Laponite as a rheology modifier of alginate solutions: Physical gelation and aging evolution

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ARTICLE INFO

ABSTRACT

The rheological behavior of alginate and Laponite/alginate solutions was studied. It was observed that the Cross viscosity model successfully describes the steady-state shear behavior of this polysaccharide. The scaling behavior analyzed for the entangled regime is in good agreement with polyelectrolyte solutions ($G_e \sim c_p^{3/2}$), with interactions generated between the alginate and the charged surfaces of the Laponite platelets. Therefore, the effect of Laponite as a rheology modifier is influenced by the alginate concentration. Higher alginate concentrations hindered the formation of the house of cards microstructure. Frequency sweep tests were performed to analyze the transition from solid-like to liquid-like behavior in a solid-like dominated domain. Soft physical gels were obtained at low alginate concentrations. The gel point was determined (1.65 wt.% of alginate and 2 wt.% of Laponite) through the Kramers–Krönig damping factor, and time sweep tests revealed the evolution of the storage (G') and loss modulus (G'') as functions of the waiting time (t_w). The growing elasticity revealed that Laponite/alginate solutions undergo aging.

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1. Introduction

Alginate is an anionic polysaccharide that can be extracted from macroalgae or bacterial cultures. It is a copolymer of (1–4)-linked β-D-mannuronate (M) and α-L-guluronate (G) residues (Gacesa, 1988; Percival, 1979). The ratio of guluronic to mannuronic acid depends on the source. Alginates are block polymers; they are linear unbranched copolymers containing similar or strictly alternating blocks: MM, GG or GM. M and G acids are covalently linked, forming different sequences or blocks. Two adjacent G blocks can be cross-linked with multivalent cations: divalent cations such as Ca^{2+}, Ba^{2+}, Fe^{2+} or Sr^{2+} or trivalent cations such as Al^{3+}. Hence, a gelling mechanism occurs when those cations take part in ionic binding zones between G blocks (Augst, Kong, & Mooney, 2006; Rezende, Bártolo, Mendes, & Maciel Filho, 2009). Thereby, a three-dimensional network is formed. Binding zones are often called "egg boxes" (Larsen, Bjørnstad, Pettersen, Tønnesen, & Melvik, 2015; Papajová, Bujdoš, Chorvát, Stach, & Lacík, 2012; Percival, 1979; Venkatesan, Bhatnagar, Manivasagan, Kang, & Kim, 2015).

Alginate is a biopolymer characterized by its hydrophilicity. It can easily form aqueous solutions in which the viscosity increases with the alginate content and its molecular weight. Aqueous alginate solutions are non-Newtonian fluids, presenting shear-thinning behavior (Rezende et al., 2009). Due to its biocompatibility, non-toxicity and gelling mechanism, alginate has been widely used in tissue engineering applications, cell encapsulation, drug and protein delivery, and as pharmaceutical excipients, among other functions (Rodríguez-Rivero, Hilliou, del Valle, & Galán, 2014). Moreover, alginate is commonly used as a gelling agent in the food industry, textile/paper industry, and for dental impressions and wound dressings (Augst et al., 2006; Fu et al., 2011).

Laponite is a layered nanosilicate with the empirical formula $Na_{+0.7}[(Mg_{5.5}Li_{0.3})Si_8O_{20}(OH)_4]^{-0.7}$ (Perkins, Brace, & Matijević, 1974; Thompson & Butterworth, 1992; Xavier et al., 2015). It is a synthetic material obtained from a combination of salts of sodium, magnesium and lithium with sodium silicate. One of the applications of Laponite is as a rheology modifier (Ruzicka & Zaccarelli, 2011). It is an additive that promotes shear-thinning and thixotropic behavior in waterborne products (Willenbacher, 1996). In recent studies, Laponite was used to reinforce hydrogels for biomedical applications (Hong et al., 2015; Shen et al., 2014). Moreover, as reported by Xavier et al. (2015), nanocomposites reinforced with Laponite can support cellular adhesion and enhance in vitro mineralization and physiological stability, which expands the applications in the tissue engineering (TE) field. Laponite platelets are nanoscale disk-like particles with an aspect

ratio of 1:25. They are formed in layers: two parallel sheets of tetrahedrally coordinated silica and a sheet of octahedrally coordinated magnesium oxide between them. Oxygen and OH^- groups are also present in the Laponite structure (Zulian, Ruzicka, & Ruocco, 2008). Furthermore, some magnesium atoms are substituted by lithium atoms. Therefore, a negative charge is on the platelet surfaces, whereas positive charges are on the rim due to the interlayer cations. In this case, the sodium ions balance the charges (Ruzicka & Zaccarelli, 2011). Conversely, when Laponite is dispersed in water, sodium ions are released, and the charges are unbalanced. Thus, the platelets adopt a negative charge on their faces, while the rims can adopt a positive or negative charge depending on the pH of the solution (Joshi, Reddy, Kulkarni, Kumar, & Chhabra, 2008; Kumar, Aswal, & Harikrishnan, 2016; Mongondry, Tassin, & Nicolai, 2005; Morariu, Bercea, & Sacarescu, 2014; Sun et al., 2012; Tawari, Koch, & Cohen, 2001).

