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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

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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).

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

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

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 $0.2 < \eta_{\text{sp}} < 1.2$ (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

E_a is activation energy. Correlation of determination (R^2; Eq. (6)) was also used as the indicator for the accuracy of the fit.

$$R^2 = \frac{\sum (M_{Ei} - M_{ave})^2}{\sum (M_i - M_{ave})^2} \tag{6}$$

where M_{Ei} is the predicted shear viscosity and M_{ave} is the average shear viscosity.

For dynamical shear measurements, dynamical frequency sweeps were conducted by applying 5% strain within the linear viscoelastic region over a frequency range between 0.1 and 100 Hz. All dynamic shear experiments were conducted at 20 °C.

2.4. Discrete relaxation spectra

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

$$G' = G_e + \sum_{i=1}^{N} g_i \frac{\omega^2 \lambda_i^2}{1 + \omega^2 \lambda_i^2} \tag{7}$$

$$G'' = G_e + \sum_{i=1}^{N} g_i \frac{\omega \lambda_i}{1 + \omega^2 \lambda_i^2} \tag{8}$$

where G' is storage modulus, G'' is loss modulus, ω is the angular frequency, the equilibrium modulus G_e equal to zero in this study, due to the viscoelastic liquid of all solutions, λ_i and g_i represent the relaxation time and the elastic modulus of the Nth Maxwell element. In this work, the Genetic Algorithm (GA) method was used to obtain discrete relaxation spectra from dynamical measurements. GA is a recently developed optimization approach, which can be used as an alternative to regression analysis to fit complex non-linear models. This method was chosen over the more widely used Levenberg–Marquardt method because the former is more robust in avoiding local optima and finding a true global solution to the problem (Haghtalab & Sodeifian, 2002; Kapanoglu, Koc, & Erdogmus, 2007; Mustapha & Phillips, 2000; Roush & Branton, 2005; Verbeeten, 2010).

2.5. Data analysis

All rheological measurements in steady and dynamical shear were performed in triplicate. Results reported were an average of three measurements. TA Rheometer Data Analysis software (TA Instruments, Shanghai, China) was used to calculate storage modulus, loss modulus and complex viscosity. The Genetic Algorithm method was adopted to analyze the data, using Matlab R2011b software (Mathworks, Inc., Natick, Massachusetts, USA).

3. Results and discussion

3.1. Intrinsic viscosity

Fig. 1 displays the variation of reduced viscosity ($\eta_{red} = \eta_{sp}/C$) as a function of polymer concentration for pullulan, alginate and blend solutions. η_{red} values of pure pullulan did not change significantly with concentration, showing that the polymer solution obeyed Huggins relationship due to the non-ionic characteristics of pullulan polymer chains (Khouryieh, 2006; Singh et al., 2008; Yuen, 1974). In contrast, pure sodium alginate solution exhibited an exponential increase on η_{red} as the polymer concentration decreased. It could be attributed to expansion of sodium alginate chains as the alginate concentration increased (Dragan, Mihai, & Ghimici, 2003; Zhong et al., 2011). Similar results have been reported in the literature for other polyelectrolyte polysaccharides (El-Hefian, Nasef, & Yahaya, 2010; Khouryieh, 2006; Yang et al., 2011).

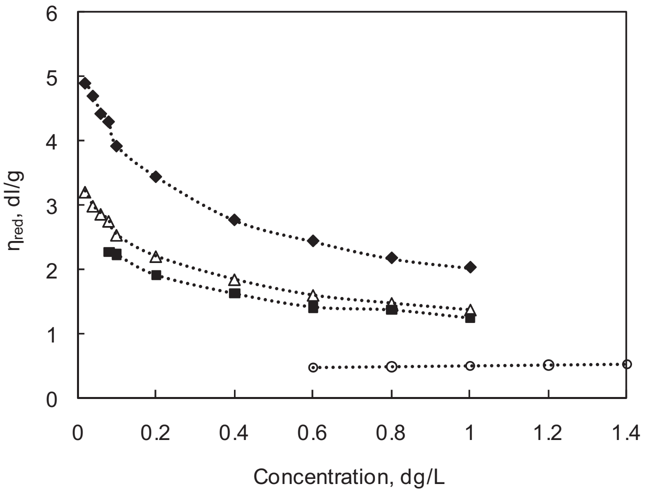

Fig. 1. Reduced viscosities ($\eta_{red} = \eta_{sp}/C$) of pullulan, alginate and blend solutions in water at 20 °C. (○) Pure pullulan; (■) pul:alg (60:40); (△) pul:alg (40:60); (♦) pure alginate.

