

# The Turbulent Drag Reduction by Graft Copolymers of Guar gum and Polyacrylamide

S. R. DESHMUKH, P. N. CHATURVEDI, and R. P. SINGH, *Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India*

## Synopsis

Commercial guar gum is known to be a shear stable drag reducing agent. However, the aqueous solutions of guar gum start degrading within 8 hrs. of their preparation and after 65 hrs., they degrade completely. In the present investigation, the graft copolymers of guar gum and polyacrylamide have been prepared. It has been shown that the purification and grafting enhance the drag reduction effectiveness and biodegradation resistance considerably in guar gum.

## INTRODUCTION

The turbulent drag reduction by polymeric additives is an active field of research.<sup>1</sup> Various polymers, soaps, fibers, and their mixtures have been found to cause appreciable drag reduction in turbulent flow of water.<sup>2</sup> However, the technical applications of these drag reducing polymers have been limited because of the fact that the drag reducing agents get degraded in the turbulent flow and thus lose their drag reduction effectiveness.<sup>3</sup> It has been found that the graft copolymers are fairly shear stable in causing drag reduction.<sup>4,5</sup> Although guar gum is a shear stable drag reducing agent, it is highly susceptible to biodegradation in aqueous solutions. It has been envisaged that the grafting of acrylamide onto guar gum will enhance the shear stability and may also impart resistance to biological degradation. Hence, graft copolymers have been synthesized by grafting acrylamide onto guar gum by ceric-ion-initiated radical polymerization in aqueous solutions.

A comparative study on the drag reduction effectiveness, shear stability, and susceptibility to biodegradation has been made on commercial guar gum (CGG), purified guar gum (PGG), and graft copolymers ( $Gm_1$ – $Gm_3$ ).

The present paper summarizes the results of the above investigations.

## EXPERIMENTAL

### Materials

Guar gum was obtained from Hindustan Gums and Chemicals, Bhiwani, India. It has been purified by method of Whitcomb et al.<sup>6</sup> The guar gum was subjected to 5 days' soxhlet extraction with 95% ethanol to remove protein and fat impurities.

Acrylamide monomer from Burgoyne Urbidges and Co., 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.

TABLE I  
The Details of Grafting Reaction<sup>a</sup>

Sample no.	Acrylamide (mol/L)	HNO <sub>3</sub> (mmol/L)	Ce(IV) (mmol/L)	Guargum (g/L)	Monomer conversion	[ $\eta$ ] <sup>b</sup> (mL/g)
Gm <sub>1</sub>	0.1408	50	2.5	10	0.53	260.0
Gm <sub>2</sub>	0.3052	50	2.5	10	0.57	272.8
Gm <sub>3</sub>	0.7004	50	2.5	10	0.77	408.7

<sup>a</sup> (i) Ceric ammonium nitrate/HNO<sub>3</sub> redox initiator system is used in the grafting reaction.  
(ii) All reactions were carried out under nitrogen atmosphere at  $29 \pm 1^\circ\text{C}$ . Reaction time was 3 h.

<sup>b</sup> For viscosity measurements, solutions were prepared in 1M NaNO<sub>3</sub> solution. Measurements were taken at 30°C.

### Graft Copolymerization

The graft copolymerization reactions were carried out under nitrogen in reaction kettle equipped, with stirrer, thermometer socket, and addition funnel. All reactions were carried out at  $29 \pm 1^\circ\text{C}$ . The following procedure has been adopted in carrying out the reactions. The purified guargum was dispersed in the distilled water, and, after flushing with nitrogen, the appropriate amounts of acrylamide and ceric solutions were added. Distilled water (100 mL) was used for each gram of guargum. In all the cases, the monomer was added before the addition of initiator. The nitrogen atmosphere was maintained throughout the reaction; the reaction time was 3 h. The reaction products were collected by precipitating the reaction mixture in excess of acetone. The products were dried in vacuum over at 45°C. The details of the reactions have been given in the Table I.

### Drag Reduction Studies

The commercial guargum, purified guargum, and graft copolymers were tested for their drag reduction effectiveness. The drag reduction studies were performed over a concentration range from 50 to 1000 ppm at Reynolds number of 14,000 by turbulent rheometer supplied by J. W. Hoyt, San Diego, CA. The results have been depicted in Figure 1.

