Drag-Reduction Efficiency, Shear Stability, and Biodegradation Resistance of Carboxymethyl Cellulose-Based and Starch-Based Graft Copolymers

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SYNOPSIS

Graft copolymers of carboxymethyl cellulose and starch with polyacrylamide have been synthesized by grafting acrylamide onto carboxymethyl cellulose and starch, respectively, using a 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 grafting enhances the drag-reduction effectiveness and shear stability and also that these factors are very much dependent on the length and number of grafts in the molecule. None of the graft copolymer solutions shows any microbial degradation up to 10 days.

INTRODUCTION

The polymeric drag reduction has shown much promise in reducing the energy requirement of crude oil and water transport through pipes. The water-soluble flexible synthetic polymers and rigid polymers from natural resources reduce drag in a turbulent flow of water. The flexible polymers like poly(ethylene oxide) and polyacrylamide cause maximum drag reduction ($\approx$ 80%) in turbulent pipe flows at the concentration of a few 10s of ppm but are easily shear degradable. On the other hand, rigid polysaccharides like guar gum, xanthan gum, carboxymethyl cellulose, and synthetic polymer [poly(vinyl alcohol)] are fairly shear stable but are relatively poor drag-reducing agents. They require much higher concentrations ($\gtrsim$ 500 ppm) to cause maximum drag reduction ($\approx$ 60%). Recently it has been shown[1-4] in the authors' laboratory that by grafting polyacrylamide chains on guar gum and xanthan gum it is possible to synthesize graft copolymers that have higher drag-reduction effectiveness than do the backbone polymers and that possess shear stability comparable to that of the backbone

polysaccharides. The maximum in drag reduction is also obtainable at concentrations around 100 ppm. The graft copolymer solutions are also more resistant toward biodegradation.

In the present investigation, graft copolymerization has been extended to carboxymethyl cellulose and potato starch using a ceric-ion-initiated solution polymerization technique. A number of graft copolymers with a varying number and length of polyacrylamide chains have been synthesized. The drag-reduction effectiveness, shear stability, and biodegradation resistance of these graft copolymers have been measured. The present paper gives a detailed account of synthesis and evaluation of the above-mentioned physical properties in terms of the existing molecular theories of drag reduction and shear stability.

EXPERIMENTAL

Materials

Sodium carboxymethyl cellulose was obtained from Supertex Ltd., India. It is purified by carboxymethylation of cellulose. The degree of substitution in the present case is 0.8. Soluble potato starch (analar grade) was obtained from Sarabhai Chemicals, India. 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 the substrate by using a ceric-ion redox initiator. The following procedure has been adopted in carrying out the reactions: One gram of purified carboxymethyl cellulose (CMC) 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 CMC solution in the Erlenmeyer flask. The mixture solution was stirred by magnetic stirrer. The flask was then sealed with a septum stopper. Nitrogen gas was then flushed through the solution by 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 a hypodermic syringe. The nitrogen flushing was continued for another 20 min; then, the needles were taken out, and flask was further sealed with Teflon tape. The reaction temperature was maintained at $30 \pm 1°C$ by immersing the flask in a constant temperature bath. The reaction mixture was stirred occasionally. The reaction was continued for 24 h and then terminated by inserting 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 a vacuum oven at 40°C.

In the case of starch, the solution was prepared by adding the starch powder to the distilled water and then heating it at 80°C for 5 min; the nitrogen gas was bubbled through the solution while it was cooling down to room temperature. The procedure afterward is the same as described above. The details of the reaction conditions are given in Tables I and II.

Drag-Reduction Studies

The solution of CMC, starch, and their graft copolymers (CAm_1–CAm_6, SAm_1–SAm_3, and SAm_6–SAm_8) 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 a turbulent flow rheometer, supplied by Dr. J. W. Hoyt, San Diego, CA. The results are shown in Figures 1–5. The first points almost on the ordinate in the drag-reduction vs. concentration plots represent drag reduction at 5 ppm.

Shear Stability Studies

The shear degradation studies have been performed on aqueous solutions of CMC, starch, and their graft copolymers (CAm_1–CAm_6, SAm_1–SAm_3, and SAm_6–SAm_8) at various concentrations. The studies were undertaken by recirculation of the same solution through the test capillary of the turbulent flow rheometer. One recirculation is depicted as a unit pass number. The results are shown in Figures 6–13.

Table I Details of Synthesis of CMC-Based Graft Copolymers (CAm_1–CAm_6)[a]

| Sample No. | Moles in Reaction Mixture | | CMC (g) | Yield (g) | % Monomer Conversion[b] | $[\eta]^c$ (mL g^{-1}) |
	Acrylamide	Ce[IV] Ion $\times 10^3$				
CAm_1	0.14	0.05	1	3.96	29.6	1150
CAm_2	0.14	0.10	1	9.17	81.7	734
CAm_3	0.14	0.20	1	9.18	81.8	605
CAm_4	0.14	0.30	1	10.00	90.0	541
CAm_5	0.21	0.10	1	13.83	85.5	850
CAm_6	0.28	0.10	1	15.48	72.4	900

[a] The reactions were carried out in nitrogen atmosphere; 300 mL of distilled water was used as solvent. Reaction temperature was $30 \pm 1°C$, and reaction time was 24 h.

[b] % Monomer conversion = $(M_0 - M_t)/M_0 \times 100$, where M_0 is the initial concentration and M_t is the concentration of unreacted monomer at the end of the reaction.

