Drag Reduction Characteristics of Graft Copolymers of Xanthangum and Polyacrylamide

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Synopsis

Graft copolymers of xanthangum and polyacrylamide have been prepared by grafting acrylamide onto xanthangum using ceric-ion-initiated solution polymerization technique. These graft copolymers have been tested for their drag reduction effectiveness, shear stability, and biodegradability. It has been shown that the grafting enhances the drag reduction effectiveness and biodegradation resistance of xanthangum considerably.

INTRODUCTION

The phenomenon of turbulent drag reduction by polymer additives has been studied extensively and several review articles have appeared on this subject.[1-3] The polymeric drag reducing agents, however, suffer from the drawback that they get degraded in the prolonged turbulent flow and thus lose their drag reduction effectiveness.[4,5] Kim et al.[6] have observed that branched polyacrylamide is more shear stable than linear polyacrylamide. However, relatively scant attention has been paid to the study of drag reduction characteristics of branched polymers and graft copolymers[7,8] in which the macromolecule contains two structurally different polymers.

Although industrial polysaccharides, like guargum and xanthangum, are fairly shear stable drag reducing agents, their solutions are highly susceptible to biological degradation. It has been envisaged[9] that the grafting of acrylamide onto these polysaccharides will enhance the drag reduction effectiveness, shear stability, and resistance to biological degradation. The graft copolymers of polyacrylamide onto guargum have been synthesized and studied for their drag reduction effectiveness, shear stability, and susceptibility to biological attack. The results have been reported earlier.[10] The similar studies have been extended to the graft copolymers of xanthangum.

Xanthangum, an extracellular polysaccharide from xanthomonas compestris, provides aqueous solutions with properties that are extremely useful in large number of industrial applications. Kenis and Hoyt[11] have studied the drag reduction characteristics of xanthangum and found it to be relatively stable drag reducing agent. In this investigation, graft copolymers of polyacrylamide and xanthangum have been prepared by grafting acrylamide onto xanthangum by ceric-ion-initiated radical polymerization in aqueous medium. Four graft copolymers of xanthangum have been prepared and studied for their drag reduction effectiveness, shear stability, and biodegradability. The present paper describes the results of the above investigation.

EXPERIMENTAL

Materials

Xanthangum (Keltrol, food grade), was procured from Kelco Division of Merck and Co. (U.S.A.). It 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 xanthangum by radical polymerization method in aqueous system using ceric ion, nitric acid redox initiator. The following procedure has been adopted in carrying out the reactions. One gram of xanthangum was dissolved in distilled water (200 mL) in an Erlenmeyer flask. The required quantity of acrylamide monomer was dissolved in distilled water (100 mL) in another flask, and the solution was added to the xanthangum solution in the Erlenmeyer flask. The mixture solution was stirred by magnetic stirrer. The flask was then sealed with septum stopper. Nitrogen gas was then flushed into the solution through a hypodermic needle. The solution was stirred for 30 min while being bubbled with nitrogen. The required amount of ceric ion solution (ceric ammonium nitrate dissolved in $1M$ HNO_3 solution) was then injected through the stopper by hypodermic syringe. The nitrogen flushing was continued for another 20 min; then the needles were taken out, and flasks were further sealed with Teflon tape. The reaction temperature was maintained at $30 \pm 1°C$ by immersing the flask in constant temperature bath. The reaction mixture was stirred occasionally. The reaction was continued for 24 h and then terminated by injecting 0.5 mL of saturated aqueous hydroquinone solution. The reaction product was precipitated in excess of isopropanol and filtered through the sintered glass filter. The precipitate was again slurried in acetone followed by filtration and finally the precipitate was dried in vacuum

TABLE I
Details of Graft Reaction[a]

Sample no.	Moles in reaction mixture		Xanthangum (g)	Monomer conversion (%)	$[\eta]$ (mL g^{-1})[b]
	Acrylamide	Ce(IV) ion $\times 10^3$			
XAm$_2$	0.14	0.10	1	47.5	1884
XAm$_3$	0.14	0.20	1	86.5	1026
XAm$_4$	0.14	0.30	1	92.0	812
XAm$_5$	0.14	0.40	1	98.8	528

[a]Distilled water (300 mL) was used as solvent. Reaction temperature was $30 \pm 1°C$, reaction time was 24 h.

