

RHEOLOGICAL BEHAVIOR OF ERWINIA GUM IN AQUEOUS SOLUTION*

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Abstract Erwinia (E) gum, an extracellular polysaccharide, is composed of fucose, galatose, glucose and glucuronic acid. Its viscosity behavior was investigated by a low-shear-rate multiball viscometer and a rotational viscometer. Its weight-average molecular weight M_w and intrinsic viscosity $[\eta]$ in 0.2 mol/L NaCl aqueous solution were measured by light scattering method at 35°C and viscometry at 25°C and found to be 1.06×10^6 g/mol and 1050 mL/g, respectively, and its aggregates in aqueous solution were proved by gel permeation chromatography (GPC). These results indicated that E gum in water has exceedingly high viscosity and exhibits Bingham fluid behavior, owing to its aggregation. The viscosity of E gum decreased with increasing temperature, and the turning point appeared at 38°C for dilute solution and 80°C for concentrated solution suggesting that the aggregates of E gum in water started to disaggregate under these temperatures. In addition, the aggregates can be disrupted by adding either acid or base. The experimental results indicated that the E gum is a good thickening agent, and its fluid behavior is similar to xanthan.

Keywords Rheological behavior, Erwinia gum, Polysaccharide, Solution properties, Molecular weight, Aggregation

INTRODUCTION

Nowadays, water soluble polysaccharides are of increasing interest as thickening agents in food and in enhanced oil recovery, because they have novel functions and belong to polymers from renewable resources. It is well known that the utilization of renewable resources not only saves the petroleum but also decreases the pollution because of their biodegradability. E gum, an extracellular polysaccharide produced by strain of *Erwinia mituyensis* 5796, has been used as an additive in food industry such as a thickening agent and stabilizer^[1]. It is composed of fucose, galatose, glucose and glucuronic acid. In general, large viscosity enhancement of the polymer is attributed to aggregation^[2-4] or large hydrodynamic volumes of polyelectrolyte caused by electrostatic force due to the charge groups in water^[5, 6]. The interchain interaction of polysaccharides is so specific that polysaccharide chains are seldom dispersed in solvent as a

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single chain^[7]. Interestingly, upon attaining the maximum ionization of acid groups in amphiphilic acrylic copolymers, the intramolecular hydrophobic interaction dominates the electrostatic repulsion. With the addition of water, the chain aggregates and changes into large macromolecular domains, resulting in a sharp decrease in viscosity. This indicates that intermolecular hydrophobic interaction dominates the rheological behavior^[8]. Therefore, an understanding of the rheological behavior of polysaccharides in aqueous solution is essential for satisfactory application. The purpose of this work is to study the viscosity behavior of E gum in water under different conditions.

EXPERIMENTAL

Materials

Erwinia (E) gum was provided by the Fourth Chemicals Department, Asahi Chemical Industry Co. Ltd. The E gum was dissolved in water to a polymer concentration of 1 wt%, then centrifuged at 5000 rpm to remove any water-insoluble gum. To prepare the sample, ethanol was added at room temperature as a precipitant until no new precipitation took place, and the precipitated product was obtained by filtration and washed with ethanol, then dried at reduced pressure. A white powder was obtained, yield 28%. The sample of xanthan was purchased from Wuhan Food Resource Co. (imported from Japan).

Characterization

The scattering light intensities were measured by DAWN DSP laser photometer (Wyatt Technology Co.) at $\lambda = 633$ nm in an angular degree from 18° to 118° at 35°C . The E gum solution was prepared with 0.2 mol/L NaCl aqueous solution. The refractive index increment (dn/dc) was 0.128 mL/g for the dialyzed solution at 633 nm.

The gel permeation chromatographic analysis of E gum in 0.2 mol/L NaCl aqueous solution was performed on a TSP P100 pump coupling with a DAWN DSP System and RI 150 refractive index detector equipped with TSK G6000 PW $\times$ L column. ASTRA software was used to calculate the GPC data.

Intrinsic viscosity $[\eta]$ of E gum in 0.2 mol/L NaCl was measured at 25°C with multiball viscometer supplied by the Institute of Chemistry, the Chinese Academy of Sciences. The intrinsic viscosity $[\eta]$ of E gum in water ($C = 0.001$ g/mL) was measured at different temperature. The $[\eta]$ were determined by the Foss Experimental equation which is adaptable for polyelectrolyte solution as following:

$$(\eta_{sp}/c)^{-1} = ([\eta])^{-1} + B ([\eta])^{-1} C^{-1/2}$$

where C is the concentration, g/mL. The $[\eta]$ of E gum in aqueous solution depended on the shear-rate $\dot{\gamma}$, thus the zero shear-rate intrinsic viscosity $[\eta]_0$ was obtained from the plots of $[\eta]$ versus $\dot{\gamma}$.

