

Drag Reduction Effectiveness, Shear Stability and Biodegradation Resistance of Guar gum-Based Graft Copolymers

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Synopsis

Guar gum is a seed galactomannan and is known to be a shear stable drag reducing agent. However, the aqueous solutions of guar gum are very susceptible to microbial degradation. In the present investigation, seven graft copolymers of guar gum and polyacrylamide have been synthesized and their drag reduction effectiveness, shear stability, and biodegradation resistance have been determined. It has been shown that the drag reduction effectiveness and shear stability of the graft copolymer depend upon the length of the graft and number of grafts in the molecule. None of the graft copolymer solutions show any microbial degradation up to 10 days.

INTRODUCTION

It is well known that the addition of very small amounts of high molecular weight polymers to solvents in turbulent pipe flow reduce the pressure drop at a given flow rate. This phenomenon is known as turbulent drag reduction by polymeric additives. The phenomenon was first reported by Toms¹ in 1948 while investigating turbulent flow of poly(methyl methacrylate) solutions in monochloro benzene. Since then the phenomenon has been studied extensively and several review articles have appeared on this subject.²⁻⁴ It was, however, found that the polymer molecules in the solutions break when subjected to high shearing encountered in turbulent pipe flow and lose their drag reduction ability within a very short time. The search for more effective and shear stable polymers has still been continuing in many laboratories. Kim et al.⁵ have observed that branched polyacrylamide is more shear stable than linear polyacrylamide. Similar results were also obtained by Singh et al.⁶; they have observed that graft copolymers of polyacrylamide and poly(vinyl alcohol) are fairly shear stable.

Certain industrial polysaccharides like guar gum and xanthan gum have been found to be fairly shear stable drag reducing agents.^{7,8} However, these polymers are less effective drag reducers than the synthetic polymers, like poly(ethylene oxide) and polyacrylamide. Furthermore, these polysaccharides also suffer from the drawback that their solutions undergo biological degradation within a very short interval of time from the time of solution preparation, and thus their drag reducing ability is impaired.

The grafting of acrylamide onto the polysaccharides was undertaken mainly to study the drag reduction behavior of graft copolymers. It was contemplated that the grafting of acrylamide onto the polysaccharides will enhance the drag

reduction effectiveness and shear stability and will impart resistance to biological degradation. The graft copolymers of xanthangum have thus been synthesized and studied for their drag reduction effectiveness, shear stability, and biodegradability, and have been reported earlier.⁹

Three graft copolymers of guar gum have been synthesized and studied for their drag reduction effectiveness, shear stability, and biodegradability.¹⁰ In this case, two of the three graft copolymers were found to be much less effective drag reducers compared to guar gum, and only one graft copolymer gave slightly more drag reduction than guar gum. However, all the graft copolymers showed good shear stability, and none of the graft copolymers showed any biodegradation up to 10 days. Hence, it has been endeavored to synthesize new graft copolymers of guar gum with increased drag reduction effectiveness and to study the effect of structural variation on the drag reduction and shear stability. Accordingly, two series of graft copolymers of polyacrylamide and guar gum have been prepared by grafting acrylamide onto guar gum by solution polymerization technique, using ceric ion redox initiator system. In the first series of graft copolymers, the number of grafting sites was varied, and, in the second series of graft copolymers, the number of grafting sites was kept the same and the length of grafts was varied. The graft copolymers were then studied for their drag reduction effectiveness, shear stability, and biodegradability. The present paper describes the results of the above investigations.

EXPERIMENTAL

Materials

Guar gum was procured from Hindustan Gums Ltd., Bhiwani, India, and was subjected to Soxhlet extraction with 95% ethanol for 5 days to remove protein and fat impurities. Acrylamide monomer from S.D. Fine Chemicals, India, was recrystallized from acetone prior to use. Ceric ammonium nitrate, reagent grade, from Loba Chemie, India and nitric acid, analar grade from BDH, India were used as received.

Graft Copolymerization

The graft copolymers have been synthesized by grafting acrylamide onto purified guar gum by radical polymerization method in aqueous medium using ceric ion/nitric acid, redox initiator. The following procedure has been used for the graft copolymerization reaction. One gram of guar gum was dissolved in 200 mL of water in an Erlenmeyer flask. The required quantity of acrylamide was dissolved in 100 mL of water, and the solution was added to the guar gum solution. The mixture solution was stirred by magnetic stirrer. The flask was sealed with a Septum stopper. The nitrogen was then flushed through the solution through a hypodermic needle. Another needle was introduced for outlet of gas. The solution was stirred for 30 min while being bubbled with nitrogen. The required amount of Ce(IV) solution (ceric ammonium nitrate dissolved in 1M HNO₃) was then injected through the stopper by hypodermic syringe. The nitrogen flushing was continued for another 10 min; then the needles were taken out, and flasks were further sealed with Teflon tape. The

