Rheological and kinetic study of the ultrasonic degradation of xanthan gum in aqueous solution: Effects of pyruvate group

Ruoshi Li, Donald L. Feke*

Department of Chemical and Biomolecular Engineering, Case Western Reserve University, Cleveland, OH 44106, USA

ABSTRACT

The influence of the pyruvate group on the efficiency of ultrasonic degradation of xanthan gum in aqueous solution has been studied. Blends of natural and pyruvate-free xanthan gums were ultrasonicated at $20\,^\circ$C for up to 30 min and evaluated for molecular-weight degradation by viscometry. Solutions of pure pyruvate-free xanthan exhibited the highest stability to degradation among all blend ratios studied. Removing the pyruvate group is believed to enable the molecular chains to adopt a more compact conformation, which renders the polymer less susceptible to ultrasonication. In addition, the effects of salt on ultrasonic degradation efficiency were studied by using 0.1, 10^{-2}, or 10^{-4} M of NaCl or Na_2SO_4 in solution prior to ultrasonication. A degradation kinetics model was developed to quantify the degradation behavior. The absence of pyruvate groups renders the xanthan gum less sensitive to the influence of salt, and hence decreases the ultrasonic degradation efficiency.

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1. Introduction

The use of ultrasound to manipulate the molecular weight of natural polymers has emerged over the last decade as a promising processing approach for oligosaccharides. Compared to traditional degradation approaches (e.g., thermal, chemical or biological processes), the use of ultrasonic techniques is viewed as being more environmentally friendly and economical. In addition, the degraded polymers can be produced with a narrow molecular weight distribution and would have the same basic chemical properties as their parent polymers (Basedow & Ebert, 1977). Thus ultrasonic degradation techniques have been receiving increasing scientific attention.

One class of natural polymers are xanthan gums, which are broadly used in modern pharmaceutical, cosmetic and food processing industries as thickeners or stabilizers due to their unusual physico-chemical properties in aqueous solutions (Lund, Lecourtier, & Muller, 1990). Owing to the stiffness of the polymer backbone, xanthan gum may undergo an order–disorder conformational transitions and thus different rheological behavior of solutions may be seen by changing the polymer concentration, or the ionic strength and pH values in aqueous solutions

(Jansson, Kenne, & Lindberg, 1975; Milas & Rinaudo, 1979; Sato, Kojima, Norisuye, & Fujita, 1984a; Sato, Norisuye, & Fujita, 1984b; Sato, Norisuye, & Fujita, 1985; Zhong, Oostrom, Truex, Vermeul, & Szecsody, 2013). Although it has been broadly accepted that the high molecular weight of xanthan gum and the rigid nature of its molecular backbone are important factors that determine its rheological properties (Kabir & Stanislav, 1980; Morris, 1977; Zirnsak, Boger, & Tirtaatmadja, 1999; Zhang et al., 1996), it has also been suggested that the pyruvate and acetate side-groups strongly influence the rheological characteristics of xanthan gum solutions or xanthan gum mixed solutions (Fitzpatrick, Meadows, Ratcliffe, & Williams, 2013; Sandford et al., 1977; Smith, Symes, Lawson, & Morris, 1981; Callet, Milas, & Rinaudo, 1987). Thus, a study of the influence of specific functional groups on ultrasonic degradation phenomena is key to optimization of such processes.

Pyruvate groups are not present on natural xanthan in stoichiometric quantities. The pyruvate group content may vary according to the strain of the bacterial source of the xanthan, as well as different fermentation conditions. As a result, the final fermentation product is composed of a mixture of polymer chains having various contents of pyruvate groups, with 14–65% of the terminal mannose residues bearing a pyruvate group (Sandford, Watson, & Knutson, 1978). The influence of pyruvate and acetate groups is also directly associated with the order–disorder transition of xanthan gum. Acetate groups, which are located closer to the center of the helix structure of the molecule, tend to stabilize the ordered form, presumably by enhancing the association of the side chains

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with the polymer backbone by hydrogen bonding and thus stimulate intramolecular interactions. On the contrary, pyruvate groups tend to favor the disordered form, due to a decrease of electrostatic repulsion when the side chains extend away from the main chain (Viebke, 2005). Since pyruvate groups are located on the periphery of the helix structure, they are more able to participate in intermolecular interactions rather than intramolecular interactions. Thus, pyruvate groups enhance the association between and structure formation among neighboring xanthan molecules through increased polymer–polymer interactions relative to polymer-solvent affinity. Consequently, pyruvate-rich xanthans tend to yield more viscous aqueous solutions than pyruvate-lean xanthans at comparable concentrations, especially in salt solutions (Smith et al., 1981). The order–disorder transition temperature of different modified xanthan gums have been screened and compared to study the contribution of acetate group and pyruvate group to the molecular backbone stability. The order of thermal stability observed experimentally was found to be: pyruvate-free xanthan gum > natural xanthan gum > acetate- and pyruvate-free xanthan gum > acetate-free xanthan gum (Dentini, Crescenzi, & Blasi, 1984).