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

Table II   Details of Synthesis of Starch-Based Graft Copolymers (SAm$_1$–SAm$_8$)[a]

Sample No.	Moles in Reaction Mixture		Starch (g)	Yield (g)	% Monomer Conversion[b]	$[\eta]^c$ (mL g^{-1})
	Acrylamide	Ce[IV] Ion × 10^3				
SAm$_1$	0.14	0.03	1	8.51	75.1	512
SAm$_2$	0.14	0.05	1	9.23	82.3	397
SAm$_3$	0.14	0.10	1	10.04	90.0	305
SAm$_6$	0.21	0.05	1	12.21	74.6	410
SAm$_7$	0.28	0.05	1	16.45	77.2	509
SAm$_8$	0.35	0.05	1	16.94	63.6	546

[a] The reactions were carried out in nitrogen atmosphere; 300 mL of distilled water was used as solvent. Reaction temperature was maintained 30 ± 1°C, and reaction time was 24 h.

[b] % Monomer conversion = $(M_0 - M_t)/M_0 \times 100$, where M_0 is the initial concentration and M_t is the concentration of unreacted monomer at the end of the reaction.

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

Biodegradation Studies

The viscosity of the solution as a function of time is taken as the criterion for the study of biodegradation as described earlier.[1,2] CMC, starch, and all their graft copolymers were tested for their biodegradability. Solutions, 0.1%, were prepared in single-distilled water, and the viscosity measurements were performed using an Ubbelohde viscometer (CS/S = 0.01) at certain intervals of time over a 10 day
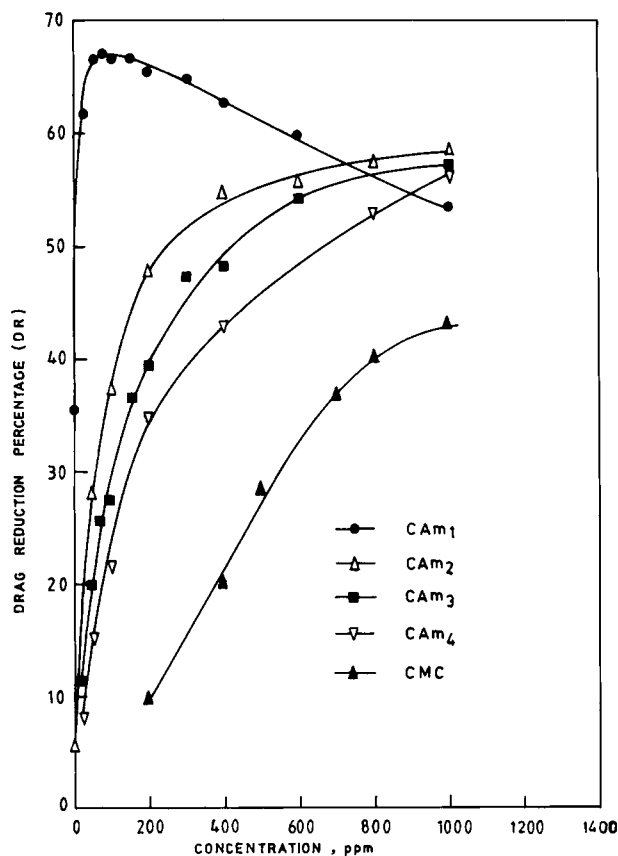

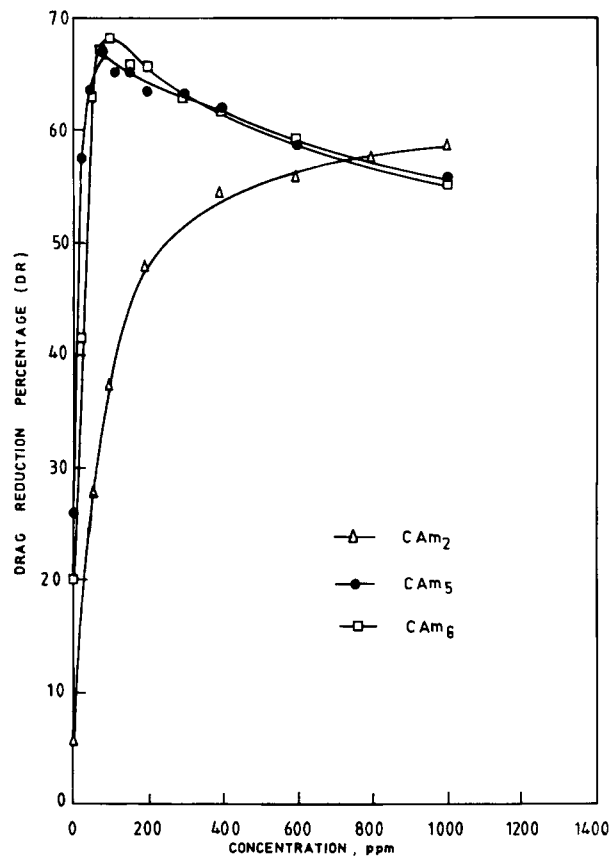**Figure 1**   Drag reduction vs. polymer concentration for CMC and its graft copolymers.

