

Research Article

Size Controlled Synthesis of Starch Nanoparticles by a Microemulsion Method

Suk Fun Chin, Aressa Azman, and Suh Cem Pang

Department of Chemistry, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak,
94300 Kota Samarahan, Sarawak, Malaysia

Correspondence should be addressed to Suk Fun Chin; sukfunchin@gmail.com

Received 14 June 2013; Revised 14 October 2013; Accepted 15 October 2013; Published 2 January 2014

Academic Editor: Santanu K. Maiti

Copyright © 2014 Suk Fun Chin et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Controllable particles sizes of starch nanoparticles were synthesized via a precipitation in water-in-oil microemulsion approach. Microemulsion method offers the advantages of ultralow interfacial tension, large interfacial area, and being thermodynamically stable and affords monodispersed nanoparticles. The synthesis parameters such as stirring rates, ratios of oil/cosurfactant, oil phases, cosurfactants, and ratios of water/oil were found to affect the mean particle size of starch nanoparticles. Starch nanoparticles with mean particles sizes of 109 nm were synthesized by direct nanoprecipitation method, whereas by using precipitation in microemulsion approach, starch nanoparticles with smaller mean particles sizes of 83 nm were obtained.

1. Introduction

Starch is one of the most commonly used biopolymers in industries because of nontoxicity, biodegradability, biocompatibility, low cost, and being renewable and abundantly available in nature [1–3]. There is a growing interest in making use of starch as precursor material for synthesizing starch-based nanoparticles for various biomedical and industry applications such as drug delivery carriers [4–7], plastic fillers [8], and biodegradable packaging materials [6, 9, 10].

Various synthetic methods for synthesis of starch nanoparticles such as high-pressure homogenization and miniemulsion cross-linking [11], nanoprecipitation [2, 12, 13], emulsion [14, 15], and microemulsion [16–18] have been explored by researchers. High-pressure homogenization is a simple technique and useful for diluted and concentrated samples; however it requires high number of homogenization cycles and possible contamination of product could occur from metal ions coming off from the wall of the homogenizers [19]. Nanoprecipitation method is a favorable method as it is very simple and straightforward method. However, in order to avoid nanoparticles aggregate formation during the precipitation process, only very low concentration of starting materials can be used [13] and large amount of nonsolvent was required in order to obtain spherical shape nanoparticles [2].

Interest in using microemulsion for nanoparticles synthesis arises mainly from the versatile nature of microemulsion system such as mild reaction conditions, simple procedure [20], cost effectiveness, and formation of very small droplet size [21–24]. Besides, microemulsion route is known to be one of the most efficient methods for stabilization of nanodroplets and controlling of particle size, morphology, and homogeneity [20, 22]. Components of microemulsion consist of water (polar phase), hydrocarbon or oil (nonpolar phase), surfactant, and in other cases also cosurfactant (short chain alcohol) [25, 26]. Normally, surfactant and cosurfactant (such as alcohol) are required for stable nanodispersions of fluids formation [20, 27].

In this work, starch nanoparticles with controllable particle size were prepared by precipitation of locally available native sago starch (*Metroxylon sagu*) solution in a water-in-oil microemulsion system. Various synthesis conditions such as stirring rates, ratios of oil/cosurfactant, types of oil phases, cosurfactants, and ratios of water/oil were found to significantly affect the particle size of starch nanoparticles.

2. Materials and Methods

2.1. Materials. Native sago (*Metroxylon sagu*) starch powder, olein palm oil, and sunflower oil (high in monosaturated

fatty acids and low in saturated fatty acids) were purchased from local market at Kuching (Sarawak, Malaysia). Hexane was supplied from PC Laboratory Reagent, while oleic acid was supplied from R&M Marketing (Essex, UK). Propanol and butanol were obtained from Fisher Scientific (Loughborough, UK). Sodium hydroxide and methanol were obtained from Merck (Darmstadt, Germany), Span 60 was received from Merck (Hohenbrunn, Germany), cyclohexane, acetone, ethanol absolute, and n-butanol were purchased from HmbG Chemicals (Hamburg, Germany), and ultrapure water (18.2 M Ω) was obtained from a Water Purifying System (ELGA, Ultra Genetic). All chemicals were used as received without further purification.

2.2. Preparation of Starch Solution. 1% (w/v) starch solution was prepared by dissolution of 0.5 g native sago starch powder in 50 mL of 0.5 M NaOH solution. The mixture was heated to 80°C in a water bath for 1 hr with magnetic stirring until all starch powder was completely dissolved and homogeneous starch solution was obtained. This starch solution was then cooled to room temperature.

2.3. Preparation of Starch Nanoparticles

2.3.1. Nanoprecipitation without Microemulsion System. Starch nanoparticles were formed when 1 mL of starch solution was added dropwise into 20 mL of absolute ethanol solution. The same procedure was repeated by varying the stirring rates (300 rpm, 600 rpm, and 900 rpm) and magnetic stirring for 1 hr in order to investigate the effect of stirring rates on the particle size and morphology of starch nanoparticles.

