Fracturing Fluid Cleanup by Controlled Release of Enzymes from Polyelectrolyte Complex Nanoparticles

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ABSTRACT: Water-based polymer gels are used widely in the oil and gas industry to viscosify fluids used in the hydraulic fracturing of production wells, where they serve to increase the force applied to the rock and to improve the transport of proppants used to maintain the fracture after formation. After fracturing, the gel must be degraded to a low viscosity with enzymes or gel breakers. Existing systems add the breaker either directly to the gelant or encapsulated in beads that are crushed when the applied pressure is released and the fractures close. In the former case, the gel may be broken prematurely, and this may prevent efficient fracture propagation and proppant transport, whereas in the latter case, the breaker may not be uniformly distributed throughout the gel, with the result that the gel is incompletely broken and the hydraulic conductivity of the well is reduced. To obtain delayed release, combined with the homogeneous distribution of enzyme throughout the gel, polyethylenimine–dextran sulfate polyelectrolyte complexes were used to entrap pectinase. Such particles were originally developed to entrap pharmaceuticals, and we previously demonstrated their ability to delay the release of gel crosslinking agents for oilfield applications. The degradation of both the viscosity and viscoelastic moduli of borate-crosslinked guar gel by pectinase loaded in polyelectrolyte nanoparticles was delayed by up to 12 h, compared to about 2 h for equivalent systems where the pectinase was not entrapped. The combination of homogeneous mixing and the delayed release of enzymes packaged in polyelectrolyte complex nanoparticles showed promise for improved cleanup after hydraulic fracturing. J Appl Polym Sci 121: 1292–1298, 2011

Key words: gels; enzymes; nanoparticle; polyelectrolytes

INTRODUCTION

The rate of oil and gas production from a well is often limited by the hydraulic conductivity of the rock immediately surrounding the production well bore. Hydraulic fracturing increases the surface area contributing to production. In hydraulic fracturing, a viscous polymeric solution is injected onto a production well at high pressure to create and propagate fracture and to transport propping agents (*proppants*).[1] A proppant such as sand is used to keep the fracture open after the injection. The fracturing fluid is usually a water-based polymer that forms filter cakes with high polymer concentration on the two faces of the fracture during the treatment.[2,3] The filter cake must be broken completely after the injection to attain high conductivity when the well is placed on production. Breakers (e.g., enzymes, oxidizers) are added to the fracturing fluid to degrade the polymer remaining in the fluid and the filter cake.

Although fracturing jobs are shifting toward lower viscosity slick-water treatments[4] for unconventional reservoirs, guar gum and its derivatives are still commonly used to viscosify water in fracturing fluids for treatments in conventional wells. Guar, a polysaccharide composed of a (1→4)-linked β-d-mannose backbone with (1→6)-linked α-d-galactose residues, can be gelled with borate ions complexing with the hydroxyl groups on the galactose (Fig. 1). The ether bonds between the sugar units on the backbone can be degraded by enzymes, which are often used as a breaker because of their low cost and because, unlike chemical breakers, they are not consumed by the reaction and so are effective at lower concentrations.

High concentrations of enzymes can cause the premature degradation of fracturing fluids. To overcome this problem, delayed release or encapsulation of the breakers has been used.[1,5] A low concentration of encapsulated breakers causes the filter cake, in particular, to break nonuniformly.[2,3,6] Delayed enzyme breakers have been developed for low pH values and cannot delay the breaking time significantly. An ideal

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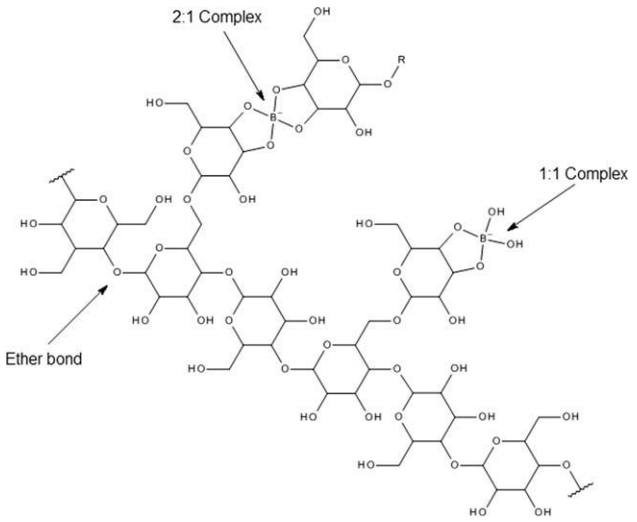

Figure 1 Chemical structure of guar showing the mechanism of crosslinking by borate and the ether bond vulnerable to cleavage by pectinase (—R denotes another guar molecule).

application would be the distribution of high concentrations of breakers (e.g., enzymes) homogeneously throughout the gel and filter cake at microscopic length scales, with controlled or delayed release.

