**Journal of Industrial Microbiology & Biotechnology (1999) 23**, 442–445
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# Evaluation of rheological properties of the exopolysaccharide of *Sphingomonas paucimobilis* GS-1 for application in oil exploration

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**Analysis of an exopolysaccharide of *Sphingomonas paucimobilis* GS-1 (EPS/GS-1) with respect to its rheological properties, cross-linking ability with chrome alum and performance test at 75 ± 5°C revealed its strong suspending ability, shear thinning property, and thixotrophic nature which are required to impart desirable rheology to drilling mud. The organism fulfilled all the specified requirements and its properties were superior to those of currently-used XC polymer (a xanthan product) for oil drilling applications. However, EPS/GS-1 was unstable in the presence of bentonite at 100 ± 5°C during performance tests, in contrast to XC polymer.**

**Keywords:** *Sphingomonas paucimobilis* GS-1 exopolysaccharide; rheological properties; biopolymer; drilling fluid; oil exploration

## Introduction

Tertiary oil recovery or enhanced oil recovery is a process wherein oil trapped in porous crevices of the reservoir can be extracted by injecting thickened water and/or gas under pressure [11]. Polymer flooding involves increasing the viscosity of water using water-soluble polymers, since the viscosity of the entrapped crude oil is very high. Water-soluble polymers are also used as a component of drilling fluids and almost 95.5% of oil wells are drilled with water-based low-solid mud systems, as these are cheaper and more environmentally acceptable than other alternatives, such as oil-based mud systems [16]. The desirable properties of polymers for polymer flooding and oil drilling fluids are: (i) high viscosity at low concentration; (ii) pseudoplastic flow behavior, enabling easy injection; and (iii) stability of the polymer viscosity to salinity, temperature, and alkaline conditions [14].

One of the classes of polymers used currently for this purpose is polyacrylamides, which are relatively less expensive and are easily synthesized. Their main limitation, however, is their sensitivity to shear and salt. Moreover, they have limited stability over a long period of time under reservoir conditions [7]. Hydroxyethyl cellulose, a low cost additive, is required in high concentrations and has low pseudoplasticity, high temperature sensitivity and poor storage stability. Biopolymers are therefore being considered as alternatives and although xanthan gum is currently an agent used for this purpose, it is not ideal as its temperature and salt sensitivity are not as low as desired [16].

Recently, an exopolysaccharide (EPS) of *Sphingomonas paucimobilis* GS-1 has been characterized chemically as well as in terms of its rheological properties such as viscosity (5.5 times that of xanthan gum), consistency index k (five times that of xanthan gum), and pseudoplasticity (better than xanthan gum). The viscosity of EPS/GS-1 was also stable up to 90°C, in the pH range 2–10 and also in the presence of NaCl up to 50 g $L^{-1}$. In contrast, the viscosity of xanthan gum (Sigma, St Louis, MO, USA) was decreased about four-fold at 90°C from that at 28 ± 2°C. Moreover, the viscosity of EPS/GS-1 was insensitive to other salts (up to 50 g $L^{-1}$) such as KCl, $CaCl_2$, $CoCl_2$, $MgCl_2$, $NH_4Cl$, $Na_2SO_2$ and $ZnCl_2$ at alkaline pH (9.0 ± 0.2) and up to 75 ± 5°C [2]. EPS/GS-1 also emulsifies a number of aliphatic and aromatic hydrocarbons more effectively than several commercially used gums such as arabic, tragacanth, karaya, and xanthan [3].

Stability of viscosity under extremes of pH, temperature and salinity, as well as emulsification ability are desirable features of a biopolymer for its application as a drilling fluid component. This communication describes the evaluation of the EPS/GS-1 for its suitability for use in drilling mud.

## Materials and methods

### *Maintenance and cultivation of the organism and extraction of EPS/GS-1*

The EPS-producing *Sphingomonas paucimobilis* GS-1 was maintained and cultivated on a minimal salts medium with nitrate and sucrose. The exopolysaccharide (8 g $L^{-1}$) was extracted from the culture broth by precipitation with acetone as described earlier [2].