2.3.2. Nanoprecipitation in Water-in-Oil (W/O) Microemulsion System. 1 mL of starch solution was added dropwise to an oil phase (15 mL of cyclohexane, 5 mL of ethanol, and certain amount of surfactant) with magnetic stirring at 900 rpm for 1 hr. The same procedure was repeated by varying the surfactants concentrations, ratios of oil/cosurfactant, oil phases (hexane, olein palm oil, sunflower oil, and oleic acid), cosurfactants (methanol, propanol, butanol, and acetone), and ratios of water/oil.

2.4. Characterization of Samples. The morphologies of samples were observed by using a scanning electron microscope (SEM) (JOEL JSM-6390 LA). The mean particles sizes of around 100 starch nanoparticles were measured randomly using SmileView software.

3. Results and Discussion

3.1. Dissolution of Starch. 0.5 M of sodium hydroxide (NaOH) was used to completely dissolve the native sago starch powder into aqueous solution with constant magnetic stirring. The dissolution of starch was carried out at 80°C in order to ensure complete solubilization of starch granules. Dissolution of starch was achieved by disrupting the starch granule to release the starch molecules into the solution. NaOH has commonly been used for dissolution of starch [28]. NaOH plays an important role to break the

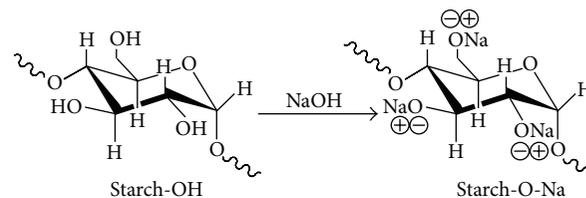


FIGURE 1: Schematic representation of alkalization reaction between starch and sodium hydroxide.

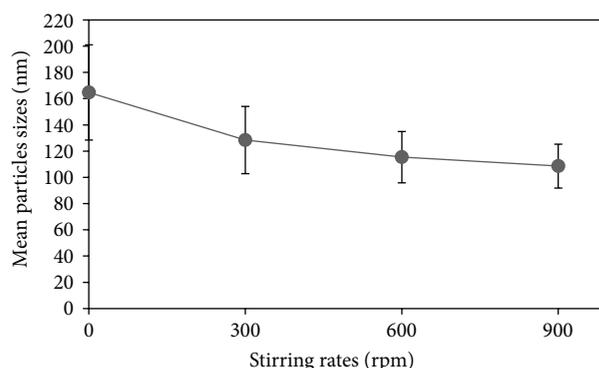


FIGURE 2: Effects of stirring rates on particles size of starch nanoparticles.

intermolecular and intramolecular hydrogen bonding between the water and starch molecules resulting in the disruption of molecular orders within the starch granule [29] thus enhancing water solubility of starch [30]. NaOH reacted with the hydroxyl groups (OH) of the starch molecules and transformed the molecules into sodium starch alkoxide (Starch-O-Na) [31], as shown in Figure 1.

3.2. Nanoprecipitation without Microemulsion System

3.2.1. Effect of Stirring Rates. Figure 2 shows effects of stirring rates on mean particles sizes of starch nanoparticles synthesized by direct nanoprecipitation of starch solution into ethanol solution. It was observed that the particle size of starch nanoparticles was affected by the stirring rates during the synthesis as evidenced by the reduction of mean particle size from 165 to 109 nm, as stirring rate increased to 900 rpm. This trend can be explained by the energy transfer differences for the different stirring rates as increasing the stirring rates has increased the energy transferred to the suspension medium which caused the reaction solution to disperse into smaller droplets and reduced the particle size [32]. For stirring rate higher than 900 rpm, bubbles were generated and splashing of the solution was observed.

As shown in Figure 3(a), native sago starch particles were observed to consist mostly of large, oval granular shape with smooth surface in range of diameter size around 20–40 μ m. Dissolving this native starch into aqueous solution and reprecipitating the starch solution into ethanol have converted the microsized starch granules into nanoparticles. Thus, nanoprecipitation technique was accessible for the