An encapsulation method originally developed for drug-delivery applications,[7] polyethylenimine (PEI)–dextran sulfate (DS) polyelectrolyte complex nanoparticles (PECNPs), was developed for oilfield applications and, for instance, can control the release of Cr(III) crosslinker to form polyacrylamide gels for conformance control.[8,9] We hypothesized that the nanoparticle system may also be capable of entrapping and releasing pectinase in a controlled manner with the potential for application in breaking fracturing fluids.[8] The use of such a carrier as a breaker in fracturing fluids would require a high entrapment efficiency (EE) of the breaker, homogeneous distribution, and a flexible release time.

Here, we present a proof-of-concept study for the application of PECNPs to entrap and release enzyme breakers for fracturing fluids. Positively charged PECNPs were made by the variation of the total concentration and charge of a polycation (PEI) and a polyanion (DS). An enzyme used in the petroleum industry to break the fracturing and drilling fluids was added to the nanoparticles either before or after the addition of DS and was entrapped in the PECNPs. EE was calculated for the nanoparticles loaded with enzymes with a viscometric assay and confirmed with sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE). Nanoparticles were then used to degrade borate-crosslinked guar solutions at 25°C. Different delay times were observed in the activity of enzymes for different PEI : DS ratios. A retardation in enzyme activity was observed by the measurement of the viscosity of the gelled guar and by the monitoring of the viscoelastic moduli of the gel over time. Delay times were compared with equivalent systems with unentrapped enzymes. The pectinase used in this study was active in environments with a maximum pH of 10 at 25°C and a maximum pH of 6 at 60°C. The temperature and pH-tolerant enzymes were typically used in the field; however, a more sensitive enzyme was selected to test the hypothesis that entrapment would protect the enzyme from extreme environmental conditions.

EXPERIMENTAL

Materials

Chemicals were used as supplied: sodium hydroxide, 1*N* hydrochloric acid, DS [weight-average molecular weight (M_w) = 500 kDa], PEI (M_w = 25 kDa), sodium thiosulfate pentahydrate, potassium chloride and sodium hydrate (Fisher Scientific, Pittsburgh, PA), guar and pectinase from *Aspergillus aculaceatus* (Sigma-Aldrich, St. Louis, MO), hydroxypropyl guar (HPG) gum blend (Jaguar 415, Rhodia, Paris, France), sodium borate (J. T. Baker Chemical Co., Phillipsburg, NJ), NuPAGE® 4–12% bis-tris gel (1.5 mL × 10 lanes), NuPAGE® MES = 2-[N-Morpholino]ethanesulfonic acid sodium dodecyl sulfate (SDS) running buffer (20×), NuPAGE® LDS = lithium dodecyl sulfate sample buffer (4×), and Mark12™ unstained buffer (1×, Invitrogen, Carlsbad, CA).

Preparation of PECNPs

Nanoparticles were made with different ratios of PEI : DS with a method presented previously.[9] In a typical formulation, 1 mL of a 1% w/w aqueous solution of DS (pH = 7.8) was added dropwise to 2 mL of a 1% w/w aqueous solution of PEI (the pH was adjusted to 8 with 4*N* HCl) with stirring. The solution was then stirred for 20 min at 600 rpm unless otherwise indicated. Pectinase was added dropwise as 0.1 mL of a 25% w/w pectinase solution either before or after DS was added (Table I). Pectinase-loaded nanoparticles were used as breakers in polymer systems at a final concentration of 0.1% w/w pectinase.

Size and ζ-potential measurement of PECNPs

A ZetaPALS ζ-potential analyzer (Brookhaven Instruments Corp., Long Island, NY) was used to measure the mean particle size of the nanoparticles. Samples of the nanoparticles were diluted approximately 40× by volume with deionized water. Recorded data were the average of three measurements by the detection of light scattering at a 90° angle. The ζ potential was also measured by phase analysis light scattering with the same instrument.

