



Scaling law and microstructure of alginate hydrogel



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ABSTRACT

The gelation of alginate in aqueous solution was studied as a function of Ca^{2+} concentration. At each given concentration of alginate, a critical gel concentration $c_{g, \text{Ca}^{2+}}$, was successfully determined for the first time using the Winter–Chambon criterion. The critical gel concentration $c_{g, \text{Ca}^{2+}}$ was found to increase linearly with alginate concentration. At the same time, the critical relaxation exponent n decreased and the critical gel strength S_g increased linearly with alginate concentration. An improved egg-box model was proposed to describe the change in gel junction and gel network. In the stable gel state, the plateau modulus G_e of alginate gel depended on Ca^{2+} concentration according to a power-law scaling, $G_e = k\varepsilon^{1.5}$, where ε is the relative distance of a gelling variable (Ca^{2+} concentration in this case) from the gel point ($c_{g, \text{Ca}^{2+}}$). The FESEM images verified the microstructure of alginate gel in which alginate chains associated into fibrils in the presence of Ca^{2+} ions. The fibrillar diameter and network density increased with increasing Ca^{2+} ion concentration while alginate concentration had a weak influence on fibrillar diameter.

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1. Introduction

Alginate is a natural polysaccharide extracted from various species of brown seaweed. It is known to be a whole family of linear copolymers containing blocks of (1→4)-linked β -D-mannuronate (M) and α -L-guluronate (G) residues, which are composed of consecutive G blocks (GG), consecutive M blocks (MM), and alternating M and G blocks (GM). Alginate extracted from different sources differs in M and G contents as well as the length of each block. The G blocks are stiffer and more extended in chain configuration than the M blocks due to a higher degree of hindered rotation around the glycosidic linkages (Gacesa, 1988). In aqueous solution, alginate is usually employed as a thickening agent to increase the viscosity of medium. In the presence of divalent cations (e.g., Ca^{2+} , Ba^{2+} , Sr^{2+} , Mg^{2+}), the carboxyl groups of alginate give it the ability to undergo a sol–gel transition (Wang, White, Konno, Saito, & Nozawa, 1995; Zheng, 1997). The G blocks are known to mainly contribute to participate in intermolecular cross-linking with divalent cations, as the structure of G blocks allows a high degree of coordination of divalent cations. That is, the G blocks of one polymer chain are connected with the G blocks of adjacent polymer chains through divalent cations, resulting in the formation of a three dimensional gel network of alginate strands. The composition and sequential

character of blocks affect the gelation behavior of alginate. G-rich alginate generally forms hard and brittle gels, while M-rich ones form soft and elastic gels. As it is easy to prepare ionotropic alginate gels under mild conditions, alginate is widely used as a gelling agent not only in foods but also in other fields such as biotechnology and biomedical engineering as scaffolds, drug delivery carriers, and cell encapsulation and transplantation (Draget, Skjåk-Bræk, & Smidsrød, 1997). However, all these properties and applications are ultimately dependent on the gelling mechanism and the gel strength.

Even though the gelation of alginate has been known for more than 40 years, there is still a continuous revision and improvement in understanding of its gelation mechanism and gel properties based on new experimental results. To obtain new insight into the sol–gel transition of alginate, numerous experimental and theoretical studies have been carried out. Morris, Rees, and Thom (1973) found that Ca^{2+} ions induce the association of G blocks and they proposed for the first time a model for the junction zone based on X-ray fiber diffraction, which is popularly known as the egg-box model. The dialysis experiment, performed by Grant, Morris, Rees, Smith, and Thom (1973) further showed that a molar ratio of 4:1 between G blocks and Ca^{2+} ions fits well with the egg-box model. Subsequently, Xinxing, Liying, Tan, and Zhen (2003) prepared alginate gels by in situ release of Ca^{2+} ions and found that much more Ca^{2+} ions are required to participate in association with G blocks for the high G block content during gelation. Lu, Liu, and Tong (2006) found that the power law is valid for the alginate gels induced by

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Ca^{2+} ions and a denser structure forms with increasing alginate concentration. Recently, a systematical studies were carried out to investigated the gelation behavior of alginate in the presence of various divalent cations and found that not only G blocks but also random GM blocks contribute to the junction zone (Donati, Benegas, Cesaro, & Paoletti, 2006; Donati, Cesaro, & Paoletti, 2006; Donati, Draget, Borgogna, Paoletti, & Skjak-Brk, 2005; Mrch, Donati, Strand, & Skjak-Brk, 2006). Although the egg-box model is popularly used for alginate gels, it has also been questioned by many researchers. For example, on the basis of calculated free energy, Braccini, Grasso, and Pérez (1999) and Braccini and Pérez (2001) found that a parallel model seems more stable than the egg-box model. All of these research works indicated that the gelation of alginate is a complex process induced by divalent cations.

