

Viscosity Profiles for Aqueous Dispersions of Extracellular Anionic Microbial Polysaccharides

INTRODUCTION

Viscosity (resistance to flow) is probably the most important property contributed by a polysaccharide to aqueous systems,¹ and the corresponding rheological (flow and deformation) properties are basic to any function served by the system.² Characterization of polysaccharides through their viscous and rheological properties, however, often has been neglected in generalized polysaccharide research. There have not been available either techniques applicable by nonspecialists or instruments of suitable design and construction that met the need for simple operation and small sample size. Of unusual significance for practical research on polysaccharides, therefore, is the technique developed by Patton³ for obtaining viscosity profiles of non-Newtonian polysaccharide solutions and rheological characterization extending into the ultralow shear-rate range by use of a commercial microcone-and-plate viscometer.

Reported here is our application of Patton's spring relaxation technique for a cone-and-plate viscometer to a series of extracellular anionic microbial polysaccharides developed in our research as hydrocolloids of possible practical utility.

EXPERIMENTAL

The polysaccharides used were products of our research (except as stated below), in the neutral K salt form, essentially free of extraneous salt and having 0.1% or less nitrogen. Their molecular weights are of the order of millions. Details of their chemical constitution and structure have been summarized.⁴ These polysaccharides, identified by the strain number in the ARS Culture Collection at the Northern Regional Research Laboratory of the yeast (Y) or bacterial (B) source, are from *Hansenula holstii* NRRL Y-2448,⁵ *Cryptococcus laurentii* var. *flavescens* NRRL Y-1401,⁶ *Xanthomonas campestris* NRRL B-1459,⁷ *Arthrobacter viscosus* NRRL B-1973,⁸ and *Arthrobacter stabilis* NRRL B-3225.⁹ Also from strain B-1459, a food-grade commercial product popularly designated xanthan and trade marked Keltrol was used after further treatment to bring it to a state of purity comparable with that of our own products. The controls used were a good grade of commercial guar gum and Gelgard M, a synthetic organic polymer from Dow Chemical Company which gives aqueous solutions having plastic rheological properties.

Homogeneous dispersions having 1% (w/w) polysaccharide concentration in deionized water were used. Samples of 1 ml were measured into the viscometer by a syringe and were maintained at 25°C. The reported experimental procedure,^{1,3} which employs the Wells-Brookfield cone-and-plate viscometer Model RVT, was followed with minor modifications. Briefly, it consists in applying shear stress to the sample by allowing the spring to relax spontaneously from an initial standard tension (dial reading 100) during a standardized length of time. Generally, the time was about 7 min or until the shear rate 0.01 sec^{-1} was reached. For dispersions of unusually high viscosity such as those of the Y-1401 polysaccharides, times of 15–20 min were necessary to reach this designated shear rate. The shear rate thus achieved is in the range from about 100 sec^{-1} to as low as 0.001 sec^{-1} . By suitable calculations, "profiles" are obtained as shown in Figure 1, where shear stress versus shear rate relations are plotted on log-log scales. Viscosity, the ratio of shear stress to shear rate, may be calculated for any point on a curve, or it may be read where any point on the flow curve coincides with or intersects constant lines along which viscosity of Newtonian solutions would fall.³

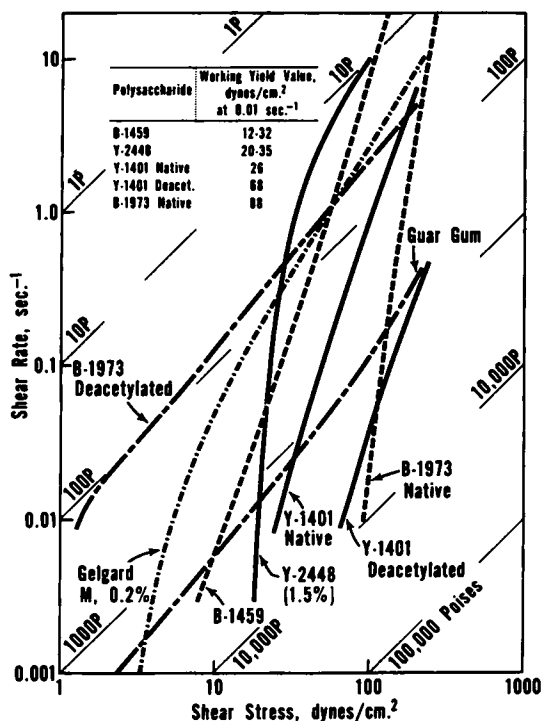


Fig. 1. Shear stress-shear rate-viscosity relations at 25°C for aqueous dispersions of extracellular anionic microbial polysaccharides. Concentrations, were 1%, except for phosphomannan Y-2448, which was 1.5%, and for Gelgard M, which was 0.2%. Type A, pseudoplastic, substances are microbial polysaccharide B-1973 deacetylated and guar gum. Type B, plastic, substances are Gelgard M and microbial polysaccharides Y-2448, Y-1401 native and deacetylated, and B-1973 native. Microbial polysaccharide B-1459 appears to have characteristics of both types A and B.