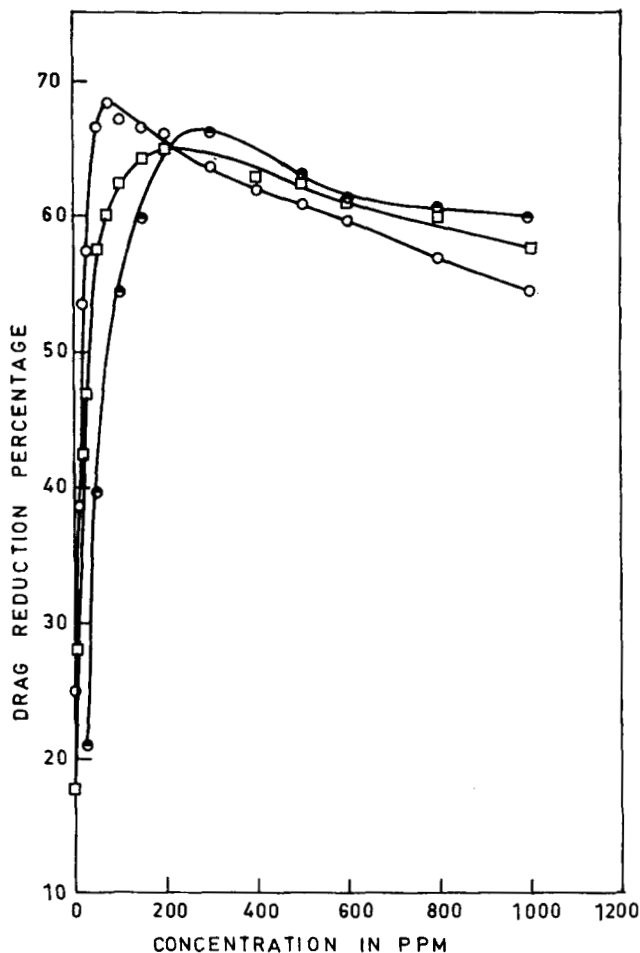[b]Viscosity measurements were carried out at 30°C using Ubbelohde viscometer (CS/S: 0.01).

Fig. 1.   Drag reduction percentage vs. concentration to study drag reduction effectiveness: (○) XAm$_2$; (□) XAm$_4$; (◕) xanthangum (XG).

oven at 40°C. The details of the reaction conditions have been given in Table I.

Drag Reduction Studies

The solutions of xanthangum and its graft copolymers, XAm$_2$–XAm$_5$, were tested for their drag reduction effectiveness. The drag reduction studies were performed over a concentration range from 5 to 1000 ppm at nominal Reynolds number of 14,000, by turbulent flow rheometer, supplied by Dr. J. W. Hoyt, San Diego, CA. The results have been depicted in Figures 1 and 2.

Shear Stability Studies

The shear degradation studies have been performed on aqueous solutions of xanthangum and its graft copolymers (XAm$_2$–XAm$_5$) at various concentra-
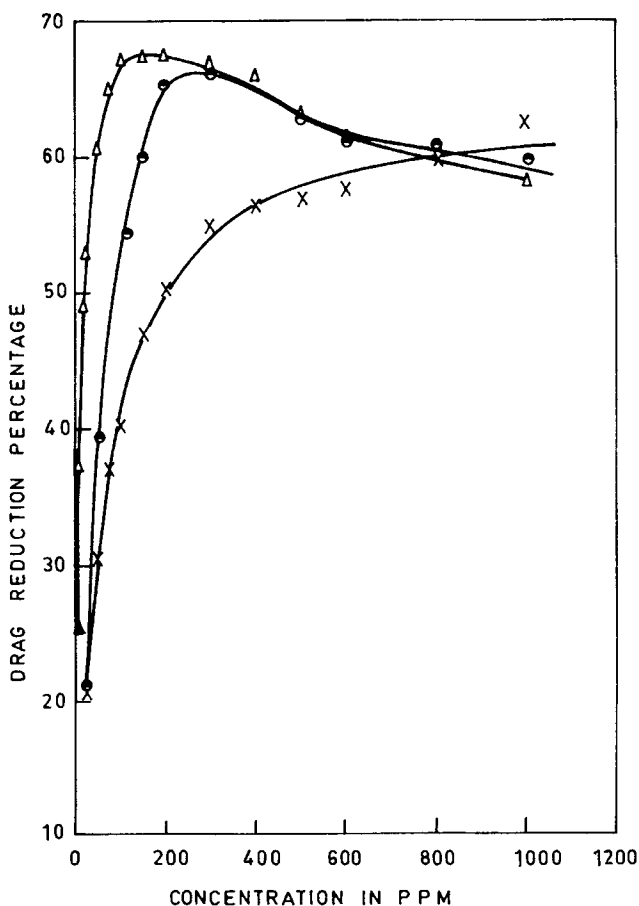
Fig. 2.   Drag reduction percentage vs. concentration to study drag reduction effectiveness: (△)
XAm₃; (X) XAm₅; (●) xanthangum (XG).

tions. The studies were undertaken by recirculation of the same solution
through the test capillary of the turbulent flow rheometer. One recirculation
is depicted as an unit pass number. The results have been shown in the
Figures 3–6.