### Shear Resistance Studies

The shear degradation studies have been performed with aqueous solutions of commercial guargum, purified guargum, and graft copolymers at 400 ppm concentration. The studies were performed 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 Figure 2.

### Biodegradation Studies

The biodegradability studies have been carried out with 0.1% solutions of commercial guargum, purified guargum, and graft copolymers over a period of 256 h. The relative viscosity is taken as the measure of biodegradation. Figure 3 depicts the results.

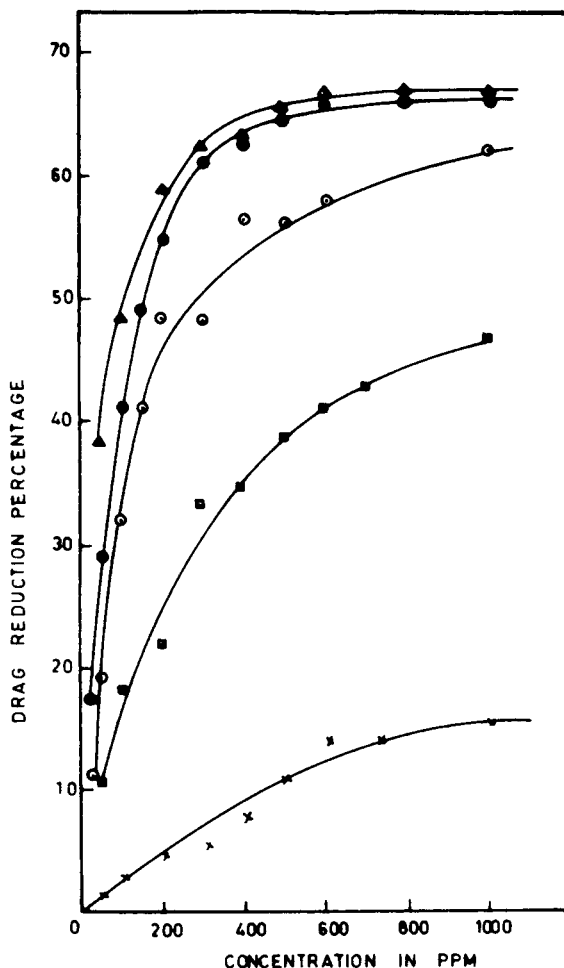


Fig. 1. Drag reduction percentage vs. concentration to study drag reduction effectiveness: (○) CGG; (●) PGG; (△) Gm<sub>3</sub>; (□) Gm<sub>2</sub>; (X) Gm<sub>1</sub>.

## RESULTS AND DISCUSSION

The ceric ion initiator system has been successfully used with a number of monomer systems to prepare polysaccharide graft copolymers; since the free radicals are formed exclusively on the chains of the substrate in this method, the grafting efficiency is higher compared to other redox systems.<sup>7</sup> The ceric ion/nitric acid initiator system has, therefore, been used in the present investigation.

The number of grafts per backbone molecule is determined by the ratio of ceric ion concentration to the concentration of backbone molecules in the reaction mixture, and the length of the grafted branch depends upon the ratio of monomer concentration to ceric ion concentration.<sup>8</sup> Preliminary experiments were carried out to optimize ceric ion concentration and nitric acid concentration on the basis of monomer conversion. Three grades of graft copolymers were then prepared by keeping all reaction parameters constant and changing only the monomer concentration. Thus the number

