



Figure 3. A plot of percentage decrease of absorbance of DMF at 220 nm versus time of exposure: ○—○, for sanguinarine and ●—●, for berberine. The percentage decrease of absorbance was calculated after subtracting the absorbance intensity at 220 nm for each sensitizer. Sanguinarine (13.8 μ M) was irradiated at 330 nm, while berberine (13.8 μ M) was irradiated at 350 nm.

$^1\text{O}_2$ generation was found to be $6.075 \times 10^{-4} \text{ s}^{-1}$ and $1.462 \times 10^{-4} \text{ s}^{-1}$ for sanguinarine and berberine, respectively. The efficiency of $^1\text{O}_2$ production by sanguinarine is four times higher than berberine but comparable to harmine²⁰. In this context, it is pertinent to point out that berberine (Structure II, Figure 1) has a partial saturation in the chemical structure and, in contrast to sanguinarine (structure I, Figure 1), has a planar and aromatic ring system like ethidium. The observed differences in the varying efficiencies of $^1\text{O}_2$ production by the two alkaloids in solution may be rationalized on the basis of their structural differences.

Several classes of tricyclic alkaloids have been shown to be toxic to a variety of organisms in the presence of light, including some furanoquinolines, β -carboline²⁰. It is known that intercalating complexes of sanguinarine-DNA or berberine-DNA are important in their antitumour and other biological activities^{5,6} even without exposure to light. Thus, in the presence of light both the alkaloids may have greater effectiveness towards their biological activities.

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Turbulent drag reduction by polymer-based mixtures and graft copolymers

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Ever since the discovery of turbulent drag reduction phenomenon, the search for materials with drag reduction effectiveness and shear stability is continuing. Polymers, soaps, fibres and their mixtures have been found to be effective drag reducers. The polymer-polymer and polymer-fibre mixtures have extensively been studied in the author's laboratory in recent years. Synergistic combinations of polymer-polymer and polymer-fibre mixtures which provide high drag reduction effectiveness and shear stability have been found. It has been shown in the author's laboratory by extensive grafting of polyacrylamide chains on to the backbones of guar gum, xanthan gum and carboxymethylcellulose as well as polymers like poly(vinyl alcohol) and low molecular compound starch that it is possible to develop graft copolymers which have high drag reduction effectiveness like

polyacrylamides and shear stability like polysaccharides at concentrations of 50–100 ppm. The graft copolymers with lower and longer chains show higher drag reduction effectiveness and shear stability. These graft copolymers have high biodegradation resistance and inertness to the presence of salts found in sea water. The present paper summarizes the details of these aspects of drag-reducing polymeric systems in terms of current molecular theories of drag reduction and shear stability.

TURBULENT drag reduction is the phenomenon of drastic reduction of drag by a factor of two or more below that of the solvent by addition of a small amount of some substances, mainly high polymers, fibres, soaps, surfactants and their mixtures. Mysels¹ and Toms² observed the phenomenon independently. The developments in this field have been recently reviewed by Singh^{3,4}, Morgan and McCormick⁵ and Kullicke *et al.*⁶. As the phenomenon has high potential for technical and industrial applications^{7,8}, the search for efficient and shear stable drag-reducing agents is continuing ever since the discovery of the phenomenon. Polymers are the most potential drag reducing agents mainly because the drag reduction of up to 80% can be obtained at concentrations of a few tens of ppm of polymer in water. But polymers suffer from mechanical degradation and biodegradation.

Several attempts have been made to enhance drag reduction and shear stability of polymeric drag reducers. It has been observed⁹ that the polymers when used in combination with drag-reducing polymers or fibres can offer combinations having synergistic effect in drag reduction and shear stability. Similarly, by grafting the chains of flexible highly effective drag-reducing polymers on rigid and shear-stable but poorly drag-reducing polymers¹⁰⁻¹⁴, it is possible to develop highly drag-reduction-effective and shear-stable drag-reducing agents. Interacting and associating polymer systems have also shown higher drag reduction efficiency and shear stabilities¹⁵. A detailed investigation has been carried out in the author's laboratory on the development of highly drag-reduction-effective and shear-stable polymeric systems. The present paper summarizes the results of this investigation.

