



Rheological and kinetic study of the ultrasonic degradation of xanthan gum in aqueous solutions



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ABSTRACT

The effectiveness of ultrasound to degrade the molecular weight of xanthan gum in aqueous solutions was investigated for sonication times up to 60 min at 20 °C and for polymer concentrations up to 0.1 g/dl. The Huggins equation was found to be applicable to the intrinsic viscosity of xanthan gum prior to sonication, while a truncated form was found to be adequate for estimating the intrinsic viscosity of the degraded xanthan. To better understand the influence of salting-in and salting-out salts (classified on the basis of the Hofmeister series) on degradation, xanthan-gum solutions were pre-mixed with 0.1, 10⁻², 10⁻³, or 10⁻⁴ M NaCl or Na₂SO₄, prior to ultrasonication. A kinetic model was developed and successfully applied to quantify and predict the degradation rates and efficiency. The various reaction rate constants and reaction orders were found to correlate with the different salt species and concentrations used, suggesting that salting-in and salting-out salts could increase or inhibit ultrasonic degradation by adjusting the molecular conformation of the xanthan.

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1. Introduction

Because of their practical significance, degradable natural polymers, such as polysaccharides and proteins, continue to attract the attention of researchers. Oligosaccharides, which are obtained from polysaccharide degradation, have been extensively used for many industrial and food applications and are considered to be products with high added-value. Among such polysaccharides is xanthan gum, which has been broadly used for food, pharmaceutical and cosmetic applications as a thickener (Lund, Lecourtier, & Muller, 1990), stabilizer, emulsifier, and foaming agent since it was first approved by the U.S. Food and Drug Administration in 1969. These applications stem from the ability of xanthan to induce high viscosity at low polymer concentration in aqueous solutions.

Xanthan is produced by aerobic fermentation of a pure culture of the bacterium *Xanthomonas campestris* (Richardson & Ross-Murphy, 1987). Xanthan, which consists of a β (1–4)-linked glucose backbone with orderly distributed trisaccharide side chains, is completely soluble in cold and hot water (Holzawarth, 1981). Xanthan gums have been shown to exhibit two different conformational structures: an ordered conformation (Jansson, Kenne, & Lindberg, 1975), which has been described as double-stranded helical structure (Sato, Kojima, Norisuye, & Fujita, 1984; Sato,

Norisuye, & Fujita, 1984; Sato, Norisuye, & Fujita, 1985), and a disordered conformation, which has been described as a single-stranded random coil (Milas & Rinaudo, 1986) or a wormlike chain with a moderate persistence length (Milas, Rinaudo, Duplessix, Borsali, & Linder, 1995). As a result, the xanthan gum may undergo a thermally induced conformational transition that depends on the salt concentration and temperature of the solvents. To date, much work has attempted to elucidate the relationship between the rheological behaviour of xanthan, conformational change, intermolecular interactions, and stability (Higiro, Herald, & Alavi, 2006; Higiro, Herald, Alavi, & Bean, 2007; Liu & Norisuye, 1988a, 1988b; Stokke, Smidsrød, & Elgsaeter, 1989; Wang, Sun, & Wang, 2001; Wang, Wang, & Sun, 2002).

Degradation of these naturally occurring biopolymers has become a key goal for xanthan studies, because the molecular weight or particle size is often required to be reduced, or to be confined within a narrow range, in order to meet the requirements of the application. Recently, several techniques for degradation have been studied and applied to xanthan, including bio-degradation (Ahlgren, 1993; Cadmus, Jackson, Burton, Plattner, & Slodki, 1982; Muchová et al., 2009), thermal degradation (Lambert & Rinaudo, 1985; Soares, Lima, Oliveria, Pires, & Soldi, 2005; Srivastava, Mishra, Singh, Srivastava, & Kumar, 2012), chemical degradation (Christensen, Smidsrød, Elgsaeter, & Stokke, 1993), and ultrasonic degradation (Milas, Rinaudo, & Tinland, 1985). Compared to other degradation techniques, ultrasonic degradation has been considered to be one of the best ways to control

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molecular weight of degradation products. In addition, under ultrasonic processing, degraded polymers have the same basic chemical structure as their parent molecule, whereas other methods might alter the chemical structure and thereby the material behaviour (Basedow & Ebert, 1977).

High intensity ultrasound generates various physicochemical effects, including radiation pressure, streaming, cavitation, and interface instabilities (Mulet, Cárcel, Benedito, Rosselló, & Simal, 2002). Cavitation is broadly accepted as the mechanism of ultrasonic degradation of polymers (Basedow & Ebert, 1977). Ultrasonic degradation of xanthan gum was recently reported by Tiwari, Muthukumarappan, O'Donnell, and Cullen (2008) and a limiting molecular weight was observed. As a result, a more thorough study of the influence of the environmental conditions within the solution on the degradation efficiency and limits is of high interest. In this work, we specifically study the influence of salt on the ultrasonic degradation of xanthan gum in aqueous solutions, which provides a potential way to achieve degradation beyond the limits seen in other degradation studies and with a faster degradation rate. Two categories of salts were used over a range of concentrations. Observation of changes in the intrinsic viscosity of the solutions was used to monitor the effectiveness of the ultrasonic degradation. A degradation kinetics model has also been developed and used to quantify and compare degradation rates under different environmental conditions.

