Turbulent Flow Friction Reduction Effectiveness and Hydrodynamic Degradation of Polysaccharides and Synthetic Polymers*

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Synopsis

Two water-soluble synthetic polymers and several polysaccharides were compared for friction reduction effectiveness during increased exposure to turbulent flow. Solutions were passed through a 0.117 × 41.0 cm fine bore tube at a constant solvent wall shear stress of 4200 dynes/cm² and wall shear rate of 4×10^5 sec⁻¹. After one pass through the tube, greatest friction reduction at low polymer concentrations was in the order poly(ethylene oxide) > polyacrylamide > bacterial polysaccharide from *Xanthomonas campestris* > guar gum. As a result of mechanical degradation, after 40 passes of 40 ppm solutions, friction reduction effectiveness was in the order polyacrylamide > polysaccharide from *Xanthomonas campestris* > poly(ethylene oxide) > guar gum. Degradation curves, the effect of concentration on degradation, and boundary layer and pipe flow applications are discussed.

INTRODUCTION

Friction-reducing polymers have a number of useful applications because of their ability to reduce hydrodynamic drag under turbulent flow conditions. In pipe flow applications, these dissolved polymers increase flow rates with less power demands on the pump. Polymers ejected into the turbulent boundary layer can increase speed or decrease power requirements for a body traveling through water.

The drag reduction phenomenon was first observed in nonaqueous systems by Mysels[1] for gasoline which contained aluminum soaps and by Toms[2] for poly(methyl methacrylate) dissolved in monochlorobenzene. In either aqueous or nonaqueous liquids, the dissolved polymer must have a high-molecular-weight linear structure to evoke drag reduction. The reader interested in the drag reduction phenomenon will find a number of interesting reports available.[3-8]

Sodium carboxymethylcellulose, ammonium alginate, and carboxypolyethylene were early water-soluble friction-reducing polymers reported.[9] A patent was awarded for reducing friction in flowing liquids with water-soluble addition polymers of monoalkenylaromatic sulfonates,[10] and another

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for a method of reducing hydrodynamic drag of objects moving through water.[11]   Among the polymers covered by the latter were guar gum, karaya gum, sodium carboxymethylcellulose, methylcellulose, ammonium alginate, and polyacrylamide.

In 1963, Fabula[8] found poly(ethylene oxide) to be the most effective drag-reducing polymer at low concentrations.   High molecular weight poly-(ethylene oxide) still remains the most effective friction-reducing polymer at low concentrations after limited exposure to turbulent flow.

In a search for other effective drag-reducing polymers, this laboratory tested polysaccharides (polymers of repeating sugar units) from sea weeds, microscopic algae, and the bacteria.   Hoyt[5] reported a number of effective algal polysaccharides, and many different bacteria were shown to produce effective friction-reducing polymers.[12,13]   The bacteria are of particular interest because large quantities of polysaccharides can be produced rapidly from simple sugars.   Also, thousands of different bacteria exist, and many synthesize a unique polysaccharide.   This great chemical and structural diversity makes the bacterial polysaccharide an interesting class of polymers for drag reduction studies.

The purpose of this investigation is to compare polysaccharides and synthetic polymers as turbulent-flow friction-reducing additives for water flow applications and to study the drag reduction properties of these polymers during increased turbulent flow exposure.   Guar gum, a polysaccharide extracted from the guar plant, bacterial polysaccharides, and two synthetic polymers, poly(ethylene oxide) and polyacrylamide, were studied.   These polymers were tested for friction reduction effectiveness after minimal turbulent flow exposure and the loss in effectiveness from mechanical degradation measured after prolonged exposure.

