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Effect of polysaccharide chain conformation on ultrasonic degradation of curdlan in alkaline solution

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ABSTRACT

This study was to investigate the effects of polysaccharide chain conformation on ultrasonic degradation of curdlan, a high MW β-glucan with wide applications. The ultrasonic degradation was performed in alkaline solution at 0.1 M and 0.3 M NaOH, in which the curdlan chain was mainly in triple helical conformation and random coil form, respectively. The degradation rate was represented by the kinetic model, $1/M_t - 1/M_o = kt$, with the rate constant k increasing with the ultrasonic power. The degradation rate was much higher in 0.3 M NaOH than in 0.1 M NaOH, suggesting that curdlan in random coil conformation was more liable to degradation than in helical conformation. Curdlan in 0.1 M NaOH was changed from triple helices to single helices and eventually to random coils with a higher solubility. In summary, ultrasonic degradation of curdlan in alkaline solution had a close and complex relationship to the chain conformation changes.

1. Introduction

Curdlan is an exopolysaccharide produced by *Agrobacterium biobar*, *Alcaligenes faecalis* and some other bacteria (Liu, Gu, Ofosu, & Yu, 2015; McIntosh, Stone, & Stanisich, 2005; Zhang & Edgar, 2014). It is a water-insoluble linear β-1,3-glucan and soluble in alkaline condition. Curdlan has a high molecular weight with an average degree of polymerization about 450 and up to 12,000 monosaccharide units (Futatsuyama, Yui, & Ogawa, 1999). It has a major application in the food industry because of the favorable rheological properties and various bioactivities (Zhang & Edgar, 2014). A useful and unique property of curdlan is its ability to form two distinct types of thermo-gels in aqueous media, high-set gel and low-set gel network (Cai & Zhang, 2017). In high-set gel, the polymer chain is predominately in triple helical conformation, while single helix is predominant in low-set gel network. In an alkaline solution, the triple helix of curdlan chain unwinds and conformational transition from helical structure to random coil occurs with increasing NaOH concentration from 0.19 M to 0.24 M (Nakata, Kawaguchi, Kodama, & Konno, 1998). Chemical modifications such as carboxymethylation, sulfation, phosphorylation, oxidation and esterification have been applied to prepare curdlan derivatives with good water solubility as well as bioactivity to widen its application (Cai & Zhang, 2017).

Power ultrasound (US) has been exploited as a simple and direct means for acceleration or activation of a wide range of chemical and physical processes (Mason & Lorimer, 2002; Tao & Sun, 2015). Depolymerization of high molecular weight polysaccharides is a useful approach for generation of lower molecular weight fractions with lower viscosity, higher water solubility and better functionality. Compared with other techniques for polysaccharide degradation, including thermal, mechanical, oxidative, and hydrolytic and high-energy radiation, US is a clean, non-hazardous, non-thermal mechanical means, which is most favorable for processing food grade products (Gogate & Prajapat, 2015). Because ultrasonic degradation of polysaccharide is mainly caused by the fluid shear forces from collapsing cavitation, it may reduce the molecular weight by splitting the most susceptible chemical bonds, but not cause significant change in chemical structure (Čížová, Bystrický, & Bystrický, 2015; Huang et al., 2015; Prajapat, Subhedar, & Gogate, 2016; Zhi et al., 2017).

The US degradation process and rate of polysaccharides can be affected by the structure and properties of polysaccharides to be degraded. Although many previous studies have been done on ultrasonic degradation of polysaccharides, few have addressed the effects of chain conformation on the degradation process (Gogate & Prajapat, 2015; Tao & Sun, 2015). There is still no reported study on the application of power US for modification or degradation of natural curdlan. This study

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aims to investigate the effect of chain conformation on the US degradation of curdlan in alkaline solution with different NaOH concentrations and to analyze the degradation kinetics and mechanism.

2. Materials and methods

2.1. Materials

Curdlan powder from *Alcaligenes faecalis* was purchased from Sigma-Aldrich, USA. The powder was stored at 4 °C before use. Curdlan solution was prepared by dissolving the sample powder in 0.1 M and 0.3 M sodium hydroxide (NaOH) solution for 2 h at room temperature with constant stirring. Aqueous solutions were prepared with ultrapure water from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Congo red was purchased from Shanghai Yuan Ye Biotechnology, Ltd. (Shanghai, China). All other reagents were of analytical grade unless otherwise specified.

2.2. Ultrasonic treatment conditions of curdlan

Ultrasonic treatment (degradation) of curdlan was performed with a Model VCX-130 ultrasonic processor of 20 kHz frequency and 130 W maximum power and a probe horn of 6 mm tip diameter (Soncis & Materials Inc., Newton, USA). The actual power at a set amplitude was determined by the calorimetric method as described previously (Cheung & Wu, 2013). The curdlan sample solution (25 mL and 2 g/L) was contained in a 50 mL plastic centrifuge bottle and the ultrasound probe was immersed in the solution at a fixed depth of 2 cm. The sample bottle was placed in an ice bath to maintain a relatively low temperature of 40 ± 5 °C throughout the US treatment. The US processor was operated at three different amplitudes of 20%, 50% and 70%, corresponding to power intensities of 10.6, 34.3 and 48.4 W/cm^2 tip surface, respectively. The treatment period was varied from 2 to 60 min, after which the US-treated curdlan solution was taken for measurement of various properties.

