



Effects of amylose content on property and microstructure of starch-graft-sodium acrylate copolymers

Zhi Zhang^{a,c}, Peirong Chen^{a,*}, Xianfeng Du^{b,**}, Zhonghua Xue^{a,c},
Shanshan Chen^a, Baojun Yang^c

^a Department of Applied Chemistry, School of Science, Anhui Agricultural University, Hefei 230036, China

^b School of Tea & Food Science and Technology, Anhui Agricultural University, Hefei 230036, China

^c Department of Chemical Processes, School of Chemical Engineering, Hefei University of Technology, Hefei 230009, China

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ABSTRACT

Starch-graft-sodium acrylate (St-g-SA) copolymers were synthesized with ammonium persulfate as an initiator. This work focused on the effects of amylose content of corn starch on the water absorbent capacity and microstructure of the St-g-SA copolymers. The water absorbent capacity of waxy, maize and high amylose St-g-SA copolymers was 1800 g/g, 1300 g/g and 1100 g/g respectively. The grafted copolymers were characterized by FTIR and solid state ¹³C NMR confirming that the graft reaction had taken place between sodium acrylate and corn starch. The surfaces and cross sections of St-g-SA copolymers were observed by SEM. Incomplete gelatinized starch aggregates increased with increasing amylose content on surfaces and cross sections of copolymers, which accorded with the water absorbent capacity and grafting ratio. DMTA results showed that the waxy St-g-SA copolymer had the highest transition temperature which indicated waxy starch had high grafting ratio.

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1. Introduction

Superabsorbent polymers are three-dimensional networks, which are composed of homopolymers or copolymers and are insoluble in all solvents. Depending on their compatibility with the solvent, they can absorb and hold a considerable volume of liquids (Athawale & Lele, 2001; Hua & Wang, 2008; Jiraprasertkul, Nuisin, Jinsart, & Kiatkamjornwong, 2006). Owing to their excellent properties of superabsorbent, superabsorbent polymers are widely used in many fields, such as flocculants for wastewater treatment (Güçlü, Güçlü, & Keleş, 2007; Güçlü et al., 2010; Jiraprasertkul et al., 2006), drug delivery systems (Ameje et al., 2001; Coucke et al., 2009), biological (Ameje et al., 2002; Eid, 2008) and hygienic products, particularly disposable diapers and napkins, in which they are used to capture secreted fluids such as urine and blood (Zou et al., 2012). St-g-SA copolymer is one of superabsorbents having a greater demand in industry due to their low cost and also because of the certain proportion of starch in these polymers which render them biodegradable and environmental friendly.

Previous reports show that properties of corn starch are different with different amylose content (Matveev et al., 2001). Furthermore, it is shown that the native granule structure, the melting thermodynamic parameters and the functional properties of starches are influenced by the amylose content (Kiseleva et al., 2005; Sang, Bean, Seib, Pedersen, & Shi, 2008). Amylose content of starches on physical properties and biodegradability of starch/PVA-blended films also exhibits a strong influence (Yun & Yoon, 2010). In addition, starch-based superabsorbent polymers grafting ratio, grafting efficiency, graft position and length of the grafted segment have recently been investigated for explaining graft reaction and performance of starch-based superabsorbents with different amylose/amylopectin ratio in starches (Zou et al., 2012). Application of starch always involves gelatinization of starch that breaks the inter-chain hydrogen bonding so as the rheological properties of starch paste can be utilized effectively and that induces a complex structural modification, leading to dramatic apparent viscosity change. Besides temperature, gelatinization behaviors of corn starches with different amylose content are also obviously different (Liu, Yu, Xie, & Chen, 2006).

St-g-SA copolymers are used extensively as superabsorbents, which show high swelling capacity. It is important to have a relatively complete cognition to internal structure of superabsorbent polymeric network because high water absorbent capacity needs high cooperative among composites that is the reflection to

* Corresponding author. Tel.: +86 551 65786121; fax: +86 551 65786121.

** Corresponding author. Tel.: +86 551 65786405; fax: +86 551 65786405.

E-mail addresses: chenpeirong@ahau.edu.cn (P. Chen), dx@ahau.edu.cn (X. Du).

internal stimuli such as osmotic pressure, amylose content of starch, et al. Therefore, it is significant and urgent to research the effect of amylose content on internal microstructure and graft ratio of St-g-SA copolymers, which is closely connected to water absorbent capacity. Corn starches with different amylose contents (waxy, 5%; maize, 27%; high amylose, 70%) were used as model materials to synthesize the superabsorbent graft copolymer using ammonium persulfate as an initiator and N,N'-methylene-bisacrylamide as a crosslinker.

2. Materials and methods

2.1. Materials

Corn starches with different amylose contents according to the manufacturer were used in the experimental work as model materials. High amylose starch (70% amylose content) was supplied by National Starch, America. Maize starch (27% amylose content) was supplied by Shandong Jincheng Co., Ltd., China. Waxy starch (5% amylose content) was supplied by Shandong Jincheng Co., Ltd., China. All other chemicals used in the work were also commercially available. Ammonium persulfate was obtained from Shantou West Long Chemical Co., Ltd. N,N'-methylene-bisacrylamide was from Sinopharm Chemical Reagent Co., Ltd. Acrylic acid (AA) was from Tianjin Guangfu Fine Chemical Research Institute. Sodium hydroxide was from Shantou West Long Chemical Co., Ltd.

