

A Structural Basis for Drag-Reducing Agents

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Synopsis

The various types of drag-reducing systems and their hydrodynamic shear degradation are briefly reviewed and some new measurements reported. The new measurements include the determination of the efficiency of drag reduction by a variety of systems ranging from fully flexible polymers, more rigid polymers, and asbestos fibers. These results, together with those of previous workers using fractionated polymers, show a good correlation between critical concentration and particle length. The results suggest that at the highest wall shear stress, the parameter governing the efficiency is the contour length of the particle, irrespective of its structure, stiffness, or diameter. At lower wall shear stresses, the shorter flexible molecules are less efficient, but the short rigid ones and the long flexible ones maintain their efficiency. The shear degradation of the systems was measured by repeated passages of the solution through the measuring apparatus at both high and low wall shear stresses. Drag reduction measured at low wall shear stresses is an extremely sensitive indicator of shear degradation of flexible polymers.

TYPES OF DRAG-REDUCING SYSTEMS

There are at least three kinds of systems capable of reducing drag in turbulent flow, namely, solutions of flexible long-chain molecules, colloidal soap solutions, and suspensions of fine, insoluble particles.¹ Attempts have been made to explain the action of long-chain polymers in terms of the viscoelastic properties of the solution,²⁻⁶ the viscoelasticity favoring oscillation of fluid elements rather than their permanent transfer by turbulence. Gadd⁷ discussed the mechanism in terms of a relaxation time following mechanical distortion. On the other hand, Peterlin⁸ considered that the viscoelastic effect in the dilute solutions concerned is too small to explain the drag reduction. He suggested that flexible molecules are deformed by the large velocity gradients set up in the vortices so that the molecules become stretched to many times their random coil length and thus introduce a greatly increased local viscosity which damps the vortex. A mechanism having as a prerequisite the extension and relaxation of flexible elements seems to be inapplicable to drag-reducing systems consisting of suspensions of substantially inelastic particles such as clay⁹ or asbestos fibers,¹⁰ and it has from time to time been suggested that there must be several essentially different mechanisms of drag reduction in order to account for the variety of materials exhibiting the phenomenon. The discovery of one unifying theory would obviously provide a more convincing

explanation, but such a theory must not only be capable of explaining why both flexible and rigid particles are active, but it must also account for the accumulated data relating to the relative effectiveness of different particle dimensions at various Reynolds numbers and velocity gradients.

Perhaps the most obvious example of two apparently different mechanisms are the data for poly(ethylene oxide) solutions on the one hand and for the 1-naphthol/cetyltrimethylammonium bromide mixture on the other. Thus, poly(ethylene oxide) solutions show relatively small drag reduction at low Reynolds numbers but increasingly large drag reduction at high Reynolds numbers, the magnitude of the effect being related directly to the wall shear stress rather than the pipe diameter or Reynolds number.⁷ The "soap" solution exhibits what at first sight seems to be the reverse behavior.¹¹ It exhibits drag reduction at low values of the wall shear stress, but beyond a certain value the solution rapidly reverts to normal turbulent behavior. These two kinds of behavior may be reconciled if it is assumed that (a) the flexible poly(ethylene oxide) molecule needs to be elongated by a large velocity gradient before its full drag-reducing capability is developed, and (b) the soap colloid particles are oriented much more easily, i.e., at lower velocity gradients, but are broken down at the high shear stresses associated with the large velocity gradients.

The early results obtained by White¹² and Ellis¹⁰ concerning the effects of tube diameter and polymer degradation on the degree of drag reduction are very relevant to this discussion. They found that freshly prepared solutions of poly(ethylene oxide) exhibited good drag reduction in both narrow-bore (of the order of 1 mm) and wide-bore (12–15 mm) tubes. White found that after storing for seven days, the solution retained this property when tested in the narrow tube, but had lost it at the intermediate Reynolds numbers when tested in the wide-bore tube. Ellis found a similar loss of efficiency in the wide-bore tube when the concentrated solution was "shear thinned" by pumping before test. Ellis proposed that the drag reduction is a "single action" phenomenon and explained his results by assuming that "shear thinning" reduces the domain size of the polymer and that the reduced domain size is adequate to interact with the largest energy-dissipating vortices in the small tube but is not large enough to interact with the larger-scale turbulence in the large tube. In Ellis's experiments, the wall shear stress in the small tube was much greater than that in the large tube, and the results could thus equally well be explained if it were the magnitude of the wall shear stress which governed the development of drag reduction rather than the size of the energy-dissipating vortices in the two sizes of tube.

The random coils of flexible molecules are undoubtedly distorted by a velocity gradient; and according to our proposed hypothesis—which is essentially an elaboration of those put forward by Peterlin⁸ and Merrill and co-workers¹³—the critical parameter of a drag-reducing particle is not simply its molecular flexibility but the maximum dimension of the shape assumed by the molecule or particle in the conditions of shear stress con-

cerned and the relationship of this dimension to the size of the vortex to be damped. On this hypothesis, the drag-reducing efficiency of a flexible molecule would increase with wall shear stress in a tube of given diameter. For polymers having equally flexible chains, the one with the longer chain would be the more easily deformed and would be expected to exhibit drag reduction at a lower value of wall shear stress. Rigid coiled polymers, for example those with strong hydrogen bonds between distant parts of the chain, will be less easily elongated and would be expected to require a higher wall shear stress before they exhibited the same degree of drag reduction. On the other hand, the drag reduction by rigid rod-shaped molecules would not be dependent on large wall shear stresses; and at small values of the latter, such rigid molecules would be more efficient drag reducers than flexible molecules of equal contour length.

These considerations had previously prompted us to investigate the drag reduction in solutions of poly(acrylic acid), a polymer whose secondary structure can be altered in a controlled manner by changing the pH value of the solution. The results obtained¹⁴ were indeed in line with the proposed hypothesis in that the drag reduction of a solution of given concentration was greatly increased at pH values at which the secondary structure of the polymer is known to change from a compact impermeable form to a relatively extended form. Evidence of the beneficial effect of rod-like conformation was also adduced from measurements of the drag reduction of solutions of DNA. In its native form, this consists of a relatively inflexible helix of great length. When the solution is denatured, the helix is converted to tightly coiled molecules of greater contour length but lower drag-reducing efficiency.