Figure 2   Drag reduction vs. polymer concentration for CMC-based graft copolymers.
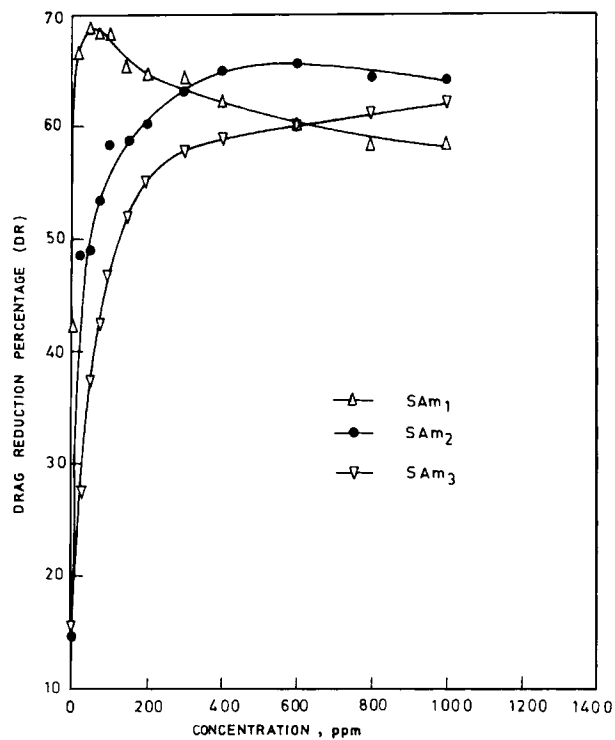
Figure 3 Drag reduction vs. polymer concentration for starch-based graft copolymers.
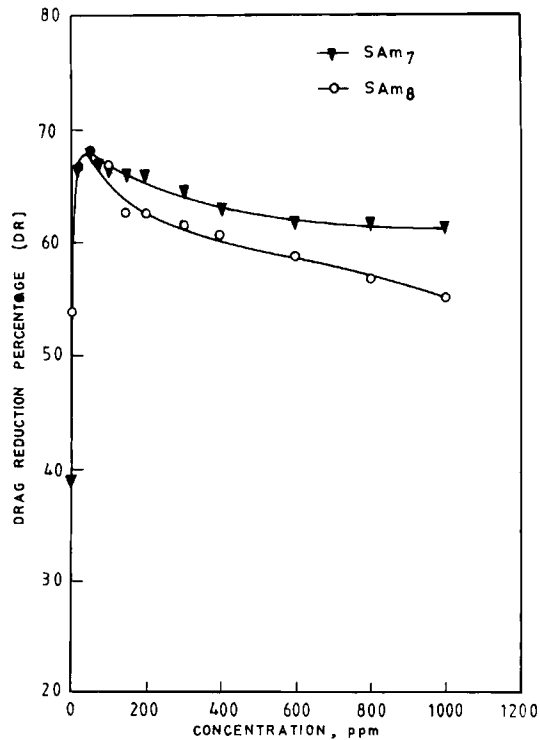

Figure 5 Drag reduction vs. polymer concentration for starch-based graft copolymers.
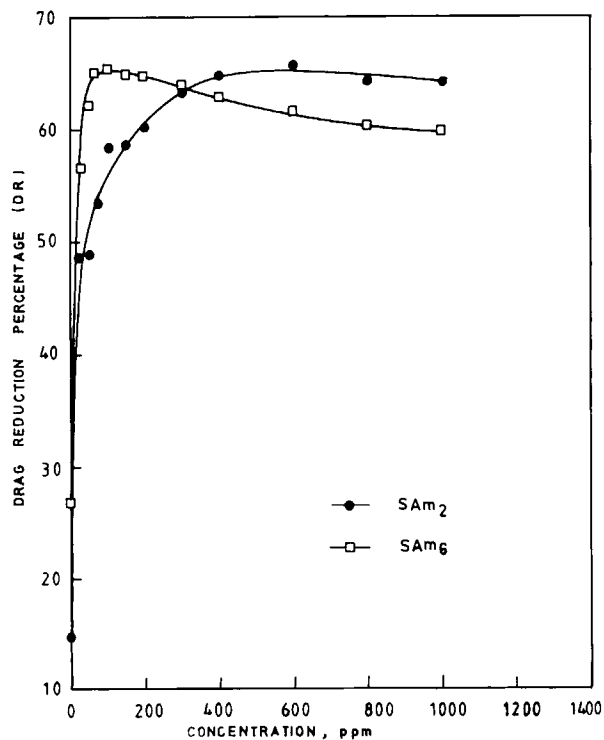

Figure 4 Drag reduction vs. polymer concentration for starch-based graft copolymers.

period. The results have been plotted as relative viscosity vs. time period (Figs. 14 and 15).

RESULTS AND DISCUSSION

The details of the graft copolymerization and the yields obtained are given in Tables I and II. For both systems, CMC and starch-based graft copolymers, two series of graft copolymers have been prepared. In the first series (CAm_1-CAm_4 and SAm_1-SAm_3), the ceric-ion concentration is progressively increased, which results in graft copolymers with an increased number of grafts per backbone molecule but with shorter chains as one goes down the series[3]; i.e., in this series, both CMC-to-acrylamide and starch-to-acrylamide ratios are kept constant (1 : 10 w/w) and the initiator concentration is varied. This is evident from the intrinsic viscosity values (Tables I and II) that go on decreasing as the number of chains increases and the length of chains decreases. With an increasing concentration of initiator, graft copolymers with lower intrinsic viscosities were obtained in both cases, due to the above-mentioned reasons.
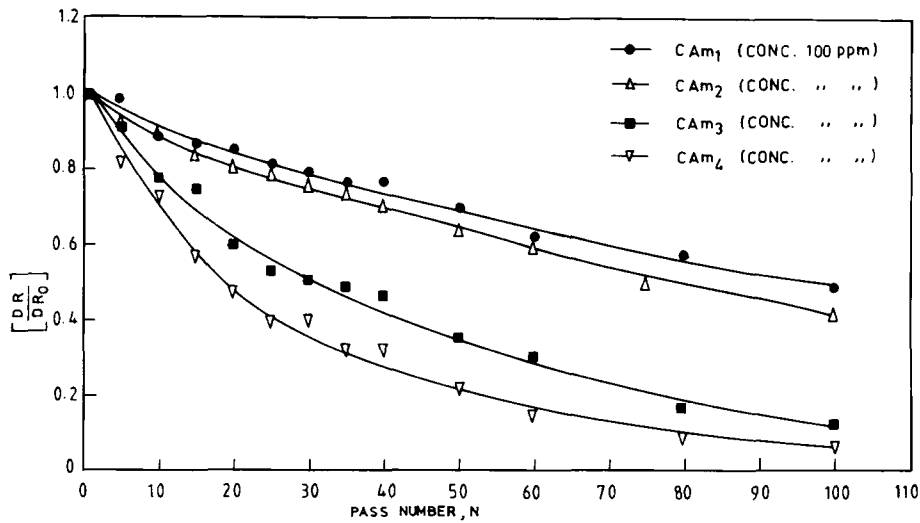
Figure 6 (DR/DR_0) vs. pass number to study shear degradation of CMC-based graft copolymers.

