



Ultrasound enhanced radical graft polymerization of starch and butyl acrylate



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ARTICLE INFO

Article history:

Received 20 October 2014

Received in revised form 3 February 2015

Accepted 5 February 2015

Available online 11 February 2015

Keywords:

Ultrasound

Graft polymerization

Starch

Radical

ABSTRACT

The graft polymerizations of starch and butyl acrylate were performed with and without ultrasound irradiation. Potassium persulfate was used as radical initiator. During the process of graft polymerization with ultrasound of 40 kHz, the effects of reaction time, temperature, initiator dosage and feeding mode on graft ratio, graft efficiency and monomer conversion were investigated. The results demonstrated that ultrasound had a strong enhanced influence on the graft reaction. Compared to the conventional graft polymerization without ultrasound, the graft ratio, graft efficiency and monomer conversion increased significantly in ultrasound fields. The radicals produced by the decomposition of initiator played an important role in propelling the graft polymerization. Furthermore, the graft ratio and graft efficiency increased when starch and initiator were pre-treated with ultrasound for a short time prior to the addition of monomer.

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1. Introduction

Starch is a natural polysaccharide and widely used in the field of food, paper, adhesive, textile industries and medical materials. However, the properties of native starch do not meet the standards necessary for industrial uses. Therefore, native starch should be modified to obtain the desired properties. Chemical modification is the common method. Graft polymerization onto starch seems to be interesting and attractive from the point of imparting incremental property of polymer to the starch chain. The starch graft copolymers are increasingly becoming important due to their potential applications in industrial, agricultural, medical and food fields [1,2]. Starch graft copolymers can be usually prepared by generating free radicals on the starch backbone and then the formed starch radicals react with monomers to produce graft chains. However, the common radical graft polymerizations have some disadvantages, such as long reaction time and low graft ratio. Therefore, it is necessary to explore a novel method to improve the graft polymerization.

Ultrasound is a kind of mechanical vibration wave with the frequency of 2×10^4 – 10^7 Hz. The application of ultrasound irradiation in chemical synthesis has been broadly researched. The advantages of ultrasound procedures are good yields, short reaction time and mild conditions [3,4]. Ultrasound can promote

the formation of metal-fluorine bond in preparation of transition metal fluoro complex [5]. Polymers can be synthesized with the ultrasound waves by solution and emulsion polymerization [6–11]. Homopolymers, block copolymers, hydrogels and polymer–inorganic composites can be prepared with the ultrasound irradiation [12–18]. Ring-opening polymerization of cyclic lactones can also be initiated by ultrasound at high-intensity fields [19,20]. The effects of ultrasound in the polymer synthesis include generation of free radicals, activation of free radical initiators, degradation of polymers to produce macroradicals and dispersion of monomer to form heterogeneous particles. These triggered us to research the graft-onto starch polymerization under ultrasound irradiation.

Ultrasound has been applied in the modification of starch in the recent years, such as carboxylation and acetylation of starch [21–24]. To our knowledge there was relatively little information on the graft polymerization of starch with ultrasound irradiation. In this work, graft copolymers of starch-g-poly(butyl acrylate) (starch-g-PBA) were synthesized in ultrasonic fields. Starch exhibits high polarity and hydrophilicity because of the abundant hydroxyl groups on the starch chains. This leads to the weak interaction between starch and non-polar compounds. It is an important method to modify starch by grafting hydrophobic polymers such as poly(butyl acrylate). It has been reported that the copolymers introduced by poly(butyl acrylate) showed improved thermal stability [25] and hydrophobicity [26,27]. It is a green and economical method to prepare starch graft polymers in gelatinized starch in water medium [1,2,28], especially for biomaterial applications. However, the insolubility of butyl acrylate has a

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negative influence on the graft polymerization. The aim of our work is expected to improve the graft reaction in water medium by the effect of ultrasound. The effects of ultrasound irradiation on the graft polymerization were investigated.

2. Experimental

2.1. Materials

Amylose starch, potassium persulfate (KPS) and butyl acrylate (BA) were purchased from Shanghai Reagent Company. KPS was of analytic grade and used as received. BA was purified by distillation under reduced pressure before use. Sodium hydroxide (NaOH), hydrochloric acid (HCl) and anhydrous ethanol were obtained from Tianjin Kemiou Chemical Reagent Company. Deionized water was used throughout the experiment.

