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Flow behavior, thixotropy and dynamical viscoelasticity of sodium alginate aqueous solutions

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ABSTRACT

Understanding of the rheological behavior of sodium alginate (SA) is fundamental either to design optimized products or to ensure stable flows. Of the SA samples tested that characterized by a M/G ratio of 0.38 and a weight–average molecular mass (*Mw*) of 1.180×10^5 g/mol, steady–shear flow, thixotropy and dynamical viscoelasticity tests were carried out to characterize rheological behavior of G–rich SA aqueous solutions as influenced by concentration (1.0–3.0%, w/v) and temperature (5–35 °C). These measurements were carried out by using an Anton Paar–Physica MCR 301 Rheometer. It was found that, above a critical shear rate, all G–rich SA solutions (1.0–3.0%, w/v) exhibited non–Newtonian shear–thinning behavior and the flow curves could be well described by the Cross model. The temperature–dependent behavior of 2.5% (w/v) SA had higher correlation to the Cross model and the Arrhenius relationship, while the flow activation energy tended to decrease with the increase of shear rate. The upward–downward rheograms showed that all the systems evaluated in this paper had a hysteresis loop which indicating strong thixotropic behavior, the higher the SA concentration, the stronger the thixotropic behavior. The dynamical viscoelastic properties characterized by oscillatory frequency sweep under small–deformation conditions showed a fluid–like viscoelastic behavior. The behavior of SA aqueous solutions was predominantly more viscous than elastic. Multiwave temperature ramp test for 2.5% SA aqueous solutions was consistent with the results from oscillatory frequency sweep test.

1. Introduction

Sodium alginate (SA) is regarded as biocompatible, non–toxic, non–immunogenic and biodegradable polymer, which makes it as an attractive candidate for biomedical applications. Bearing in mind of its gelling ability, stabilizing properties and high viscosity in aqueous, SA and its derivatives are widely used in food, cosmetics, biomedical and pharmaceutical industries, as well as sewage–treating industries (Funami et al., 2009; Gao, Liu, Chen, & Zhang, 2009). It is also used as artificial skin in healing of split–thickness skin graft donor sites (Giele, Tong, & Huddleston, 2001; Vanstralen, 1992). Most applications of SA are based on its gel–forming ability through cation binding, the transition from water-soluble SA to water–insoluble calcium alginate. In molecular terms, SA is an unbranched binary copolymers of (1–4)–linked β–D–mannuronic acid (M) and α–L–guluronic acid (G) residues as monomers, constituting of M–, G–, and MG sequential block structures (Moe, Draget, Skjak Braek, & Smidsrod, 1995). The G–block is stiffer and more extended in chain configuration than the M–block due to a higher degree of hindered rotation around the glycosidic linkages (Braccini, Grasso, & Perez, 1999). The physical properties, the ability to form gels and the strength of SA gels depend not only upon the uronic acid composition and the relative proportion of the three types of blocks, but also on the molecular weight and molecular weight distribution of SA, the source of calcium ions and the methods of preparation (Sosa-Herrera, Lozano-Esquivel, Ponce de León-Ramírez, & Martínez-Padilla, 2012; Zhong, Huang, Yang, & Cheng, 2010).

Rheological characteristics correlate to the textural attributes of the products, which, in turn, determine its sensory characteristics and consumer acceptability. The most important rheological characteristics are its flow behavior, thixotropy and dynamical viscoelastic properties. The flow behavior data are required as an indicator of product quality, for calculation in any process involving fluid flow

