Lowering mechanical degradation of drag reducers in turbulent flow

Witold Brostow[a)] and Haley E. Hagg Lobland
Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas, Denton, Texas 76203-5310

Taruna Reddy
Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, India

Ram P. Singh
Office of the Vice Chancellor, University of Lucknow, Lucknow 226 007, India

Leslie White
Laboratory of Advanced Polymers & Optimized Materials (LAPOM), Department of Materials Science and Engineering, University of North Texas, Denton, Texas 76203-5310

Drag reduction (DR) agents are used in several ppm concentrations to accelerate significantly the flow through conduits in oil pipelines, oil well operations, flood water disposal, fire fighting, field irrigation, transport of suspensions and slurries, sewage systems, water heating and cooling systems, airplane tank filling, marine systems, and also in biomedical systems including blood flow. The drag reduction agents are typically high molecular mass polymers; in industrial applications they undergo mechanical degradation in turbulent flow. We provide an equation that describes quantitatively the degradation, thus predicting drag reduction as a function of time and of the concentration of the drag reduction agent. We report how grafting a polymer on the backbone of a different polymer affects the drag reduction efficacy. Our grafted polymer undergoes degradation by flow turbulence more slowly and also provides high levels of drag reduction efficacy at much lower concentrations than homopolymers do.

I. INTRODUCTION

Drag reduction (DR) as defined in the above abstract has many applications in a variety of fields.[1–4] To give an example, large urban agglomerations in India (and by no means only in India) find their sewer systems inadequate in the face of doubled or tripled populations. An alternative to digging out the entire municipal sewer system and replacing it by pipes with larger diameters is the use of DR agents. This is not just a much faster and cheaper solution. Larger diameter sewage pipes would have to be replaced periodically by still larger ones. By contrast, when the population continues to grow still more as it always does, a DR agent at increasing concentrations can continue to keep the sewer situation under control for a much longer time, provided a sewer network exists. DR has been discovered as occurring 'by itself' in human and animal blood flow[5,6] and consequences of this fact are of staggering proportions. Without DR, humans and animals would have to eat multiple amounts of food compared with their current food consumption. Otherwise the blood circulation would be far from adequate and living organisms other than plants would disappear. The fact that we know about DR occurrence in blood makes possible atherosclerosis prevention.[5,6]

In industrial applications (such as the Alaska pipeline) we have typically mechanical degradation in flow (MDF); DR decreases with time—a consequence of scission of polymeric chains caused by flow turbulence.[3,4] For all applications, this situation behooves us to develop new DR agents with slower MDF. So as not to develop them by trial and error, we need sufficient understanding of the mechanism of DR.

Given the many fields in which the DR phenomenon is used to advantage, various explanations as to how it occurs have been advanced. Models based on fluid mechanics did not take into account the polymer + solvent interactions and were not successful for that reason. In their classical work Zakin and Hunston[7,8] reported that poor polymer solvents require higher DR agent concentrations than good ones and also that MDF of the drag reducer chains is faster in poor solvents; particularly the latter finding seemed contradictory to intuition. By definition, in poor solvents the liquid volume pervaded by each polymer chain is small; for a good discussion of the solvent effects see for instance the book by Lucas and colleagues[9] or the book by Gedde.[10] The chains "keeping

their own company" were expected to defend themselves against MDF better than those in good solvents; the latter are extended over large volumes and thus were expected to be "attacked" more by flow turbulence.

In 1980 one of us developed a model[11] assuming in each polymer chain the existence of two kinds of sequences, good (oriented along the flow direction or close to it, and strongly solvated) and poor (oriented approximately perpendicularly to the flow, poorly solvated). The model explained all the phenomena observed, but it was a hypothesis without experimental evidence supporting it. Statistical mechanical calculations based on that model, showing for instance effects of variation of the proportion of good/poor sequences on solution properties[12–14] did not change this situation. (Engineers in industry are not massive supporters of statistical physics.) Indirect support for the model was provided by Springer and coworkers[15,16] who reported the existence of *long-range heterogeneities* in polymer solutions. Brownian dynamics computer simulations of flowing dilute polymer solutions[17,18] have shown that at short times and high shear rates the polymer chains become less entangled and less intertwined, thus enlarging their pervaded volumes. This agrees with the DR model and with experimental results of Kulicke and coworkers[2] that single chains can also cause DR; practical applications of the DR phenomenon involve sometimes concentrations as low as 10 ppm. However, only in 1999 did some of us obtain direct experimental evidence[19] for the 1980 model. The model[11] assumes that the larger the volume pervaded by polymer chains, the higher is the DR. Acoustic measurements of the solvation numbers and of DR efficacy show that indeed the solvation numbers go symbatically with that efficacy.[19]