### *Testing of EPS/GS-1 for its application in oil drilling fluid*

The tests were performed according to specifications laid down by Oil and Natural Gas Commission, Dehradun, India

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Received 14 April 1999; accepted 26 July 1999

(ONGC), for testing XC polymer, a xanthan product for oil drilling applications for its use in oil drilling fluids [1]. XC polymer was used as a control for comparison.

### *Rheological properties*

Polymer solution (0.5% w/v) was prepared in distilled water by stirring it in a Hamilton Beach mixer at medium speed for 20 min. While stirring, NaCl (4.0% w/v) was added and the pH was adjusted to $9.0 \pm 0.2$ with 1 N NaOH. Rheology was determined using an NL Baroid rheometer (Houston, Texas, USA), at 0, 100, 200, 300, 600 rpm and $28 \pm 2$°C. $Gel_0$ and $Gel_{10}$ were measured by vigorously stirring the sample and keeping the solution static for 10 s and 10 min, respectively, before taking readings. The deflection in the dial reading was further recorded at 3 rpm and expressed as lb per 100 sq ft.

### *Crosslinking ability of EPS/GS-1*

A solution of polymer (0.5% w/v), fused $CaCl_2$ (3.0% w/v) and chrome alum (0.2% w/v) was prepared by stirring it at medium speed in a Hamilton Beach mixer for 20 min. The pH was adjusted to $9.0 \pm 0.2$ using 1 N NaOH. The rheology was determined as specified earlier.

### *Rheological parameters*

Basic concepts and definitions of rheological parameters (such as apparent viscosity, plastic viscosity, yield point, and 'n' value), measured here, have been explained previously [4]. Rheological parameters were measured using simplified conventional procedures based on the Reiner–Riwlin equation and a direct-indicating viscometer [8,9].

### *Borate sensitivity test*

A polymer solution (0.5% w/v) that contained $Na_2B_4O_7$ (2% w/v) was prepared and stirred for 5 min. It was observed visually for up to 24 h for gelation. No stiff gel formation should take place.

### *API filtration loss*

API filtration loss is the measure of the fluid retention capacity of a polymer as defined by the American Petrochemical Institute (API). The polymer-bentonite sample was filtered through Whatman No. 50 filter paper (9.0 cm diameter circle) having a filtration area of 45.8 $cm^2$ at 100 psi pressure for 30 min. The volume of the filtrate was noted as the fluid loss of the drilling mud.

### *Performance test with EPS/GS-1 and XC polymer*

ONGC-approved bentonite powder (3.0% w/v) was mixed with 500 ml of 0.5% w/v polymer solution, stirred in a Hamilton Beach mixer at medium speed for 20 min. The pH was adjusted to $9.0 \pm 0.2$. The formulation was subsequently aged in a rolling oven at $75 \pm 5$°C for 20 h and was then cooled to room temperature. Rheology and API filtration loss were measured before and after aging.

### *Reproducibility*

All the experiments were performed three times and values represent their average.

## Results and discussion

### *Rheological and crosslinking properties*

The flow properties of a drilling fluid play a vital role in the success of the drilling operation. These properties are primarily responsible for the 'cuttings carry capacity' of drilling fluid and thereby for the removal of the drill cuttings. Addition of organic polymers helps in achieving desirable flow properties. Rheological characterization of the polymer in terms of apparent viscosity (AV), flow index 'n', yield point (YP), plastic viscosity (PV), and gel strength provides the information necessary for day-to-day control of mud rheology.

Xanthan gum's major application in low-solid drilling mud is that of a suspending agent to impart 'cuttings carry capacity' to the drilling mud. The suspending ability of a polymer solution is directly related to the low shear rate viscosity of the solution. It is reported, with respect to suspending ability, that xanthan gum surpasses that of any other polymer currently used in drilling fluid. Either the high YP/PV ratio or a low flow index, 'n', is used to characterize the shear thinning properties (pseudoplasticity) of the mud and this property is desirable for the better hole cleaning capacity, easy injectivity and improved drilling rate.

