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Preparation and characterization of starch nanoparticles in ionic liquid-in-oil microemulsions system

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ABSTRACT

A novel ionic liquid microemulsion consisting of 1-octyl-3-methylimidazolium acetate ([Omim]Ac, an ionic liquid), native corn starch, surfactant TX-100, 1-butanol and cyclohexane was prepared. The ionic liquid-in-oil (IL/O), bicontinuous, and oil-in-ionic liquid (O/IL) microregions of the microemulsions were identified by conductivity measurements. The formation of IL/O microemulsion was confirmed by UV–vis spectrophotometry using the methyl orange (MO) as absorption probes and dynamic light scattering (DLS) analysis. Starch nanoparticles were prepared with epichlorohydrin as crosslinker through 3 h IL/O microemulsion-crosslinking reaction at 50 °C. The results of Fourier transform infrared spectroscopy (FTIR) demonstrated the formation of crosslinking bonds in starch molecules. Scanning electron microscope (SEM) data revealed that starch nanoparticles showed aggregation or cluster formation. Starch nanoparticles with a mean diameter of 96.9 nm and narrow size distribution were confirmed by the results of DLS.

1. Introduction

As a cheap, abundant and renewable natural material, starch has been modified through physical, chemical or enzymatic processes to improve its properties for many years (Malafaya et al., 2001; Raina et al., 2006). Various kinds of starch derivatives have been investigated, among which crosslinked starch microspheres show high stability towards swelling, high shear, high temperature and acidic conditions (Kim and Lee, 2002). Besides, crosslinked starch microspheres possess good performance in their total biodegradability, biocompatibility, stability on storage, cost-effectiveness as well as simple fabrication method (Mundargi et al., 2007). In view of the good properties, starch microspheres had been widely used in biology and medicine in many aspects. Several years ago, it was shown that starch microspheres possess unique features which suggest their use as an excipient for the manufacturing of controlled release solid drugs (Mundargi et al., 2007). Lately, Stertman et al. (2006) also discovered that starch microspheres could act as an effective adjuvant in biology and medicine. Nowadays, studies on starch microspheres as drug carriers tend to be a popular topic for their extensive use in medicine. However, the application of starch microspheres in drug delivery systems is not ideal due to their poor appearance in particle size and size distribution which mainly affect their adsorption and release properties. Therefore, the quality of starch microspheres is desperately expected to be improved in order for better application.

Several preparation approaches of starch microspheres have been investigated, such as precipitation, spray drying, solvent evaporation and emulsion-crosslinking technique, among which water-in-oil (W/O) emulsion-crosslinking technique has been extensively used. However, starch microspheres obtained from W/O emulsion-crosslinking approach still appears relatively big size. Fang et al. (2008) prepared starch microspheres with the average diameter of 19 μm through W/O emulsification-crosslinking method. Franssen and Hennink (1998) also preformed the preparation of starch microspheres with the volume mean diameter ranging from 2.5 μm to 25 μm through emulsion-crosslinking method. Starch nanoparticles (StNPs) are nano-sized (1–1000 nm in the pharmaceutical field) particulates of starch prepared by chemically crosslinking starch molecules with appropriate crosslinkers (Shi et al., 2011). However, researches on synthesis of starch nanoparticles have rarely been reported. Therefore, there is a strong incentive to develop a new strategy for the synthesis of starch nanoparticles and research their properties.

Room-temperature ionic liquids (ILs) have been considered as possible green and effective replacements for their unique properties, such as recyclability and designability (Sheldon, 2001; Welton, 1999). Progress in applying ILs into starch chemistry mainly focuses

Abbreviations: [Omim]Ac, 1-octyl-3-methylimidazolium acetate; DLS, dynamic light scattering; MO, methyl orange; FTIR, Fourier transform infrared spectroscopy; SEM, scanning electron microscopy; IL/O, ionic liquid-in-oil; O/IL, oil-in-ionic liquid; W/O, water-in-oil; [Bmim][BF_4], 1-butyl-3-methyl-imidazolium tetraflouroborate; ILs, ionic liquids; AGU, anhydroglucose units.

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on dissolution and esterification of starch (Lu et al., 2012; Luo and Zhou, 2012; Xie and Wang, 2011). However, researches on synthesis of starch microspheres in ILs system have rarely been reported, much less the starch nanoparticles. Recently, many documents showed that ILs could substitute polar phase, non-polar phase or surfactant to prepare ionic liquid microemulsions (Cheng et al., 2007, 2008; Gao et al., 2004; Yan and Texter, 2006). Meanwhile, many literatures also reported that ionic liquid microemulsions could be used as reaction system of the preparation of nanometer materials (Dixit et al., 1998; Gan et al., 1997; Qiu et al., 1999; Song and Kim, 1999; Zhang et al., 2009, 2012). However, there is no report about the preparation of starch nanoparticles in ionic liquid based on microemulsion system until now. Accordingly, it is essential to research on possibility of the preparation of starch nanoparticles in ionic liquid microemulsion reaction system.

In this study, 1-octyl-3-methylimidazolium acetate ([Omim]Ac)-starch/surfactant TX-100+1-butanol/cyclohexane microemulsions were prepared and investigated by phase behavior, conductivity measurements, UV–vis spectrophotometry and dynamic light scattering (DLS). Starch nanoparticles were prepared by [Omim]Ac-starch/cyclohexane microemulsion-crosslinking method with native corn starch as raw material, epichlorohydrin as a crosslinker. Starch nanoparticles were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and DLS. This work may provide an efficient pathway to prepare starch nanoparticles which could be expected to be well used in drug delivery system.

