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Effect of intermolecular cross links on drag reduction by polymer solutions

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Summary

In this work we explore the effect of a cross-linking agent on the drag reduction capability of hydroxypropyl guar and guar gum solutions in turbulent flow through horizontal pipes. The results show that the addition of a cross-linking agent (borax) to solutions with concentrations below those required for gel formation enhances drag reduction due to the increased dimensions of the macromolecules in the presence of intermolecular cross links. The flow-induced degradation of the polymers is not appreciably affected by the addition of cross-linking agent.

Introduction

The use of small amounts of high molecular weight polymeric additives in turbulent pipe flows causes the well known effect of drag reduction. This effect has been extensively studied due to its wide range of technical applications. Extensive reviews of the subject are available (1-4).

The extent of drag reduction increases with the molecular weight of the polymer. However, the use of extremely high molecular weight polymers is limited by their susceptibility to flow-induced degradation. Reversible intermolecular associations in solution increase the apparent molecular weight of the polymer and can provide mechanical stability, which leads to an enhanced drag reduction efficiency. Kowalik et al (5) used hydrocarbon-soluble polymers with small amounts of polar associating groups to induce ionic associations in solution. They showed that the formation of intramolecular associations reduced the extent of drag reduction. On the other hand, the formation of interpolymer complexes by ionic associations of a cationic group in one chain with an anionic group in another one, lead to enhanced drag reduction with higher resistance to degradation. In their study, Kowalik et al employed three different associating polymers: an octyl-methyl undecenoate-undecenoic acid terpolymer, a styrene-vinylpyridine copolymer and a zinc salt of a sulfonated ethylene-propylene-diene terpolymer. More recently, Malik and Mashelkar (6) reached the same conclusions about the effect of secondary associations on drag reduction, using a poly (dodecyl acrylate-co-sodium methacrylate) and a poly (dodecyl acrylate-styrene-vinyl pyridine). On the other hand, Deshmukh et al (7) have shown that grafting polyacrylamide on carboxymethyl cellulose and starch enhances the drag reduction efficiency and mechanical stability.

Commercial polysaccharides have been used as drag reducing agents (1,8). These polymers have the advantage that they are highly stable with regards to mechanical degradation when compared to flexible polymers of similar molecular

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weight. However, their drag reduction ability is typically lower than that of available commercial samples of synthetic polymers (eg, high molecular weight hydrolyzed polyacrylamide (HPAA) and poly(ethylene oxide)). They are also more susceptible to biological degradation. Examples of commercial polysaccharides are xanthan gum, guar gum and hydroxypropyl guar (HPG).

Guar gum and HPG can be cross linked in solution in the presence of various transition metal ions, and also in the presence of borate ions. If the polymer and cross linker concentrations are sufficiently high, gels are formed. The ability to form gels is commercially used in the petroleum industry, particularly in hydraulic fracturing, where it is used to stimulate recovery from oil or gas bearing rock beds. Gel formation requires more than two intermolecular cross links per chain so that a three dimensional network of polymer molecules can be formed. As the polymer concentration in the solution is decreased, a point is reached at which the network losses its connectivity, and the intermolecular cross links are merely intermolecular associations which lead to an apparent increase in the molecular weight and to a possibly branched topology. It is important to point out that the effect of cross links at these concentrations on the rheological properties of the solution might not be equivalent to the use of a linear HPG of higher molecular length. Since HPG in aqueous solution is an expanded coil, further reduction in polymer concentration (below the coil overlap concentration, c^*) in the presence of the cross-linking agent leads to the formation of intramolecular cross links, which reduce the coil size (9).

Pruitt and Crawford (cited in 1) performed drag reduction experiments with guar gum solutions cross linked with borate ions at a concentration of 2000 ppm. They observed that the drag reduction capability of the polymer was greatly lowered.

In this work we study the drag reduction capabilities of guar gum and HPG in the concentration regime at which intermolecular cross links are formed but there is no gel formation, in order to assess the effect of these associations on drag reduction efficiency.