2. Materials and methods

2.1. Materials and solution preparation

Xanthan gum (of molecular weight, ranging from 13,000 to 50,000 kDa) was purchased from Sigma–Aldrich (St. Louis, MO). Sodium chloride (NaCl) and sodium sulphate (Na₂SO₄) were purchased from Fisher Scientific (Fair Lawn, NJ). Solutions were prepared by dispersing 100 mg of dried xanthan gum in 100 ml of deionized distilled water, followed by heating to 40 °C and stirring for 60 min. After cooling to room temperature, the solutions were transferred into two 50 ml centrifuge tubes, and spun at 2200 rpm for 15 min to remove air bubbles. After centrifuging, the solutions were ready for ultrasonic processing. To understand the influence of ionic strength on the ultrasonic degradation of xanthan gum, the solutions were pre-mixed with either 0.1, 10⁻², 10⁻³, or 10⁻⁴ M NaCl or Na₂SO₄ before sonication.

2.2. Density measurement

The amount of dissolved xanthan gum was measured by filtering small samples of the centrifuged xanthan gum solutions with a Tisch Scientific 0.22 μm Nylon syringe filter (North Bend, OH). Aliquots were added to small vials and heated overnight at 80 °C to evaporate the solvent, and the amount of dissolved material was determined gravimetrically. All the measurements were performed in triplicate.

2.3. Sonication treatment and viscosity measurement

The xanthan gum solutions (25 ml, 0.10 g/dl) were transferred into a cooling cell, and sonicated by using a Cole-Parmer ultrasonic processor Model CP750 (Vernon Hills, IL) fitted with a horn, which has a diameter of 0.5 in and a nominal power output of 750 W. The frequency of the amplifier was fixed at 20 kHz, and the amplitude was fixed at 35%, which corresponds to approximately 92 W of power. The water–ice bath was replenished as needed in order to control the temperature of the solutions in the cell. After sonication treatment, the salt concentrations of all solutions were adjusted to 0.1 M through addition of corresponding salts, in order

to make sure that all viscosity measurements were taken at the same ionic strength. Each sample was diluted by using the corresponding salt solution with the concentration of 0.1 M, to produce concentrations of xanthan gum in the range of 0.10–0.02 g/dl. The viscosity of the solutions was determined using Cannon Ubbelohde viscometers (State College, PA) at 25 °C. Origin 8.5.1 (Origin Lab, Northampton, MA) was used to plot viscosities against concentrations, 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.

2.4. Intrinsic viscosity determination

The goal of the rheological measurements is to determine the intrinsic viscosity [*η*] of the solutions as a function of ultrasonication in order to quantify the degradation process. The intrinsic viscosity measures the contribution of individual polymer molecules to the solution viscosity. As indicated in Eqs. (1)–(3), to obtain the value of intrinsic viscosity, solution-viscosity measurements are extrapolated to zero shear-rate (*q* → 0) and infinite dilution (*C* → 0) in order to eliminate the interaction effects between the polymer molecules. Here, *η*_{sp} is the specific viscosity, *η*_{rel} is the relative viscosity, *η*_s is the viscosity of the solvent, and *η* is the viscosity of the solution. The intrinsic viscosity is determined by measuring the specific viscosities of a solution at its original polymer concentration, diluting it several times with solvent and measuring and calculating the specific viscosity after each dilution, and extrapolating the course of specific viscosity results to zero concentration. The zero-concentration intercept value is the intrinsic viscosity of the polymer.

$$[\eta] = \lim_{\substack{q \rightarrow 0 \\ C \rightarrow 0}} \frac{\eta_{sp}}{C} \quad (1)$$

$$\eta_{sp} = \eta_{rel} - 1 = \frac{\eta - \eta_s}{\eta_s} \quad (2)$$

$$\eta_{rel} = \frac{\eta}{\eta_s} \quad (3)$$

The relationship between dilute polymer solution viscosity and concentration can be described by many empirical forms, the most common of which is the Huggins equation (Huggins, 1942), as shown in Eq. (4), wherein *k* is the Huggins constant.

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]^2 C \quad (4)$$

For very dilute solutions, the Huggins equation can be simplified, removing the second-order term and, in this case, the intrinsic viscosity can be determined from the slope of a plot of polymer concentration against relative viscosity (Tanglerpaibul & Rao, 1987).

$$\eta_{rel} = 1 + [\eta]C \quad (5)$$

2.5. Ultrasonic degradation kinetics

In general, the rate of degradation can be modelled as an *n*th-order reaction, based on total molar concentration of the polymer, as is shown in Eq. (6). Here [*M*]_{*t*} is the total concentration of polymer molecules (and fragments) at time *t*, *k'* is the degradation rate constant, and *n* is the order of reaction (Taghizadeh & Mehrdad, 2003).

$$\frac{d[M]_t}{dt} = k' [M]_t^n \quad (6)$$

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