HYDRODYNAMIC SHEAR DEGRADATION OF LONG-CHAIN POLYMERS

The fact that the hydrodynamic forces on long-chain polymer molecules could be sufficiently strong to break covalent bonds was first pointed out by Frenkel¹⁵ and was investigated in more detail by Levinthal and Davison,¹⁶ who treated the molecule as a long, thin rod and calculated the maximum tension experienced by a molecule of given dimensions in laminar flow through a tube. They predicted a critical laminar flow rate in a given tube below which the molecules would be unaffected. They determined the critical flow rate experimentally using DNA of known molecular weight and confirmed their theoretical predictions.

The shear degradation of synthetic water-soluble polymers in turbulent flow has been investigated extensively during the last few years in connection with the drag-reducing properties exhibited by these materials. White¹⁷ attributed the rapid degradation of poly(ethylene oxide) to direct oxidation by dissolved oxygen initiated by high-frequency turbulent eddies. Elliott and Stow¹⁸ followed up the work of Ellis¹⁰ on the effect of the pipe diameter on the drag reduction. They compared the drag reduction in

narrow (1.2 mm) and wide (23.6 mm) tubes using poly(ethylene oxide) and anionic acrylamide copolymers prepared under low and high shear conditions. Rheological measurements demonstrated that high shear caused a decrease in size of the polymer units, particularly with poly(ethylene oxide). Shear had no effect on the measurements in the narrow tube but considerable effect on the measurements in the wide tube. Elliott and Stow suggested that the effects were due to polymer supermolecular structure. However, like Ellis their measurements were not carried out at the same wall shear stress in each tube.

Measurements of the drag reduction and shear degradation of poly(ethylene oxide) and polyacrylamide were made by Kenis¹⁹ and Fisher and Rodriguez.²⁰ Both found that poly(ethylene oxide) degraded more rapidly than polyacrylamide. Barnard and Sellin²¹ postulated that shear degradation is due to scission of molecular entanglements or breaking of individual molecular chains, probably caused by elongation of a single molecule or cluster of molecules by shear stresses associated with the local velocity gradient. They assumed that the region of turbulent flow in which the degradation occurs is confined to the viscous sublayer or at least to a region comparatively close to the wall. Patterson and Abernathy²² found that the drag reduction of poly(ethylene oxide) depended critically on the concentration of the highest molecular weight species present in the molecular weight distribution. Degradation in turbulent flow was severe with high molecular weight polymers, causing appreciable changes in drag reduction and molecular weight. They concluded that drag reduction is due to an interaction of individual molecules with the surrounding solvent and that the extent of drag reduction is relatively independent of pipe diameter when the comparison is made at the same solvent wall shear stress.

The object of the present work was to compare a variety of types of drag-reducing systems in order to obtain further information about the relationship between particle stiffness and length and the drag reduction at high and low wall shear stresses, to attempt to determine the relevance of the tube diameter, and to correlate this information with hydrodynamic shear degradation of the particles.

EXPERIMENTAL

Materials

The poly(ethylene oxide) was a Union Carbide product WSR301. The poly(acrylic acids) and polyacrylamides were supplied by Allied Colloids, Bradford; and the asbestos fibers, by Turner Bros (Asbestos), Rochdale. The poly(acrylic acid) S25 was provided in partly neutralized form. The sodium and the volatile matter were determined and allowed for in preparing standard solutions. The remaining poly(acrylic acids) were provided as concentrated solutions. Portions of these were dried to constant weight to determine the concentrations of the polymers.

The T7 bacteriophage DNA was provided by Microbiological Research Establishment, Porton, where the DNA was separated from the protein by the usual process of phenol extraction. The specimen was obtained from MRE in the form of a 4-ml quantity of aqueous solution which was transported to AML packed in ice. After phenol extraction, the aqueous phase had been dialyzed at Porton over the weekend against a phosphate buffer at 4°C. The buffer contained 0.00677*M* NaH₂PO₄ 0.0311*M* Na₂HPO₄ and had a pH of 7.4. The residual phenol and ethanol had been diluted 100 times by the process of dialysis. The concentration of the solution provided was found by MRE from measurement of optical absorption to be 0.66 mg/ml (optical density per cm of a 10 mg/ml solution at 260 nm was assumed to be 260). The calf thymus DNA was obtained from BDH Chemicals Ltd. Poole.

Determination of Molecular Weight

The average molecular weights of the synthetic polymers were estimated from their intrinsic viscosities $[\eta]$. The latter were obtained by extrapolating the value of $(\eta - \eta_0)/\eta_0 c$ to zero, where η and η_0 are the viscosities of solution and solvent and c is the polymer concentration in g/dl. The viscometer used was type BS/IP/MSL suspended level, size 1, as described in reference 23. The molecular weights were calculated from the values of $[\eta]$ using the following data:

Poly(ethylene oxide)²⁴ in water at 30°C:

$$[\eta] = 1.25 \times 10^{-4} M^{0.78} \quad (1)$$

Nonionic polyacrylamide²⁵ in water at 25°C and ionic polyacrylamide in 0.2*M* Na₂SO₄ at 25°C:

$$[\eta] = 6.31 \times 10^{-5} M^{0.80} \quad (2)$$

Poly(acrylic acid)²⁶ in 2 × 10⁻³*N* HCl at 30°C:

$$[\eta] = 7.3 \times 10^{-4} M^{0.50} \quad (3)$$

The values obtained are recorded in column 2 of Table I. The molecular weight of T7 phage DNA²⁷ is known to be 25 × 10⁶, and the contour length was calculated from this on the basis of 0.34 nm per average base pair of molecular weight 618.

Preparation of Solutions

The solid polymers were taken into solution by slowly adding a weighed amount of polymer to the required volume of water with agitation until the powder was evenly dispersed. The dispersion was then rotated end-over-end (30 rpm) overnight. The poly(acrylic acid) solutions were diluted approximately, a portion dried under vacuum, weighed, and the volume of solution adjusted to give a known, convenient concentration of stock solution.

