



Influence of reaction parameters on carboxymethylation of rice starches with varying amylose contents



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ABSTRACT

The influence of reaction parameters on the carboxymethylation of rice starches with different amylose contents was investigated. Rice starches with varying amylose contents showed various degrees of susceptibility to the reaction conditions. The maximum degree of substitution (DS) for all three rice starches was obtained under similar reaction conditions which involved a reaction medium consisting of isopropanol–water at the ratio of 90:10, a molar ratio of NaOH:AGU at 1.5 and a reaction temperature and time of 40 °C and 3 h. Under these conditions, the DS for all rice starches was similar; however, when the reaction was performed under conditions using lower NaOH concentration, the effect of starch types on the DS was observed. The results could be explained in terms of the granular/structural features of the different rice starches, their degrees of granular swelling as influenced by the reaction conditions and the accessibility of the etherifying reagents to starch molecules.

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1. Introduction

Starch is a major natural polymer that has been used for a long time in both food and non-food applications. However, certain undesirable characteristics of native starch such as insolubility in cold water and sensitivity of cooked starch to high temperature, low pH and shear have limited its wider industrial use. The common approach to overcome such drawbacks is by physical or chemical modification to alter the molecular structure and thus improve the properties to suit specific applications. Carboxymethyl starch (CMS) is an important modified starch widely used in many fields. CMS is used as a disintegrant (called sodium starch glycolate) in the pharmaceutical industry (Shah & Augsburger, 2002), and as a sizing and printing agent in the textile industry (Ragheb, El-Sayiad, & Hebeish, 1997; Roberts, 1967; Tatongjai & Lumdubwong, 2010). Recently, with an increasing interest in novel environmentally friendly products, CMS has found innovative applications as a raw material for the development of biodegradable bio-based hydrogels (Lawal et al., 2009) and of a sustained-release device for

drugs and bio-active compounds (Lemieux, Gosselin, & Mateescu, 2009; Mihaela Friciu, Le Tien, Ispas-Szabo, & Mateescu, 2013).

CMS is usually produced by the reaction of starch with monochloroacetic acid or sodium monochloroacetate (SMCA) based on Williamson's ether synthesis. The reaction is carried out in the presence of alkali in order to increase the nucleophilicity of the hydroxyl group and to aid the swelling of the starch granules. However, a side reaction between sodium hydroxide and SMCA can also occur (Bhattacharyya, Singhal, & Kulkarni, 1995). Since CMS becomes soluble in water when the degree of substitution is higher than 0.1 (Roberts, 1967), the reaction is usually carried out in an aqueous organic solvent, in most cases alcohol. The presence of alcohol prevents starch from gelatinizing and preserves the granular form of starch; thus, the side products and reagent residues can easily be washed out (Tijssen, Kolk, Stamhuis, & Beenackers, 2001). However, the alcoholic hydroxyl groups may compete with the starch for etherification with SMCA (Ambjörnsson, Schenzel & Germgård, 2013).

Due to the presence of an anionic functional group, CMS possesses unique properties such as solubility in cold water, improved storage stability of paste and increased paste and film clarity. Beside the botanical source of native starch, the properties of CMS are dependent on the DS (Sangseethong, Ketsilp, & Sriroth, 2005; Spsychaj, Wilpizewska, & Zdanowicz, 2013; Tatongjai &

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Lumdubwong, 2010). Although the synthesis of CMS was first reported in the literature in 1924 (Chowdhury, 1924) and the commercial product has long been available, it has continued to be a subject of many research studies (Bhattacharyya et al., 1995; Heinze, Pfeiffer, & Lazik, 2001; Jie, Wen-ren, Manurung, Ganzeveld, & Heeres, 2004; Kooijman, Ganzeveld, Manurung, & Heeres, 2003; Lawal, Lechner, & Kulicke, 2008; Li et al., 2010; Tijssen et al., 2001; Volkert, Loth, Lazik, & Engelhardt, 2004; Wang, Pan, Hu, Miao, & Xu, 2010). Most of these previous studies have focused on the reaction parameters that affect the DS of CMS and the optimization of CMS production from a specific type of starch; however, studies of the influence of the botanical source and structural parameters of the native starch on the carboxymethylation process have been relatively limited.

Bhattacharyya et al. (1995) studied the conditions for the carboxymethylation of common corn and waxy amaranth starches and found that the optimal reaction conditions for the two starches differed considerably. For comparison, the authors also included rice starch having a granule size similar to amaranth starch but an amylose (AM):amylopectin (AP) ratio similar to corn; and potato starch having a granule size larger than both corn and amaranth starch but an AM:AP ratio close to corn starch. However, it was not possible to draw a conclusion regarding the relationship between the DS of CMS and the size of the starch granule or the AM:AP ratio; probably because all four starches were from different botanical sources. Kittipongpatana, Chaitep, Kittipongpatana, Laenger, & Sriroth (2007) prepared CMS from rice starches and found that there was a positive correlation between the AM content in the native rice starch and the DS of the obtained CMS. On the other hand, Tatongjai and Lumdubwong (2010) reported that AM did not affect the DS of CMS prepared from rice starches with varying AM contents. The discrepancy between the previous reports might be due to the different sets of reaction conditions used in those studies.