Biodegradation Studies

The viscosity of the solution as a function of time is taken as the criterion
for the study of biodegradation. All the graft copolymers synthesized were
tested for their biodegradability. 0.1% solutions were prepared in the distilled
water and the viscosity measurements were performed using Ubbelohde
viscometer (cs/s: 0.01) over the time period of 10 days. All measurements were
carried out at 30°C. The results were plotted as relative viscosity vs. time
period (Fig. 9).

In the case of xanthangum, viscosity measurements were carried out by
coaxial cylinder type rotary viscometer, Rheotest II (MLW, GDR). The
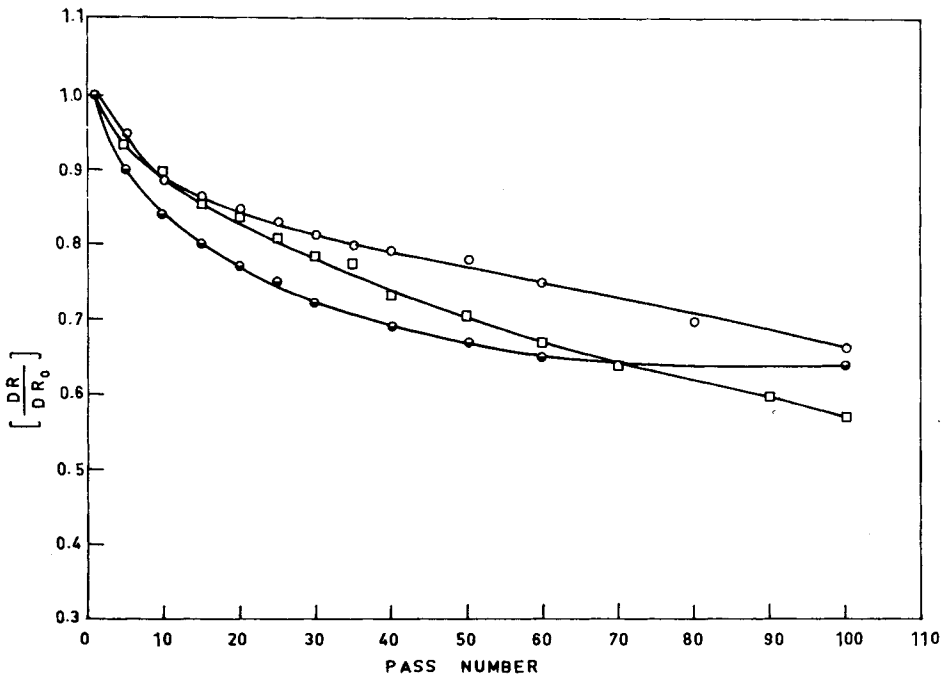viscosity measurements were carried out with 0.1% solution of xanthangum in