The difference between the initial gel strength and that taken after a 10-min rest period indicates the thixotrophic nature of the polymer and may be used to judge how thick the mud will become to keep drill cuttings suspended when circulation is stopped. A polymer with a higher yield point exhibits higher gel strength, which imparts a desirable structural property to the mud [10].

Cross-linking between chromic ion and xanthan gum significantly increases the viscosity as well as the structural property. This property of xanthan gum has been exploited to plug very permeable streaks (thief zones) in reservoirs in order to exert more pressure on the oil-bearing areas [13].

Analysis of rheological parameters as such (Table 1) and after cross linking with chrome alum (Table 2) revealed that EPS/GS-1 met all the specified requirements, in contrast to XC polymer. In rheological terms, ie apparent viscosity, pseudoplasticity, thixotrophy, gel strength, and also in terms of cross linking ability with chrome alum, EPS/GS-1 was found better than the XC polymer as it imparted a more desirable rheology to drilling mud than XC polymer. Succinoglycan and rhamsan have also been reported as

**Table 1** Rheological properties of the exopolysaccharide

| Samples | Parameters | |
|---|---|---|
| | Apparent viscosity (cPs) | n value |
| EPS | 27 | 0.311 |
| XC polymer | 13 | 0.500 |
| Desired value[a] | >15 | <0.400 |

The rheology of EPS (0.5% w/v) solution was tested in the presence of 40 g $L^{-1}$ NaCl, at pH $9.0 \pm 0.2$ and $28 \pm 2$°C as described in the Materials and Methods section.

[a] 'Desired value' indicates the requirement in terms of rheological properties of the polymer, under testing, for its efficient performance as a drilling fluid component [1].

**Table 2** Crosslinking ability of polymers with chrome alum

| Samples | Apparent viscosity (cPs) | Yield point 1b per 100 sq ft | $Gel_0$ lb per 100 sq ft | $Gel_{10}$ lb per 100 sq ft |
|---|---|---|---|---|
| EPS | 45.5 | 45.0 | 24.5 | 45.0 |
| XC polymer | 13.5 | 11.0 | 10.0 | 14.5 |
| Desired value[a] | >30.0 | >30.0 | >15.0 | >30.0 |

Crosslinking of the polymers (5.0 g $L^{-1}$) was carried out with chrome alum (2.0 g $L^{-1}$) in the presence of $CaCl_2$ (3.0% w/v) at pH 9.0 ± 0.2.

[a] 'Desired value' indicates the requirement in terms of rheological properties of the polymer, under testing, for its efficient performance as a drilling fluid component [1].

strong viscosifiers and better suspending agents than xanthan gum [13].

### Borate sensitivity test

EPS/GS-1 was insensitive to sodium tetraborate (2.0%), whereas XC polymer gelled instantly. Borate is a component of sea water, and gelation in the presence of borate is not a desirable property as it impairs the injectivity in reservoirs through the formation of microgels. This problem is encountered with some types of xanthan gums [13].

### Performance tests

Temperatures and pressures higher than ambient are encountered during drilling operations and reduction in rheological functions of the polymers under extreme conditions affects their performance as a viscosifier. Other organic polymers such as acrylamides and xanthan gum used in drilling mud are hydro-colloids and under extreme drilling conditions, ie high temperature and pressure, increased water loss of the polymers (measured in terms of filtration loss) leads to hydration of the clay particles. Thus, the permeability of sand particles is reduced, which in turn reduces the flow of oil through sand layers and thereby oil productivity. Hence, characterization of the polymer-bentonite sample is required in terms of its rheological and filtration properties after aging at higher temperature.