TABLE I
Dimensions of Drag-Reducing Particles

Material	Molecular weight $\times 10^{-6}$	Contour length, ^a μm	Diameter, ^b nm
Poly(ethylene oxide) Polyox WSR 301	1.7	14	0.5
Polyacrylamide Magnafloc R351	4.4	16	0.7
Polyacrylamide Magnafloc R155	6.4	23	0.7
Poly(acrylic acid) Versicol E17	5.5	19	0.7
Poly(acrylic acid) Versicol E21	8.9	31	0.7
Poly(acrylic acid) Versicol S25	39	140	0.7
DNA T7 phage	25	14	2.0
Asbestos fibrils No. 6 (see also Table III)	—	1600	40

^a The contour lengths of the flexible polymers were calculated from $L_c = \frac{M}{m} \Sigma l \sin \frac{1}{2}\theta$, where M and m are the molecular weights of polymer and monomer, Σl is the sum of the bond lengths for one monomer unit, and θ is the mean bond angle. The values of Σl and θ are 0.440 nm and 108° for poly(ethylene oxide) and 0.308 and 109.5° for the others.

^b Unsolvated.

The concentrated solution of T7 phage DNA was diluted with acetate buffer (pH 5.7) equivalent to a final concentration of 0.009*N* sodium acetate, 0.001*N* sodium chloride, and 0.001*N* acetic acid. The BDH calf thymus DNA was dissolved directly in the same buffer.

The asbestos fibers were provided as dispersions in a 0.5% w/v solution of Manoxol OT. (The asbestos concentrations were calculated from the magnesium contents of the dispersions. The magnesium was determined by atomic absorption after treating the ignited residue with HF-H₂SO₄.) Dilutions were made into the same concentration of dispersing agent. The solutions of the poly(acrylic acids) were in most tests adjusted to a pH value of 5.8 by the addition of a small quantity of sodium hydroxide.

Drag-Reducing Efficiency

The effect of the solutes in reducing the turbulent drag was determined by observing the rate of flow of solution through a cylindrical glass tube of the chosen diameter and length when driven by a constant gas pressure which could be set at a value between 0.02 and 0.34 MN/m² (approximately 3–50 psi). Thus, in effect, the "drag," as measured by the wall shear stress (S), was maintained constant and the increased rate of flow caused by the presence of the drag-reducing agent was determined by observing the time for a constant volume of liquid (500 ml except for T7 phage DNA, where 250 ml was used) to be ejected. The electronic timer was controlled by pulses produced by the passage of the meniscus in front of illuminated photo-transistors situated at positions in the long, narrow reservoir, separated by a distance of 630 mm corresponding to a volume of 500 ml.

The Reynolds number with water varied between 3,500 and 29,000 with tube diameter and applied pressure. The rate of flow could be measured with a standard deviation of between 0.47% and 0.54% for a single determination. Values of "relative drag" were calculated from the square of the ratio of the time of flow of solution (t_s) to that of water (t_w). The significance of this relative drag value is as follows. For flow through a tube, Fanning's friction factor f is defined by

$$f = S/^{1/2}\delta v^2 = K(\text{Re})^n \quad (4)$$

where S is the wall shear stress, δ is the density of the fluid, v is the mean velocity, and Re is the Reynolds number. For turbulent flow of a homogeneous Newtonian fluid K and n have the values 0.064 and -0.23 , respectively. The time of flow for a given volume was measured at constant driving pressure, i.e., constant S , and hence (since the density of the solutions was almost identical with that of water

$$f \propto 1/v^2 \propto t^2 \quad (5)$$

Hence the relative friction factor at constant shear stress is given by

$$(f_s/f_w)_s = (t_s/t_w)^2. \quad (6)$$

This is the parameter we call "relative drag."

Choice of Tube Dimension

The objects of the present experiments were (a) to observe how the drag reduction varied when the wall shear stress in a tube of given diameter was varied; (b) to observe the variation in drag reduction when the diameter of the tube was varied while the wall shear stress was kept constant; and (c) to observe the degree of degradation of the polymers when subjected to various degrees of wall shear stress. The wall shear stress S is expressed in terms of applied pressure p , tube diameter d , and length l by the equation

$$S = pd/4l. \quad (7)$$

Thus, if tubes of varying diameters all have the same value of d/l , they will all subject the solution to the same value of wall shear stress when the same pressure is applied.

It has been shown by Levinthal and Davison¹⁶ that, for a given length of polymer chain and tensile strength of bond, there is, in laminar flow, a limiting value of wall shear stress below which shear degradation of the polymer will occur to a negligible extent. In turbulent flow, the situation is more complex, but it is still reasonable to assume that bond breaking occurs only in the region of high shear stress near the wall of the tube and that the total number of bonds broken is proportional to the shear energy dissipated per unit volume once the critical value of wall shear stress is exceeded. The shear energy dissipated per unit volume is equal to $4Sl/d$,

and thus for tubes of constant l/d value, the shear energy dissipated per unit volume will be constant if the wall shear stress is maintained constant. Here, the four tubes used in the experiments were chosen to have the same value of l/d , and their actual dimensions were governed by the range of pressures that the apparatus was capable of applying. The diameters finally chosen were 1, 2, 3, and 6 mm. The relevant parameters of these tubes are shown in Table II. In the event, it was decided to make the 6-mm tube about 10% shorter than the calculated value in order to avoid the necessity of having an extra join in the precision bore glass tubing.

The values of shear stress calculated from the applied pressure via eq. (7) were between 6% and 13% greater than those calculated from the flow rate via the Reynolds equation (see Table II). This difference gives an indication of the magnitude of the contribution of the inlet losses to the total pressure drop.