Fig. 3. $[DR/DR_0]$ vs. pass number to study shear stability of 100 ppm solutions of: (○) XAm_2; (◖) xanthangum (XG); (□) XAm_4.
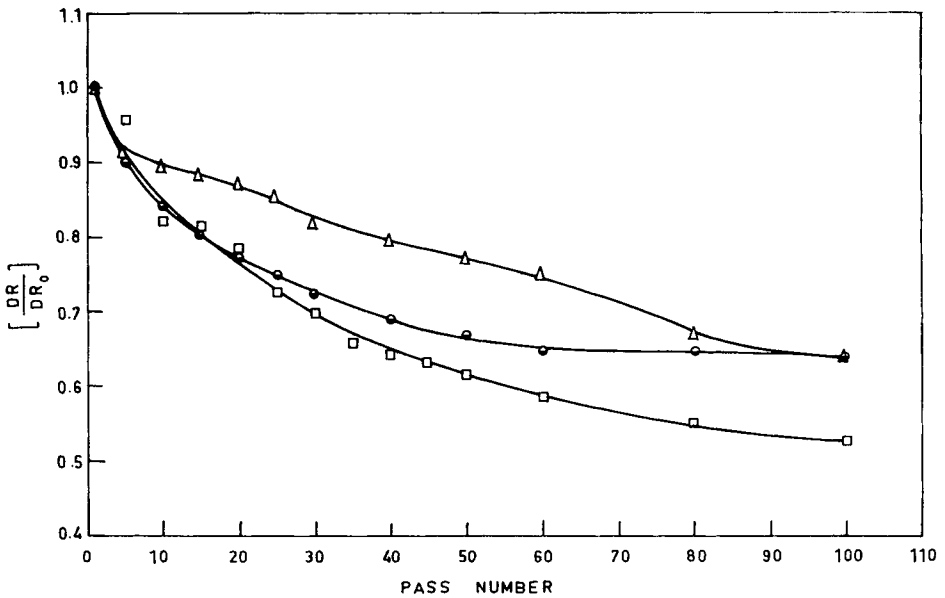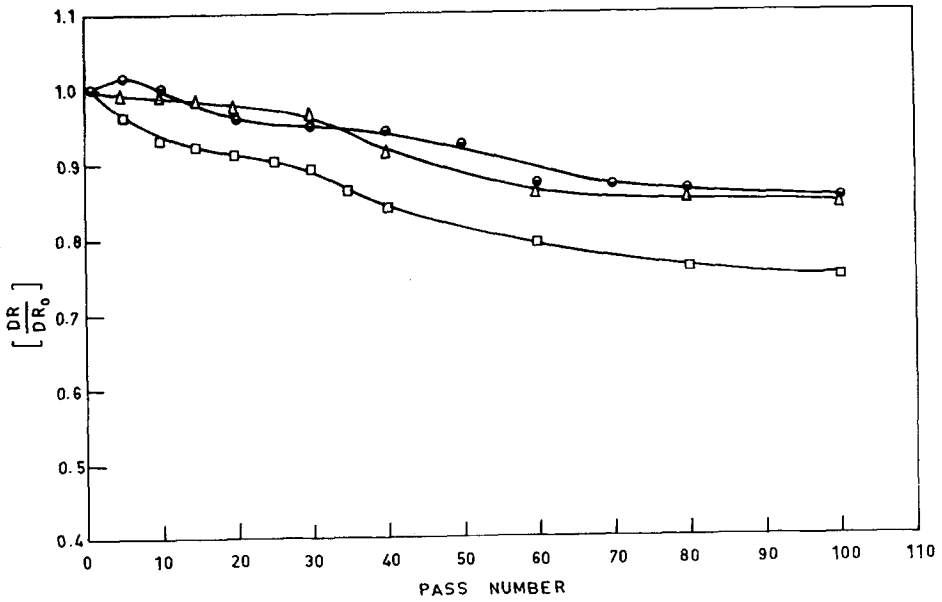

Fig. 4. $[DR/DR_0]$ vs. pass number to study shear stability of 100 ppm solutions of: (◖) xanthangum (XG); (△) XAm_3; (□)XAm_5.

Fig. 5. [DR/DR$_0$] vs. pass number to study shear stability of 400 ppm solution of: ($\bigcirc$) xanthangum (XG); ($\triangle$) XAm$_3$; ($\square$) XAm$_5$.
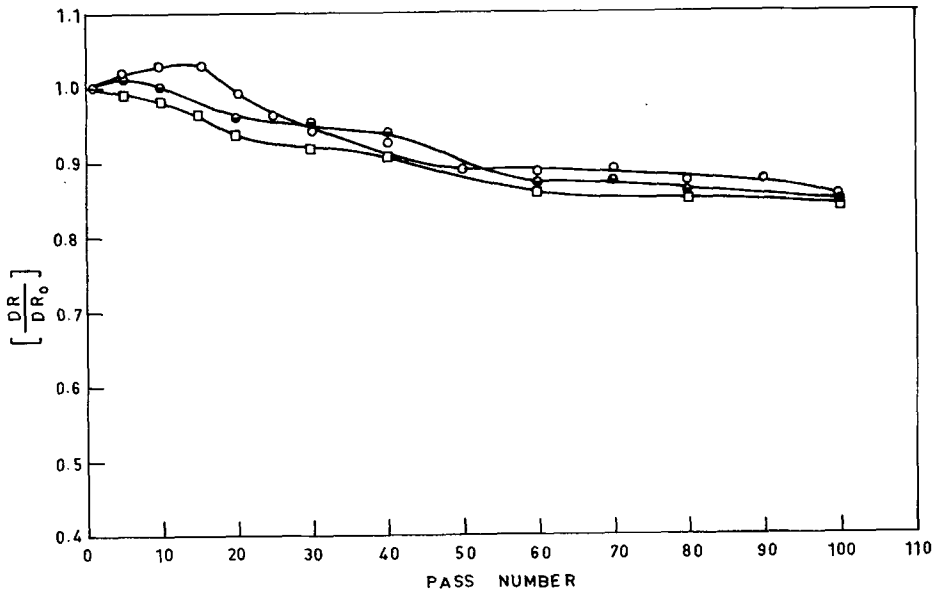
Fig. 6. [DR/DR$_0$] vs. pass number to study shear stability to 400 ppm solutions of: ($\bigcirc$) XAm$_2$; ($\square$) XAm$_4$; ($\bullet$) xanthangum (XG).

distilled water at shear rate of 1312 S^{-1} and temperature 30°C. The results were plotted as absolute viscosity vs. time period in Figure 10.

