

Turbulent Drag Effectiveness and Shear Stability of Xanthan-Gum-Based Graft Copolymers

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Synopsis

A number of graft copolymers of xanthan gum and polyacrylamide have been synthesized by grafting acrylamide onto xanthan gum using the ceric-ion-initiated solution polymerization technique. The effects of various synthesis parameters such as amount of catalyst, reaction time, and ratio of xanthan and acrylamide on drag reduction effectiveness of the graft copolymers have been studied. The scaling up of grafting reaction has been accomplished in 40-L reactor. The drag reduction effectiveness of the graft copolymers is investigated over a wide range of concentrations and Reynolds numbers. It is shown that the maximum drag reduction obtainable in xanthan gum solutions above 300 ppm can be obtained in solutions of graft copolymers at concentrations of 100–150 ppm. The grafting also improves the shear stability at higher Reynolds numbers. The shear stability of the graft copolymers at constant wall stress has been found to be superior to polyacrylamide and the mixtures of polyacrylamide and xanthan gum. In general, the shear stability of graft copolymers and polyacrylamide is shown to increase with concentration. The drag reduction characteristics and shear stability have been discussed in terms of structural features of the graft copolymers. The drag reduction characteristics of the graft copolymers are found to be similar to those of flexible polymers.

INTRODUCTION

The turbulent drag reduction is caused by addition of very small amount of high molecular weight polymers to a solvent in turbulent flow.¹⁻³ Both flexible synthetic polymers and rigid polymers from natural resources are found to be effective drag reducers.^{4,5} The flexible polymers cause maximum drag reduction ($\approx 80\%$) in turbulent pipe flows at the concentration of few tens of ppm but are easily shear degradable. Thus they have limited applications in long unidirectional or recirculatory flows due to this severe limitation.⁶ On the other hand, rigid polymers such as guar gum, xanthan gum, and carboxymethylcellulose are fairly shear stable but cause maximum drag reduction (60%) at the concentration of few hundred ppm.⁷ Recently it has been shown⁸⁻¹¹ that, by grafting polyacrylamide chains on guar gum, xanthan gum, and carboxymethylcellulose macromolecules, it is possible to synthesize graft copolymers which are more drag reducing than the backbone polymers and have shear stability of the order of the backbone polymers. The maximum in

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drag reduction is also obtainable for concentrations close to 100 ppm. These graft copolymers exhibit also higher resistance to biodegradation.

The grafts of xanthan and polyacrylamide are synthesized by grafting acrylamide onto xanthan gum using the ceric-ion-initiated solution polymerization technique,¹²⁻¹⁵ which is a simple and controllable method. Deshmukh and Singh¹⁰ had synthesized graft copolymers of xanthan gum (Kelco) and polyacrylamide and studied the drag reduction effectiveness and shear stability of the graft copolymers at $Re = 14,000$ based on the solvent (water) viscosity.

In the present investigation, the graft copolymers have been synthesized using xanthan gum (Trade name Rhodopol from Rhone Poulenc, France) but varying various graft reaction parameters such as amount of catalyst, reaction time, and ratio of xanthan gum and polyacrylamide. The synthesis has also been scaled up in a 40-L reactor. The drag reduction characteristics and shear stability of these graft copolymers have been studied over a wide range of Reynolds numbers (based on solution viscosity) and concentrations. As the grafting of polyacrylamide chains on xanthan gum introduces flexibility in the graft copolymer, an attempt is made to explain the various features of these characteristics based on the molecular structures of xanthan gum, polyacrylamide, and their mixtures.

EXPERIMENTAL

Materials

Xanthan Gum (Rhodopol) was procured from Rhone Poulenc, France. It was subjected to Soxhlet extraction with 95% ethanol for 5 days to remove protein and fat impurities. Acrylamide monomer, nitric acid (fuming) and ceric ammonium nitrate, all of analar quality from Merck, F.R.G. were used as received. It has been observed that if extracted xanthan gum is stored at room temperature for a few months, it loses its characteristic properties due to biodegradation. Its storage in refrigerator is recommended.

Graft Copolymerization

The graft copolymers have been synthesized by grafting purified xanthan gum by the radical polymerization method in aqueous solutions using ceric ammonium nitrate as initiator, following the procedure of Deshmukh and Singh¹⁰ with slight modifications. First various solutions have been prepared, 4 g of xanthan is dispersed in 50 mL deionized water and stirred at 300 rpm in a 1-L globular flask; 9.7 mL of 65% (by weight) nitric acid is dissolved in deionized water to make 100 mL 1M nitric acid solution. Then 5.4823 g ceric ammonium nitrate is dissolved in 100 mL of 1M nitric acid. Acrylamide (10 g) is dissolved in 50 g deionized water. For drag reduction measurements, polyacrylamide (AP 45) is first dispersed in the same quantity of isopropanol prior to its dissolution in water. This solution is stirred in a 10-L vessel at the lowest revolution number of the stirrer for 10 h.

Acrylamide solution (50 mL) is mixed with 50 mL xanthan gum solution and deionized water is added to make a total amount of 1-L solution in an Erlenmeyer flask. Nitrogen is bubbled inside the flask during mixing and for

TABLE I
The Comparison of the Chosen Concentrations and Parameters with Those in the Literature