η_{int} is a characteristic property of an isolated polymer molecule in a given solvent. It is related to the hydrodynamic volume occupied by the polymer and can be used to detect the conformational changes in individual polysaccharides (Kasaai, 2006). The measured and calculated η_{int} of all samples are listed in Table 1. The η_{int} values of pullulan and sodium alginate in water were 0.436 and 7.340 dl/g, respectively, which were comparable to those reported by Kasaai (2006), Mancini et al. (1996), and Nishinari et al. (1991). The η_{int} value of sodium alginate determined was 7.340 dl/g, which was comparable to those reported for other linear polysaccharides, such as κ-carrageenan in 0.05 M NaCl and locust bean gum in 0.2 M NaOH (Chronakis, Doublier, & Piculell, 2000; Launay, Cuvelier, & Martinez-Reyes, 1997; Morris & Ross-Murphy, 1981). Compared with pullulan solution, sodium alginate solution had a much higher η_{int} value, which might be attributed to the higher molecular weight and chain stiffness of sodium alginate (Morris, Cutler, Ross-Murphy, Rees, & Price, 1981). In water, polymer chains of sodium alginate tend to adopt an extended configuration due to electrostatic charge repulsion (Smidsrød, 1970; Yolacan, 2006). In contrast, pullulan behaved as a typical random coil in water at this temperature. Similar results have been reported by Kasaai (2006) and Nishinari et al. (1991).

3.2. Steady shear properties

As shown in Fig. 2a, the shear stress versus shear rate curves for all tested solutions recorded in forward and reverse scans varied by less than 5%. This implied that samples did not show time-dependent rheological phenomena; they recovered instantaneously to their original viscosity when the shear was removed.

Table 1
Intrinsic viscosity for pure pullulan, alginate and blend dilute solutions.

Samples	Intrinsic viscosity $[\eta]_{exp}$ (dl/g)
Pure pullulan	$0.436^a \pm 0.012$
Pul:alg (60:40)	$3.148^b \pm 0.054$
Pul:alg (40:60)	$4.396^b \pm 0.038$
Pure alginate	$7.340^b \pm 0.096$

[a] Values obtained from the Huggin's equation (Eq. (1)).
[b] Values obtained from the simplified Fuoss equation (Eq. (2)).

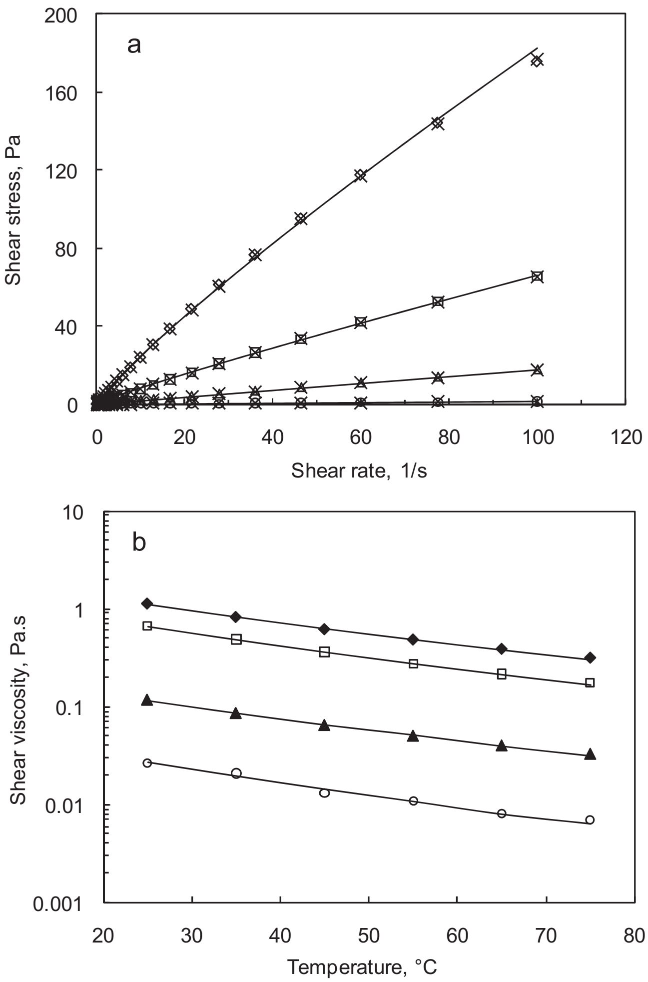

Fig. 2. Steady shear characterization of pure pullulan, sodium alginate and blend film forming solutions at 4% (w/w) polymer concentration. (a) Shear stress as a function of shear rate for all solutions. (○) Pure pullulan up; (△) pul:alg (60:40) up; (□) pul:alg (40:60) up; (◇) pure alginate up; (**X**) down (solid lines representing the fitted curves based on power law model); (b) temperature dependence of viscosity of all solutions for a fixed shear rate 5 s^{-1}. (○) Pure pullulan; (▲) pul:alg (60:40); (□) pul:alg (40:60); (♦) pure alginate (solid lines representing the fitted curves based on Arrhenius equation).