2. Materials and methods

2.1. Materials

Native corn starch was obtained from ChangChun DaCheng Corn Products Co. (Changchun, China) and dried at 50 °C for 24 h before using. 1-Octyl-3-methylimidazolium acetate ([Omim]Ac, >99%) was purchased from Lanzhou Institute of Chemical Physics (Lanzhou, China). All other chemicals were of analytical grade.

2.2. Preparation of ionic liquid microemulsions containing native corn starch

Dried corn starch (0.5 g) was added into [Omim]Ac (9.5 g) in a three-neck round flask which was continuously purged with gaseous N_2, and the starch concentration was kept at 5%. The mixture were stirred for homogeneous mixing and heated in an oil bath at 135 °C for 2.5 h. Subsequently, [Omim]Ac-starch (10 g) and cyclohexane (68.6 g) were added into the small beaker, and their masses were determined by an analytical balance (FA1104N, Shanghai Balance Instrument Co., Shanghai, China) with a resolution of 0.0001 g. The temperature was controlled by a thermostatic magnetic stirring apparatus (DF-II, Shanghai Yuzheng Instrument Co., Shanghai, China). After thermal equilibrium, the solution was then titrated by the mixture of TX-100 (35.1 g) and 1-butanol with the mass ratio of TX-100 to 1-butanol at 3:1 until the hierarchical and hazy liquid solution became transparent, which was indicative of the formation of the single phase.

2.3. Phase behavior and structure of ionic liquid microemulsion

2.3.1. Phase diagram determination

The pseudo-ternary phase diagram of the [Omim]Ac-starch/TX-100+1-butanol/cyclohexane system was determined at 25 °C by direct visual observation as described in Section 2.2. A series of microemulsions were prepared through changing the mass ratio of cyclohexane/[Omim]Ac-starch at 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, respectively. The corresponding composition of the solution was remarked as the phase boundary. Phase diagram could be used to characterize the system further and choose the proper reaction system for the preparation of starch nanoparticles.

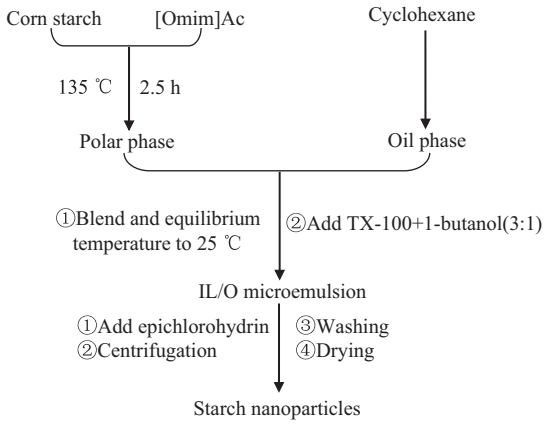

Fig. 1. Scheme of microemulsion-crosslinking reaction of starch.

2.3.2. Conductivity

Conductivity is frequently used to investigate structure and structural changes in microemulsions. Conductivity measurements were taken with a conductometer (DDSJ-308A, Shanghai Precision Scientific Instrument Co., Shanghai, China) at 1 kHz using a dip-type cell of cell constant 0.971 cm^{-1}. The errors in the conductivity measurements were ±0.5%. The cyclohexane was progressively added to the mixture of [Omim]Ac-starch, TX-100 and 1-butanol, and the conductivity was measured after thorough mixing and temperature equilibrium.

2.4. The formation of IL/O microemulsion

2.4.1. UV–vis spectrophotometry

UV–vis absorption spectroscopy is a powerful tool for characterizing the microenvironment of microemulsion. The UV–vis spectra were performed on a computer-controlled UV–vis spectrometer (TU-1901, PGENERAL Co., Beijing, China). The path length of the quartz cell used in this experiment was 1 cm. Operation process is as follows, appropriate amounts of methyl orange (MO) were mixed with measured ionic liquid microemulsions in advance and then added to the quartz cell. The experiments were carried out at room temperature.

2.4.2. Dynamic light scattering

Measurements were conducted using a particle size analyzer (Nano ZS, Malvern Instrument Ltd., Worcestershire, UK) at a wavelength of 633 nm. The scattering angle was set at 90°. Samples were maintained at 25.0 °C during the experiments.

2.5. Preparation of starch nanoparticles

Starch nanoparticles were prepared according to [Omim]Ac-starch/cyclohexane microemulsion-crosslinking method with native corn starch as raw material, epichlorohydrin as a crosslinker. The reaction scheme for crosslinked starch nanoparticles was depicted in Fig. 1. After [Omim]Ac-starch/cyclohexane microemulsion ($R = 0.21$, R represents $W_{[Omim]Ac\text{-}starch}/W_{TX\text{-}100+1\text{-}butanol}$) was obtained along line a, 2% (w:w) epichlorohydrin was added to the above microemulsion as a crosslinker. The mixture was stirred at the speed of 1200 rpm at 50 °C for 3 h. After the completion of the reaction, the reaction solution was cooled to room temperature and starch nanoparticles were subsequently precipitated with