	U.S. Pat. ¹²	Deshmukh and Singh ¹⁰	Own
Concentration of xanthan gum	10,000–30,000 ppm	3300 ppm	1000 ppm
Concentration of catalyst	0.002–0.006 mol/L	0.0003–0.0013 mol/L	0.0001–0.0004 mol/L
Ratio xanthan gum–monomer	No statement	1 : 10 by weight	1 : 10 by weight
Ratio moles catalyst: g xanthan gum	2×10^{-4}	9.1×10^{-5} – 3.9×10^{-4}	10^{-4} – 4×10^{-4}
pH	2–5	No statement	3.5–4
Reaction time	2–3 h	24 h	2–24 h

another 30 min. Then a certain amount of catalyst is added by 10-mL pipette (see Tables I and II). The stirring is continued for another 5 min. The number of revolutions of the stirrer is reduced so that the liquid is seen in motion in all parts of the flask. The bubbling of N₂ is continued for the whole reaction at approximately two bubbles per second. All the time the temperature inside the flask is maintained at 30°C. To examine the influence of reaction time on yield and drag reduction effectiveness, test fractions are taken out by a 25-mL pipette. To these fractions, 0.1 mL saturated aqueous hydroquinone is added. The reaction product is precipitated in excess of isopropanol. The separation of the precipitate from the liquid is tried by filtration under vacuum in a Buchner funnel using Schwarz band filter paper. Usually filtering is not possible for the graft copolymers after short reaction times because the filter pores get blocked in a few seconds. Then the thread types of polymers are rolled up with a glass rod, and the rest is allowed to precipitate for 12 h. The remaining polymer is separated by decanting. The white polymer is washed with acetone, which dissolves unconverted acrylamide. It was left in acetone for 3 h, and finally it is dried at 40°C in vacuum for 24 h. The solid product is usually hard and brittle and is crushed to powder form in a mortar.

TABLE II
Monomer Conversion and Its Dependence on Synthesis Parameters^a

Reaction time (h)	1 g xanth. + 10 g Am + 1 mL cat. (%)	1 g xanth. + 10 g Am + 2 mL cat. (%)	1 g xanth. + 10 g Am + 4 mL cat. (%)	2 g xanth. + 10 g Am + 4 mL cat. (%)	0.5 g xanth. + 10 g Am + 1 mL cat. (%)
2	0	0	18.4	11.1	
4	11	11.8	30.7	18.8	
8	11.2	18	50.8	45.9	
12	23.9				34
24	34.6	34.1	59.7	55.1	

^aExplanation: all quantities are related to 1 L solution, Am = acrylamide.

The monomer conversion(MC) is defined as follows:

$$MC = \frac{\text{wt graft copolymer} - \text{wt xanthan gum}}{\text{wt acrylamide}}$$

Later on, the synthesis was repeated several times with 1 mL catalyst, 12-h reaction time, and a ratio of xanthan gum and acrylamide of 1:10. The monomer conversions were 38.4, 32.6, and 39.6%. The monomer conversions given in Table II are in general low because the various samples were taken from the same reactor at different intervals of times, which causes leakage of traces of oxygen, resulting in poor monomer conversion. The most probable reasons for variation in MC may be that the pHs of deionized water in various syntheses are different and also there is the possibility of very slow biodegradation of extracted xanthan gum.

After crushing to pieces of max 3 mm diameter, the polymer is suspended in 1 L deionized water and stirred for 7–12 h at 300 rpm in a 1-L flask to provide homogeneous solution for measurements.

Scaling Up to 40-L Reactor

The grafting reaction was later on accomplished in a 40-L reactor. It consists of a cylindrical vessel ($d = 378$ mm, $h = 465$ mm) made of polypropylene which has a copper heat exchanger. A glass beaker of 10 L was placed inside the copper spiral in the cylindrical vessel. The vessel can be closed by a flat perspex cover provided with holes for a stirrer, gas inlet and outlet, and for injector of catalyst, respectively. The reaction is carried in the same way as in the 1-L Erlenmeyer flask, keeping the ratio of reactants the same. The conversion was of order of 40%. This is in the same range as obtained by latter experiments. The real conversion should be more because in separation by decanting some part of the product is lost.

Rheological, Drag Reduction and Shear Stability Parameters Measuring Techniques

The shear viscosity was measured for low shear rates (< 1 s⁻¹), medium shear rates (0.1–100 s⁻¹) by Low Shear 100 (Contraves), Low Shear 2 (Contraves), and Rotovisko (Haake) viscometers, respectively.

The pressurized capillary flow system was used for drag reduction measurements. The friction factor was evaluated from the pressure drop and volume of flow measurements at various Reynolds numbers. Viscosity-corrected Reynolds numbers have been used in the present investigation by taking the shear viscosity as measured in laminar flow at the same wall shear stress in a viscometer. The schematic diagram of the experimental setup is shown in Figure 1.

The shear stability of polymers in aqueous solution was measured by estimating the friction factor when the same solution was recirculated through the test capillary at a constant wall shear stress (= 37.5 Pa). One circulation is depicted as a unit pass number.

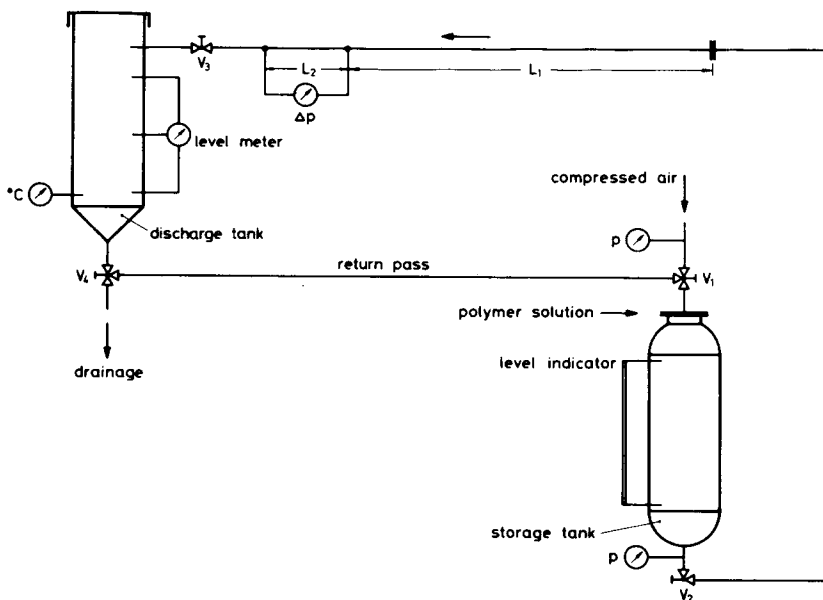


Fig. 1. The schematic diagram of pressurized capillary flow system.