RESULTS AND DISCUSSION

The details of the graft copolymerization reaction and the yields obtained are given in the Table I. Numerous methods have been reported in the literature for initiating graft copolymerization.[12,13] When polyol type of polymers, such as polysaccharides are the substrates, the ceric ion initiation method has been used extensively.[14-16] Since the free radicals are formed exclusively on the chains of the substrate in this method, the grafting efficiency is higher in this method compared to other redox systems.[17]

In the present investigation, four graft copolymers of xanthangum and polyacrylamide have been prepared by grafting acrylamide onto xanthangum using ceric ion initiator. All the graft copolymers have been prepared by keeping the ratio of xanthangum and acrylamide constant (1 : 10 w/w) and varying the initiator concentration. With increased initiator concentration, graft copolymers with lower intrinsic viscosities were obtained. These results are again in accordance with results obtained by Meister[18] on graft copolymers of starch. By increasing the initiator concentration, the number of grafts per backbone molecule increases but the length of grafts decreases; hence, the polymers with lower intrinsic viscosity were obtained.

The graft copolymers (XAm_2–XAm_5) and xanthangum were tested for their drag reduction effectiveness and the results have been plotted in Figures 1 and 2. It has been found that xanthangum and all the graft copolymers except XAm_5 showed enhancement in the drag reduction with the increase in the concentration reaching a maximum value. Beyond this concentration, the drag reduction was found to be decreasing with further increase in the concentration. Lyashev et al.[19] 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[20] studied the rheology of drag reducing polymers and explained the effect of concentration on 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. Since turbulent drag increases with an increase in viscosity and decreases with an increase in elasticity, there should be an optimum concentration corresponding to maximum drag reduction. Our results of drag reduction effectiveness studies as well as shear stability studies amply support the above view.

The graft copolymer XAm_5 shows continuous increase in drag reduction with increase in concentration up to 1000 ppm, which means the maximum drag reduction level is above 1000 ppm concentration.

It is apparent from the Figures 1 and 2 that, at lower concentrations, XAm_2, XAm_3, and XAm_4 are more effective drag reducing agents than xanthangum while XAm_5 was found to be less effective drag reducing agent. By increasing the initiator concentration in the reaction mixture and keeping all other parameters constant, graft copolymers with larger number of grafts
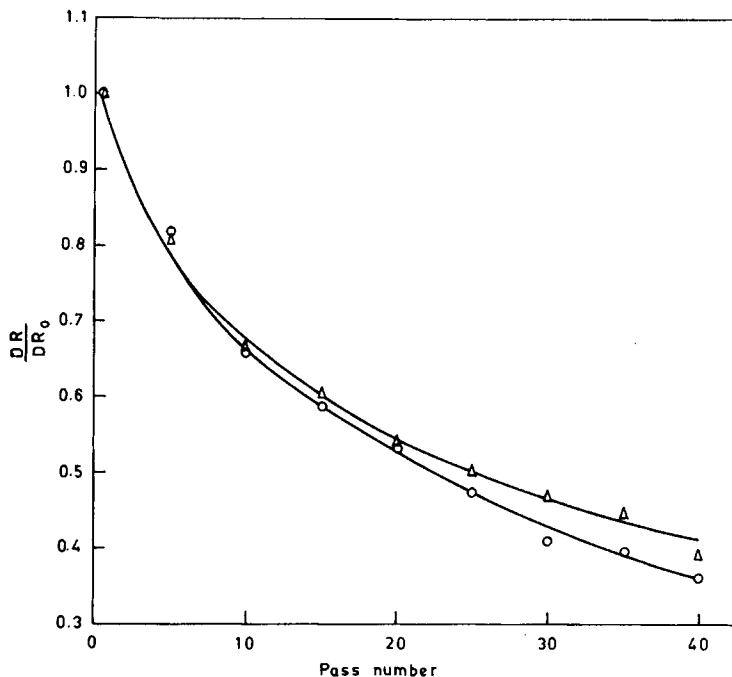
Fig. 7. [DR/DR$_0$] vs. pass number to study shear stability of 22 ppm XAm$_3$ (○) and 35 ppm of XAm$_4$ (△) solutions.

