Polymerization Processes of Emulsifier-free Pickering Emulsion Stabilized by Nanocrystalline Cellulose

Heng Zhang,[a,b,]* Hongkun Gao,[a] Zhe Wang,[a] and Xiaolong Zhu [a]

Styrene was used as the monomer, ammonium persulfate as the initiator, and the nano-cellulose (NCC) obtained by hydrolyzing microcrystalline cellulose with sulfuric acid was used as the stabilizer for solid particles. Then the Pickering emulsion, which can be stable for a certain time, was prepared by emulsifier-free emulsion polymerization by ultrasonic homogenization. The solid content and conversion and emulsion rates were calculated. The material was examined by infrared spectroscopy and scanning electron microscopy. Its stability and other characteristics were described. The average NCC particle size was 187.2 nm, and the particle size distribution coefficient of PDI was 0.394. The styrene Pickering emulsion was stable for 20 d, and the emulsion rate was stable at approximately 0.7. The conversion rate of the polymerization emulsion was approximately 80%. When the content of NCC was approximately 3% to 4%, the maximum degree of sizing was approximately 42 s, and the water resistance was better than Pickering emulsion with other NCC additions.

Keywords: NCC; Styrene; Pickering emulsion; Soap-free polymerization

*Contact information: 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*

INTRODUCTION

Pickering emulsion is a special emulsion that is stabilized by solid particles instead of a surfactant. A Pickering emulsion possesses the basic characteristics of a traditional emulsion, but it also has the unique properties. It is environmentally friendly, lacks emulsifiers, and possesses a stable emulsion phase. Also the emulsion is little influenced by pH, ionic concentration, temperature, and emulsion composition. The properties of a Pickering emulsion are affected by the properties of the solid particles (Binks and Lumsdon 2001). The wettability of particles that are hydrophilic and hydrophobic directly influences the stability of the emulsion on the surface of the droplet. When the contact angle of the solid particles ($\theta < 90°$), an o/w (oil in water) emulsion tends to form. The stabilizer particles form a dense film with one or more layers on the droplet surface through the interaction among particles to inhibit emulsion droplet coalescence (Nasser *et al.* 2015), which stabilizes the emulsion. When the contact angle of the solid θ is less than 90°, a w/o (water in oil) emulsion usually forms, and the solid particles form a dense bridged monolayer to achieve a stable emulsion.

Various types of organic or inorganic solid particles are used to prepare stable emulsions. Abundant natural polymers such as cellulose can be used as stabilizers for preparing Pickering emulsions. Wen *et al.* (2014) synthesized a highly stable nanocellulose/D-limonene Pickering emulsion using ultrasonic homogenization; the nanocellulose was obtained by hydrolysis of corn cellulose with ammonium persulfate.

Nasser *et al.* (2015) reported the latest method for the synthesis of blowing agents for synthesizing expandable nonvolatile organic compounds, such as polystyrene droplets, that contain uniformly dispersed water droplets. Asim *et al.* (2017) developed hybrid membranes integrated with nanocrystalline cellulose (NCC)/Gum Arabic (GuA) conjugates; such membranes enhanced the hydrophilic character, resulting in increased permeation flux rate as well as having great potential for boron removal.

The use of nanocellulose or cellulose derivatives, such as microfibers, as solid particles to stabilize Pickering emulsions has been examined, but these studies explored emulsification stages only. Some studies have focused on the polymerization stage, while the obtained styrene Pickering emulsion cannot be stable for a long time. Thus, they are not applied in emulsion polymerization processes.

This study used styrene as a monomer, ammonium persulfate as the initiator, and nanocellulose (NCC) as a stabilizer to prepare styrene Pickering emulsions through ultrasonic homogenization soap-free emulsion polymerization. The prepared emulsion was studied for its solid content, conversion, and emulsification rates, and it was characterized by infrared spectroscopy, scanning electron microscopy (SEM), and stability tests.

EXPERIMENTAL

Materials and Equipment

Styrene was purchased from a chemical reagent factory (Tianjin Damao, Tianjin, China). Ammonium persulfate was obtained from a chemical reagent company (Tianjin Guangcheng, Tianjin, China). Sodium bicarbonate was provided by Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Concentrated sulfuric acid was purchased from Yantai Sanhe Chemical Reagent Co., Ltd. (Yantai, China). Ethylenediamine tetraacetic acid was obtained from Tianjin Bodi Chemical Co., Ltd. (Tianjin, China). Ferric chloride was provided by Tianjin BASF Chemical Co., Ltd. (Tianjin, China). Ammonium thiocyanate was purchased from Tianjin Dengke Chemical Reagent Co., Ltd. (Tianjin, China). All of the above chemical reagents were of analytical grade. The microcrystalline cellulose, which was from Chengdu Kelon Chemical Reagent Factory (Tianjin, China), was of medicinal grade.