Experimental

The polymers used in the experiments were guar gum and HPG. The HPG used was provided by Dowell Schlumberger in unpurified powder form. The weight-average molecular weight of the polymer is approximately 2.5×10^6 (9). The guar gum was a commercial sample used in oil recovery operations, provided by Alliburton.

The polymer solutions were prepared in a beaker by dispersing the powder on the surface of deionized water whilst stirring with a magnetic stirrer to produce a deep vortex. After dispersing the powder, gentle stirring followed for periods between 12 and 24 hours. Owing to the sensitivity of these polymers to biological degradation small amounts of sodium azide: 2.5 mg of sodium azide/g of polymer were added to the solutions.

The cross-linking agent used was borate ion, provided by an aqueous solution of sodium tetraborate decahydrate (borax). The polymer solutions in the presence of cross-linking agent were prepared as follows: first, the required amount of polymer to prepare the desired solution was dissolved in approximately 90% of the final solution volume by means of the procedure described above. Second, a borax solution was prepared in 10% of the final solution volume, using the desired total amount of borax. Both solutions were mixed, and the pH of the final solution was adjusted to a value of 11 by adding small amounts of 1 M NaOH, in order to promote the existence of free borate ions in solution (10). In all cases, the amount of borax used was large enough to assure an excess of borate ions for the cross-linking process (9).

The drag reduction experiments were carried out in a turbulent flow apparatus. A batch of approximately 70 liters of the polymer solution was placed in a stainless steel feed tank in each experiment. Turbulent flow was established by means of a positive displacement pump (progressive cavity pump Netzsch model NE30A) through a horizontal pipe with an internal diameter of 3.5 cm and a total length of 4.7 m. The pipes transporting fluid to and from the horizontal pipe had internal diameter of 5.3 cm and were made of stainless steel. The horizontal pipe was divided in two sections: an entrance section, made of stainless steel, with a length of 3.5 m, to ensure the development of the flow, and a test section, with a length of 1.2 m, between whose extremes the pressure drop was measured. The test section was made of plexiglas, so that it could be considered to be a smooth pipe. The flow rate was controlled by means of a recycle to the feed tank with the purpose of diminishing restrictions to the flow in order to minimize possible mechanical degradation of the polymer. The experiments were conducted at 25°C.

Results and Discussion

Figure 1 shows the pressure drop across the test section of the horizontal pipe as a function of average velocity for HPG solutions in highly turbulent flow. The solid line corresponds to a fit of experimental results obtained in this work with pure water, which coincide with Colebrook's equation for turbulent flow in smooth pipes. The polymer solutions yield pressure drops equal to those of water at low velocities until an onset of drag reduction behavior occurs (at approximately 1.8 m/s). It has been argued in the literature (11) that such behavior is typical of coiled macromolecules, presumably since a critical local elongation rate must be attained to deform the coil before drag reduction occurs. Tatham et al (9) have shown, by means of ideal elongational flow experiments, that HPG adopts an expanded coil conformation in aqueous solutions, and it is capable of undergoing a coil-stretch transition. The maximum level of drag reduction obtained in the velocity range studied is around 15% in terms of pressure drop reduction. A slight increase in drag reduction is observed as the concentration increases.

