Measurement of Shear-Dependent Intrinsic Viscosities of Carboxymethyl Cellulose and Xanthan Gum Suspensions

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SYNOPSIS

A rotational rheometer with cone and plate fixtures was used to measure the intrinsic viscosities of aqueous suspensions of xanthan gum and carboxymethyl cellulose (CMC). The reduced viscosities or hydrodynamic volumes of CMC suspensions increased with dilution. However, the reduced viscosities of xanthan gum suspensions decreased with dilution within the concentration range of 0.1–0.06% and increased with dilution within the concentration range of 0.04–0.01%. When the gums were suspended and diluted with 0.06 *M* sodium acetate, the reduced viscosities of all the xanthan gum and CMC suspensions decreased upon dilution. The intrinsic viscosities of xanthan gum and CMC suspensions decreased with increasing the shear rate, showing a dependence of hydrodynamic volume on shear rate.

INTRODUCTION

The viscosities of non-Newtonian high molecular weight polymer solutions decrease with an increasing shear rate because of orientation of chains in the direction of flow. Intrinsic viscosity is a function of the molecular shape and size[1] and should also be a function of shear rate. The evaluation of this functionality could be a useful tool for the study of polymer conformation in solution.

Conventional intrinsic viscosity measurements are made with a capillary viscometer. Easy handling and low cost are advantages of this viscometer. However, the requirement of a varying pressure head to obtain a range of shear rates is a disadvantage. The shear rate is also a function of the radial position within the capillary, which is an another disadvantage. To study the deformation of molecules as a function of shear rate, it is important to be able to apply a constant shear rate throughout a flow field during a measurement. This can be done with cone and plate fixtures on a rotational rheometer.[2] This has not been commonly used because the limitation of the sensitivity of rotational rheometers. However, with computer control and electronic signal, averaging the sensitivity can be enhanced. The purpose of this study was to determine the shear-dependent intrinsic viscosities of carboxymethyl cellulose and xanthan gum suspensions with such a modified cone and plate rheometer.

EXPERIMENTAL

Xanthan and CMC (high viscosity) were purchased from Sigma. Stock suspensions of 0.1% (w/v) CMC and xanthan gum were prepared with deionized water. A series of CMC and xanthan gum dilutions were made with deionized water. A second set of 0.1% (w/v) suspensions and dilutions were made with 0.06 *M* sodium acetate.

Rheological measurements were carried out with a Carri–Med Weissenberg R20A rheogoniometer (Mitech Corp., Twinsburg, OH) at 25°C. The cone angle was 2°, and the diameter of platens was 7.5 cm. For temperature control, a bottom plate was fabricated so that fluid from a controlled temperature bath was circulated immediately below the flat surface on which the sample was placed.[3] For the purposes of automatic control and data acquisition, this rheometer was interfaced to an LSI 11/23 microprocessor (Digital Equipment Corp., Mayard,

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Table I Viscosities of Sucrose Solutions Measured by Weissenberg Rheometer and Capillary Viscometer

	Viscosity × 10^2 (dyne s/cm^2)			
Sucrose (%)	Weissenberg Rheometer	SD	Capillary Viscometer	SD
5	1.074	0.063	1.086	0.012
10	1.268	0.088	1.217	0.011
20	1.506	0.03	1.542	0.011
30	2.196	0.047	2.107	0.008

MA). The sensitivity of this modified rheometer was determined by comparing the viscosities of different concentration of sucrose solutions (5, 10, 20, 30%) measured on this rheometer and a capillary viscometer (Cannon–Fenske, No. 50) at 25°C.

The relationship between dilute solution viscosity and polymer concentration, c, has been described by Huggins' equation[4]:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$$

where k' is the Huggins slope constant, $[\eta]$ is intrinsic viscosity, and specific viscosity η_{sp} is defined as

$$\eta_{sp} = \frac{(\eta - \eta_s)}{\eta_s}$$

where η is the viscosity of solution and η_s is the viscosity of solvent. Intrinsic viscosity was obtained by extrapolating to zero concentration from a plot of reduced viscosity, η_{sp}/c, against c in a very dilute solution region.

RESULTS AND DISCUSSION

The viscosity differences of sucrose solutions measured by rotational rheometer and capillary viscometer were less than 5% (Table I). This suggested that modified rotational rheometer was quite sensitive to low-viscosity fluids. Because of linearities of the shear stress–shear rate plot for different concentrations of sucrose solutions, the inertia effect was considered negligible for these low-viscosity fluids for shear rates up to 300 s^{-1} (Fig. 1).