per backbone molecule are obtained as higher number of grafting sites are generated on the backbone. However, the length of graft decreases as the monomer to backbone ratio was kept constant. The drag reduction effectiveness was found to be decreasing with increasing number of grafts per backbone molecule and with decreasing the length of graft. Thus the drag reduction effectiveness was found to be in the following order:

$$XAm_2 > XAm_3 > XAm_4 > XAm_5$$
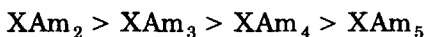
Shear degradation (Figs. 3–6) was studied up to 100 pass numbers in the case of xanthangum and other graft copolymer solutions at two concentrations, i.e., 100 ppm (Figs. 3 and 4) and 400 ppm (figs. 5 and 6). In the cases of XAm$_3$ and XAm$_4$, the degradation studies have also been performed on their solutions at 22 and 35 ppm concentrations, respectively, to study the concentration effect (Fig. 7). The concentrations have been chosen where DR is almost same in both the cases.

The degradation was found to be more at 100 ppm than at 400 ppm in all the polymers studied. In the cases of XAm$_3$ and XAm$_4$, the degradation was carried out at three concentrations, and the results show that the degradation rate decreases with increase in the concentration of the solution (Fig. 8). The similar results have been obtained in the case of guargum and its graft copolymers[21] and polyacrylamide.[22] The negative dependence of degradation rate on concentration was also shown by many investigators.[23–27] Hunston and Zakin[28] studied degradation of monodisperse polystyrene samples in good solvent (toluene) and "poor solvent" (52% toluene and 48% iso-octane) and
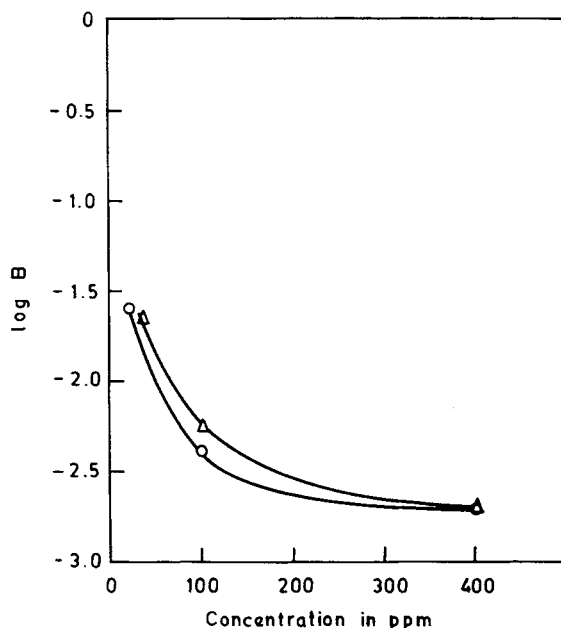
Fig. 8. Log B vs. concentration to study effect of concentration on shear degradation in the cases of XAm_3 (○) and XAm_4 (△).

observed that in "poor solvent" there is very little effect of concentration on the degradation. However, in good solvent they have also observed similar negative dependence of degradation rates on concentration.

The negative dependence of degradation rate on concentration reflects that the "entanglements" is not the only factor governing the degradation, as was thought by Bueche.[29] Yu, Zakin, and Patterson[27] suggested that "Stretching" of the individual molecules could be another factor involved in degradation of molecules apart from the entanglements as stretching has a negative concentration dependence.

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

$$DR/DR_0 = Ae^{-BN} \tag{1}$$

where DR is the drag reduction at particular pass number, DR_0 is the initial drag reduction, N is pass number, and A and B are empirical parameters. B is a parameter which gives rate of loss of drag reduction activity—hence rate of degradation. The values of A and B were computed from the least-squares fit of the eq. (1) with the experimental results and are given in Table II.

The B values for all the polymers show that the rate of shear degradation is in the following order:

$$XAm_5 > XAm_4 > XG > XAm_3 > XAm_2$$

XAm_2 being most shear stable and XAm_5 being least shear stable, of all the polymers studied.

