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Interactions between wheat starch and cellulose derivatives in short-term retrogradation: Rheology and FTIR study

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ABSTRACT

The understanding of the interactions between starch and cellulose hydrocolloids is crucial for equipment design and definition of operation parameters in the food industry. In the present study, the possible interactions of wheat starch (WS) with different levels (2–10%) of carboxymethyl cellulose (CMC) or microcrystalline cellulose (MCC) in short-term retrogradation were explored by dynamic rheological and Fourier transform infrared spectrum (FTIR) measurements. The chains of water-soluble CMC could creep into the continuous phase during paste gelation. It was found the amylose network structure was broken and the inter- and intra-molecular hydrogen bond of WS were weaken after gelation. Moreover, there were interactions between the chains of CMC and chains of amylose at higher CMC concentration. On other hand, water connected with $-COO^-$ groups blocked the interactions between CMC chains and amylose, and the interactions among CMC chains. The amorphous phases of high crystalline MCC were just swollen during paste gelation. It results that heterogeneous microstructure with amylose and MCC domains unevenly distributed was in WS/MCC paste.

1. Introduction

Starch is widely used in the food industry, either as a main raw material or as a food additive (Huc et al., 2014; Sun, Si, Xiong, & Chu, 2013). Wheat starch is composed of linear chains of amylose and highly branched chains of amylopectin (Miyazaki & Morita, 2005). However, inherent properties of the native starch are undesirable for most food products. Most of production processes involve thermo-mechanical treatments, the starches present swelling capacity when heated in excess water. Further heating leads to the breakdown of the granules and tendency to exhibit a decrease in viscosity (Eliasson, 1986; Lawal, 2009; Song, Kwon, Choi, Kim, & Shin, 2006). Moreover, the use of starches alone is limited due to their tendency to syneresis and retrogradation during cooling, leading to changes in texture and to a short-shelf life (J. Singh, Kaur, & McCarthy, 2007; Techawipharat, Suphantharika, & BeMiller, 2008). Therefore, combinations of starches and hydrocolloids have arisen interest of food scientist and technologists. Hydrocolloids, such as CMC, guar gum, methylcellulose, xanthan, were found to improve stability and thickening properties, regulate moisture and water mobility, and optimize applicability of starch based systems (Kim & Yoo, 2006; Kim & Yoo, 2011; Rosell, Yokoyama, & Shoemaker, 2011; Sarker et al., 2013). These showed that the interactions occur between starches and hydrocolloids in the process of starch gelatinization, but the interactions are specific for a particular starch and particular hydrocolloid combination (Aguirre-Cruz, Méndez-Montealvo, Solorza-Feria, & Bello-Pérez, 2005; H.-S. Kim & BeMiller, 2012; Rosell et al., 2011). Moreover, most of hydrocolloids, such as guar gums, xanthan and carrageenan are often restricted by geographical and source factors. Nevertheless microcrystalline cellulose (MCC) and carboxymethyl cellulose (CMC) are safe and extensively used as food additives (Arancibia, Bayarri, & Costell, 2013; Correa, Añón, Pérez, & Ferrero, 2010). In the food industry, cellulose derivatives are widely used as thickener, suspending agent, stabilizer, emulsifier (Mariotti, Lucisano, Pagani, & Ng, 2009; Tiwari, Muthukumarappan, O'Donnell, Chenchaiah, & Cullen, 2008). In addition, they are also used as dietary fiber to reduce calories and meet the demand of special groups (Correa et al., 2010). The blending of starches and cellulose derivatives is in accordance with the modern health-conscious food industry development (Techawipharat et al., 2008). Therefore, the understanding of the interaction between cellulose derivatives and wheat starch is important in order to improve product quality and regulate production processes.

Rheology contributes to the knowledge of the materials structure. In food industry, rheological measurements were widely used to study the interaction between starches and non-starch polysaccharides (Choi & Yoo, 2009; Kim & Yoo, 2011; Sarker et al., 2013).

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Techawipharat et al. (2008) reported that CMC increased the peak and final viscosities, but addition of CMC did not significantly affect storage modulus(G′), loss modulus(G″) and tanδ values of waxy rice starch, indicating a similar microstructure of these pastes. Aguirre-Cruz and his coworkers investigated the effect of CMC addition on maize masa through dynamic studies performed in a rheometer. These authors observed that in the rheological profiles recorded throughout heating, cooking and cooling during which the gel built up. The G′ value for maize masa with 2% CMC were higher than that of the starch, possibly because at this concentration, the molecular mobility is restricted by the network formed, increasing the rigidity of the system.

Another widely used technique to study the intermolecular interactions of starches is Fourier transform infrared spectroscopy (FTIR). Different from the abovementioned rheological measurements, FTIR measures interactions by detecting the characteristic bands of chemical groups (Goodfellow & Wilson, 1990; Kizil, Irudayaraj, & Seetharaman, 2002). Kizil et al. (2002) investigated comprehensive characterization of six selected irradiated starch samples. On the basis of that characterization specific chemical groups and linkages corresponding to radiochemical changes were identified (Kizil et al., 2002). Bello-Pérez, Ottenhof, Agama-Acevedo, and Farhat (2005) have used FTIR to study the retrogradation of amylose and amylopectin of banana starch because the spectra were sensitive to short-range order. However, these studies did not involve the interactions between starch and hydrocolloids determined by FTIR (Bello-Pérez et al., 2005).