Drag reduction by a large number of polymer–polymer mixtures has been studied by several workers³. The synergism in drag reduction has been obtained only by those mixtures in which either both of the components or at least one of the components in the mixture has a rigid structure. In the author's laboratory, mixtures of relatively shear-stable polymers such as polyacrylamide, guar gum, xanthan gum and carboxymethylcellulose have been investigated¹⁶. Both positive and negative deviations from linearly additive straight line have been observed in drag reduction caused by polymer–polymer mixtures, depending upon their compositions, flow rate and the

polymer species in the mixtures. Drag reduction by mixtures has been predicted by using the simple mixture rule equation having an interaction parameter, i.e.

$$DR_M = DR_1 W_1 + DR_2 W_2 + I W_1 W_2, \quad (1)$$

where DR_M is the drag reduction percentage by the mixture and DR_1 , DR_2 , and W_1 , W_2 , are the drag reduction percentages and weight fractions of component 1 and 2, respectively, in mixtures. I is the interaction parameter believed to depend on the interaction in the polymer mixture. The random coil size, solvation and rigidity of the polymer molecules appear to be responsible for synergism observed in drag reduction caused by mixtures. In the above study, the concentrations and Reynold's numbers were higher, i.e. 200–1000 ppm and 20,000–60,000, respectively. However, when the studied concentrations were in tens of ppm¹⁷, synergism was obtained only in those mixtures where both the constituents are rigid and cause the same order of drag reduction individually. From these studies, it appears that synergism is a function of concentration as well. Recently, it has been observed¹⁵ that interacting polymers can cause high drag reduction (up to 90% with higher shear stability) at concentrations of a few tens of ppm in organic solvents. Hence, a detailed study has been conducted in the author's laboratory¹⁸ to find the pairs of water-soluble interacting drag-reducing polymers. The study of drag reduction by such interacting polymers is under progress.

Although polymer–fibre mixtures cause high drag reduction¹⁹, very limited work has been reported. A detailed study of drag reduction by polymer–fibre systems was undertaken in the author's laboratory. Reddy and Singh¹⁶ found strong synergistic effects with both guar gum and xanthan gum in combination with asbestos fibres. A 50–50 mixture by weight gives the maximum synergism in both cases. Malhotra *et al.*^{17,19} observed that a 50–50 mixture of guar gum and asbestos fibres shows synergism in drag reduction even at a very low concentration of 50 ppm. The random coil extension of polymers and rigidity of fibres appear to be responsible for synergistic drag reduction observed by them. These investigations also have a bearing on the mechanism of drag reduction as observed by Hoyt²⁰. "Singh *et al.*²¹ show strong additive effects with both guar and xanthan polymers in combination with asbestos fibres – a 50–50 mixture (by weight) being the best in each case. This additive effect of combining high-mass fibres and long-length polymers seems to indicate the importance of both mass and length in interfering with the $\vec{u}\vec{v}$ fluctuations."

The flexible polymers like polyacrylamide and poly(ethylene oxide) cause maximum drag reduction (80% in turbulent pipe flows) at concentrations of a few tens

of ppm but are easily shear-degradable. On the other hand, rigid polymers such as polysaccharides like guar-gum, xanthangum and carboxymethylcellulose show high shear stability but are relatively poor drag-reducing agents, requiring much higher concentrations (few hundreds of ppm) to achieve maximum drag reduction (40–60%). They are susceptible to biodegradation in aqueous solutions. Thus, there exists a scope to develop new drag-reducing agents having reasonable shear stability, high drag reduction effectiveness and low cost. An extensive investigation^{10–14} was undertaken in the author's laboratory to develop graft copolymers of polyacrylamide/guargum, xanthangum, carboxymethylcellulose, poly(vinyl alcohol) and low molecular weight starch. These graft copolymers have the shear stability of polysaccharides and drag reduction effectiveness of polyacrylamide. On grafting, alteration of the structure of polysaccharides also reduces their biodegradability.

A large number of graft copolymers were synthesized by changing the length and number of grafted chains. The graft copolymers with longer chains cause more drag reduction and have higher shear stability. Their molecular behaviour is also akin to flexible molecules. The maximum in drag reduction is also obtained at concentrations of 50–100 ppm. The drag reduction characteristics of these graft copolymers show inertness to the presence of salts found in sea water²². Regarding the above approach, the observations of Choi *et al.*²³, recently there have been some attempts to improve the effectiveness of synthetic polymers to shear degradation by altering their chemical structures. Kowalik *et al.*¹⁵ reported that the interpolymer complexes formed by one polymer with the anionic groups and the other with the cationic groups increase the polymers' resistance to degradation in turbulent flows. Deshmukh and Singh¹¹ tried to take advantage of the fact that natural polymers such as guar are quite resistant to mechanical degradation. They grafted polyacrylamides to guar backbone and found that the synthetic polymer became more robust to shear degradation than without the graft.