TABLE II
Flow Characteristics With Water

Parameter	Driving pressure, MN/m ²	Tube diameter and length, m			
		0.0010 0.502	0.0020 1.006	0.0030 1.505	0.0060 2.715
Flow time t , sec	0.0237	—	—	46.9	10.2
	0.0330	—	89.2	38.8	8.48
	0.141	173.7	39.7	16.9	3.71
	0.348	104.9	23.9	10.2	—
Volume Qt , m ³ × 10 ³	0.0237	0.500	0.500	0.500	0.500
	0.0330				
	0.141				
	0.348				
Flow rate Q , m ³ s ⁻¹ × 10 ³	0.0237	—	—	0.0107	0.0489
	0.0330	—	0.00561	0.0129	0.0590
	0.141	0.00288	0.0126	0.0295	0.135
	0.348	0.00477	0.0209	0.0490	—
Mean velocity v , ms ⁻¹	0.0237	—	—	1.51	1.73
	0.0331	—	1.78	1.82	2.09
	0.141	3.67	4.01	4.18	4.77
	0.348	6.07	6.66	6.93	—
Reynolds number (vd/ν)	0.0237	—	—	4,520	10,400
	0.0330	—	3,570	5,470	12,500
	0.141	3,670	8,020	12,500	28,600
	0.348	6,070	13,300	20,800	—
Shear stress s ($pd/4l$), N/m ²	0.0237	—	—	11.8	13.1
	0.0331	—	16.4	16.4	18.2
	0.141	70.2	70.1	70.3	77.9
	0.348	173	173	173	—
Shear stress calcd. from Reynolds equation, N/m ²	0.0237	—	—	10.5	11.4
	0.0331	—	15.4	14.6	16.0
	0.141	65.3	65.1	63.9	68.7
	0.348	159	160	156	—

EFFECT OF CONCENTRATION

It is well known that as the concentration of a drag-reducing agent is increased from very low values, the degree of drag reduction at first increases, passes through a maximum, and at very high concentrations of the polymer decreases again. The shape of this curve is due to the combination of two factors: the drag-reducing property of the solute, and the increasing viscosity of the solution, which becomes significant at high concentrations of polymer. When investigating the effect of other variables on the drag-reducing capability, it is clearly necessary to work at concentrations on the upward slope of the curve and not at the maximum or beyond, where the effect of other parameters is obscured by the saturation of the solution with drag-reducing agent. The optimum concentration will, of course, vary considerably with the kind of material used; and to choose suitable concentrations, concentration plots of all the polymers were first determined. Typical concentration plots are shown in Figures 1, 2, and 3. The measurements were carried out under two conditions, viz., those thought to represent the two extremes, i.e., narrowest tube and high wall shear stress, and widest tube and lowest wall shear stress. Figure 1 compares the results obtained with three poly(acrylic acids) of varying molecular weight in neutral solution where their chains are relatively stiffly extended and they exhibit the highest degree of drag reduction. These curves already give an indication of one of the main findings of this whole investigation, that is, that high molecular weight material (e.g., the polymer S25) gives good drag reduction at either high or low wall shear stress, whereas the lower molecular weight materials gives much less effect at low wall shear stress.

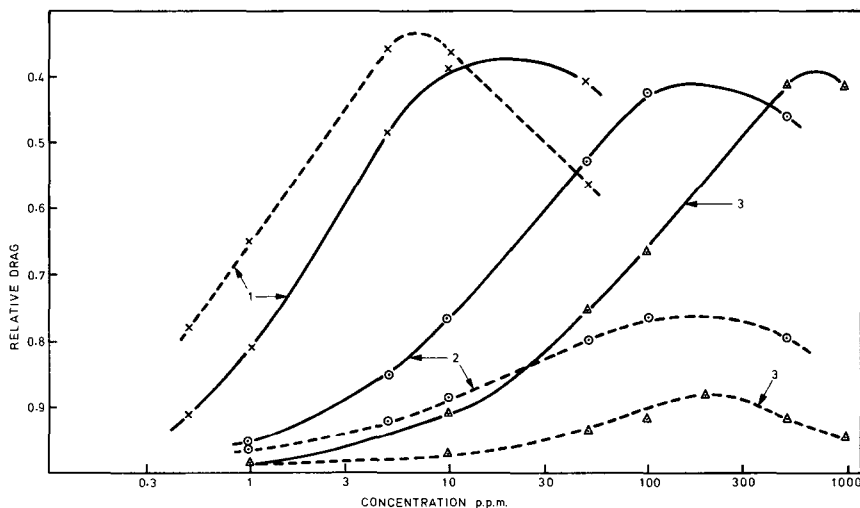


Fig. 1. Relationship between relative drag and concentration. Full lines are measurements at high shear stress; pecked lines at low shear stress: curves 1, poly(acrylic acid) S25; curves 2, poly(acrylic acid) E21; curves 3, poly(acrylic acid) E17.

It also illustrates very well the marked dependence of efficiency of drag reduction (as measured by the concentration of agent required to produce say, a relative drag value of 0.7) on the average molecular weight of the polymer.

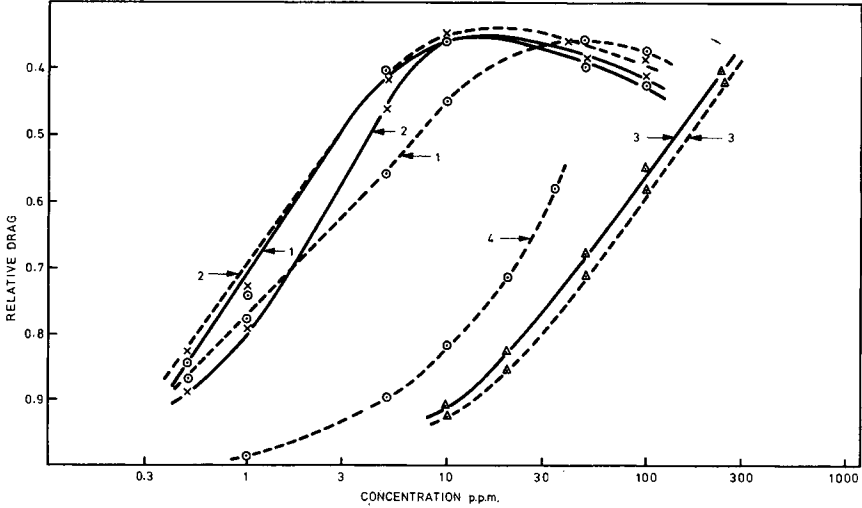


Fig. 2. Relationship between relative drag and concentration. Full lines are measurements at high shear stress; pecked lines at low shear stress: curves 1, poly(ethylene oxide) WSR301; curves 2, polyacrylamide R351; curves 3, calf thymus DNA; curve 4, T7 phage DNA.

