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Palm olein-in-water Pickering emulsion stabilized by Fe_3O_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_3O_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.

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 (Frelichowska 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, Chon, & Sangwai, 2015; Tang et al., 2015), drug delivery (Frelichowska 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: ρ, density; μ, viscosity; A, cross-sectional area; ANOVA, analysis of variance; C_D, drag coefficient; CNC, cellulose nanocrystal; d, droplet diameter; F_D, drag force; Fe, iron; $FeCl_2.4H_2O$, iron (II) chloride tetrahydrate; $FeCl_3.6H_2O$, iron (III) chloride hexahydrate; FE-SEM, field emission scanning electron microscope; MCNC, Fe_3O_4-cellulose nanocrystal; MNPs, Fe_3O_4 nanoparticles; M_s, saturation magnetization; O/W, oil-in-water; Re, Reynolds number; TGA, thermogravimetric analysis; u, velocity; VSM, vibrating sample magnetometry.

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particle that undergo some physical or chemical transformation under responses to external triggers that, in turn, changing its wetting ability. This can ultimately result in generating remote controllable Pickering emulsion. To date, various responses such as thermosensitive (Tang et al., 2014; Zoppe, Venditti, & Rojas, 2012), pH responsive (Lan et al., 2007; Tang et al., 2014), and magnetic responses (Lan et al., 2007; Zhou et al., 2011), have been attempted for Pickering emulsions preparation. In fact, Pickering emulsions with multiple stimuli responses were also demonstrated (Tang et al., 2014). One of the popular material that has gained attentions for its stimuli responsive properties is the Fe_3O_4 nanoparticles (MNPs). Besides being known for its superparamagnetic properties, recent study by Lan et al. (2007) demonstrated that oleic acid stabilized MNPs experienced several phase transition when the pH was adjusted from acidic to alkali condition. However, study by Zhou et al. (2011) showed that pure MNPs were only able to stabilize certain non-polar oil based Pickering emulsion. This highly constrained the uses of MNPs for the as-mentioned applications.

In search for approaches to improve the feasibility of MNPs to stabilize more types of oil-based Pickering emulsion, cellulose nanocrystal (CNC), was one of the most widely investigated Pickering stabilizer due to its biocompatibility, biodegradability, non-toxicity, and sustainability (Capron & Cathala, 2013; Kalashnikova, Bizot, Cathala, & Capron, 2011; Zoppe et al., 2012). In literature, CNC had been reported to exhibit remarkable performance as Pickering stabilizer for emulsion. Furthermore, it was reported that CNC can undertake variety of responses when incorporated with fillers with respective responses (Wu, Jing, Gong, Zhou, & Dai, 2011). In fact, literature evidence have proven that the incorporation of MNPs into CNC matrix give rise to magnetic cellulosic materials with great dispersion stability (Liu, Nasrallah, Chen, Huang, & Ni, 2015). Despite the wide documentation of CNC-based stimuli responsive Pickering emulsions, magneto-responsive Pickering emulsions based on Fe_3O_4-CNC (MCNC) nanocomposites has, however, not been adequately explored.

This leads to the objective of this paper where preparation of magneto-responsive Pickering emulsions stabilized by MCNC nanocomposite is studied. In addition, the pH responses of MCNC stabilized Pickering emulsion is also studied in the current work with an ultimate aim in preparing dual-responsive Pickering emulsions using MCNC nanocomposites as Pickering stabilizer.

2. Materials and methods

2.1. Materials

Iron (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, ≥99%), iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99%), ammonium hydroxide (28% NH_3 in H_2O), nile red (for microscopy), calcofluor white (for microbiology), and potassium hydroxide were purchased from Sigma-Aldrich. CNC (Freeze dried, rod structure with diameter of 5 nm and length of 150–200 nm, 0.96 wt% sulfur content) was obtained from University of Maine. Red palm superolein (melting point 19 °C) was purchased from Sime Darby Jomalina Sdn Bhd (Malaysia). All water used in this experiment are ultrapure water obtained from Milli-Q® Plus apparatus (Millipore, Billerica, USA). Ethanol (AR standard), 1 M hydrochloric acid (HCl), and sodium hydroxide (NaOH) procured from R & M Chemical (Syarikat Saintifik Jaya, Malaysia). All experiments were conducted on an ultrasonic horn (20 kHz, 100 w system, NexTgen ultrasonic platform, Sinaptec, France) under pulse mode (15 s pulse on, 10 s pulse off). All chemicals used in this study were analytical grade.

2.2. In-situ synthesis of MCNC composite

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^{3+}/Fe^{2+} 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 washes 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 sonochemically prepared MCNC were analyzed using Hitachi SU8010 field emission scanning electron microscope (FE-SEM) (Hitachi, Japan) at 15 kV. Hydrodynamic 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 ($\phi_{oil} = 0.3$) 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 14th 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 calcofluor 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-