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Anti-thixotropic properties of waxy maize starch dispersions with different pasting conditions

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ABSTRACT

The effects of pasting conditions, testing temperature, and shear rate on the anti-thixotropy of waxy maize starch (WMS) dispersions were investigated in this study. Activation energy and viscoelastic properties of the WMS dispersions were also determined to understand the anti-thixotropy of these dispersions. The WMS dispersions (5.0 wt.%) displayed both thixotropic and anti-thixotropic properties in loop and shear recovery tests, depending on pasting conditions and testing temperature. The standard anti-thixotropy test indicated anti-thixotropy of WMS dispersions only appeared at a certain shear rate range. When WMS dispersion was pasted more completely, the shear rate range for anti-thixotropy became wider, also the sample showed improved heat stability. The anti-thixotropy of the WMS dispersions was ascribed to re-range of the amylopectin molecules under appropriate shear rates. The normal maize starch (NMS) dispersion (5.0 wt.%) could not display anti-thixotropy here, due to a different paste structure formed by amylose in the continuous phase.

1. Introduction

Waxy maize starch (WMS), which contains about 99% amylopectin, is an essentially amylose-free starch (Achayuthakan & Suphantharika, 2008). Because of its unique composition, WMS has many specific attributes such as swelling easily, giving sticky texture, hardly retrograding, and better digestibility than normal starches (Enes, Panserat, Kaushik, & Oliva-Teles, 2006; Hibi, 2001), making it a promising raw material in food, medicine, and cosmetic industries (Lehmann, Volkert, Fischer, Schrader, & Nerenz, 2008; Sands, Leidy, Hamaker, Maguire, & Campbell, 2009; Wang et al., 2009a).

The rheological properties of starches are very important, which could determine their value and understand their behavior during the process. For example, in food technology, specific adjustment of the flow behavior of starch gels is significant in order to regulate production processes and to optimize applicability, stability, and sensory properties of the end products (Kulicke, Eidam, Kath, Kix, & Kull, 1996). In paper making and textile industries, the rheological properties of starch solutions could determine the loss of momentum during pipe transportation and the quality of final production. As a result, for a successful product formulation and engineering scale up, the knowledge about rheological properties of starch solutions is necessary (Bhandari, Singhal, & Kale, 2002).

In our last paper, the anti-thixotropic behavior of WMS dispersions was reported in the steady flow and in-shear structural recovery measurements (Wang et al., 2009a). Anti-thixotropy, which is also known as rheopexy (Dewar & Joyce, 2006), is just opposite to thixotropy of solutions or suspensions. It was reported that an anti-thixotropic behavior is observed when viscosity increases with time at a fixed shear rate, while a thixotropic effect is described as a viscosity decrease with time at a constant shear rate (Gouveia, Muller, Marchal, & Choplin, 2008). Besides, the anti-thixotropic properties could also be determined through a steady shear tests involving a rate ramp up to a peak shear rate, then a ramp down back to zero; and the fluids with such properties could display an anti-hysteresis in the form of a counterclockwise loop (Achayuthakan & Suphantharika, 2008; Acquarone & Rao, 2003; Tattiyakul & Rao, 2000; Wang et al., 2009a). Anti-thixotropy of liquids or suspensions has important significance in industries, such as cement with rheopectic property which can be used in building a bridge pier underwater, or molding plaster with anti-thixotropic behavior, which could accelerate solidification and molding under shaking.

Till now, only limited messages were given about the anti-thixotropy of starch dispersions. In our last study, it was found that the anti-thixotropy of WMS dispersions had some relationships with pasting conditions. It seems WMS dispersions only displayed such

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Nomenclature

E_a	activation energy (J/mol)	R	gas constant (J/mol K)
G'	storage modulus (Pa)	R^2	correlation coefficient (dimensionless)
G''	loss modulus (Pa)	T	absolute temperature (K)
K'	index (Pa s^n)	$\dot{\gamma}$	shear rate (s^{-1})
K''	index (Pa s^n)	η_a	apparent viscosity (Pa s)
n'	frequency exponent (dimensionless)	η_∞	frequency factor (dimensionless)
n''	frequency exponent (dimensionless)	ω	angular frequency (rad/s)

properties after being sufficiently pasted (Wang et al., 2009a). Since there are still many questions about this problem, the anti-thixotropy of WMS dispersions was further investigated in this study, which will help to provide useful messages for the industrial production of the WMS based foods.

During the study, the effects of several factors (such as pasting conditions, testing temperature, shear rate, etc.) on the anti-thixotropy were investigated. In previous reports, the anti-thixotropy of starch dispersions was mainly reported of waxy starches or modified waxy starches (Tattiyakul & Rao, 2000). Therefore, in order to determine whether such a behavior was unique to waxy starch, normal maize starch (NMS) was also used as a reference. Besides, the effect of temperature on apparent viscosity, viscoelastic properties, and micro-structure of the samples were also studied to understand the anti-thixotropy of starch dispersions.