The relation between the pressure Δp in a length l of capillary of diameter d and wall shear stress τ_w is given by

$$\begin{aligned}\tau_w d \pi l &= \Delta p \pi (d^2/4) \\ \tau_w &= \Delta p d / 4l\end{aligned}\quad (1)$$

The friction factor f is given by the following equation:

$$f = \frac{\Delta p d}{2l \rho u^2} = \frac{2\tau_w}{\rho u^2}\quad (2)$$

where ρ is the density of the liquid and u is the average velocity. The Reynolds number is given by $Re = ud/\nu$, where ν is the kinematic viscosity ($\nu = \eta/\rho$; η is the shear viscosity). The drag reduction DR is defined in the following way: $DR = 1 - f_s/f_0$, where f_s and f_0 are the friction factors for solution and solvent, respectively, at constant flow rate.

The magnitude of drag reduction depends on the Reynolds number Re , the additive concentration c , the pipe diameter d , and the molecular parameters of the additive. It has been shown by Virk² that there exists a limit of maximum drag reduction in pipe flows given by

$$1/\sqrt{f} = 19 \log(Re \sqrt{f}) - 32.4\quad (3)$$

This maximum drag reduction asymptote has been confirmed by measurements of several authors. Therefore, all plots of the friction behavior contain this maximum drag reduction asymptote besides the friction curves for New-

tonian fluids

$$f = 16/\text{Re} \quad (4)$$

for a laminar pipe flow and the Prandtl-Kármán law

$$1/\sqrt{f} = 4 \log(\text{Re} \sqrt{f}) - 0.4 \quad (5)$$

for a turbulent flow in smooth pipes.

RESULTS AND DISCUSSION

The Monomer Conversion and the Effect of Synthesis Parameters on Drag Reduction

Various methods are available for initiating graft copolymers. In case of the backbone polymers containing polyols such as polysaccharides, the ceric ion initiation method has been extensively used.⁸⁻¹⁵ Here free radicals are formed at glucose unit containing diol by ring opening in the presence of ceric ion initiator. Polyacrylamide chains can be grafted here as shown first by Mino, Kaizerman, and Rasmussen.¹⁶ This method was later on adopted by Petit¹² and Deshmukh and Singh¹⁰ with some modifications to graft polyacrylamide chains on xanthan gum. The same method has been followed in the present investigation. However, when the grafting was tried at the same concentration of the purified xanthan gum as reported by Deshmukh and Singh,¹⁰ the resulting graft copolymer had very poor solubility. Hence it was suspected that some crosslinking may take place among the graft copolymer as was noticed by Wade¹⁷ in the synthesis of graft copolymers of poly(vinyl alcohol) and acrylamide. Hence, in the present investigation, the concentration of xanthan gum was lowered to avoid the possibility of crosslinking among graft copolymers during the grafting reaction. The comparison of the chosen concentration and parameters with literature is shown in Table I.

The monomer conversion is shown to increase with increasing amount of catalyst, mainly because of the increase in number of free radicals. McDowall et al.,¹⁵ who summarized the reports from various authors, show that there is a catalyst concentration which gives maximum conversion because the catalyst in excess enhances the termination reactions as well. The amount of catalyst was varied between 1 and 4 mL (Table II). The order of drag reduction caused by consequent graft copolymers is 1 ml > 2 ml > 4 ml, as shown in Figure 2. At $\text{Re} = 27,000$, the difference disappeared. Less amount of catalyst amounts to larger but fewer side chains.^{8-11,17} Larger chains enhance the flexibility of macromolecule and hence drag reduction.⁷ Even with large monomer conversion, the number of chains does not increase the lengths in the presence of large amount of catalyst. This does not change the nature of rigid xanthan molecules; hence one gets lower drag reduction. Also better solubility in earlier case favors higher drag reduction effectiveness. Similar behavior has been obtained in graft copolymers of guar gum/poly(vinyl alcohol) and polyacrylamide by Deshmukh and Singh,^{8,9} Wade,¹⁷

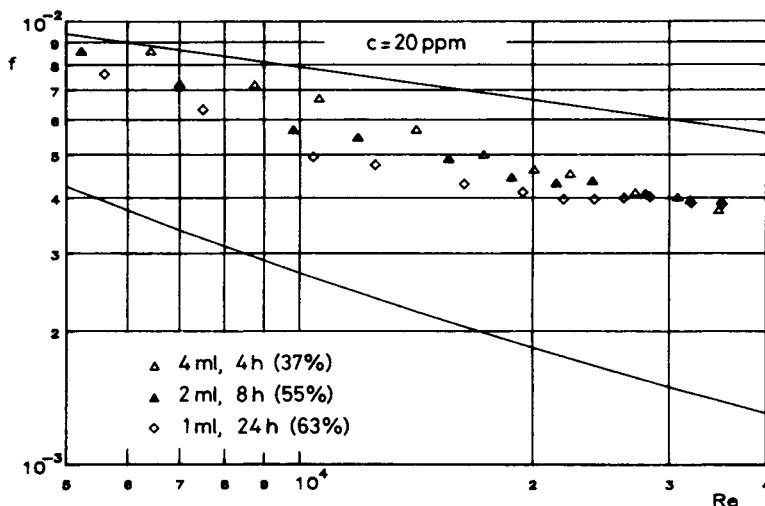


Fig. 2. The effect of catalyst on friction factor vs. Reynolds number characteristics of the graft copolymers: (Δ) 4 mL, 4 h (37%); (\blacktriangle) 2 mL, 8 h (55%); (\diamond) 1 mL, 24 h (63%).

and Majumdar.¹⁸ The monomer conversion increases rapidly with time in all cases, but, after 12 h, the monomer conversion rate becomes very small. Figure 3 shows the effect of the reaction time on the drag reduction vs. Reynolds number characteristics. It can be seen that at lower Reynolds numbers, the drag reduction is higher for graft copolymers with 8 h reaction time than for the graft copolymers with 4 and 24 h reaction times. For Reynolds numbers $Re \geq 15,000$, the drag reduction is almost the same for all the graft copolymers. As in the present case, the concentration of catalyst is higher, some possibility of crosslinking among graft copolymers is not denied, which makes