The equipment used were a Fourier infrared spectrometer (VECTOR22, Germany Brooke Co., Ettlingen, Germany), particle size tester (ZetaSizer Nano-Zs900, Malvern Instrument Co., Shanghai, China), AIDA centrifuge (TD5G, Hunan Kaida Scientific Instrument Co., Hunan, China), ultrasonic cleaning machine (M2000, Suzhou Creative Electronics Co., Suzhou, China), homogenizer (T10, Janke and Kunkel KG.IKA-werk, Guangzhou, China), freeze dryer (FD-1A-50, Shanghai Bilan Instrument Manufacturing Co., Shanghai, China), and optical microscope (PM6000, Nanjing Jiangnan Yongxin Optical Co., Nanjing, China).

Emulsification - Styrene Monomer Stabilized by Nanocellulose Solid Particles

A certain concentration (0.5 g/L, 0.75 g/L, 1 g/L, 2 g/L, 3 g/L, 4 g/L, or 5 g/L) of nanocellulose (sulfuric acid hydrolyzed microcrystalline cellulose) was placed in a four-necked flask with a stirrer. While stirring, the styrene monomer was uniformly dropped into the four-necked flask through a constant pressure funnel, and the dropping time was set to 2 h to ensure even stirring. The mixed solution of monomer and nanocellulose were processed in the homogenizer for 30 min, and a stable Pickering emulsion was obtained.

Pickering Emulsion Polymerization

The prepared Pickering emulsion was placed in a four-necked flask equipped with a constant pressure funnel, a thermometer, a spherical condenser, and a stirrer. The temperature was raised to 60 °C with constant stirring. A small amount of ammonium persulfate initiator was added dropwise, and the temperature was raised to 86 °C. The dropping reaction was conducted for 4 h and then maintained at this temperature for an additional 1 h. A small amount of the initiator was reserved during the dropwise addition, then added to this system during the holding time. The mixture was cooled to room temperature, adjusted to a pH 7 to 8, and filtered to obtain a styrene Pickering emulsion.

Characterization of Pickering Emulsion

Determination of particle size and potential of Pickering emulsions

A small amount of emulsions was diluted in distilled water at a ratio of 1:10 until it was transparent. The particle size distribution and potential of the latex particles were measured by the Malvern ZetaSizer Nano-ZS90 laser particle size analyzer (Shanghai, China).

Infrared spectroscopy

The Pickering emulsion was dried and powderized using the KBr pelletizing method. The suspension was then poured onto the KBr sheet, and the solvent was evaporated to form a thin uniform layer of powder prior to infrared spectroscopy with a resolution of 4 cm^{-1} in the region of 4000 to 500 cm^{-1}(GB/T 6040, 2002).

SEM analysis

The Pickering styrene emulsion was dried thoroughly to preserve the surface structure of the sample well. Samples measuring 1 cm were fixed on the sample plate and underwent electrical processing to ensure sample conductivity before SEM.

Determination of emulsification rate

The emulsification ratio is defined as the ratio of the volume of oil to that of the emulsion. The Pickering emulsion, which stabilized the NCC suspension in different amounts, was centrifuged at 4000 r/min. The centrifuged emulsion was placed in a separate funnel, and 200 mL of the underlying emulsion was removed. Finally, the emulsification ratio was measured and calculated using a visible spectrophotometer.

Determination of solid content and conversion rate of styrene polymeric emulsion

The styrene monomer was mixed with the NCC suspension at a volume ratio of 10/90 and subjected to continuous ultrasonic shock (continuous intermittent ultrasound 5 min, static 3 min, ultrasonic frequency 40 KHz) to obtain a Pickering emulsion. The Pickering emulsion polymerization was obtained with the use of ammonium persulfate. A total of 1 g to 2 g of the polymerized Pickering emulsion was placed in a dry box at 75 °C for drying and then weighed. The actual solid content was calculated according to Eq. 1,

$$X(\%) = \frac{M_1}{M_2} \times 100\% \tag{1}$$

where X is the emulsion solid content, M_1 is the weight of the dry sample, and M_2 is the sample weight before drying.

The conversion rate of the polymer Pickering emulsion was calculated according to Eq. 2,

$$C = \frac{S_1}{S_0} \quad (2)$$

where C is the monomer conversion rate, S_0 is the theory emulsion solid content, and S_1 is the actual emulsion solid content.

Optical microscopic analysis of styrene polymerized emulsion

The morphology of the styrene polymer emulsion was measured using a high-power optical microscope. Low-magnification observation was initially applied. The object was located and moved to the center of the field of vision. The converter was turned to high magnification (1000x) to observe.

Determination of sizing degree of styrene polymer emulsion

The sizing degree of the prepared Pickering emulsion was measured by the liquid permeation method in accordance with GB/T 5405 (2002), and the recording time was accurate to 1 s.