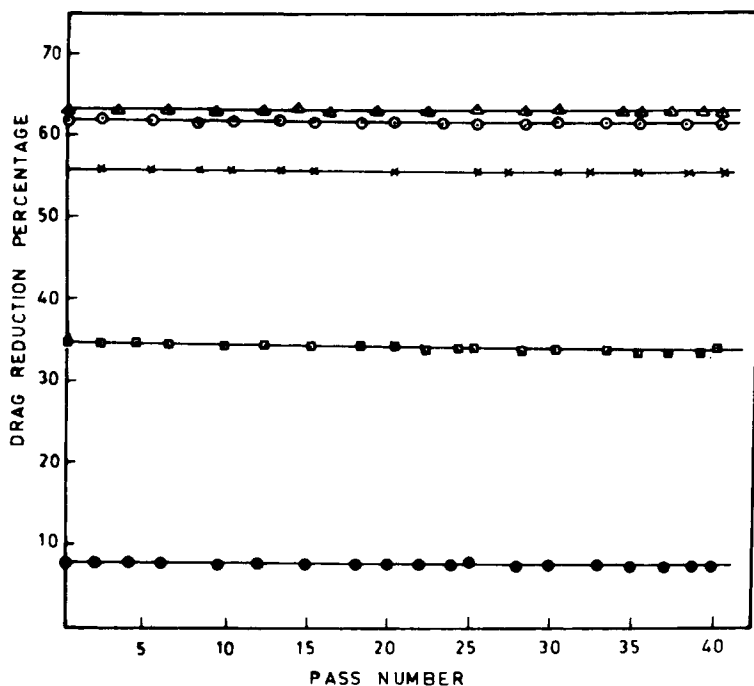


Fig. 2. Drag reduction percentage vs. pass number to study shear stability: (○) PGG; (X) CGG; (●) Gm<sub>1</sub>; (□) Gm<sub>2</sub>; (△) Gm<sub>3</sub>.

of graft sites was kept constant, and the chain length of the graft was increased. This has been confirmed by increase in the viscosity with increasing monomer concentration. However, it has been observed that the degradation of guar gum molecules occurs during the grafting reaction. This is possibly due to the acidic medium of the reaction and the continuous stirring. The conversion of the monomer was determined from nitrogen analysis data after appropriate corrections for moisture content.

The drag reduction effectiveness studies show that one of the graft copolymers (Gm<sub>3</sub>) with higher graft content is more effective than purified guar gum whereas the other two graft copolymers were less effective drag reducing agents. It is possibly due to the fact that during the grafting reaction, degradation of the original backbone molecule occurs. However, with increasing polyacrylamide content, i.e., by increasing the length of the graft, the drag reduction effectiveness has been found to be enhanced. The purified guar gum was found a more effective drag reducing agent than commercial guar gum. This is obvious as purification removes protein and fat impurities, leaving behind drag reducing polysaccharide.

According to Beuche's midpoint break theory<sup>9</sup> the polymers degrade under the high shear gradients almost at the midpoint. Hence, it was thought<sup>4</sup> that highly branched structures may offer fairly shear stable drag reducing system. It has been found in the present investigation that the graft copolymers have shown good shear stability up to pass number 40, and thus the results amply support the above viewpoint.

The biodegradation studies have been carried out over a period of 256 h. It has been found that commercial guar gum gets degraded first followed