TABLE I
The Details of Graft Reaction

Sample no.	Moles in reaction mixture		Guargum (g)	Monomer conversion (%)	[η] (mL g ⁻¹)
	Acrylamide	Ce(iv) ion ($\times 10^3$)			
GAm ₁	0.14	0.02	1	nil	—
GAm ₂	0.14	0.03	1	nil	—
GAm ₃	0.14	0.05	1	78.3	834
GAm ₄	0.14	0.10	1	100.0	688
GAm ₅	0.14	0.20	1	100.0	478
GAm ₆	0.14	0.25	1	87.0	319
GAm ₇	0.14	0.30	1	86.0	280
GAm ₈	0.07	0.05	1	50.0	703
GAm ₉	0.21	0.05	1	66.0	938

^a300 mL of distilled water was used as solvent. Reaction temperature was $30 \pm 1^\circ\text{C}$ and reaction time was 24 h.

^bViscosity measurements were carried out at 30°C using an Ubbelohde viscometer (cs/s: 0.01).

reaction temperature was maintained at $30 \pm 1^\circ\text{C}$ by immersing the flask in water bath. The reaction mixture was stirred occasionally. The reaction was continued for 24 h. The reaction was terminated by injecting 0.5 mL of saturated aqueous solution of hydroquinone. The polymer solution was precipitated in excess of acetone and then filtered. Again copolymer was slurried in acetone followed by filtration and ultimately dried in a vacuum oven at 40°C . Further details of graft copolymerization reaction are given in Table I.

Similarly, control experiments were carried out in the absence of guargum. Other reaction parameters were maintained the same as given in Table I.

Drag Reduction and Shear Stability Studies

The solutions of guargum and the graft copolymers (GAm₃–GAm₉) were tested for their drag reduction effectiveness. The drag reduction studies were performed over a concentration range from 5 to 1000 ppm using turbulent flow rheometer, supplied by Dr. J. W. Hoyt, San Diego, CA. The apparatus operates at nominal Reynolds number of 14,000. In this apparatus, the test solution is forced to pass through a capillary tube of 0.1575 cm diameter; the pressure at two taps can be recorded on the recorder. The experiment is to be repeated with distilled water alone and drag reduction percentage (DR) can be calculated from the formula

$$\text{DR} = \frac{\Delta P_w - \Delta P_p}{\Delta P_w} \times 100$$

where ΔP_w = pressure drop in water and ΔP_p = pressure drop in test solution. The apparatus has been described in detail elsewhere.¹¹ The results are depicted in Figures 1 and 2.

The shear degradation studies have been performed with aqueous solutions of guargum and its graft copolymers (GAm₃–GAm₉) at 100 ppm and 400 ppm concentrations. The studies were performed by recirculation of the same

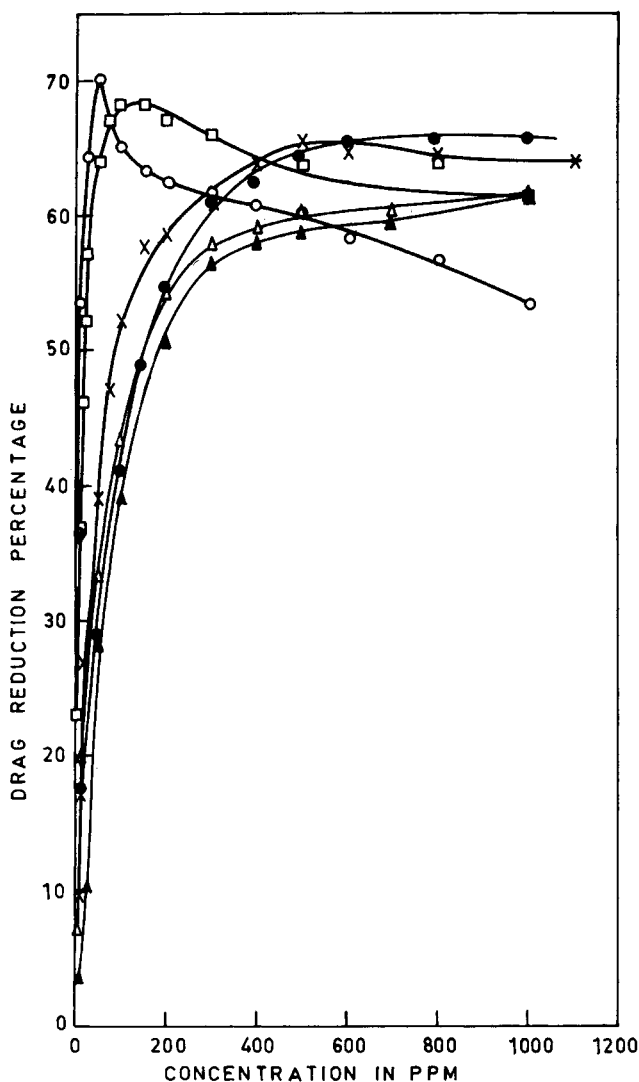


Fig. 1. Plot of drag reduction vs. concentration to study drag reduction effectiveness in the cases of purified guar gum (●), and graft copolymers GAM₃ (○), GAM₄ (□), GAM₅ (×), GAM₆ (△), and GAM₇ (▲).