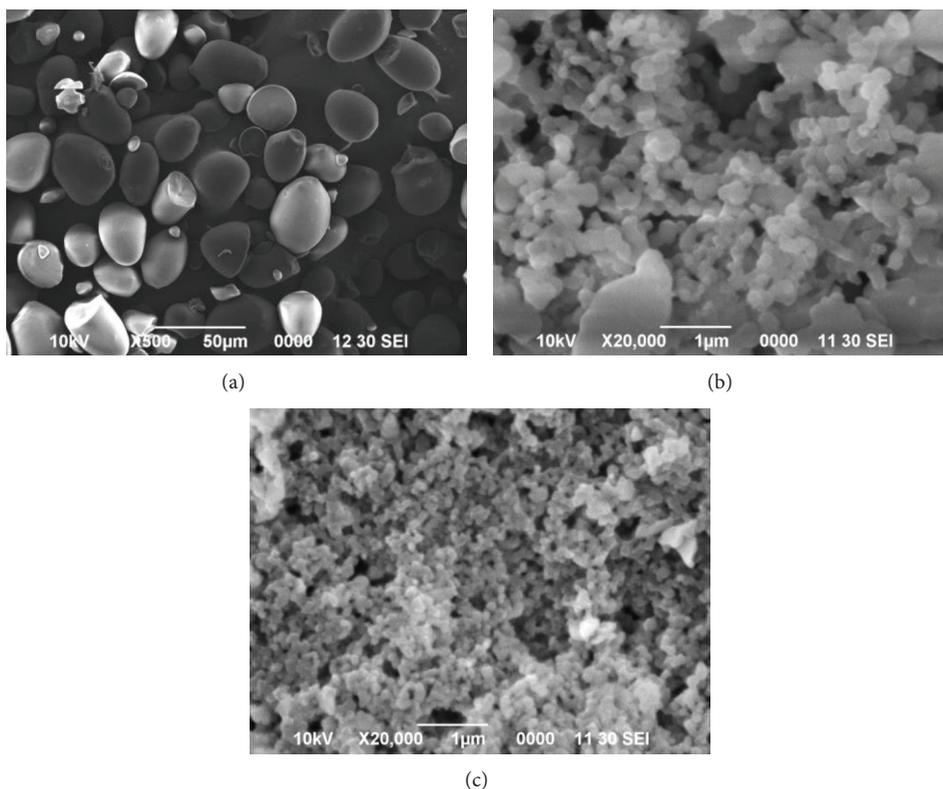


FIGURE 3: SEM micrographs of (a) native sago starch; starch nanoparticles prepared (b) without stirring; and (c) with stirring rate at 900 rpm.

nanoparticle formation. The stirring rate was also found to affect the morphology of starch nanoparticles as more aggregated and wider particle size distribution nanoparticles were produced without stirring (Figure 3(b)) as compared to when stirring was used during the synthesis (Figure 3(c)). At low stirring rates, the nucleation species were not dispersed uniformly throughout the solution thus leading to agglomeration of particles compared to higher stirring rates which gave rise to more uniform, homogeneous dispersion and smaller nanoparticles due to enhanced mobility of nucleated species in the reaction solution [33].

3.3. Nanoprecipitation in Microemulsion System

3.3.1. Effect of Surfactant Concentrations. The effects of surfactant concentrations on the particles sizes of starch nanoparticles were investigated by using various concentrations of span 60 (3:1 ratio of cyclohexane and ethanol) as shown in Figure 4. The mean particles sizes of starch nanoparticles decreased from 140 to 96 nm as the concentration of span 60 increases up to 3% (w/v). However, further increase of span 60 concentration from 5 to 9% (w/v) did not significantly affect the particles sizes. Smallest particle size was achieved at 3% (w/v) of span 60 concentration.

In the presence of surfactant, the particle sizes of starch nanoparticles sizes were observed to decrease since surfactant reduced the interfacial tension between oil and water phases and stabilized the dispersed phase against coalescence once it was formed [34]. However, 1% (w/v) of span 60 was not

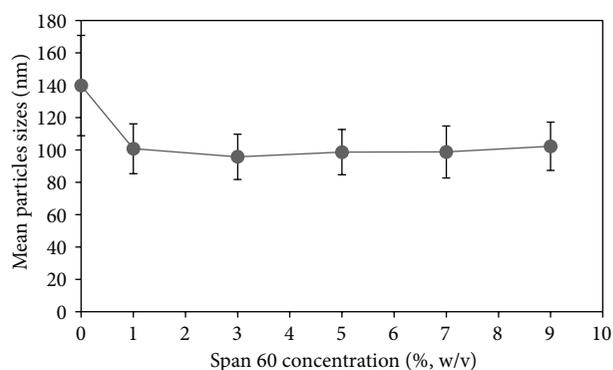


FIGURE 4: Effect of various span 60 concentrations on the mean particles sizes of starch nanoparticles.

enough to produce very small nanoparticles since the amount of surfactant was insufficient to cover the surface area of the droplets; therefore the droplet tends to aggregate to reduce the surface area [11]. The aggregated nanoparticles then fused with each other and slightly larger nanoparticles were formed. 3% (w/v) of span 60 has produced smaller particles sizes of starch nanoparticles with more discrete nanoparticles due to optimum amount of span 60 that has completely coated the entire surface area of droplets and gave high stability against droplets coalescence and thus generated smaller droplet size [11]. Besides, more monodispersed particles were obtained