Rotation Viscosity

E gum was dissolved in distilled water to prepare its aqueous solution with the concentration of 1 g/mL. The viscosity of E gum solutions was measured at 30°C under different conditions using an NDJ-4 rotational viscometer (Shanghai Balance Instrumental Manufacturer). By changing the temperature, concentration, pH and shear-rate of the E gum solution, their apparent viscosity (η_a) was measured. The pH of the solution was adjusted by adding sodium hydroxide or hydrochloric acid, and monitored by PHS-10B meter (XiaoShan Scientific Instrument Factory).

RESULTS AND DISCUSSION

Figure 1 shows a Zimm plot of E gum in 0.2 mol/L NaCl aqueous solution at 35°C . The measured values of weight average molecular weight M_w , second virial coefficient A_2 and radius of gyration $\langle S^2 \rangle^{1/2}$ are 1.06×10^6 g/mol, 0.44×10^{-4} cm³ mol g⁻² and 90 nm, respectively.

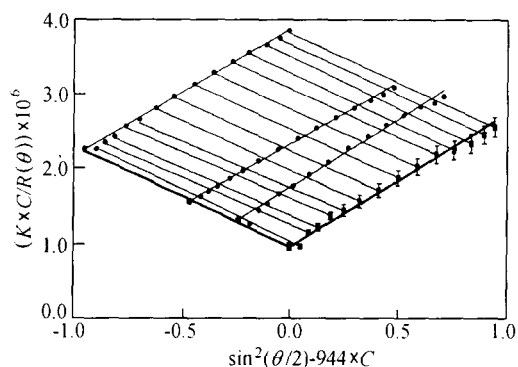


Fig. 1 Zimm plot of E gum in 0.2 mol/L NaCl aqueous solution at 35°C

GPC of E gum in 0.2 mol/L NaCl at 35°C and 50°C are shown in Fig. 2, indicating that the shoulder peak corresponding to the aggregates of higher molecular weight, decreased at 50°C, and the M_w changed from 1.06×10^6 to 6.03×10^5 g/mol, suggesting the aggregates were disrupted with increasing temperature.

Figure 3 shows the temperature dependence of zero-shear-rate intrinsic viscosity ($[\eta]_0$) of E gum dilute solution in water. The turning point existed on the curve line, suggesting a change from order to disorder conformation or from aggregation to disaggregation start at 38°C. The conformation change from triple-stranded helix to single chain for schizophyllam in water takes place at 130°C^[9]. However, the change from aggregation to disaggregation of sodium poly-*bis*-carboxylatophenoxy-phosphatezene in water is at 63°C^[10]. The turning point at 38°C for E gum in water was attributed to the change from aggregation to disaggregation.

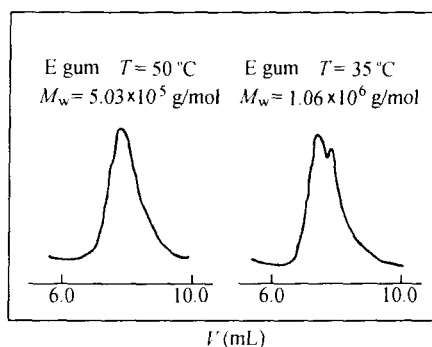


Fig. 2 GPC of E gum in 0.2 mol/L NaCl at 35°C and 50°C, respectively

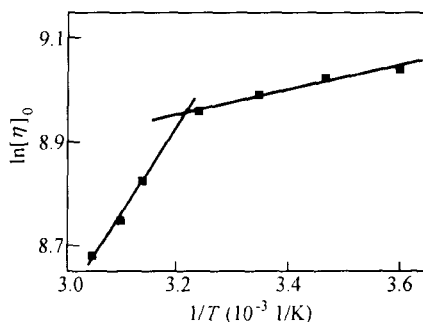


Fig. 3 plots of $\ln[\eta]_0 - 1/T$ for E gum in water

Concentration dependence of apparent viscosity (η_a) of E gum and xanthan in water are shown in Fig. 4. E gum and xanthan solutions all exhibited exceedingly high viscosity, but the η_a of E gum increased more significantly than xanthan with increasing concentration. Interestingly, η_a of E gum enhanced by a factor of 25 on passing from 0.3 to 0.9 g/mL of concentration. It is well known that xanthan is a good thickening agent, and has long been used as additive in foods, detergents and cosmetics. However, maximized concentration (0.005 g/mL) obtained from the xanthan in water was much lower than from E gum. In addition, $[\eta]_0$ of E gum in 0.2 mol/L NaCl aqueous solution was measured and found to be 1050 mL/g, which is similar to the value of xanthan^[11]. Therefore, E gum is an ideal thickening agent.

