



The rheological behavior of native and high-pressure homogenized waxy maize starch pastes

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ABSTRACT

Both steady and large amplitude dynamic rheological testes were carried out in hydrothermally gelatinized waxy maize starch (WMS) pastes. The concentration of WMS was maintained at 6.0% (w/w) throughout these tests. The WMS pastes exhibited shear thickening behavior during the first up curve in steady shear tests. The shear thickening behavior was found to be irreversible and could not be retained after equilibrating the pastes beyond 6 h. The change in the shape of Lissajous curves was insignificant during strain sweeps at higher angular frequencies. This arose because of slow response of WMS pastes to oscillatory strain within a period of oscillatory shear, which can be attributed to the domination of rheological properties by amylopectin in continuous phase. High-pressure homogenization (HPH) was found to significantly reduce the apparent viscosity of the WMS pastes. After HPH, the WMS pastes behaved like typical Newtonian fluids.

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1. Introduction

Starch is a main component of foods and it is also commonly used as an ingredient for thickening and gelling. Since the rheological behavior of starch paste and suspensions is very important in processing, the rheological properties of starch pastes or suspensions are quite intensively investigated. Unlike normal starch (amylose content between 20 and 30%, w/w) and high-amylose starch (amylose content >50%, w/w), waxy starch contains only traces of amylose (Achayuthakan & Supphantharika, 2008; Preiss, 1991). Due to the unique composition (i.e. 100% amylopectin), waxy starch is reported to be a promising raw material in food, medicine, and cosmetic industries (Lehmann, Volkert, Fischer, Schrader, & Nerenz, 2008; Sands, Leidy, Hamaker, Maguire, & Campbell, 2009). The knowledge of rheological behavior of the food ingredients (such as starch pastes) is important to optimize applicability, stability and sensory properties of end products (Kulicke, Eidam, Kath, Kix, & Kull, 1996). Waxy starch paste is an ideal biphasic model for rheological study. This is because the pastes of waxy starch contain both degraded starch granules and a continuous matrix of amylopectin, which makes such suspensions ideal model for

the investigation of rheological properties of biphasic model fluids (Rodríguez-Hernández, Durand, Garnier, Tecante, & Doublier, 2006). In these systems, due to the absence of amylose, the complexity of the paste system can be simplified. In addition, to waxy starch pastes the effects of gelation and retrogradation on the rheological properties caused by amylose can also be avoided.

Because of the purity of amylopectin, the paste obtained from waxy starch is reported to have quite different rheological properties from those obtained from common starch and high-amylose starch. For examples, waxy starch pastes have different thixotropic properties from the pastes obtained from the corresponding common and high-amylose starches. The anti-thixotropic property which features a counter-clockwise loop of shear stress/apparent viscosity versus shear rate during the steady shear cycle (involving a rate ramp up to a peak shear rate, then a ramp down back to zero) is mostly reported for waxy starches (Wang, Li, Wang, & Özkan, 2010). Furthermore, shear thickening property is essentially reported for waxy starch during the shear tests, indicating the existence of quite different flow properties in waxy starch compared to other starches (Wang, Wang, Dong Li Zhou, & Özkan, 2011).

The investigation of the shear-thickening behavior of waxy maize starch (WMS) pastes with relatively low concentrations (<10%, w/w) was initiated by Dintzis et al. (Dintzis & Bagley, 1995; Dintzis, Berhow, Bagley, Wu, & Felker, 1996). Dintzis and Bagley (1995) showed that the waxy starch suspensions (3%, w/w) gelatinized using 0.2 M sodium hydroxide (without starch particle

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Nomenclature

K	consistency index, Pa s^n
n	flow behavior index, dimensionless
R^2	correlation coefficient, dimensionless
$\dot{\gamma}$	shear rate, s^{-1}
γ	shear strain, dimensionless
γ_0	maximum shear strain within a period of oscillatory shear, dimensionless
η^*	complex viscosity, Pa s
η_a	apparent viscosity, Pa s
τ	shear stress/oscillatory stress, Pa
τ_0	maximum oscillatory stress within a period of oscillatory shear, Pa
ω_0	constant angular frequency in strain sweep, rad/s

ghosts) can display shear-thickening behavior. When the amylose and amylopectin fractions were separated from normal potato starch and the rheological behavior of each fractions were investigated, it was found that only the dispersed amylopectin fraction displayed shear thickening behavior (Dintzis et al., 1996). As a result, shear thickening was ascribed to free amylopectins by Dintzis et al. (1996). In subsequent study, Kim, Willett, Carriere, & Felker (2002) reported similar shear thickening behavior in starch pastes obtained using gentle alkali-gelatinization, and ascribed shear thickening in these pastes to the breaking up of the highly concentrated gel-like starch clusters during the tests, which caused increase in effective starch concentration. Wang et al. (2011) gelatinized the waxy maize starch using hydrothermal method coupled with strong agitation and found that the pastes obtained in this way also displayed shear-thickening behavior. They also found that the shear thickening behavior was related to both temperature during the tests and starch concentration used.