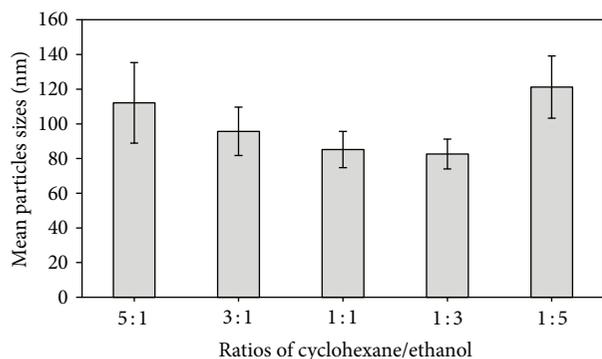


FIGURE 5: Effect of various ratios of cyclohexane/ethanol on the mean particles sizes of starch nanoparticles.

due to the surfactant layer that created the steric stabilization which prevented the aggregation of nanoparticles [22] besides providing tridimensional stabilization of the system [35]. At the surfactant concentration above 3% (w/v), all surfaces of nanoparticles were completely covered by the surfactant and the nanoparticles were fully stabilized; thus the particle sizes would remain almost constant.

3.3.2. Effect of Oil/Cosurfactant Ratios. As can be observed from Figure 5, increasing the amount of ethanol (cosurfactant) up to 1:3 cyclohexane/ethanol could reduce the particles sizes of starch nanoparticles from 112 nm to 83 nm. The observed decrease in mean particle size of nanoparticles could be attributed to sufficient amount of ethanol having reduced the interfacial tension of the microemulsion system and the radius of the droplets [35]. Starch nanoparticles obtained from 1:3 ratio of cyclohexane/ethanol were more homogeneous in nature as can be inferred from smaller range of standard deviation compared to others ratios which gave greater range of standard deviation that indicated the particles were nonhomogeneously distributed. Increase of cosurfactant partition has resulted in increase of the fluidity of the interface and thus increased the kinetics of the intermolecular exchange and gave more homogeneous repartition of microemulsion droplets [36] which, in turn, resulted in the homogeneous distribution of starch nanoparticles.

However, increase of cosurfactant up to 1:5 ratio of cyclohexane/ethanol resulted in larger particle size of around 121 nm due to dilution effect of microemulsion as high cosurfactant volume led to destruction of the microemulsion droplets [37, 38]. Besides, if amount of ethanol present was too small such as in 5:1 ratio of cyclohexane/ethanol system, the particles sizes of starch nanoparticles grew larger because small amount of ethanol as cosolvent might not mix uniformly in the bulk of the oil phase [39]. Higher oil content in the microemulsion system was not required to produce smaller particle size. Thus, 1:3 ratio of cyclohexane/ethanol was preferred for formulation of microemulsion system for synthesis of smaller sizes of starch nanoparticles.

3.3.3. Effect of Types of Oil Phases. Figure 6 presents the mean particle size of starch nanoparticles prepared in various types

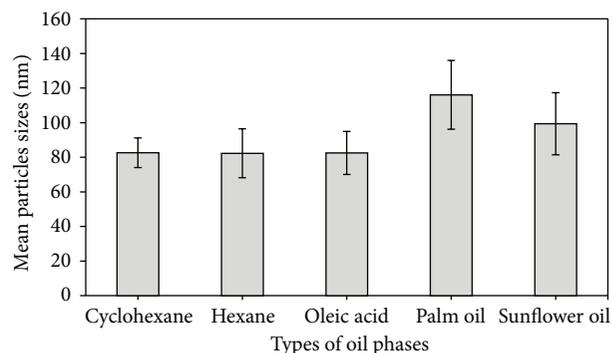


FIGURE 6: Effect of types of oil phases on the mean particles sizes of starch nanoparticles.

of oil phases (cyclohexane, hexane, oleic acid, olein palm oil, and sunflower oil) and in 1:3 ratio of oil/ethanol system with 3% (w/v) of span 60. It was observed that smaller starch nanoparticles were obtained when cyclohexane, hexane, and oleic acid were used as the oil phase, as compared to palm oil and sunflower oil. As can be seen in Figure 7, these three types of oil phase (cyclohexane, hexane, and oleic acid) gave almost similar particle sizes of starch nanoparticles; however their morphologies were greatly distinct.

Starch nanoparticles prepared using cyclohexane and hexane produced smaller nanoparticles; however the particles were observed to be more aggregated. When oleic acid was used, more monodispersed and discrete nanoparticles were formed due to the more hydrophobic nature of oleic acid. However, oil with excessive long hydrocarbon chains or high molecular weight such as palm oil and sunflower oil was difficult to microemulsify [40]. Thus, the system was not optically clear and stable as the water droplets become much larger [41]; this, in turn, has resulted in larger particles with wider particles sizes distribution.