In the second series of graft copolymers (CAm$_2$, CAm$_5$, CAm$_6$, SAm$_2$, SAm$_6$, and SAm$_8$), only acrylamide concentration is increased down the series. As a result, the number of grafts per backbone is constant but the length of the graft increases with an increase in acrylamide concentration.[3] 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 increasing acrylamide concentration in both the systems.

The graft copolymers (CAm$_1$-CAm$_6$, SAm$_1$-SAm$_3$, and SAm$_6$-SAm$_8$), and both CMC and starch were tested for their drag-reduction effectiveness, and the results are plotted in Figures 1-5. In CMC-based graft copolymers, it was found that all the grafts were more effective than was CMC itself. For these copolymers, the drag-reduction effectiveness varies in two different ways with an increase in concentration. In one series (CAm$_1$-CAm$_4$), except for CAm$_1$, the drag reduction increases continuously with an increase in the concentration even up to 1000 ppm. The continuous increase in drag reduction
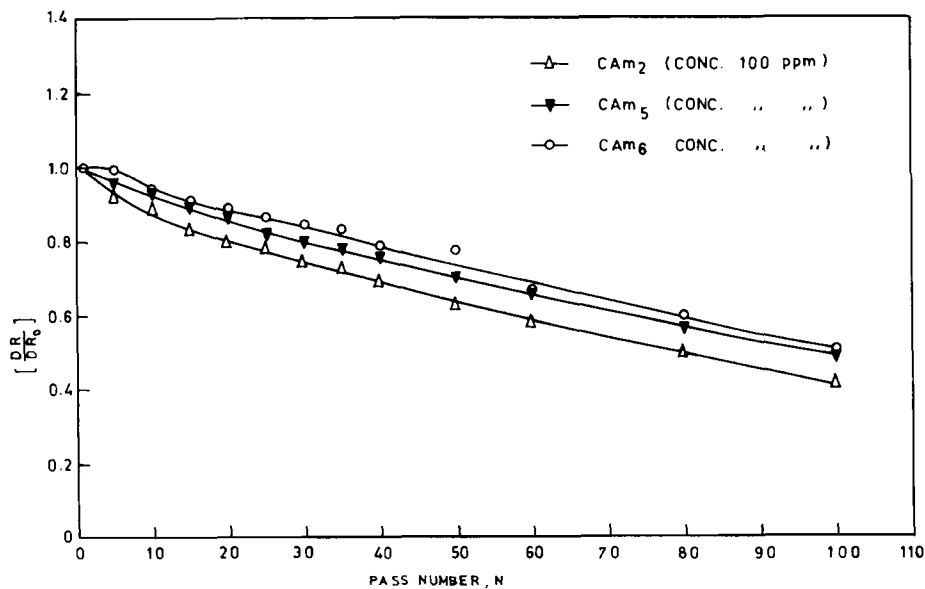

Figure 7 (DR/DR_0) vs. pass number to study shear stability of CMC-based graft copolymers.
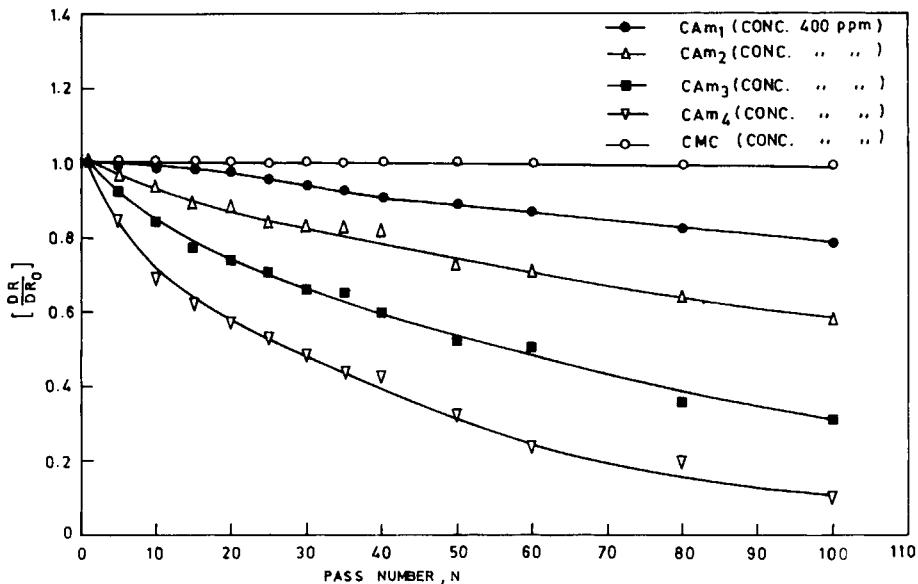
Figure 8 (DR/DR_0) vs. pass number to study shear degradation of CMC and its graft copolymers.