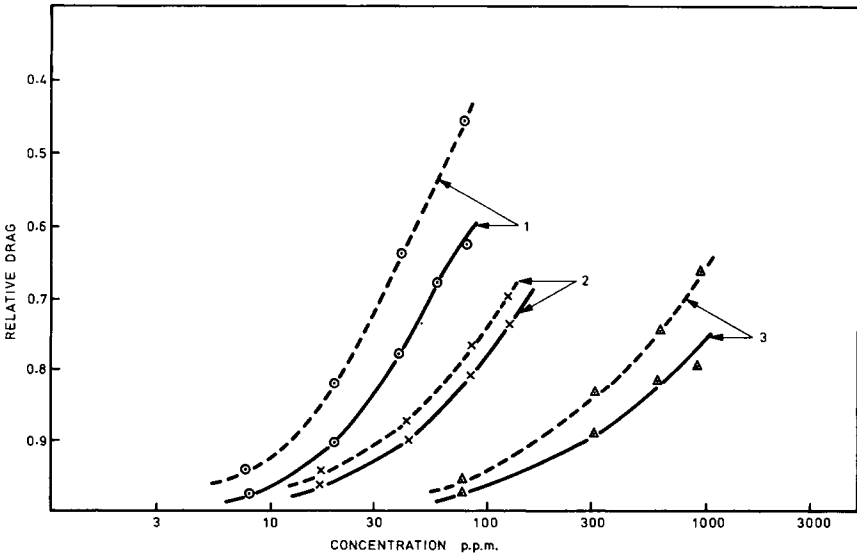


Fig. 3. Relationship between relative drag and concentration. Full lines are measurements at high shear stress; pecked lines at low shear stress: curves 1, asbestos fibers No. 6; curves 2, asbestos fibers No. 4; curves 3, asbestos fibers No. 2.

Thus, even at high wall shear stresses the reduction in molecular weight by a factor of about 4 resulted in a tenfold decrease in the efficiency of drag reduction. At low wall shear stresses the lower molecular weight material never achieved 0.7 relative drag at any concentration. The behavior of three other types of system are compared in Figures 2 and 3. Here again, the high-polymer solutions achieve a relative drag of better than 0.4 at the maxima in the curves. The polyacrylamide does equally well, if not better, at low wall shear stress; the poly(ethylene oxide) is somewhat less efficient at low wall shear stress; the calf thymus DNA and the asbestos fibrils behave similarly to high molecular weight polymers in being equally efficient or somewhat more efficient at low wall shear stress.

If indeed the extended length of the molecule or the particle is the critical parameter governing the degree of drag reduction, it would be better to compare concentrations not in terms of weight but in terms of number of molecules or particles per unit volume of solution. This value is simply calculated by dividing the weight concentration by the weight per particle. The particle concentrations of the materials required to produce a relative drag value of 0.7 (at the most favorable value of shear stress) are listed in column 4 of Table III. These results show a good correlation with contour lengths of the particles, as can be seen more clearly from the log plot in Figure 4 (graph 1). The values of contour length L_c can be represented in terms of the critical particle concentration n , by the equation

$$L_c = 30n^{-0.37} \quad (8)$$

with a correlation coefficient for the log plot of 0.94.

It is interesting to compare these results with those reported by Morgan and Pike.²⁸ These workers determined the drag reduction in tube flow of specimens of poly(ethylene oxide) and polyacrylamide having narrow ranges of molecular weight. They made measurements at two values of wall shear stress, viz., 100 and 400 N/m², compared with the largest value of 173 N/m² in the present experiments. They expressed their results in terms of a relative drag-reduction efficiency, denoted by E , defined as the reciprocal of the average relative concentration with reference to a standard (a particular specimen of Polyox WSR 301 having $[\eta] = 13.6$ dl/g corresponding to an average molecular weight of 2.9×10^6) giving the same drag reduction. Considering only the results at high shear stress (for which the drag reduction will more closely approach to maximum efficiency), Morgan and Pike found the following relationship between efficiency and viscosity:

$$E \propto [\eta]^{2.3} \quad (9)$$

for values of $[\eta]$ between 1.5 and 13.5 (molecular weight 0.17 to 2.8×10^6). Now, for poly(ethylene oxide),

