

Preparation and Characterization of Amphiphilic Starch Nanocrystals

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ABSTRACT: In this article, amphiphilic starch nanocrystals were synthesized by graft copolymerization of starch nanocrystals with styrene in aqueous emulsion system. The starch nanocrystals of size around 50 nm were used, which were prepared by acid hydrolysis of corn starch. The structure of starch-g-polystyrene nanocrystals was characterized by Fourier transform infrared and ¹H nuclear magnetic resonance (¹H NMR). The crystalline structure as well as its particle morphology was studied by X-ray diffraction and scanning electron microscopy, respectively. The results indicated that the amphiphilic starch nanocrystals obtained

exhibit the size around 80–100 nm. Its crystalline structure is basically not changed after grafting polystyrene suggested that the polystyrene was essentially grafted on the surface of starch nanocrystals. Wettability experiments indicated that the prepared starch-g-polystyrene nanocrystals can be uniformly dispersed both in water phase and oil phase revealing excellent amphiphilicity. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 418–422, 2008

Key words: polysaccharides; graft copolymers; polystyrene; amphiphilic starch nanocrystals

INTRODUCTION

Starch is a natural polymer consisting of α -D glucose units.¹ Native starch occurs in the form of discrete and semi-crystalline microscopic granules. By submitting native starch to acid hydrolysis below the gelatinization temperature, the amorphous regions are hydrolyzed allowing the separation of crystalline residues.² Putaux et al.³ and Angellier et al.⁴ prepared starch nanocrystals by the acid hydrolysis of waxy starch using hydrochloric acid and sulfuric acid, respectively. The use of starch nanocrystals as reinforcing agents in polymer composites led to a desirable reinforcing effect. Angellier et al.⁵ substituted starch nanocrystals for carbon black as green fillers of natural rubber. When the content of starch nanocrystals was below 20 wt %, it had an obvious reinforcing effect as its weight concentration increased. However when the content was above 20 wt %, the reinforcing effect decreased instead. This is because the hydrophilic character of starch, attributed to abundant hydroxyl groups, decreases the interface compatibility between hydrophilic starch nanocrystal filler and hydrophobic rubber matrix. To

improve the hydrophobic character of starch nanocrystals for enhancing its compatibility with polymer matrix, amphiphilic starch nanocrystals were prepared and studied in this article.

In the past decades, various hydrophobic modifications of native starch have been developed, for example, hydroxypropyl starch,⁶ benzyl starch,⁷ and starch acetate.⁸ Amphiphilic starch nanocrystals can be prepared by introducing hydrophobic groups or polymer chains onto the polysaccharides backbone. Recently, Angellier et al.⁹ conducted chemical modification with starch nanocrystals using alkenyl succinic anhydride and phenyl isocyanate. Maybe because they are small molecular reagent, the hydrophobic modification is not remarkable. In this article styrene was graft copolymerized with starch nanocrystals to prepare amphiphilic starch nanocrystals.

EXPERIMENTAL

Materials

Corn starch, water content 14%, was the product of Beijing Hongxing starch company, China. Styrene, the product of Tianjin No. 1 chemical reagent factory and used as received. Potassium persulfate, sodium dodecylbenzene sulfonate, sulfuric acid, acetone, and toluene were all of analytical grade, produced by Beijing chemical reagent company, Distilled water was used for graft copolymerization.

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Preparation of amphiphilic starch nanocrystals

Preparation of starch nanocrystals: It was prepared by acid hydrolysis of native starch according to Angellier et al.⁴ Starch powder (36 g) were mixed with 250 mL of 2.87 mol/L sulfuric acid solution. The suspension was placed at 45°C hydrolyzed for 7 days under stirring, then washed successively by deionized water and centrifugation until neutrality. An ultrasonic treatment was then employed to ensure better dispersion of starch nanocrystals.

