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Pickering emulsion polymerization of styrene stabilized by nanocrystalline cellulose

Xue Song[a], Mingqin Lin[a], Changsheng Song[a], Zipei Shi [a], Heng Zhang [a,b]*

a) College of Marine Science and Biological Engineering, Qingdao University of Science & Technology, Qingdao, Shandong, 266042 China;
b) State Key Laboratory Base of Eco-chemical Engineering, Qingdao, Shandong, 266042 China

**Corresponding author:hgzhang@sina.com*

ABSTRACT

In this work, polystyrene-based oil-in-water Pickering emulsion stabilized by nanocrystalline cellulose (NCC) was formulated. The NCC was prepared by sulfuric-acid-catalyzed hydrolysis of microcrystalline cellulose, with a yield of 60% and an average particle size of about 152.9 nm. When the content of NCC was 5 g/L, the surface tension was 54.58 mN/m, and stable styrene-based Pickering emulsion was prepared using NCC as the stabilizer. The presence of NCC particles in the emulsion system resulted in high resistance against creaming. Due to improved stability, the conversion efficiency of styrene was higher in the polymerization process of the styrene-based Pickering emulsion.

Keywords: Soap-free emulsion polymerization; Nanocrystalline cellulose; Stabilizer; Pickering emulsion

1. INTRODUCTION

An emulsion is a system of dispersed droplets of one immiscible liquid in another.[1] Principally, emulsions are thermodynamically unstable systems. The addition of surfactants and solid particles or a mixture of surfactant with other amphiphilic polymers can kinetically stabilize the emulsions.[2] When solid particles are used to stabilize emulsions, solid particles have been shown to adsorb at fluid interfaces, forming so-called Pickering emulsion.[3] The properties of these systems are somehow due to the irreversible absorption nature of such particle.[4-6] Stabilization of solid particles at the interface is generally considered to be directed by particle wettability. [1] For particles with contact angle of less than 90°, the dispersed system tends to be an o/w emulsion, and the particles forma densely packed film (monolayer or more than one layer) around the droplets due to particle interactions. This crusty film can sterically inhibit the coalescence of emulsion droplets.[7-9] In contrast, for w/o emulsion, of which the contact angle of colloidal particles is above 90° , the particles can stabilize the droplets by bridging stabilization.[10] It has been proposed that the sparsely covered emulsion droplets with strongly repulsive particles are stabilized by forming a dense bridging monolayer. [10]

Recently, many types of particles, either inorganic or organic, have been used to produce stable emulsion. Nanocrystalline cellulose (NCC) is a biodegradable material derived from lignocellulosic resources.[11] Currently, published works indicate that NCC has a high specific surface area[12] and high strength[13.] NCC is effective in mechanical reinforcement because of its high modulus.[14] It can be chemically modified and functionalized because of its abundant hydrophilic groups.[15] Several researchers have used NCC as filler to fabricate composite materials, which have been widely applied in various fields, such as catalysis.[16,17] Furthermore, NCC could be used as scaffold in polymeric materials, [18] carriers or emulsion stabilizers for medicine tablets, [19] or hydrogel-based products.[20,21]

Interestingly, NCC has been studied as stabilizer in the formulation of Pickering emulsion. For example, Chun et al.[10] investigated the formulation of NCC-stabilized D-limonene Pickering emulsion with the aid of ultrasonic homogenization. This NCC was prepared by ammonium persulfate hydrolysis of corncob. The stabilizing effect of NCC on was identified.

In this study, NCC-assisted in-situ o/w polymerization of styrene was used to formulate Pickering emulsion. NCC was prepared via sulfuric acid hydrolysis of microcrystalline cellulose. Then, NCC-stabilized styrene Pickering emulsion was successfully prepared with the aid of sonication, and its properties were studied.