3.3.4. Effect of Types of Cosurfactants. Figure 8 shows the mean particles sizes of starch nanoparticles synthesized using various types of cosurfactants, namely, methanol, ethanol, propanol, butanol, and acetone in 1:3 ratio of oleic acid/cosurfactant with 3% (w/v) span 60. Starch nanoparticles prepared in methanol and ethanol produced smaller particles with mean particles sizes of 84 and 83 nm, respectively, as compared to those prepared with propanol, butanol, and acetone. It was observed that when n-propanol and n-butanol were used, starch nanoparticles obtained were more discrete; however the particles sizes distribution was very wide as shown in larger range of standard deviations.

Increase of alcohol chain used for synthesis has resulted in increase of the particles sizes of starch nanoparticles. This could be due to the lipophilicity of the cosurfactant that increased with the carbon chain length from propanol to butanol and the longer the alcohol chain, the less effective the cosurfactant because it is more soluble in the oil phase [39]. Furthermore, it was also due to the dielectric constants of longer aliphatic chain such as propanol and butanol that were lower than methanol, ethanol, and acetone thus resulting in

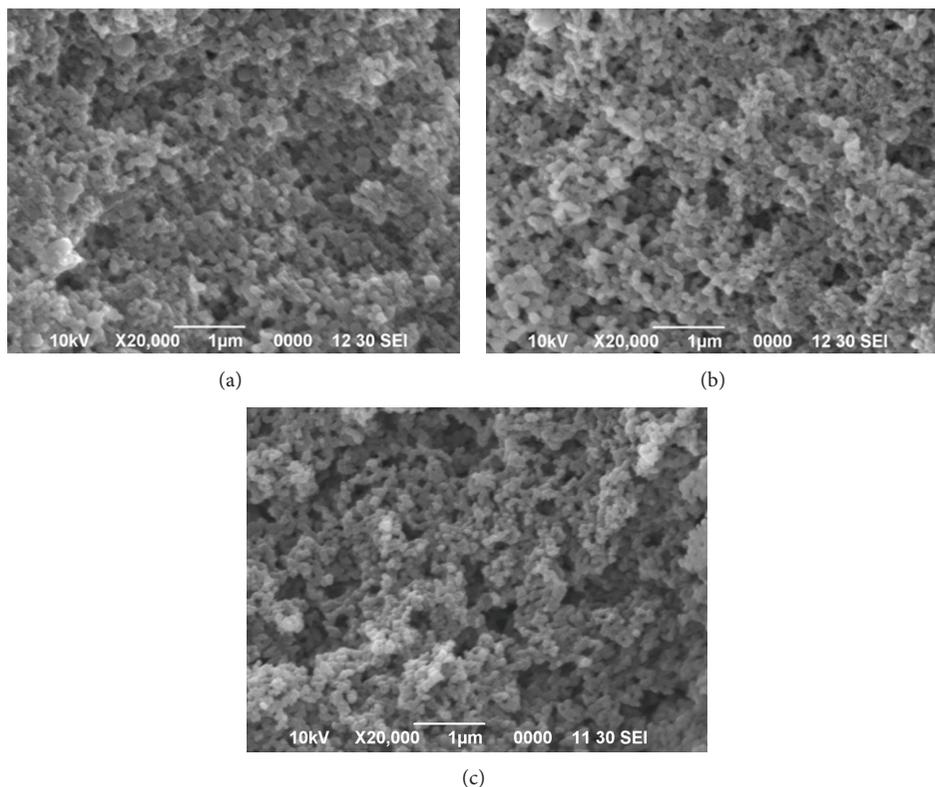


FIGURE 7: SEM micrographs of starch nanoparticles prepared in various oil phases: (a) cyclohexane, (b) hexane, and (c) oleic acid.

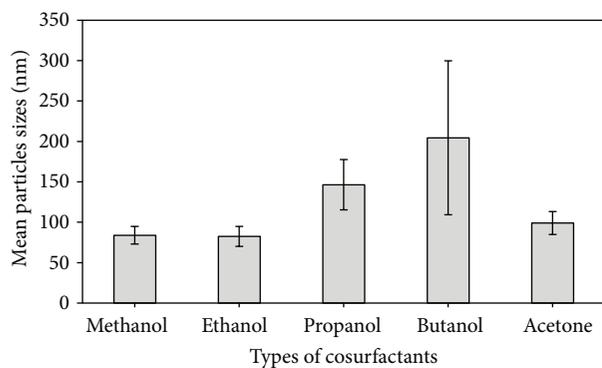


FIGURE 8: Effect of types of cosurfactants on the mean particles sizes of starch nanoparticles.