Given the understanding provided by the model, we should be able to develop DR agents with enhanced efficacy. Along these lines, taking a polymer and grafting on its chains a second polymer should increase the solvent volume pervaded and thus enhance DR—unless the solvent is a poor one for the grafted polymer. This line has been followed by one of us including cooperation with Choi and coworkers.[20–25] An alternative is formation of intermolecular associations in solution that can be destroyed by turbulent flow—but then are re-formed for thermodynamic reasons as reported by Kowalik and coworkers.[26] Choi and coworkers have shown that calf-thymus DNA is also a drag reducer[27,28] unless DNA denaturation into two single strand molecules occurs.[27] There is also another approach proposed by Bello and coworkers[29] consisting in crosslinking DR polymers at concentrations below those required for gel formation. Thus, longer polymeric chains are formed, DR enhanced, but so far that approach did not decrease MDF. Thus, the problem of slowing down MDF remains.

The present work addresses at least three issues: Can we predict MDF as a function of flow time? If yes, how can we slow MDF down, so as to retain reasonable levels of DR? Since DR agents cause additional costs in fluid transport, what are the additive concentrations sufficient to achieve useful levels of DR?

II. EXPERIMENTAL

Homopolymers tested were amylopectin (Am, a branched polysaccharide from Aldrich), and polyacrylamide (PAM, Separan AP-273 from Dow Chemical Co., molecular mass $\approx 5 \times 10^6$). Solution polymerization was used to graft acrylamide monomer (from Merck) onto amylopectin in the presence of Ce^{+4} initiator. Details of the graft procedure have been described previously.[21,24]

To achieve full dissolution of a given drag reducing agent in water, each solution was kept under slow stirring for 6–24 h (the time dependent on the additive and its concentration). There are several techniques to determine DR, including a rotating disk apparatus of Choi and coworkers.[30–32] We have used a turbulent flow rheometer based on the classical design of Hoyt.[33] There is a motor-driven syringe; the delivery rate of the syringe is controlled by the ¼ hp motor speed. A linear actuator drives the syringe plunger and is coupled to the motor. The flow pipe is a stainless steel capillary tube with the diameter $d = 1.6$ mm. Our polymers were subjected to turbulent flow at the Reynolds number maintained at $N_{Re} \approx 14000$. $N_{Re} = du\rho/\eta$, where u is the average flow velocity (in cm/s), ρ is the solution mass density (in g/cm), and η is viscosity (in Pa/s). Input concentrations of the polymers varied from 50–5000 ppm. Samples of the solutions were withdrawn from the rheometer at pass numbers 10, 20, 30, 40, and 50. Absolute viscosities of the solutions were determined at 25 °C with an Ubbelhode viscometer as described for instance by Lucas, Soares, and Monteiro.[9]

Changes in viscosities η of the solutions with time t are clearly caused by MDF and result in lowered DR efficacy λ. Thus, we write

$$\lambda/\lambda_0 = \eta/\eta_0 \quad , \quad (1)$$

λ_0 and η_0 pertain to the solution that has just begun to flow ($t = 0$). Thus, the key property we seek is the change of the ratio in Eq. (1) with time; in our experiments t is proportional to the number of passes. An analysis of this problem[11] was based on consideration of the number of bonds $a(t)$ broken by turbulence per unit volume of the solution as

$$a = cN_A(1/M - 1/M_0) \quad , \quad (2)$$

where c is the polymer concentration in g/cm^{-3} and N_A is the Avogadro number; M and M_0 are the molecular masses of the polymer while the index 0 has the same meaning as in Eq. (1). We similarly define M_∞ as the

molecular mass at the time that mechanical degradation does not occur anymore. In other words, the chains became so short that the flow turbulence does not cause any more scission. We then define the average number of vulnerability points per chain in terms of M_0 and M_∞, namely

$$M_\infty = M_0/(1 + W) \quad , \tag{3}$$

W depends on the good/poor sequences ratio. Thus for example, $W = 4$ means that the original chain will eventually break into five pieces. We then assume that

$$dU/dt = -U/h \quad , \tag{4}$$

where U is the energy provided by turbulence that is available for bond scission while h is a parameter dependent on the liquid + drag reducer pair and on c. Clearly U depends on the Reynolds number N_{Re}. Integrating Eq. (4) with respect to time t, taking into account the definitions of a in Eq. (2) and of W in Eq. (3),[11] we obtain