Preparation of starch-g-polystyrene nanocrystals: The preparation method used was similar to Cho and Lee.¹⁰ Emulsion polymerization was conducted in a 250-mL three-neck flask equipped with a magnetic stirrer and a condenser. Under magnetic stirring, suspension containing 2.0 g of starch nanocrystals (dry weight), 60 mL of deionized water, 2.0 g of styrene, 50 mg of NaHCO₃ were charged into the flask, and sparged further with nitrogen for 10 min at 40°C (bath temperature). 30 mg of sodium dodecylbenzene sulfonate and 2 mg of potassium persulfate were added. The reaction mixture was then heated to 70°C for 8 h. After cooled down to room temperature, several drops of acetone were added under stirring. The crude product starch-g-polystyrene nanocrystals were separated from emulsion by centrifugation and washed with deionized water. The polystyrene homopolymer as byproduct in crude product was isolated from graft copolymer by Soxhlet extraction with toluene for 24 h. Then the purified copolymer was dispersed in ethanol to get the emulsion of starch-g-polystyrene nanocrystals.

Characterization of starch-g-polystyrene nanocrystals

Fourier Transform Infrared (FTIR) spectra in the range of 400–4000 cm⁻¹ were recorded on FTIR TENSOR 27 spectra (Germany BRUKER). KBr pellet was used for sample preparation.

¹H NMR spectrum of starch nanocrystals and starch-g-polystyrene nanocrystals were collected on a Bruker AV400 spectrometer (Bruker AXS, Germany) at room temperature using DMSO-d₆ and DMSO-d₆/CDCl₃ as solvents respectively and tetramethylsilane as an internal reference.

Wide-angle X-ray diffraction data of starch nanocrystals before and after graft modification were obtained on Rigaku D/max-2500 X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu-K α radiation at 40 kV and 200 mA. The diffractograms were recorded at room temperature over the 2 θ range of 2–40°.

Microstructure and particle size of native starch and starch nanocrystals before and after grafting were observed by scanning electron microscope (SEM,

Japan Hitachi, S-4300F) with the highest distinguishability of 1.5 nm. The sample surface was first coated with a thin layer of gold.

RESULTS AND DISCUSSION

Discussion on graft copolymerization

In this article the emulsion graft polymerization of styrene with starch nanocrystals was a heterogenous system. There are mainly two kinds of mechanism for the emulsion polymerization of starch-g-polystyrene nanocrystals. One is the grafting occurs by the polymerization of styrene induced by the free radical on the starch backbone, as reported by Mehrotra and Ranby.¹¹ The other is that a growing chain free radical of polystyrene in a micelle is adsorbed onto starch surface and attached to an oxy radical at the surface. Although it is hard to figure out a proper reaction path for the graft polymerization in emulsion at present,¹⁰ in our case the graft copolymerization was mainly occurred at the surface of nanocrystals, because starch nanocrystals were used instead of native starch. As it may imagine if native starch was used, in it exists amorphous region, the grafting might more easily occur in the amorphous region of starch, and the homopolymers also might be produced in this region and stayed inside of the starch graft copolymer.

In graft copolymerization by free radical mechanism the homopolymer usually occurred along with graft copolymer. It was found homopolystyrene can generally be removed by toluene in Soxhlet extraction just as Cho and Lee¹⁰ and Fanta et al.¹² had reported. The homopolystyrene located inside the starch and entangled with grafted chains may not be removed entirely. These were thought to be unavoidable factors. However in our case since almost no amorphous region was present in starch nanocrystals and the homopolystyrene located inside graft copolymer become negligible, only the entanglement factor still exists. So in our system relatively more pure graft copolymer might be obtained.

FTIR spectrum analysis

FTIR spectra of native starch, starch nanocrystals and starch-g-polystyrene nanocrystals were shown in Figure 1 respectively.