2.2. Synthesis of starch graft copolymer

5.00 g starch and 50 mL deionized water was put into a round flask equipped with thermometer, mechanical stirrer and reflux condenser. The mixture was heated at 80 °C for 30 min in order to obtain gelatinized starch. Then the starch solution (9.09%) was cooled to room temperature and immersed in an ultrasonic tank. The ultrasonic generator was a typical ultrasonic bath vessel. The equipment consisted of two layers stainless steel body with a tank of 5 L. The reactor had a constant operation frequency at 40 kHz with an output of 150 W. The nitrogen atmosphere was maintained in the system by purging the nitrogen gas in the reactor. When KPS (0.25 g, 5% weight of starch) and BA (5.00 g) were added into the flask, the polymerization started under ultrasonic irradiation at a predetermined temperature. Starch could act like a stabilizer in the heterogeneous system. After a certain time, the mixture solution was put into anhydrous ethanol slowly and stirred violently. The formed white precipitate was filtered and then dried at 60 °C until the weight was a constant. The crude product of starch-g-poly (butyl acrylate) (starch-g-PBA) was obtained. The product was often mixed with poly(butyl acrylate) (PBA) homopolymer. The homopolymer could be separated by Soxhlet extraction for 12 h using acetone as a solvent. The obtained pure graft copolymer was filtered, washed with anhydrous ethanol, and dried at 60 °C to a constant weight.

2.3. Analysis and characterization

The chemical structures of starch and graft polymer were recorded on a Bruker Vector 22 Fourier transform infrared (FTIR) spectrometer, using KBr pellets at the range of 400–4000 cm⁻¹.

The graft ratio of graft copolymer was evaluated using weight method. Pure graft copolymer was weighted accurately and dispensed in 100 mL 1 mol/L HCl solution. The mixture was refluxed at 100 °C. After a certain time several drops of the solution was extracted by a dropping pipette and added into an I₂-KI solution until the solution did not turn blue. Then the solid content was filtered, washed and dried at 60 °C to a constant weight. Since starch, the main chains of the copolymer, was degraded completely in HCl solution, the white solid was the PBA that was the grafted part of the copolymer.

The graft ratio (GR), graft efficiency (GE) and monomer conversion (MC) were calculated as follows:

$$GR = \frac{\text{the weight of grafted polymer}}{\text{the weight of starch chain}} \times 100\% \quad (1)$$

$$GE = \frac{\text{the weight of grated polymer}}{\text{the weight of monomers reacted}} \times 100\% \quad (2)$$

$$MC = \frac{\text{the weight of monomer reacted}}{\text{the weight of monomer taken}} \times 100\% \quad (3)$$

3. Results and discussions

The graft polymerization of starch and butyl acrylate initiated by KPS in ultrasonic field was studied under different experimental conditions in order to evaluate the effects of ultrasound on the graft reaction.

3.1. Chemical structures of starch and graft copolymer

The FTIR spectra of starch and a representative graft copolymer (GR = 31.7%) are presented in Fig. 1. The characteristic absorptions of starch are: 3200–3500 cm⁻¹ (O–H bond stretching vibrations), 2927 cm⁻¹ (C–H bond stretching vibrations), 1016–1158 cm⁻¹ (the skeletal stretching vibrations of starch) [2,21]. The graft copolymer not only reserved the characteristic absorptions of starch but also showed new band at 1730 cm⁻¹ coming from the C=O bond stretching vibration of ester group. Since the homopolymer had been removed during purification process, it was certain that the new band was from the PBA chains grafted on the starch molecules. Meanwhile, the stronger peak around 2900 cm⁻¹ of the copolymer was due to more C–H bonds in the graft copolymer.

3.2. Effect of reaction time on graft polymerization

The concentrate of gelatinized starch solution was 9.09% (5.00 g starch was dispensed in 50 mL distilled water) and the monomer was 5.00 g. KPS was 5% weight of starch. The reaction was carried out at 60 °C. Since ultrasonication was often accompanied by local temperature increasing, the temperature was carefully monitored and controlled within 60 ± 1 °C through the experiments. The reaction time was from 15 to 90 min. The effects of ultrasound on the graft polymerization are illustrated in Fig. 2. The graft ratios were found to increase with the reaction time going on both with and without ultrasound irradiation. At the same reaction condition

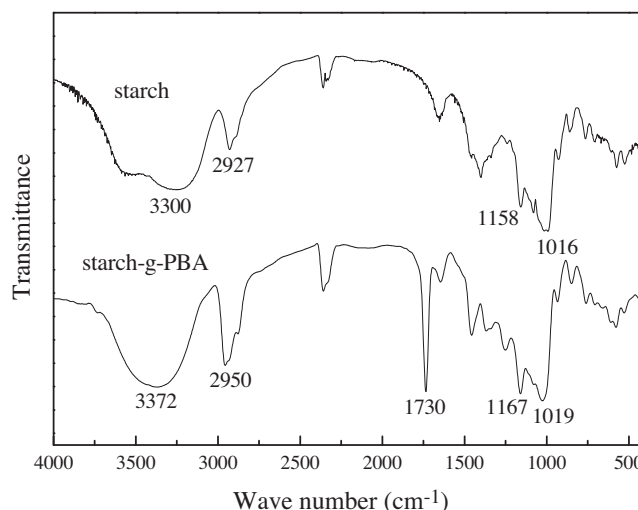


Fig. 1. FTIR spectra of starch and starch-g-PBA.

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