Similar results were reported for 0.5% κ-carrageenan and HPPS blend solutions (Lafargue, Lourdin, & Doublier, 2007).

The shear data were analyzed by fitting power law flow models to the data. The power law parameters are summarized in Table 2. Newtonian flow behavior was observed for pullulan solution alone (Fig. 2a), with a power law index (n) of 0.99. The pure pullulan solution also exhibited relatively low intrinsic viscosity in water at 20 °C due to the lower molecular weight and flexible molecular conformation. These results suggested that pullulan chains were overlapping each other to form a transient network in this concentration that was disrupted readily during shear (Ioan, Aberle, & Burchard, 2000). In contrast, alginate polymer chains adopted a more entangled network in the solution wherein alginate chains intertwined with each other. The disruption of the chain entanglement when the solution was sheared could be the main contributor to the decreased apparent viscosity with increasing shear rate (Graessley, 1974). Similar behaviors were reported for CMC, glucomannan, rice starch-sucrose composites, and so on (Lue & Zhang, 2009; Yasar, Kahyaoglu, & Sahan, 2009; Yoo & Yoo, 2005). As shown in Table 2, this shear thinning behavior is reflected by the lower n value (0.868) for the pure alginate solution. Increasing the sodium alginate content in the blend solutions led to decreasing n value, implying that the solution exhibited more non-Newtonian flow behavior.

Table 2
Power law parameters (K, n) of pullulan, alginate and blend solutions at 20 °C.

Samples	Power law parameters		
	K (Pa s^n)	n	SEE
Pure pullulan	0.013 ± 0.002	0.994 ± 0.003	0.637
Pul:alg (60:40)	0.199 ± 0.009	0.974 ± 0.005	1.740
Pul:alg (40:60)	0.977 ± 0.010	0.916 ± 0.003	4.971
Pure alginate	3.348 ± 0.027	0.868 ± 0.002	6.490

Table 3
Values of activation energy and constant for pullulan, alginate and blend film forming solutions.

Samples	A ($\times 10^{-5}$ Pa s)	E_a (kJ/mol)	R^2
Pure pullulan	0.12 ± 0.009	24.85 ± 0.352	0.99
Pul:alg (60:40)	1.27 ± 0.026	22.58 ± 0.449	0.99
Pul:alg (40:60)	4.61 ± 0.046	23.74 ± 0.174	0.99
Pure alginate	12.6 ± 0.173	22.51 ± 0.063	0.99

3.3. *Effect of temperature on viscosity*

At a fixed shear rate of 5 s^{-1}, increasing the temperature from 25 to 75 °C resulted in significant decrease in shear viscosities for all solutions tested (Fig. 2b). The decrease in η could be attributed to the increased intermolecular distances as a result of thermal expansion with increasing temperature (Constenla, Lozano, & Crapiste, 1989; Kim & Yoo, 2009; Yoo, 2006). The behavior was similar to most other water-soluble polysaccharides (Farhoosh & Riazi, 2007; Lapasin, Pricl, Graziosi, & Molteni, 1988; Park, Chung, & Yoo, 2004; Yang & Zhu, 2007). The temperature-dependent behavior was well described by the Arrhenius relationship with R^2 of 0.99 for all solutions tested (Table 3). The E_a of pullulan (24.85 kJ/mol) was higher than that of sodium alginate (22.51 kJ/mol), indicating that the viscosity of pullulan was more sensitive to temperature change as compared to sodium alginate in the given temperature range tested.

3.4. *Dynamical shear properties*

At 4% concentration level, due to the low viscosity of the pure pullulan solution, reliable determination of storage modulus data was difficult. Therefore, modulus data are not reported for pullulan solution (Fig. 3). Within the tested frequency range, the G'' is larger than G' and both modulus had a tendency to approach each other at high frequency. The tangent δ values of 40:60 pullulan:alginate and pure sodium alginate solutions (not shown), were not subtantially different. These results indicated the existence of a similar microstructure. For sodium alginate solutions, the G'' was significantly larger than the G', especially at low frequencies, implying that the majority of the energy was dissipated by viscous flow. At lower deformation rate, alginate polymer chains had more time to relax to a more favourable state by slippage of the entanglement point of alginate chains. However, as the sweeping frequency increased, the available time for the polymer chain to relax declined. Here, the alginate chains could no longer slip past one another as readily; the entanglement points acted more like fixed network anchors. Consequently, the ability of this entanglement alginate network to temporarily store the imposed energy increased, and it behaved more like elastic solid (Clasen & Kulicke, 2001; Doi & Takimoto, 2003; Ferry, 1980).

