Carbohydrate Polymers 99 (2014) 385–393

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Physicochemical properties of granular and non-granular cationic starches prepared under ultra high pressure

Yoon-Je Chang[a], Hyun-Wook Choi[a], Hyun-Seok Kim[b], Hyungjae Lee[c], Wooki Kim[a], Dae-Ok Kim[a], Byung-Yong Kim[a], Moo-Yeol Baik[a,*]

[a] Department of Food Science and Biotechnology, Institute of Life Science and Resources, Kyung Hee University, Seochun 1, Yongin, Gyeonggi-do 446-701, Republic of Korea
[b] Department of Food Science and Biotechnology, Andong National University, 1375 Gyeongdongro, Andong, Gyeongsangbuk-do 760-749, Republic of Korea
[c] Department of Food Engineering, Dankook University, Cheonan, Chungnam 330-714, Republic of Korea

ARTICLE INFO

Article history:
Received 25 February 2013
Received in revised form 2 September 2013
Accepted 4 September 2013
Available online 9 September 2013

Keywords:
Non-granular and granular cationic starch
Ultra high pressure (UHP)
UHP-assisted cationization reaction
Physicochemical properties
Flocculating activity

ABSTRACT

Granular and non-granular cationic starches were prepared through the reaction of tapioca and corn starches with 2,3-epoxypropyl trimethyl ammonium chloride (ETMAC) using conventional and ultra high pressure (UHP)-assisted reactions. The cationic starches were characterized with respect to morphology, degree of substitution (DS), FT-IR, ^{13}C NMR, X-ray diffraction pattern, solubility and swelling power, pasting viscosity, and flocculating activity. Non-granular (relative to granular) cationic starches possessed higher DS values. While DS values of non-granular cationic starches were lower for UHP-assisted (relative to conventional) reaction, granular cationic starches did not differ for both reactions. For flocculation activity, granular cationic starches with lower solubility and higher swelling power were higher than non-granular counterparts with reversed patterns in solubility and swelling power, regardless of conventional and UHP-assisted reactions. Overall results suggested that flocculation activity of cationic starches may be directly associated with their swelling powers (relative to DS values).

1. Introduction

Starch is one of the most abundant natural polymers and a common carbohydrate source in staple foods such as corn, wheat, potato, rice, and tapioca. Starch and its chemically and physically modified products have been widely used in industrial applications, due to their low cost and biodegradation. However, the utilization of native starch is limited, due to its cold-water insolubility, uncontrolled consistency of starch pastes and higher tendency to retrogradation and gel formation. Thus, native granular starch is chemically and/or physically modified to improve and extend their physicochemical properties depending on demands of industrial applications (Song, 2010; Wang & Xie, 2010).

Chemically modified starches are commonly prepared by treating native starch granules with reacting reagents that can react with hydroxyl groups on starch molecules. One of the chemically modified starches, cationic starches possess positively charged groups such as amino, imino, ammonium and phosphonium, and are widely used for wastewater purification and non-food products (e.g., papers, textiles and cosmetics). Cationic starches are generally synthesized by reaction of native starch with cationic reacting reagents such as 2,3-epoxypropyl trimethyl ammonium chloride (ETMAC) and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC). Cationic starch derivatives are effective flocculants for negatively charged organic and inorganic colloidal particles over a wide range of pH (Pal, Mal, & Singh, 2005; Wei, Cheng, & Zheng, 2008; Zhang et al., 2012). Most of cationic starches are present in non-granular forms due to the use of excessive NaOH for purpose to enhance their degree of substitution (Wang et al., 2009). However, limited information is available on physicochemical properties of granular-type cationic starch.

UHP or high hydrostatic pressure (HHP) technology is an attractive non-thermal technique as minimal processing technique of food systems, in particular for sterilization, enzyme inactivation, enzyme activity modulation, and bioactive compound extraction (Kim, Kim, & Baik, 2012). More recently, UHP-assisted derivatization of starch granules has been developed using UHP equipment as a reactor. This developed technique has been successfully applied for preparation of chemically modified starches (e.g., acid-thinned starch, starch acetate, phosphorylated cross-linked starch, phosphorylated starch, and hydroxypropylated starch) (Choi, Kim, Park, Kim, & Baik, 2009; Kim, Choi, Kim, & Baik, 2010; Kim, Choi, Kim, & Baik, 2011; Kim, Hwang, Kim, & Baik, 2012; Kim, Kim, et al., 2012; Lee et al., 2006). In acetylation and hydroxypropylation

---

* Corresponding author. Tel.: +82 31 201 2625; fax: +82 31 204 8116.
E-mail address: mooyeol@khu.ac.kr (M.-Y. Baik).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.09.010

reactions, starch reactivities in UHP-assisted (relative to conventional) derivatization were around 25% lower, while reaction time was dramatically reduced at similar reactivity levels (Choi et al., 2009; Kim et al., 2010; Kim et al., 2011; Kim, Kim, et al., 2012). For UHP-assisted $POCl_3$ starch derivatives, significant differences in swelling, gelatinization, and pasting viscosity properties were not observed depending on pressurizing levels (Kim, Hwang, et al., 2012), though influenced by cross-linking reagent addition levels (Hwang, Kim, & Baik, 2009). Nevertheless, UHP-assisted (relative to conventional) cross-linking reaction shortened reaction time, and UHP-assisted $POCl_3$ starch derivatives prepared at pressure ranges of 300–400 MPa revealed similar swelling, gelatinization, and pasting viscosity properties to those of conventional $POCl_3$ starch derivatives (Kim, Hwang, et al., 2012). To date, however, UHP-assisted derivatization is not applied to preparation of cationic starch derivatives, though many studies have been conducted with respect to synthesis of cationic starch derivatives using conventional method (i.e., thermal processing at atmospheric pressure).