2. EXPERIMENTAL

2.1 Materials

Microcrystalline cellulose was obtained from Chengdu Kelon Chemical Reagent Co. Ltd. Sulfuric acid was obtained from Yantai Sanhe Chemicals Co. Ltd. Styrene, ammonium persulfate and ammonium bicarbonate were all of reagent grade and purchased from Tianjin Chemicals Co. Ltd.

2.2 NCC Preparation and Contact Angle Measurement

2.2.1 NCC Preparation

Firstly, 4.5 g of microcrystalline cellulose was added to 135 g of 65 wt% sulfuric acid solution. Hydrolysis of microcrystalline cellulose was conducted 40℃for 3 h. A dispersion of NCC was then obtained. Distilled water was added to NCC dispersion to stop the reaction. Acid was removed by successive centrifugation during 10 min at 10000 g, and redispersion of solid materials in ultrapure water by ultrasound treatment for a few minutes. The resulting suspension was then dialyzed in Distilled water to remove any contaminants.

2.2.2 Contact Angle Measurement

A few drops (about 0.016 mL) of NCC dispersion were placed on a flat glass. The contact angle of NCC film was measured with a JY-82-C Video Contact Angle Meter.

2.3 Preparation and Characterization of NCC-stabilized styrene emulsion

2.3.1 Preparation of NCC-stabilized styrene emulsion

The o/w emulsion was prepared using styrene and NCC aqueous suspension. The emulsion was prepared with oil to aqueous liquid ratio of 10/90. Practically, 1ml of styrene was added to 9 ml of aqueous suspension in a plastic vial, and the mixture was sonicated with an ultrasonic device. After that, the emulsion was subjected to micro-creaming for a few minutes. Finally, the resulting emulsion was sonicated again to obtain a Pickering emulsion.

2.3.2 Stability Test

The stability of the emulsion was tested by centrifugation for 5 min at 4000 g. The emulsion volume and drop size were measured, and results indicated that they were kept stable under various centrifugation times from 30s to 40 min. Photographs of the vials containing the emulsions were taken with a digital camera.

2.4 Preparation of NCC-stabilized polystyrene emulsion

2.4.1 Polymerization

NCC-stabilized styrene emulsion was added to a four-necked flask placed in water bath, and then the temperature of the water bath began to increase. When the temperature was 60 ℃, the system was timed after ammonium persulfate was added to start the reaction, with continued heating to 75 ℃. Within 4 h, ammonium persulfate was added at a constant speed, and then the mixture was incubated for 1 h. During the heat preservation time, a given amount of initiator was added. At the end of the reaction, the emulsion was cooled to room temperature.

2.4.2 Stability Test

According to the requirements of stability determination, 40 ml of deionized water was added to 10 ml of each sample. After the mixed solution was stirred, it was sealed and kept t for 2 d. Finally, the stability of the Pickering emulsion was evaluated.

2.4.3 Determination of monomer conversion efficiency and solid content

The solid content of Pickering emulsion was determined according to the following equation:

$$X(\%) = \frac{M_1}{M_0} * 100\% \tag{1}$$

Where: X - solid content, %; M_1 - sample weight after evaporation, g; M_0 - sample weight before evaporation, g.

The monomer conversion efficiency in the process of polymerization is the ratio of actual solid content versus theoretical solid content. This parameter was calculated according to the following equation:

$$C = \frac{S_1}{S_0} \tag{2}$$

Where: C- monomer conversion efficiency, %; S_0 - theoretical solid content of the emulsion, %; S_1- actual solids content of the emulsion, %.

3. RESULTS AND DISCUSSION

3.1 NCC preparation and contact angle

In this work, NCCs were isolated by sulfuric acid hydrolysis to remove the amorphous part of the microcrystalline cellulose. The yield of NCC, under specified reaction condition (40℃, 3 h), was 60%. The average size of NCC was determined to be around 152.9 nm. Water contact behavior of NCC film is shown in Fig 1. Contact angle measurements were conducted to evaluate the mechanism of stabilization of Pickering emulsion. The contact angle was about 59°. For particles with a water contact angle of less than 90°, the emulsion tends to be in o/w form by generating a densely close-packed film (monolayer or more than one layer) around the droplets due to particle interactions. [7-9] The impact of NCC on the surface tension is shown by the contact angle of a water drop on the NCC film (Fig. 2).