with concentration up to 1000 ppm indicates that the maximum drag-reduction level of these polymers lies beyond 100 ppm. In the case of CAm_1, the drag-reduction effectiveness increases with an increase in concentration up to 75 ppm, where it gives maximum drag reduction, and with a further increase in the concentration, the drag reduction decreases. It was also observed that CAm_1 seems to be the most effective in the series, and CAm_5 to be the least effective, at lower concentrations below drag-reduction maxima; i.e., the drag-reduction effectiveness

seems to be in the following order at lower concentrations below drag-reduction maxima:

$$CAm_1 > CAm_2 > CAm_3 > CAm_4$$

In the second series of graft copolymers (CAm_2, CAm_5, and CAm_6), it was observed that except in CAm_2 the drag reduction increases with an increase in the concentration of the solution, reaches the maximum value at a certain concentration, and then decreases with a further increase in concentration.
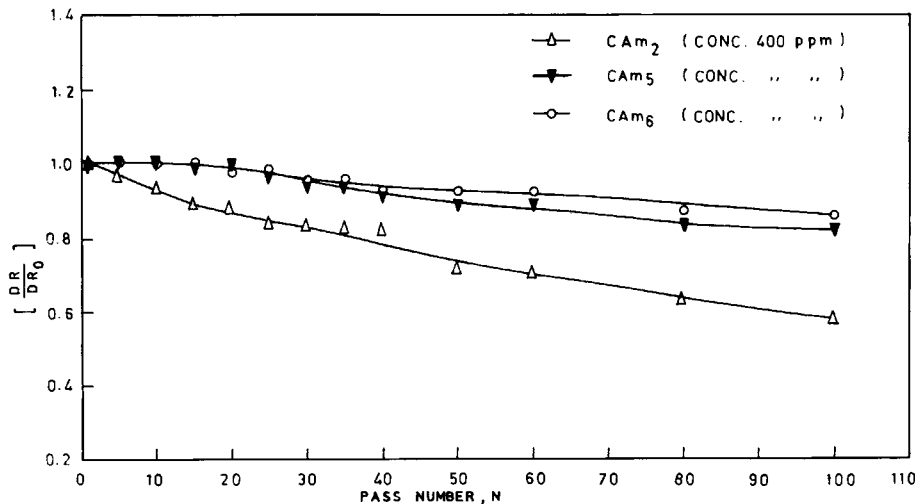

Figure 9 (DR/DR_0) vs. pass number to study shear degradation of CMC-based graft copolymers.
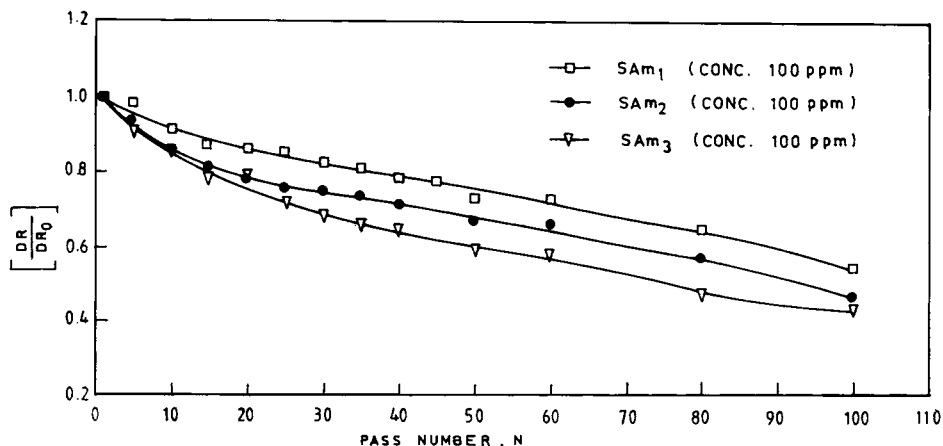
Figure 10 (DR/DR_0) vs. pass number to study shear degradation of starch-based graft copolymers.

Thus, the maximum drag reduction was observed at concentrations of 75 and 100 ppm in cases CAm_5 and CAm_6, respectively. In the case of CAm_2, the drag reduction continues to increase even up to 1000 ppm. For this series, the drag-reduction effectiveness of CAm_5 and CAm_6 is larger than that of CAm_2.

In the case of purified CMC, it was observed that the drag-reduction effectiveness is much less. The drag reduction at 1000 ppm is only 40%.