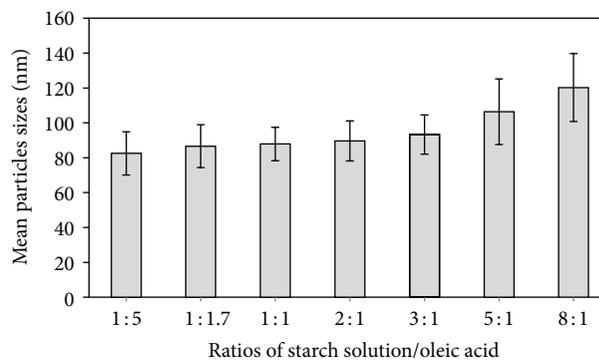


FIGURE 9: Effect of various ratios of starch solution/oleic acid on the mean particles sizes of starch nanoparticles.

larger particles sizes [42]. Although methanol and acetone also have high dielectric constant [43], ethanol was preferred amongst various cosurfactants because of less toxicity and giving the smallest particles sizes.

3.3.5. Effect of Water/Oil Ratios. Figure 9 illustrates the mean particle size of starch nanoparticles obtained at various ratios of starch solution to oleic acid at constant ratio of oleic acid/ethanol 1:3 system with 3% (w/v) span 60. The mean particles sizes were observed to increase when higher water content to oil ratio was used in microemulsion system. The mean particles sizes of nanoparticles have slightly increased

from 83 nm to 90 nm as the volume of starch solution increased up to double the amount of oil (2:1 ratio of starch solution/oleic acid). Subsequently increasing the ratio of starch solution/oleic acid to 8:1 in the microemulsion system drastically increased the mean particles sizes up to 120 nm with more aggregated and wider particles distributions.

For synthesis of smaller nanoparticles, it is essential to maintain low water/oil ratio as increase of water fraction in the microemulsion system would increase the particles sizes of starch nanoparticles due to reinforcement of the interfacial tension between water and oil in the microemulsion system [44]. At high water content, water droplets fused with each

other to form bigger microemulsion droplets which gave rise to larger starch nanoparticles.

4. Conclusions

Controllable particles sizes of starch nanoparticles were successfully synthesized by precipitation in microemulsion system under controlled conditions. All of the starch nanoparticles obtained were spherical in shape and have uniform particles sizes distribution. Direct nanoprecipitation method without microemulsion produced larger particle size in the range of 108.6 ± 16.7 nm, while in microemulsion system, smaller nanoparticles in the range of 82.5 ± 12.4 nm were obtained. This study demonstrated that particle size of starch nanoparticles can be controlled by judicious choice of the surfactants, stirring rates, cosurfactant, oil phases, compositions of oil/cosurfactants, and water/oil of the microemulsion system.

Disclosure

The authors of this paper have no direct financial relation with the commercial entities mentioned in this paper.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of the paper.

Acknowledgments

Financial support by Ministry of Higher Education (MOHE) Fundamental Research Grant Scheme (FRGS), Grant no. 01(17)746/2010(32), and MyBrain (My Master) Programme for graduate scholarship were gratefully acknowledged.