$$[\eta] \propto M^{0.78} \quad (10)$$

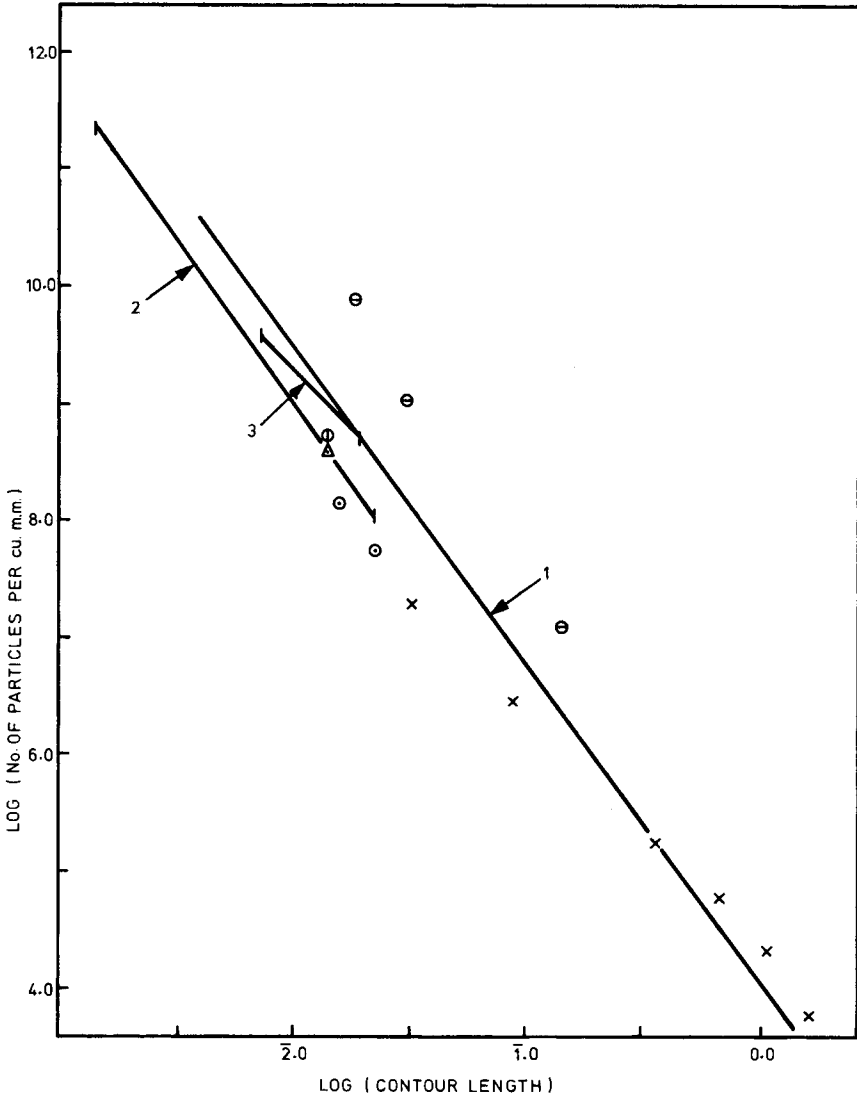


Fig. 4. Relationship between critical concentration and contour length (for relative drag value of 0.7): (Δ) poly(ethylene oxide); (\odot) polyacrylamide; (\ominus) poly(acrylic acid); (\oplus) DNA; (\times) asbestos fibers. Graph 1, mean of above data; graph 2, data of Morgan and Pike for poly(ethylene oxide); graph 3, data of Morgan and Pike for polyacrylamide.

and since for the critical concentration c

$$E \propto 1/c \quad (11)$$

and

$$n \propto c/M \quad (12)$$

TABLE III
 Drag Reduction Lengths (Calculated for a Relative Drag of 0.7)^a

Material	Contour length L_c , mm	Critical concentration, ppm	Particle concentration n , mm ⁻³	Drag reduction length L_D , mm	L_D/L_c
Poly(ethylene oxide)					
Polyox WSR 301	0.014	1.1	3.9×10^8	0.0014	0.100
Polyacrylamide					
Magnafloc R351	0.016	1.0	1.4×10^8	0.0019	0.119
Polyacrylamide					
Magnafloc R155	0.023	0.58	5.5×10^7	0.0026	0.113
Poly(acrylic acid)					
Versicol E17	0.019	73	8.0×10^9	0.00050	0.026
Poly(acrylic acid)					
Versicol E21	0.031	16	1.1×10^9	0.00097	0.031
Poly(acrylic acid)					
Versicol S25	0.140	0.78	1.2×10^7	0.0044	0.031
DNA T7 phage	0.014	22	5.3×10^8	0.0012	0.086
Asbestos 1	0.030	1900	1.9×10^7	0.0037	0.123
Asbestos 2	0.088	780	2.7×10^6	0.0072	0.082
Asbestos 3	0.35	190	1.7×10^5	0.018	0.052
Asbestos 4	0.67	130	5.9×10^4	0.026	0.038
Asbestos 5	1.06	74	2.1×10^4	0.036	0.034
Asbestos 6	1.60	30	5.7×10^3	0.056	0.035

^a The average lengths of the fibers were determined by Turner Brothers (Asbestos) Co. Ltd. by methods previously described.²⁹ The particle concentrations of the asbestos suspensions were calculated from the weight concentrations by assuming a diameter²⁹ of 40 nm and a density of 2.6.

it follows that

$$M \propto n^{-0.36} \quad (13)$$

Or, in terms of contour length L_c :

$$L_c = Kn^{-0.36} \quad (14)$$

Now, the molecular weight of the specimen used in the present tests was 1.7×10^6 , for which n was found to be 3.9×10^8 from which the value of K can be calculated to give

$$L_c = 17.3n^{-0.36} \quad (15)$$

These data are included in Figure 4 as graph 2.

Morgan and Pike reported similar though less extensive data for nonionic polyacrylamide. These fitted the relationship

$$E = 0.015[\eta]^{1.44} \quad (16)$$

in which

$$E = c_0/c = n_0M_0/nM \quad (17)$$

where c_0 is the concentration of standard poly(ethylene oxide) required to give the same degree of drag reduction. The standard had $[\eta] = 13.6$ dl/g corresponding to $M_0 = 2.9 \times 10^6$ and $L_c = 0.023$, for which eq. (15) indicates that $n_0 = 9.7 \times 10^7$. For polyacrylamide, we have (see eq. (2))

$$[\eta] = 6.31 \times 10^{-5} M^{0.80} \quad (18)$$

Hence, from eqs. (16), (17), and (18)

$$L_c = 191 n^{-0.46} \quad (19)$$

These data are included in Figure 4 as graph 3.

Considering the wide variety of materials represented and the uncertainties in particle size distribution, the data in Figure 4 fall sufficiently close to the same line to suggest that the proposed hypothesis of a single mechanism of drag reduction based directly on particle length is a reasonable one. The exponents in eqs. (8) and (15) are sufficiently close to the value $-1/3$ to suggest the idea that the influence of the drag-reducing particles extends over a domain equal to the cube of the length to which the rotating particles are extended in the velocity gradient concerned, i.e., that drag reduction becomes significant when the concentration has risen to a value where the volumes swept out by the individual rotating particles start to overlap. To make quantitative comparison, we therefore define a "drag reduction length" denoted by the symbol L_D equal to the cube root of the volume occupied per particle at some chosen critical concentration. If we choose as the critical concentration the value required to give a residual drag value of 0.7, the values of L_D may be calculated from those in column 4 of Table III by the relationship $L_D = n^{-1/3}$. Values of L_D calculated in this way are given in column 5 of Table III. The drag-reduction lengths lie between 3% and 12% of the contour lengths when the actual values of contour lengths vary by a factor of 100.