solution through the test capillary of the turbulent flow rheometer. One recirculation is depicted as a unit pass number. The results are shown in the Figures 3-6.

Biodegradation Studies

As earlier,^{9,10} the viscosity of the solution as a function of time is taken as the criterion for the study of biodegradation. Guar gum and all the graft copolymers were tested for their biodegradability. 0.1% solutions were prepared in the distilled water, and the viscosity measurements were performed using an Ubbelohde viscometer (CS/S = 0.01) at certain interval of times,

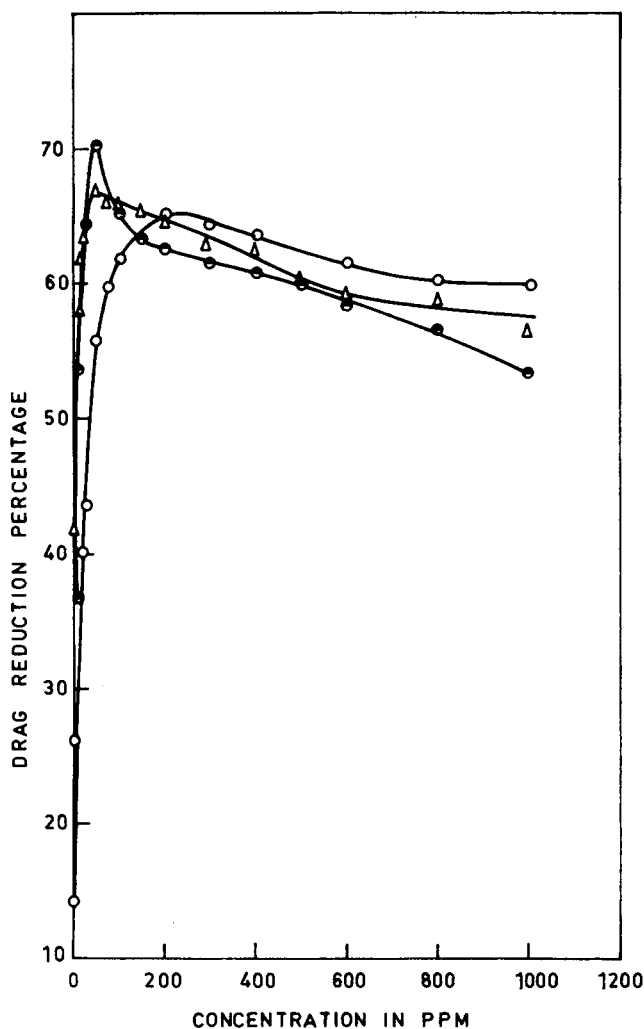


Fig. 2. Plot of drag reduction vs. concentration to study drag reduction effectiveness in the cases of graft copolymers GAM₃ (●), GAM₈ (○), and GAM₉ (△).

over the time period of 10 days. The results have been plotted as relative viscosity vs. time period (Fig. 7).

RESULTS AND DISCUSSION

The details of the graft copolymerization reaction and the yields obtained are given in Table I. Numerous methods have been reported in the literature for initiating graft copolymerization.^{12,13} When the polyol type of polymers, such as polysaccharides, are the substrates, the ceric ion initiation method has been used extensively.¹⁴⁻¹⁶

To study the homopolymer formation, control reactions were carried out in the absence of guar gum. The initiator and monomer concentrations were taken as given in Table I. No homopolymer was formed in any of the control