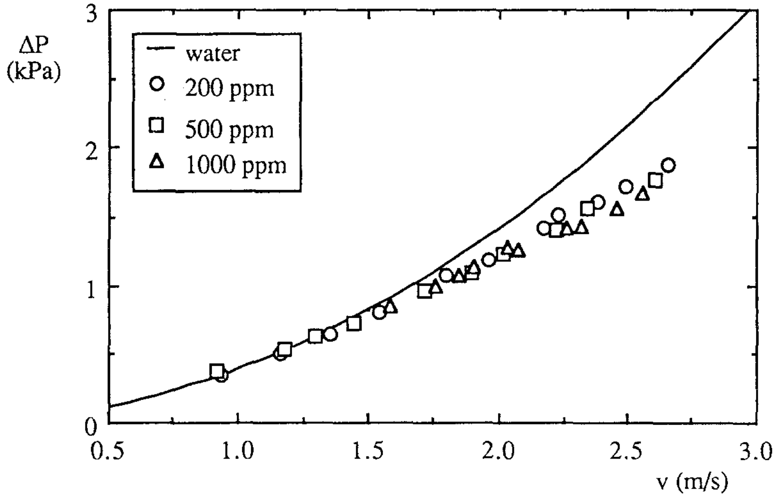

Figure 1. Drag reduction of HPG solutions.

Guar gum exhibits a behavior which is qualitatively similar to that of HPG at concentrations below 2000 ppm, as shown in figure 2. In the range of concentrations employed, the drag reduction efficiency increases with polymer concentration up to 500 ppm. At concentrations between 500 and 1500 ppm the pressure drop reduction saturates at a level around 22% at high velocities. At higher concentrations, 2000 ppm, the pressure drop increases, which is a result of the high viscosity level of the solution whose effect overcomes the drag reduction capability of the polymer. Notice that, for this concentration, the pressure drop at low velocities is higher than water.

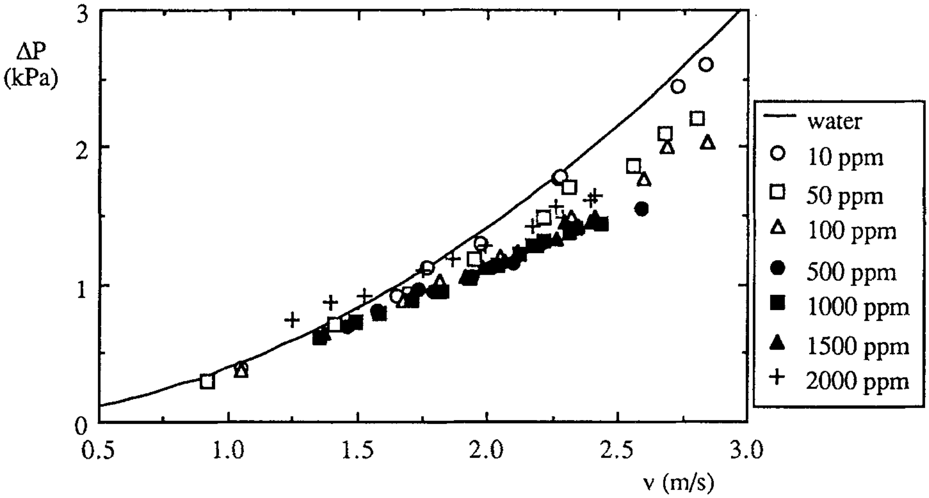

Figure 2. Drag reduction of guar gum solutions.

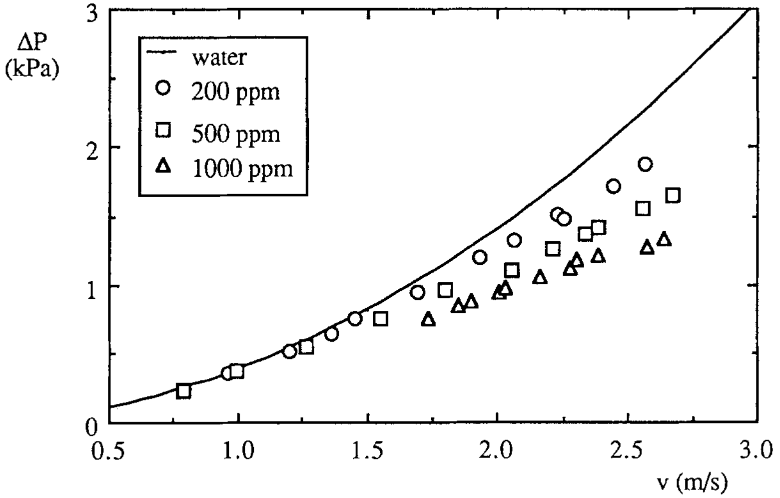

Figure 3. Drag reduction of HPG solutions with cross-linking agent.