RESULTS AND DISCUSSION

Particle Size of Nanocellulose

The nanocellulose was prepared under optimal conditions where the sulfuric acid concentration was 60%, reaction time was 2.5 h, and the reaction temperature was 45 °C. The average particle size of NCC was 187 nm, the yield was 56.04%, and the particle size distribution coefficient PDI was 0.394 (<1). The size distribution of the prepared NCC was relatively narrow; a smaller the PDI value indicates more uniform particle sizes.

Pickering Emulsion Ratio

As shown in Fig. 1, when NCC content was below 2 g/L, the emulsion ratio was low, at less than 0.1. However, with an increase in NCC content, the emulsifiability increased and finally stabilized to a fixed value of approximately 0.7. When the NCC content was below 2 g/L, the oil and water phases were separated and coalesced by centrifugal force.

When the NCC content was large, the oil phase was trapped in the emulsion, whose value would increase rapidly to approximately 0.7. At this point, the NCC content or increase in centrifugation speed could not lead to an increase in the emulsification ratio. Furthermore, the centrifuge could distort the droplets and remove the layers of the interface without damaging the structure of the droplets.

This finding showed that when the NCC content was above 2 g/L, the styrene Pickering emulsion had good space resistance for deformation and coalescence in a certain time.

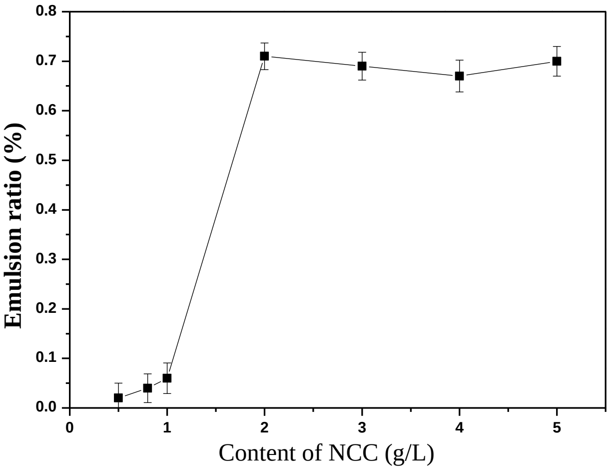

Fig. 1. Effect of NCC content on emulsion rate of styrene in Pickering emulsion

Particle Size of Pickering Emulsions

The particle size of the styrene Pickering emulsion changed with increased NCC content (Fig. 2). With an increase in NCC content, the emulsion particle size decreased. When the NCC content was higher than 2 g/L, the emulsion particle size gradually stabilized, and the increase in NCC content had only a small effect on the particle size. This result suggests that the low NCC content had a weak effect on emulsification and dispersion, and the styrene monomer that was dispersed was not uniform. A low NCC content is prone to aggregation, which leads to enlarged emulsion droplet size. With increased NCC content that exceeded 2 g/L, the particle size of the Pickering emulsion gradually stabilized at approximately 4 µm, and this result may be related to the manner of obtaining the emulsion. Emulsification with ultrasound produces a large o/w surface. Consequently, the NCC could be effectively covered, the solid NCC particles adsorbed on the surface of the droplets played an important part in dispersion, and the styrene could be emulsified and dispersed, such that the size of the emulsion droplets was reduced and could be stabilized. With further increases in the NCC content, the excess NCC did not stabilize the emulsion and was free in the solution.

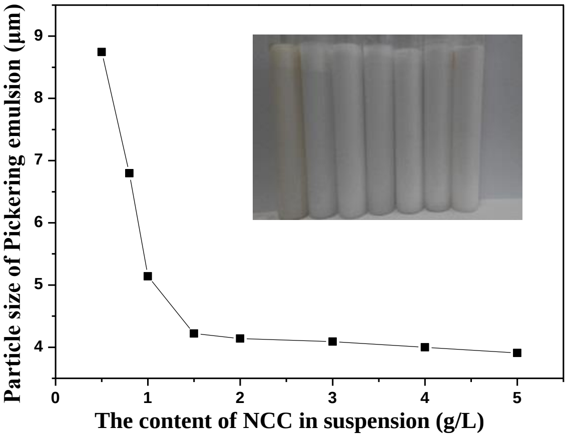

Fig. 2. Effect of NCC content on Pickering emulsion particle size

Determination of Surface Tension and Contact Angle of NCC Suspension

Results from the determination of the surface tension and contact angle of the NCC suspension with different contents are shown in Fig. 3. The surface tension of the NCC suspension with different contents decreased with increased NCC content, and the contact angle increased with decreased surface tension. Meanwhile, the contact angle of the NCC suspension in 2 g/L was measured using the volume angle method. The result was 59°, and the surface tension was 64.49 mN/m. The size of the contact angle was used mainly to evaluate the water affinity of the solid particles and the stability of the Pickering emulsion. According to Nasser *et al.* (2015), the emulsion form becomes o/w when the contact angle of solid particles is $\theta < 90°$. The solid particles adsorbed on the droplet surface, which formed one or more layers of encapsulation film, rely on molecular force between particles (van Edward force), thereby stopping the condensation of the emulsion drop in space. The contact angle of the NCC particles was 59° (< 90°), and the surface had a large number of negative charges. Particles with the same charge repelled each other and allowed the NCC to be stably adsorbed on the surfaces of the styrene droplets.