$$\frac{\lambda}{\lambda_0} = \frac{1}{1 + W\left[1 - e^{-t/(h_0 + h_1 c + h_2 c^2)}\right]} \quad , \tag{5}$$

h_i parameters are constants for a given Reynolds number and the polymer + solvent pair. Eq. (5) contains the quadratic term absent before[11] to take now into account the overlap between polymer chains that affects their pervaded volumes.[34] Thus, a single equation for DR takes care of both time and the additive concentration variables. An exponential decay function used instead of Eq. (5) provides acceptable results only in certain cases but not in general.[35] This while Eq. (5) without the quadratic term has been used with good results in all cases it was applied, also by Lim, Choi, Biswal, and one of us.[25]

III. RESULTS AND CONCLUSIONS

In Fig. 1 we display the λ/λ_0 ratio as a function of time (the number of passes) for aqueous solutions of polyacrylamide for the PAM concentrations 500, 2000, 3000, and 5000 ppm. Continuous lines are drawn according to Eq. (5) while the points represent experimental values. We see that the equation is obeyed within the limits of the experimental accuracy. The same conclusion is reached on the basis of results for other materials investigated, but these results are not included here for brevity.

Given that we can handle quantitatively DR as a function of time, the next obvious question is: Can we get better drag reducers, that is with MDF as slow as possible? It is for this reason that a technique of grafting homopolymers has been developed by some of us[24] leading to the graft copolymer Am-g-PAM. In Fig. 2 we compare the relative DR defined by Eq. (1) as a function of time for aqueous solutions of that graft copolymer and
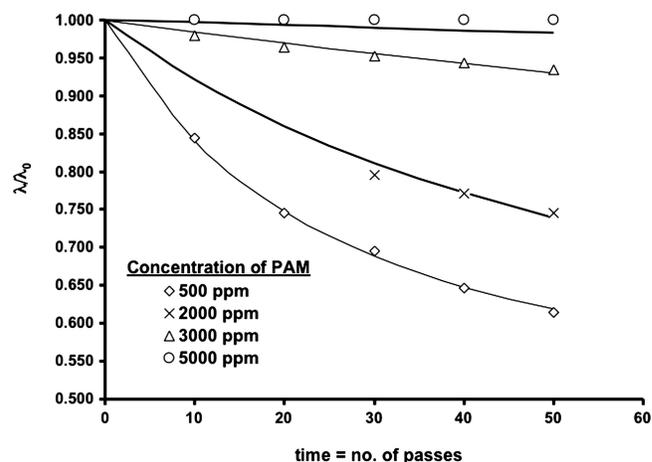

FIG. 1. Relative drag reduction λ/λ_0 for aqueous solutions of polyacrylamide (PAM) as a function of time (time represented by the number of passes) for several concentrations of the PAM drag reducer. Points are experimental, continuous lines calculated from Eq. (5).
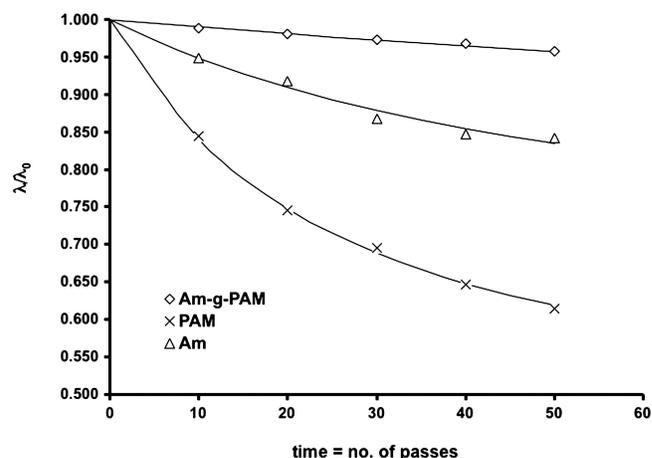

FIG. 2. Relative drag reduction λ/λ_0 for aqueous solutions of the Am-g-PAM graft copolymer and for the respective homopolymers as a function of time for 500 ppm concentrations of each drag reducer. Points are experimental, continuous lines calculated from Eq. (5).

of the respective homopolymers, with the concentration of each DR agent equal to 500 ppm. Again, continuous lines are drawn using Eq. (5).