TABLE I
Nanoparticle Systems Differences in the Ratio of PEI, DS, and Pectinase and the Order of Addition

System	1% w/w PEI (aqueous, mL)	1% w/w DS (aqueous, mL)	25% w/w pectinase (aqueous, mL)	Order of addition
A	2.0	1.0	0.10	PEI, DS, pectinase
A′	2.0	1.0	0.10	PEI, pectinase, DS
B	3.0	1.0	0.10	PEI, DS, pectinase
B′	3.0	1.0	0.10	PEI, pectinase, DS
C	4.0	1.0	0.10	PEI, DS, pectinase
C′	4.0	1.0	0.10	PEI, pectinase, DS
D	2.0	1.0	0.07	PEI, DS, pectinase
E	3.0	1.0	0.06	PEI, DS, pectinase

Samples were diluted approximately 20× with a 1.0 m*M* KCl solution. Three measurements were averaged for each sample. The ζ potential was estimated with the Smoluchowski approximation from the previously measured hydrodynamic diameter and the electrophoretic mobility of the nanoparticles.

Separation of the nanoparticles

Samples of the enzyme-loaded nanoparticles were centrifuged at 14,000 g for 1.5 h at 4°C. Supernatants were then separated from the nanoparticles for activity measurements.

Determination of the enzyme activity of the nanoparticles and their supernatants

Two grams of either 5000-ppm guar or HPG solution was mixed with 0.5 g of the diluted nanoparticles or supernatants at room temperature. After mixing, 1.5 mL of the solution was placed between the plates of a parallel-plate Bohlin CS rheometer (Malvern Instruments, Malvern, England), and the viscosity of the solution was measured over time at 25°C. The time for the viscosity of the solution to fall to 50% of its initial value [$t_{1/2}$ (h)] was used to calculate the activity of the nanoparticles after the method reported by Bell and Etchells.[11] The activity was defined as the reciprocal of $t_{1/2}$. The activity of the free enzyme was also calculated with the same method. The entrapment efficiency based on enzyme activity (EE_A) was calculated with the activities of the supernatant and free enzyme, as in eq. (1):

$$EE_A = \frac{A_E - A_S}{A_E} \times 100\% \quad (1)$$

where A_E is the activity of the equivalent enzyme concentration added to the nanoparticles and A_S is the activity of the supernatant.

Determination of enzyme concentration with SDS-PAGE

We performed SDS-PAGE analysis with a NuPAGE® kit, following the manufacturer's instructions. SDS-PAGE is a type of gel electrophoresis technique that uses the SDS to separate proteins by size, independent of their net charge. This technique works by the binding of the negatively charged SDS molecule to the hydrophobic side chains of a protein. On average, one SDS molecule binds to every two residues of a typical protein; this gives it a large overall negative charge proportional to the length of the protein.[12] Samples, including several concentrations of pectinase and supernatants, were first diluted (30 μL of sample + 10 μL of buffer). One lane was loaded with a mixture of protein markers of known molecular weights (MWs) to calibrate the gel and determine the weights of the unknown proteins. After the electrophoresis, the gel was stained, destained, and optically measured. The area under the intensity–distance curve was measured for different intensity peaks.

The calibration curves of peak area against enzyme concentration were generated to determine the concentration of enzyme in the supernatants. The entrapment efficiency of the enzyme in the nanoparticles based on concentration (EE_C) was calculated with eq. (2):

$$EE_C = \frac{C_E - C_S}{C_E} \times 100\% \quad (2)$$

where C_E is the enzyme concentration added to the nanoparticle system and C_S is the concentration of enzyme in the supernatant.

Preparation of guar and HPG solutions

A sufficient mass of polymer to create a 5000-ppm guar or HPG solution was added slowly to the shoulder of a vortex of a vigorously (800 rpm) stirred solution of 2% KCl and 1.35 g/L of sodium thiosulfate in a 1-L beaker. The solution was stirred for 5 min after the addition of guar. Then, the stirring rate was reduced to 600 rpm for another hour and allowed to become hydrated for another 24 h at 200 rpm. Guar solutions were centrifuged at 9600 g for 1.5 h at 25°C to separate the residue.[13]

TABLE II
Mean Diameter Versus Time for 10 Samples of the System A Nanoparticles

Time (h)	Mean diameter (nm)	Standard deviation
0	461	10.2
1	473	13.8
2	463	16.9
5	473	16.1
13	472	12.4
24	460	15.1

Preparation of borate-crosslinked guar/HPG

Twenty-four milliliters of the 5000-ppm HPG or guar was mixed with 7.5 mL of the diluted enzyme-loaded nanoparticles or an aqueous solution with an equivalent concentration of pectinase (final concentration = 0.1% w/w pectinase). A 1000 or 2000 ppm borax aqueous solution (7.5 mL) was added to the mixture, and the pH was adjusted to 8.8 with 0.1*M* NaOH. Gel samples were incubated on a table shaker (LAB-LINE 3520 JR, Melrose, IL) at 150 rpm and 25°C.