There was almost no difference between Figure 1(a), the corn starch and Figure 1(b), the starch nanocrystals as was expected. Figure 1(c) clearly indicated the absorption of aromatic ring stretching vibration at 3027 cm⁻¹. The absorption peaks between 1452 and 1645 cm⁻¹ attributed to the benzyl ring backbone vibration. A strong and sharp signal at 698 cm⁻¹ arising from the out-of-plane vibration

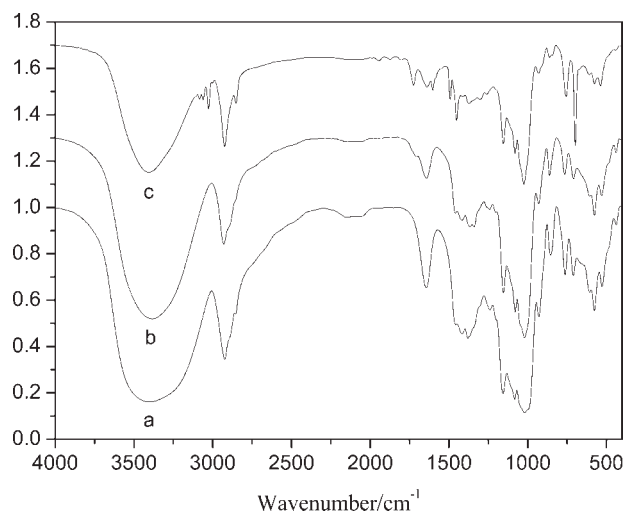


Figure 1 FTIR spectra of corn starch (a), starch nanocrystals (b), and starch-g-polystyrene nanocrystals (c).

of C—H in aromatic ring. As compared with Figure 1(b), the intensity of the O—H stretching vibration in Figure 1(c) decreased and the peak's maximum of hydroxyl group was shifted towards higher wave number, from 3383 to 3392 cm^{-1} for starch-g-polystyrene nanocrystals. This is because there was a decrease in the intermolecular force of hydroxyl groups due to the grafted polystyrene chains.

^1H NMR analysis of amphiphilic starch nanocrystals

The structures of starch nanocrystals before and after graft modification were also evaluated by ^1H NMR, see Figure 2.

In Figure 2(b) the peaks at 6.4–7.1 ppm is assigned to be the protons of the aromatic ring, peaks at 1.84 and 1.45 ppm own to the protons of —CH— and —CH₂—, respectively. The peak area ratio of chemical shift at 6.4–7.1, 1.84, and 1.45 ppm is 5 : 1 : 2. In Figure 2(a), the peaks at 3.5, 4.5, 5.0, and 5.4 ppm corresponding to the non-hydroxyl protons in glucose units are consistent with that in native corn starch.^{13,14} After grafting polystyrene, the peaks of non-hydroxyl protons were shifted slightly to 3.7, 4.6, 5.1, and 5.6 ppm, and the absorption peak of hydroxyl group was around 3.3 ppm. On the basis of the group compare of aromatic ring and glucose backbone, the molar ratio of the grafted styrene to glucose unit is around 1.

X-ray diffraction analysis

The X-ray diffraction patterns (XRD) of starch nanocrystals and starch-g-polystyrene nanocrystals were shown in Figure 3.

As it can be seen in Figure 3(a), the clear sharp diffraction peaks, at which 2θ values equal to 15°, 17°, 18°,

20°, and 23°, are characteristic for the starch nanocrystals structure.¹⁵ In Figure 3(b), the corresponding 2θ values for starch-g-polystyrene nanocopolymer are the same as equal to 15°, 17°, 18°, and 23°. It is apparent after grafting the crystalline structure was almost kept intact. This result is in consistent with that waxy starch nanocrystals modified by using long chain stearic acid chloride and poly(ethylene glycol).¹⁶ In this article after grafting polystyrene, the relative crystallinity of starch nanocrystals decreased slightly and the polystyrene crystallinity, characteristic diffraction peak at about 20°,¹⁷ reduced dramatically. It suggested that the polystyrene side chains were mainly grafted on the surface of starch nanocrystals and arranged irregularly on the polysaccharides backbones.

Morphology and particle size

The morphology and particle size of corn starch, starch nanocrystals, and starch-g-polystyrene nanocrystals were studied by SEM respectively and shown in Figure 4.