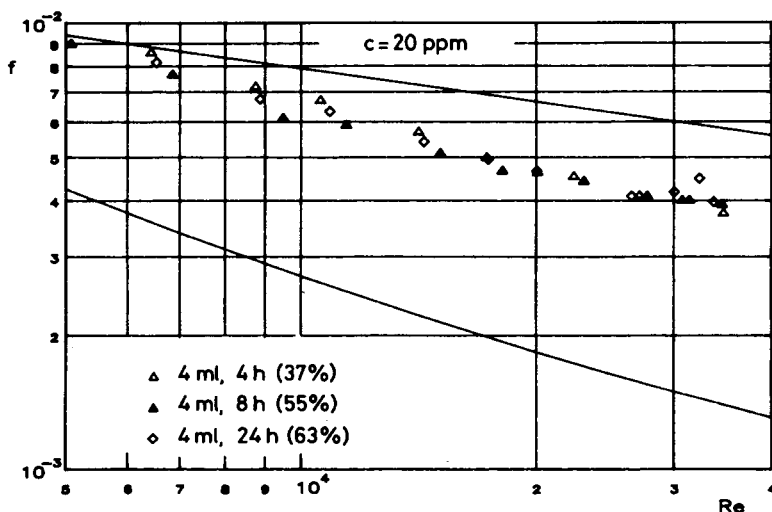


Fig. 3. The effect of reaction time on friction factor vs. Reynolds number characteristics of the graft copolymers: (Δ) 4 mL, 4 h (37%); (\blacktriangle) 4 mL, 8 h (55%); (\diamond) 4 mL, 24 h (63%).

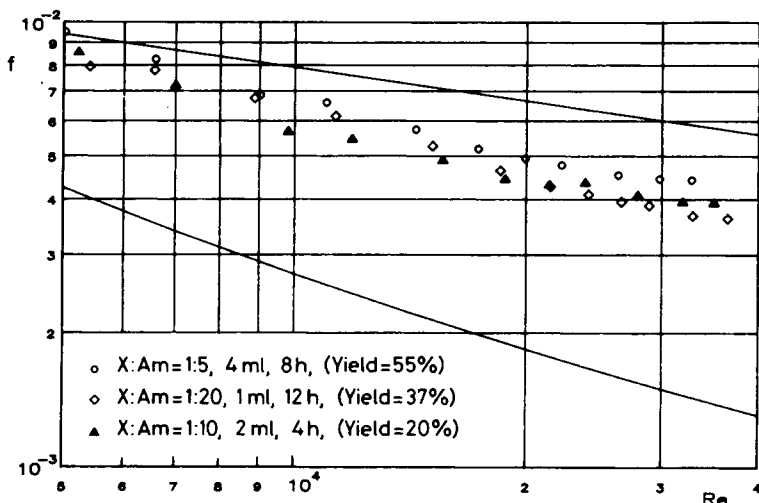


Fig. 4. The influence of length of the grafted chains on friction factor vs. Reynolds number characteristics of the graft copolymers: (○) X : Am = 1 : 5, 4 mL, 8 h (yield = 55%); (◇) X : Am = 1 : 20, 1 mL, 12 h (yield = 37%); (▲) X : Am = 1 : 10, 2 mL, 4 h (yield = 20%).

the drag reduction lower than the graft copolymers prepared at optimum reaction time of 8 h. When these crosslinks are broken at higher Reynolds number, all three graft copolymers give almost equal drag reduction. In this case the effect of shearing will be lowest in graft copolymers of lower molecular weight prepared after 4 h, and degradation will be highest in the larger crosslinked grafts.¹⁹ Hence all three graft copolymers show the similar behavior.

Figure 4 shows the influence of length of the grafted chains on drag reduction vs. Reynolds number characteristics. Here it is evident that the graft copolymer with shortest but large number of side chains is least effective as drag reducer (XG : AM, 1 : 5). The graft copolymer with longest and fewest chains shows higher drag reduction at higher Reynolds numbers.

The Drag Reduction Characteristics of Graft Copolymers and the Concentration Effect

Deshmukh and Singh¹⁰ reported a considerable increase of drag reduction effectiveness if polyacrylamide chains are grafted onto xanthan gum backbone. They measured the drag reduction and its dependence on concentration at a constant Reynolds number of $Re = 14,000$. They obtained the drag reduction maximum between 75 and 300 ppm, depending on the synthesis parameters. On the other hand, purified xanthan gum shows maximum drag reduction at a concentration not below 300 ppm. Figure 5 shows the drag reduction vs. concentration characteristics of graft copolymers of the present investigation at $Re = 14,000$. Here the drag reduction maximum is obtained at 100 ppm, and at higher concentrations no change is observed. In the present investigation at $Re = 14,000$, the drag reduction is about 10% less than that of Deshmukh and Singh.¹⁰ This difference may be due to some

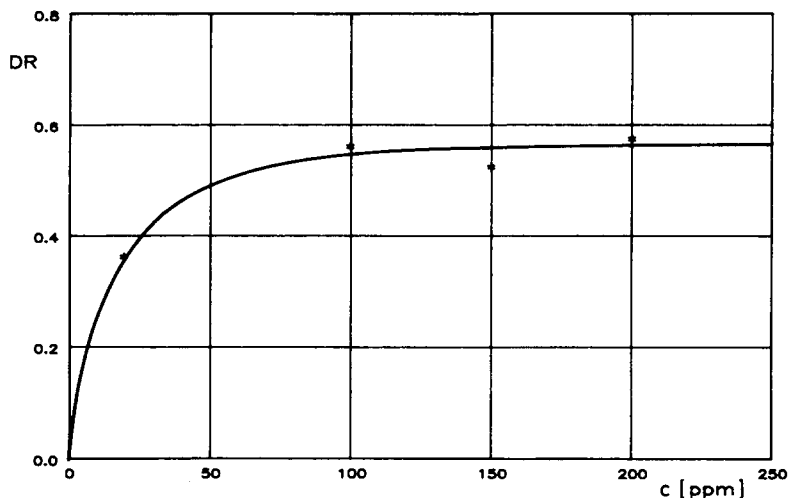


Fig. 5. The effect of concentration on drag reduction by the graft copolymer at $Re = 14,000$.