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TABLE II
Computed Values of Constants A and B [eq. (1)]
for Xanthangum and Its Graft Copolymers

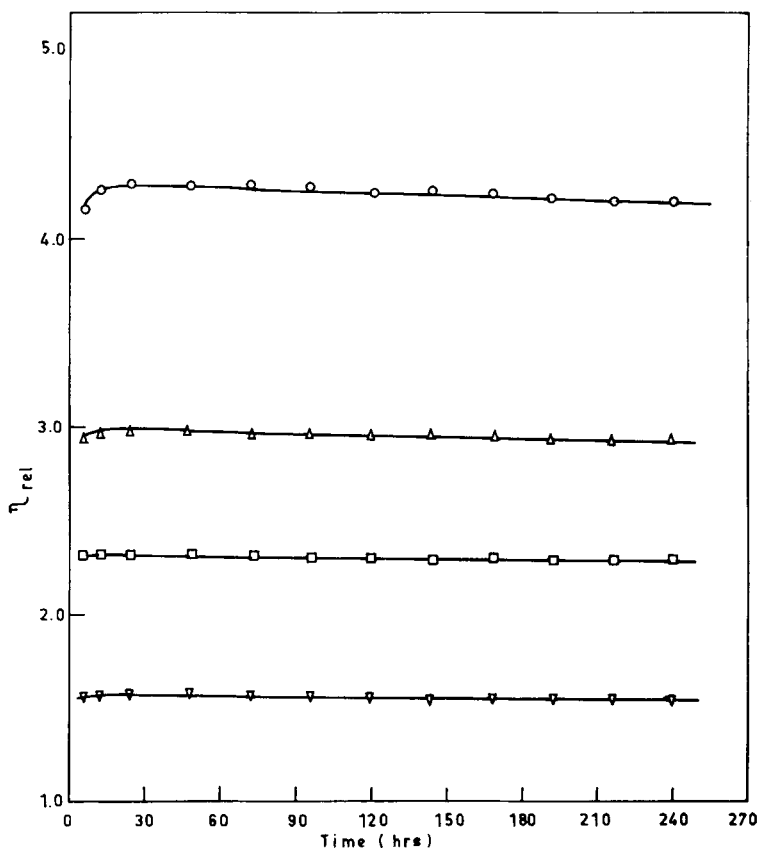| Polymer	Concentration of the solution (ppm)	A	B	Correlation coefficient r
Xanthangum	100	0.8652	4.165×10^{-3}	−0.858
	400	—	—	—
XAm$_2$	100	0.9404	3.948×10^{-3}	−0.960
	400	—	—	—
XAm$_3$	22	0.9041	24.717×10^{-3}	−0.982
	100	0.9399	4.109×10^{-3}	−0.980
	400	1.001	1.905×10^{-3}	−0.973
XAm$_4$	35	0.8871	21.412×10^{-3}	−0.975
	100	0.9466	5.578×10^{-3}	−0.987
	400	0.9921	1.962×10^{-3}	−0.970
XAm$_5$	100	0.9046	6.826×10^{-3}	−0.949
	400	0.9730	3.049×10^{-3}	−0.977

Fig. 9. Relative viscosity (η_{rel}) vs. time period to study biodegradability of 1000 ppm solutions of: (○) XAm$_2$; (△) XAm$_3$; (□) XAm$_4$; (▽) XAm$_5$.
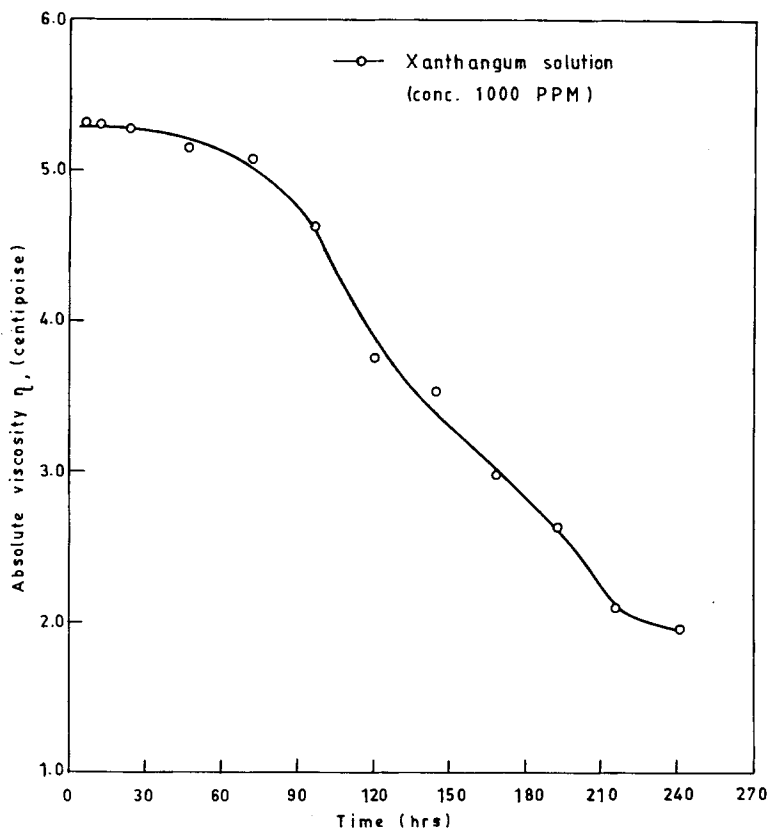
Fig. 10. Absolute viscosity (η) vs. time period to study biodegradability of 1000 ppm xanthangum solution (o).