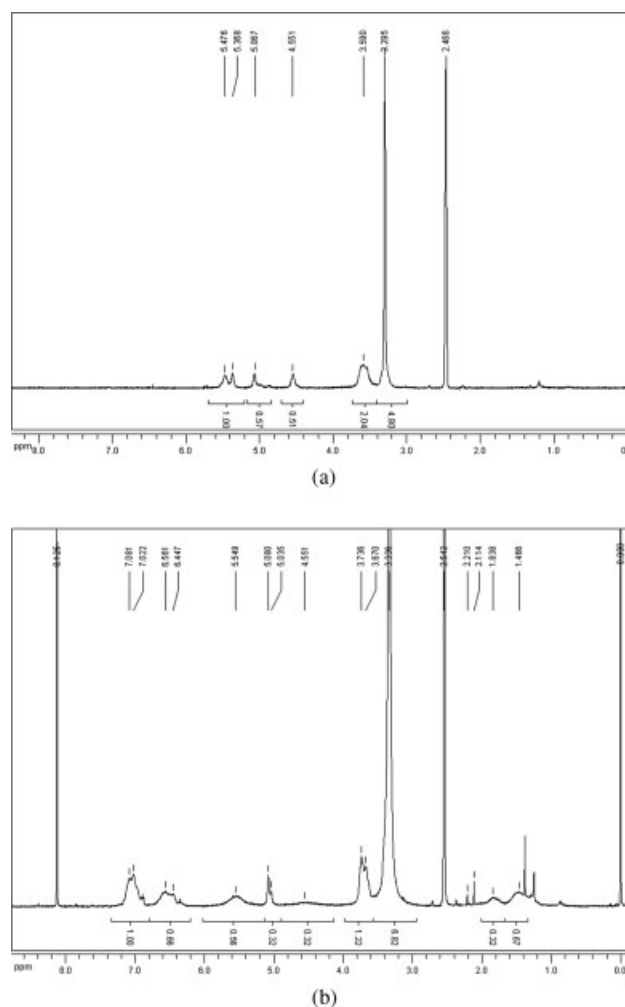


Figure 2 ^1H NMR spectra of starch nanocrystals (a) and starch-g-polystyrene nanocrystals (b).

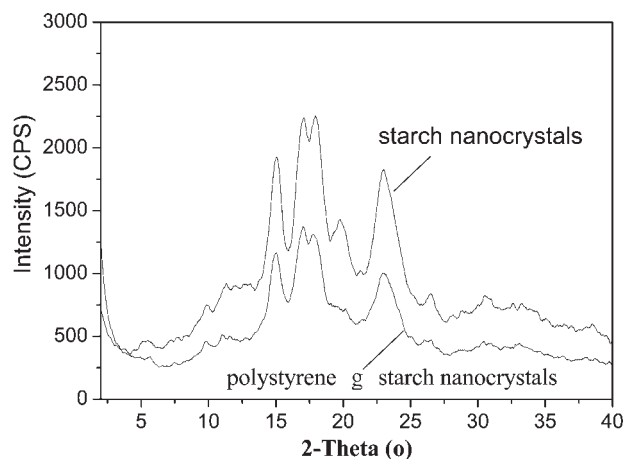


Figure 3 XRD patterns of starch nanocrystals (a) and starch-g-polystyrene nanocrystals (b).

According to SEM, the particles size of native starch is 5–40 μm [Fig. 4(a)], the obtained starch nanocrystals around 50 nm [Fig. 4(b)] after 7 days of

sulfuric acid hydrolysis. The particles size of the resulted starch-g-polystyrene nanocrystals increased to 80–100 nm [Fig. 4(c)] due to the graft copolymerization with styrene.

Wettability experiments

A simple and valuable experiment was used to evidence the amphiphilicity of starch-g-polystyrene nanocrystals. It was to mix the grafted starch nanocrystals with two immiscible solvents having both different polarities and densities to observe the wettability with these solvents. This can qualitatively indicate the different affinities between grafted starch nanocrystals and solvents of different polarities. Because of the strong hydrophilic character of starch, the unmodified starch nanocrystals can only stay in the aqueous medium of a mixed solvent system even after several times of shaking.⁹ Here four kinds of solvent systems were taken, that were distilled water ($d = 1 \text{ g cm}^{-3}$), toluene ($d = 0.866 \text{ g cm}^{-3}$), the