chemical modifications present in xanthan gum from Rhone-Poulenc and also because of the larger diameter used in the present investigation than that ($d = 1.574$ mm) used by Deshmukh and Singh.¹⁰

Figure 6(a) shows the friction factor vs. Re characteristics for two different concentrations of the graft copolymer, xanthan gum, and a mixture of polyacrylamide and xanthan gum over a wide range of Reynolds numbers. Figures 7(a) and (b) depict effect of concentration of drag reduction characteristics of the same systems. While the 20 ppm solution shows lesser drag reduction, at higher concentrations (> 100 ppm) the similar drag reduction is shown, which is an indication of maximum drag reduction reached at concentrations near 100 ppm as shown in previous figure at $Re = 14,000$. The higher concentrations show the onset of shear degradation at higher Reynolds numbers. In the above diagram, the mixture of xanthan gum and polyacrylamide in weight ratio 1 : 3 is depicted. This ratio is also present in graft copolymer because the xanthan gum and polyacrylamide were used in ratio 1 : 10 for synthesis and monomer conversion was about 30%.

From Figures 6(a) and (b) it is self-evident that the drag reduction effectiveness of the xanthan gum Rhodopol is enhanced by grafting polyacrylamide chain on it. The graft copolymer solutions show a linear dependence between $\log f$ and $\log Re$ but with steeper slope than that of Prandtl-Kármán line. Their onset from the Prandtl-Kármán line is also near the critical Reynolds number, but for 20 ppm it seems to be at a higher Reynolds number. The mixture produces high drag reduction. The mixture first follows the maximum drag reduction asymptote up to $Re = 10^4$, and then it shows a leveling off due to shear degradation. This behavior could also be observed with polyacrylamide at 10 ppm. The graft copolymer solutions do not reach maximum drag reduction asymptote even up to 200 ppm. The 200 ppm solution shows no degradation up to the Reynolds number of 30,000.

The fact that the graft copolymers are not as effective as the mixture of backbone polymer (XG) and branch polymer (PAM) can be explained by two

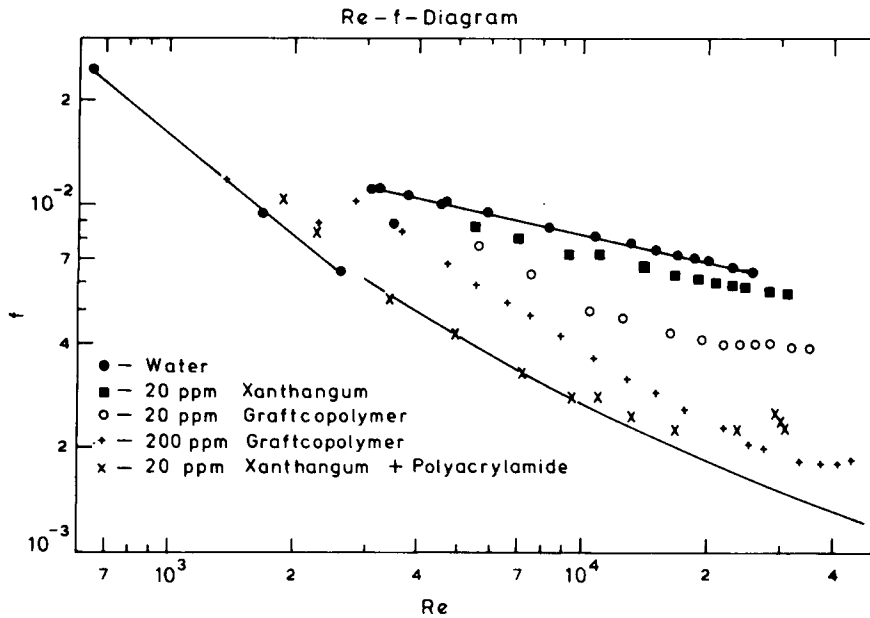


Fig. 6(a). The friction factor vs. Reynolds number characteristics of xanthan gum, graft copolymer and the mixture of graft copolymer and xanthan gum: (●) water; (■) 20 ppm xanthan gum; (○) 20 ppm graft copolymer; (+) 200 ppm graft copolymer; (×) 20 ppm xanthan gum + polyacrylamide.

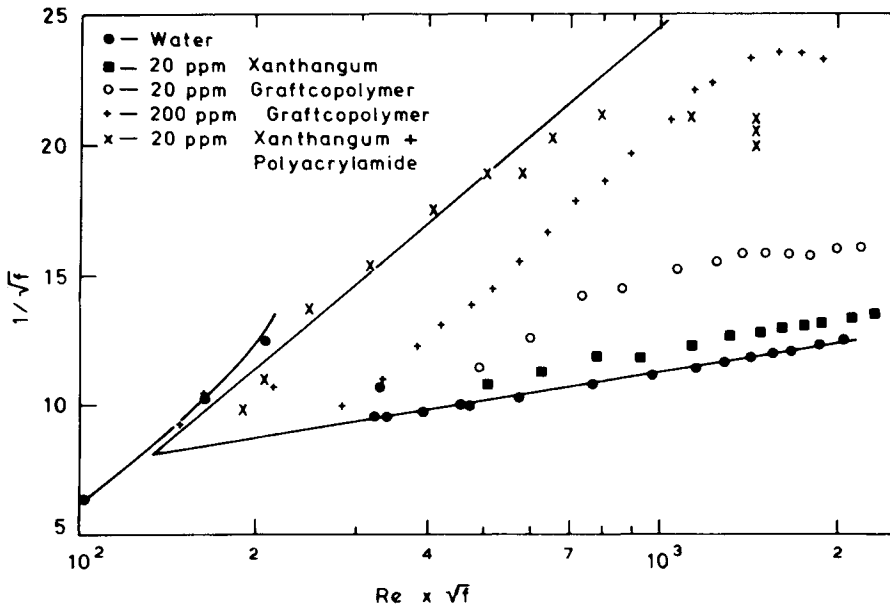


Fig. 6(b). The $1/\sqrt{f}$ vs. $Re\sqrt{f}$ characteristics of xanthan gum, graft copolymer, and the mixture of xanthan gum and polyacrylamide: (●) water; (■) 20 ppm xanthan gum; (○) 20 ppm graft copolymer; (+) 200 ppm graft copolymer; (×) 20 ppm xanthan gum + polyacrylamide.