EFFECT OF VARIATION OF WALL SHEAR STRESS AND TUBE DIAMETER

The concentrations of the various polymers were chosen to give relative drag values between 0.4 and 0.6 at the highest wall shear stress. At this constant concentration, the relative drag values were measured in each of the four tubes at each of the four applied pressures with the exception that in the narrowest tubes the lowest pressures were omitted because the solution did not become turbulent, and the highest pressure in the largest tube was also omitted because the rate of flow was too rapid. The results on each polymer were then expressed in the form of a block, as shown in Table IV, in which horizontal rows represent values obtained at constant wall shear stress with varying tube diameter and vertical columns represent varying wall shear stress with constant tube diameter.

With the exception of the poly(acrylic acid) measured in sodium sulfate solution, it will be observed that the diameter of the tube has relatively little effect on the value of relative drag although there is a tendency for the

values to be lower in the narrow tube. With the materials of long chain length, the wall shear-stress also has a comparatively minor effect on the relative drag but with the particles of shorter length, for example, the poly-(acrylic acids) E21 and E17, the drag reduction capability is very much less

TABLE IV
Effect of Shear Stress and Tube Diameter

Material and concentration	Driving pressure, MN/m ²	Relative drag in tube of indicated diam.			
		1 mm	2 mm	3 mm	6 mm
Poly(ethylene oxide) Polyox WSR 301, 5 ppm	0.0237	—	—	0.52	0.55
	0.0331	—	0.45	0.47	0.47
	0.141	0.42	0.39	0.45	0.51
	0.348	0.40	0.47	0.45	—
Polyacrylamide Magnafloc R351, 5 ppm	0.0237	—	—	0.41	0.43
	0.0331	—	0.45	0.38	0.42
	0.141	0.40	0.38	0.44	0.39
	0.348	0.45	0.50	0.53	—
Polyacrylamide Magnafloc R155, 2.5 ppm	0.0237	—	—	0.42	0.41
	0.0331	—	0.45	0.42	0.42
	0.141	0.50	0.50	0.52	0.52
	0.348	0.62	0.61	0.64	—
Poly(acrylic acid) Versicol E17, 200 ppm	0.0237	—	—	0.87	0.89
	0.0331	—	0.90	0.89	0.88
	0.141	0.70	0.67	0.69	0.72
	0.348	0.56	0.58	0.62	—
Poly(acrylic acid) Versicol E21, 50 ppm	0.0237	—	—	0.81	0.80
	0.0331	—	0.80	0.78	0.77
	0.141	0.61	0.62	0.63	0.66
	0.348	0.53	0.55	0.57	—
Poly(acrylic acid) Versicol E21 in 0.2M Na ₂ SO ₄ , 100 ppm	0.0237	—	—	0.97	0.87
	0.0331	—	0.94	0.92	0.80
	0.141	0.48	0.65	0.67	0.62
	0.348	0.41	0.55	0.58	—
Poly(acrylic acid) Versicol S25, 2.5 ppm	0.0237	—	—	0.45	0.46
	0.0331	—	0.47	0.52	0.57
	0.141	0.50	0.49	0.52	0.54
	0.348	0.60	0.59	0.61	—
Poly(acrylic acid) Versicol S25, 50 ppm after 60 passes at 0.348 MN/m ²	0.0237	—	—	0.61	—
	0.0331	—	—	0.61	—
	0.141	—	—	0.57	—
	0.348	—	—	0.54	—
DNA Calf thymus, 100 ppm	0.0237	—	—	0.43	0.46
	0.0331	—	0.46	0.42	0.46
	0.141	0.44	0.41	0.43	0.46
	0.348	0.40	0.43	0.45	—
DNA T7 phage, 20 ppm	0.0237	—	—	0.72	—
	0.0331	—	—	0.70	—
	0.141	0.64	0.64	0.66	0.69
	0.348	—	—	0.61	—
Asbestos fibrils No. 6, 75 ppm	0.0237	—	—	0.46	0.50
	0.0331	—	0.43	0.49	0.52
	0.141	0.54	0.51	0.54	0.59
	0.348	0.60	0.61	0.64	—

(higher relative drag) at the lower values of wall shear stress. The same applies to a less extent to poly(ethylene oxide). Molecular stiffness also seems to play a part. For example, the poly(acrylic acids) in neutral solution take up a relatively rigid extended form due to electrostatic repulsion of the anionic groups. Addition of high concentrations of salt are known to cause the collapse of such structures to a much more flexible form and the addition of 0.2*M* sodium sulphate to poly(acrylic acid) E21 reduces the drag reduction even at high wall shear stress (100 ppm is now required to produce a relative drag of 0.58 in comparison with 50 ppm in the absence of salt); and at the low wall shear stress, the drag-reducing capability almost disappears.

It will be noted that the relative drag of the long-chain polymers and asbestos fibers actually decreases as the wall shear stress is reduced. This was partly due to the fact that some shearing action took place during the single pass of the solution through the tube. The investigation of this effect is described in the following section.

EFFECT OF MECHANICAL SHEARING

The effects of repeated passage through the test apparatus at high and low values of shear stress are shown in Figure 5. The solution containing asbestos fibers was practically unaffected at low shear stress, but it showed a steadily decreasing drag-reduction efficiency (increasing values of relative drag) at high shear stress. The solutions of the high polymers showed an increasing value of relative drag when subjected to either high or low shear stress. That shearing converts a high polymer to one of lower molecular weight is confirmed by the results of tests on the sheared solutions at various values of shear stress (see Table V). Thus, the drag-reduction efficiency of polyacrylamide solution after subjection to high shear stress disappeared completely when measured at low shear stress (relative drag 0.99), although it was still appreciable when measured at high shear stress. The other materials also showed a greater degradation when measured at low shear stress.

