO sheets that are not enough to enwrap the oil droplets. However, there are some GOLCsPE droplets present in the continuous phase. Other than $GOLCsPE_{1.0}$, all samples show successful self-organized GO sheets around the linseed oil droplets, although the birefringence becomes faint due to the viscosity of the emulsions.

The average size obtained from the POM images shows that there is some reduction in emulsions size as the concentration of GO sheets increased. The decreased in Cv values (Table- II) as the concentration of GO increased indicates a better droplet size distribution. A study by Wu et al. [21] also suggested that the increase in stabilizing particles decrease the formed droplet diameter and improve the surface coverage. Besides, the excess particles allow the formation of a network structure around the oil droplets which further improves the emulsion stability.

Based on these findings, it is safe to conclude that the GO concentration plays a more important role in maintaining the stability of the emulsion, rather than controlling the linseed oil droplet size. The formation of GOLCsPE can be separated into two important stages. First, is the breaking of the linseed oil phase and second, is the stabilization of oil droplets by the GO sheets. Based on these two important stages, the oil droplet size is first determined by the dispersed speed, and whether the resultant droplets maintained their size depends on the stabilizing particles. This finding also showed that the shear speed and stabilizing moieties go hand in hand and controlling only the GO concentration to obtain small sizes emulsion is not enough to produce a stable oil-in-water emulsion.

C. Particle Size Analyzer (PSA)

As compared to average size based on POM images, PSA analysis gives an inverse result. Fig. 3 shows the droplet size distribution for all samples. There are some discrepancies in GOLCsPE sizes obtained from both POM and PSA. It should be noted that the size of GOLCsPE in POM images was measured based on the bright ring shell, while PSA measured the size of the linseed oil droplets. The GOLCsPE size increased as the concentration increased. It is postulated that as the GO concentration increased, more GO sheets are laden around the oil droplets. This also suggested that PSA may not be suitable to measure the size of the GOLCsPE, as the high concentration of GO may give some inconsistent data. This statement also can be supported by several past studies that measured the

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size of graphene oxide liquid crystals solely based on the optical microscope images [1, 13-14].

Nevertheless, droplets size distribution is found to be improved by increasing the GO concentration based on the narrow peak. Although the $GOLCsPE_{1.0}$ gives the smallest microcapsule's size (around 300 nm), there are about 2-3% of GOM's with a diameter around 5000 nm is also observed. It should be noted that all samples were taken from the continuous phase of the emulsion, excluding the creaming part, which results in small size droplet distribution for $GOLCsPE_{1.0}$ through PSA.

Fig. 4 shows the average droplet size comparison based on POM and PSA. Considering the physical attributes and both POM and PSA analysis, $GOLCsPE_{3.7}$ possesses a good emulsion consistency, stability, a relatively small microcapsule, and even size distribution. These characteristics are essential emulsion attributes. Poor stability with uneven emulsion size distribution will disrupt the performance of the application that employed this type of emulsion. Hence, 3.7 mg/ml was chosen as an ideal GO concentration for the preparation of the emulsion for further tests.

Table- II: C_v values for emulsions prepared with varied GO concentration

Sample	Coefficient of Variation (C_v)
$GOLCsPE_{1.0}$	0.39
$GOLCsPE_{3.7}$	0.31
$GOLCsPE_{5.0}$	0.22
$GOLCsPE_{7.0}$	0.23

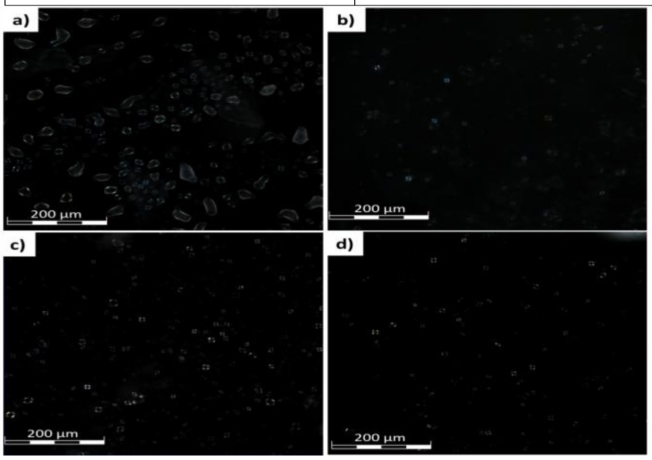

Fig. 2. Digital image of the emulsions formed with different GO concentration, a) $GOLCsPE_{1.0}$, b) $GOLCsPE_{3.7}$, c) $GOLCsPE_{5.0}$, d) $GOLCsPE_{7.0}$