Performance tests carried out by aging at 75 ± 5°C (Table 3) indicated superior behaviour of EPS/GS-1 over that of XC polymer in terms of all three parameters studied. The apparent viscosities of EPS/GS-1 and XC polymer were reduced marginally ie by 9–14% of original viscosity, while the water-binding ability of EPS/GS-1 was not affected. The higher viscosity of EPS/GS-1 (about four times that of XC polymer) observed after aging would mean that a lesser amount of EPS/GS-1 would be required for unit applications. As polysaccharides are marketed on the basis of their ability to alter viscosity power, higher viscosity per unit weight is an advantageous feature [13]. Unlike EPS/GS-1, XC polymer decreased pseudoplasticity and water-binding ability, which are not desirable. The viscosity of EPS/GS-1 was, however, affected by aging at 100 ± 5°C, whereas that of XC polymer was stable (data not shown). Hot rolling in the presence of bentonite at 100°C for 20 h at pH 9.0 ± 0.2 affected the rheology of EPS/GS-1. The ordered conformation of polysaccharides in solution, when subjected to heat, melts into a disordered one at the critical temperature, Tm. It should be noted that EPS/GS-1 was stable up to 90°C, while xanthan was not stable up to that temperature, as described previously [2]. However, xanthan was stable to temperature in the presence of NaCl. XC polymer, used here for comparison, is a trade name of a product developed from xanthan specifically for oil drilling [12] and contains additional chemicals to improve/stabilize rheological properties under extreme conditions. It should be possible to improve the thermal stability of EPS/GS-1 by adding low molecular weight solutes or by chemical modification. The Tm for xanthan can be adjusted from ambient to over 200°C, by addition of appropriate salts [5,6]. Improved thermostable, viscous xanthan gum solutions have been obtained by heat treatment of the polymer in the presence of C1–C10 alkyl amines [17].

**Table 3** Performance test

| Samples | Treatment | Apparent viscosity (cPs) | n value | API filtration loss (ml) |
|---|---|---|---|---|
| EPS | Before aging | 92.0 | 0.66 | 12.0 |
| | After aging | 84.0 | 0.54 | 11.5 |
| XC Polymer | Before aging | 24.5 | 0.24 | 17.5 |
| | After aging | 21.0 | 0.52 | 31.0 |

Polymer samples (5.0 g $L^{-1}$) were mixed with 3.0 g $L^{-1}$ ONGC-approved bentonite and the pH was adjusted to 9.0 ± 0.2. Aging was done for 20 h at 75 ± 5°C in a hot rolling oven. Requirements: There should be no loss in rheology and no increase in the filtration rate of a formulation.

Xanthan is used frequently in drilling fluids, either in combination with the traditional thickener, bentonite clay, or alone in clear muds [13]. As EPS/GS-1 alone, ie without bentonite, was stable up to 90°C it may perform well, without loss of rheology, in clear muds.

The greatest application of succinoglycan is for workover and completion operations in the oilfield [13] where use is made of its relatively low (~70°C) transition temperature (Tm). The transition temperature for EPS/GS-1 of around 75°C observed during performance tests in the presence of bentonite could be exploited in a manner similar to succinoglycan.

Reservoir temperatures range from ambient to over 150°C. However, for all practical purposes the application of 'polymer flooding' is restricted to reservoirs containing oil with viscosities in the range of 10–100 cP at temperatures below 80°C [16]. Further, on the Indian subcontinent, approximately 40% of the reservoirs have temperatures around 70–80°C. Under these conditions, the application of EPS/GS-1 as a viscosifier can be envisaged.

The potential of deacylated EPS from *S. paucimobilis* GS-1 as a gel-forming polymer superior to agar-agar was reported recently [2]. Gellan is a deacylated polymer from another strain of *S. paucimobilis* marketed as 'Kelcogel', which suggests that technology for mass production of exopolysaccharide of *S. paucimobilis* is already available [15]. The work presented here has shown the potential of native EPS/GS-1 for application in drilling fluid in preference to XC polymer. This should be explored further.

## Acknowledgements

The authors acknowledge SS Negi for the tests carried out at Oil and Natural Gas Commission (ONGC), Baroda, India and the partial financial assistance received from the Department of Biotechnology, India. AAA acknowledges receipt of a fellowship from the University Grants Commission, India.

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