EXPERIMENTAL

Friction-Reducing Polymers

Poly(ethylene oxide) was obtained from Union Carbide Chemicals Co., New York (Polyox WRS 301); and polyacrylamide, from Stein, Hall and Co., New York (Polyhall 295).   Both polymers are recommended by their respective manufacturers for use as friction reduction additives.   The plant-derived polysaccharide, guar gum (J2S1), was also obtained from Stein, Hall and Co., and is recommended as a friction reduction additive. The bacterial polysaccharide from *Xanthomonas campestris* was provided by Kelco Co., San Diego; and bacterial polysaccharide from *Arthrobacter viscosus*, by the Northern Regional Research Laboratory, U.S.D.A., Peoria, Illinois.   Two other bacteria, *Pseudomonas* sp. and *Neisseria* sp., were grown in a medium containing sugars and protein hydrolysates, the cells removed by centrifugation, and the polysaccharide precipitated from the supernatant with acetone.

All polymers were dried at 60°C for 3 hr to remove excess moisture, and 0.1000 g was weighed on an analytical balance and added to a 1-liter flask

containing several hundred milliliters of deionized water. Polymer was allowed to dissolve for 16 hr with no agitation, then agitated gently by swirling, and the flask was filled to the 1-liter mark and shaken gently several times. Excessive agitation must be avoided with some long-chain polymers to prevent mechanical degradation. The 100-ppm solution was diluted with deionized water to obtain lower polymer concentrations.

Friction Reduction Measurements and Polymer Degradation

A turbulent flow rheometer, a miniature pipe flow apparatus, was used to measure friction reduction effectiveness of polymer solutions and to mechanically degrade these solutions.[14] The turbulent flow rheometer is a valuable tool for the study of high-molecular-weight linear polymers as friction reduction is often produced by polymer concentrations far below those which can be detected by viscometry techniques. In addition, the constant mean flow speed provided by the rheometer adds another useful parameter in characterizing long-chain polymers by relating loss in friction reduction effectiveness to total turbulent flow exposure.

Polymer solution was withdrawn into a 100-cc syringe and forced through a fine bore tube (0.117 × 41.0 cm) at a constant mean flow speed of 1,100 cm/sec. The corresponding solvent wall shear stress is 4200 dynes/cm^2, a wall shear rate of 4×10^{-5} sec^{-1}, and a Reynolds number of 13,000. Two pressure transducers placed 13 cm apart measured the pressure drop along the tube. Per cent friction reduction was computed from the expression

$$\text{per cent friction reduction} = [1 - (\Delta P_s / \Delta P_r)]100$$

where ΔP_s is the pressure drop for the sample and ΔP_r is the pressure drop for the deionized water reference. The maximum friction reduction obtainable for any polymer, computed from the above formula, is about 65% at the flow conditions used in this study.

Polymer solution was withdrawn into the syringe from the filling reservoir through a filling tube rather than the fine bore tube. The filling tube provided for withdrawal of polymer solution into the syringe without excessive shear and therefore minimized mechanical polymer degradation. Loss in friction reduction effectiveness due to hydrodynamic polymer degradation was caused and measured by repeatedly passing the polymer solution through the fine bore tube of the turbulent flow rheometer and measuring the pressure drop during each pass. All testing took place 24 hr after dry polymer was dissolved, and all mechanical degradations occurred in less than 1 hr.