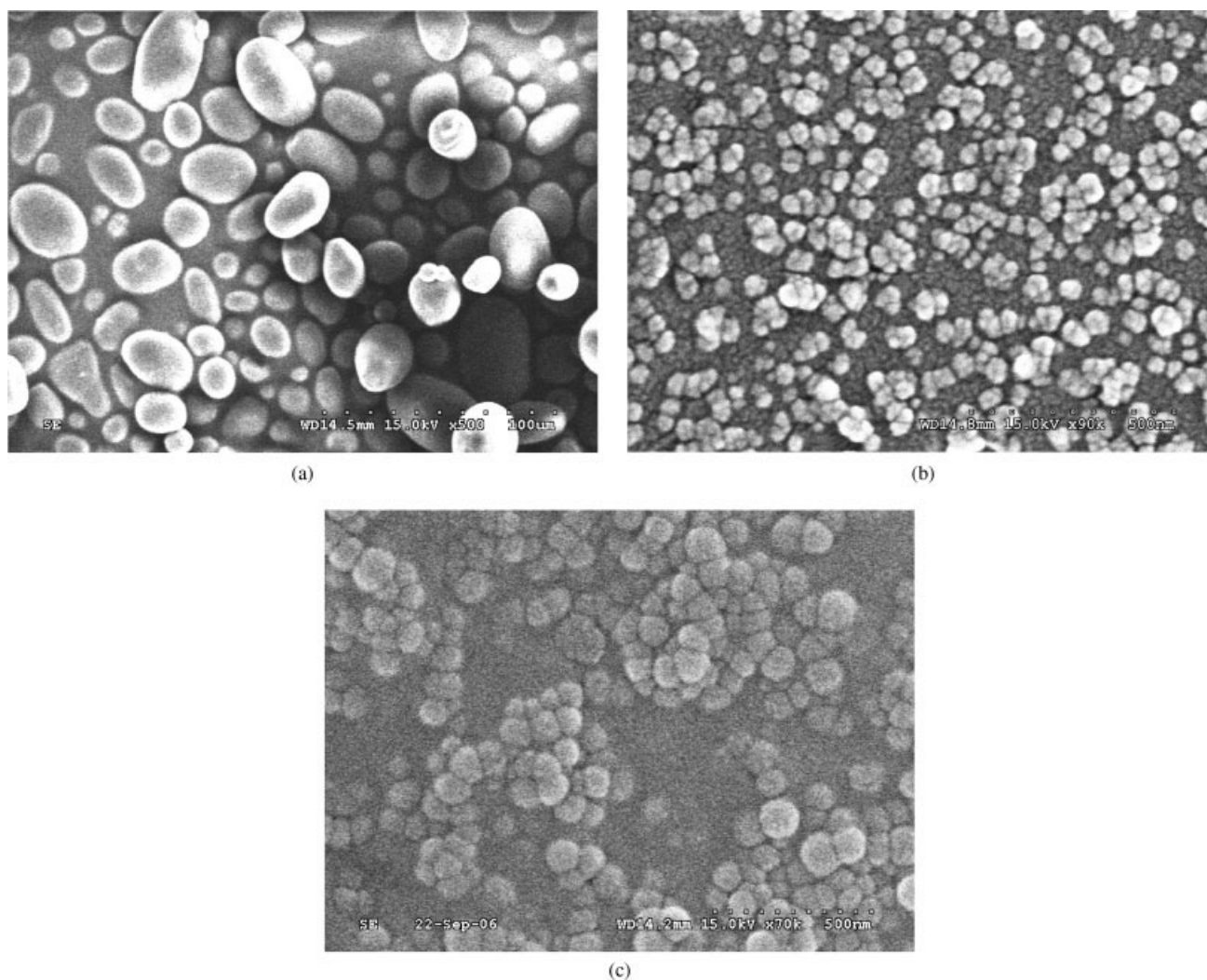


Figure 4 SEM micrographs of corn starch (a), starch nanocrystals (b), starch-g-polystyrene nanocrystals (c).