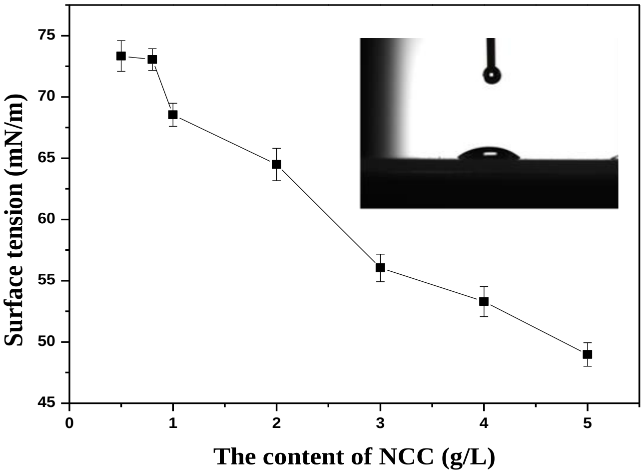

Fig. 3. Effect of NCC content on Pickering emulsion particle size

Determination of Zeta Potential of NCC Suspension and Pickering Emulsions

The Pickering emulsions stabilized with NCC particles were obtained by ultrasonic and micro-emulsification with an o/w ratio of 10:90 in different amounts of NCC suspension. The zeta potential was measured, as shown in Fig. 4. With an increase in NCC content, the zeta (negative) potential, which is related to emulsion stability, increased gradually. A higher absolute value of zeta potential results in a more stable system (Yin *et al.* 2009; Shariffa *et al.* 2016). The large number of negative charges were caused by the large amounts of hydroxyl radicals that formed on the surfaces of the cellulose nanoparticles during sulfation. The adsorption of the NCC on the surfaces of the droplets, and the zeta potential increased with the NCC content. Moreover, the repulsion between particles and the dispersion increased with the absolute value of the zeta potential. The zeta potential measured the potential of the stern layers on the particle surfaces, and the amount of charged particles indicated the stability of the system. Therefore, a higher absolute value of the zeta potential on the droplet surfaces indicated higher stability of the corresponding Pickering emulsion.

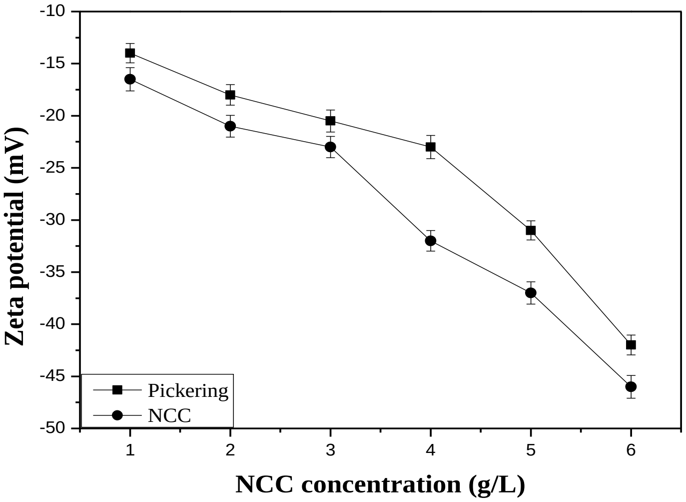

Fig. 4. Effect of NCC content on zeta potential of Pickering emulsion

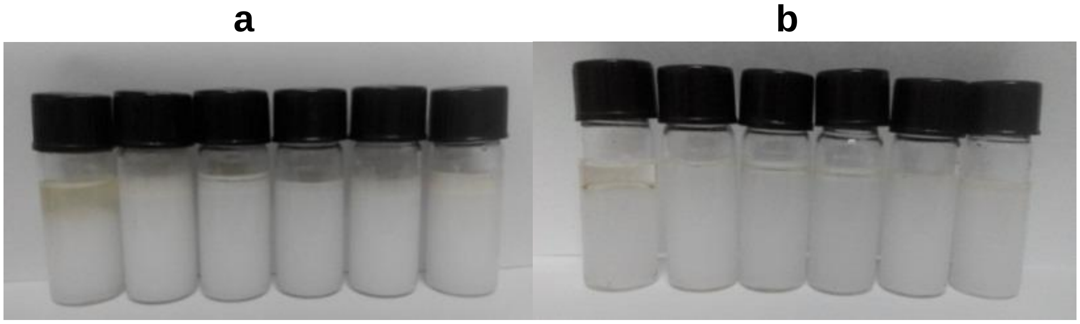

Fig. 5. Styrene/aqueous NCC o/w emulsion stability (a) before centrifugation and (b) after centrifugation at 4000 r/min for increasing NCC concentration in water phase