RESULTS AND DISCUSSION

Figure 1 illustrates the friction reduction effectiveness of several polymers during one pass through the fine bore tube. Poly(ethylene oxide) was the most effective, reducing friction 56% at 5 ppm and 65% at 10
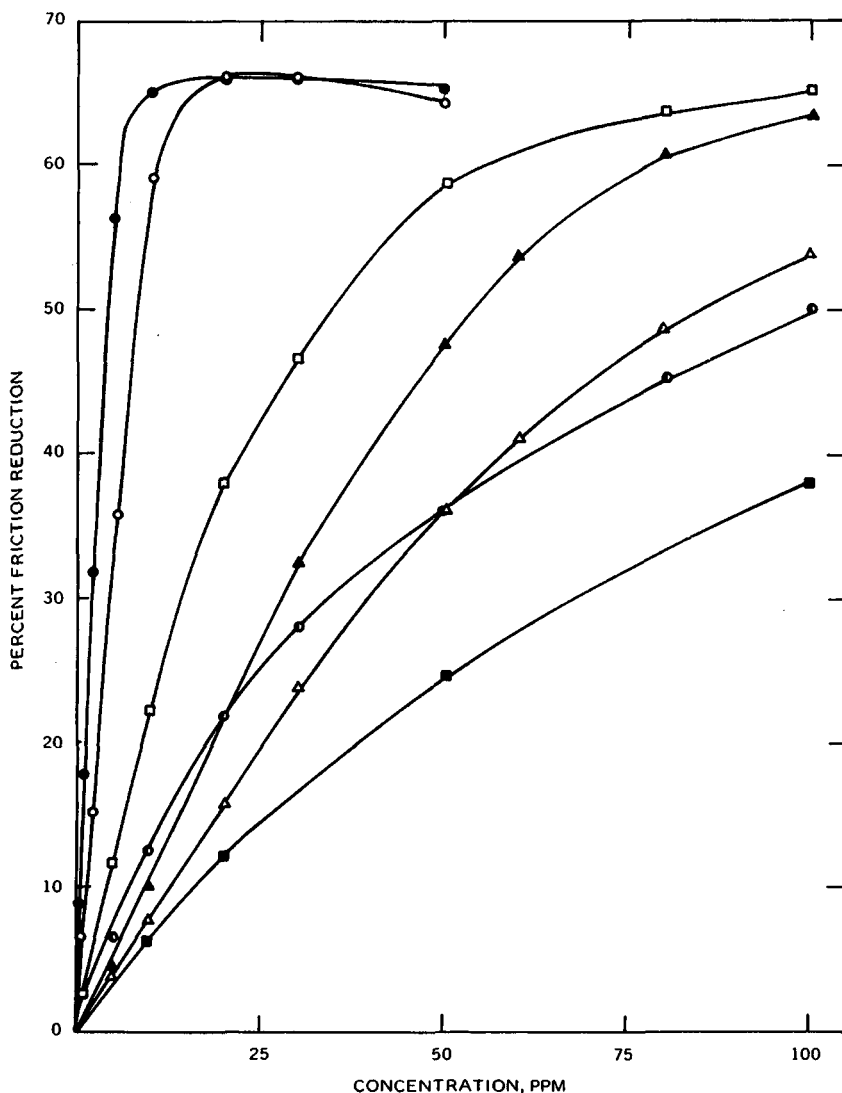
Fig. 1. Friction reduction effectiveness of synthetic polymers and polysaccharides during one pass through the turbulent flow rheometer: (●) poly(ethylene oxide); (O) polyacrylamide; Polysaccharides: (□) *Xanthomonas campestris;* (▲) *Pseudomonas* sp.; (△) *Neisseria* sp.; (■) *Arthrobacter viscosus;* (◐) guar gum.

ppm. Polyacrylamide, the second most effective, reduced friction 36% and 59% at 5 and 10 ppm, respectively.

The polysaccharides were less effective than the synthetic polymers during one pass through the fine bore tube (Fig. 1). Polysaccharide from the bacterium *Xanthomonas campestris* was the most effective, reducing friction 65% at 100 ppm. Polysaccharides from two other bacteria, *Pseudomonas* sp. and *Neisseria* sp., were less effective than polysaccharide from *X. camp-*

estris, but more effective than guar gum. Guar gum reduced friction 50% at 100 ppm, followed in effectiveness by a bacterial polysaccharide from *Arthrobacter viscosus*, which reduced friction 38% at 100 ppm.

It should be noted that friction reduction effectiveness of a polymer may vary from lot to lot. For example, a different lot of bacterial polysaccharide from *X. campestris* tested previously was found to be less effective than the lot tested in this report.[12] To insure maximum polymer efficiency, each polymer lot intended for friction reduction applications should be tested and rated.

