Scaling law, fractal analysis and rheological characteristics of physical gels cross-linked with sodium trimetaphosphate

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ARTICLE INFO

ABSTRACT

The scaling behavior and fractal analysis of basil seed gum (BSG) cross-linked with sodium trimetaphosphate (STMP) have been investigated by rheological small amplitude oscillatory shear measurements. Storage modulus and critical strain (γ_o) of the gels exhibited power law relationships with BSG concentration. Based on the power-law exponent values, the fractal dimension (d_f) of gels was estimated using scaling models, revealed the weak-link regime of BSG. The d_f values lied well within the range of fractal dimension values (1.5–2.8) reported for protein gels. However, they slightly differed from d_f for diffusion-limited and reaction limited cluster-cluster aggregation processes. Stress sweep test was shown that STMP addition to BSG made a stronger gel than that of BSG lacking STMP. Mechanical spectrum of gels was also revealed that adding STMP can improve the elasticity of gels. BSG had a tan δ of >0.1, indicating paste-like weak gel, while tan δ of BSG-STMP has approached to 0.1 exhibited the character of a cross-linked network near to "true gel". BSG-STMP was also recognized as a thermo-reversible physical gel, which gelation and thermal properties did not affect by STMP. Therefore, the scaling behavior can be applied for hydrocolloids gels to extract structural information through rheological measurements. Moreover, the rheological characteristics of BSG-STMP showed it can be used as a proper hydrogel in food and pharmaceutical applications.

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1. Introduction

Basil seed gum (BSG) is a natural, water-soluble polysaccharide which is extracted from the outer pericarp of basil seeds (*Ocimum basilicum* L.), can be soaked in water, swells into a gelatinous mass and forms a colloidal gel (Rafe & Razavi, 2012). It is a renewable hetero-polysaccharide that contains glucomannan, xylan and glucan (Tharanathan & Anjaneyalu, 1974), and can be formed a suitable hydrogel at alkaline conditions, particularly at pH 8.0 (Rafe & Razavi, 2013). The frequency and easily extraction of BSG make it as an excellent opportunity to be utilized in many functions such as lubricant (Zhang, Liu, Chen, & Liu, 2016), emulsifying agent (Hosseini-Parvar, Osano, & Matia-Merin, 2016), thickening or stabilizing agent (Hosseini-Parvar, Matia-Merino, Goh, Razavi, & Mortazavi, 2010; BahramParvar & Goff, 2013). As BSG has a weak network structure, it is essential to improve its gelling strength by applying some chemical cross linkers in order to elaborate BSG hydrogels in food and pharmaceutical applications.

Sodium trimetaphosphate (STMP) is a safe, non-toxic cross-linking agent suitable for polysaccharides matrices elaboration which approved by the Food and Drug Administration (FDA, 1995). It has been used as a phosphorylation agent for both protein and sugars as a means of enhancement to improve their functional properties (Li, Enomoto, Ohki, Ohtomo, & Aoki, 2005, 2010). It works by linking the polymer chains with phosphates (Autissier, Letourneur, & Le Visage, 2006; Lack et al., 2004), and is mainly used to prepare food-grade phosphorylated starches (Khondkar, Tester, & Karkalas, 2009). Although, many researchers have mainly used STMP on starches (Carmona-Garcia, Sanchez-Rivera, Mendez-Montealvo, Garza-Montoya, & Bello-Perez, 2009; Sang, Prakash, & Seib, 2007, 2010; Woo & Seib, 2002), but it has also been utilized for guar gum (Gliko-Kabir et al., 2000), carboxy methyl cellulose (Leone, Torricelli, Giardino, & Barbucci, 2008), konjac glucomannan (Liu, Fan, Wang, & He, 2007), hyaluronan (Dulong et al., 2004), xanthan (Bejenariu, Popa, Dulong, Picton, & Le Cerf, 2009) and pullulan (Dulong, Forbice, Condamine, Le Cerf, &

Picton, 2011; Lack, Dulong, Picton, Le Cerf, & Condamine, 2007, 2004). The mechanism of the reaction of STMP with some hydrocolloids has been described in the literature (Dulong et al., 2011; Lack et al., 2007).

Fractal analysis through rheological experiments has been attracted a great deal of interest as a simple quantitative procedure to characterize physical properties of macromolecules such as the elasticity of gels (Mandelbrot, 1982; Stauffer & Aharony, 1994). A fractal is a self-similar structure which can be characterized by a noninteger dimension; the fractal dimension d_f (Mandelbrot, 1982; Viscek, 1989). It can be measured by small amplitude oscillatory shear (SAOS) methods using the dynamic shear storage modulus, G', as an indicator of the connectivity of the gel network. The fractal structures of gels formed by aggregation have been investigated on gold (Weitz & Oliveria, 1984), bovine serum albumin and β-lactoglobulin (Hagiwara, Kumagai, & Matsunaga, 1997; 1998), caseinate gel by glucono-δ-lactone (Bremer, Bijsterbosch, Schrijvers, van Vliet, & Walstra, 1990; 1993), boehmite alumina colloidal gels (Shih, Shih, Kim, Liu, & Aksay, 1990) and egg white protein (Ould Eleya, Ko, & Gunasekaran, 2004).