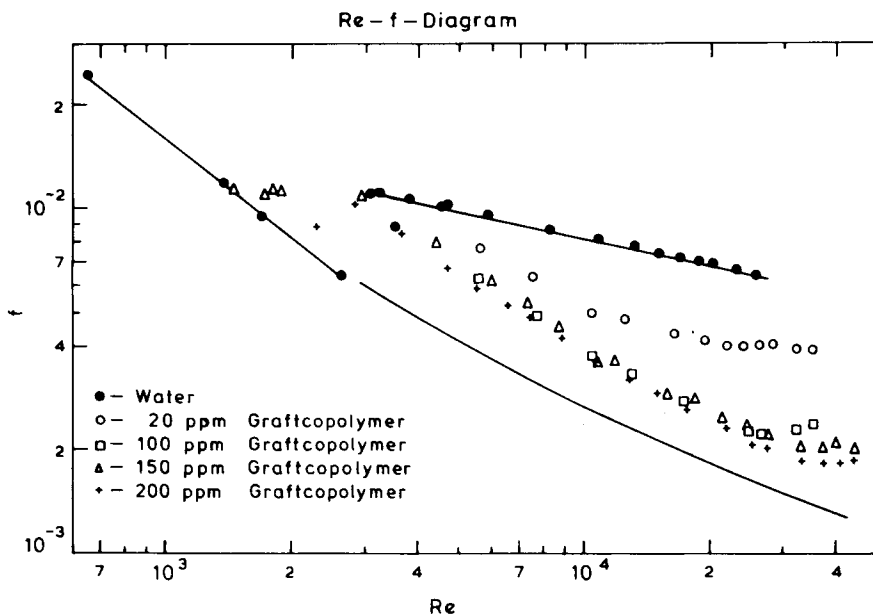


Fig. 7(a). The effect of concentration on friction factor vs. Reynolds number characteristics of graft copolymer and friction factor vs. Reynolds number characteristics of the mixture of xanthan gum and polyacrylamide: (●) water; graft copolymer (ppm); (○) 20; (□) 100; (Δ) 150; (+) 200.

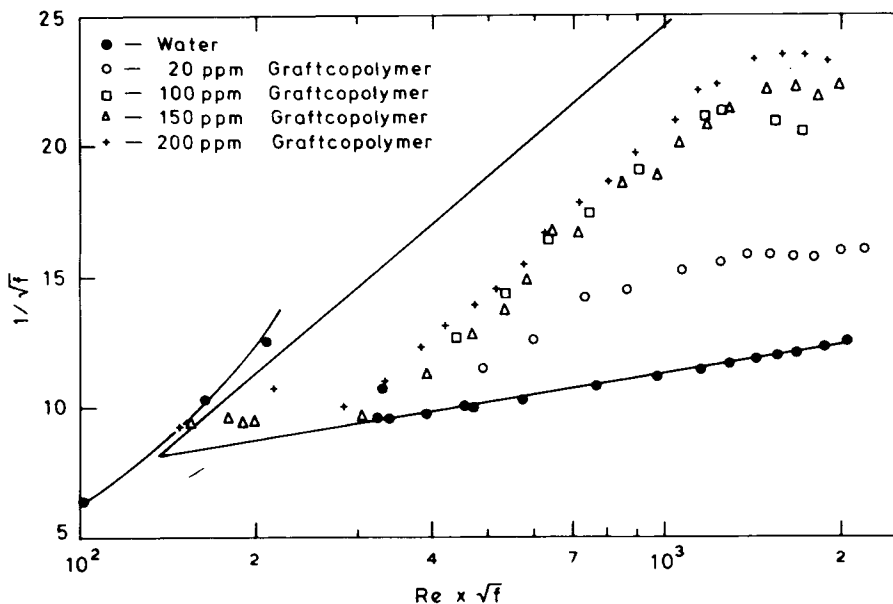


Fig. 7(b). The effect of concentration on $1/\sqrt{f}$ vs. $Re \sqrt{f}$ characteristics of the graft copolymer and $1/\sqrt{f}$ vs. $Re f^{1/2}$ characteristics of the mixture of xanthan gum and polyacrylamide: (●) water; graft copolymer (ppm); (○) 20; (□) 100; (Δ) 150; (+) 200.

reasons:

- i. Linear polymers of large molecular weights are more efficient than the branched one, in which both the polymers may be of shorter lengths.⁵
- ii. Between graft copolymers some crosslinking may also take place which may reduce the drag reduction capability.¹⁷

Shear Stability of Graft Copolymers in Comparison with Xanthan Gum Polyacrylamide and Their Mixtures

In order to examine the shear stability in details, various solutions were forced to pass through the same pipe several times at a constant wall shear stress. As the drag reduction goes on decreasing, with increasing pass number, it is extremely difficult to take measurement at a particular Reynolds number. The wall shear stress equal to 37.5 Pa was chosen below which no degradation is supposed to take place. The shear stability tests were performed in capillary of 6 mm ID and at the concentration of 40 ppm of drag reducers. The ratio of DR at a pass number n and DR_0 at first pass vs. pass number is plotted in Figure 8. The shear stability of xanthan gum and graft copolymer at 40 ppm seems to be similar, although, at highest pass numbers, the graft copolymer seems to be more stable. On the contrary, the polymer mixture described earlier shows a sharp decrease at the first five passes similar to the behavior of the pure polyacrylamide solutions. At higher Reynolds numbers due to the presence of xanthan gum, the mixture shows higher stability than PAM. Lowering the concentration of mixtures to 20 ppm also lowers the shear stability.

