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Pullulan-sodium alginate based edible films: Rheological properties of film forming solutions

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ABSTRACT

Rheological properties of pullulan, sodium alginate and blend solutions were studied at 20 °C, using steady shear and dynamic oscillatory measurements. The intrinsic viscosity of pure sodium alginate solution was 7.340 dl/g, which was much higher than that of pure pullulan (0.436 dl/g). Pure pullulan solution showed Newtonian behavior between 0.1 and 100 s^{-1} shear rate range. However, increasing sodium alginate concentration in pullulan–alginate blend solution led to a shear-thinning behavior. The effect of temperature on viscosities of all solutions was well-described by Arrhenius equation. Results from dynamical frequency sweep showed that pure sodium alginate and blend solutions at 4% (w/w) polymer concentration were viscoelastic liquid, whereas the pure pullulan exhibited Newtonian behavior. The mechanical properties of pure sodium alginate and pullulan–alginate mixture were analyzed using the generalized Maxwell model and their relaxation spectra were determined. Correlation between dynamic and steady-shear viscosity was analyzed with the empirical Cox–Merz rule.

1. Introduction

Pullulan is an extracellular and neutral microbial polysaccharide produced by *Aureobasidium pullulans* in starch and sugar cultures. The linear polymer mainly consists of maltotriose units interconnected to each other by α-(1,6) glycosidic bonds. This unique linkage pattern endows pullulan with good solubility in water compared with other polysaccharides (e.g., amylose). Pullulan molecules behave as flexible random coils in water, resulting in solutions that exhibit Newtonian or Newtonian-like flow behavior at low polymer concentration (Rees, 1977). The viscosity of pullulan solutions was relatively low, which was similar to gum Arabic (Leathers, 2003). Aqueous pullulan solutions can be cast into water-soluble films upon drying. However, when maintained under dry conditions, the films are strong, transparent, and exhibited low permeability against oil and oxygen (Izydorczyk, Cui, & Wang, 2005; Singh, Saini, & Kennedy, 2008; Yuen, 1974).

Alginate, a linear polysaccharide extracted from brown seaweed, is composed of variable proportions of β-D-mannuronic acid (M block) and α-L-guluronic acid (G block) linked by 1–4 glycosidic bonds. The block copolymer consisted of homopolymeric regions of M- and G-blocks, separated by regions that contain M and G units (Fu et al., 2011; Hay, Rehman, Ghafoor, & Rehm, 2010). The proportion and distribution of these blocks determine the physicochemical properties of the biopolymer. Sodium alginate is a polyelectrolyte with negative charges on its backbone (Zhong, Huang, Yang, & Cheng, 2011). The polymer dissolves readily in water to form homogeneous film-forming solutions, which upon drying can yield coherent films that have a wide range of food and non-food applications (Çaykara, Demirci, Eroglu, & Güven, 2005; Skjak-Bræk, Moe, Smidsrød, & Ingar Draget, 2006).

In the previous study, we observed that the material properties of the pullulan:alginate blend films were significantly affected by the polymer ratios. Incorporation of alginate into pullulan film increased the tensile strength and elastic modulus, but decreased the elongation at break of the composite films at low to intermediate water activity (Tong, Xiao, & Lim, 2008; Xiao, Lim, & Tong, in press). Cuq, Aymard, Cuq, and Guilbert (1995) and Peressini, Bravin, Lapasin, Rizzotti, and Sensidoni (2003) reported that rheological property of the fish myofibrillar proteins or starch–methylcellulose based film forming solutions was an important property for casting process of pre-formed films. They also indicated that the gel type

Abbreviations: η_{sp}, specific viscosity; η_{int}, intrinsic viscosity; η_{red}, reduced viscosity; η, shear viscosity; n, flow behavior index; K, consistency index; SEE, standard error of estimate; E_a, activation energies; R^2, correlation of determination; HPPS, acid hydrolyzed hydroxypropylated pea starch; CMC, sodium carboxymethyl cellulose; GA, Genetic Algorithm; G^*, complex modulus; G', storage modulus; G'', loss modulus; g_i, elastic modulus; λ_i, relaxation times; $\eta^*(\omega)$, complex viscosity; $\eta(\dot{\gamma})$, steady shear viscosity.

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structures or high viscosity of film forming solution would make it difficult to eliminate air bubbles and hinder casting in thin layers. Thus pseudoplastic, viscoelastic and thixotropic properties of film forming solutions were the most important elements for most coating systems.

Several researchers have studied the basic rheological properties of pullulan and sodium alginate solutions. According to Lazaridou, Biliaderis, and Kontogiorgos (2003), the intrinsic viscosity (η_{int}) of pullulan ranged from 0.38 to 0.70 dl/g, as the molecular weight of the polymer increased from 100 to 560,000 Da. In addition, the critical concentration (C^*), which marks the point where the individual coils begin to entangle and the onset of significant coil overlap and interpenetration, were within the range for 1.4–3.1 dl/g. The relatively low η_{int} values for pullulan solution, as compared to those for other biopolymers (such as alginate) were attributed to its low molecular weight and to the relatively high chain flexibility of pullulan originating from the α-(1,6) linkage (Kato, Okamoto, Tokuya, & Takahashi, 1982). Additionally, η_{int} and hydrodynamic volume of pullulan solution are not affected by ionic strength, since pullulan is a nonionic polysaccharide (Kasaai, 2006). In comparison, typical η_{int} values for sodium alginate solution range from 6.2 to 12.1 dl/g. The higher η_{int} values for sodium alginate than pullulan suggested that the former has a more open, stiffer chain structure when dissolved in water. In the concentration range of 0.125–1.5%, sodium alginate solutions exhibit pseudoplastic shear flow behavior (Mancini, Moresi, & Sappino, 1996). Moreover, the greater the concentration of the alginate solutions, the greater the decrease in viscosity as temperature increases (Duggirala & Deluca, 1996).