Many studies have also been devoted to reveal the physical properties of alginate gels in the stable state, because G block length, the ratio of G to M blocks, molecular weight of alginate, type and amount of divalent cations and alginate concentration in aqueous solution are critical factors affecting the physical properties of alginate gels. For example, Simpson, Stabler, Simpson, Sambanis, and Constantinidis (2004) found that alginate possessing a high G block content developed more porous gels which maintained their integrity for longer periods of time. During cationic cross-linking, they did not undergo excessive swelling and subsequent shrinking, thus they could better maintained their form. Drury, Dennis, and Mooney (2004) found that alginate gels with the high ratio of G to M blocks at a given molecular weight showed a relatively high stiffness, which could effectively control the rate of drug release. With increasing Ca^{2+} ion content, Yuguchi, Urakawa, Kajiwara, Draget, and Stokke (2000) found through small angle X-ray scattering (SAXS) that the addition of much Ca^{2+} ions in aqueous solution induces the lateral association of G block, which results in the formation of multimer and the increase in the dimension of the junction zone. The similar experimental results have also been reported by Draget, Stokke, Yuguchi, Urakawa, and Kajiwara (2003) and Maki et al. (2011). From the preceding works, it can be found that the gel strength is strongly dependent on the formation of various junction zones. However, no studies have shown directly the evolution of microstructures of alginate gels so far.

Rheology is a powerful tool to study the sol–gel transition and properties of gels. During gelation, storage modulus G' and loss modulus G'' would simply increase or decrease depending essentially on various gelation mechanisms. For example, for methylcellulose (MC), the gelation is achieved by the hydrophobic association of MC chains (Arvidson et al., 2013; Desbrieres, Hirrien, & Ross-Murphy, 2000; Kobayashi, Huang, & Lodge, 1999; Li, 2002), where G' and G'' increased upon heating and MC gels showed an excellent thermal thermoreversibility through a thermal cycle of heating to cooling. However, for the kappa-carrageenan gel system (Parker, Brigand, Miniou, Trespoey, & Vallee, 1993; Ramakrishnan & Prud'homme, 2000; Souza, Hilliou, Bastos, & Goncalves, 2011), the formation of the double-helix aggregation during cooling led to the increase of viscoelastic moduli. A number of studies have been carried out to characterize rheological properties of alginate gels that are stable over the temperature range from 0 to 100 °C. Stokke et al. (2000) found that alginate gels become independent of the oscillation frequency at high Ca^{2+} ion contents, which is similar to the rheological characteristics of classical gels. Webber, De Carvalho, and Barreto (2012) reported that the viscoelastic response at high strains seems coherent with an interconnected rod-like structure. In general, different viscoelastic properties reflect different gelation mechanisms and gel microstructures.

In the present work, we have systematically studied the gelation behavior of alginate and its structure property. The rheological scaling law has been examined and discussed for

understanding of the gelation of alginate which is induced by Ca^{2+} ions. In the stable gel state, the feature of alginate gel microstructure has been demonstrated by field emission scanning electron microscopy (FESEM) and the evolution of the plateau modulus has been observed, which could correlate viscoelastic properties with microstructures. The possible mechanism for the formation of the unique microstructures during the sol–gel transition has been proposed and discussed.

2. Experimental

2.1. Materials and solution preparation

Sodium alginate was obtained from Sigma–Aldrich (Singapore). According to the supplier, the molecular weight of sodium alginate ranged from 100,000 to 150,000 g/mol and G block content of was 50–60%. Calcium chloride with 99% ACS grade was also purchased from Sigma–Aldrich (Singapore). All materials were used without further purification.

Aqueous solutions of alginate with four concentrations, 2 wt%, 3 wt%, 4 wt% and 5 wt%, were prepared with deionized water from a Millipore water purifier. Solutions were mechanically stirred for 24 h under ambient condition. After then, aqueous solutions of calcium chloride with various molar concentrations were added to each concentration of alginate solution. The final alginate/calcium chloride solutions were stirred at room temperature for 2 days to achieve a homogeneous dissolution of Ca^{2+} ions in aqueous solutions of alginate. The concentrations of alginate and calcium chloride used in this study were expressed in wt%.

2.2. Rheological measurement

The rheological measurements were performed on a rotational rheometer (DHR, TA Instruments, USA) with a parallel plate geometry of 40 mm in diameter and a gap of 0.55 mm. The sample for rheological measurement was transferred directly from a glass bottle to the bottom plate of rheometer using a pipette for dilute solutions and a spoon for solid-like gels. Strain sweeps in the range of 0.1–100% at frequencies of 0.1–2 Hz were carried out to determine the linear viscoelastic range of the solution in both sol and gel states. A low-viscosity silicone oil was placed to the sample's perimeter to prevent water evaporation during measurement. Frequency sweeps for a given alginate solution with various Ca^{2+} contents in the angular frequency range of 0.1–100 rad/s were carried out at a constant strain of 1% and a fixed temperature ($T=20\text{ }^\circ\text{C}$).

2.3. Morphological characterization

The morphology of alginate gels was observed using a field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan). The samples for FESEM were prepared by freeze drying as follows. About 10 μL of an alginate solution was dripped on the surface of aluminum foil and was frozen under the refrigerator of $-20\text{ }^\circ\text{C}$ for about 24 h. After then the frozen samples were quickly transferred into a vacuum freeze dryer (Telstar cryodos-80, Telstar industrial, Spain) and dried at $-80\text{ }^\circ\text{C}$ for about one week. The final dried sample was sputtered with gold on its surface in vacuum and examined by FESEM with an accelerating voltage of 5 kV. For the cross-sectional structures, the freeze dried samples were fractured in liquid nitrogen and sputtered with gold in vacuum and then mounted vertically on a sample holder. They were observed using FESEM with an accelerating voltage of 2 kV.

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