The shear degradation which could be detected in the $Re-f$ diagram as a leveling off the curves at higher Reynolds number was observed for polyacrylamide and graft copolymers solutions. At 20 ppm the degradation began

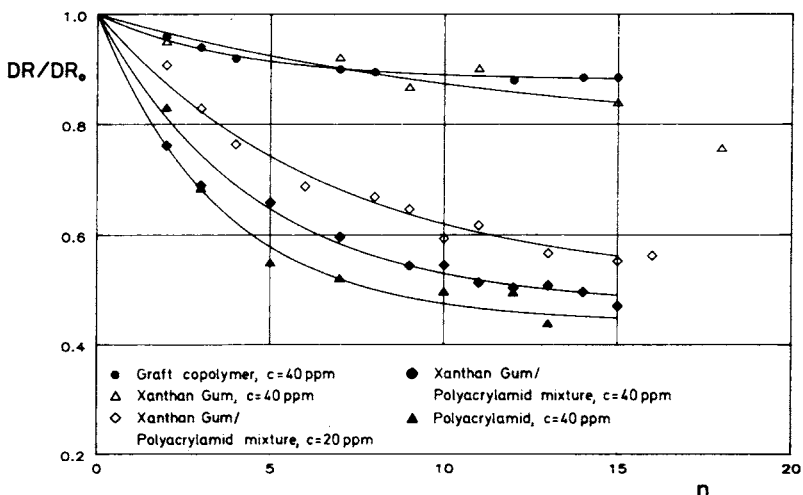


Fig. 8. The effect of pass numbers on the DR/DR_0 for graft copolymer [(●), $c = 40$ ppm], xanthan gum and the mixture of xanthan gum and polyacrylamide. [(◇) $c = 20$ ppm; (◆) $c = 40$ ppm]; (▲) polyacrylamide, $c = 40$ ppm.

at $Re = 21,900$ for the graft copolymer and at $Re = 16,700$ for the mixture. For higher concentrations of the graft copolymer, degradation starts at $Re = 26,665$ (100 ppm), $Re = 33,050$ (150 ppm), and $Re = 37,320$ (200 ppm). The degradation in the turbulent flow has been convincingly demonstrated due to midchain scission of extended molecules.¹⁹⁻²² When branches are present, the shear or extensive forces acting on the polymers are distributed among the individual branches. Any reduction in the molecular weight probably corresponds to that of an individual branch rather than one half of the molecule; hence graft copolymers in general show higher shear stability. In the present case, xanthan gum itself is fairly shear stable. Its shear stability is supposed to be due to strong bonds between monomeric units due to intermolecular and intramolecular interactions. The graft copolymerization reduces its inherent strength by ring opening, but also shifts the scission on branches. Due to the interplay of these two effects, resulting graft copolymers show slightly higher shear stability at higher Reynolds numbers.

To further check the degradation beyond the critical one, 200 ppm solution was first studied up to $Re = 5.5 \times 10^4$ and then again the drag reduction characteristics were measured up to the same Reynolds number in a row (Fig. 9). At the second pass, the onset was considerably pushed to higher Re numbers, meaning thereby to higher onset wall shear stress, although the slope remains the same. This indicates that polymer has degraded. The onset wall shear stress is commonly related to a characteristic length or time of molecule, which in reverse are related to the molecular weight [2]. Mathematically drag reduction ratio vs. time is given by following equation²⁰:

$$\frac{DR}{DR_0} = \left(1 - \frac{DR_\infty}{DR_0}\right) e^{-RT} + \frac{DR_\infty}{DR_0} \quad (6)$$

The constant R is the measure of decay of drag reduction effectiveness and hence of molecular time. By replacing T by n , the same equation also fits the present experimental results. Table III gives the various constants.

To further examine the effect of concentration on the degradation, the polyacrylamide solutions at four concentrations have been studied in a 3.15 mm pipe. Although the wall shear stress was held constant, the degradation was lower than that in the bigger pipe at the same pass number. At concentrations of 20 and 40 ppm, which lie near the maximum drag reduction concentration (10 ppm), the degradation is evident while, beyond 100 ppm, no degradation is observed up to 40 pass numbers. This behavior may be due to two reasons:

- i. The concentrations beyond 100 ppm are much higher than the maximum drag reduction concentration (≈ 10 ppm), so if degradation takes place, there is a reserve of effective large unbroken molecules.⁸ Accordingly, the degradation may be observed at higher pass numbers when this reserve is depleted below the maximum drag reduction concentration.
- ii. The polymer molecules in excess could also exert on each other a shielding effect¹⁹ so that the mechanical stress on a single molecule could not exceed a critical value. In view of this reason, the drag reduction should remain constant even for higher pass numbers.