Almost the same type of behavior is observed in the case of starch-based graft copolymers. Here, also, all the graft copolymers were found to be more effective than was starch itself, which is not drag-reducing. In the first series of copolymers (SAm_1–SAm_3), except for SAm_1, it was observed that the drag-reduction effectiveness increases continuously

with an increase in the concentration even up to 1000 ppm, indicating that the maximum drag-reduction level lies beyond 1000 ppm for these copolymers. For SAm_1, it was observed that the drag-reduction effectiveness increases with concentration and reaches its maximum level at 50 ppm and then decreases with a further increase in the concentration. The drag-reduction effectiveness below 250 ppm seems to be in the following order:

$$SAm_1 > SAm_2 > SAm_3$$

In the second series (SAm_2, SAm_6, SAm_7, and SAm_8), except in SAm_2, it was observed that the drag-reduction effectiveness increases with the concentration, reaches its maximum value, and then
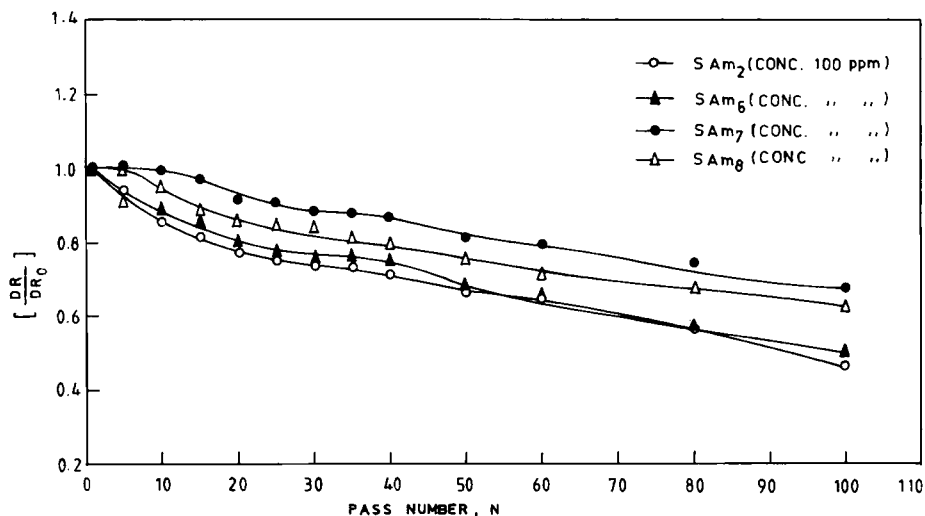

Figure 11 (DR/DR_0) vs. pass number to study shear degradation of starch-based graft copolymers.
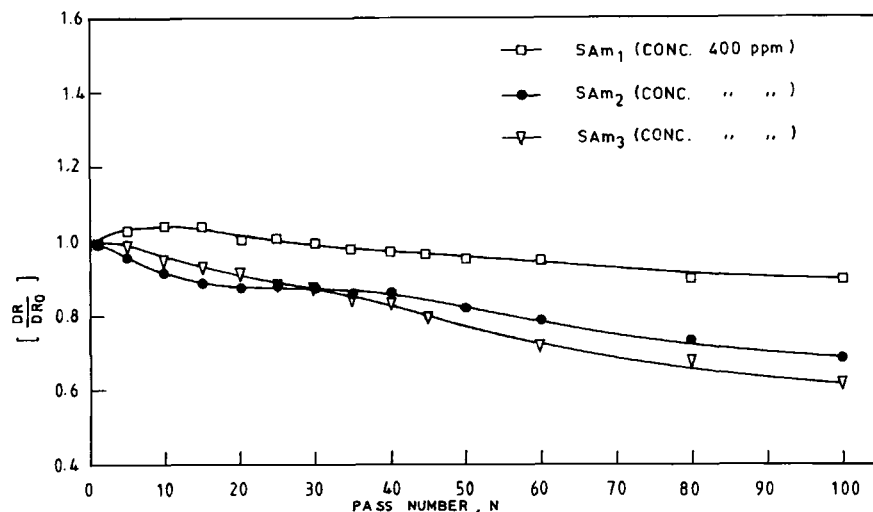
Figure 12 (DR/DR_0) vs. pass number to study shear degradation of starch-based graft copolymers.

decreases with a further increase in concentration. Thus, the maximum drag-reduction effectiveness was obtained at 100, 50, and 50 ppm for SAm_6, SAm_7, and SAm_8, respectively. In the case of SAm_2, the drag-reduction effectiveness increases with concentrations up to 400 ppm, then it almost levels off with a further increase in the concentration. After 400 ppm, it was observed that the drag-reduction effectiveness decreases only slightly with a further increase in concentration. For this series, the drag-reduction effectiveness below drag-reduction maxima seems to be in the following order:

$$SAm_8 > SAm_7 > SAm_6 > SAm_2$$

For starch, it was found that it did not give any drag reduction even up to 2000 ppm.

For both systems, in the first series, the increase in the ceric-ion concentration results in graft copolymers with a large number of shorter grafts. As the length of the graft decreases, the radius of gyration also decreases, which is indicated by a decrease in drag-reduction effectiveness as we go down the series in both CMC and starch-based graft copolymer systems. As mentioned earlier,[4] drag-reduction effectiveness of graft copolymers will depend on the length of the grafts: Longer grafts will contribute more toward drag reduction, and shorter grafts will contribute less. Below a certain length of
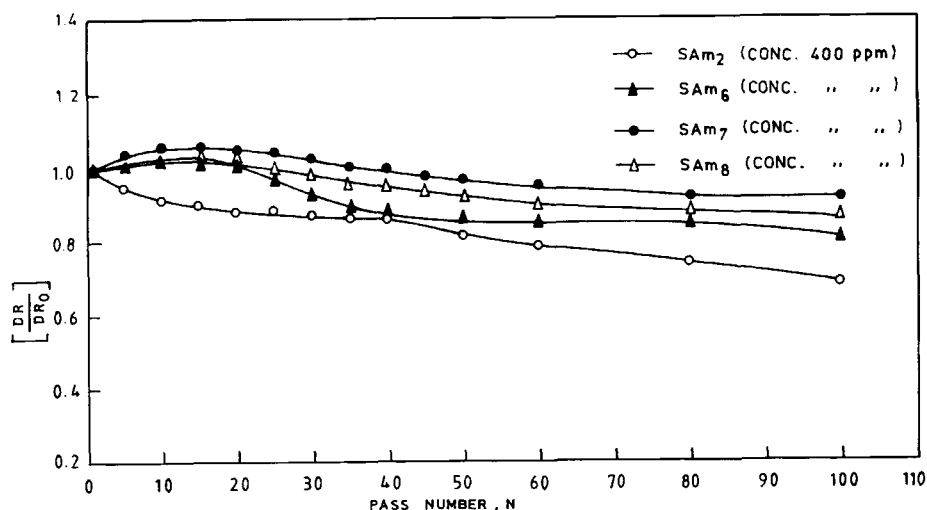

