



Rheological properties of an amorphous cellulose suspension



Xuejuan Jia^a, Yingwen Chen^a, Chong Shi^a, Yangfan Ye^a, Muhammad Abid^{a,b},
Saqib Jabbar^a, Peng Wang^a, Xiaoxiong Zeng^a, Tao Wu^{a,*}

^a College of Food Science and Technology, Nanjing Agricultural University, Weigang 1, Nanjing 210095, People's Republic of China

^b Department of Food Technology, Pir Mehr Ali Shah Arid Agriculture University, Rawalpindi, Pakistan

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ABSTRACT

Amorphous cellulose was prepared by the dissolution of microcrystalline cellulose with phosphoric acid and subsequent regeneration in water. The rheological properties of the aqueous suspension as affected by the concentration of cellulose, ionic strength, pH and temperature were studied. Amorphous cellulose forms a three-dimensional (3D) network, which displays typical shear-thinning behavior with little thixotropic tendency, at concentrations above 0.71%. Its flow properties are similar to that of microfibrillated cellulose, as determined by a three-region (shear thinning – plateau or shear thickening – shear thinning) viscosity profile, in which ionic strength and pH have little influence. However, increasing the temperature causes a decrease in the viscosity in both low and high shear rate regions. A viscoelastic analysis confirms that the ionic strength and pH have no influence, but increasing the temperature decreases the storage modulus, which is explained by the weakening or disruption of intermolecular interactions at elevated temperatures.

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1. Introduction

Cellulose is a linear biopolymer of glucose that exists mainly in higher plants as a structural component of cell walls. It is considered to be the most abundant biomass on earth, with an annual biosynthesis of 7.5×10^{10} tons (Habibi, Lucia, & Rojas, 2010). Various cellulose and cellulose-derivative products have been successfully commercialized and have applications in the food, pharmaceutical and chemical industries for thickening, gelling and emulsion stabilization (Habibi et al., 2010; Klemm et al., 2011; Lima & Borsali, 2004). Native cellulose has both crystalline and amorphous regions, of which the former can be isolated by chemical or mechanical methods to produce a series of products in the form of crystalline cellulose, such as microcrystalline cellulose (MCC), nanocrystalline cellulose (NCC), microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC) or bacterial nanocrystalline cellulose (BNC), depending on the preparation methods and sources (Habibi et al., 2010). Among these forms, MCC has been successfully commercialized and used in the form of a powder as an anti-caking agent and emulsifier or co-processed with a hydrophilic dispersant, such as sodium carboxymethyl cellulose (CMC), to obtain a colloidal form used in thickening and gelling (Tuason, Krawczyk, & Buliga,

2009). No other crystalline celluloses have been produced on a large scale either because the yield is too low or because the energy consumption is very high, although significant progress has been made recently towards the commercialization of these products (Sandquist, 2013). Nevertheless, a number of studies have been conducted to investigate the rheological properties of these celluloses by trying to probe their microstructure change and the associated consequences during processing, handling and application (Agoda-Tandjawa et al., 2010; Chen et al., 2013; Derakhshandeh, Petekidis, Sabet, Hamad, & Hatzikiriakos, 2013; Shafiei-Sabet, Hamad, & Hatzikiriakos, 2012; Urena-Benavides, Ao, Davis, & Kitchens, 2011).

Generally, MCC or NCC suspensions are shear-thinning and thixotropic, but the extent varies with the preparation methods. For example, a suspension of MCC prepared by HCl hydrolysis is more shear-thinning than is a suspension prepared by H₂SO₄ hydrolysis. The former is thixotropic at concentrations higher than 0.5% (w/v), but the latter is not (Araki, Wada, Kuga, & Okano, 1998). The suspensions of NCC prepared by H₂SO₄ hydrolysis behave as conventional isotropic polymer solutions at concentrations up to 3 wt%, phase-separate into isotropic and liquid crystalline biphasic suspensions that display a typical three-region viscosity profile at higher concentrations and behave as rheological gels that display a single shear-thinning behavior at even higher concentrations (Shafiei-Sabet et al., 2012). Temperature has a profound influence on the rheological properties of NCC suspensions depending on

* Corresponding author. Tel./fax: +86 25 84395671.

E-mail addresses: twu@njau.edu.cn, wutao007@hotmail.com (T. Wu).

cellulose concentrations, shear rates and tested temperature ranges (Liu, Chen, Yue, Chen, & Wu, 2011; Shafiei-Sabet et al., 2012; Urena-Benavides et al., 2011). This temperature dependence of the rheological properties is attributed to the change in the relative fractions of isotropic and liquid crystalline regions (Shafiei-Sabet et al., 2012; Urena-Benavides et al., 2011).

MFC or NFC suspensions are usually shear-thinning and also display a three-region viscosity profile with both flow and viscoelastic properties that are influenced by the ionic strength, pH and temperature (Karppinen et al., 2012; Lowys, Desbrieres, & Rinaudo, 2001). As the ionic strength increases, both viscosity and moduli (storage and loss) are increased due to the screening of electrostatic repulsions, resulting in enhanced fiber–fiber interactions and stronger gel-like behavior (Agoda-Tandjawa et al., 2010; Lowys et al., 2001). The pH dependency varies with the source of the MFC. For an MFC containing a high content of hemicellulose and lignin, increasing the pH leads to higher electrostatic repulsion and results in a lower fiber–fiber interaction and reduced viscosity (Paakko et al., 2007). However, for sugar beet MFC, the viscoelastic properties are independent of pH from 4.5 to 9 (Agoda-Tandjawa et al., 2010). With regard to the effects of temperature, contradictory results can be found in the literature. Some studies reported a reduction of the viscosity with increasing temperature, but others reported that the storage and loss moduli were unaffected by temperature or slightly increased with increasing temperature (Chen et al., 2013; Iotti, Gregersen, Moe, & Lenes, 2011; Lowys et al., 2001; Paakko et al., 2007).