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(e.g. pump sizing, extraction, filtration, extrusion, purification) and for the analysis of flow conditions in product processes such as pasteurization, evaporation, drying and aseptic processing (Cevoli, Balestra, Ragni, & Fabbri, 2013; Gómez-Díaz & Navaza, 2003). Thixotropy can give clues to product stability after stirring and help to adapt food texture by stirring or by resting. Oscillatory frequency sweep is extremely sensitive to the physical structure and chemical composition of the sample, which makes it useful for evaluating gelation kinetics, and it can provide abundant additional information, including data on the structure and energy consumption. So, understanding rheological properties is essential to predict, design and characterize most of its applications. In previous studies, the basic rheological properties of low–concentration SA solutions have been studied extensively using fundamental rheological measurements (e.g. rotational viscometer; capillary viscometer) though many aspects of these solutions are still in the focus of polymer research. Both high–M and high–G of SA in aqueous dispersions exhibited non–Newtonian shear–thinning behavior when the SA concentrations and temperatures ranged from 0.125 to 1.5% (w/v) and from 5 to 35 °C, respectively. The lower concentrations of SA solutions exhibited pseudo plastic shear flow behavior (Mancini, Moresi, & Sappino, 1996). Moreover, the greater the concentration of SA solutions, the greater the decrease in viscosity would be as temperature increased (Duggirala & Deluca, 1996). Solutions of 0.1% SA were low viscosity Newtonian fluids for shear rate more than 10 s^{-1}, which indicating no intermolecular interactions owing to electrostatic repellence (Yang, Chen, & Fang, 2009). However, when SA was dissolved in acetate buffer (pH 5.4), lower shear viscosity was detected compared to those in water. Addition of 5 mM $CaCl_2$ to 0.1% SA solutions induced shear–thinning behavior as well as the development of viscoelasticity, and the sample showed a Hershel–Bulkley behavior. But when SA was dissolved in acetated buffer (pH 5.4) with 5 mM $CaCl_2$, non–Newtonian behavior was observed, with a moderate increase in viscosity instead (Sosa-Herrera et al., 2012). Solutions of 0.05–0.5% (w/v) SA belonged to shear–thinning and non–Newtonian fluid, the viscosity fluctuated with temperature and increased with stirring time (Wang, Li, & Zhang, 2008). The viscose flow activation energy increased with the increase of SA concentration, and structural viscosity index increased when the relative molecular weight of SA was raised (Guo, Zhu, Wang, Zhan, & Zhang, 2007). The G–rich SA (0.5%, w/v) was higher in elasticity with rod–like molecular assemblies in presence of 15 mM $CaCO_3$, while the M–rich SA (0.5%, w/v) was higher in elasticity with network–like molecular assemblies at 3.75 mM $CaCO_3$ (Funami et al., 2009). According to Qian Xiao, SA and pullulan–SA blend solutions at 4% (w/w) polymer concentration were viscoelastic liquid, whereas the pure pullulan exhibited Newtonian behavior. But SA polymer chains adopted a more entangled network in the solution wherein SA chains intertwined with each other. Pullulan solutions agreed well with the Cox–Merz superposition rule, while SA and their blend solutions showed considerable departure from the Cox–Merz rule (Xiao, Tong, & Lim, 2012). However, there were few reports about SA aqueous solutions on thixotropy and dynamical viscoelasticity properties in literature, and most flow behavior research reports were based on low–concentration of SA aqueous solutions using rotational viscometer or capillary viscometer. The main purpose of this research was to provide, evaluate and correlate a complete and comprehensive rheological investigation of SA aqueous solutions (1.0–3.0%, w/v) as influenced by concentration and temperature. These measurements were carried out by using an Anton Paar–Physica MCR 301 Rheometer (Anton Paar, GmbH, Germany). This characterization of SA aqueous solutions was based on: i) measurement of steady–shear flow properties to find a well rheology model; ii) evaluation of the thixotropy and dynamical viscoelasticity properties at different concentrations and temperatures; and iii) comprehensive analysis of the rheological properties using multiwave–temperature ramp test under the condition of temperature and frequency changed synchronously. This work will allow to further extend the experimental investigation of SA additive products in order to better understand the physical phenomena responsible for the changes induced by the addition of SA on the rheological and colloidal properties of the products.

2. Materials and methods

2.1. Materials and sample preparation

The SA was a chemically pure product purchased from the Kaixin Chemical Industry Co., LTD. Tianjin, China. It was purified further before measurements with the reported method (Yuan & Chen, 2002). SA solutions with different concentrations (1.0%, 1.5%, 2.0%, 2.5%, 3.0%, w/v) were prepared by dissolving a proper amount of SA powder in 100 mL deionized water. The whole gum dispersions were kept on a magnetic stirrer at room temperature and gently stirred for 6 h. Later, the system was allowed to stand at 4 °C for 24 h to enable biopolymer hydration and removal of bubbles.

2.2. Characterizations of SA

The average molecular weight and polydispersity index of SA were determined by size exclusion chromatography (SEC) coupled with multiangle laser light scattering photometer (MALLS, $\lambda = 690$ nm; DAWN EOS, Wyatt Technology Co., USA) using a refractive index of 1.33. An ultrahydrogel™ column (7.8 mm × 300 mm, Waters, USA) was used as the SEC instrument. An optilab refractometer (Dawn, Wyatt Technology Co., USA) was simultaneously connected. The SA samples with desired concentrations were prepared and optical clarification of the samples was achieved by filtration into a scattering cell. The injection volume was 50 μL and the flow rate was 1.0 mL/min. The refractive index increment (dn/dc) value of the sample was determined, by using an optilab refractometer at 690 nm and 25 °C, to be 0.14 mL/g.

The composition ratio of mannose and gulose of SA was analyzed according to the earlier report from our laboratory (Wang et al., 2010; Zhang et al., 2007). Briefly, 10 mg of SA was dissolved in 4 mL of 4 M trifluoroacetic acid acetate (TFA) in a test tube and then hydrolyzed at 120 °C for 10 h under airtight conditions. TFA was then evaporated through decompression and distillation. When the tube was dry, 10 mg of oxammonium hydrochloride and 0.5 mg pyridine were added and allowed to react in a 90 °C water bath for 30 min. Then 0.5 mL of cold (kept at 4 °C in a refrigerator) acetic anhydride was added to the test tube and the mixture was incubated in the 90 °C water bath for a further 30 min to allow the acetylation reaction to complete. The end product was decompressed and distilled to dryness. The acetate derivatives were extracted by chloroform and filtered with 0.22 μm microfilter. Then the acetate derivatives were analyzed by GC–MS (Thermo Focus GC–Polaris Q MS) system equipped with a TR–5MS SQC capillary column (30 m × 0.25 mm × 0.25 μm). The MS was operated in the electron ionization mode at 70 eV and the acquisition mode was scan mode. The ion source temperature was 250 °C. The oven temperature was programmed as follows: initial temperature of 120 °C was held for 3 min and then increased to 250°C with an increment of 5 °C/min and held for 5 min. The injector temperature was 250 °C and helium was used as the carrier gas at a constant column flow rate of 1.0 mL/min. 0.5 μL of the sample extract was injected in the split mode and the split–flow ratio was 1:50. The standard monosaccharides were measured following the same procedure.