With the increase of NCC content, the contact angle decreased, and the surface tension was reduced, and the wettability was enhanced. Therefore, during the Pickering emulsion polymerization process, NCC formed a layer or layers of dense film on the surface of the droplets due to the small contact angle. NCC could suppress the coalescence of emulsion droplets and improve the stability of the emulsion.

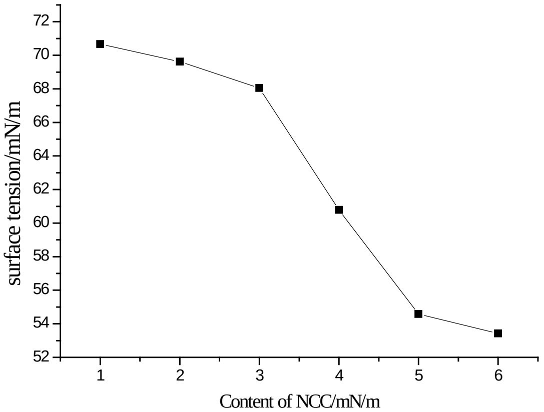

Fig. 2. Effect of NCC content on the surface tension

When the dosage of NCC was 5 g/L, the surface tension was 54.58 mN/m. When the content of NCC was above 6 g/L, surface tension did not change significantly.

Fig.1. The contact angle of a water drop on the NCC film

3.2. Formation of NCC-stabilized styrene emulsion

For each sample of tested emulsions, the aqueous phase, consisted of NCC dispersed in water at the required concentration. And then styrene was slowly added afterwards. The biphasic system was then sonicated, resulting in a stable oil/water emulsion. Pickering emulsions were formulated at a 10/90 ratio (o/w), with about 5g/L suspension of NCC in water phase. These conditions were used to test stability under various centrifugation conditions. Very high stability was observed. The ability of NCC to stabilize the droplets was assessed by varying the concentration of NCC in the aqueous suspension from 1 to 6 g/L. In Fig.3, before centrifugation (a), the emulsion of 1g/L suspension of NCC was stratified, while others were stable. After centrifugation at 4000 rpm, the emulsion of 1 g/L of NCC “broke up”; above 2g/L of NCC dense emulsions were obtained, which shows resistance to the stress induced by centrifugation. [1]

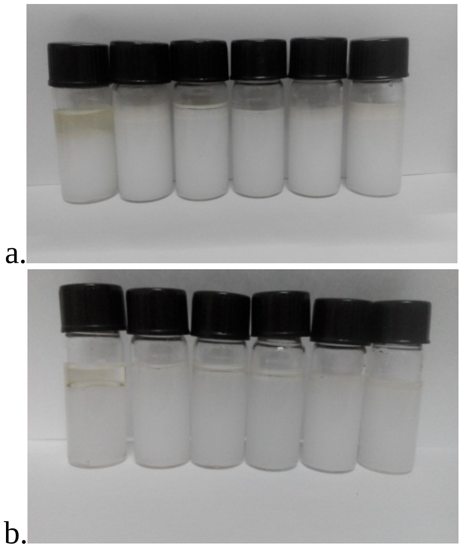

Fig.3. NCC-stabilized styrene emulsions: (a) before centrifugation and (b) after centrifugation. From left to right: PCC contents varied from 1 to 6 g/L.

3.3 Impact of PCC dosage on particle size of styrene emulsion

Droplet size variations were monitored by measuring the surface mean diameter and varying concentrations of NCC in the water phase for a fixed amount of oil. Results are given for a ratio of 10/90 (oil/water) (Fig. 4).