Stability of Pickering Emulsions

All Pickering emulsions showed no stratification during preparation, but 5 min after preparation, various degrees of stratification occurred. The stratification tended to stabilize after 24 h. There have been previous reports on the rapid delamination of Pickering emulsions stabilized by BC and starch particles in the early stages of preparation (Jia *et al.* 2013; Marefati *et al*. 2015). As shown in Fig. 5(a), NCC stationary styrene Pickering emulsion was stationary up to 20 d in the presence of ultrasonic and high-pressure homogenization. There was stratification only with 1% NCC content. The stability of the styrene Pickering stabilized with different amounts of NCC (1, 2, 3, 4, 5, and 6 g/L) was determined. Figure 5(b) depicts the styrene Pickering emulsion after centrifugation; the stability of the Pickering emulsion increased gradually with the NCC content. This finding suggests that the content of NCC affects the stability of the NCC Pickering emulsion. NCC first formed a layer or multi-layer compact membrane on the surface of the droplet to prevent the coalescence of droplets and then intertwined the fiber into the 2D network structure. A more compact network structure indicates a more stable Pickering emulsion (Nasser *et al.* 2015). Wen *et al*. (2014) concluded that when the content is low in the NCC stable D-limonene Pickering emulsion, the molecular interaction between NCC with weak network structure formation is weak, and the emulsion is not stable. However, with an increase in NCC content, the bonding force between particles increases, and the net structure is strengthened, which improves the stability of the emulsion.

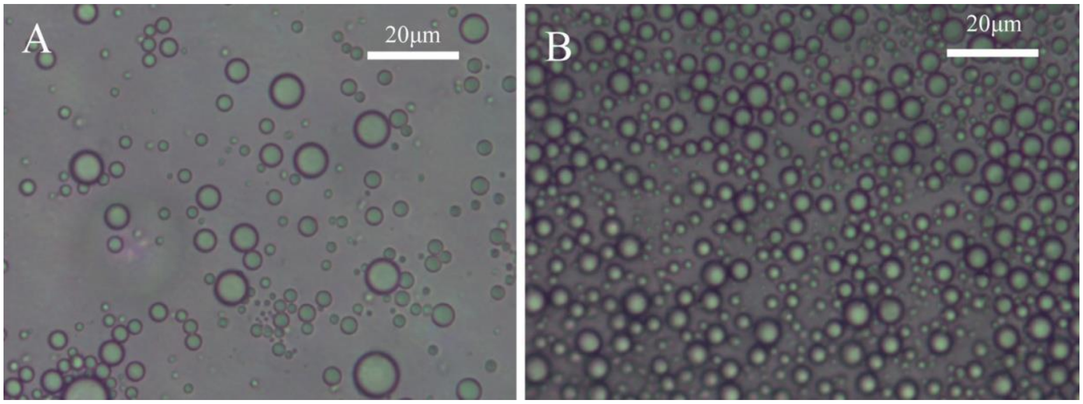

Fig. 6. Optical microscopy images of styrene Pickering emulsions prepared with (a) 1 g/L of NCC and (b) 3 g/L of NCC (o/w ratio of 1:9)

Microscopic View of Styrene Pickering Emulsion

Figure 6 shows the optical microscope morphology of the styrene Pickering emulsion droplets with an NCC content of 1 and 3 g/L and illustrates that the styrene monomer is dispersed into small droplets and the NCC is covered on the droplet surfaces. The particle size of the droplets of the 3 g/L NCC stabilized Pickering emulsion (Fig. 6(b) was significantly lower than that of the stable Pickering emulsion (1 g/L) in Fig. 6(a). The effects of the different levels of NCC on the particle size of the emulsion were determined by the particle size distribution curve of the styrene Pickering emulsion (Fig. 2). With an increase in NCC content, the particle size of the dispersed droplets of styrene was gradually reduced. As shown in Fig. 5, with an increase in NCC content, the stability of the emulsion was enhanced and the stability of the small droplets can be higher than that of the large droplets. Combined with the styrene Pickering emulsion particle size distribution shown in Fig. 2, the stability depicted in Fig. 5, and the optical microscope morphology illustrated in Fig. 6, it is apparent that the particle size and stability of the emulsion droplets were affected by NCC content.

Where there was an increase in NCC content, the particle size of the Pickering emulsion droplets gradually decreased and the stability gradually increased. Bortnowska *et al.* (2014) reported that when pre-gelatinized corn starch stabilizes an o/w Pickering emulsion, the droplet size increases with the amount of starch due to the non-covalent effect of starch molecules. Kalashnikova *et al.* (2011) reported that when NCC stabilizes a styrene Pickering emulsion, the resistance of the emulsion to coalescence increases due to its dense cellulosic film and compact fibrous network, which indicates that the particle diameter of the emulsion droplets decreases with increasing NCC content. The solid NCC particle-stabilized Pickering emulsion had better stability, lower foaming properties, less solid particulate stabilizer, and was more environmentally friendly than emulsions formed by conventional surfactants. Therefore, this stabilized emulsion had better prospects in the field of emulsification.

