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Effect of microwave-assisted dry heating with xanthan on normal and waxy corn starches

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ABSTRACT

Normal corn starch (CS) and waxy corn starch (WCS) were impregnated with xanthan gum (1% based on starch) and heat-treated using a microwave in a dry state for 0, 4, or 6 min (CS-X0, CS-X4, CS-X6, WCS-X0, WCS-X4, WCS-X6), respectively. Effects of the microwave-assisted dry heating (MADH) on pasting, morphological, and structural properties were evaluated. The results revealed that the viscosity of both the CS and WCS with xanthan increased compared with untreated samples after MADH, and the effect on WCS was more obvious. The syneresis values showed that the water-holding ability of CS-X6 and WCS-X6 increased, and that value of CS was lower than that of WCS after MADH with xanthan. The MADH with xanthan reduced the T_o, T_c, T_p, and ΔH values of both the CS and WCS. After MADH, the particle morphology of the starch–xanthan connected more densely, especially WCS, and the gelatinized samples exhibited a strong and smooth laminar structure. The Fourier transform Infrared Spectroscopy (FTIR) displayed that the absorption peak width of both CS-X6 and WCS-X6 became larger. X-ray diffraction showed that the crystallinity of CS-X6 and WCS-X6 decreased slightly as a result of MADH, and the crystalline pattern remained A-type.

1. Introduction

With the concept of "green chemistry," starch, as a kind of natural high-molecular compound, becomes a kind of ideal green raw material, due to its high yield and low cost, and because it is easily biodegradable and harmless to the environment. It has a wide range of applications, such as thickener, colloidal stabilizer, gelling agent, bulking agent, and water-holding agent [1]. However, native starch has some undesirable defects, such as poor solubility, uncontrolled paste consistency, and low freeze–thaw stability of pastes. Therefore, chemical modifications of starch are widely used to improve and enhance its inherent properties in accordance with the intended purposes [2]. However, these applications are often restricted due to some shortcomings, such as residual chemical reagents and associated environmental pollutants [3]. Dry heating treatment is a physical modification that changes the physicochemical properties of starch without destroying its granule structure [2]. Compared with chemical methods, dry heat is a simple, safe, and healthy method. Chiu et al. [4] introduced a dry heating process for formulating physically modified starches. They reported that thermally treated starches yield a functionality equivalent to that obtained by chemical cross-linking [4,5]. Dry heat treatment with xanthan provides the most substantial changes in the paste viscosity of starches, which increases the peak viscosity of starches [6]. Waxy rice starch heated with a mixture of phosphate salts and xanthan has been shown to exhibit a continuous increase in pasting viscosity [7]. After dry heat treatment, the gel structure of potato starch heat-treated with CMC becomes more compact and forms into many small lumps [8]. The pasting and rheological properties of waxy rice starch change greatly, and the gel forming ability of the waxy rice starch becomes stronger after dry heat treatment with xanthan [5].

To sum up, dry heat treatment with ionic gums is a good method to physically modify starch, but such dry methods require a high temperature of 130 °C and a long time (2–4 h), which does not conform with the concept of energy savings and emissions reduction. The advantage of a microwave-assisted reaction is that it provides fast and uniform heating [9], and it is economical and environmentally friendly, as it minimizes energy consumption [10]. In this study, normal corn starches (CS) and waxy corn starches (WCS) were heat-treated by microwave in a dry state after being impregnated with xanthan gum. The effects of the microwave-assisted dry

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heating (MADH) treatment on the pasting behavior, morphology, and structural properties of the samples were evaluated.

2. Materials and methods

2.1. Materials

The CS (26.55% amylose content) and WCS (0.54% amylose content) used in this study were from Shandong Zhucheng Starch Company, Weifang, China. Xanthan was purchased from Zhengzhou Shun Da Chemical Co. Ltd., Zhengzhou, China. All other reagents were of analytical grade.

2.2. Methods

2.2.1. Starch modification by MADH treatment with xanthan gum

The starches were modified by dry heating with gums according to the procedures of Lim et al. [6], with some modifications. Xanthan gum (0.5 g, db.) was slowly added to distilled water (100 mL) with vigorous stirring. After the gum was completely dissolved, granular starch (45.5 g, db.) was dispersed into the gum solution. The dispersion was stirred for 30 min at room temperature and then transferred to a glass dish and dried at 45 °C in a convection oven until the moisture content reached about 5%. The dried starch gum mixture was ground to a powder and passed through a 100-mesh sieve.

The starch–gum mixture was placed in a Petri dish and sealed with plastic wrap, which was then pricked to allow steam to escape. The dish was heated in the microwave oven at 600 W for 4–6 min. An untreated sample and native starch were used as control. Each dried starch sample was kept in a hermetic container at room temperature for further analysis.