In our previous work, we have reported the influence of different salt species on ultrasonic degradation of xanthan gum solutions (Li & Feke, 2015). In this work, we focus on the specific influence of the pyruvate group on ultrasonic degradation of xanthan gums and a thorough study of the effect of this group on degradation efficiency is of high interest. Here, blends of natural and pyruvate-free xanthan gum dissolved in salt-free or salt solutions were used to investigate how the pyruvate group influences the ultrasonic degradation efficiency.

2. Materials and methods

2.1. Preparation of pyruvate-free xanthan gum

Xanthan gum was purchased from Sigma-Aldrich (St. Louis, MO). Trifluoroacetic acid (TFA) and sodium carbonate (Na_2CO_3) were purchased from Fisher Scientific (Fair Lawn, NJ). Xanthan gum was dissolved in deionized distilled water, and stirred at 40 °C to prepare xanthan gum solutions at a polymer concentration of 0.50 g/dl. Then, 5 mM of TFA was added into the solutions, and the mixture was stirred at 100 °C for 90 min. During treatment of large volumes (400 ml) of solutions, a temperature of 94–98 °C was normally achieved. After the mixture was cooled down to room temperature, it was neutralized to pH 7.0 with a 0.1-M solution of Na_2CO_3, as monitored by an Accumet pH/ion Meter Model 25 (Hayward, CA). After that, the mixture was diluted and washed with deionized distilled water, filtered, and dried. NMR studies of the modified xanthan revealed negligible TFA or Na_2CO_3 residue in the samples.

2.2. Preparation of xanthan gum blends and solutions

Sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) were purchased from Fisher Scientific (Fair Lawn, NJ). Stock solutions (0.10 g/dl) were prepared by dispersing 100 mg of dry natural xanthan gum or pyruvate-free xanthan gum in 100 ml of deionized distilled water. The solutions were stirred at 40 °C for 60 min. After a complete cool-down to room temperature, the solutions were transferred to two 50-ml centrifuge tubes, and spun at 2200 rpm for 15 min to remove air bubbles. Then the stock solutions were used in the following blend ratios (by volume) of natural to pyruvate-free xanthan: 100:0, 80:20, 20:80, and 0:100. To understand the influence of salt on the ultrasonic degradation of the xanthan gum blends, the solutions were pre-mixed with 0.1, 10^{-2}, or 10^{-4} M of NaCl or Na_2SO_4 before ultrasonication.

2.3. 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.

2.4. Ultrasonication treatment and viscosity measurement

The xanthan gum blend 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 had a diameter of 12.7 mm and a nominal power output of 750 W. The frequency of the amplifier was fixed at 20 kHz, and the power was fixed at 35% of maximum, 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 ultrasonication, the concentration of salt in all solutions was adjusted to 0.1 M through addition of corresponding salts, so that viscosity measurements would be taken at the same ionic strength. Each sample was diluted by using the corresponding salt solution (0.1 M) to produce concentrations of xanthan gum in the range of 0.10 to 0.02 g/dl for the determination of intrinsic viscosity. Solution viscosity was determined using Cannon Ubbelohde viscometers (State College, PA) at 25 °C. Dynamic viscosity measurements were precise to within $\pm 10^{-6}$ Pa·s, which leads to high accuracy in the determination of the intrinsic viscosity of the polymers. Origin 8.5.1 (Origin Lab, Northampton, MA) was used to plot solution viscosity against polymer concentration, as well as to perform linear and nonlinear regressions and evaluate correlation coefficients (R^2) in order to assess the best model.

2.5. Intrinsic viscosity determination

The intrinsic viscosity of the polymer (η) was determined using the Huggins equation (Eq. (1)) where k is the Huggins constant and η_{sp} is specific viscosity of the solution (Huggins, 1942). The intrinsic viscosity is obtained by measuring the specific viscosity of the original 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 measurements to zero concentration. The intercept value obtained is the intrinsic viscosity of the polymer. The specific viscosity of solutions is obtained from Eqs. (2) and (3), where η_{rel} is relative viscosity, η is the viscosity of the solution, and η_s is the viscosity of the pure solvent:

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

$$\eta_{sp} = \eta_{rel} - 1 = \frac{\eta - \eta_s}{\eta_s} \tag{2}$$

$$\eta_{rel} = \frac{\eta}{\eta_s} \tag{3}$$

2.6. Salt tolerance (S) and relative stiffness (B) parameters

The influence of ionic strength on the molecular chain stiffness can be analyzed by measuring solution viscosity in an isoionic dilution procedure. The intrinsic viscosity can be correlated with ionic strength through Eq. (4), where $[\eta]^\infty$ is the intrinsic viscosity at infinite ionic strength (Smidsrød & Haug, 1971).

$$[\eta] = [\eta]^\infty + S\frac{1}{\sqrt{I}} \tag{4}$$