Hydrodynamic Degradation

A dissolved long-chain polymer is a fragile molecule and quite subject to hydrodynamic degradation. Scission in the polymer chain results when sufficient stress is placed on a portion of the polymer molecule. Shin[15] noted increased molecular scission in the high molecular weight poly(ethylene oxides) and less scission at low molecular weights. Shin found the higher molecular weight poly(ethylene oxide) polymers to degrade in laminar flow in the capillary of the Ubbelohde viscometer at wall shear rates greater than 1500 sec^{-1}. Lower molecular weight poly(ethylene oxide) was not degraded at these shear rates. Hoyt and Fabula[3] demonstrated mechanical degradation of high molecular weight poly(ethylene oxide) by rotating a disc at several thousand rpm in the solution and measuring the increase in torque. No increase in torque was found for guar gum solutions, indicating insignificant mechanical degradation. White and McEligot[16] mentioned the need to use fresh polymer solutions for each pipe flow pass in transition experiments in order to eliminate molecular weight effects due to degradation. A comprehensive study was made by Paterson[7] on the shear degradation of poly(ethylene oxide), but no comparison was made with other polymers.

An important consideration in evaluating the friction reduction effectiveness of polymers is the extent of turbulent flow exposure. A polymer may be more effective after minimal exposure but less effective after greater exposure, as discussed subsequently.

Degradation of Poly(ethylene Oxide) and Polyacrylamide

At equal concentrations, under conditions of limited turbulent flow exposure, poly(ethylene oxide) was a more effective friction-reducing polymer than polyacrylamide; however, polyacrylamide was more effective after prolonged exposure (Fig. 2). After 20 passes through the fine bore tube, poly(ethylene oxide) and polyacrylamide reduced friction at the following concentrations, respectively: 5 ppm, 19% and 16%; 10 ppm, 28% and 30%; 20 ppm, 36% and 46%; and 40 ppm, 46% and 59%.

Friction reduction-versus-molecular weight data for poly(ethylene oxide) can be used to help explain the hydrodynamic degradation of this polymer. Hoyt[17] plotted the average molecular weight of various poly(ethylene oxide)

samples of known molecular weight as a function of friction reduction at
several concentrations.   The same turbulent flow rheometer was used in the
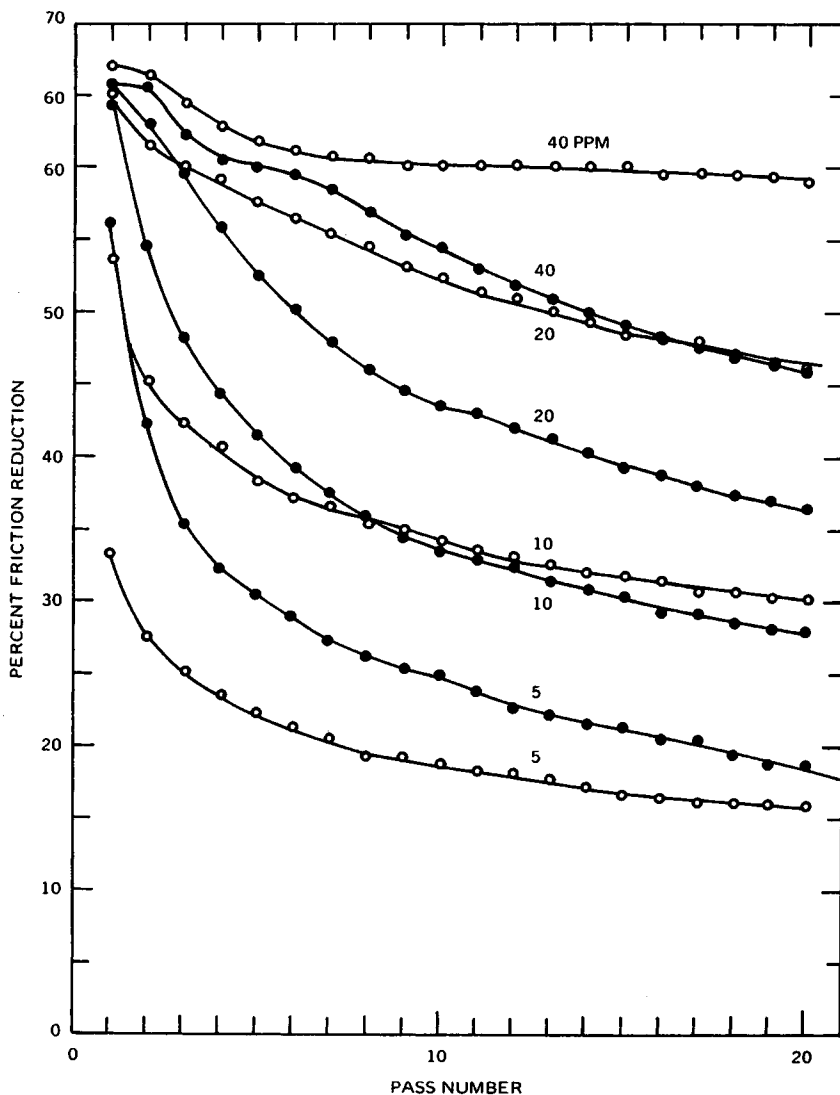present investigation at identical flow rates as in Hoyt's experiments.