These results apparently show contradictory behavior. XAm_5, with highly branched structure among all the studied graft polymers, should offer more resistance to shear degradation and XAm_2 with least number of grafts should be more prone to the degradation.

Kim et al.[6] observed that branched polymer shows improved shear stability over that of the linear polymer at the same concentration. However, the drag reduction effectiveness of both the polymers, i.e., linear and branched poly-acrylamides, which they have used was more or less the same. On the contrary, the drag reduction level of the polymers studied in this investigation is different for all the polymers. The anomalous results obtained can be explained as below. Maximum drag reduction was obtained at 75, 100, 150, and 300 ppm in the cases of XAm_2, XAm_3, XAm_4, and XG. In the case of XAm_5, maximum drag reduction was not obtained even up to 1000 ppm. Thus XAm_2 and XAm_3 have optimum concentrations, much smaller than those of XAm_4, XAm_5, and XG. When shear stability runs were made at 100 and 400 ppm, XAm_2 and XAm_3 appeared more shear stable because relatively these are higher concentrations for them. In other words, they contain more "effective drag reducing fractions" than XG, XAm_4, and XAm_5 at these

concentrations. Thus, they can afford to be sheared off but still remain to be effective to give high DR/DR_0. But the experimental concentration were far smaller than the optimum ones for XAm_4, XAm_5, and XG. They cannot afford to be sheared off; hence, on shearing, they lose the effective drag reducing fractions earlier and thus the observed behavior is exhibited.

These results also indicate that it is more appropriate to take an equal drag reduction level as a criterion for comparing degradation rather than equal concentration.

In the case of XAm_3 and XAm_4 degradation was studied at 22 and 35 ppm. In both cases, initial drag reduction was more or less the same. In this case, it was observed that XAm_4 with more branches is more resistant to degradation that XAm_3 with relatively less number of branches. B values obtained are 2.471×10^{-2} and 2.141×10^{-2} for 22 ppm XAm_3 and 35 ppm XAm_4 solutions, respectively. It appears that if the comparison of degradation is made at equal level of drag reduction, then one may get different trends in shear stabilities.

Somewhat different degradation behavior was observed in the cases of 400 ppm solutions of xanthangum and graft copolymer, XAm_2 (Fig. 6). It was found that the drag reduction was increasing with the degradation for the first few pass numbers and after that again they showed the normal behavior, i.e., loss of drag reduction with successive shear degradation. Darby and Chang[30] have shown that the 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 following relationship exists between these three parameters:

$$N_{DC} \propto \left(\lambda/\eta_0^4 \right)^K \tag{2}$$

where $K = 1/12$. Thus the degree of drag reduction increases with increase of λ and decreases with increase in η_0, but there is a fourth order greater sensitivity to changes in η_0 than to the changes in λ. For more concentrated solutions, the effect of degradation on drag reduction can also be explained in terms of the relative changes in the parameters 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 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.

The biodegradation studies have been carried out for a period of 10 days (Figs. 9 and 10). Xanthangum like other polysaccharides is very prone to biodegradation, and it was found that within 24 h it starts degrading and at the end of 10 days the solution showed considerable loss of viscosity (Fig. 10). All the graft copolymers were similarly studied for biodegradation, and no graft copolymer solution shows any loss of viscosity up to 10 days (Fig. 9). 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 molecule and increasing the ratio of inert polyacrylamide in graft copolymer, it can be made less susceptible to bacterial attack.[31]

Thus by grafting polyacrylamide onto xanthangum, more effective drag reducing agents with good shear stability can be prepared. These graft copolymers show less susceptibility for biodegradation.

APPENDIX: NOMENCLATURE

XAm_2, XAm_3, XAm_4, XAm_5	graft copolymers of xanthangum and acrylamide
DR	drag reduction percentage
DR_0	initial drag reduction percentage at first pass
XG	xanthangum
η_{rel}	relative viscosity
η	absolute viscosity
$[\eta]$	intrinsic viscosity

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