The aim of this work was to study the carboxymethylation of rice starches containing different AM contents. The factors expected to affect the carboxymethylation process including the type of solvents, the water content in the reaction medium, the molar ratio of NaOH to AGU ($n_{\text{NaOH}}:n_{\text{AGU}}$) and the reaction temperature and time were systematically investigated. The results will provide insights into the structural aspect of starch that affects the carboxymethylation process and allows the determination of the optimal operating conditions to achieve carboxymethyl rice starches (CMRS) with a high degree of substitution.

2. Materials and methods

2.1. Materials

Three types of commercial rice starch were used in this study. Normal rice starch (NRS) was kindly provided by General Food Products Co., Ltd., Nakhon Rachasima, Thailand. Jasmine rice starch (JRS) and glutinous rice starch (GRS) were obtained from Bangkok Starch Industrial Co., Ltd., Nakhon Pathom, Thailand. Sodium monochloroacetate was obtained from Fluka Analytical (Buchs, Switzerland). Ethanol (95% purity) used to wash CMRS was of technical grade. All other chemicals used in the study were of analytical grade.

2.2. General analytical methods

The contents of fat, ash and moisture were examined according to AOAC methods 2003.05, 923.03 and 925.10 (2012). The nitrogen content of the rice starches was determined by the AOAC Kjeldahl method 2001.11 (2012) and converted to protein contents using

a factor of 5.95. The apparent amylose content was determined according to the colorimetric method of Juliano (1971).

2.3. Preparation of carboxymethyl starch

The method for the carboxymethylation of rice starches was based on our previous report (Sangseethong et al., 2005) with slight modification. The reaction was performed in aqueous-organic liquid media. The organic solvents used in this experiment were methanol, ethanol and isopropanol. The reaction was carried out in a 250 mL two-necked round-bottom flask equipped with a motor-driven stirrer. In the first step, 12.5 g of starch (10% w/w of starch–aqueous–alcohol mixture) was dispersed in the organic solvents (being varied between 70 and 95% according to the specified content of water in the aqueous–alcohol solution). While the starch slurry was vigorously stirred at 250 rpm, an aqueous solution of NaOH (0.5–3.0 mol/mol AGU) was added drop-wise. The amount of water used to prepare the NaOH solution was varied (5–30% w/w of aqueous–alcohol solution) according to the experimental plan in Table 1. The reaction mixture was then heated to the target temperature (30, 40 and 50 °C). After stirring for 10 min, SMCA powder (1 mol/mol AGU) was added to the mixture. The mixture was stirred at the defined experimental conditions for a certain period of time (0.5–5 h). At the end of the reaction period, the starch slurry was filtered, and the recovered product was suspended in 95% ethanol and neutralized (pH 5.5–6.5) with aqueous HCl solution. Following filtration, the starch was dispersed again in 85% ethanol, and the suspension was filtered. This process was continued until the silver nitrate test for chloride in the filtrate was negative. The starch was then washed with absolute ethanol twice and dried in an oven at 40 °C for 16 h. The compilation of experimental conditions for this study is given in Table 1.

2.4. Determination of degree of substitution (DS)

The Na-form of CMRS was first converted to the acid form (H-CMRS) by the method described by Stojanovic, Jeremic, Jovanovic, and Lechner (2005) with slight modification. CMRS (3 g) was dispersed in acetone (90 mL) by stirring with a magnetic stirrer and then converted to the acid form (H-CMRS) by adding 6 M HCl (7.5 mL). After being stirred for 30 min, the dispersion was filtered; the recovered product was redispersed in 80% ethanol, and the product was recovered from the suspension by filtration. This process was repeated until the filtrate became neutral. The H-CMRS was then dispersed in absolute ethanol, recovered by filtration, dried at 50 °C and ground. The H-CMRS was then used for the DS determination by back titration according to ISO-11216 (1998). About 0.5 g (accuracy of weighing ± 0.1 mg) of the H-CMRS was dissolved in 25 mL of 0.1 M NaOH. Deionized water (75 mL) was then added. The excess NaOH was back-titrated with standardized 0.1 M HCl using phenolphthalein as the indicator. A blank titration was also conducted. The DS was calculated from the following equation:

$$DS = \frac{w_c \times 162}{(100\% - w_c) \times M_c}$$

where 162 g/mol is the molar mass of AGU, M_c is the molar mass of the carboxymethyl group (58 g/mol) and w_c (% by mass) is the carboxymethyl group content calculated from the following equation:

$$w_c = \frac{c_{\text{HCl}} M_c \times (V_b - V_s) \times 100\%}{m} \times \frac{100\%}{100\% - w_m}$$

where c_{HCl} (mol/L) is the HCl concentration, V_b (mL) is the volume of HCl used for the blank titration, V_s (mL) is the HCl volume used for

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