Thus, the objectives of this study were to synthesize granular and non-granular forms of cationic starch (tapioca and corn) derivatives using conventional and UHP-assisted derivatization reactions, and characterize their physicochemical properties and flocculating activities for waste water treatment.

2. Materials and methods

2.1. Materials

Tapioca and normal corn starches were purchased from Sing Song Industrial Co. (Seoul, Republic of Korea) and Shin Dong Bang CP Co. (Seoul, Republic of Korea), respectively. Tapioca and normal corn starches were 12.7 and 12.3% (wet basis or w.b.), respectively, for their moisture contents, and 24.6 and 26.5% (dry basis or d.b.), respectively, for their amylose contents. 2,3-Epoxypropyl trimethyl ammonium chloride (ETMAC) (60% solution) as an etherifying agent was purchased from KCI Co. (Ansan, Republic of Korea). Kaolin was obtained from Sigma–Aldrich Co. (St. Louis, MO, USA). Sodium hydroxide and isopropanol were obtained from Daejung Chemical & Metals Co. (Incheon, Republic of Korea).

2.2. Synthesis of conventional non-granular cationic starch

Conventional non-granular cationic starch was synthesized according to Wang et al. (2009). Starch (20 g, d.b.) was dissolved in a mixture of distilled water (90 g) and 10% sodium hydroxide solution (10 g), and stirred at 60 °C for 1 h. ETMAC (45 g) was added to starch solution, and reaction was conducted at 60 °C for 5 h. After completion of reaction, the resultant starch derivatives were precipitated with addition of isopropanol, and recovered by centrifugation (3000 × g, 20 min). The recovered cationic starch derivatives were washed three times with isopropanol and dried at 105 °C for 12 h. Dried samples were ground, passed through 60-mesh standard sieve, and stored at room temperature for further analysis.

2.3. Synthesis of UHP-assisted non-granular cationic starch

Starch (20 g, d.b.) was dissolved in a mixture of distilled water (90 g) and 10% sodium hydroxide solution (10 g), and stirred at 60 °C for 1 h. ETMAC (45 g) was added to starch solution. The reaction mixture was immediately transferred into a retortable pouch and hermetically sealed using a heat sealer. It was pressurized in UHP unit (Ilshin Autoclave, Daejeon, Republic of Korea) using distilled water as a pressure medium. During pressurization, the UHP unit was maintained at room temperature (25 °C). The UHP treatments were conducted at 500 MPa for 15 min. After UHP treatment, the resultant starch derivatives were post-treated as previously mentioned in Section 2.2.

2.4. Synthesis of conventional granular cationic starch

ETMAC (38.27 g) was dissolved in distilled water (41.316 g), and then starch (20 g, d.b.) was slowly added to a reaction medium under continuous stirring. The pH of a reaction mixture was adjusted to 11.0 using 25% (w/v) sodium hydroxide solution. Reaction was conducted at 25 °C for 18 h under continuous stirring, after which the resultant starch derivatives were recovered by centrifugation (3000 × g, 20 min). The recovered starch derivatives were washed three times with isopropanol, dried at 105 °C, ground, passed through 60-mesh standard sieve, and stored at room temperature for further analysis.

2.5. Synthesis of UHP-assisted granular cationic starch

ETMAC (38.27 g) was dissolved in distilled water (41.316 g), and then starch (20 g, d.b.) was slowly added to a reaction medium under continuous stirring. The pH of a reaction mixture was adjusted to 11.0 using 25% (w/v) sodium hydroxide solution. The reaction mixture was immediately transferred into a retortable pouch and hermetically sealed using a heat sealer. It was pressurized in UHP unit (Ilshin Autoclave, Daejeon, Republic of Korea) using distilled water as a pressure medium. During pressurization, the UHP unit was maintained at room temperature (25 °C). The UHP treatments were conducted at 500 MPa for 15 min. After UHP treatment, the resultant starch derivatives were post-treated as previously mentioned in Section 2.4.

2.6. Scanning electron microscopy (SEM)

Morphological characteristics of native and cationic starches were viewed using scanning electron microscopy (TM3000, Hitachi, Tokyo, Japan). The starch samples were dusted onto a conductive double glued carbon tape on a cylindrical aluminum tray, and coated to 20 nm thickness using a sputtering coater with gold-palladium (60:40). All specimens were observed at an accelerating voltage of 15 kV.

2.7. Nitrogen content and degree of substitution (DS)

The nitrogen content of native and cationic starches was determined by a semi-micro Kjeldahl method. Degree of substitution (DS) was calculated as following:

$$\mathrm{DS} = \frac{162 \times N\%}{14 \times 100 - (151.5 \times N\%)}$$

where 14 is the molecular weight of nitrogen, 162 is the molecular weight of an anhydrous glucose unit (AGU) of starch, and 151.5 is the molecular weight of ETMAC.

2.8. FT-IR spectroscopy

FT-IR analysis of ETMAC, and native and cationic starches was conducted using Spectrum One System (Perkin-Elmer, Waltham, MA, USA). The starch samples were mixed with potassium bromide (KBr), and pelleted. The spectra were examined with a resolution of 4 cm^{-1} and a wavelength range of 400–4000 cm^{-1}.

2.9. ^{13}C nuclear magnetic resonance (NMR) spectroscopy

NMR spectra of native and cationic starches were recorded on a 300 MHz nuclear magnetic resonance spectrometer (JNM-AL300,