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Molecular weight distribution, rheological property and structural changes of sodium alginate induced by ultrasound

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ABSTRACT

In this study, the effects of ultrasound with different ultrasonic frequencies on the properties of sodium alginate (ALG) were investigated, which were characterized by the means of the multi-angle laser light scattering photometer analysis (GPC-MALLS), rheological analysis, circular dichroism (CD) spectrometer and scanning electron microscope (SEM). It showed that the molecular weight (M_w) and molecular number (M_n) of the untreated ALG was 1.927×10^5 g/mol and 4.852×10^4 g/mol, respectively. The M_w of the ultrasound treated ALG was gradually increased from 3.50×10^4 g/mol to 7.34×10^4 g/mol while the M_n of ALG was increased and then decreased with the increase of the ultrasonic frequency. The maximum value of M_n was 9.988×10^4 g/mol when the ALG was treated by ultrasound at 40 kHz. It indicated that ultrasound could induce ALG degradation and rearrangement. The number of the large molecules and small molecules of ALG was changed by ultrasound. The value of d_n/d_c suggested that the ultrasound could enhance the stability of ALG. Furthermore, it was found that ALG treated by ultrasound at 50 kHz tended to be closer to a Newtonian behavior, while the untreated and treated ALG solutions exhibited pseudoplastic behaviours. Moreover, CD spectra demonstrated that ultrasound could be used to improve the strength of the gel by changing the ratio of M/G, which showed that the minimum ratio of M/G of ALG treated at 135 kHz was 1.34. The gel-forming capacity of ALG was correlated with the content of G-blocks. It suggested that ALG treated by ultrasound at 135 kHz was stiffer in the process of forming gels. The morphology results indicated that ultrasound treatment of ALG at 135 kHz increased its hydrophobic interaction and interfacial activity. This study is important to explore the effect of ultrasound on ALG in improving the physical properties of ALG as food additives, enzyme and drug carriers.

1. Introduction

Sodium alginate (ALG) is one of the widely used polysaccharides as an enzyme carrier and food additives, which is made up of mannuronic acid (M) and guluronic acid (G) as two kinds of structure units, forming a kind of no linear block copolymer of branched chain. It is easy to form hydrogels in the presence of divalent cations, such as calcium, which can act as cross-linkers between the functional groups of alginate chains [1]. It has been demonstrated that alginate is promising as a bioactive compound carrier due to its nontoxic and inexpensive [2,3]. Furthermore, ALG is widely used as stabilizers, thickeners or gelling agents in products such as sauces, soups and beverages [4,5]. However, it was proved that the physical properties, the ability to form gels and the strength of ALG gels depended not only upon the ratio of M/G, but also on the physical properties of ALG such as molecular weight and distribution [6].

Ultrasonic refers to the acoustic frequency is higher than the threshold of human hearing (in general, >20 kHz). The main mechanism responsible for the effect of ultrasound on liquid systems is the physical forces generated by acoustic cavitation such as microjets, shear, shockwaves and acoustic streaming [7,8]. The shear forces resulted from the collapse of the bubbles may break the covalent bonds in polymeric materials [9,10]. The process of the cavitation in liquid systems was presented in Fig. 1. The asymmetric collapse of a cavitation bubble leads to a liquid jet rushing through the centre of the collapsing bubble. Ultrasound can effectively improve and strengthen the physical and chemical properties of some solutions, which is attributed to the shear stress

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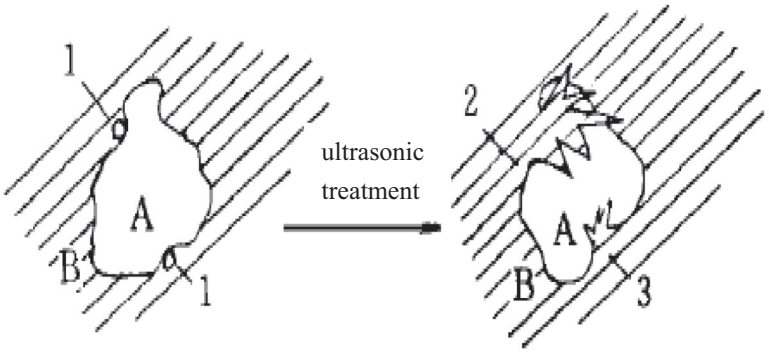

Fig. 1. The process of cavitation. 1. Cavitation nuclear. 2. Micro jet. 3. Erosion, broken. A: the polymers molecules B: the solvent molecules.

generated by the high temperature and high pressure accompany with the collapse of cavitation bubbles [11]. Under such conditions, molecules trapped in the bubble (water vapor, gases and vaporized solutes) can be brought to an excited-state and dissociate [12]. Lu et al. reported that ultrasound could enhance the porosity of alginate scaffold based on acoustic cavitation [13]. In addition, many process and treatment parameters affect the ultrasound output and its effect on the properties of polysaccharide in liquid media. Several studies have shown that the reduction of macromolecular chains of the polysaccharides may be obtained by the ultrasound method [9,14].