Figure 13 (DR/DR_0) vs. pass number to study shear degradation of starch-based graft copolymers.
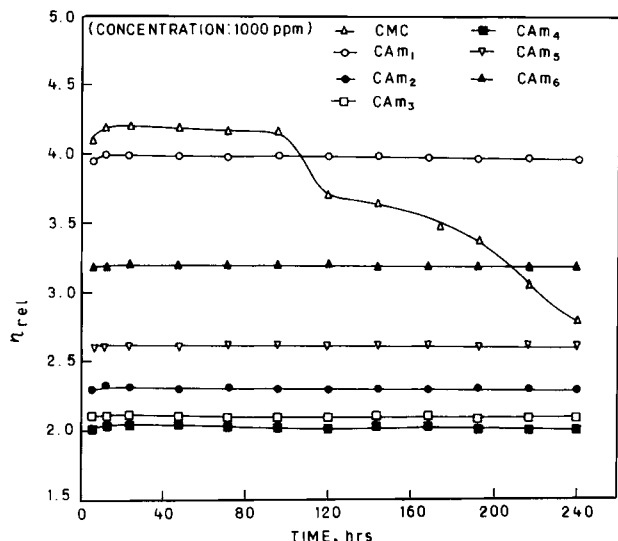
Figure 14 η_{rel} vs. time period to study biodegradation of CMC-based graft copolymers.

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

$$DR/DR_0 = A \cdot e^{-BN} \qquad (1)$$

where DR is the drag reduction at a particular pass number (N), DR_0 is the initial drag reduction, and A and B are empirical parameters. B is a parameter that expresses the rate of loss of drag-reduction activity—hence, the rate of degradation. The values of A and B were computed from the least-squares fit of eq. (1) with the experimental results and are given in Tables III and IV. The degradation rates were higher at 100 ppm than at 400 ppm (Tables III and IV) in both systems.

In the case of the CMC-based graft copolymers, in the first series (CAm$_1$–CAm$_4$) at 100 ppm (Fig. 6), CAm$_1$ was found to be more shear resistant and

graft, the contribution of grafts in drag-reduction effectiveness of graft copolymers will be insignificant. However, a number of such short grafts per backbone molecule will significantly contribute to the molecular weight of the molecule.

These facts are well reflected in both CMC and starch-based copolymers: As we go down the series, the drag-reduction effective concentration decreases. Also, the decrease in the drag reduction, in the case of the second series of graft copolymer based on CMC and starch, with an increase in concentration beyond the optimum level can, again, be explained on the reasonings given by Lyashev et al.,[5] i.e., the reduction is due to the association of molecules after the optimum level. The absolute viscosity of the solution also increases with the concentration. This lowers the effective Reynolds number, with a consequent decrease in drag reduction. The same explanation as given earlier by Chang and Darby[6,7] also holds true for the present system regarding the drag-reduction effectiveness behavior of these systems with an increase in the concentration. The detailed description of the dependence of elastic and viscous properties on concentration and their effect on turbulent drag have been reported elsewhere.[8] Our results of drag-reduction effectiveness studies as well as shear stability studies support the view of Chang and Darby.[6,7]

Shear degradation studies were performed for both CMC and starch-based systems up to 100 pass numbers. Concentrations used were 100 ppm (Figs. 6, 7, 10, and 11) and 400 ppm (Figs. 8, 9, 12, and 13) for both systems. In the present systems, the
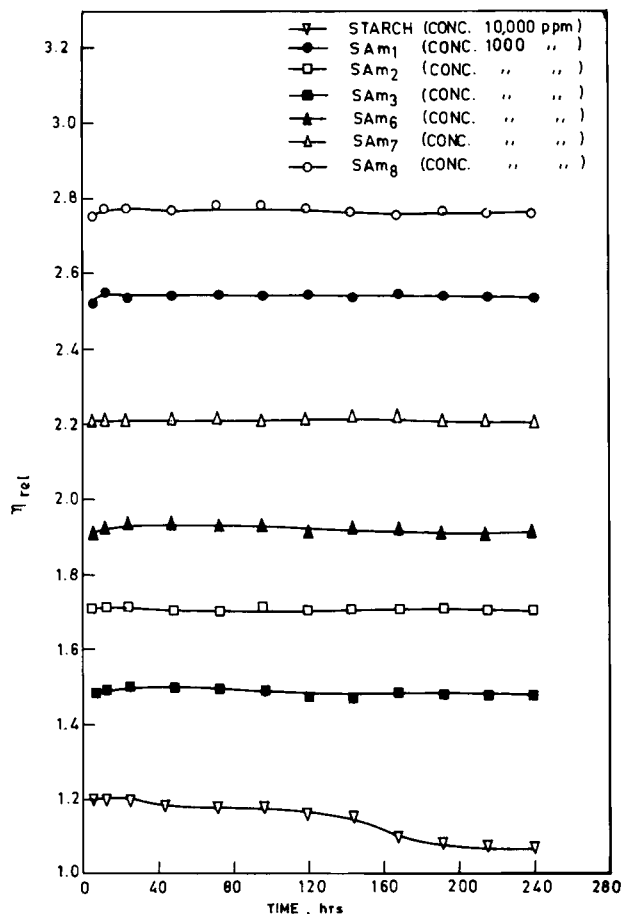

Figure 15 η_{rel} vs. time period to study biodegradation of starch and its graft copolymers.