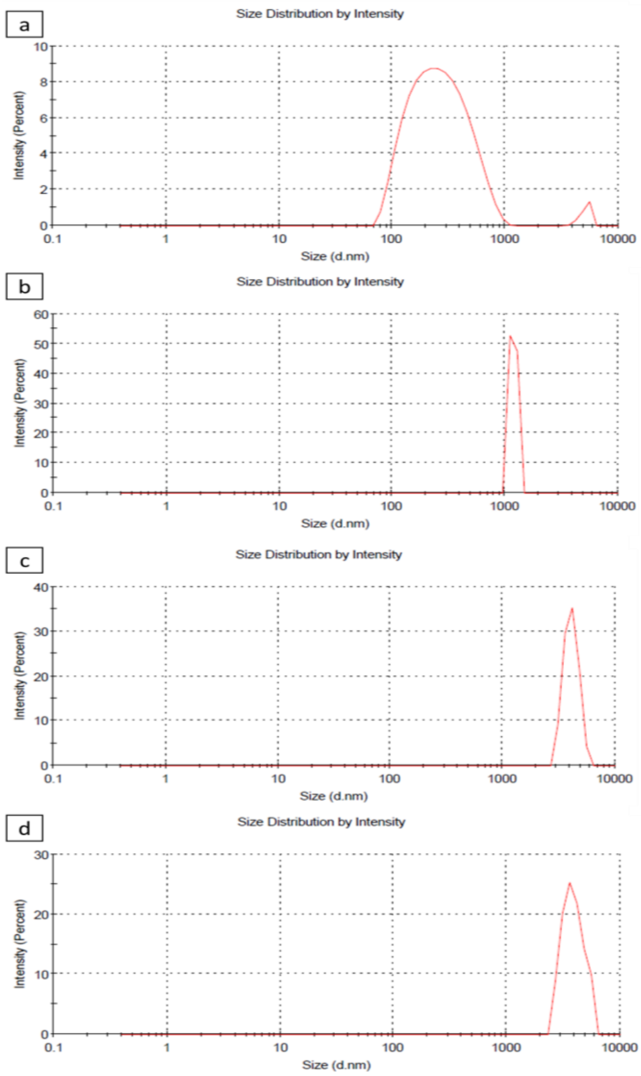

Fig. 3. Droplet size distribution, a) $GOLCsPE_{1.0}$, b) $GOLCsPE_{3.7}$, c) $GOLCsPE_{5.0}$, d) $GOLCsPE_{7.0}$

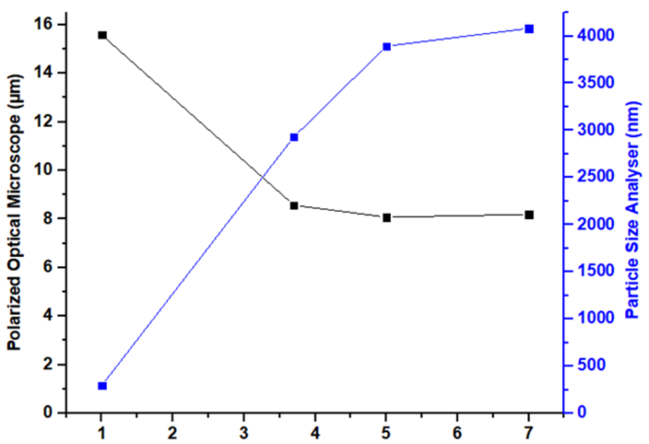

Fig. 4. Average droplet size comparison

IV. CONCLUSION

In summary, it can be demonstrated that the graphene oxide liquid crystals Pickering emulsion (GOLCsPE) was successfully synthesized based on the cross-shape birefringence. The ability of GO sheets to assemble themselves around the oil-water interface is a proof that GOLCs formed a lyotropic liquid-crystalline phase. Higher GO concentration led to the thickening of the emulsion and improved its stability. POMs analysis revealed that the higher GO concentration decreased the droplet size and reduced the C_v. However, PSA analysis showed an increased pattern in droplets size. This could be due to more GO sheets enwrapped and laden the oil droplets. Nevertheless, as the GO concentration increased, the GOLCsPE size distribution is also improved based on the narrow peak in PSA graph. GO concentration plays a more important role in maintaining the GOLCsPE's size, rather than reducing it. From the physical attributes, POM and PSA analysis, it can be deduced that GOLCsPE prepared with GO concentration of 3.7 mg/ml produced a satisfying size (8.5µm), low C_v (0.31), good size distribution and stability to be used for further test in self-healing coating application. Small, even size distribution and good stability are crucial for emulsion to be used in self-healing coating to avoid any adverse effect that will disturb the barrier properties of the coating itself.

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