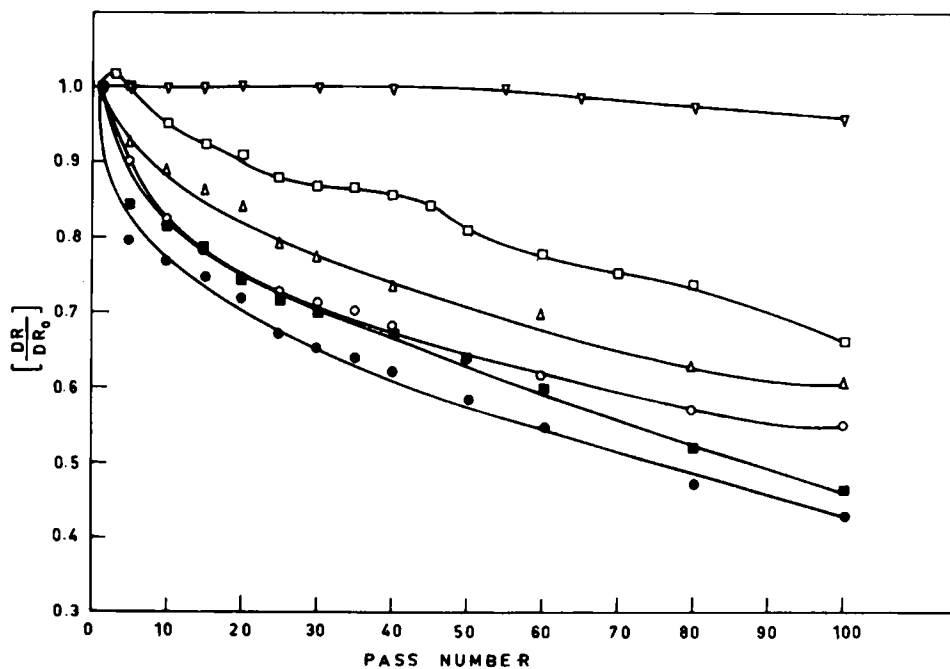


Fig. 3. Plot of DR/DR_0 vs. pass number to study shear stability of 100 ppm solutions of guar gum (∇) and graft copolymers GAm_3 (\square), GAm_4 (Δ), GAm_5 (\circ), GAm_6 (\blacksquare), and GAm_7 (\bullet).

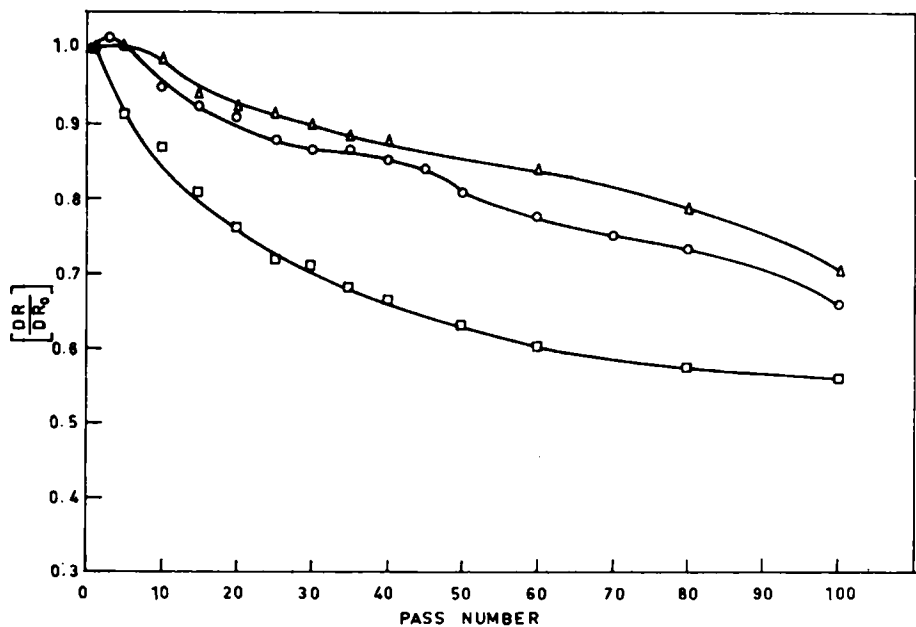


Fig. 4. Plot of DR/DR_0 vs. pass number to study shear stability of 100 ppm solutions of graft copolymers GAm_3 (\circ), GAm_8 (\square), and GAm_9 (Δ).