The application of ultrasound to modify biopolymers is increasingly studied. To investigate the impact of different ultrasonic frequencies on characteristics of ALG by using the complementary techniques of gel permeation chromatography coupled with a multiangle laser light scattering photometer analysis (GPC-MALLS) in combination with structure evaluation techniques including circular dichroism (CD) and scanning electron microscope (SEM). The measurement of molecular weight can be accomplished without using standard solutions or polymers [15]. The viscosity data of ALG induced by ultrasound was obtained from rheological measurements. The aim of this work was to investigate the effect of ultrasound on physical properties and structural changes of ALG in order to extend the application of ultrasound in the formation of gel and improvement of the ALG additive products.

2. Materials and methods

2.1. Materials and sample preparation

Sodium alginate (ALG, $M_w = 1.93 \times 10^5$ g/mol, M/G = 1.51, 200 ± 20 mPa.s viscosity) was purchased from Aladdin Reagent Company (Shanghai, China). ALG solutions (0.95 wt%) were prepared in 0.1 M phosphate buffer solution at pH 7.0. Samples were stirred with heating at 50 °C to ensure complete dispersion and hydration, and then cooled to the room temperature. All other chemicals and solvents used were of analytical grade.

2.2. Ultrasound treatment

An assemble ultrasonic bath system equipment with two sets of JXD-02 multi-frequencies processing system and the low temperature circulating water tank was employed (JXD-02, Beijing Jinxing Ultrasonic Equipment Technology Co., Ltd., China). The experimental ultrasound apparatus used in this work has been described in detail in our previous work [16]. ALG solutions prepared with ultrasound treatment were carried out at different frequencies, 0.25 W/cm^2, 50 °C for 20 min, respectively. The ultrasonic equipment could deliver four different frequencies (28, 40, 50,135 kHz).

2.3. Gel permeation chromatography coupled with a multiangle laser light scattering photometer analysis (GPC-MALLS)

The molecular weight and molecular mass distributions of ALG were determined by GPC-MALLS (Wyatt Technology Co, USA). The GPC-MALLS system consists of a Waters 2690D separations module, a Waters 2414 refractive index detector (RI) and a Wyatt DAWN EOS MALLS detector. ALG solutions treated by different ultrasonic frequencies were analyzed after diluted two times. All samples (300 μL) were injected at 0.5 ml/min after passing through a 0.22 μm nylon filters. Then the molecular weight and molecular mass distribution of ALG were determined through the designated software.

2.4. Rheological measurement

Steady shear measurements were conducted in a rheometer (Haake MARS III, Thermo Scientific, Germany) using a cone-and-plate geometry, with a cone angle of 1° and a diameter of 60 mm. Viscosity analyses were recorded by using a steady state flow ramp in the 0.1–1000 s^{-1} range of shear rate. The measuring device was equipped with a temperature unit that gave good temperature control (25 ± 0.05 °C) over an extended time in this work.

Oscillatory (dynamic) tests were performed inside the linear viscoelastic region, and the storage modulus (G′) and loss modulus (G″) were recorded versus frequency. Frequency sweeps were done from 0.1 to 10 Hz.

2.5. Circular dichroism analysis

The composition ratio of mannose acid (M) and gulose acid (G) of ALG was analyzed according to CD spectra. It was recorded by spectropolarimeter (optical physics applications, British; Chirascan), using a quartz cuvette of 1 mm optical path length at room temperature (25 ± 1 °C). ALG solutions were scanned in the far UV range (190–260 nm) with three replicates at 0.1 nm as band width. All spectra were corrected by subtracting the baseline. The relative amounts of D-mannuronate and L-guluronate residues (the ratio of peak height and trough depth) could be calculated by the following equation [17]:

$$\text{Mannuronate/guluronate} \approx 2.0\,(\text{peak/trough}), \quad \text{if peak/trough} < 1 \tag{1}$$

$$\%\,\text{Mannuronate} \approx 27(\text{peak/trough}) + 40, \quad \text{if peak/trough} > 1 \tag{2}$$