To further investigate the influence of sodium alginate on the viscoelastic properties and relaxation processes of the polymer

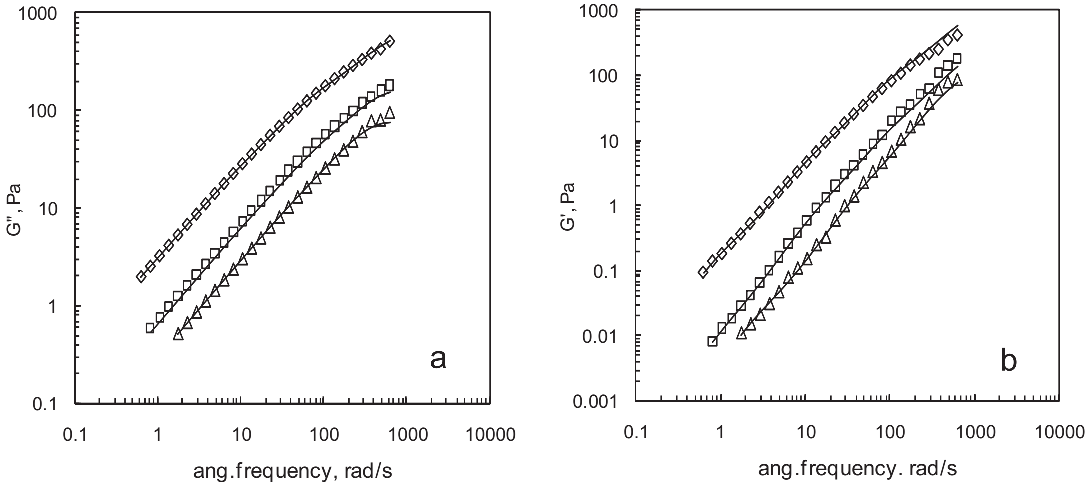

Fig. 3. Dynamical modulus of pullulan, alginate and blend film forming solutions at 20 °C. (a) Loss modulus; (b) storage modulus. (△) Pul:alg (60:40); (□) pul:alg (40:60); (◇) pure alginate (solid lines representing the fitted curves based on generalized Maxwell model).

solutions, the experimental data were fitted by the generalized Maxwell models. In Fig. 3a and b, the experimental G' and G'' data were compared with predictions from the generalized Maxwell model. Modeling of the pure pullulan data could not be performed since the polymer solution was Newtonian at 4% concentration. As shown, the model predicted the experimental data well. The relaxation spectra were showed in Table 4. As shown, all g_i value decreased with increasing λ_i. Moreover, the relaxation times spanned a range from 0.001 to 1 s for all samples. Similar relaxation times span have been reported for purified tara gum solutions at the concentration from 0.78% to 1.03% (Sittikijyothin, Torres, & Gonçalves, 2005). For the 60:40 pullulan:alginate solutions, six elements of Maxwell model provided a satisfactory fit. However, five Maxwell elements were needed to fit the data of 40:60 pullulan:alginate and pure alginate solutions satisfactory, suggesting that the relaxation processes for these solutions could be different. According to Mours and Winter (2000), small-scale relaxation processes are associated with molecular strands or subunits of molecules. On the other hand, long-range relaxation processes are related to macromolecular motions or physical aggregation. For 60:40 pullulan:alginate solutions, four relaxation times were detected at small-scale relaxation processes (relaxation time span from 0.001 to 0.01), whereas three relaxation time constants are predicted for 40:60 pullulan:alginate and pure alginate solutions. These observations might be attributed to the difference of molecular structure, conformation or molecular weight of pullulan and sodium alginate. As sodium alginate content increased, g_i values significantly shifted to higher values at the long-range relaxation processes. It suggested that long-range relaxation processes that dominate by stress slowed down with increasing sodium alginate content, due to formation entanglement networks. This is consistent with the results of dynamical frequency sweep testes.