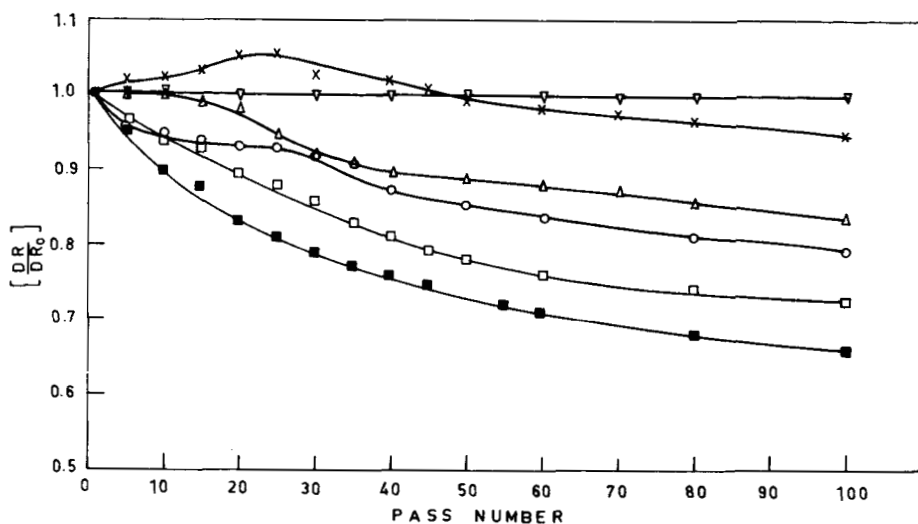


Fig. 5. Plot of DR/DR_0 vs. pass number to study shear stability of 400 ppm solutions of guar gum (∇) and graft copolymers GAM_3 (\times), GAM_4 (Δ), GAM_5 (\circ), GAM_6 (\square), and GAM_7 (\blacksquare).

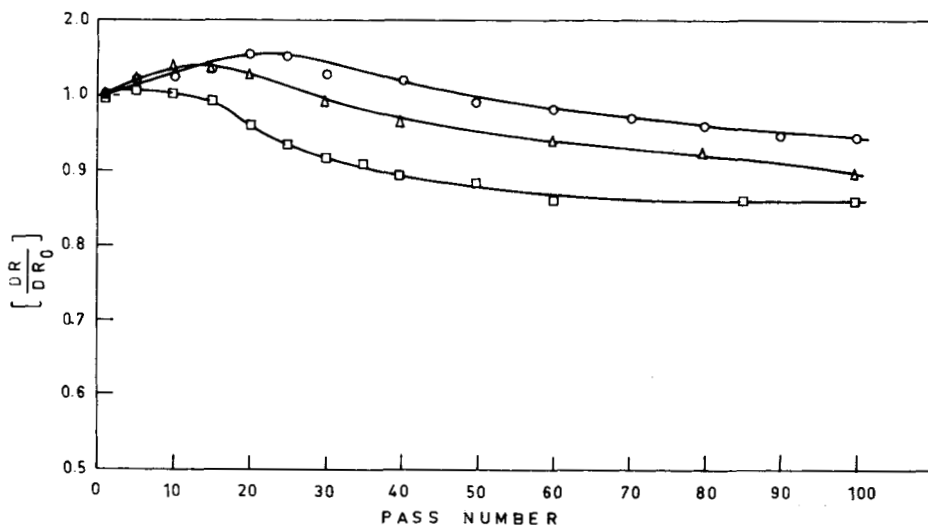


Fig. 6. Plot of DR/DR_0 vs. pass number to study shear stability of 400 ppm solutions of graft copolymers GAM_3 (\circ), GAM_8 (\square), and GAM_9 (Δ).

experiments. These results are in agreement with the results of Owen and Shen.¹⁷ They have observed that control experiments with acrylamide concentrations of less than $2.0M$, nitric acid concentrations of less than $1.2M$, and ceric ion concentrations of less than $0.01M$ resulted in no homopolymerization. This indicates that free radicals are exclusively formed on the backbone molecules, guar gum molecules in this case.

Although the rate of oxidation of hemiacetal unit, i.e., reducing end group, was found to be 360 times that of C_2-C_3 hydroxyls,¹⁸ yet the presence of relatively large number of latter groups in guar gum molecule compared to the