The reduced viscosities of CMC suspensions increased with dilution (Fig. 2), a typical phenomenon for most polyelectrolytes,[5] which might have been due to several reasons. One was because the counterion electrostatic shielding effect was reduced upon dilution with water and the CMC molecular chain expanded; hence, the hydrodynamic volume increased. The others included the effects of the intramolecular osmotic pressure that was due to fixed ionic charges on the polymer and the solvation effect. The hydrodynamic volume of the CMC molecule at each dilution was found to increase as the shear rate was reduced.

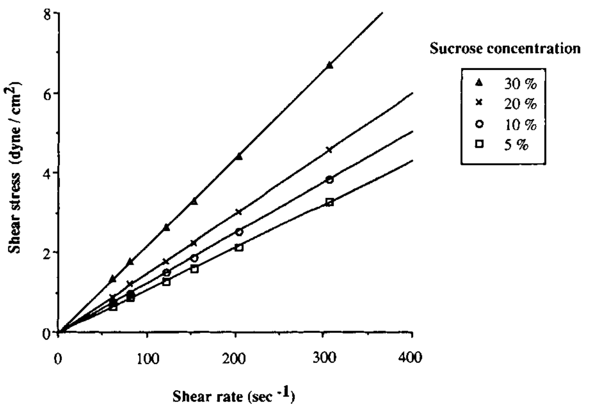

Figure 1 Shear stress-shear rate plots of different concentration of sucrose solutions.

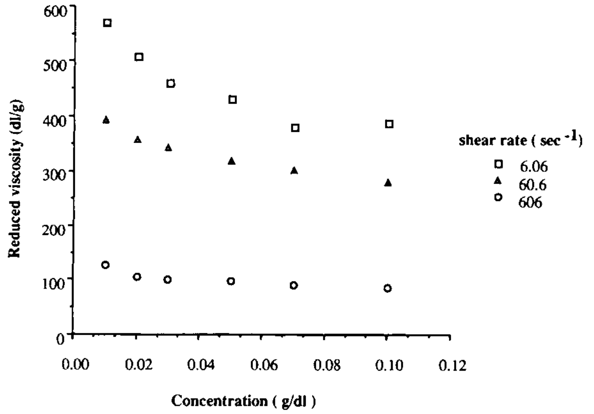

Figure 2 Reduced viscosities of aqueous carboxymethyl cellulose.

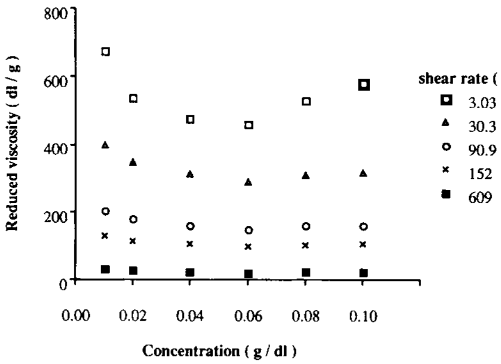

Figure 3 Reduced viscosities of aqueous xanthan gum.

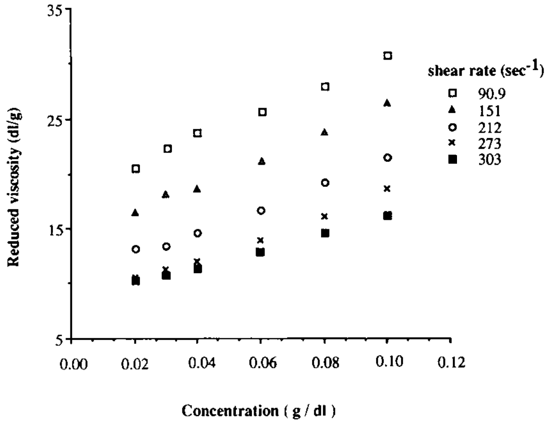

Figure 5 Reduced viscosities of CMC in 0.06 *M* sodium acetate solutions.