Table 4
Discrete relaxation spectra for pure alginate and pullulan alginate blend film forming solutions at 4% (w/w) polymer concentration.

i	Pul:alg (60:40)		Pul:alg (40:60)		Pure alginate	
	λ_i (s)	g_i (Pa)	λ_i (s)	g_i (Pa)	λ_i (s)	g_i (Pa)
1	0.001	54.847	0.001	159.243	0.001	717.032
2	0.0017	35.046	0.0015	158.324	0.0015	693.663
3	0.0018	34.256	0.009	19.569	0.01	124.089
4	0.0021	29.987				
5	0.019	2.135	0.059	1.198	0.079	7.712
6	0.344	0.025	0.823	0.013	0.957	0.248

λ_i relaxation times of the *i*th Maxwell element.
g_i elastic modulus of the *i*th Maxwell element.

3.5. Cox–Merz rule

Empirically it has been observed that the complex viscosity $\eta^*(\omega)$ is approximately equaled to steady shear viscosity $\eta(\dot{\gamma})$ when the frequency and shear rate are equaled. This empirical relationship is known as the Cox–Merz rule (Eq. (9)), which has been applied for studying many polysaccharide solutions (Da Silva & Rao, 1992; Lopes da Silva, Goncalves, & Rao, 1993; Park et al., 2004; Wen, Lin, Li, & Hua, 2004).

$$|\eta^*|(\omega) = \eta(\dot{\gamma})|_{\omega=\dot{\gamma}} \tag{9}$$

As shown in Fig. 4, the curves of $\eta^*(\omega)$ versus radial frequency could be superimposed on the curves of $\eta(\dot{\gamma})$ versus shear rate. It appeared that pullulan solution obeyed the Cox–Merz rule, indicating that no long range interactions were detected. As discussed above, pure pullulan behaved as flexible coils in water that formed a transient weak network at the concentration of 4%, leading to $\eta(\dot{\gamma})$ and $\eta^*(\omega)$ at equivalent numerical values of shear-rate and frequency. In contrast, sodium alginate and blend solutions showed

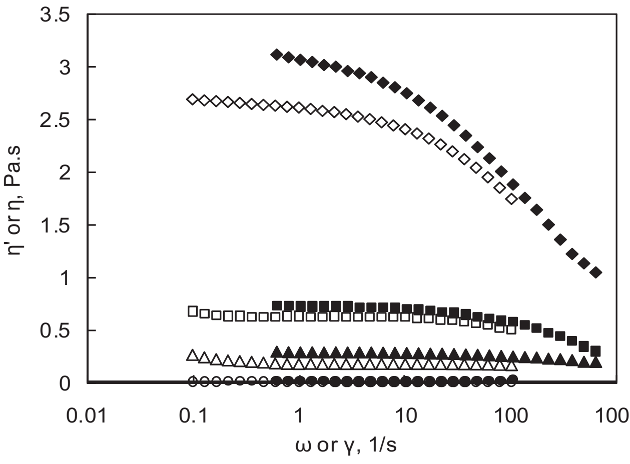

Fig. 4. Cox–Merz plots of the pullulan, alginate and blend film forming solutions. (○) Pure pullulan; (△) pul:alg (60:40); (□) pul:alg (40:60); (◇) pure alginate (solid circles refer to the complex viscosity and open circles to the shear viscosity).

considerable departure from the Cox–Merz rule. It was observed that the deviation between $\eta(\dot{\gamma})$ and $\eta^*(\omega)$ increased as the alginate content increased from 40% to 100%. These results may be explained on the basis that specific interactions between alginate-alginate or alginate-pullulan chains were disrupted during the rotational measurements (Chamberlain & Rao, 1999; Verbeeten, 2010; Yasar et al., 2009). The plots for alginate and blend solutions tended to superimpose as the shear rate increased, which might be attributed to the increasing deformation of chain entanglement network.

4. Conclusion

In this study, rheological properties of pullulan, sodium alginate and blend film forming solutions were investigated. In diluted solution, pullulan chains behaved as a typical random coil, however, sodium alginate chains tended to adopt an extended configuration. Newtonian flow behavior was observed for pure pullulan solution at the concentration of 4%. In contrast, increasing the sodium alginate content led to non-Newtonian behaviors at the same concentration. These data indicated that pullulan chains were overlapping each other to form a transient network, but alginate polymer chains adopted a more entangled network in the solution wherein alginate chains intertwined with each other. Based on dynamical rheological analysis, G' and G'' significantly increased, as sodium alginate content increased from 40% to 60%. Furthermore, discrete relaxation spectral data showed that both g_i and λ_i increased as sodium alginate content increased from 40% to 60%, suggesting that relaxation processes slowed down with increasing sodium alginate content, due to formation entanglement networks. Pullulan solution agreed well with the Cox–Merz superposition rule, but considerable deviation was observed as the sodium alginate content increased in the polymer solutions.

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