However, the dynamic rheological behavior of BSG at different conditions such as pH, ion strength and concentrations have been studied (Rafe & Razavi, 2012, 2013), but the scaling law and fractal analysis of polysaccharides such as BSG did not consider yet and most studies have been carried out on protein gels and fat crystal networks (Hagiwara et al., 1997; 1998; Ould Eleya, Ko, & Gunasekaran, 2004; Tang & Marangoni, 2006). Moreover, the fractal dimension of BSG and BSG cross-linked with STMP as a polymer gel will be precious in controlling macroscopic physical properties of the gel. Therefore, the relationship between the structure of the aggregates and the macroscopic physical properties were explored. Furthermore, the influences of BSG concentration and temperature on the chemical crosslinking during heating, cooling and reheating of such gels by dynamic rheology were investigated.

2. Materials & methods

2.1. Fractal models

When colloidal gels are far from its gelation threshold, the scaling law for the elasticity and the limit of linearity (γ_o) can be considered by the fractal nature of the colloidal flocs (Shih et al., 1990). Depending on the strength of inter and intra-floc links, there are two regimes, including strong-link regime (inter-floc links have higher elasticity than those in the intra-floc links) and weak link regime (inter-floc links are weaker than intra-floc links).

In the strong-link regime, the dependency of the elasticity and the limit of linearity of the gels on the particle concentration (φ) can be described as follows:

$$G' \sim \varphi^{(d+x)/(d-d_f)} \tag{1}$$

$$\gamma_0 \sim \varphi^{-(1+x)/(d-d_f)} \tag{2}$$

In the weak-link regime:

$$G' \sim \varphi^{1/(d-d_f)} \tag{3}$$

$$\gamma_0 \sim \varphi^{1/(d-d_f)} \tag{4}$$

where d is the Euclidean dimension, d_f is the fractal dimension of the flocs ($d_f \leq 3$), and x is the fractal dimension of the floc backbone ($1 \leq x < d_f$) (Shih et al., 1990).

Recently, Wu and Morbidelli (2001) have extended the Shih et al. model by considering an appropriate effective microscopic elastic constant α (where $\alpha \in [0, 1]$) to estimate the fractal dimension for both inter- and intra-floc links. It indicates the relative importance of these two contributions and lets identifying different gelation regimes prevailing in the system.

$$G' \sim \varphi^{\beta/(d-d_f)} \tag{5}$$

$$\gamma_0 \sim \varphi^{(d-\beta-1)/(d-d_f)} \tag{6}$$

$$\beta = (d-2) + (2+x)(1-\alpha) \tag{7}$$

2.2. Materials

Basil seeds (Isfahan variety) were purchased from the local markets of Mashhad, Iran. Sodium trimetaphosphate (STMP), Sodium hydroxide and Hydrochloric acid in analytical grade were purchased from Alfa Aesar (Lot No, 5002, Lancashire, United Kingdom) and from the Merck Company (Merck KgaA, Darmstadt, Germany), respectively.

2.3. Basil seed gum preparation

Basil seed gum was prepared according to our previous work, which extracted at optimum conditions (temperature 68 °C, water to seed ratio 65:1 and pH 8) (Rafe & Razavi, 2012). Based on the previous works, the carbohydrate to protein ratio of BSG was obtained 2.7 for our variety (Razavi et al., 2009). BSG suspensions at various concentrations (0.5, 1, 1.5 & 2% w/v), were prepared by dispersing appropriate amounts of BSG powder to a portion of alkaline water (pH 8.0) that contained 0.02% sodium azide as an anti-microbial preservative. These solutions were made in stock solutions then divided into smaller stocks (with and without STMP). For STMP, an aqueous solution of STMP (10% w/v) was added and the reaction mixture was stirred one minute (Woo & Seib, 1997; Lack et al., 2007). Then, the solutions were agitated for 2 h at room temperature and shook by a roll mixer overnight to complete the hydration. These samples were kept in a refrigerator at 5 °C before the experiments.

2.4. Dynamic oscillatory measurements

Rheological measurements were performed with an AR2000-EX rheometer from TA instrument (New Castle, New Jersey, US) using parallel plate geometry (diameter 40 mm, gap 1 mm). The linear viscoelastic region (LVE) is determined by amplitude sweep tests in controlled shear stress (CSS) mode at 20 °C and 1 Hz. The viscoelastic parameters, such as the storage modulus (G'), the loss modulus (G'') and tan δ, were calculated using the manufacturer's software (US200 Physica® version 3.40 Anton Paar GmbH, Germany).

In order to study thermo-reversibility of BSG, the solutions were heated on the rheometer *in situ* from 20 to 90 °C during the temperature sweep and held at this temperature for 10 min, followed by a cooling down to 20 °C, to observe thermal hysteresis and gel forming characteristics of BSG. Then, the samples were subjected to a stress sweep at a constant frequency of 1 Hz. The strain values were measured and critical strain or the limit of linearity (γ_o) was determined from the G'-strain profiles of the gels. In order to study gel melting; the temperature was increased to 90 °C. All heating and cooling processes were performed at a rate of 5 °C/min. Gelling