Table III   Computed Values of Constants A and B [eq. (1)] for CMC-Based Graft Copolymers

Polymer	Concentration of the Solution (ppm)	A	$B \times 10^3$	Correlation Coefficient (r)
CAm_1	100	0.9580	5.037	−0.984
	400	1.0064	2.251	−0.992
CAm_2	100	0.9355	5.581	−0.986
	400	0.9713	4.187	−0.986
CAm_3	100	0.8420	8.555	−0.946
	400	0.8988	6.649	−0.971
CAm_4	100	0.7375	8.643	−0.898
	400	0.7851	8.000	−0.931
CAm_5	100	0.9679	5.058	−0.994
	400	1.0147	2.070	−0.987
CAm_6	100	0.9946	4.926	−0.994
	400	1.0106	1.586	−0.979

CAm_4 was found to be the least shear resistant. The shear stability seems to be in the following order:

$$CAm_1 > CAm_2 > CAm_3 > CAm_4$$

A similar trend was also observed for 400 ppm solutions (Fig. 8). In the second series, the shear stability indicates the following order for both 100 ppm and 400 ppm solutions (Figs. 7 and 9):

$$CAm_6 > CAm_5 > CAm_2$$

With starch-based graft copolymers, in the first series (SAm_1–SAm_3), SAm_1 was found to be the most stable and SAm_3 was found to be least stable at both concentrations (Figs. 10 and 12). The shear stability, at both concentrations, seems to be in the following order:

$$SAm_1 > SAm_2 > SAm_3$$

In the second series (SAm_2, SAm_6–SAm_8), the shear stabilities for 100 ppm solutions (Fig. 11) seems to be in the following order:

$$SAm_7 > SAm_8 > SAm_6 > SAm_2$$

and for 400 ppm solution (Fig. 13), the shear stabilities indicate the following order:

$$SAm_8 > SAm_7 > SAm_6 > SAm_2$$

Thus, at 100 ppm concentration, SAm_7 was found to be more shear stable than was SAm_8, whereas at 400 ppm, SAm_8 was more shear stable than was SAm_7. However, the difference in the shear stability of SAm_7 and SAm_8 is very small at both concentrations.

Table IV   Computed Values of Constant A and B for Starch-Based Graft Copolymers

Polymer	Concentration of the Solution (ppm)	A	$B \times 10^3$	Correlation Coefficient (r)
SAm_1	100	0.9635	4.271	−0.985
SAm_2	100	1.1111	8.022	−0.952
	400	0.9577	2.770	−0.978
SAm_3	100	0.8915	5.282	−0.958
	400	0.9865	3.888	−0.987
SAm_6	100	0.9300	4.5288	−0.979
SAm_7	100	1.000	3.360	−0.989
SAm_7	100	0.9119	2.353	−0.616

It has been seen from the above results that the degradation rate decreases with an increase in the concentration of the solution in all the cases. Similar results have been obtained in the case of guar gum, xanthan gum, and their graft copolymers[2,8,9] and polyacrylamide.[9] The negative dependence of the degradation rate on concentration was shown by many workers.[10-12]

The above findings reflect the fact that for these systems, also, the explanations given by Bueche[12] and Yu et al.[10] for the negative dependence of the degradation rate on concentration along with the role of the individual molecule "stretching" are the relevant reasons for the observed behavior.

Even though the drag-reduction effectiveness of CMC is very low, however, the 400 ppm solution of CMC was found to be extremely shear stable and the degradation at the end of 100 pass number is insignificant (Fig. 8).

The biodegradation studies have been carried out for a period of 10 days (Figs. 14 and 15) for both CMC-based and starch-based systems. The results obtained indicate that like guar gum and xanthan gum,[2,8] CMC and starch also are susceptible to biodegradation. All the graft copolymers were similarly studied for biodegradability, and no graft copolymer solution showed any loss of viscosity up to 10 days (Figs. 14 and 15). Thus, all the graft copolymers were found to be less susceptible to biodegradation. The improvement in biodegradation resistance might be due to the following reasons: The structural change due to grafting and the incorporation of relatively inert polyacrylamide chains in graft copolymers have enhanced the resistance to biodegradation, i.e., these modifications resulted in systems that are less susceptible to bacterial attack.[13]

Thus, the grafting of polyacrylamide chains onto CMC and starch resulted in systems that are more effective drag-reducing agents with good shear stability than those of unmodified CMC and starch. These graft copolymers also show less susceptibility to biodegradation.

NOMENCLATURE

CAm_1, CAm_2, CAm_3, CAm_4, CAm_5, CAm_6	Graft copolymers of carboxymethyl cellulose and acrylamide
SAm_1, SAm_2, SAm_3, SAm_6, SAm_7, SAm_8	Graft copolymers of starch and acrylamide
DR	Drag-reduction percentage
DR_0	Initial drag reduction percentage
CMC	Carboxymethyl cellulose
η_{rel}	Relative viscosity
η	Absolute viscosity
$[\eta]$	Intrinsic viscosity

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