Fig. 2. Friction reduction effectiveness of synthetic polymers at various concentra-
tions for multiple passes through the turbulent flow rheometer: (●) poly(ethylene oxide);
(○) polyacrylamide.

The friction reduction-versus-molecular weight curves are valid for deter-
mining the molecular weight of shear-degraded samples if it is assumed that
the molecular weight distribution in the degraded samples influences friction

similarly to the molecular weight distribution of Hoyt's reference polymers of known molecular weight. If this is assumed, then the friction reduction values for degraded samples can be converted directly to molecular weights using Hoyt's 5- and 10-ppm curves. For a polyacrylamide sample, Hoyt found close agreement of the manufacturer's estimated molecular weight with the corresponding molecular weight inferred from his curves for poly-(ethylene oxide). These curves can therefore be used to estimate the molecular weights of degraded polyacrylamide solutions if the same limitations are realized.

Based on Hoyt's curves, the initial molecular weights were about 7,000,-000 for poly(ethylene oxide) and about 2,000,000 for polyacrylamide. After six passes through the fine bore tube, poly(ethylene oxide) was degraded from a molecular weight of 7,000,000 to 1,500,000 and polyacrylamide was degraded from 2,000,000 to 1,000,000. This represents a respective 4.7- and 2.0-fold decrease in molecular weight for the two polymers. As it might be predicted, the longer, higher molecular weight molecules were many more times subject to hydrodynamic degradation than the smaller molecular fragments.

The results in Figure 2 show greater degradation of poly(ethylene oxide) than of polyacrylamide at increased concentrations. For example, after 20 passes at 5 ppm, poly(ethylene oxide) reduced friction greater than polyacrylamide, while at 10, 20, and 40 ppm, polyacrylamide became increasingly more effective than poly(ethylene oxide). Other data, not shown in this report, showed a decrease in degradation of both polymers at increased concentrations. A 20- or 10-ppm solution, passed 19 times through the fine bore tube, diluted to 5 ppm, and passed for the 20th time, produced more friction reduction than a 5-ppm solution after 20 passes. A. G. Fabula (personal communication) suggested that the decreased degradation at higher polymer concentrations was due to lower turbulent intensity with these concentrations.