Effect of Different NCC Contents on Sizing Degree and Conversion Rate of Styrene Pickering Emulsion

Figure 7 shows that the sizing degree increased first and then decreased with an increase in NCC content. The sizing degree reached approximately 42 s when the NCC content was approximately 3% to 4%. The stability of the styrene polymer emulsion was mainly caused by the solid particle stabilizer on the droplet surfaces, which formed a 2D mesh structure that suppressed the emulsion droplets between mutual coalescence and achieved stability. Figure 7 shows that when the NCC content was small, the surface tension was large, the wettability of the droplet surface was poor, the adsorption capacity of the solid particles on the droplet surface was low, and the number of solid particles was not sufficient to cover all of the latex particles. Consequently, the interaction among the solid particles was weak and the droplets easily collided and agglomerated, which increased the Pickering emulsion particle size.

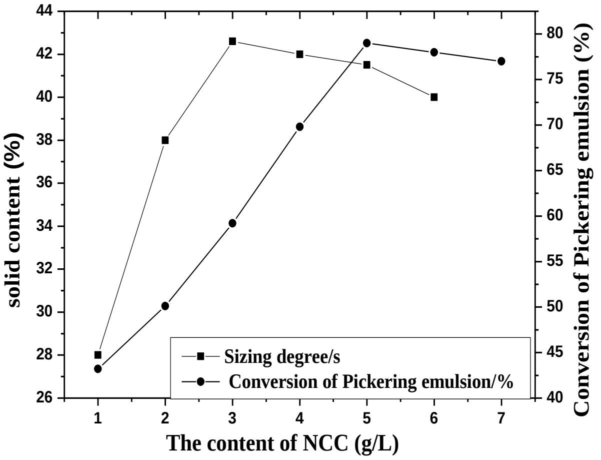

Fig. 7. Effect of NCC content on sizing degree and conversion rate of styrene polymer emulsion

However, the large particle size of the pre-polymerization Pickering emulsion was not conducive to penetration and film formation of the polymer on the paper surface. Thus, the paper sizing was low and water resistance was poor. With an increase in NCC content, the surface tension of the NCC solution decreased and the wettability, adsorption capacity, and the coating capacity of the solid particles on the droplet surfaces increased. Consequently, the particles on the interface could form a stable network structure, thereby stabilizing the system. The Pickering emulsion particle size was reduced, which accelerated the penetration and film formation of the polymer on the surface of the paper, increased the paper sizing, and enhanced the water resistance.

As depicted in Fig. 7, the conversion of the polymer emulsion increased with the NCC content. When the NCC content exceeded 5 g/L, the conversion rate of approximately 80% did not change considerably. This finding reflects that the Pickering emulsion showed varying degrees of static time with varying degrees of instability. During the formation of the Pickering emulsion, NCC acted as an emulsifying and dispersing monomer droplet. As shown in Figs. 2 and 6, when the NCC content was small, the emulsifying and dispersing effects were weak, and the monomer droplets were large. The larger monomer droplets were prone to instability, which would result in flocculation, affect the polymerization of the droplets, and consequently decrease the conversion of styrene polymerization. However, with an increase in NCC content, the particle size of the monomer droplets gradually decreased. Its dense cellulose membrane and compact fiber network structure increased the emulsion agglomeration resistance, the emulsion increasingly stabilized, and the degree of polymerization of the styrene droplets under the action of the initiator increased. However, an increase in NCC content would only be in the form of free suspension in aqueous solution. An excessive amount of NCC could not achieve emulsification and dispersion. Thus, the styrene monomer (as initiator) could not polymerize and the change of conversion rate was not noticeable.

Analysis of Infrared Spectrum of Styrene Polymer Emulsion

Figure 8 shows the infrared spectrum of the styrene polymer emulsion. There was a skeleton vibration peak of the benzene ring at 1601 cm^{-1}. Within the range of approximately 3030 cm^{-1} to 3125 cm^{-1}, there were three or four peaks, which are the characteristic peaks of the benzene ring. A stretching vibration peak of C=C was present at 3025 cm^{-1}. These observations indicated the existence of benzene rings and double bonds in polymers. The absorption peak of the NCC was at approximately 3439 cm^{-1}, and this position indicated a stretching vibration peak of alcohol hydroxyl in the NCC. NCC had absorption peak of C=O at approximately 1710 cm^{-1}, and the presence of these absorption peaks in 1493 and 1452 cm^{-1} indicated that the NCC was a cellulose I type. The infrared spectrum of the styrene polymer emulsion showed that a simple physical adsorption occurred between the styrene and the NCC, and no new chemical bonds or other polymerization occurred. Thus, the effect of the NCC was only stability and emulsification.