2.2.2. Pasting properties

The pasting properties of the modified starches were determined using a rapid viscosity analyzer (RVA) (Master; Newport Scientific, Pty Ltd, Australia). Deionized water (25 ml) was added to the starch (3.0 g, 14 g/100 g moisture basis) in the RVA canister to obtain a total constant sample weight of 28 g. The slurry was then manually homogenized using a plastic paddle to avoid lump formation before the RVA run. The starch slurry was heated from 50 °C to 95 °C at a rate of 12 °C/min, maintained at 95 °C for 2.5 min, then cooled to 50 °C at the same rate, and held at 50 °C for 2 min. Parameters were recorded, including peak viscosity; viscosity at the end of the hold time at 95 °C, or trough viscosity; final viscosity at the end of cooling; and breakdown, setback, and pasting temperatures. All tests were replicated three times.

2.2.3. Syneresis properties

Syneresis was measured using the method of Mohammed [11], with some modifications. Starch slurry (6 wt%) was pasted by RVA. Gels obtained from the RVA canisters were shifted to graduated centrifuge tubes and stored in a freezer at −20 °C. After four days of storage, the gels were placed in a water bath at 50 °C for 30 min and centrifuged at 3000 × *g* for 15 min. The water was separated from the gel via centrifugation. The amount of water separated from the gels was recorded, and the gels were restored in the freezer for another four days. Water separation after eight days was recorded using the same procedure. The syneresis percentages recorded for the two freeze–thaw cycles were reported on the fourth day and four days after that, and the total after eight days was recorded. The syneresis percentage was calculated using Eq. (1):

$$SV\% = \left(\frac{W_s}{W}\right) \times 100 \quad (1)$$

where SV is the syneresis value, W_s is the weight of the water separated from the gels, and W is the weight of the gel obtained from the RVA canisters.

2.2.4. Thermal properties

The thermal properties of the products produced via heat treatment described above were investigated using a differential scanning calorimeter (DSC 1; Mettler–Toledo, Schwerzenbach, Switzerland) as described by Chanvrier et al. [12], with minor modifications. Indium was used as the calibration standard. Each product sample (approx. 4 mg) was placed in a stainless steel pan, extra water was added (8 ml), and the container was hermetically sealed. The scan was carried out immediately to minimize retro gradation. The samples were heated at 5 °C/min, from 25 °C to 115 °C, to observe the presence of any residual enthalpy gelatinization.

2.2.5. Scanning electron microscopy (SEM)

The surface topography of the samples was observed by SEM, using the method of Kim et al. [13], as starch granule samples can be observed directly with that method. Normal corn starch and WCS pastes were gelatinized with RVA, and then put into an ultra-low temperature freezer and freeze dried for 48 h. A dry, finely ground sample was placed on double-sided Scotch tape, mounted on an aluminum specimen holder, and coated with a thin film of gold, under vacuum. Samples were observed under a Jeol scanning electron microscope (JSM 840; Jeol, Japan).

2.2.6. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of the samples were recorded with an FTIR spectrometer (NEXUS-870; Thermo Nicolet Corporation). The dried samples were mixed with KBr, ground, and formed into pellets. The FTIR spectra were ranged from 500 cm^{-1} to 4000 cm^{-1}.

2.2.7. X-ray diffraction analysis

The X-ray patterns of starches were obtained with an X-ray diffractometer (Rigaku Miniflex, Japan). The starch powder was packed tightly in small holders. The scanning range was 4–40° of 2θ values. The overall degree of crystallinity was quantified as the ratio of the area of crystalline reflections to the overall diffraction area. The relative crystallinity was calculated according to the literature [14].

2.2.8. Statistical analysis

All experiments were conducted at least in triplicate, and the experimental data were analyzed by analysis of variance (ANOVA), using the Origin Pro 8.0 statistics program, and expressed as mean ± standard deviation. Differences were considered significant at a 95% level ($p < 0.05$).

3. Results and discussion

3.1. Pasting properties

Paste viscogram data of the starches before and after MADH with 1% xanthan are shown in Table 1. We could see that MADH with xanthan decreased the pasting temperatures of the samples (Table 1). Lim et al. [6] reported that waxy maize starch displayed similar results after heat treatment. A possible explanation might be that the water absorption of xanthan is strong, which inhibits the interaction between starch particles and water, but under MADH conditions, starches interact with xanthan in such a way that the inhibition effect is lower and the pasting temperatures decrease.

The paste viscosity was substantially changed by MADH when xanthan was present. The viscosity value of the starch–xanthan mixture was similar to that of native starch, but the viscosities increased significantly as the MADH time was prolonged.