Droplet size showed a clear tendency to coalescence at the lowest concentration of NCC. Then sizes decreased to a plateau value of about 4 um diameter for all emulsions containing more than 2g/L of NCC in the water phase. Below 2g/L, the increasing amount of NCC particles resulted in decreasing average droplet size which led to a larger interfacial area and thus to a higher emulsion volume. [1]

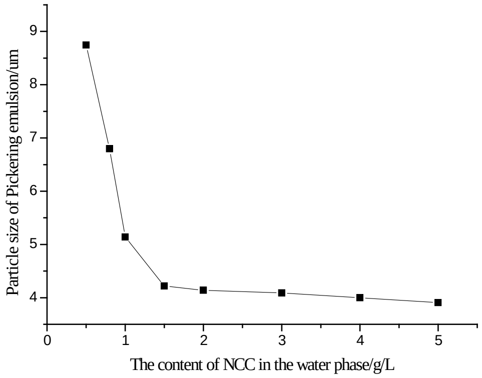

Fig.4. Effect of NCC content on particle size of Pickering emulsion

3.4 Formation of polystyrene emulsion stabilized by NCC

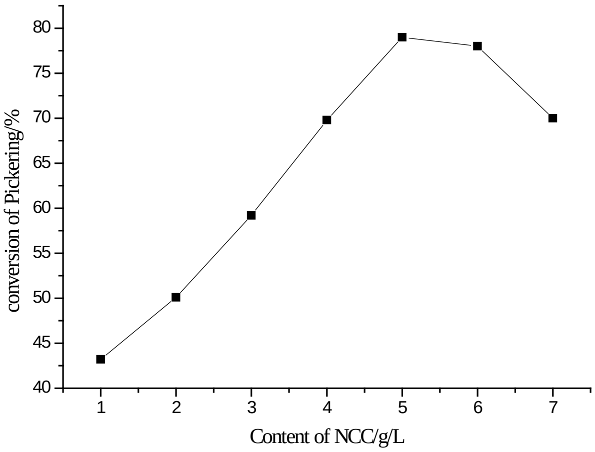

Fig.5. Effect of NCC content on the conversion efficiency of monomer

Polystyrene emulsion was successfully synthesized through surfactant-free inverse Pickering emulsion polymerization in o/w system using NCC as the stabilizer. During the polymerization process, NCC stabilized the styrene Pickering emulsion by forming a densely close-packed film around the droplets thanks to the strong particle interaction of NCC. In this study, when the amount of NCC was 5g/L, the emulsion conversion efficiency reached 79%. The solids content of the Pickering emulsion increased with increasing NCC content, as shown in Fig.5. This is due to the fact that the solids content and the conversion of the emulsion can be governed by the wettability of NCC. The surface tension gradually decreased with increasing NCC content, thereby enhancing surface wettability, which in turn improved the adsorption of solid particles on the surface of the liquid droplets. On the other hand, NCC, as emulsion stabilizer, may play a role in emulsification, stabilization, and dispersion. When insufficient amount of NCC was present the surface wettability was low due to higher surface tension. Under these conditions, the ability of the solid particle was weak in emulsifying/stabilizing Pickering emulsions, which restrained the latex particle micelle formation in micelle formation. As a result, nuclear reaction was unable to continue growing, resulting in a lower conversion efficiency of the monomer.

4. CONCLUSION

In this study, a stable styrene Pickering emulsion was prepared for high efficient emulsion polymerization, using nanocrystalline cellulose (NCC) as the stabilizer. The NCC which was produced by sulfuric acid hydrolysis of microcrystalline cellulose had an average size of about 150 nm. It was found that at a dosage of 5g/L NCC, the obtained Pickering emulsion exhibited high stability against creaming. It was also found that during the polymerization of the NCC-stabilized styrene Pickering emulsion, the conversion efficiency of styrene monomers improved markedly compared with the control.

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