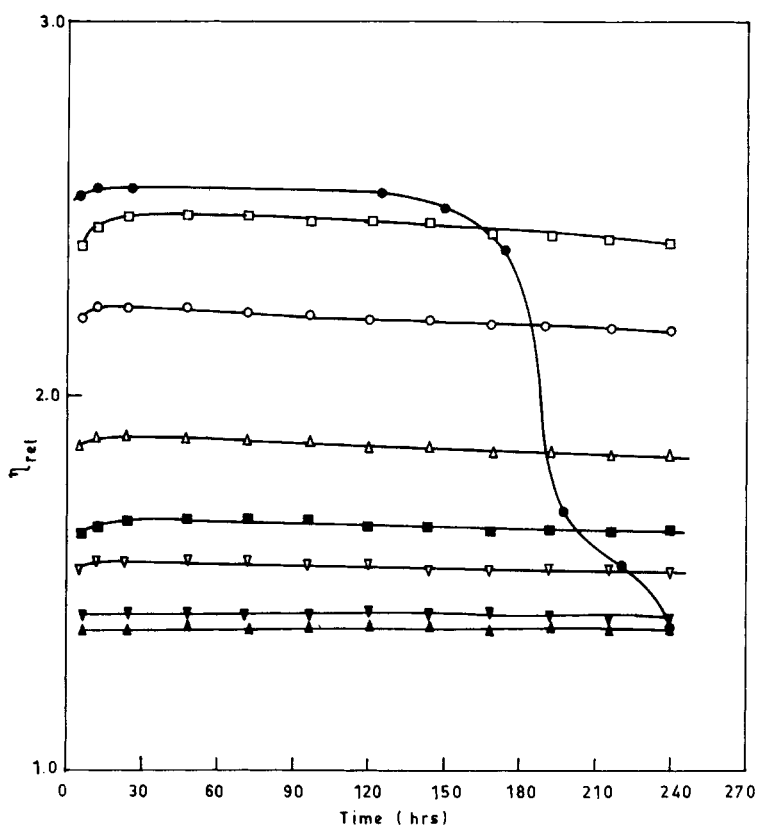


Fig. 7. Relative viscosity (η_{rel}) vs. time period to study biodegradability of 1000 ppm guar gum (●) and graft copolymers: (○) GAm₃; (■) GAm₄; (▽) GAm₅; (▼) GAm₆; (▲) GAm₇; (Δ) GAm₈; (□) GAm₉.

end groups indicates that they are still probable reaction sites. Thus, most probable graft sites should be C₂ and C₃ carbons of both the galactose and mannose units.

In the present investigation, two series of graft copolymers of guar gum and polyacrylamide have been synthesized by grafting acrylamide onto guar gum using ceric ion initiator. In the first series (GAm₃-GAm₇), the graft copolymers have been prepared by keeping the ratio of guar gum and acrylamide constant (1 : 10 w/w) and varying the initiator concentration. With increased initiator concentration, graft copolymers with lower intrinsic viscosities were obtained. The average number of grafting sites per guar gum molecule depends on the ratio of concentration of ceric ion to guar gum in the reaction medium. As the ratio increases, the number of grafting sites increases. The length of graft, on the other hand, depends on the ratio of concentration of acrylamide monomer to ceric ion. As the ratio decreases the length of graft also decreases. Thus, when the ceric ion concentration was increased, keeping the concentration of guar gum and acrylamide in the system constant, the graft copolymers with more number of grafts per backbone molecule were obtained, but the length of graft decreased; hence the polymers with lower intrinsic viscosity were obtained.

In the other series (GAM₃, GAM₈, GAM₉), the ratio of concentrations of ceric ion to guar gum in the reaction system was kept constant, thereby keeping the grafting sites per backbone molecule the same, the ratio of concentration of acrylamide monomer to ceric ion was increased. Thus, in this series the number of grafting sites was kept constant for all three copolymers whereas the length of the graft was varied. Thus, by increasing the acrylamide concentration graft copolymers with longer grafts were obtained. This is supported by the fact that the intrinsic viscosity of graft copolymers was found to be increasing with increase in the acrylamide concentration in the reaction system. Similar results were obtained by Meister¹⁹ for synthesis of graft copolymers of starch.

The guar gum and its graft copolymers were tested for their drag reduction effectiveness and the results are plotted in Figures 1 and 2. All the graft copolymers except GAM₆ and GAM₇ were found to be more effective drag reducers than purified guar gum. It was found in all the graft copolymers except GAM₆ and GAM₇ that drag reduction effectiveness increases with increasing concentration, attains a maximum value, and then decreases with increase in the concentration. Thus, the maximum drag reduction was obtained at concentrations of 50, 75, 400, 200, and 50 ppm in the cases of GAM₃, GAM₄, GAM₅, GAM₈, and GAM₉ respectively. Lyashev et al.²⁰ ascribed this decrease in the drag reduction with increase in the concentration beyond the optimum level to the association of molecules. As the association of molecules starts, the decrease in the drag reduction occurs. Chang and Darby^{21,22} studied the rheology of drag reducing polymers and explained the effect of concentration on the drag reduction in the following way.

Both elastic and viscous properties increase in magnitude with concentration. These properties as well as the drag reduction increase with concentration due to the presence of very high molecular weight species, although not in the same ratio. They have shown that degree of drag reduction increases with N_{DC} , a dimensionless relaxation time parameter (Deborah number). N_{DC} was found to be dependent upon viscosity (η_0) and elasticity (λ), and the following relationship exists between these three parameters:

$$N_{DC} = (\lambda/\eta_0^4)^K \quad (1)$$

where $K = 1/12$.

Thus, the degree of drag reduction increases with increase of elasticity (λ) and decreases with increase in viscosity (η_0). As both these parameters are concentration-dependent, the degree of drag reduction also depends on concentration, and there should be an optimum concentration corresponding to maximum drag reduction. Our results of drag reduction effectiveness and shear stability studies on graft copolymers amply support the above view.

