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Rheological and kinetic study of the ultrasonic degradation of locust bean gum in aqueous saline and salt-free solutions

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ABSTRACT

The ultrasonic degradation of locust bean gum (LBG) in aqueous solutions has been studied at 25 °C for ultrasonication times up to 120 min. Although LBG is not a polyelectrolyte, the degradation extent and kinetics were found to be somewhat sensitive to the ionic conditions in solution, and this is attributed to changes in molecular conformation that can occur in different salt environments. Ultrasonic degradation was tracked by rheological measurements that lead to the determination of intrinsic viscosity for the LBG molecules. A kinetic model was also developed and successfully applied to characterize and predict the degradation results.

1. Introduction

Locust bean gum (LBG), also known as carob bean gum, is obtained from the endosperm of the seed of the locust (carob) tree, an evergreen of the legume family, *Ceratonia siliqua* L. LBG and its derivatives are broadly used in a variety of applications, such as the papermaking, mining and textile industries as well as in food processing [1]. Moreover, LBG is also commonly used in conjunction with other gums, such as guar gums, κ-carrageenan gums [2], and xanthan gums [3] because of its unique swelling and water-binding properties.

LBG is composed of 1–4-linked β-D-mannopyranose, and randomly distributed 1–6-linked α-D-galactopyranose side chains with an approximate ratio of 4:1 (see Fig. 1). The reported molecular weight of LBG is in the range of 300–360 kDa [4]. As a typical galactomannan, the physicochemical properties of locust bean gum are highly dependent on the distribution of galactose moieties, because longer galactose side chains generate stronger synergistic interactions with other polymers and result in greater functionality [5,6]. In recent years, the molecular structures and rheological properties of LBGs in aqueous solutions have been studied using various characterization methods [3,7–11] and LBG is considered to behave in aqueous solution as disordered random coils [12]. Because LBG is only slightly soluble in water at ambient temperature, it does not easily form gels by itself. However, LBG could interact synergistically with other polysaccharides, such as guar gums, tara gums, xanthan gums, and κ-carrageenan gums, and perform as a gelation enhancer by binding double helices of these polysaccharides in solution into a continuous network and increase the gel strength [13–16].

To meet the requirements of an application, it is often necessary that the molecular weight or particle size of the LBG be adjusted to yield macroscopically observable behavior within a proper range. Thus the degradation (depolymerization) of LBG has been studied in recent years [11,17,18] and is considered as a key question for LBG studies. However, traditional chemical and thermal degradation techniques will change the fundamental structure of the polymers, and subsequently change their chemical or biological properties. Ultrasonication degrades the polymers primarily through a mechanical mechanism associated with the collapse of cavitation bubbles [19,20] and is considered to be a promising technique for modifying the molecular weight of LBGs without changing its chemical properties.

The effects of salt on LBG molecules in solution have been reported in several previous studies [8,21–23]. The results suggested that addition of salts may have some effect on the hydrodynamic volume of LBG molecules, but not as much effect as is seen for polyelectrolytes. Previous studies of ultrasonic degradation of native xanthan gum solutions and native/depyruvate xanthan gum blends have shown that degradation rates are affected by molecular conformation which can be manipulated through the salt concentrations and choice of salt species [24,25]. Thus, in this work, we study the ultrasonic degradation of LBG in aqueous

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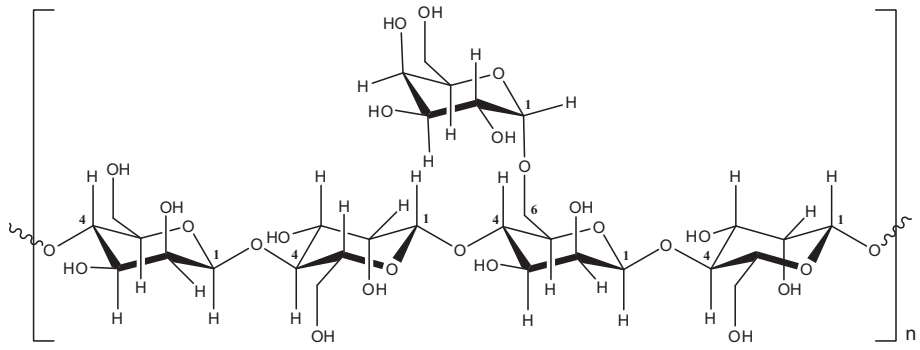

Fig. 1. Molecular structure of the repeat unit for LBG, which has a molecular weight of around 900 Da, and a ratio of mannose to galactose of about 4:1.

solutions containing various concentrations of salt to investigate the degree of sensitivity of degradation efficiency to the ionic conditions. Observation of changes in the intrinsic viscosity of the solutions was used to monitor the degradation process. An intrinsic viscosity estimation model and a degradation kinetics model have also been developed and used to quantify and compare degradation rates under different environmental conditions.