Measurement of the viscosity and viscoelastic moduli

Guar/HPG solution

A Bohlin CS10 rheometer was used to measure the viscosity of the guar and HPG solutions. All of the viscometric assays were performed under a shear rate of 90 s^{-1}, except for the shear sensitivity analysis, in which the viscosities were also measured at 180 and 270 s^{-1}.

Gelled guar

A digital cone-and-plate viscometer (DVII+ Pro, SP-40 0.8° cone, Brookfield Engineering, Middleboro, MA) was used to monitor the viscosity of the gelled guar at 0.6 rpm (4.5 s^{-1}) versus time. This technique was convenient because of the closure surrounding the platens that kept the gel in place and is a method of choice in industry. It was included here to allow comparison to existing data. However, viscosity is not strictly a property of gels, and so, in addition, a Bohlin CS10 rheometer was used to measure the elastic modulus (G') and viscous modulus (G'') for 30-mL gel samples over time at a frequency of 1 Hz, a strain of 0.1 Pa, and an initial stress of 0.1 Pa in autostress mode. The double-gap configuration of Couette geometry was used to measure G' and G''.

TABLE III
Mean Particle Diameter and ζ Potential Versus Time for the Nanoparticles (pH = 8.7)

	8 h		32 h	
Nanoparticle system	Diameter (nm)	ζ (mV)	Diameter (nm)	ζ (mV)
A	433	29.4	408	35.0
A′	435	36.3	424	34.9
B	370	28.3	362	29.6
B′	313	28.2	292	24.3
C	250	27.4	238	17.5
C′	239	18.7	235	10.4

TABLE IV
Activity and EE Values of Pectinase-Loaded Nanoparticles and Their Supernatants with Viscometric Assay

Nanoparticle system	Activity of nanoparticle suspension (h^{-1})	Activity of supernatant (h^{-1})	EE_A (%)
B	1.24	1.11	60
A	0.87	1.00	65
B′	0.91	0.75	73
A′	0.68	0.70	75
D	1.75	0.86	88
E	1.33	1.00	81

Temperature = 25°C, pH = 8.8. Centrifuged 5000-ppm guar prepared in deionized water was used for this assay.

RESULTS AND DISCUSSION

Preparation and characterization of the nanoparticles

Preparation of the pectinase-loaded PECNPs

Formulations varied in PEI : DS ratio and in the order of addition, as shown in Table I. The repeatability of the formulation procedure was demonstrated by the preparation of 10 samples under identical conditions and the measurement of their size over time (Table II). The size and ζ potential were measured periodically to demonstrate the stability of the nanoparticles over time (Table III). The size and charge of the nanoparticles decreased with increasing PEI : DS ratio.

The nanoparticles were diluted to reach a specified enzyme concentration. In addition, 1-mL samples of undiluted nanoparticles were centrifuged, and the supernatants were diluted by the same dilution factor (8× for systems A and A′ and 6× for systems B and B′). Viscometric assay was performed for the nanoparticle suspensions, supernatants, and enzymes with concentrations equivalent to those of the diluted nanoparticles. Table IV shows the EE values of nanoparticles loaded with pectinase with different PEI : DS ratios. The nanoparticle systems with a 2 : 1 PEI : DS ratio (systems A and A′) showed the highest EEs of the systems prepared with 0.1 mL of pectinase. EE_A of the nanoparticles decreased with increasing PEI : DS ratio in the range studied. Nanoparticles that were prepared by the addition of

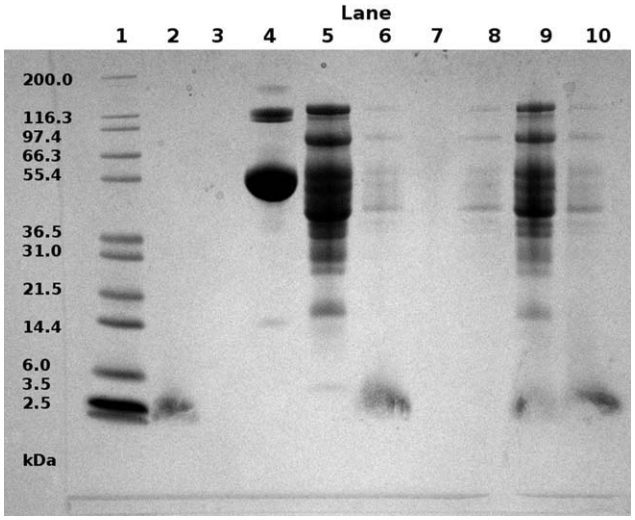

Figure 2 SDS-PAGE gel. The contents of each lane are described in Table II. The numbers on left are the MWs of the marker proteins in lane 1.

pectinase to PEI before the addition of DS (systems A′ and B′) showed higher EE_A values compared to the nanoparticles prepared by the addition of pectinase to preformed PEI–DS nanoparticles (systems A and B).