It is clear from Fig. 2 that grafting has resulted in significantly slower MDF compared with the respective homopolymers. Thus, grafting a polymer "on the back" of another one seems a viable way to slow down the degradation in turbulent flow. In terms of the original model,[11] this can be explained by a contribution of the grafted side chains to solvation and thus to DR. The side chains also enhance the overall resistance of macromolecular chains to scission caused by flow turbulence.

We now recall also that the model developed in Ref. 11 and confirmed experimentally in Ref. 19 is based on considering the volumes pervaded by the macromolecular chains; hence the quantity $a(t)$ defined by Eq. (2).

Thus, higher polymer concentrations should result in more DR—until chain overlap occurs to a significant degree.[34] In Fig. 3 we show the λ/λ_0 ratios for aqueous solutions of Am-g-PAM as a function of the copolymer concentration for several turbulent flow times. Also here the continuous lines are obtained by using Eq. (5), with $W = 0.251$, $h_0 = 57.5$, $h_1 = 0.218$, and $h_2 = 0.00036$. This value of W means that on the average one macromolecular chain in four undergoes scission at one location. Some purely mechanistic models were assuming that the scission occurs exactly at the midpoint of the chain. There is of course no reason for this assumption; the scission location depends on the local magnitudes of turbulence. We also provide in Fig. 3 calculated curves for $t = 25$ and $t = 60$ for which no experiments were made, thus demonstrating the predictive capabilities of Eq. (5).

It is instructive to compare the value of W for the copolymer with those for the homopolymers. The respective values are $W = 0.870$ for PAM and $W = 0.355$ for Am. Thus, using amylopectin as the backbone and grafting acrylamide on it is preferred, rather than doing the opposite. The grafted copolymer has the slowest mechanical degradation (Fig. 2) while its lowest W value agrees with this fact also.

The use of drag reducers raises the costs of the liquid transport. For a proven drag reducer one thus wants as low concentration of the additive as possible. We see from Fig. 3 that applying concentrations of the graft copolymer higher than 1000 ppm is not worthwhile; a further improvement in retaining drag reduction for longer times is not achieved. The chain overlap has been seen also in Brownian dynamics computer simulations.[17,18] Apparently, above 1000 ppm, "new" polymer chains

added have little effect on the chain stability with respect to MDF—a consequence of the overlap.

For brevity we do not include here diagrams for the homopolymers analogous to Fig. 3. However, the plateau seen in Fig. 3 around 1000 ppm is in those cases reached only around 2000 ppm or more of the DR additive; see the curve for 5000 ppm in Fig. 1. Thus, our graft copolymers as DR agents have one more advantage over homopolymers for the same purpose. Not only do we get more stability with time against chain degradation by turbulent flow. Also the concentration needed to achieve the stability is for the graft copolymer around one half or less of the concentrations needed for homopolymers— with obvious consequences for the cost of applying a DR additive.

To conclude, let us provide a broader perspective on these results. As pointed out by Rustum Roy[36] and also by Roald Hoffmann,[37] various groups try to compartmentalize disciplines of science and engineering and cut them into pieces for their own convenience or benefit. Our work described briefly in this article goes in the opposite direction, toward integration of several ostensibly "unconnected" disciplines named in the abstract and in the beginning of this article.
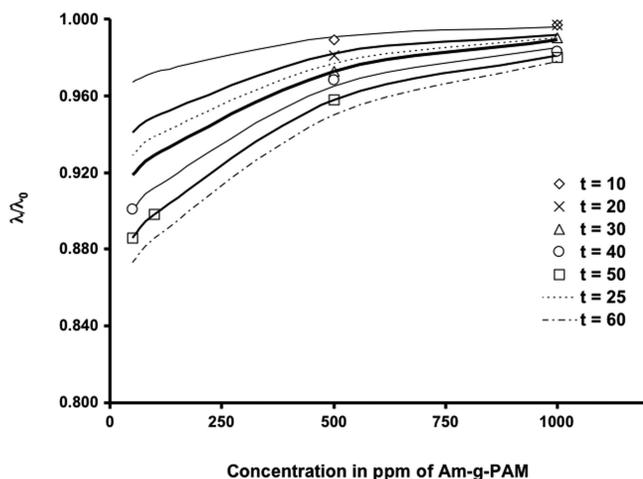
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FIG. 3. Relative drag reduction λ/λ_0 for aqueous solutions of the Am-g-PAM graft copolymer subjected to turbulent flow for varying amounts of time as a function of the polymer concentration. Points are experimental, continuous lines calculated from Eq. (5). Patterned lines are predicted from calculation.

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60

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