The effect of addition of cross-linking agent to HPG solutions is presented in figure 3. Upon comparison with the results presented in figure 1, at 200 ppm, the presence of cross-linking agent has no effect on the pressure drop. At higher concentrations, the drag reduction efficiency of the solutions is appreciably increased with respect to the unmodified polymer solution. The results can be interpreted if one considers that at 200 ppm, intermolecular cross links are either not present or their number is too small to cause an effect whereas at higher concentrations their number increases, yielding a macromolecular structure with an apparently higher molecular weight, and hence increased drag reduction capability. It should be pointed out that changes in polymer concentration which produce small effects in the unmodified solution (figure 1) induce noticeable changes in the solution with cross-linking agent (figure 3).

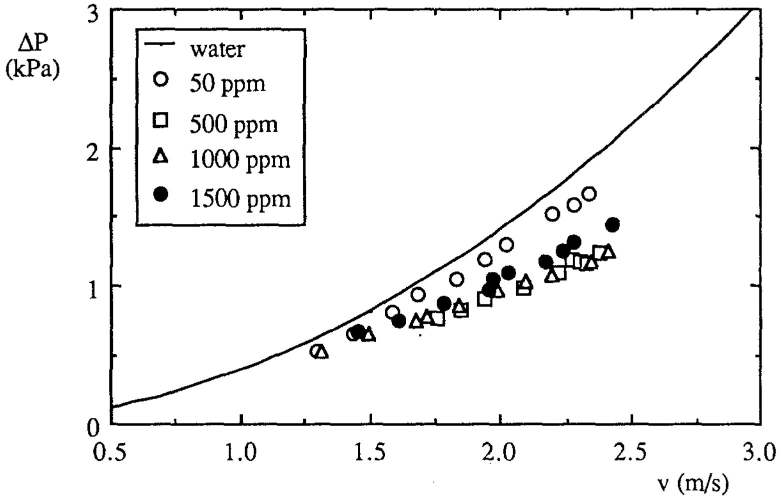

Figure 4. Drag reduction of guar gum solutions with cross-linking agent.

Figure 4 shows the drag reduction results for guar solutions with borax. At a concentration of 50 ppm, the results are similar to those reported in figure 2 (without cross-linking agent), as it happened with the 200 ppm HPG solution. At higher concentrations the drag reduction levels are appreciably higher than those obtained in the absence of cross linker. As in the case of HPG this increase in drag reduction can be interpreted in terms of the formation of intermolecular cross links. At 500 and 1000 ppm the drag reduction effect has reached a saturation level. At an even higher concentration, 1500 ppm, the pressure drop values are higher, which indicates that the increase of the viscosity of the solution is overcoming the drag reduction effect. It is interesting to point out that, in the absence of cross linker, this viscosity effect is not exhibited at 1500 ppm (figure 2) but at 2000 ppm. This was expected, since the solution with cross-linking agent should have higher shear viscosities at the same concentration than the solution without cross-linking agent. At concentrations higher than 1500 ppm, the guar gum solutions with cross-linking agent formed gels which could not even be pumped through the system.

The effect of polymer concentration on drag reduction as a function of concentration is presented in figure 5, for a constant flow velocity. The percentage of drag reduction is defined by

$$\%DR = \frac{\Delta P_w - \Delta P}{\Delta P_w} \times 100 \qquad (1)$$

where ΔP is the pressure drop of the polymer solution, and ΔP_W is the pressure drop of pure water at the same velocity. Figure 5 summarizes the effects discussed above. First, the curves exhibit the typical trend produced by drag-reducing polymers: the drag reduction efficiency increases at low concentrations; it then levels off to a plateau value that indicates that the maximum drag reduction ability of the polymer has been reached; and, finally, the drag reduction efficiency decreases at high concentration, as a consequence of a substantial increase in shear viscosity. The latter is only observed for guar gum solutions, in the range of concentrations employed.