The preceding considerations are not sufficient to explain the apparent greater stability of polyacrylamide on a molecular basis. The relative length-to-width ratios and the number and type of cleavable bonds must be considered, since these parameters are important criteria for hydrodynamic degradation. Pruitt and Crawford[18] have computed the length-to-width ratios for extended poly(ethylene oxide) and polyacrylamide molecules of various molecular weights. The length-to-width ratio per monomeric unit of poly(ethylene oxide) of molecular weight 44 is 1.2100. Polyacrylamide has a molecular weight of 71 per monomeric unit with a length-to-width ratio of 0.6155. For each monomeric unit of poly(ethylene oxide) in the polymer chain, four bonds of two types are subject to scission. In each monomeric unit there is one C–C bond and one C–O bond, and the same two bonds exist between monomeric units. Scission in the polyacrylamide monomer is always between two carbons, one of which has an amide group attached, or between monomeric units for a total of three identical cleavable bonds.
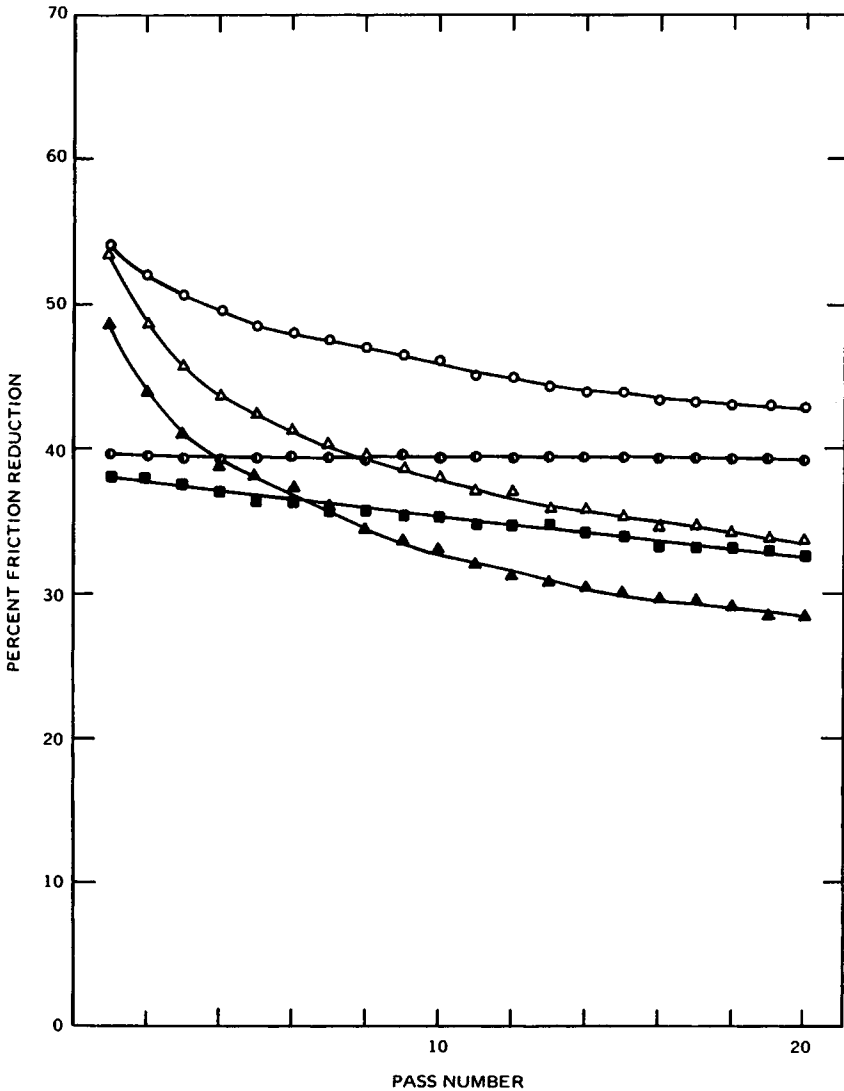
Fig. 3. Friction reduction effectiveness of bacterial and guar polysaccharides for multiple passes through the turbulent flow rheometer. Polysaccharide from: (■) *Arthrobacter viscosus*, 100 ppm; (△) *Pseudomonas* sp., 60 ppm; (▲) *Neisseria* sp., 80 ppm; (○) *Xanthomonas campestris*, 40 ppm; (◐) guar, 60 ppm.

The length-to-width ratio of each monomeric unit in the poly(ethylene oxide) molecule is almost twice that of the polyacrylamide monomeric unit, and the molecular weight per monomeric unit in poly(ethylene oxide) is about one half that of polyacrylamide. Therefore, at equal polymer concentrations, poly(ethylene oxide) provides almost four times the effective length-to-width ratio as does polyacrylamide. This greater total length-to-

width ratio and additional number of bonds present for a given concentration of poly(ethylene oxide) may explain its increased hydrodynamic degradation over polyacrylamide at the same concentration. Further speculation on the stabilities of these two polymers to hydrodynamic degradation will not be attempted.

