



Gamma radiation-induced grafting of acrylamide and dimethyl diallyl ammonium chloride onto starch

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ABSTRACT

Corn starch graft copolymers were prepared from acrylamide/dimethyl diallyl ammonium chloride binary monomers (AM/DMDAAC) by a simultaneous radiation grafting method, and were characterized by FTIR and ¹H NMR techniques, weight measurement and titration method. The copolymers with high grafting ratio and high grafting efficiency of binary monomers were achieved at absorbed doses of 2 kGy and 3 kGy using a 6:9.8:4.2 (w/w/w) ratio of starch/AM/DMDAAC, but their cationic degrees were low. Grafting ratio, grafting efficiency and cationic degree of the copolymers increased with increasing AM content in comonomer mixtures and then decreased at 3 kGy using a 6:14 ratio of starch:total comonomers, but their cationic degrees generally decreased with increasing AM content. The grafting ratio, the grafting efficiency and the cationic degree of the copolymers increased, but the grafting efficiency of DMDAAC decreased with varying starch/(AM + DMDAAC) ratio from 6:3 to 6:18 at 3 kGy by using a fixed 7:3 ratio of AM:DMDAAC.

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1. Introduction

Starch comprises a mixture of two polysaccharides: amylose (a linear polysaccharide) and amylopectin (a branched polysaccharide). Molecules of the former polysaccharide consist of weakly branched polysaccharide chains composed of glucose residues linked by valence bonds, while the latter has a more complicated structure of branched chains. As one of the most abundant substances in nature, starch is not only the primary source of food for the humans, but can also be regarded as renewable resource that may be utilized in many industrial applications. But native starches have limited usage due to its inherent weakness of hydration, swelling and structural organization. In order to enhance viscosity, texture, stability among many desired functional properties desired for many food and industrial applications, starch and their derivatives are modified by chemical, physical and biotechnology means. Starch modification involving the alteration of the physical and chemical characteristics of specific industrial applications,

Abbreviations: AM, acrylamide; DMDAAC, dimethyl diallyl ammonium chloride; St-g-p(AM-co-DMDAAC), starch-graft-poly(acrylamide-co-dimethyl diallyl ammonium chloride).

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is generally achieved through derivatization such as esterification, etherification, cross linking, acid hydrolysis, enzymatic hydrolysis, heat treatment and grafting of starch (Singh, Nath, & Singh, 2010).

As an important aspect of starch modification, graft copolymerization of starch with a variety of vinyl monomers is initiated either by a chemical free radical initiator (e.g. ceric ammonium nitrate or ammonium persulfate) (Athawale & Lele, 2000; Chen, Park, & Park, 1999) or by high energy radiation (e.g. gamma ray or electron beam) (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002; Song, Zhang, Ma, Wang, & Yang, 2007). The chemical free radical initiator is used to generate free radical sites on the polysaccharide backbones, where the monomers are added up to form the graft chain. This method of synthesis has low reproducibility and is not very suitable for commercial scale synthesis. A better method of graft copolymer synthesis is by using high energy radiation as the free radical generator. Radiation-induced grafting is of high efficiency and does not cause any further contamination associated with chemical initiators (Khalek & Mahmoud, 2011). On the other hand, there are four methods of grafting of starch: dry, semi-dry and wet processes. Dry and semi-dry processes are more efficient and more ecological than wet process. But wet process is more mature than others, including the more heterogeneous reactions of granular starch in a slurry and the more homogeneous reactions of gelatinized starch in a paste, which is referred to as the slurry process and the paste process. Reactive extrusion is an efficient approach for starch graft copolymers because it is easy, inexpensive and has a short processing time. Although

reactive extrusion has numerous advantages one of the limitations is degradation of the polymer under the high temperatures and mechanical stresses encountered (Kalambur & Rizvi, 2006; Moad, 2011; Nakason, Wohmang, Kaesaman, & Kiatkamjornwong, 2010; Xie, Yu, Liu, & Chen, 2006).

Cationic starches, which are widely used in many fields (Haack, Heinze, Oelmeyer, & Kulicke, 2002; Khalil & Aly, 2001), can be obtained through the grafting reaction of starch with an ethylenically unsaturated monomer having cationic groups initiated either by gamma irradiation (Carr, 1994; Fanta, Burr, Doane, & Russell, 1974; Jones & Elmquist, 1973; Jones & Jordan, 1971; Peoria, 1984) or by a chemical free radical initiator (Liu, Li, & Xu, 2011; Lu, Lin, & Yao, 2004). In general, cationic groups may be amino, immonium, ammonium, sulphonium or phosphonium. Compared with amino and immonium groups, quaternary ammonium group is preferred because the final product does not require any further cationization.