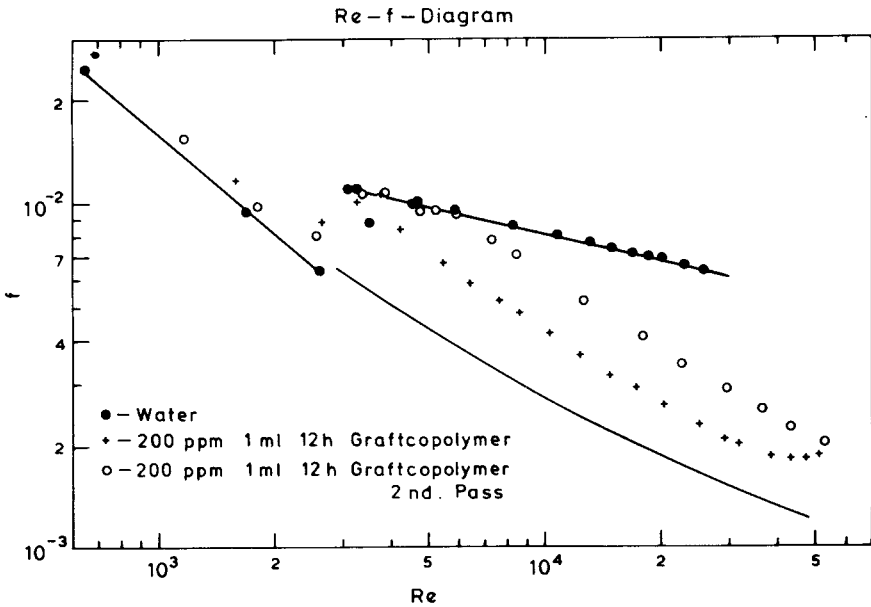
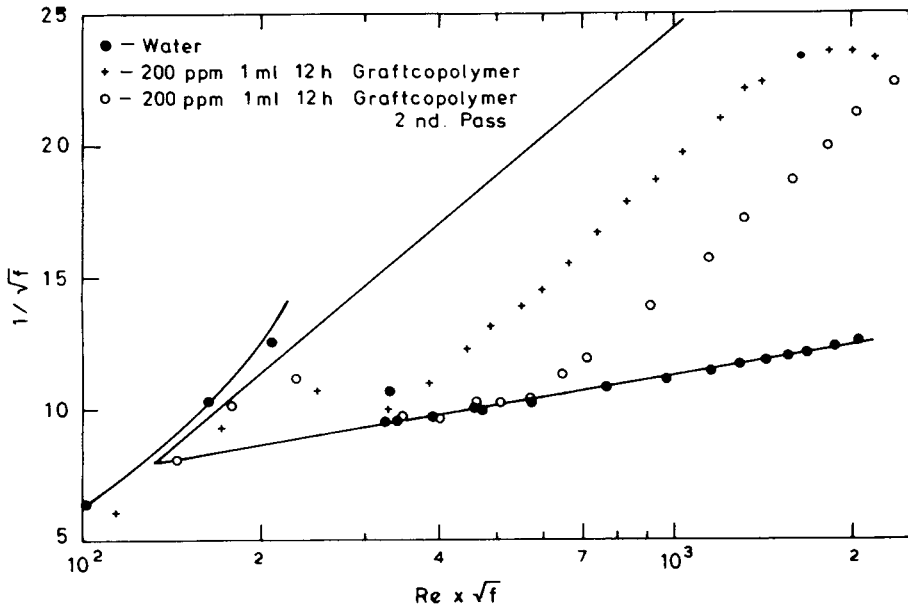


Fig. 9. The effect of degradation on friction factor vs. Reynolds number characteristics for two consecutive circulations of graft copolymer solution through experimental pipe: (●) water; (+) graft copolymer, 200 ppm, 1 mL, 12 h; (○) graft copolymer 2nd pass, 200 ppm, 1 mL, 12 h.

TABLE III
 Constants for the Degradation Behavior at a Constant Wall Shear Stress

Polymer	Concentration (ppm)	DR ₀ (%)	DR _∞ (%)	R
Graft copolymer	40	32.9	29.0	0.25
Xanthan gum	40	24.3	18.7	0.08
Xanthan gum/ polyacrylamide mixture	20	50.3	22.1	0.28
	40	66.8	34.1	0.15
Polyacrylamide	40	75.6	35.6	0.22

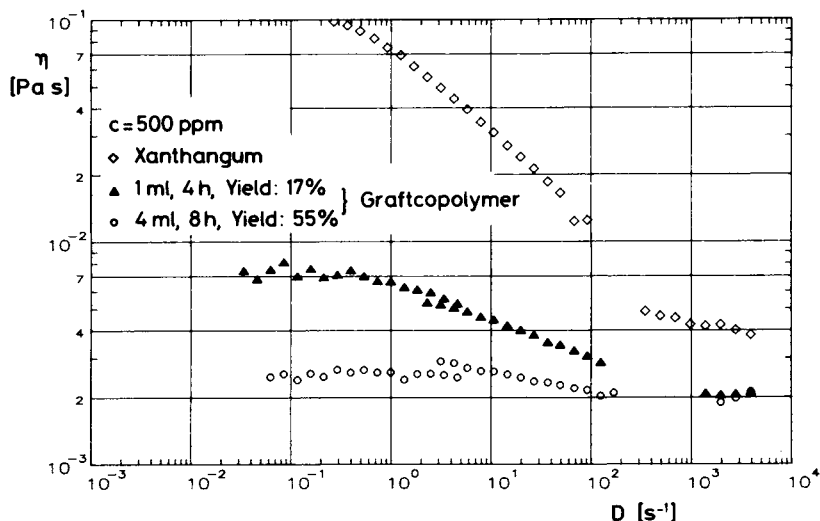


Fig. 10. The variation of shear viscosity as a function of the shear rate for xanthan (\diamond) and graft copolymer solution of 500 ppm concentration [(\blacktriangle) 1 mL, 4 h, yield = 17%; (\circ) 4 mL, 8 h, yield = 55%]. $c = 550$ ppm.

The dependence of shear viscosity on shear rate is shown in Figure 10. The graft copolymers do not show the marked shear thinning properties of xanthan, explained by its rigid structure and strong hydrogen bonding. The flexibility of graft copolymers imparts the low viscosity to their solutions. In the case of first graft copolymer (1 mL, 4 h, yield = 17%) the branches are few but long. While in other graft copolymers, the branches are more but also long due to high yield; hence this results in lower viscosity. At 100–200 ppm concentrations the graft copolymers show nearly shear independent viscosity of 1.4×10^{-3} Pa s. This value corrected with temperature dependence of water viscosity was used to calculate the Reynolds number. At concentrations up to 40 ppm of graft copolymer and for all polyacrylamide solutions, the water viscosity was used.

CONCLUSIONS

It may be concluded on the basis of above investigation that grafting of polyacrylamide chains onto the backbone of xanthan gum increases the drag

reduction effectiveness of xanthan gum over the extended range of Reynolds numbers. The concentration of maximum drag reduction in the case of graft copolymers is obtained around 100 ppm, which is found in case of xanthan gum above 300 ppm. The shear stability of the graft copolymers is similar to that of xanthan gum and much better than those of polyacrylamide and xanthan polyacrylamide mixtures. The ceric-ion-initiated solution polymerization technique may be scaled up to synthesize larger quantities of graft copolymers. The rheological and drag reduction behavior of the graft copolymers depend on the synthesis parameters influencing the number and the length of grafted chains. The graft copolymers with fewer and longer chains of polyacrylamide behave like flexible polymers. The shear stability of graft copolymers and polyacrylamide increases with concentration. It may be possible to make use of graft copolymer for drag reduction in larger pipes.

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