



# Rheological properties of pullulan-sodium alginate based solutions during film formation



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## ABSTRACT

During film formation, the rheological properties of pullulan, sodium alginate, and blends, dried at 50 °C were studied using an oscillatory rheometer. According to the drying curves, the drying process of pullulan, alginate, and blend films was divided into three stages. At the first drying stage, four samples exhibited typical liquid-like viscoelastic behavior. As the drying proceeded (polysaccharide concentration up to 75%), pure pullulan chains formed an entangled network, whereas coupling of alginate molecules gave a weak gel. At this drying stage, complex viscosity data for 75% alginate and blends were fitted with the power law equation. The effects of drying on the mechanical properties of pullulan-sodium alginate based samples were analyzed using the generalized Maxwell model, and their relaxation spectra were determined. The rheological properties during drying obtained from this study is essential for understanding film-forming mechanism and predicting the properties of pullulan-sodium alginate based edible films.

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## 1. Introduction

Edible films are thin edible layers that can be used to separate food components, to deliver active compounds as carriers, or to contain and protect food products as packaging. They can prevent deterioration and prolong the shelf life of food products by acting as selective barriers against moisture, gases, and vapors (Giancone et al., 2008). Biopolymers, including polysaccharides, proteins, lipids, and combinations, can be used to prepare edible films (Gennadios, Weller, Hanna, & Froning, 1996). Many studies have been performed to characterize the mechanical, barrier, thermal and structural properties of edible films. The structure and properties of films depend on the process by which they are formed (Denavi et al., 2009; Mayachiew & Devahastin, 2008; Perez-Gago & Krochta, 2000; Petersson & Stading, 2005; Srinivasa, Ramesh, Kumar, & Tharanathan, 2004). Therefore, understanding

the formation of edible films is critical to predict their potential applications and to tailor their properties.

The formation of edible films involves various physical complexes processes. The dynamic properties of polymer chains, as well as their conformational transitions, change as the solvent evaporates. Several researchers have studied the formation of edible films. Ghoshal, Mattea, Denner, and Stapf (2010) reported that drying of gelatin solutions took place heterogeneously, but the resulting films appeared to be homogeneous. Starch showed heterogeneous molecular dynamics during film formation. Moreover, the microscopic arrangement of starch chains was influenced by this dynamic heterogeneity, and determined the final structure of the films (Ghoshal, Ardelean, Ritter, & Stapf, 2012). As the film formation continued, hydrogen-bonded intermolecular  $\beta$ -sheet structures in glycinin solutions acted as junction zones forming a network (Subirade, Kelly, Guéguen, & Pézolet, 1998). For amylose and amylopectin films, both coil-to-helix transition and aggregation of double helices occurred during the film formation (Liu & Han, 2005).

According to Löfflath and Gebhard (1997), the rheological properties of polymer solutions must be known to predict the properties of the resulting films. In particular, the glossiness and distinctiveness of films depend on variations in the rheological properties of solutions during drying. From a rheological standpoint, the drying of polymer films can be divided into three stages (Kornum, 1979). In the first stage, solvent evaporates at a constant rate and the solution

**Abbreviations:** HPSEC-MALLS-RI, high-performance size exclusion chromatography system equipped with multi-laser scattering and refractive index detectors; DSS, 4, 4-dimethyl-4-silapentane-1-sulfonic acid;  $M_w$ , weight average molar mass;  $M_w/M_n$ , polydispersity index;  $R_g$ , radius of gyration;  $n$ , Power law index;  $K$ , consistency index; GA, genetic algorithm;  $G'$ , storage modulus;  $G''$ , loss modulus;  $g_i$ , elastic modulus;  $\tau_i$ , relaxation times;  $h^*$ , complex viscosity.

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behaves as a liquid. The rate of evaporation then increases dramatically, and the samples undergo a second transition, becoming an elastic solid. The last stage involves the slow diffusion of solvent out of the solidified film. In summary, samples exhibit liquid or elastic behavior in the first and second drying stages, but form free-standing films in the last stage.

Pullulan is a water-soluble extracellular polysaccharide produced by *Aureobasidium pullulans* in starch and sugar cultures. The linear polymer mainly consists of maltotriose units interconnected to each other by an  $\alpha$ -(1,6) glycosidic bond (Singh, Saini, & Kennedy, 2008). Alginate, a linear polysaccharide extracted from brown seaweed, is composed of variable proportions of  $\beta$ -D-mannuronic acid and  $\alpha$ -L-guluronic acid linked by 1–4 glycosidic bonds (Fu et al., 2011). Sodium alginate is a polyelectrolyte with a negatively charged backbone (Zhong, Huang, Yang, & Cheng, 2010). Although the properties of pullulan and sodium alginate solutions and films have been investigated in great detail in many studies (Kristo, Biliaderis, & Zampraka, 2007; Leathers, 2003; Singh, Saini, & Kennedy, 2008; Tong, Xiao, & Lim, 2008; Xiao, Lim & Tong, 2012a; Xiao, Tong, & Lim, 2012b), information on the formation of pullulan-alginate based films has not been reported yet.

To more precisely investigate the formation of pullulan-alginate based films, it is necessary to measure the rheological properties of film-forming solutions during drying. This information is important as it can reveal the film-forming mechanism, as well as predict the properties of pullulan-sodium alginate based edible films. Therefore, the objective of this study was to characterize the rheological properties of aqueous pullulan, sodium alginate and blends upon drying at 50 °C.