References

- [1] H. Y. Kim, J. H. Lee, J. Y. Kim, W. J. Lim, and S. T. Lim, "Characterization of nanoparticles prepared by acid hydrolysis of various starches," *Starch*, vol. 64, no. 5, pp. 367–373, 2012.
- [2] S. F. Chin, S. C. Pang, and S. H. Tay, "Size controlled synthesis of starch nanoparticles by a simple nanoprecipitation method," *Carbohydrate Polymers*, vol. 86, no. 4, pp. 1817–1819, 2011.
- [3] F. Geng, P. R. Chang, J. Yu, and X. Ma, "The fabrication and the properties of pretreated corn starch laurate," *Carbohydrate Polymers*, vol. 80, no. 2, pp. 361–366, 2010.
- [4] A. Rodrigues and M. Emeje, "Recent applications of starch derivatives in nanodrug delivery," *Carbohydrate Polymers*, vol. 87, no. 2, pp. 987–994, 2012.
- [5] J. Han, G. Borjihan, R. Bai, X. Chen, and X. Jing, "Synthesis and characterization of starch piperinic ester and its self-assembly of nanospheres," *Journal of Applied Polymer Science*, vol. 108, no. 1, pp. 523–528, 2008.
- [6] C. K. Simi and T. Emilia Abraham, "Hydrophobic grafted and cross-linked starch nanoparticles for drug delivery," *Bioprocess and Biosystems Engineering*, vol. 30, no. 3, pp. 173–180, 2007.
- [7] D. Yu, S. Xiao, C. Tong, L. Chen, and X. Liu, "Dialdehyde starch nanoparticles: preparation and application in drug carrier," *Chinese Science Bulletin*, vol. 52, no. 21, pp. 2913–2918, 2007.
- [8] J. Y. Kim and S. T. Lim, "Preparation of nano-sized starch particles by complex formation with n-butanol," *Carbohydrate Polymers*, vol. 76, no. 1, pp. 110–116, 2009.
- [9] H. Horchani, M. Chaàbouni, Y. Gargouri, and A. Sayari, "Solvent-free lipase-catalyzed synthesis of long-chain starch esters using microwave heating: optimization by response surface methodology," *Carbohydrate Polymers*, vol. 79, no. 2, pp. 466–474, 2010.
- [10] Q. Gong, L. Q. Wang, and K. Tu, "In situ polymerization of starch with lactic acid in aqueous solution and the microstructure characterization," *Carbohydrate Polymers*, vol. 64, no. 4, pp. 501–509, 2006.
- [11] A. M. Shi, D. Li, L. J. Wang, B. Z. Li, and B. Adhikari, "Preparation of starch-based nanoparticles through high-pressure homogenization and miniemulsion cross-linking: influence of various process parameters on particle size and stability," *Carbohydrate Polymers*, vol. 83, no. 4, pp. 1604–1610, 2011.
- [12] S. H. Tay, S. C. Pang, and S. F. Chin, "Facile synthesis of starch-maleate monoesters from native sago starch," *Carbohydrate Polymers*, vol. 88, no. 4, pp. 1195–1200, 2012.
- [13] C. Gavory, A. Durand, J. L. Six, C. Nouvel, E. Marie, and M. Leonard, "Polysaccharide-covered nanoparticles prepared by nanoprecipitation," *Carbohydrate Polymers*, vol. 84, no. 1, pp. 133–140, 2011.
- [14] C. A. Dai, C. J. Chang, H. Y. Chi, H. T. Chien, W. F. Su, and W. Y. Chiu, "Emulsion synthesis of nanoparticles containing PEDOT using conducting polymeric surfactant: synergy for colloid stability and intercalation doping," *Journal of Polymer Science A*, vol. 46, no. 7, pp. 2536–2548, 2008.
- [15] H. Y. Koo, S. T. Chang, W. S. Choi, J. H. Park, D. Y. Kim, and O. D. Velev, "Emulsion-based synthesis of reversibly swellable, magnetic nanoparticle-embedded polymer microcapsules," *Chemistry of Materials*, vol. 18, no. 14, pp. 3308–3313, 2006.
- [16] C. Tojo, M. de Dios, and F. Barroso, "Surfactant effects on microemulsion-based nanoparticle synthesis," *Materials*, vol. 4, no. 1, pp. 55–72, 2011.
- [17] M. Ethayaraja, K. Dutta, D. Muthukumaran, and R. Bandyopadhyaya, "Nanoparticle formation in water-in-oil microemulsions: experiments, mechanism, and Monte Carlo simulation," *Langmuir*, vol. 23, no. 6, pp. 3418–3423, 2007.
- [18] M. A. López-Quintela, "Synthesis of nanomaterials in microemulsions: formation mechanisms and growth control," *Current Opinion in Colloid and Interface Science*, vol. 8, no. 2, pp. 137–144, 2003.
- [19] J. Chingunpituk, "Nanosuspension technology for drug delivery," *Walailak Journal Science and Technology*, vol. 4, no. 2, pp. 139–153, 2007.
- [20] S. P. Moulik, A. K. Rakshit, and I. Capek, "Microemulsions as templates for nanomaterials," in *Microemulsions: Background, New Concepts, Applications, Perspectives*, C. Stubenrauch, Ed., p. 180, John Wiley & Sons, Chichester, UK, 2009.
- [21] J. P. Rao and K. E. Geckeler, "Polymer nanoparticles: preparation techniques and size-control parameters," *Progress in Polymer Science*, vol. 36, no. 7, pp. 887–913, 2011.
- [22] M. A. Malik, M. Y. Wani, and M. A. Hashim, "Microemulsion method: a novel route to synthesize organic and inorganic nanomaterials," *Arabian Journal of Chemistry*, vol. 5, no. 4, pp. 397–417, 2012.