The effect of shearing poly(acrylic acid) is also shown by the results in Table IV, obtained with a 50-ppm solution of poly(acrylic acid) S25, which

TABLE V
Effect of Shear Degradation

Driving pressure MN/m ²	2.5 ppm S25		5 ppm R351		75 ppm Asbestos	
	Before	After ^a	Before	After ^a	Before	After ^a
0.0237	0.45	0.82	0.41	0.99	0.47	0.72
0.0331	0.48	0.80	0.40	0.98	0.52	0.79
0.141	0.54	0.79	0.44	0.89	0.58	0.80
0.348	0.61	0.79	0.53	0.80	0.66	0.82

^a After 10 passes through the 3-mm tube at 0.348 MN/m².

had been subjected to 60 passes through the apparatus at high shear stress. The value of relative drag was now similar to that obtained with the poly(acrylic acid) of lower molecular weight (E21); and like the latter, the relative drag *increased* when the test was carried out at lower shear stress.

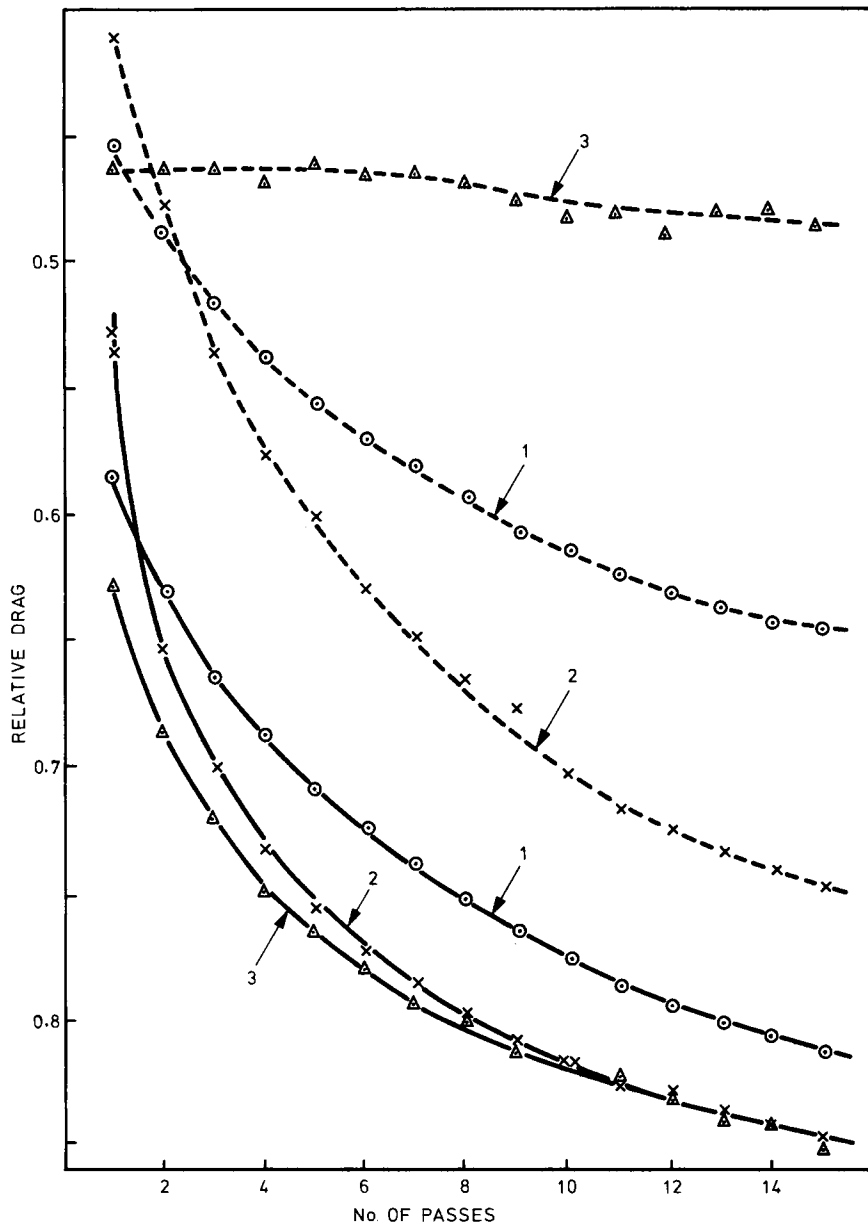


Fig. 5. Effect of repeated shearing. Full lines are sheared and measured at high shear stress; pecked lines are sheared and measured at low shear stress: curves 1, 2.5 ppm of poly(acrylic acid) S25; curves 2, 5 ppm of polyacrylamide R351; curves 3, 100 ppm of asbestos fibers No. 6.

The fact that the relative drag (at low shear stress) of the poly(acrylic acid) and asbestos fibers is less affected by mechanical shearing than that of polyacrylamide is attributed to the relative rigidity of the former after shearing; the shorter particles of the rigid materials retain the ability to extend at low shear stress, but the shorter particles of the more flexible polyacrylamide do not.

CONCLUSIONS

At constant wall shear stress, the relative drag value obtained with a particular concentration of any agent is substantially independent of tube diameter within the range of 1–6 mm.

Drag-reducing agents may be divided into two classes. Materials in class 1 have drag-reducing capabilities which are either independent of wall shear stress (within the range of 12–170 N/m²) or are more efficient at low wall shear stress. Materials in class 2 give very much lower drag-reduction efficiency at low wall shear stress. Class 1 includes linear flexible molecules of high molecular weight, and it is possible to convert these to class 2 materials by subjecting them to mechanical shearing forces. The class into which the drag-reducing agent falls is decided not only by the chain length of the molecule or particle but also by its rigidity. The effect of rigidity in determining the class can be illustrated by changing the environment of a class 1 polymer so that it becomes increasingly flexible and therefore more collapsed in solution. (If the polymer is caused to assume a rigid *compact* structure, its drag-reducing efficiency becomes less; this has been previously demonstrated with poly(acrylic acid) or DNA.)

The values of relative drag obtained at high wall shear stress may be correlated for all materials of both classes, and the correlation may be interpreted by a physical picture in which the effective domain occupied by the particles is proportional to volume swept by their rotating extended lengths, and drag reduction becomes significant when the effective domains start to overlap.

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