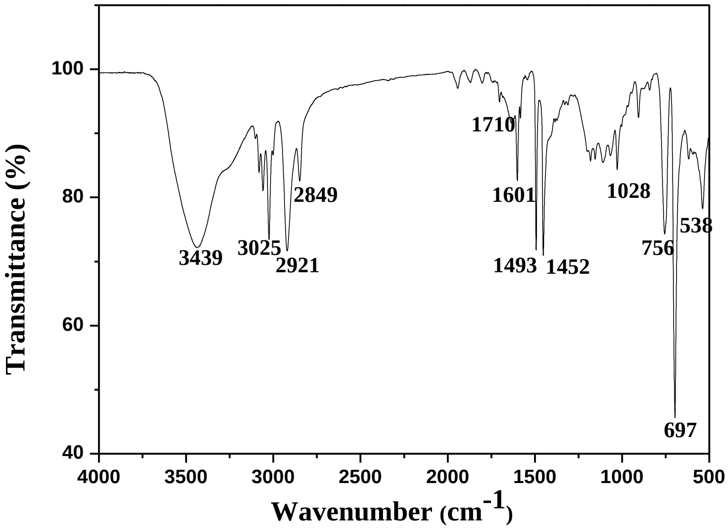

Fig. 8. Infrared spectrum of styrene polymer emulsion

SEM Diagram of Styrene Polymerization Emulsion

As shown in Fig. 9, NCC formed a network structure adsorbed on the droplet surfaces. Moreover, NCC was bent on the spherical surface of the styrene, which stabilized the emulsion and showed that the NCC was flexible enough to bend on the spherical surface to stabilize the emulsion (Wei 2015).

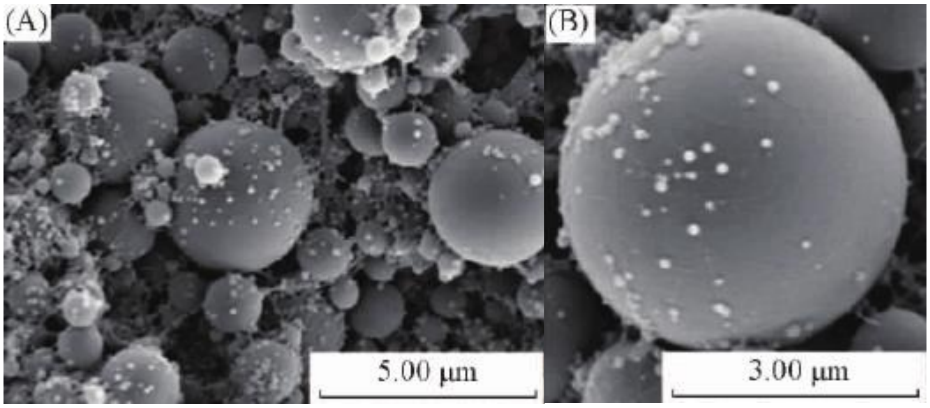

Fig. 9. SEM image of NCC on polystyrene surface

Dilution and Ca^{2+} Stability of Styrene Polymer Emulsion

As shown in Table 1, when the Pickering emulsion obtained by polymerization of NCC (as solid particle stabilizer) was tested for dilution and Ca^{2+} stability, there was slight flocculation when the content of NCC was 1 g/L. With an increase in NCC content, the stability of the Pickering emulsion increased but no delamination occurred. The increase in NCC content improved the stability of the styrene copolymer emulsion possibly because the NCC played the role of emulsifying and dispersing monomer droplets in the process of pre emulsification, and it could adsorb on droplet indication and form the 2D network structure, which prevents droplet coalescence and achieving stability. When the NCC content was low, it was not sufficient to adsorb completely on the droplet surfaces. Thus, the emulsion was unstable. However, with an increase in NCC content, the amount of NCC adsorbed on the droplet surfaces and the bonding force between the particles increased. Thus, the network structure was strengthened, and improved the emulsion stability (Kalashnikova *et al.* 2011).

Table 1. Effect of NCC Dosage on Emulsion Stability

Dosage of NCC	1 g/L	2 g/L	3 g/L	4 g/L	5 g/L
Dilution stability	Not stratified and slightly flocculated	Not stratified, stable	Not stratified, stable	Not stratified, stable	Not stratified, stable
Ca^{2+} stability	Not stratified and slightly flocculated	Not stratified, stable	Not stratified, stable	Not stratified, stable	Not stratified, stable

CONCLUSIONS

1. Nanocrystalline cellulose (NCC) was prepared through the sulfuric acid hydrolysis of a microcrystalline cellulose. The average grain size was approximately 187 nm, the yield was 56.0%, and the particle size distribution coefficient PDI value was 0.394. NCC prepared by hydrolysis of sulphuric acid was used as a solid particle to emulsify the styrene monomer, and a Pickering emulsion was obtained that was stable for 20 d. The emulsion ratio stabilized at approximately 0.7.