Graft copolymerization of starch with acrylamide (AM) and dimethyl diallyl ammonium chloride (DMDAAC) was reported to be carried out using a complex initiation system (Liu et al., 2011; Lu et al., 2004). And a series of cationic starch graft copolymers have been developed by gamma-ray irradiation of starch and quaternary ammonium salt monomers (Fanta et al., 1974; Jones & Elmquist, 1973; Jones & Jordan, 1971; Peoria, 1984). But the graft copolymerization of starch with AM and DMDAAC initiated by gamma irradiation has not been previously reported. Furthermore, Tanaka had investigated the radical copolymerization of DMDAAC (M_1) with acrylamide (M_2) at pH 6.1 in aqueous solutions, and the reactivity ratios were determined to be 0.58 and 6.7 for the pair of monomers (Tanaka, 1986), which implies that DMDAAC is prone to copolymerization with AM instead of homopolymerization due to the electrostatic repulsion between the charged monomer and the charged radical chain end. Therefore, the presence of AM in the graft copolymerization of starch with DMDAAC is expected to facilitate graft copolymerization of DMDAAC onto starch.

Based on the existing literature, the present study has been conducted to synthesize cationic starch by graft copolymerization of starch, AM and DMDAAC by means of simultaneous gamma irradiation. The effects of the reaction parameters, such as the total absorbed dose, mass ratio of AM to DMDAAC, mass ratio of starch to comonomers, and monomer concentration on the grafting parameters were systematically investigated.

2. Experimental

2.1. Materials

Food grade corn starch powder was supplied from Henan Yongchang Starch Sugar Co., Ltd. Dimethyl diallyl ammonium chloride (DMDAAC, AR grade) was purchased from Shandong Luyue Chemical Co., Ltd. Acrylamide (AM, AR grade) was obtained from Tianjin No. 3 Chemical Reagent Factory. All other chemicals were A.R. grade. Double distilled water was used for preparation and measurements.

2.2. Radiation induced graft polymerization

A mixture of corn starch powder and distilled water was continuously stirred using a mechanical stirrer under nitrogen atmosphere in water bath at 85 °C for 30 min. The obtained gelatinized corn starch was mixed with AM and DMDAAC, and continuously stirred to form a homogenous mixture under nitrogen atmosphere. Thereafter, the homogenous mixture was transferred into a wide-mouth, screw-cap glass bottle and repressured with nitrogen four times to remove dissolved oxygen. The bottle was

tightly closed with a cap, irradiated with cobalt 60 to a required absorbed dose at 40 Gy/min dose rate, and allowed to stand at ambient temperature for 2 h.

2.3. Determination of grafting ratio and grafting efficiency of total monomers

The rubbery product obtained was broken up, washed with ethanol, vacuum-dried at 60 °C and ground into fine powder. The powder was extracted continuously for 18 h in a Soxhlet extractor with a mixture of acetone and glacial acetic acid (1:1, v/v), and thus ungrafted poly(AM-co-DMDAAC) and unreacted monomers were removed from the powder. The graft copolymer St-g-p(AM-co-DMDAAC) after solvent extraction was dried in a vacuum oven at 60 °C to a constant weight.

Grafting performance in terms of percentage grafting ratio and grafting efficiency of binary monomers was determined by weight measurement. The percentage grafting ratio was calculated as shown in Eq. (1).

$$\text{Grafting ratio} = \frac{\text{Weight of starch grafted copolymer}}{\text{Weight of starch}} \times 100\% \quad (1)$$

The percentage grafting efficiency of total monomers was calculated by Eq. (2).

$$\text{Grafting efficiency of total monomers} = \frac{\text{Weight of starch grafted copolymer} - \text{Weight of starch}}{\text{Weight of AM} + \text{Weight of DMDAAC}} \times 100\% \quad (2)$$

2.4. Determination of cationic degree and grafting efficiency of DMDAAC

Cationic degree of St-g-p(AM-co-DMDAAC) copolymer was determined by titration (Mohr's method) (Block & Waters, 1967), which depended upon the amount of DMDAAC units incorporated into the copolymer. The starch graft copolymer was weighed into 250 ml Erlenmeyer flask and dissolved in 100 ml of distilled water, and then the pH value of the solution was adjusted between 6.5 and 7.2. Potassium chromate served as the end point indicator in the titration of chloride ions with a silver nitrate standard solution, and the color changed from yellow to brick-red which signaled the end point of this titration. Cationic degree used in m mol/g was calculated by Eq. (3).

$$\text{Cationic degree} = \frac{\text{Molarity of AgNO}_3 \times (V_{\text{AgNO}_3} - V_{\text{AgNO}_3}^0)}{\text{Weight of starch grafted copolymer}} \quad (3)$$

where Molarity of AgNO_3 is used in mol/l or m mol/ml, V_{AgNO_3} is the volume of the silver nitrate standard solution consumed during titration used in ml, $V_{\text{AgNO}_3}^0$ is the volume of the silver nitrate standard solution consumed during blank titration used in ml.

Based on the value of cationic degree, corresponding grafting efficiency of DMDAAC alone was calculated by Eq. (4).

$$\text{Grafting efficiency of DMDAAC alone} = \frac{M_{\text{DMDAAC}} \times \text{Cationic degree}}{1000} \times \frac{\text{Total weight of starch and monomers}}{\text{Weight of DMDAAC}} \times 100\% \quad (4)$$

where M_{DMDAAC} is molecular weight of DMDAAC. Grafting efficiency of DMDAAC with excluding AM implied the ratio of the weight of grafted DMDAAC monomer to the total weight of initial DMDAAC monomer.

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