Palm olein-in-water Pickering emulsion stabilized by Fe$_3$O$_4$-cellulose nanocrystal nanocomposites and their responses to pH

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**Abstract**
We studied the formation of palm olein-in-water (O/W) Pickering emulsion stabilized by Fe$_3$O$_4$-cellulose nanocrystals (MCNC) nanocomposites obtained by ultrasound assisted in-situ co-precipitation method. The synthesized MCNC nanocomposites successfully stabilized Pickering emulsion with dual responses. The magnetic tests revealed a direct-relation between attractability of MCNC-stabilized Pickering emulsions and the emulsion droplet diameter. The Pickering emulsions were stable under pH ranging from 3 to 6. The stability substantially reduced around pH 8–10, and regained slowly when approaching pH 13. From microscopic and mastersizer analysis, monodisperse emulsion droplets were noticed at pH 3–6, and 13, while polydisperse emulsion were obtained at pH 8–12. The Pickering emulsions prepared at pH 6 are stable up to 14 days, while Pickering emulsions at pH 8 experienced coalescence. In this study, the dual stimuli-responsive Pickering emulsion stabilized by MCNC may hold potentials for biomedical and drug delivery as new generation of smart nanotherapeutic carrier.

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1. Introduction

Emulsion is compose of two immiscible liquids in which one of the liquid is dispersed in the other. Generally, conventional emulsions were stabilized by surfactants. However, the cost of surfactant is normally high, and their recovery is not practical (Binks, 2002; Tang et al., 2015). Furthermore, some surfactants may also induce tissue irritation and cell damage (Tang et al., 2015). Therefore, the use of solid particles as emulsifier is getting more attentions recently due to their low cost, low toxicity, and their remarkable resistance against coalescence compared to the conventional emulsions stabilized by surfactant (Fredlichowska et al., 2009a; Pickering, 1907; Ramsden, 1903). The solid-stabilized emulsions system, termed as Pickering emulsion were pioneered by Ramsden (1903) and Pickering (1907) back in the 19th century. Their findings allowed the generation of surfactant-free emulsions. This is vitally useful especially in various health and cosmetics applications where the use of lethal surfactants are undesirable. By definition, the advanced resistances to de-stabilization of Pickering emulsions were due to the irreversible adsorption of colloidal solid particles onto the interfaces of two immiscible liquids (Binks & Lumsdon, 2001; Cunha, Mougel, Cathala, Berglund, & Capron, 2014; Tambe & Sharma, 1993). The strong shielding effects imparted by the solid particles, however, have restricted the employment of the Pickering emulsion in various applications that requires temporal stabilization and subsequent demulsification. This includes oil recovery (Sharma, Velmurugan, Patel, Chiu, & Sangwai, 2015; Tang et al., 2015), drug delivery (Fredlichowska et al., 2009a;b; Marku, Wahlgren, Rayner, Sjöö, & Timgren, 2012; Tang et al., 2015), and emulsion polymerization (Chen, Cheng, Chiu, Lee, & Liang, 2008; Tang et al., 2015; Zhang, Wu, Meng, Guo, & Chen, 2009).

The stabilization of Pickering emulsion is normally affected by the surface wettability of particles (Binks & Lumsdon, 2000). Hence, nanoparticles with switchable partial surface wetting properties are desirable. This can be done by designing Pickering stabilizer that responds to external stimuli. Generally, this requires

**Abbreviations:**

d. density; \( \mu \), viscosity; S, cross-sectional area; ANOVA, analysis of variance; \( C_0 \), drag coefficient; CNC, cellulose nanocrystal; d, droplet diameter; \( D_0 \), drag force; Fe, iron; FeCl$_3$, 4H$_2$O, iron(III) chloride hexahydrate; FeCl$_3$, 6H$_2$O, iron(III) chloride hexahydrate; FE-SEM, field emission scanning electron microscope; MCNC, Fe$_3$O$_4$-cellulose nanocrystal; MNPs, Fe$_3$O$_4$ nanoparticles; \( M_r \), saturation magnetization; O/W, oil-in-water; Re, Reynolds number; TGA, thermogravimetric analysis; u, velocity; VSM, vibrating sample magnetometry.

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McNC composites were prepared by ultrasound assisted in-situ co-precipitation methods. In particular, CNC was first dispersed in water under 0.05 wt% via ultrasonic cavitation for 2 min. Next, iron (III) and iron (II) chloride (1.5/1 Fe(III)/Fe(II) mol ratio) were added into the CNC dispersed water. Consequently, the mixtures were stirred and heated to 45 °C. Then, the mixtures were sonicated in the presence of ammonium hydroxide (2.2 ml) for 5 min. After the process, the mixtures were precipitated with ethanol. The resulted MCNC were magnetically separated and washed 3 times with ethanol to remove all ammonium hydroxide. Lastly, the remained MCNCs were centrifuged at 4500 rpm for 20 min, and dried in an oven overnight. The dried samples were stored for characterization.

2.3. Characterization of MCNC

Size and surface morphology of the sonoochemically prepared MCNC were analyzed using Hitachi SU8010 field emission scanning electron microscope (FE-SEM) (Hitachi, Japan) at 15 kV. Hydromagnetic size and zeta potential were measured utilizing Zetasizer Nano ZS 90 (Malvern instruments, UK), at 25 °C. Magnetic properties via vibrating sample magnetometry (VSM) (Lakeshore 7400 Series). Chemical composition and thermal stability was evaluated by thermogravimetric analysis (TGA) using Q50 TGA (TA instrument, USA).

2.4. Formation of MCNC stabilized Pickering emulsion

Preparation of MCNC stabilized Pickering emulsion was carried out using ultrasound methods. For instance, the resulted MCNC samples (0.05 wt%) were re-dispersed in water. Oil phase of a fixed volume fraction (ϕwl = 0.3) were added to the MCNC dispersion, and emulsified using ultrasonic horn at room temperature for 3 min. Pickering emulsion images were captured immediately, 7, and 14 days after synthesis to determine the storage stability of MCNC stabilized Pickering emulsions in different system.

2.5. Characterization of MCNC stabilized Pickering emulsion

MCNC stabilized Pickering emulsion droplets diameter was measured using a Mastersizer (Mastersizer 3000, Malvern Instruments, UK) equipped with a Hydro EV wet dispersion unit. The emulsions were analyzed periodically up to 14 days of preparation to determine the storage stability of the emulsions. Stability of Pickering emulsions were checked via traces of phase separation or coalescence of the emulsions. Visualization of Pickering emulsion droplets were performed using an inverted optical microscope (Nikon Eclipse TS100, Nukon Instruments Inc., USA) at 10× magnification. Localization of MCNC at the oil/water interface were checked using inverted fluorescent microscope (Nikon Eclipse Ti-E, Nukon Instruments Inc., USA) at 10× magnification. The emulsions sample for fluorescent microscopy were prepared at pH 6 with double staining. Red palm oil were stained with nile red prior to emulsions preparation. After preparation, the Pickering emulsions were diluted 30 times with water. The MCNC were then stained with calcicour white.

2.6. Responses of MCNC stabilized Pickering emulsion under external magnetic field

The motion of MCNC-PE under an external magnetic field was evaluated based on a method similar to that by Lin, Yang, Petit, & Lee (2015) on examination of motion of MRGO-Pickering emulsion under an external magnetic field. For instance, 50 μl of the MCNC-
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