In the present work, FTIR spectroscopic and rheology studies to characterize the interactions then may develop in the WS/CMC and WS/MCC system. These two methods combine molecular vibration with mechanical analysis to clarify the interactions. The finding will reveal the network characteristics of starch pastes containing cellulose-derivatives, which could guide the food formulations and processing, and promote starch-containing cellulose for industrial applications in food industry.

2. Materials and methods

2.1. Materials

Wheat starch (WS) were purchased from Dongguan Hui Mei starch technology Co., Ltd., (Guangdong province, China). The WS contained 12.1% moisture, 0.19% protein, 0.33% fat, 32.1% amylose. Carboxymethyl cellulose (CMC, Degree of substitution = 0.89) (coronet cellulose Co., Ltd., Shandong province, China). Microcrystalline cellulose (MCC, average degree of polymerization = 150) (Hu Zhou prospect pharmaceutical Co., Ltd., Zhejiang province, China).

2.2. Preparation of wheat starch-cellulose gum mixture pastes

WS slurry (8.0%, w/w) was dispersed in deionized water under strong mechanical stirring. Once dispersed, milder stirring was continued for 30 min at room temperature. In order to avoid the entry of air into the sample (Choi & Yoo, 2008 and Kim & Yoo, 2011), the sample was then heated from room temperature to 90 °C with magnetic stirring in a thermostat water bath, After 30 min stirring, the sample was cooled immediately and storage at 4 °C for 8 h until further testing. This procedure was used to ensure starch gelatinization, then the sample was named as control.

Starch-hydrocolloid slurries (8.0%, w/w) were prepared by mixing starch with CMC or MCC in deionized water under strong mechanical stirring, respectively. The dosage of CMC and MCC are 2.0%, 4.0%, 6.0%, 8.0%, 10.0% (w/w, dry basis). Once dispersed, milder stirring was continued for 30 min at room temperature. Then the thermal treatment procedures were the same as the control's as described. These procedures were used to ensure starch gelatinization, CMC dissolution and MCC swelling. Then these samples were marked as WS + 2CMC, WS + 4CMC, WS + 6CMC, WS + 8CMC, WS + 10CMC, respectively, or WS + 2MCC, WS + 4MCC, WS + 6MCC, WS + 8MCC, WS + 10MCC, respectively.

2.3. FTIR measurements

The specimens were ground into powder after freeze-drying and were analyzed using a Bruker TENSOR 27 Fourier transform infrared spectrometer. The samples were mixed with KBr and then the mixture was tableted by a machine under a 15 t/cm^2 pressure for 1 min to keep all pellets in the same thickness and uniformity as possible. The spectra were obtained after 32 scans, and the range of the spectra is 4000–400 cm^{-1} with the resolution of 4 cm^{-1}. FTIR spectra were recorded as transmission mode spectra against a KBr background.

2.4. Dynamic rheological measurements

The dynamic rheological properties of wheat starch-cellulose gum mixture pastes were determined according to Kim and Yoo (2011). The data were obtained using a rheometer (AR 550, TA Instruments, New Castle, DE, USA) with a parallel plate system (40 mm dia.) at a gap of 500 μm. Each sample was equilibrated at 25 °C. Dynamic rheological data were obtained from frequency sweeps over the range of angular frequency (1–100 rad s^{-1}) at 1% strain, which was in the linear viscoelastic region. The storage modulus (G′), loss modulus (G″), complex viscosity (η*), and loss tangent (tanδ) were calculated by TA Data Analysis software (version 5.7.0.3).

2.5. Statistical analysis

All samples were analyzed in triplicate and the results were reported as the mean. Statistical analysis was performed by IBM SPSS V.18.0 statistical software (SPSS Inc., Chicago, USA). A one-way analysis of variance (ANOVA) and Duncan's Test were used to describe the significance of differences among the mean values. Significant differences were defined as $P \leq 0.05$.

3. Results and discussion

3.1. FTIR spectroscopy

The FTIR spectra (4000–400 cm^{-1}) of CMC, MCC, the control and different proportion WS/CMC and WS/MCC mixtures are showed in

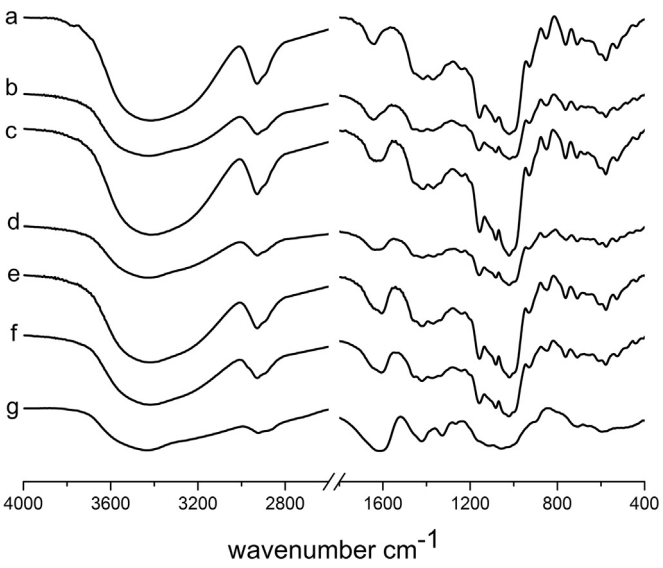

Fig. 1. The FTIR spectra of CMC, the control and CMC/WS mixtures (a: control, b: WS + 2CMC, c: WS + 4CMC, d: WS + CMC, e: WS + CMC, f: WS + CMC, g: CMC).