RESULTS AND DISCUSSION

Grossly, the flow curves differ in the rapidity of decrease in flow rate with decrease in shear stress, that is, in the resistance the solutions present to the shearing force. The curves appear to differentiate into two general categories characterized by (A) concavity to the shear rate scale and tending asymptotically to parallel the viscosity lines of constant Newtonian flow that run at 45° angles to the perpendicular, and (B) convexity to the shear rate scale and tending asymptotically to become perpendicular to the shear stress axis at ultra-low shear rates.¹ Type A dispersions are pseudoplastic and appear to be continuously deformable under shear stress; the corresponding macromolecules possess approximately linear backbone structure and are flexible, and their solution configuration may be that of a random coil. Type B dispersions are plastic; at or below a definite shear stress they do not continue to flow, and the rate of shear decreases rapidly toward zero. Flow behavior of plastic dispersions differ most strikingly from the Newtonian. The corresponding macromolecules may be relatively stiff or involved in cross-linked colloidal networks or other structured aggregates that resist shearing stress.¹ The rheological classification of a substance, however, is influenced by concentration and, with sufficient decreases in concentration, may change from plastic through pseudoplastic to Newtonian.^{1,3}

The flow curves for deacetylated polysaccharide B-1973 and guar gum accord with the the general criteria for pseudoplastic substances (and are strikingly similar in slope); those for Gelgard M and microbial polysaccharides Y-2448, Y-1401, and native B-1973 accord with the criteria for plastic substances. The flow curve for polysaccharide B-1459 seems to be a composite; its slight concavity identifies it with the pseudoplastic substances, but its exceptionally sharp decrease in viscosity with shear and its almost perpendicular approach to the shear stress axis are distinguishing characteristics of plastic-type substances. Its molecules also show some characteristics of each rheological type: a linear backbone structure carries occasional side chains one unit long,⁴ and the molecules appear to be stiff⁷ and to associate in elongated birefringent supramolecular forms.¹⁰ Molecular structures of the other polysaccharides also accord with the generalizations concerning their respective types: guar gum has a linear backbone with frequent one-unit-long branches; deacetylated polysaccharide B-1973 has no branches or substituent groups, and molecular cohesion is strong;⁴ and native polysaccharide B-1973 has 50% of its hydroxyl groups esterified by acetyl groups⁴ and forms birefringent supramolecular forms in aqueous dispersions.¹⁰ Polysaccharide Y-2448 appears to form aqueous dispersions that are three-dimensionally crosslinked and to show birefringence effects comparable to "liquid crystals."¹⁰

The shear stress at zero rate of shear is defined as the yield value. Since it often is impractical to actually reach this point for measurement, Patton defines a practical or "working" yield value as the shear stress required to produce a shear rate of 0.01 sec⁻¹.³ Microbial polysaccharides having significantly high working yield values are tabulated on Figure 1 along with the corresponding values. Polysaccharide B-3225,⁹ which has a working yield value of 26, is not shown in the figure. With the exception of polysaccharide B-1459, all of these polysaccharides having high yield values are plastic-type substances. This is a further exhibition by polysaccharide B-1459 of plastic-type characteristics. Working yield values for various preparations of polysaccharide B-1459 have been in the range 12 to 32; those for polysaccharide Y-2448 have been 20 to 35. The striking plastic behavior of phosphomannan Y-2448 appears to result from electrostatic charge effects since, in the presence of 0.1% KCl, viscosity is diminished below the range of measurement. The anionic constituent of this polysaccharide is orthophosphoric acid, in contrast to glucuronic^{6,7,9} and manuronic⁶ acids, pyruvic acid ketal,^{7,9} and half-ester succinic acid⁹ in the other polysaccharides as indicated by the references.

All of these substances having high yield values are excellent suspending agents in keeping with the established relation between suspending power and yield values. The demonstrated superiority of polysaccharide B-1459 for suspending heavy particles is the basis for numerous patented applications^{4,11} in petroleum drilling fluids, paints, glazes, abrasives, explosives, and cements, as well as for applications in the food¹² and metal beneficiation¹³ industries.

In the presence of 0.5% KCl, the respective working yield values for polysaccharide B-1459, B-1973, and B-3225 are increased five-, two-, and fourfold. After being heated to 80°C and tested at 25°C, the value for B-1459 increases if 0.5% KCl is present during heating but decreases if it is absent. Working yield values of polysaccharides B-1459 and B-3225 are increased significantly in the presence of locust bean gum and, to a lesser extent, guar gum.

Removal of O-acetyl groups from polysaccharide B-1973 (25% O-acetyl)⁸ and both O-acetyl (5.0%) and half-ester succinic acid (3.5%) substituents from B-3225⁹ changed the rheological class of the polysaccharides from plastic to pseudoplastic and decreased the apparent working yield values to 1.6 and 2.5, respectively. Deacetylation of polysaccharide Y-1401 (6% O-acetyl),⁸ however, increased the working yield value as shown in Figure 1. Deacetylation of polysaccharide B-1459 (4.5% O-acetyl) gives a pseudoplastic-type substance with working yield value 20.5.

Patton^{1,3} obtained a measure of thixotropy from the ratio of working yield value determined before and after shearing the sample. The microbial polysaccharide dispersions were sheared in the viscometer for 5 min at 100 rpm (384 sec⁻¹); the thixotropic index

has been no more than 1.1 to 1.15. Thus, although all the microbial polysaccharides with the exception of deacetylated B-1973 show rapid decrease in viscosity with increase in shear stress (Fig. 1), all regain the initial viscosity without lag when shear ceases. This ease of thinning while under shear is cited frequently as an unusual property of xanthan¹¹⁻¹⁴ as well as of polysaccharide B-1973.¹⁵ Reversible shear-thinning is a valuable property in operations that involve movement of dispersions such as flow of food-stuffs¹² or paints,³ flow through pipes^{11,12} or orifices,^{11,14,15} and centrifugal separations.¹³

Viscosity values reported previously⁴⁻⁹ for the polysaccharides used in this study were measured with a Brookfield LVT at 30 rpm, which corresponds approximately to 1 rpm or 3.84 sec⁻¹ on the microcone-and-plate viscometer. The practical equivalence of these conditions for viscosity measurements is confirmed by the correspondence of viscosity values taken from Figure 1 at 3.84 sec⁻¹ with those reported previously.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

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