Figure 5 shows the temperature dependence of η_a of E gum in water. The turning point at

80°C suggested that a chain entanglement occurred in the aggregates, resulting in a sharply decreased viscosity. The turning point at 80°C was much higher than that at 38.5°C in dilute solution. This result indicated that it is more difficult to destroy aggregation in concentrated solution.

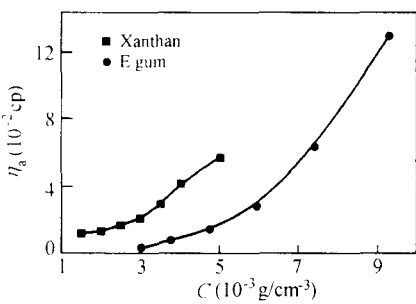


Fig. 4 concentration dependence of η of E gum and Xanthan in water at 30°C, $\gamma = 12.7$

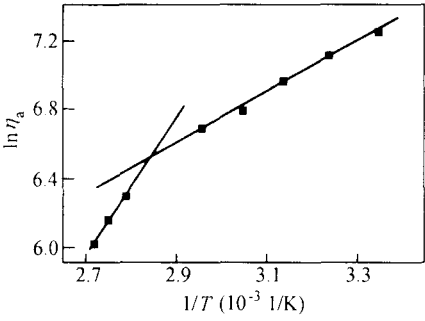


Fig. 5 Plot of $\ln \eta_a - 1/T$ for concentrated solution of E gum in water, $\gamma = 12.7$

Figure 6 shows the shear-rate (γ) dependence of η_a of E gum and xanthan in water at 30°C, respectively. The curves in Fig. 6 indicated that E gum and xanthan all exhibited Bingham-type fluid behavior in the aqueous solution. Compared with xanthan gum, the viscosity of E gum decreased sharply, giving further evidence that the shear force broke the aggregates of E gum, resulting in the decreasing of η_a . This suggested that the aggregates of E gum were disrupted more easily than the double helix of xanthan^[12] with increasing shear force.

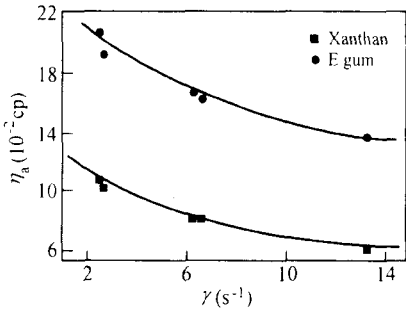


Fig. 6 γ dependence of η_a of E gum and Xanthan in water at 30°C

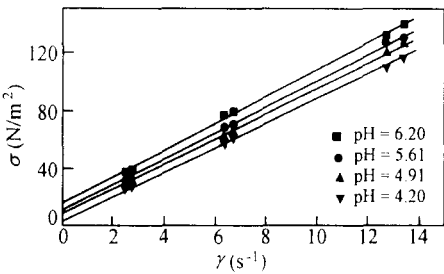


Fig. 7 σ - γ relation curve of E gum in water at pH from 6.2 to 10.4, $T = 30^\circ\text{C}$

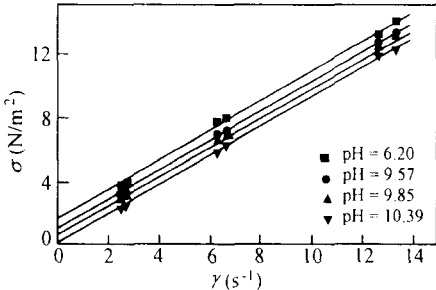


Fig. 8 σ - γ relation curve of E gum in water at pH from 6.2 to 4.2, $T = 30^\circ\text{C}$

Figures 7 and 8 show the plots of γ versus shear stress (σ) for E gum in water at 30°C at different pH. σ values achieved a maximum at pH = 6.2, and then decreased with either increasing

or decreasing pH, suggesting that the aggregates and the entanglement could be disrupted by acid or base. Interestingly, the σ - γ relation curve of the E gum solution was close to that of Newtonian fluid by decreasing or increasing pH. At pH = 4.2 or pH = 10.4, the E gum solution exhibited Newtonian fluid behavior.

CONCLUSION

E gum in water can form aggregates which started to be disrupted at 38°C for dilute solution and at 80°C for concentrated solution. E gum aqueous solution has extremely high viscosity, and exhibits Bingham-type fluid behavior at 30°C, due to the aggregation. Addition of acid or base could break the aggregates, and E gum fluid behaves in a similar way to Newtonian fluid at pH = 4.2 or pH = 10.4. The experimental results indicated that the E gum is a good thickening agent, and its fluid behavior is similar to that of xanthan.

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