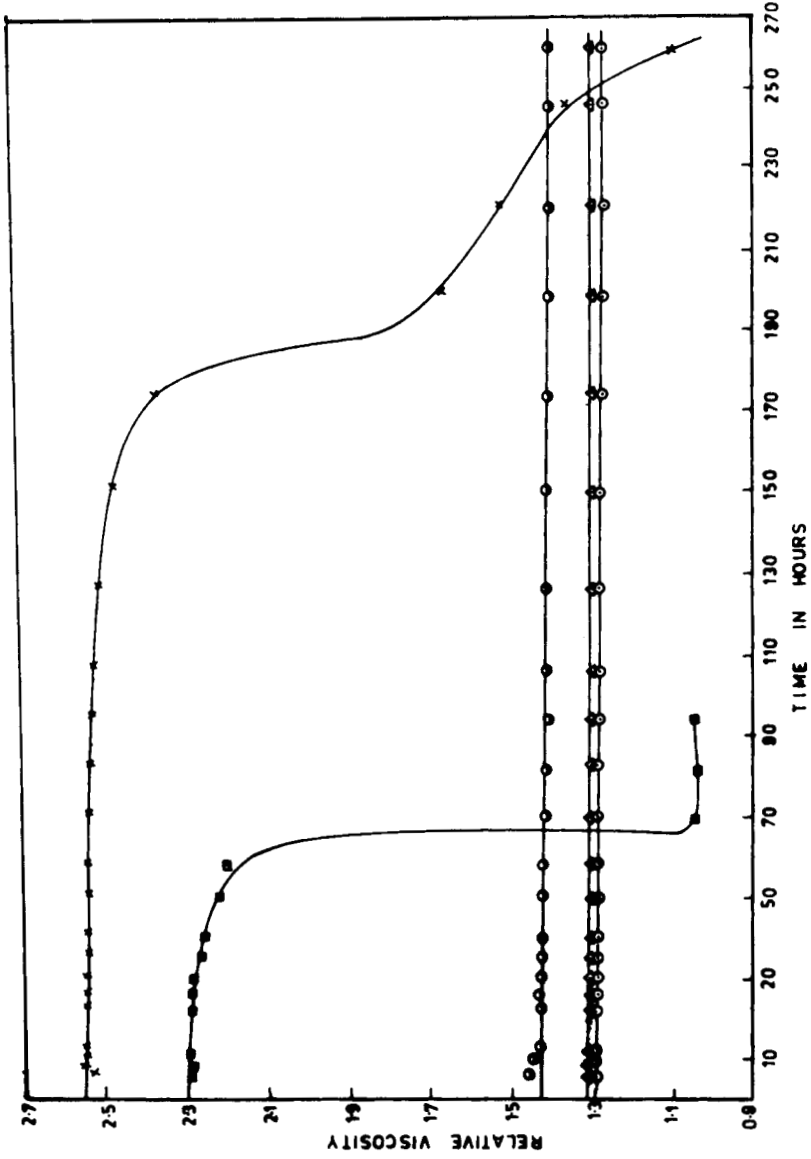


Fig. 3. Relative viscosity vs. time to study biodegradability: (X) PGG; (●) CGG; (△) Gm<sub>2</sub>; (◊) Gm<sub>3</sub>; (○) Gm<sub>1</sub>.

by purified guar gum whereas graft copolymers show no degradation during the entire period of experimentation. This is quite reasonable because the commercial guar gum contains protein impurities and hence act as a better culture media as compared to purified guar gum. Besides this, it also contains hydrolyzing enzymes which help in fast degradation. The graft copolymers did not show biodegradation over the period of experimentation. This is in agreement with the fact that by altering the structure of guar gum molecule it can be made less susceptible to bacterial attack.<sup>10</sup>

The financial support to this work by Department of Science and Technology, Government of India, is gratefully acknowledged.

### References

1. B. A. Toms, in *Proceedings First International Congress on Rheology*, North-Holland, Amsterdam, 1948, Vol. II, p. 135.
2. J. W. Hoyt, *Polymer Drag Reduction, A Literature Review, 1975-76, Drag Reduction*, BHRA Fluid Engineering, Cranfield, Bedford, U.K., 1977.
3. A. T. Ellis, R. Y. Ting, and R. H. Nadolink, *J. Hydronaut.*, **6**, 66 (1972).
4. R. C. Little, R. J. Hansen, D. L. Hunston, O. K. Kim, R. L. Patterson, R. Y. Tang, *Ind. Eng. Chem. Fundam.*, **14**, 283 (1975).
5. R. P. Singh, S. Majumdar, and G. V. Reddy, in *Proceedings IUPAC-82*, University of Massachusetts, Amherst, 1982, p. 726.
6. P. J. Whitcomb, J. Gutowski, and W. W. Howland, *J. Appl. Polym. Sci.*, **25**, 2815 (1980).
7. A. Y. Kulkarni, A. G. Chitale, B. K. Vaidya, and P. C. Mehta, *J. Appl. Polym. Sci.*, **7**, 1581 (1983).
8. J. J. Meister, *J. Rheol.*, **25**, 487 (1981).
9. F. Beuche, *J. Appl. Polym. Sci.*, **4**, 101 (1960).
10. *Handbook of Water Soluble Gums and Resins*, R. L. Davison, Ed., McGraw-Hill, New York, 1980, p. 69.

Received October 15, 1984

Accepted January 21, 1985