## 2. Materials and methods

### 2.1. Materials

Pullulan PI20 was purchased from Hayashibara Biochemical Lab. Inc. (Shanghai, China). Sodium alginate A2158 was obtained from Sigma-Aldrich Co. Shanghai (Shanghai, China).

### 2.2. Structural and characterization of pullulan and sodium alginate

The molecular weight distributions of pullulan and alginate were determined using the high-performance size exclusion chromatography system equipped with multi-laser scattering and refractive index detectors (HPSEC-MALLS-RI) (Wyatt Technology Corp., Santa Barbara, USA), as described by Lazaridou, Biliaderis, Roukas, and Izydorczyk (2002) and Yang, Campanella, Hamaker, Zhang, and Gu (2013). Chromatography was performed at room temperature. The mobile phase consisted of a 0.15 M NaNO<sub>3</sub> solution containing 0.02% NaN<sub>3</sub> (vacuum-filtered through a 5- $\mu$ m filter) at a flow rate of 1.3 mL/min. The HPSEC column was PL aquagel-OH MIXED-M (7.5  $\times$  300 mm<sup>2</sup>, bead diameter: 8  $\mu$ m, Agilent Technologies Co. Ltd, Beijing, China) analytical  $M_w$  range from 10<sup>3</sup> to 5  $\times$  10<sup>5</sup> g/mol based on Dextran T-40 (Pharmacia Biotech, Uppsala, Sweden). The weight-average molar mass ( $M_w$ ), number-average molar mass ( $M_n$ ), and radius of gyration ( $R_g$ ) of the polysaccharides were calculated using the ASTRA 5.3.4 software (Wyatt Technology Corp., Santa Barbara, USA).

Chemical composition of the sodium alginate was analyzed by the Grasdalén's method (Grasdalén, Larsen, & Smidsrød, 1979) using a Bruker 400 MHz NMR spectrometer (Bruker, Karlsruhe, Germany). Sodium alginate were partly degraded in a hydrochloric acid solution at pH=3.0 at 100 °C for 30 min, dialyzed, and freeze dried. The pre-treated alginate sample was dissolved in D<sub>2</sub>O to make a solution of 15 mg/mL for NMR tests at 80 °C. The 4,

4-dimethyl-4-silapentane-1-sulfonic acid (DSS) was used as internal reference for the spectra (0 ppm).

### 2.3. Preparation 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 60 mL of distilled water, and mixed for 3 h at 1300 rpm by magnetic stirrer (DF-101B, Yueqing, Zhejiang, China) to form homogeneous solutions.

### 2.4. Drying curves

Pullulan, alginate and blended solutions (10 g), prepared as outlined in Section 2.3, were poured into petri dishes and dried in an environmental chamber (PQX-300A, Ningbo Southeast Instrument Company, Ningbo, China) at 50 °C and 55% RH. Moisture loss was periodically weighed by taking out the petri dishes and weighing it on the electronic balance (ME54, Mettler Toledo, Shanghai, China) with a precision of 0.00001 g. Three replications of each sample was performed, and the data given was an average of these results. The reproducibility of the experiments was within the range of  $\pm 4\%$ . The end point of drying was taken to be when no further changes of weight were observed. All weighing processes were completed in less than 10 s during the drying process.

### 2.5. Rheological properties

Rheological properties of pullulan, alginate and blended film-forming solutions dried at 50 °C were measured with a rheometer (AR G2, TA Instruments, Shanghai, China) equipped with a parallel plate (60 mm diameter; 56  $\mu$ m gap). A thin layer of silicon oil (viscosity 20cP) was placed around the sample to prevent the evaporation of water during the test. The extent of the linear viscoelastic region was determined by strain sweep at a frequency of 5 Hz. A dynamic frequency sweep was conducted by applying oscillation amplitude within the linear viscoelastic region (8% strain) over a frequency range between 0.1 to 100 Hz at 50 °C.

Complex viscosity ( $\eta^*$ ) was estimated as follows (Eq. (1)):

$$\eta^* = \frac{\sqrt{(G')^2 + (G'')^2}}{\omega} \quad (1)$$

where,  $G'$  is storage modulus,  $G''$  is loss modulus, and  $\omega$  is the angular frequency.

The relationships between  $\eta^*$  and  $\omega$  were analyzed using the power law model (Eq. (2)):

$$\eta^* = K\omega^n \quad (2)$$

where,  $K$  is the consistency index (Pa s <sup>$n$</sup> ),  $\omega$  is the angular frequency, and  $n$  is the power law index.

### 2.6. Discrete relaxation spectra

Discrete relaxation spectra were derived from dynamic measurements using a generalized Maxwell model comprising an appropriate number of Maxwell elements in parallel (Ferry, 1980).

$$G' = G_e + \sum_{i=1}^N g_i \frac{\omega^2 \lambda_i^2}{1 + \omega^2 \lambda_i^2} \quad (3)$$

$$G'' = \sum_{i=1}^N g_i \frac{\omega \lambda_i}{1 + \omega^2 \lambda_i^2} \quad (4)$$

where,  $G'$  is storage modulus,  $G''$  is loss modulus,  $\omega$  is the angular frequency,  $G_e$  is the equilibrium elasticity modulus, and  $\lambda_i$  and  $g_i$

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