2.2. Preparation of copolymers

A 250 mL four-neck round-bottom flask equipped with a mechanical stirrer (Gongyi SZCL-3A, two blade propeller type, 400 rpm) and a nitrogen line was charged with 120 mL of water and 5.00 g of waxy or maize starch and the mixture was stirred for 30 min at 100 °C, while the high amylose starch was heated and stirred in an autoclave for 30 min at 120 °C. The gelatinized starch was subsequently cooled to room temperature. Then after adding ammonium persulfate (0.16 g) and N,N'-methylene-bisacrylamide (0.012 g), 95% neutralized acrylic acid (20.00 g) regarded as monomer was added to the flask. The mixture was heated in thermostatic water bath at 65 °C for 5 h under nitrogen atmosphere to obtain hydrogel, as reported previously (Cao, Xu, Feng, & Wang, 2005; Hua & Wang, 2008; Wu, Wei, Lin, & Lin, 2003). Poly (sodium acrylate) (PSA) hydrogel was synthesized under the same conditions with no added starch. These obtained hydrogels were further processed.

A portion of hydrogels were washed with distilled water and rewashed with ethanol to remove ungrafted molecules and acrylic acid homopolymer to achieve the grafted copolymers (Jyothi & Carvalho, 2013; Lanthong, Nuisin, & Kiatkamjornwong, 2006; Wu, 2005; Zhang, Wang, & Wang, 2007; Zou et al., 2012). The grafted copolymers were dried at 105 °C, crushed and sieved through a 200-mesh (75 μm-mesh) screen to obtain powders for FTIR analysis and grafting ratio calculation, respectively. Another portion of hydrogels were washed thoroughly by acetone to remove unreacted acrylic acid and homopolymer until the precipitate agglomerates. Both the grafted copolymer and maybe ungrafted starch were separated by centrifugation. The precipitate was dried in a vacuum oven at 60 °C until constant weight. The dried samples were crushed and sieved through a 200-mesh screen to obtain powders for the ¹³C NMR analysis (Witono, Marsman, Noordergraaf, Heeres, & Janssen, 2013). The remainder hydrogels were poured onto a polytetrafluoroethylene dish and were dried at 65 °C to solid state, then dried at 105 °C to a constant weight to form the films for characterizations of the water absorbent capacity, SEM, DMTA and mechanical properties.

2.3. Characterizations

2.3.1. Fourier transforms infrared spectrometer (FTIR)

The starches, grafted copolymers and PSA were characterized by Nicolet-Nexus 670 model FTIR spectrophotometer using KBr pellets.

2.3.2. Solid state ¹³C NMR spectroscopy

Solid state ¹³C NMR spectra were recorded on Bruker AV400 spectrometer operating at 100.62 MHz. The powders of starch, copolymers, and PSA were packed into 4 mm rotors and spun at speeds of 5 kHz and a fixed CP contact time of 2 ms was used in all the experiments.

2.3.3. Water absorbent capacity of copolymers

The water absorbent capacity of copolymer was measured by a filtration method. St-g-SA copolymers films were bended to break into small pieces, 0.10 g of several pieces of dry film was put into distilled water, and completely immersed in excess water for 24 h to reach swelling equilibrium at ambient temperature (Lanthong et al., 2006; Wu et al., 2003). The fully swollen copolymer gels were filtered through a 100-mesh (150 μm-mesh) nylon screen to remove the residual water. The absorption capacity *Q* (g/g) was calculated as shown in Eq. (1) (Cao et al., 2005; Lanthong et al., 2006; Zhang et al., 2007).

$$Q = \frac{M_2 - M_1}{M_1} \quad (1)$$

where *M*₁ (g) is the weight of the dry film sample, *M*₂ (g) is the weight of the swollen gel sample.

2.3.4. Grafting ratio

In a 125 mL Erlenmeyer flask mounted with a condenser, 0.5 g of the grafted copolymer was refluxed in 50 mL of 1 M HCl at 100 °C for 2 h (Lanthong et al., 2006). The polymer was filtered and washed with distilled water to a pH of 7, and then it was dried at 105 °C to obtain grafted polymer. Iodine solution was applied to observe the completion of acid hydrolysis starch reaction. The grafting ratio (GR) was calculated by Eq. (2) (Jyothi & Carvalho, 2013; Lanthong et al., 2006; Zhu, Li, & Jin, 2009; Zou et al., 2012).

$$GR(\%) = \frac{W_1}{W_0} \times 100\% \quad (2)$$

where *W*₁ (g) is the weight of grafted polymer and *W*₀ (g) is the weight of starch.

2.3.5. Field emission scanning electron microscope (SEM)

The morphology observation was carried out by Sirion200 Scanning Electron Microscopy (SEM). Firstly, St-g-SA copolymers films obtained by drying the synthesized hydrogels were directly bended to break into pieces, then these pieces of dry film were coated with gold. Finally, the film upper surface contacted with the air during drying process and the film broken cross section were observed to take images for surface and cross section, respectively.

2.3.6. Dynamic mechanical thermal analysis (DMTA)

St-g-SA copolymers and PSA films (30 mm × 5 mm × 1 mm) were performed on DMA 242E (Netzsch) analyzer at a frequency of 1 Hz and a displacement of ±60 μm (about 0.1 N in force), from room temperature to 180 °C at a heating rate of 5 °C/min under nitrogen atmosphere (100 mL/min), using the single cantilever bending mode.

2.3.7. Mechanical properties of copolymers

Elongation at break and tensile strength were evaluated for St-g-SA copolymers and PSA films (50 mm × 5 mm × 1 mm) using the

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