In the case of purified guar gum, it was observed that the drag reduction increases with concentration, attains maximum value at 600 ppm, and remains constant with further increase in the concentration up to 1000 ppm, while, in the cases of GAM₆ and GAM₇, the drag reduction was found to be increasing with increasing concentration and has not reached its maximum value even up to 1000 ppm.

In the first series of graft copolymers of guar gum, in which the number of grafting sites was increased and the length of graft was decreased, it has been

observed that the graft copolymers with less number of longer grafts per backbone molecule were more DR-effective than the graft copolymers with more number of short grafts per backbone molecule. Thus, the drag reduction effectiveness was found to be in the following order:

$$\text{GAm}_3 > \text{GAm}_4 > \text{GAm}_5 > \text{GAm}_6 > \text{GAm}_7$$

Higher drag reduction effectiveness of GAm_3 can be explained by the large radius of gyration of GAm_3 molecule because of the long and flexible grafted polyacrylamide chains. As the length of graft decreases, the radius of gyration also decreases, which is reflected by a decrease of DR effectiveness as we go from GAm_3 to GAm_7 . Drag reduction effectiveness of graft copolymers will depend on the length of its grafts: Longer grafts will contribute more towards drag reduction, and shorter grafts will have less of a contribution in drag reduction. Below a certain length of graft, the contribution of grafts in drag reduction effectiveness of graft copolymer will be insignificant. However, number of such short grafts per backbone molecule will significantly contribute to the molecular weight of the molecule. Now, observation that the drag reduction effectiveness of GAm_6 and GAm_7 is less than that of guar gum can be explained on the basis that the short grafts contribute more towards increase in molecular weight of the molecule without contributing much towards drag reduction. As a result, the effective concentration (no. of drag reducing molecules per unit weight of substance) will be much less in GAm_6 and GAm_7 . As a result, the drag reduction by GAm_6 and GAm_7 was found to be less than that of guar gum at equal concentrations.

In the second series of graft copolymers the number of grafts was kept same. In the three graft copolymers GAm_8 , GAm_3 , and GAm_9 , the length of grafts was ascending in order; the drag reduction effectiveness was also found to be in the same order, i.e.,

$$\text{GAm}_9 > \text{GAm}_3 > \text{GAm}_8$$

Once again, this behavior can be explained on the basis of presence of longest PAM grafts in GAm_9 and shortest grafts in GAm_8 . GAm_3 lies in between.

Shear degradation studies were performed up to 100 pass number with solutions of guar gum and its graft copolymers. Concentrations used were 100 ppm (Figs. 3 and 4) and 400 ppm (Figs. 5 and 6). The degradation rates were higher at 100 ppm than at 400 ppm (Table II). These results are in accordance with the results obtained by Nakano and Minoura²³ and Yu et al.²⁴ Nakano and Minoura studied shear degradation of polystyrene and poly(methyl methacrylate) solutions prepared in various solvents. They observed that the rate of shear degradation increases with decrease in the concentration. Yu, Zakin, and Patterson²⁴ have studied the effect of concentration on shear degradation of polyisobutene in aromatic mineral oil. They have explained their results on the assumption that "stretching" of the individual molecules could be a factor involved in degradation. The inhibition of molecular extension by surrounding molecules will be greater in more concentrated solutions, which explains the negative dependence of degradation on concentration.

In the first series of graft copolymers, the rate of shear degradation was found to be in the following order, $\text{GAm}_7 > \text{GAm}_6 > \text{GAm}_5 > \text{GAm}_4 >$

TABLE II
 Computed Values of Constants *A* and *B* [Eq. (2)] for Graft Copolymers

Polymer	Concentration of the solution (ppm)	<i>A</i>	<i>B</i>	Correlation coefficient
GAm ₃	100	0.9887	3.99×10^{-3}	-0.9928
	400	—	—	—
GAm ₄	100	0.9423	4.979×10^{-3}	-0.972
	400	1.0037	2.074×10^{-3}	-0.966
GAm ₅	100	0.8969	5.983×10^{-3}	-0.945
	400	0.9765	2.329×10^{-3}	-0.9793
GAm ₆	100	0.8679	6.318×10^{-3}	-0.9521
	400	0.9663	3.525×10^{-3}	-0.9600
GAm ₇	100	0.8212	6.444×10^{-3}	-0.8955
	400	0.9284	4.1629×10^{-3}	-0.937
GAm ₈	100	0.8992	5.99×10^{-3}	-0.9332
	400	0.9977	2.005×10^{-3}	-0.9290
GAm ₉	100	0.9954	2.984×10^{-3}	-0.9882
	400			