The shear stability of drag-reducing systems in general has been studied by recirculating the same solution through the pipe of turbulent flow rheometers and monitoring the drag reduction with the time of recirculation or pass number. One recirculation is depicted as a unit pass number. The following equation represents the loss of drag-reducing ability by mechanical degradation during turbulent flows:

$$\frac{DR}{DR_0} = \left(1 - \frac{DR_\infty}{DR_0}\right) \times e^{-RT} + \frac{DR_\infty}{DR_0} \quad (2)$$

where DR is drag reduction, T is the time and the subscripts ∞ and 0 refer to infinite and zero times. The constant R is a measure of the rate of decay of drag reduction effectiveness. As DR_∞ tends to zero,

$$\frac{DR}{DR_0} = e^{-RT}. \quad (3)$$

The above equation in terms of the pass number N can be written in the following form:

$$\frac{DR}{DR_0} = A e^{-BN}, \quad (4)$$

A is found to be nearly equal to 1. An alternate equation has been proposed by Brostow²⁴.

$$\frac{DR}{DR_0} = [1 + W(1 - e^{-ht})]^{-1}, \quad (5)$$

where W and h are parameters defined by the Brostow theory²⁴. An investigation has been undertaken in the author's laboratory to study the shear stability of polymer–polymer, polymer–fibre mixtures. The results of such an investigation are summarized below.

The mixtures exhibiting synergism in causing drag reduction are found to be more stable. Equations (2)–(5) can explain the results mathematically. The shear stability of highly efficient but highly degradable polymer polyacrylamide can be improved by incorporation of more shear-stable polymers such as guar-gum and xanthangum. Similarly, the shear stability of asbestos fibres suspension can be improved by incorporation of guar-gum or xanthangum.

In the cases of graft copolymers of polyacrylamide with guar-gum/xanthangum/carboxymethylcellulose/poly(vinyl alcohol)/starch, equation (4) can explain the results.

It was observed that the graft copolymers having fewer number of longer grafts showed more shear stability than the graft copolymers with more number of shorter grafts^{10–14}. The shear stability of xanthangum graft copolymers is comparable with xanthangum. However, the guar-gum and CMC were found to be more shear-stable than their graft copolymers. The graft copolymers of xanthangum are more shear-stable than the mixture of xanthangum and polyacrylamide having the same composition as in the graft copolymers¹³.

Recently, the Brostow model of drag reduction has been applied²⁵ to study the time dependence of drag reduction in terms of the Brostow equation (5). A large number of the drag-reducing polymers, polymer–polymer and polymer–fibre mixtures²⁵ studied in the author's laboratory provide excellent fit to the Brostow equation, thus giving credence to general applicability of the Brostow model for flowing solutions²⁴.

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Trenching in the Koyna area

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The results of excavating a trench to uncover fissures associated with the 1967 Koyna earthquake suggest that evidence of prehistoric earthquakes can be preserved in fissures. Future paleoseismological investigations can be used to seek evidence of prehistoric earthquakes in the Koyna-Warna area and at other locations.

THE Killari earthquake of September 1993 was the most recent reminder that peninsular India is not immune to moderate to large earthquakes. Kutch was the site of a major (M_w 7.8) earthquake in 1819. Mid-plate earthquakes (also called stable continental interior earthquakes) occur much less frequently than their plate boundary counterparts. They account for about 0.5% of the seismic energy release but account for a disproportionate amount of damage and destruction. Besides these two events, the M 6.3 Koyna earthquake of 1967 was the most destructive earthquake in peninsular India. Although the temporal and spatial pattern of seismicity near the Koyna Reservoir strongly suggest that it was induced (see e.g. ref. 1 for a comprehensive review), this view is not universally shared.

The objective of the studies reported here was to see if evidence of large prehistoric earthquakes and their rates of recurrence can be documented by identifying the evidence of their occurrence in the shallow sediments. That is, could the nascent science of paleoseismology, the search for prehistoric earthquakes, be a feasible approach in the Koyna-Warna area in particular and other areas in the Deccan Traps in general?

To accomplish this, we decided to trench in the Koyna area to see if ground fissures that were widely observed in 1967 are preserved in the shallow soil and if they could be used to identify the evidence of earlier earthquakes.

Fissures associated with the 1967 earthquake

Following the disastrous magnitude 6.3, 1967 Koyna earthquake, widespread fissuring was observed in the *meizoseismal* area by Sathé *et al.*² Although some of these fissures were associated with slumping of land forms along hill slopes, several fissures were a direct consequence of the earthquake. Among these was a very well-developed system of fissures about 20 km in length from Nanel and Baje on the SE shore of Shivajisagar (reservoir impounded by Koyna dam), SSW to near Randhiv (Figure 1).

The fissures were mapped in detail by the Geological Survey of India (GSI) and it was thought possible to locate them in the field based on the descriptions in the GSI report.