2. The styrene emulsion was polymerized using ammonium persulfate, and the monomer conversion rate was approximately 80%. An SEM analysis of the styrene emulsion showed that on the droplet surfaces, the NCC formed a network structure and was adsorbed. An infrared spectrum analysis showed that a simple physical adsorption occurred between the styrene and the NCC, but no new chemical bonds and other polymerization were found. Measurements of the emulsion and Ca^{2+} stability showed that flocculation occurred only at 1 g/L. With an increase in NCC content, the stability of the styrene polymerization Pickering emulsion increased and no stratification occurred. When the NCC content was approximately 3% to 4%, the maximum degree of sizing was approximately 42 s, indicating that the water resistance was improved.

ACKNOWLEDGMENTS

This work was supported by Shandong Provincial Natural Science Foundation of China (Grant No. ZR2017MC032), Open Fund of State Key Laboratory Base of Eco-Chemical Engineering (Grant No. KF1706), and Projects of College Students' Innovative and Entrepreneurial Training Plan (Grant No. 201710426031).

REFERENCES CITED

Asim, S., Wasim, M., Sabir, A., Shafiq, M., Andlib, H., Khuram, S., Ahmad, A., and Jamil, T. (2017). "The effect of nanocrystalline cellulose/gum arabic conjugates in crosslinked membrane for antibacterial, chlorine resistance and boron removal performance," *Journal of Hazardous Materials* 343, 68. DOI: 10.1016/j.jhazmat.2017.09.023

Binks, P., and Lumsdon, S. O. (2001). "Pickering emulsions stabilized by mono-disperse latex particles: Effects of particle size," *Langmuir* 17(15), 4540-4547. DOI: 10.1021/la0103822

Bortnowska, G., Balejko, J., Tokarczyk, G., Romanowska-Osuch, A., and Krzeminska, N. (2014). "Effects of pregelatinized waxy maize starch on the physicochemical properties and stability of model low-fat oil-in-water food emulsion," *Food Hydrocolloid* 36(2), 229-237. DOI: 10.1016/j.foodhyd .2013.09.012

GB/T 5405 (2002). "Paper – Determination of the sizing value (Liquid permeance method)," Standardization Administration of China, Beijing, China.

GB/T 6040 (2002). "General rules for infrared analysis," Standardization Administration of China, Beijing, China.

Jia, Y. Y., Wan, T., Huo, M. M., and Zhou, Y.-L. (2013). "Stabilization of oil/water emulsions by microfibrillized bacterial cellulose," *Chemical Journal of Chinese Universities-Chinese* 34(6), 1475-1482. DOI: 10.7503/cjcu20120935

Kalashnikova, I., Bizot, H., Cathala, B., and Capron, I. (2011). "New Pickering emulsions stabilized by bacterial cellulose nanocrystals," *Langmuir* 27(12), 7471-7479. DOI: 10.1021/la200971f

Marefati, A ., Sjöö, M ., Timgren, A., Dejmec, P., and Rayner, M. (2015). "Fabrication of encapsulated oil powders from starch granule stabilized W/O/W Pickering emulsions by freeze-drying," *Food Hydrocolloids* 51, 261-271. DOI: 10.1016/j.foodhyd.2015.04.022

Nasser, N., Nader, T. Q., and Yulin, D. (2015). "Surfactant free Pickering emulsion polymerization of styrene in w/o/w system using cellulose nanofibrils," *European Polymer Journal* 64, 179-188. DOI: 10.1016/j.eurpolymj.2015.01.007

Shariffa, Y. N., Tan, T. B., Abas, F., Mirhosseini, H., Nehdi, I. A., and Tan, C. P. (2016). "Producing a lycopene nanodispersion: The effects of emulsifiers," *Food & Bioproducts Processing* 98, 210-216. DOI:10.1016/j.fbp.2016.01.014

Wei, F. (2015). *Study on Pickering Emulsions Stabilized by Bacterial Cellulose Nanofibrils*, Master's Thesis, Tianjin University of Science & Technology, China.

Wen, C. X., Yuan, Q., Liang, H., and Vriesekoop, F. (2014). "Preparation and stabilization of D-limonene Pickering emulsions by cellulose nanocrystals," *Carbohydrate Polymers* 112(2), 695-700. DOI: 10.1016/j.carbpol.2014.06.051

Yin, L. J., Chu, B.-S., Kobayashi, I., and Nakajima, M. (2009). "Performance of selected emulsifiers and their combinations in the preparation of β-carotene nanodispersions,"*Food Hydrocolloids* 23(6), 1617-1622. DOI:10.1016/j.foodhyd.2008.12.005

Article submitted: January 15, 2018; Peer review completed: March 5, 2018; Revised version received and accepted; March 22, 2018; Published: April 20, 2018.
DOI: 10.15376/biores.13.2.4132-4144