In many physiological processes such as mastication and swallowing, the deformation is large and rapid. This necessitates that the non-linear viscoelastic characteristics be measured and quantified. Large amplitude oscillatory shear (LAOS), which is normally generated by a strain sweep test, can produce a measurable non-linear material response in the fluids (Hyun, Kim, Ahn, & Lee, 2002; Hyun et al., 2011). LAOS behavior of the fluids was reported to be associated with formulation details (material composition and microstructure), and is very sensitive to the interactions or the shear-induced formation of microstructures of complex fluids (Hyun et al., 2002; Leblanc, 2007). The LAOS behavior of the WMS pastes was also studied in this study.

After gelatinization, mechanical treatments during downstream processing such as mixing, extrusion, pumping and homogenization directly affect the rheological properties of starch pastes or suspensions. It is reported that shear rates of 1 to 10^2 s^{-1} in extrusion, 1 to 10^3 s^{-1} in tube flow mixing and pumping and up to 10^5 s^{-1} in high-pressure homogenization (HPH) are very common in food industry (Barnes, Hutton, & Walters, 1989; Loh, 1992; Nayouf, Loisel, & Doublier, 2003). Due to very high energy input per mass of a product, HPH can usually introduce new and surprising changes in products. To our knowledge, only limited studies are so far carried out in order to study the effect of HPH on rheological properties of polysaccharide solutions. Viturawong, Achayuthakan, and Supphantharika (2008) prepared xanthan gum solutions of different molecular weights by using HPH at 70 MPa with different numbers of passes. This study showed that the addition of xanthan gum with a higher molecular weight had a more pronounced effect on rheological properties of rice starch pastes. Che et al. (2009) applied HPH up to 100 MPa in 2.0% (w/w) potato and cassava starch slurries, and reported significant decrease in apparent viscosity. However, the

effect of HPH on rheological properties of waxy starches or special starches which have no amylose is still unavailable.

The objectives of this study were to investigate the effects of pre-shearing and conditioning time, testing mode (steady shear/large amplitude oscillatory shear), as well as homogenization pressure on rheological properties of the waxy maize starch pastes. We believe this study provides comprehensive understandings and new insights into rheological properties of WMS pastes which can be applied to various production processes in food processing industries.

2. Materials and methods

2.1. Materials

Commercial waxy maize starch (amylose content <1%, w/w) was purchased from Jinan Jinwang Food Co., Ltd. (Shandong Province, China). The moisture content of the starch was determined by drying sample in an air-oven maintained at 105°C to constant weight. Triplicate drying experiments were carried out and the average value of those experiments was 9.71% (w/w). Commercial normal maize starch (22% amylose, w/w) was purchased from Weizhiyuan Food Co., Ltd. (Beijing, China), and the moisture content was determined to be 11.35% (w/w).

2.2. Preparation of waxy maize starch (WMS) suspensions

The WMS slurries with WMS concentration of 6.0% (w/w) were prepared by dispersing calculated amount of WMS (dry basis) into distilled water to make a total weight of 150 g. Subsequently, the well mixed WMS slurry (150 g) was transferred to a conical flask (250 ml), and heated in a water bath at 95°C for 40 min. The mixing rate was 450 rpm during gelatinization. The mixing/agitation rate during the gelatinization process was controlled by a digital mixer (EUROSTAR, IKA Instruments, Germany). Once the pasting/gelatinization process was completed, the samples were rapidly cooled in another water bath. For reference, the 6.0% (w/w) normal maize starch (NMS) pastes were prepared in the same way. The cooled samples were equilibrated in an incubator at 25°C for 2 h before measurement. For replicate tests, fresh samples were prepared to ensure the consistency and accuracy.

2.3. Steady shear test of WMS pastes

Steady flow properties of the samples were determined using an AR2000ex rheometer (TA Instruments Ltd, Crawley, UK) at 25°C . An aluminum parallel plate geometry (40 mm diameter) was used and the gap size was set as 1.0 mm during all the tests. Before testing, a thin layer of silicone oil was applied on the edge of the sample in order to prevent moisture evaporation. Continuous-ramp steady shear measurements of the WMS pastes (6.0%, w/w) were performed at 25°C to obtain shear stress/apparent viscosity versus shear rate data.

Both the logarithmic mode and linear mode of shear rate ramp were adopted. For the tests conducted in log mode, the stepped-ramp shear rate was programmed to logarithmically increase from 0.1 to 500.0 s^{-1} followed immediately by a logarithmic reduction in the shear rate from 500.0 to 0.1 s^{-1} . Fourteen points were collected per decade for both the ramping-up and ramping-down steps. In the case of linear mode, the shear rate was programmed to linearly increase from 1.0 to 500.0 s^{-1} within 6 min. It was followed immediately by a linear decrease from 500.0 to 1.0 s^{-1} at the same time scale. For comparison, continuous-ramp steady shear measurements of the NMS pastes (6.0%, w/w) were performed at 25°C in linear mode.

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