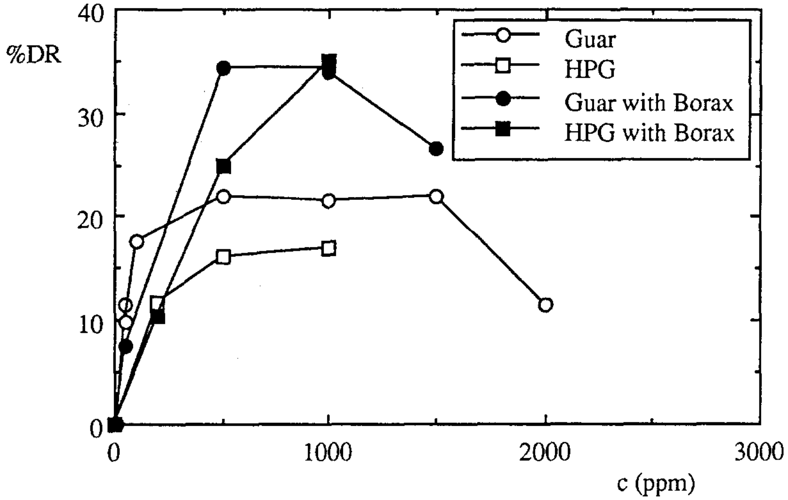

Figure 5. Drag reduction percentage at v=2.2 m/s.

The results presented in figure 5 show that the addition of cross-linking agent to guar and HPG solutions at relatively low concentrations produces a sizable increase in the drag reduction efficiency of the solution. For HPG, the addition of cross linker duplicates the drag reduction percentage at 1000 ppm, whereas for guar at the same concentration, the drag reduction percentage increases from slightly over 20% to 35%.

For the polymer solutions employed in this work we performed degradation studies under turbulent flow conditions. These experiments consisted in passing the solution through the horizontal tube continuously while keeping the flow velocity constant at the highest possible value. Such extreme conditions were chosen to maximize degradation and its effects. The pressure drops were recorded as a function of time. The pressure drops increased slowly with time, which presumably indicated that the polymer degraded during the course of these experiments. Since the degradation might occur not only in the test section but in other sections of the equipment, such as the pump, we performed experiments passing the solution through the pump only except at short intervals in which the solution was passed through the test section to record the pressure drop. Using this procedure we inferred that around 40% of the change in pressure drop with time was caused by degradation in the test section. The rest of the change is mostly induced by degradation in the pump where the fluid is subjected to sudden contractions and expansions in turbulent flow. It is important to keep in mind that the results presented below include the degradation in the pump; however, a substantial contribution to the degradation is caused by the turbulent flow in the test section.

In the degradation experiments, we found that the drag reduction percentage decreased exponentially with time, according to

$$\%DR = (\%DR)_0 \, e^{-kt} \tag{2}$$

where $(\%DR)_0$ is the drag reduction percentage at the beginning of the experiment. This trend has been reported in previous works (12). Table 1 presents the values of the rate coefficient k for the solutions employed in this work. The order of magnitude of the rate coefficient indicates that degradation was very slow compared to the typical time interval required for a complete ΔP vs v experiment. These experiments lasted less than 1 hour. For the 200 ppm HPG solution, the rate of degradation is appreciably higher than for the rest of the solutions. This is consistent with previous results in elongational flow experiments with flexible polymers, in which degradation rates decrease upon increasing concentration in the semi-dilute regime (13). Table 1 also shows that the rate of degradation does not change significantly with the addition of cross-linking agent to the solution. This indicates that the intermolecular cross links do not break faster than the polymer molecules, which is an added advantage to the use of cross linking agent.