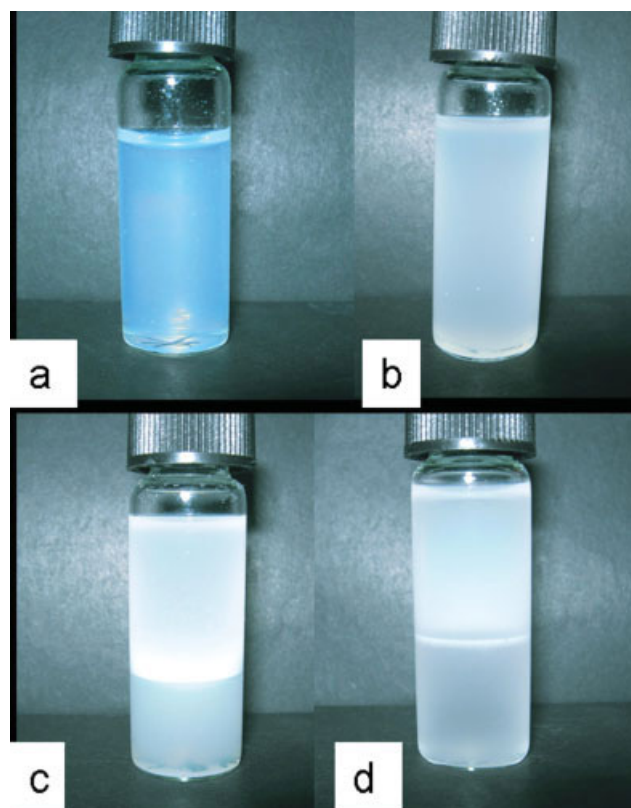


Figure 5 Wettability tests of starch-g-polystyrene nanocrystals: (a) in distilled water; (b) in toluene; (c) in water/toluene, and (d) in water/dichloromethane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mixture of water with toluene (water/toluene) and the mixture of water with dichloromethane ($d = 1.335 \text{ g cm}^{-3}$) (water/dichloromethane), seen in Figure 5.

As it can be seen in Figure 5(a) the polystyrene grafted starch nanocrystals can disperse well in water and so keep a good affinity with polar substance. Figure 5(b) indicated that this grafted starch nanocrystals can also well disperse in nonpolar solvent of toluene. Figure 5(c,d) showed the dispersion of grafted starch nanocrystals in water/toluene and in water/dichloromethane, respectively. These tests revealed that the grafted starch nanocrystals have good affinity both with polar and nonpolar solvents. The excellent amphiphilicity of the polystyrene grafted starch nanocrystals can be explained that in water medium the hydrophobic polystyrene side chains will be rolled up, and the hydrophilic starch backbone is in extended form showing hydrophilic character. On the contrary, in oil medium (toluene or dichloromethane) the hydrophilic hydroxyl groups of starch tend towards inside of starch while the hydrophobic grafted polystyrene side chains will be in stretched form showing hydrophobic character.

CONCLUSIONS

An amphiphilic starch nanocrystal copolymer was prepared by the graft copolymerization of starch nanocrystals with styrene. The starch nanocrystals used in this article were prepared by acid hydrolysis of corn starch. During hydrolysis process the amorphous region of starch was hydrolyzed and removed, the crystal particles with the size of 50 nm was thus obtained as starch nanocrystals. Since there is no amorphous region in starch nanocrystals, the polystyrene side chains were essentially grafted on the surface of starch nanocrystals. The wide angle X-ray diffraction data supported this speculation. SEM pattern revealed that the particle size of amphiphilic starch nanocrystals was around 80–100 nm.

The amphiphilic starch nanocrystals can well disperse both in polar and nonpolar solvents. Its excellent amphiphilic character attributes to the different conformation variation of the hydrophobic polystyrene side chains and the hydrophilic starch backbone when in polar or nonpolar solvent.

The amphiphilic starch-g-polystyrene nanocrystals prepared in this article may be used as the fillers of polymer matrix, such as natural rubber, polylactic acid, and polycaprolactone for getting nanocomposites with unique properties.

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