GAm₃, GAm₃ being the most shear stable and GAm₇ being the least stable among the series. This can be explained on the basis of the chain scission concept. According to Beuche's midpoint break theory,²⁵ polymer chain breaking does not take place at random along the chain but occurs predominantly in the central portion of the chain. This theory of chain scission was well supported by the results obtained by Zakin and Hunston²⁶ with polystyrene in toluene and the results obtained by Horn and Merrill²⁷ for the degradation behavior of polystyrene in chloroform. In the case of GAm₃, where the grafted branches are sufficiently long, the shear forces acting on the polymer are distributed among the individual branches. Any reduction in molecular weight, when it occurs, would probably correspond to that of an individual branch rather than one-half of the molecule and the scissioned molecules would still be effective in drag reduction.

In the case of GAm₇, where numerous small branches have been grafted onto the guar gum molecule, the branches being very short and molecular weight being low, the shear forces acting on polymer are concentrated on the main chain. Any reduction in the molecular weight due to degradation will therefore correspond to that of the main chain rather than the graft branches. Thus, the chain scission will result in formation of smaller molecules, less effective or noneffective as a drag reducer. Similar results were also obtained for a second series of graft copolymers. Graft copolymer with shorter grafts was found to be the least stable, and graft copolymer with longer branches was found to be the most shear stable among the series. The rate of shear degradation was found to be in the following order: GAm₈ > GAm₃ > GAm₉.

In the cases of 100 ppm and 400 ppm solutions of GAm₃ and 400 ppm solutions of GAm₉, it was observed that in the initial stage of shearing (first few pass numbers) the drag reduction effectiveness was found to be increased; after that, again they showed normal behavior, i.e., loss of drag reduction effectiveness with further shearing. Darby and Chang²² have shown that the

degree of drag reduction increases with increase in Deborah number N_{DC} , which itself depends upon elasticity and viscosity [eq. (1)]. For more concentrated solutions, the effect of degradation on drag reduction can also be explained in terms of the relative changes in the parameter η_0 and λ . With degradation both η_0 and λ decrease, but, since N_{DC} is more sensitive (fourth order) to changes in η_0 , so that the net effect is an increase in drag reduction with degradation. Once the viscosity of solution approaches to that of solvent viscosity, then there is not much change in η_0 but elasticity continues to decrease and thus drag reduction starts decreasing. This explains the loss of drag reduction if the degradation is continued. The present results support the above theory of drag reduction given by Chang and Darby.^{21,22}

The plots of $\ln(DR/DR_0) = F(N)$ were found to be linear in all the cases except 100 and 400 ppm GAm₃ and 400 ppm GAm₉, and thus it follows that the degradation can be best explained mathematically by the empirical equation

$$\frac{DR}{DR_0} = Ae^{-BN} \quad (2)$$

where DR is the drag reduction at a particular pass number. DR_0 is the initial drag reduction, N is the pass number, and A and B are empirical parameters. Values of A and B were computed from least square fit and are given in Table II. B gives the rate of shear degradation.

All the graft copolymers were found to be less shear stable than guar gum. This might be due to incorporation of polyacrylamide grafts into the guar gum molecule in the graft copolymers. Polyacrylamide chains are more prone to degradation than the robust guar molecule. In graft copolymers, shearing causes rupture of these chains, thereby decreasing the drag reduction effectiveness of the graft copolymer, whereas the robust guar gum molecule offers more resistance to shear degradation.

The biodegradation studies have been carried out for a period of 10 days (Fig. 7). Guar gum solution, like other polysaccharide solutions, is very prone to biodegradation, and it was found that, within 24 h of its preparation, it starts degrading and at the end of 10 days the solution showed considerable loss of viscosity. All the graft copolymers were similarly studied for biodegradation, and no graft copolymer solution showed any loss of viscosity up to 10 days (Fig. 7). These results show that the graft copolymers are less susceptible to biodegradation. This is in agreement with the fact that by altering the structure of polysaccharide molecules and incorporating relatively inert polyacrylamide chains in graft copolymer, it can be made less susceptible to bacterial attack.²⁸

Thus, it can be concluded that, by incorporation of polyacrylamide graft onto polysaccharide molecule through graft copolymerization, the drag reduction effectiveness can be enhanced and biodegradation can be minimized.

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APPENDIX: NOMENCLATURE

PGG	purified guar gum
GAM ₃ , GAM ₄ , GAM ₅ , GAM ₆ , GAM ₇ , GAM ₈ , GAM ₉	graft copolymers
ppm	parts per million
DR, DR%	drag reduction percentage
DR ₀	initial drag reduction
N _{DC}	Deborah number
N	pass number
λ	elasticity
η ₀	viscosity
η _{rel}	relative viscosity
[η]	intrinsic viscosity

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