Table 1. Rates of degradation at v=2.2 m/s.

c (ppm)	$k \times 10^3$ (s^{-1}) HPG	HPG with borax	Guar	Guar with borax
200	3.5	3.0	-	-
500	1.2	0.6	0.9	0.7
1000	1.7	1.1	0.8	1.7
1500	-	-	0.1	0
2000	-	-	0.8	-

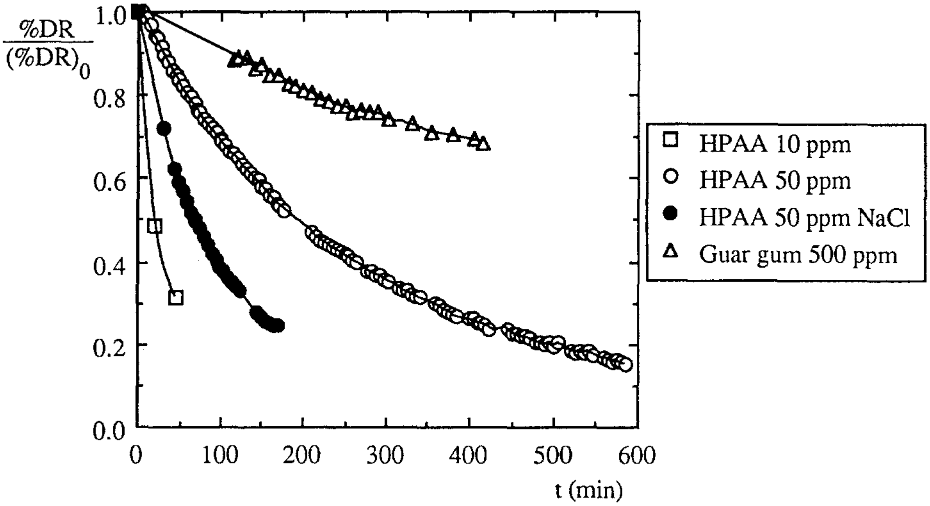

Figure 6. Drag reduction loss as a function of time at v=2.2 m/s.

In order to establish a comparison of the degradation rates of the polymers employed in this work, we performed experiments with a commercial sample of HPAA of very high molecular weight (ALCOFLOOD 1175A, provided by Allied Colloids). Solutions of 10 and 50 ppm HPAA in deionized water were employed, as well as a 50 ppm solution in 0.5 M NaCl in order to evaluate the effect of ionic environment since the HPAA is a polyelectrolyte whose coiled conformation depends on ionic strength (14). At v=2.2 m/s, the three HPAA solutions exhibited drag reduction at levels between 62 and 65%. Figure 6 shows the decrease in drag reduction efficiency as a function of time of the HPAA solutions, and one of the guar gum solutions. If we associate a decrease of drag reduction efficiency with flow-induced molecular scission, it is clear that the HPAA degrades faster than the guar gum. It is interesting to notice that the HPAA degrades faster at lower concentrations, which is similar to the trends observed in table 1. Furthermore, figure 6 shows that, for HPAA, the ionic environment affects degradation rates since using 0.5 M NaCl as solvent leads to a faster decrease in drag reduction efficiency. Notice that the time scale of degradation for the HPAA solutions is in the same order of magnitude as the typical duration of a ΔP vs v experiment.

Conclusions

The drag reduction capability of hydroxypropyl guar and guar gum can be increased by the addition of a cross-linking agent such as borax to solutions with concentrations below that required for gel formation. This enhancement is due to the higher apparent molecular weight obtained when intermolecular cross links are present. The intermolecular bonds are stable to flow-induced degradation, since their presence does not alter significantly the degradation rate. Even though the drag reduction efficiency of HPG and guar gum with cross-linking agent is not as high as that obtained with high-molecular weight synthetic polymers (such as polyacrylamide and poly(ethylene oxide)), their relatively low degradation rate makes them attractive for practical applications.

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