In comparison with a substantial number of studies on crystalline cellulose, amorphous cellulose has received less attention as a functional material. During the preparation of crystalline cellulose, amorphous cellulose is usually hydrolyzed by acid and discarded as waste. However, the yield of crystalline cellulose such as NCC is generally low, which was reported to be around 30% even after the optimization of preparation method (Bondeson, Mathew, & Oksman, 2006). This means a great portion of cellulose biomass, probably mainly amorphous cellulose has been lost. Therefore, production of amorphous cellulose as a functional material may provide a profitable solution to the cellulose industry. It is known that dissolving cellulose with a solvent and subsequently regenerating it with an anti-solvent can result in amorphous cellulose (Ciolacu, Ciolacu, & Popa, 2011; Mori et al., 2012). However in published literatures, either toxic organic solvents or expensive ionic liquids have been used to prepare amorphous cellulose, which may not be practical if the targeted application is food industry. In our work, we have chosen phosphoric acid as a solvent to prepare amorphous cellulose. It is benign and has good solubility for cellulose when it is used in high concentration and at low temperature (Zhang, Cui, Lynd, & Kuang, 2006). In the past, it has only been used for cellulose depolymerization to enhance enzymatic saccharification (Zhang et al., 2006). The functional properties of the resulting amorphous cellulose remain unexplored so far.

Bearing in mind that the main applications of crystalline celluloses are for thickening and gelling, for which desired rheology properties, such as high zero-shear viscosity, marked shear thinning properties at higher shear rates and significant viscoelasticity are required, amorphous cellulose, aimed to use as an alternative product of crystalline cellulose must demonstrate similar or better rheology properties. Therefore, in this paper, we have studied the rheological properties of amorphous cellulose by steady flow and dynamic rheological test and compared it with that of crystalline cellulose. The effects of concentration, ionic strength, pH and temperature on the flow and viscoelastic properties of amorphous cellulose suspensions are reported.

2. Experimental details

2.1. Materials

Microcrystalline cellulose powder (MCC), 85% phosphoric acid (H_3PO_4) and other common chemicals were purchased from Sino-pharm Chemical Reagent Co, Ltd. (Shanghai, China). Deionized water was used throughout the experiment unless specified.

2.2. Preparation method of amorphous cellulose

Phosphoric acid was pre-cooled to 4 °C in a refrigerator (Haier, China). Two grams of MCC was wetted with 6 ml of deionized water and mixed with 50 ml of 85% phosphoric acid by vortex to obtain a homogenous suspension, followed by the addition of another 50 ml of phosphoric acid. The resulting cellulose suspensions were incubated in a shaking bath at a temperature 0 °C and a speed of 150 rpm for 24 h to obtain a clear solution. Five hundred milliliters of deionized water was used to dilute the cellulose solution to obtain a milky suspension, followed by centrifugation at $16,700 \times g$ for 20 min (Beckman, JLA-91000, USA) and washing with deionized water repeatedly until a constant pH was obtained. The concentration of cellulose in the final suspension was determined gravimetrically to be 2.23% w/v and the yield of the amorphous cellulose reached 87% constantly.

2.3. Transmission electronic microscopy (TEM)

Twenty microliters of a 0.01% (w/v) cellulose suspension was deposited on a carbon-coated copper grid (400 mesh), dried at room temperature and negatively stained by 2% uranyl acetate for 1 min. A TEM analysis was performed using an H-7650 TEM (Hitachi, Japan) at 80 kV.

2.4. ^{13}C CP/MAS NMR spectroscopy

The solid state ^{13}C CP/MAS NMR (cross polarization magic angle spinning nuclear magnetic resonance) spectra were obtained on a Bruker Advance III 400 MHz NMR spectrometer (Bruker, Switzerland) at a frequency of 100.62 MHz. Analyses of the original MCC powder and freeze-dried amorphous cellulose were performed using a 4-mm MAS probe and ZrO_2 rotors.

2.5. Rheological measurements

Three minutes of shearing at 10,000 rpm (IKA T18 homogenizer, Germany) was applied to disrupt any weakly flocculated aggregates prior to any measurements. Rheological measurements were performed by a rotational Physical MCR 301 rheometer (Anton Paar, Graz, Austria) using a 50 mm diameter parallel plate (PP50) with the gap fixed at 1 mm. The temperature was maintained as desired with an accuracy of ± 0.1 °C. To minimize dehydration, the samples were sealed by silicone oil. All rheological tests were repeated three times to ensure reproducibility.

Thixotropic-loop tests were performed to plot the shear stress versus the shear rate ($2\text{--}50 \text{ s}^{-1}$) for the cellulose suspensions at concentrations of 0.77 and 2.23% w/v. The viscosity against the shear rate ($0.1\text{--}1000 \text{ s}^{-1}$) was recorded at 25 °C at concentrations from 0.36 to 2.23% w/v. The effects of ionic strength and pH on the viscosity curve were also tested at cellulose concentrations of 0.77 and 2.23% w/v. Ionic strengths from 0 to 0.1 M were adjusted by solid sodium chloride, and the pH was adjusted from 2 to 8 using 1 N HCl or 1 N NaOH, respectively.

The linear viscoelastic region (LVR) was analyzed at 1 Hz by amplitude sweep tests. Oscillatory measurements of the storage

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