2. Materials and methods

2.1. Materials

Commercial WMS (10.04 wt.% moisture (wet basis) and trace amount of amylose) was purchased from Jinan Jinwang Food Co., Ltd. (Shandong Province, China). Commercial NMS (12.43 wt.% moisture (wet basis) and 22% amylose) was purchased from Weizhiyuan Food Co., Ltd. (Beijing, China).

2.2. Preparation of WMS and NWS dispersions with different pasting conditions

WMS suspension (5.0 wt.%) was prepared by adding 7.5 g WMS into 142.5 g deionized water at room temperature (about 25 °C). Three different pasting methods were adopted to study the effect of pasting conditions on the rheological properties of WMS dispersions (A): Well mixed WMS suspension (150 g) in conical flask was heated in a water bath at 95 °C for 6 min with a constant mixing rate of 200 rpm controlled by a digital mixer (EUROSTAR, IKA Instruments, Germany). (B): Well mixed WMS suspension (150 g) was heated in a water bath at 95 °C for 40 min with a constant mixing rate of 200 rpm. (C): Well mixed WMS suspension (150 g) was heated in a water bath at 95 °C for 40 min with a constant mixing rate of 400 rpm. (D): As a reference, well mixed NMS suspension (150 g, 5.0 wt.%) was pasted with the same procedure as (C). Then the dispersions from (A)–(C) were rapidly cooled in another water bath, and stored in an incubator (GP-01, Hubei Province, China) at 25 °C for 2 h before testing. After pasting, the dispersion of NMS was rapidly cooled in another water bath, and then stored in the incubator at 40 °C for 2 h before measurements. The storage temperature of 40 °C was chosen in order to prevent gel formation of NMS dispersion (Pongsawatmanit, Temsiripong, & Suwonsichon, 2007). The dispersions pasted from procedures (A)–(D) were signed as the dispersions A–D, respectively.

2.3. Rheological tests

Rheological properties of all samples were measured using AR2000ex rheometer (TA Instruments Ltd., Crawley, UK) with aluminum parallel plate geometry (40 mm diameter, 1 mm gap). The temperature was controlled by a water bath connected to the Peltier system in the bottom plate. A thin layer of silicone oil was applied on the surface of the samples in order to prevent evaporation. For each sample, steady flow tests, in-shear structural recovery, standard anti-thixotropy, effect of temperature on apparent viscosity, and viscoelastic properties were determined.

2.3.1. Steady flow measurements

Steady flow measurements were performed at 25 °C, 50 °C and 75 °C to obtain shear rate versus shear stress data. The sample was placed in the rheometer and pre-sheared at 100 s^{-1} for 30 s, and then it was equilibrated at the testing temperatures for 5 min before measurement. The shear rate was programmed to increase from 0 to 300 s^{-1} in 3 min, then followed immediately by a reduction from 300 to 0 s^{-1} in the next 3 min.

2.3.2. In-shear structural recovery measurements

In-shear structural recovery of the samples was determined according to the procedure of Mezger (2002) with some modifications. The sample was loaded into the rheometer and pre-sheared at 100 s^{-1} for 30 s, and subsequently it was equilibrated at the testing temperature (i.e. 25, 50 and 75 °C) for 5 min before measurement. A three stepped shear flow test was performed as follows: (1) a constant shear rate of 1 s^{-1} was applied for 120 s and subsequently (2) a constant shear rate of 300 s^{-1} was applied for 60 s, and then (3) a constant shear rate of 1 s^{-1} was applied for 180 s. The in-shear recovery value was calculated as the ratio of average apparent viscosity (η_a) obtained during the first 120 s of the third step to the average η_a value determined in the first step.

2.3.3. Standard anti-thixotropy test

The definition of anti-thixotropy is an increase in apparent viscosity with time under constant shear rate (Ferguson & Kembowski, 1995; Gouveia et al., 2008). In this test, the samples were sheared at a fixed shear rate (1, 10, 50, 100 s^{-1}, etc.) for a specific amount of time (10 min 30 s), and the viscosity was recorded in order to determine the anti-thixotropic behavior of the samples.

2.3.4. Effect of temperature on apparent viscosity

The sample was loaded into the rheometer and equilibrated at the testing temperature (5, 15, 25, 35 and 45 °C, respectively) for 5 min before measurement, and then the apparent viscosity ($\eta_{a,10}$) was determined as the average value of the first two minutes at a constant shear rate of 10 s^{-1}. Arrhenius equation was used to determine the activation energy (E_a) and to investigate the temperature dependency of the apparent viscosity of all samples (Pongsawatmanit, Temsiripong, Ikeda, & Nishinari, 2006; Wang, Wang, Li, Xue, & Mao, 2009b). The effect of temperature