2. Materials and methods

2.1. Preparation of LBG solutions

LBG (molecular weight ~310 kDa) was purchased from Sigma–Aldrich (St. Louis, MO). To prepare the solutions, 120 mg of LBG was dissolved in 100 ml of cold deionized distilled water, followed by heating to 85 °C and stirring for 60 min. After a complete cool down to room temperature, the solutions were transferred to centrifuge tubes, and spun at 2200 rpm for 15 min. Subsequently, the supernatant was analyzed by filtering small samples with a 0.22-μm syringe filter. Aliquots were added to small vials and heated overnight at 80 °C to evaporate the water. The mass of the vials was measured before and after heating to determine the amount of dissolved material. All the measurements were performed in triplicate. Typically, the centrifuged solutions were found to have a polymer concentration of ~1.0 g/l (which indicates that about 83% of the original LBG could be dissolved).

To understand the influence of ionic strength on LBG before and after sonication treatment, the solutions were pre-mixed with either 0.5, 0.1, 10^{-2}, or 10^{-4} M of NaCl (a typical salting-in salt) or Na_2SO_4 (a typical salting-out salt) before ultrasonication.

2.2. Sonication treatment and viscosity measurement

The LBG-salt mixtures or salt-free LBG solutions (25 ml, 1.0 g/l) were transferred into a glass tube with a dimension of 24 × 106 mm (O.D. × length), and were sonicated by using a Cole-Parmer ultrasonic processor Model CP750 (Vernon Hills, IL) which operates at a fixed 20 kHz frequency and has a maximum power output of 750 W. The processor was fitted with a horn having a diameter of 12.5 mm and was operated at 35% of maximum amplitude. Since the output power is proportional to the square of the amplitude, this condition corresponds to approximately 92 W of power. The tip of the horn was placed just below the surface of the fluid in the tube, and the ultrasonic field was applied for a specific duration of time. The water bath was replenished as needed in order to control the temperature of the solution in the tube at a relatively constant temperature of ~25 °C. After sonication, the salt concentration in all solutions was adjusted to 0.1 M with additional amounts of the corresponding salt, in order to ensure that viscosity measurements were performed at the same ionic strength. Each sample was then diluted by using aliquots of the corresponding 0.1 M salt solution to produce solutions with LBG concentrations in the range of 1.0 to 0.2 g/l. Solution viscosity was determined using Cannon viscometers of Ubbelohde type (State College, PA). The sample volume was ~15 ml for each viscosity measurement, and the temperature of water bath was fixed ~25 °C. Origin 8.5.1 (Origin Lab, Northampton, MA) was used to plot viscosity against concentration, as well as to obtain linear and nonlinear regression lines with the corresponding equations and correlation coefficients (R^2) in order to assess the best model.

2.3. Intrinsic viscosity determination

Since the intrinsic viscosity of a polymer in solution is directly related to its molecular weight, rheological measurements of sonicated solutions were used to monitor the ultrasonic degradation process. The intrinsic viscosity is a measure of the contribution of the polymer itself to the solution viscosity. The intrinsic viscosity is obtained from specific viscosity measurements extrapolated to zero shear rate and infinite dilution since under those conditions the effects caused by the rotation of polymers relative to the solvent are eliminated.

Many empirical forms have been used to characterize the relationship between the viscosity of polymer solutions and the polymer concentration. The most broadly accepted one is the Huggins equation [26] shown in Eq. (1), where k is the Huggins constant. The intrinsic viscosity can be obtained by measuring the specific viscosity of a solution, and then diluting it several times with solvent, measuring and calculating the specific viscosity after each dilution, and extrapolating the course of specific viscosity to zero concentration. The intercept values obtained are intrinsic viscosities of the polymer in the original solution:

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]^2 C \tag{1}$$

If the solution is very dilute or the interaction between molecular chains is negligible, the Huggins' equation can be simplified by neglecting the second-order term, and thus the intrinsic viscosity can be determined from the slope of a plot relative viscosity vs. polymer concentration [27]:

$$\eta_{rel} = 1 + [\eta]C \tag{2}$$

In this study, both Eqs. (1) and (2) were applied for estimation of intrinsic viscosities of LBG solutions and statistically compared in order determine the quality of fit.

2.4. Salt tolerance (S) and relative stiffness parameter (B)

To analyze the results of ultrasonic degradation on LBG solutions, salt tolerance and relative stiffness parameters were