- [23] S. Talegaonkar, A. Azeem, F. J. Ahmad, R. K. Khar, S. A. Pathan, and Z. I. Khan, "Microemulsions: a novel approach to enhanced drug delivery," *Recent Patents on Drug Delivery and Formulation*, vol. 2, no. 3, pp. 238–257, 2008.
- [24] F. Wang, B. Fang, Z. Zhang, S. Zhang, and Y. Chen, "The effect of alkanol chain on the interfacial composition and thermodynamic properties of diesel oil microemulsion," *Fuel*, vol. 87, no. 12, pp. 2517–2522, 2008.
- [25] R. Gannu, C. R. Palem, V. V. Yamsani, S. K. Yamsani, and M. R. Yamsani, "Enhanced bioavailability of lacidipine via microemulsion based transdermal gels: formulation optimization, ex vivo and in vivo characterization," *International Journal of Pharmaceutics*, vol. 388, no. 1-2, pp. 231–241, 2010.
- [26] R. Nagarajan and E. Ruckenstein, "Molecular theory of microemulsions," *Langmuir*, vol. 16, no. 16, pp. 6400–6415, 2000.
- [27] R. Dave and D. Madamwar, "Candida rugosa lipase immobilized in Triton-X100 microemulsion based organogels (MBGs) for ester synthesis," *Process Biochemistry*, vol. 43, no. 1, pp. 70–75, 2008.
- [28] M. B. Cardoso, J. L. Putaux, D. Samios, and N. P. da Silveira, "Influence of alkali concentration on the deproteinization and/or gelatinization of rice starch," *Carbohydrate Polymers*, vol. 70, no. 2, pp. 160–165, 2007.
- [29] K. Neelam, S. Vijay, and S. Lalit, "Various techniques for the modification of starch and the applications of its derivatives," *International Research Journal of Pharmacy*, vol. 3, no. 5, pp. 25–31, 2012.
- [30] J. A. Han and S. T. Lim, "Structural changes in corn starches during alkaline dissolution by vortexing," *Carbohydrate Polymers*, vol. 55, no. 2, pp. 193–199, 2004.
- [31] P. Rachtanapun, P. Simasatitkul, W. Chaiwan, and Y. Watthanasakun, "Effect of sodium hydroxide concentration on properties of carboxymethyl rice starch," *International Food Research Journal*, vol. 19, no. 3, pp. 923–931, 2012.
- [32] J. Sun, S. Zhou, P. Hou et al., "Synthesis and characterization of biocompatible Fe₃O₄ nanoparticles," *Journal of Biomedical Materials Research A*, vol. 80, no. 2, pp. 333–341, 2007.
- [33] U. S. Khan, N. S. Khattak, A. Rahman, and F. Khan, "Optimal method for preparation of magnetite nanoparticles," *Journal of the Chemical Society of Pakistan*, vol. 33, no. 5, pp. 628–633, 2011.
- [34] R. Pal, "Rheology of simple and multiple emulsions," *Current Opinion in Colloid and Interface Science*, vol. 16, no. 1, pp. 41–60, 2011.
- [35] Y. Sun, G. Guo, Z. Wang, and H. Guo, "Synthesis of single-crystal HAP nanorods," *Ceramics International*, vol. 32, no. 8, pp. 951–954, 2006.
- [36] M. A. López-Quintela, C. Tojo, M. C. Blanco, L. García Rio, and J. R. Leis, "Microemulsion dynamics and reactions in microemulsions," *Current Opinion in Colloid and Interface Science*, vol. 9, no. 3-4, pp. 264–278, 2004.
- [37] S. Hickey, S. A. Hagan, E. Kudryashov, and V. Buckin, "Analysis of phase diagram and microstructural transitions in an ethyl oleate/water/Tween 80/Span 20 microemulsion system using high-resolution ultrasonic spectroscopy," *International Journal of Pharmaceutics*, vol. 388, no. 1-2, pp. 213–222, 2010.
- [38] M. J. Lawrence and G. D. Rees, "Microemulsion-based media as novel drug delivery systems," *Advanced Drug Delivery Reviews*, vol. 45, no. 1, pp. 89–121, 2000.
- [39] J. L. Salager, R. Anton, A. Forgiarini, and L. Marquez, "Formulation of microemulsions," in *Microemulsions: Background, New Concepts, Applications, Perspectives*, C. Stubenrauch, Ed., pp. 105–106, John Wiley & Sons, Chichester, UK, 2009.
- [40] V. B. Patravale and A. A. Date, "Microemulsions: pharmaceutical applications," in *Microemulsions: Background, New Concepts, Applications, Perspectives*, C. Stubenrauch, Ed., pp. 259–266, John Wiley & Sons, 2009.
- [41] N. Savco, *The role of inverse nonionic microemulsion in the synthesis of SiO₂ nanoparticles [Ph.D. thesis]*, University of Trieste, Trieste, Italy, 2010.
- [42] S. Schubert, J. T. Delaney Jr., and U. S. Schubert, "Nanoprecipitation and nanoformulation of polymers: from history to powerful possibilities beyond poly(lactic acid)," *Soft Matter*, vol. 7, no. 5, pp. 1581–1588, 2011.
- [43] M. Mohsen-Nia, H. Amiri, and B. Jazi, "Dielectric constants of water, methanol, ethanol, butanol and acetone: measurement and computational study," *Journal of Solution Chemistry*, vol. 39, no. 5, pp. 701–708, 2010.
- [44] Y. Li, Y. Tan, Z. Ning, S. Sun, Y. Gao, and P. Wang, "Design and fabrication of fluorescein-labeled starch-based nanospheres," *Carbohydrate Polymers*, vol. 86, no. 1, pp. 291–295, 2011.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