The reduced viscosities of xanthan gum suspensions decreased with dilution with water within the concentration range of 0.1–0.06 g/dl and then increased with further dilution from 0.04 to 0.01 g/dl, (Fig. 3). These observations were in partial agreement with Gelman and Barth's data,[6] which were measured with a capillary viscometer. Agreement was found within the concentration range of 0.1–0.06 g/dl. Upon further dilution, Gelman and Barth found the reduced viscosity leveled off; they suggested that the backbone was rigid enough so that it was not affected by the repulsive forces between the anionic groups. In this study, the reduced viscosity increased with dilution within the concentration range of 0.04–0.01 g/dl, which indicated that the xanthan molecule was not rigid as Gelman and Barth's data suggested. This may because a higher averaged shear rate was probably applied with the capillary viscometer. The reduced viscosities of xanthan gum in our study also started to level off with dilution when measured at 609 s^{-1}. However, at lower shear rates, an increase in hydrodynamic volume was observed, suggesting that the xanthan backbone was flexible enough to be affected by charge repulsions among the anionic side groups.

To obtain the intrinsic viscosities of xanthan gum and CMC suspensions by using Huggins' equation, the effect of electrostatic repulsive force should be excluded or at least kept constant. Keeping ionic strength constant by adding salt not only decreased electrostatic repulsive force but also decreased the thickness of the counterion layer. Therefore, the reduced viscosities of xanthan gum suspensions decreased with dilution with 0.06 *M* sodium acetate (Fig. 4). Similar trends were found for the CMC suspensions (Fig. 5).

The intrinsic viscosities of xanthan gum and CMC suspensions within the experimental shear rates (Fig. 6) agreed with the values in the literature,[6-8] where molecular weights of xanthan gum and CMC were about 10^6. The Huggins' slope constants k' (Table II) of both polymers increased with increasing shear rates, which indicated that molec-

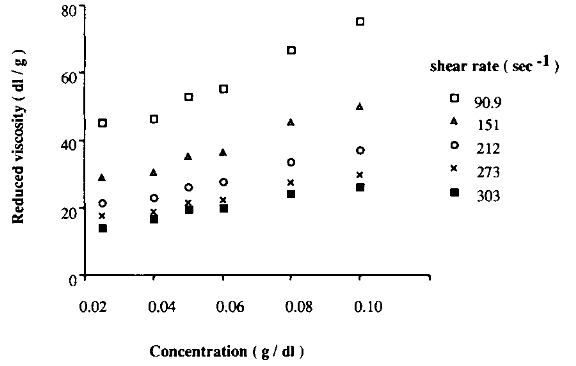

Figure 4 Reduced viscosities of xanthan gum in 0.06 *M* sodium acetate solutions.

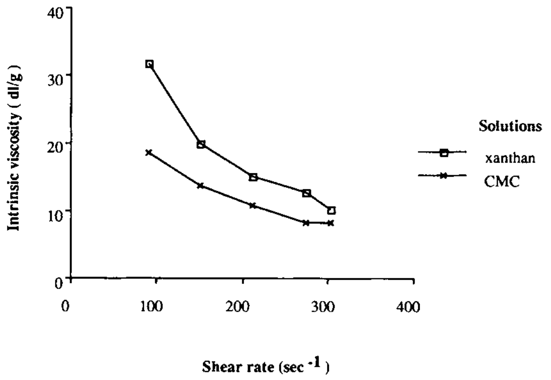

Figure 6 Shear-dependent intrinsic viscosities of xanthan gum and CMC solutions.

Table II Huggins' Slope Constants k' of Xanthan Gum and CMC at Different Shear Rates

Shear Rates (s^{-1})	Huggins' Slope Constant k'	
	Xanthan Gum	CMC
90.9	0.42	0.35
151	0.76	0.66
212	0.99	0.93
273	1.05	1.02
303	1.60	1.35

ular chains of both polymers were not entangled as suggested by Lohmander and Svensson.[9]

The intrinsic viscosities of both molecules decreased with increasing shear rate because the molecules were deformed more under higher shear forces. The intrinsic viscosities of xanthan gum suspensions were higher than those of CMC at all shear rates, which may be because the xanthan molecule is branched with uniformly distributed trisaccharide side chains that make the structure of xanthan more rigid than that of CMC.[6] The differences between the intrinsic viscosities of these two polymers increased at lower shear rates, which illustrates the increased rigidity of the xanthan molecule.

CONCLUSION

Determination of intrinsic viscosity as a function of shear rate is important for the study of the rigidity of polymer molecules. The intrinsic viscosity measured with a capillary viscometer is at an relatively high averaged shear rate, and the differences between polymer conformations are not likely to be observable because of the flow-induced alignment. Intrinsic viscosity measurements at lower shear rates can provide valuable data in the study of polymer conformation in solution.

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