Degradation of Polysaccharides

The polysaccharides exhibited varying stabilities to turbulent flow exposure (Fig. 3). Guar gum was least influenced showing little loss in friction reduction effectiveness after 20 passes through the fine bore tube. Bacterial polysaccharide from *A. viscosus* showed slightly less stability. Bacterial polysaccharide from *X. campestris*, *Pseudomonas* sp., and *Neisseria* sp. showed an initial decrease in friction reduction ability after the first several passes through the tube, and less of a change after subsequent passes. This initial decrease in friction reduction is likely due to the greater fragility of the longer polymer chain, and the increased stability after subsequent passes is due to the more stable, shorter chains.

It is interesting that polysaccharide from *A. viscosus* was apparently degraded more than guar gum, and polysaccharide from *Pseudomonas* sp. and *Neisseria* sp. more than polysaccharide from *X. campestris* (Fig. 3). The greater friction reduction ability of guar gum and polysaccharide from *X. campestris* (Fig. 1) suggests that the former is a longer molecule than polysaccharide from *A. viscosus* and the latter, longer than polysaccharides from *Pseudomonas* sp. and *Neisseria* sp. The longer polymer chains would be expected to be more amenable to hydrodynamic degradation. Their increased stability, however, may be due to stronger bonds between monomeric units or from decreased stresses placed on these bonds as a result of intra- and intermolecular interactions. Also, this anomaly may reflect different molecular weight distributions. The structures for guar gum and polysaccharides from *A. viscosus* and *X. campestris* have been determined.[19-21]

Comparative Degradation of Polysaccharides and Synthetic Polymers

Figure 4 shows friction reduction effectiveness after 40 passes through the fine bore tube for poly(ethylene oxide), polyacrylamide, and two effective polysaccharides, guar gum and bacterial polysaccharide from *X. campestris*. After 40 passes, a 40-ppm solution of poly(ethylene oxide) was slightly less effective than the same concentration of polysaccharide from *X. campestris* and slightly more effective than guar gum. Polyacrylamide was the most effective friction-reducing polymer after 40 passes; however, it has not been determined how polyacrylamide will compare to the polysaccharides after even more extensive turbulent flow exposure, say, after 100 or several thousand passes.

Applications

More insight may be gained into the physical chemistry of long-chain polymers utilizing friction reduction-versus-concentration curves combined with friction reduction-vs-shear curves.   As mentioned previously, friction
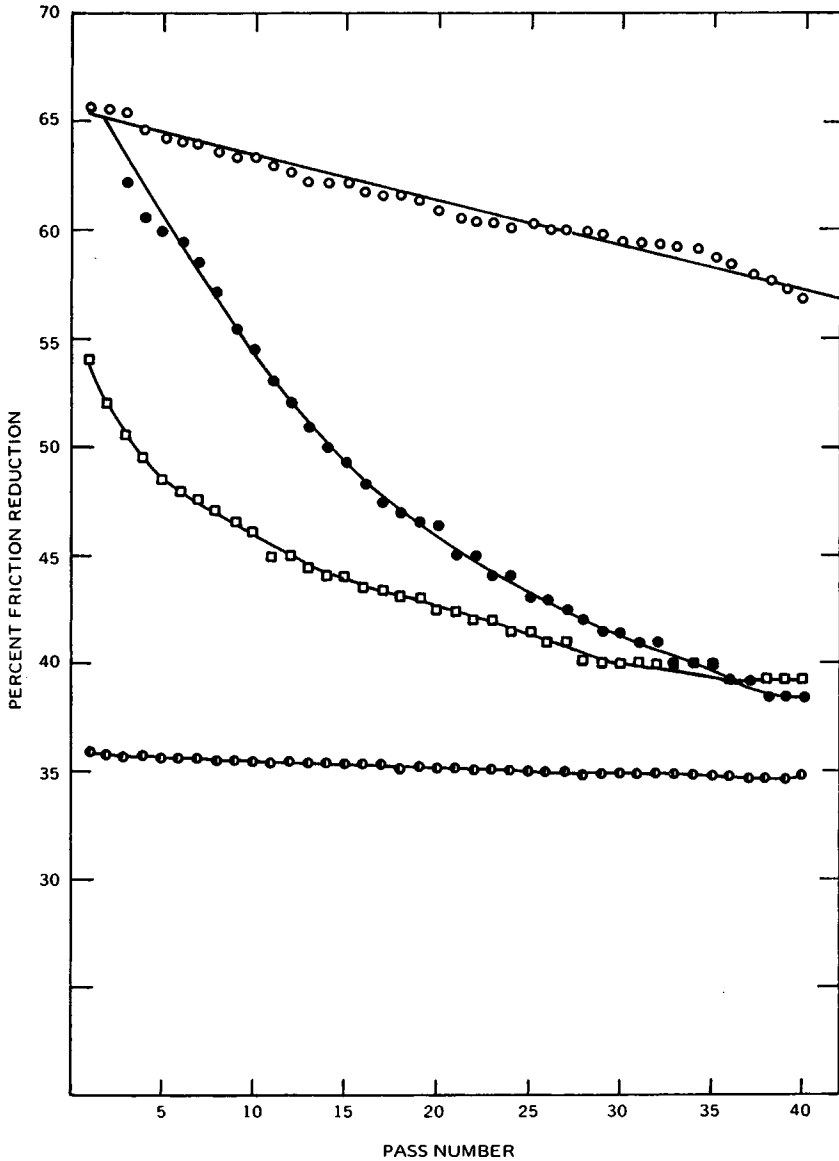