Aqueous Laponite dispersions undergo physical aging because they are out of thermodynamic equilibrium. Hence, the microstructure of these dispersions progressively evolves to a lower level of energy (Jatav & Joshi, 2014; Shahin & Joshi, 2010). Thermal motion and particle aggregation due to the electrostatic forces between them influence physical aging (Jatav & Joshi, 2014; Labanda & Llorens, 2008), as do the Laponite concentration and the addition of polymers, salts or other components. It is reported in the literature that the intensity of the positive charges on the rims decreases as the pH increases; the rim is positively charged at pH $\leq$ 11 (Shahin & Joshi, 2010; Sun et al., 2012). With positive rims, a "house of cards" microstructure is formed by the platelets due to the electrostatic interactions between them and the faces (Liu & Bhatia, 2015; Mongondry et al., 2005). This microstructure is also responsible for the viscosity increase and the shear-thinning effect of aqueous Laponite dispersions (Mongondry et al., 2005). Under low shear rates, the house of cards structure is adopted, but it collapses at high shear rates. In this case, the platelets are oriented in the flow direction, and the viscosity decreases. Contrariwise, the negative charges on the rims have an influence on the elastic behavior of the dispersion due to the repulsion between platelets.

The electrostatic interaction between Laponite platelets and the mechanism of the formation of the microstructures are yet a matter of debate. The Laponite concentration plays an important role in the dispersion microstructure. Below a 2 wt.% Laponite concentration, the house of cards microstructure is suggested. Conversely, above this concentration, two proposals are suggested in the literature: (i) a house of cards or (ii) a Wigner repulsive glass microstructure. This latter takes into account the repulsion between Laponite platelets (Jatav & Joshi, 2014; Zulian et al., 2008). These microstructures evolve due to aging and can be destroyed by applying a deformation onto the sample, in a process called rejuvenation. The applied deformation should generate a stress greater than the yield stress of the sample (Jatav & Joshi, 2014). To perform rejuvenation, pre-shear or shear melting processes are carried out before the rheological studies. Sun et al. (2012) studied the aging phenomena in aqueous Laponite dispersions containing polyethylene glycol (PEG) and NaCl. To rejuvenate the samples to set a reference initial condition for the tests, a uniform shear field was applied. As observed in the dynamic time sweep test, a reproducible liquid state was achieved. Nevertheless, it is observed that the aging is partially irreversible, as described by Jatav and Joshi (2014); a shear melting process was previously applied to the rheological characterization of aqueous Laponite dispersions. In this case, an oscillatory shear stress was applied to rejuvenate the samples. As demonstrated, the shear melting rejuvenates the sample, although not completely; a slight difference is observed in comparison with a freshly prepared sample (Jatav & Joshi, 2014; Shahin & Joshi, 2010).

As previously described, the addition of salts and polymers modifies the aging of dispersions. Salt reduces the electrostatic repulsion between Laponite platelets, accelerating the aggregation for low concentrations of Laponite because the surface charge is screened (Sun, Wang, Wang, Liu, & Tong, 2013). The addition of salt also modifies the microstructure from glass-like to gel-like. The gel state has a fractal network, while the glass state does not have an ordered microstructure (Joshi et al., 2008).

The pronounced shear-thinning and solid-like behaviors provide interesting results for additive manufacturing (AM) applications in tissue engineering. Solutions rheologically modified could easily flow through nozzle tips due to the shear rate generated along their walls. Once out of a nozzle, the material could maintain its shape as result of the high viscosity (Barry et al., 2009; Hong et al., 2015). Subsequently, a crosslinking process can be applied to form hydrogels, thereby improving the geometric accuracy. In this work, the rheological behavior of alginate aqueous solutions and Laponite/alginate solutions was studied. A steady-state shear master curve for alginate solutions was obtained. When Laponite was added to the alginate solutions, a pronounced shear-thinning behavior was observed in steady-state shear tests. Then, frequency sweep tests were performed to analyze the physical gelation due to the electrostatic interactions between the Laponite platelets and alginate chains. The damping factor of the solutions was analyzed as a function of the alginate concentration, where the gelation mechanism, which arises due to the dispersed Laponite platelets, was studied. Finally, time sweep tests were performed to analyze the aging evolution of the Laponite/alginate samples under the gel point concentration.

2. Experimental

2.1. Materials and solution preparation

Medium-viscosity sodium alginate from brown algae was purchased from Sigma–Aldrich Corp., USA. Its molecular weight ranges between 80,000 and 120,000 g mol^{-1}, and it is composed of approximately 61% mannuronic acid and 39% guluronic acid. Laponite XLG was obtained from Southern Clay Products, Inc., USA. Sodium chloride was purchased from Labsynth, Brazil. 0.1 M NaCl was added to the dilute alginate solutions to determine the viscosity-average molecular weight using the Mark–Houwink–Sakurada correlation, which is given by

$$[\eta] = KM^{\alpha} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity, $K = 7.3 \times 10^{-3}$ g ml^{-1} and $\alpha = 0.92$ for an M/G ratio of 1.56 (Thu et al., 1996). The specific and reduced viscosities are given by Eqs. (2) and (3), respectively,

$$\eta_{sp} = \frac{\eta_0 - \eta_s}{\eta_s} \tag{2}$$

$$\eta_{red} = \frac{\eta_{sp}}{c_p} \tag{3}$$

where η_0 is the zero shear viscosity, η_s the solvent viscosity ($\eta_s = 0.001003$ Pa s at 20 °C) and c_p the polymer concentration. The intrinsic viscosity is given by

$$[\eta] = \lim_{c_p \to 0} \left(\frac{\eta_{sp}}{c_p} \right) \tag{4}$$

All solutions were prepared using deionized water without added NaCl, except that to determine the viscosity-average molecular weight. Alginate solutions and Laponite/alginate solutions were prepared using a magnetic stirrer for 6 h with a plate temperature of 60 °C to ensure homogeneity. All samples were stored for 16 h before the rheological tests. The Laponite/alginate solutions were prepared using 2 wt.% Laponite. The alginate concentration was varied in the range of 0.25–4 wt.% for the steady-state shear and