2.3. Molecular weight determination by intrinsic viscosity measurement

Intrinsic viscosity [η] of curdlan solution in NaOH was determined by the dilution method (Yang & Zhang, 2009) and the viscosity was measured using an Ubbelohde viscometer at 25.0 ± 0.1 °C in a water bath. The viscosity-average molecular weight (M_v) of curdlan was determined according to Mark-Houwink equation,

$$[\eta] = KM_v{}^a, \quad (1)$$

where $K = 0.0079$ and $a = 0.78$ for curdlan dissolved in 0.3 M NaOH at 25 °C (Nakata et al., 1998), or $K = 0.0032$ and $a = 0.85$ for curdlan dissolved in 0.1 M NaOH at 25 °C (Futatsuyama et al., 1999).

2.4. Ultrasonic degradation kinetic model

The reduction of curdlan molecular weight (M_v) with time during the US was fitted to the following kinetic model for ultrasonic degradation process of polymer originally derived by Malhotra (1986),

$$\frac{1}{M_t} - \frac{1}{M_0} = kt \quad (2)$$

where t is the sonication time (min) and k is the rate constant (mol/g min) of the ultrasound degradation process, and M_0, M_t are the viscosity-average molecular weights (mol/g) at time 0 and time t, respectively. The value of k at a given US power intensity (W/cm^2) was determined by linear regression fit of experimental data according to Eq. (2).

2.5. Gel formation by acidification

A weak gel is usually formed when curdlan in alkaline solution is neutralized with the addition of acid, due mainly to the single and triple-helical conformation of curdlan polymer chain (Kanzawa, Harada, Koreeda, & Harada, 1987; Saito, Ohki, & Sasaki, 1977). For evaluation of the US effect on the solubility of curdlan molecules in a neutral solution, 36% HCl was added at an equal mole to NaOH to the US-treated curdlan solution immediately after the US treatment for neutralization. The gel formed after the neutralization was separated from the liquid solution by centrifugation at 6000 rpm for 15 min, and then dried at 70 °C for 2 days for weight measurement.

2.6. Congo red-curdlan complex test

Congo red test is a simple and useful measurement of the high-ordered conformation of polysaccharide chain in alkaline solution (Ogawa & Hatano 1978; Saito et al., 1977). The test was performed of the curdlan solution before and after sonication at various NaOH concentrations. Congo red was mixed with curdlan of 0.2% in 25 mL NaOH solution from 0.05 to 0.5 M NaOH before and after various sonication periods at a power intensity of 48.6 W/cm^2. The solution was maintained at room temperature for 1 h and the absorbance spectrum from 400 to 700 nm was recorded on a UV–vis spectrometer for detection of the maximum absorbance wavelength (λ_{max}).

3. Results and discussion

3.1. Effect of ultrasonic power on intrinsic viscosity of curdlan

Fig. 1 shows the decrease of intrinsic viscosity of curdlan with sonication time in 0.1 M and 0.3 M NaOH. The initial intrinsic viscosity of curdlan on 0.1 M NaOH (4.25 dL/g) was higher than that in 0.3 M

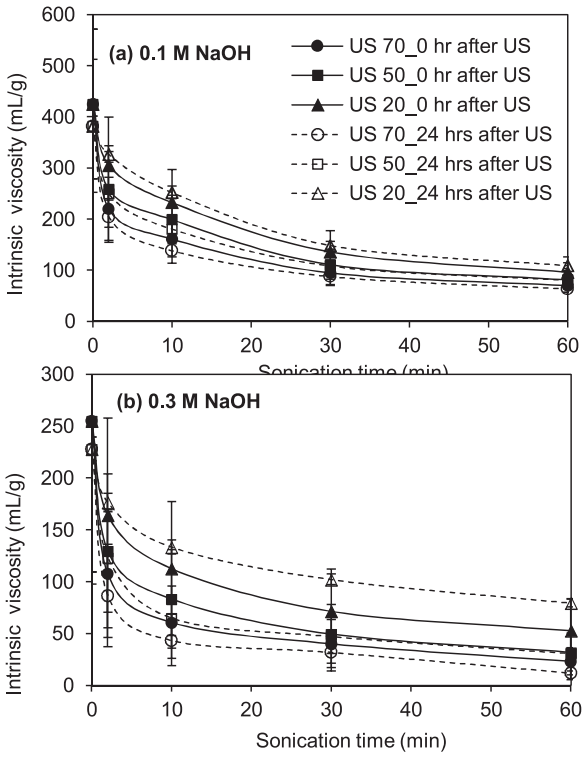

Fig. 1. Intrinsic viscosity change of curdlan solution with sonication time in (a) 0.1 M and (b) 0.3 M NaOH caused by ultrasound treatment at various power intensity (solid line: measured immediately after US treatment; dash line: measured 24 h after US treatment).