Although basic rheological properties of respective pullulan and alginate solutions have been investigated to great detail in many studies, information related to pullulan–alginate blend solution is not currently available. Researchers have observed that blending of different polysaccharides with complementary structural properties can result in synergistic effects that are desirable for specific applications. Blend polymer systems reported in the literature include xanthan/CMC, xanthan/locust bean gum, xanthan/galactomannan, xanthan/methylcellulose, and hydroxypropyl guar gum/CMC (Florjancic, Zupancic, & Zumer, 2002; Mannion et al., 1992; Rinaudo & Moroni, 2009; Zhang & Kong, 2006). In many cases, polysaccharide mixtures exhibited flow behaviors which are not a simple linear combination of individual contributions. Due to the complex interactions between the polymers involved, rheological studies on blend solution are important to develop better understanding on global properties of the mixed systems.

In our previous studies, we observed that mixtures of pullulan and alginate resulted in film-forming solutions could be cast into pullulan–alginate films of desirable mechanical and water sorption properties (Tong et al., 2008). However, rheological properties of the film-forming solutions have not been investigated. This information is important as it can reveal the underlying mechanisms on different phenomena in food, as well as predict the effects of processing treatments. Therefore, the objective of this paper is to characterize the rheological properties of aqueous pullulan, sodium alginate and blend solutions under small amplitude oscillatory and large-deformation shear conditions.

2. Materials and methods

2.1. Materials

Pullulan PI20 (MW 200,000 Da) was purchased from Hayashibara Biochemical Lab. Inc. (Shanghai, China). Sodium alginate was obtained from Sigma–Aldrich Co. Shanghai (Shanghai, China).

2.2. Intrinsic viscosity

Pullulan and alginate were dissolved separately in deionized distilled water to form 0.2% (w/w) solutions, and then mixed to give pullulan:alginate blends at 100:0, 60:40, 40:60 and 0:100 weight ratios. Solutions were mixed for 1 h under shear at 20 °C to form homogeneous solutions, and tested immediately to determine their specific viscosity (η_{sp}) using an Ubbelohde capillary viscometer (Sinopharm Chemical Reagent Co., Ltd., Shaighai, China), with a capillary diameter of 0.5 mm. Kinetic energy was negligible and therefore correction was not made.

The η_{int} values of pullulan solutions were determined by Huggins equation (Eq. (1)) (Huggins, Sun, & Davis, 1942). For sodium alginate solutions, since they are polyelectrolyte, their η_{int} values were determined by Fuoss equation (Eq. (2)) (Fuoss & Strauss, 1948).

$$\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 C \tag{1}$$

$$\frac{C}{\eta_{sp}} = \frac{(1 + KC^{0.5})}{[\eta]} \tag{2}$$

where η_{sp}, η_{int}, K', K and C are the specific viscosity, intrinsic viscosity, Huggins' coefficient, Fuoss constant, and solution concentration, respectively. Eqs. (1) and (2) have been shown to be useful for fitting specific viscosity data of dilute polymer solutions with $0.2 < \eta_{sp} < 1.2$ (Da Silva & Rao, 1992; Higiro, Herald, & Alavi, 2006). In the present study, all samples were diluted to within this η_{sp} range.

2.3. Rheological properties of film-forming solutions

Pullulan and sodium alginate powders (4%, w/w) were mixed at four pullulan:alginate weight ratios (100:0, 60:40, 40:60 and 0:100), dispersed in distilled water, and mixed for 3 h under shear to form film forming solutions. Rheological properties for all fresh samples were studied by a rheometer (AR G2, TA Instruments, Shanghai, China) equipped with a cone-and-plate geometry (60 mm diameter; 56 μm gap; cone angle 2°). For steady-shear measurements, all samples were sheared continuously at shear rates ranging from 0.1 to 100 s^{-1} at 20 °C. Flow behaviors of the solutions were analyzed using the power law model (Eq. (3)):

$$\sigma = K\dot{\gamma}^n \tag{3}$$

where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency index (Pa s^n), and n is the flow behavior index (dimensionless). Standard error of estimate (SEE; Eq. (4)) was used as the indicator for the accuracy of the fit.

$$\text{SEE} = \sqrt{\frac{\sum (M_i - M_{Ei})^2}{n}} \tag{4}$$

where M_i is the experimental shear stress for experiment i, M_{Ei} is the predicted shear stress, and n is the number of data points.

Additional shear experiments were conducted at different temperatures (25–75 °C) using a shear rate of 5 s^{-1}. A thin layer of silicon oil (viscosity 20cP) was placed around the sample to avoid water evaporation during measurements. Arrhenius equation (Eq. (5)) was fitted to the temperature-dependent viscosity data:

$$\eta = A \times \exp\left(\frac{E_a}{RT}\right) \tag{5}$$

where η is the shear viscosity at 5 s^{-1}, A is the pre-exponential constant, T is the absolute temperature, R is the gas constant, and