Fig. 4. Comparative friction reduction effectiveness of synthetic polymers and polysaccharides at 40 ppm for multiple passes through the turbulent flow rheometer: (●) poly(ethylene oxide); (O) polyacrylamide; Polysaccharides: (□) *Xanthomonas campestris;* (◐) guar gum.

reduction-versus-concentration plots can be used to estimate molecular weights of long-chain polymers.[17]   This information, combined with hydrodynamic degradation and other data, may help reveal the nature of bonding, molecular interactions, and molecular weight distributions in solutions of long-chain polymers.

A. G. Fabula, in a personal communication, has suggested that multiple-pass testing of friction-reducing solutions in the turbulent flow rheometer is not directly relevant to friction reduction on typical marine vehicles.   He bases his conclusions on consideration of the magnitudes of wall shear stress and specific energy dissipation (the energy dissipated per unit of discharged volume) which are believed to control the degree of mechanical degradation. The wall shear stresses in the turbulent flow rheometer used in the present study are fairly high (about 4200 dynes/cm² for water flow) compared to typical values in larger pipes and in marine boundary layers.   More significantly, the specific energy dissipation due to wall friction alone is about 50 times greater than in typical marine boundary layers.   Furthermore, it seems likely that there is also mechanical degradation of polymer molecules in the rheometer in the entry to the fine bore tubing, since the test fluid is subjected there to a rapid, major elongational deformation.   Thus, Fabula suggests that the multiple-pass results are more relevant to degradation in recirculating systems and long pipe lines rather than in marine boundary layers.

In an attempt to assess the relative degree of degradation during flow through the turbulent flow rheometer, Fabula further calculated the energy dissipation from entrance loss, wall friction loss, and jet dissipation, the sum of which is the pressure drop from the syringe to the atmosphere. For water, wall frictional loss contributes about 87%, and for a polymer solution with 60% friction reduction, the loss is still about 70% of the total energy dissipated, if Newtonian-fluid entrance loss is assumed.

In the selection of a friction-reducing polymer for a given hydrodynamic application, a number of considerations must be made in addition to the friction reduction effectiveness as a function of concentration and shear. The polymer must have satisfactory solution properties for the system; it must be sufficiently stable to thermal, chemical, and biologic degradation; and it must be priced economically.   Approximate prices for friction-reducing polymers used in this study in bulk are: poly(ethylene oxide), 85¢/lb; polyacrylamide, $1.40/lb; guar gum, 60¢/lb; and bacterial polysaccharide from *X. campestris*, $1.60/lb.   As friction-reducing polymers find more applications, these parameters will have to be more seriously considered.

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