To increase EE_A, the amount of pectinase added to the nanoparticles was reduced from 0.1 to 0.07 and 0.06 mL of 25% w/w pectinase for system A and B nanoparticles. Nanoparticles prepared with less pectinase (systems D and E) showed improved EE_A's of 88 and 81%, respectively.

SDS-PAGE was used to measure the MW of the pectinase and to compare PEI, DS, pectinase, and supernatants from centrifuged nanoparticle samples (Fig. 2; the lane contents are reported in Table V). A marker containing proteins of a range of known MWs was run in lane 1. Lane 5 showed the MW distribution of pectinase. Distinct peaks were seen at 116 and 66 kDa. PEI traveled (lane 2) off the end of the gel; this suggested a low MW. Lane 10 is the supernatant of the 2 : 1 : 0.1 nanoparticles (PECNP system A), in which low concentrations of pectinase were observed. Lane 3 showed no peaks because the NuPAGE® 4–12% bis-tris gel accepted proteins with a maximum M_w of 200 kDa, whereas M_w of DS was 500 kDa.

SDS-PAGE was also performed for different pectinase concentrations (gel not shown), and the area of the most distinct absorbance peak ($\sim$ 116 kDa) of pectinase was plotted versus the pectinase concentration to yield a calibration curve. The area under the intensity–distance peak for the supernatant of the nanoparticle systems was correlated with the concentration of the enzyme.

The concentration of pectinase in the supernatant, as measured by SDS-PAGE, was used to calculate EE_C of the nanoparticles from eq. (2). The calculated EEs were verified by measurement of the activity of the enzyme in the supernatant [eq. (1)]. The EE_C values were slightly higher than the EE_A values (Table VI).

Effect of shear during the preparation of the pectinase-loaded nanoparticles

Batches of system A nanoparticles were prepared with stirring at 300, 600, and 900 rpm at 25°C and pH 8.8. There was no relationship between the preparation shear and size, ζ potential, or EE of the nanoparticles within this range (data not shown).

Effect of applied shear on the activity of the nanoparticles

Viscometric assays were performed on samples from the system A nanoparticles, which were prepared with stirring at 600 rpm. The activity of the nanoparticles was determined from $t_{1/2}$ of a 5000-ppm HPG solution in 2% KCl. Figure 3 shows that when the shear applied during the experiment increased, the activity of the nanoparticles decreased. However, the activity of the pectinase also decreased with the same trend; this indicated that any additional release

TABLE V
Samples in the SDS-PAGE Lanes

Lane	1: MW marker	2: Diluted PEI	3: Diluted DS	4: BSA	5: Pectinase	6: Diluted PEI + pectinase	7: Diluted DS + pectinase	8: Diluted pectinase	9: 50 : 50 PEI : pectinase	10: Supernatant (A)
MW marker	3.1	—	—	—	—	—	—	—	—	—
25% w/w pectinase	—	—	—	—	3.1	0.1	0.1	0.1	1.55	0.1
1% w/w PEI	—	2.0	—	—	—	2.0	—	—	1.55	2.0
1% w/w DS	—	—	1.0	—	—	—	1.0	—	—	1.0
BSA	—	—	—	3.1	—	—	—	—	—	—
Deionized water	—	1.1	2.1	—	—	1.0	2.0	3.0	—	—

BSA = bovine serum albumin.

TABLE VI
EE and Enzyme Concentration Values for Different Supernatants with the First Intensity Peak

PECNP system	Pectinase concentration in nanoparticle suspension (% w/w)	Pectinase concentration in supernatant (% w/w)	EE (%)
A	0.81	0.22	72
B	0.61	0.23	62

of pectinase from the nanoparticles caused by an increase in the shear was insignificant. The shear rates were chosen to be broadly representative of the shear rates encountered by the gel in the field.[1]

Characterization of borate crosslinked guar/HPG gels degraded by pectinase-loaded nanoparticles

A 5000-ppm solution of guar in 2% KCl was used to prepare borate (1000 ppm) crosslinked gels. Diluted nanoparticles with different ratios of PEI : DS were mixed with the guar before the addition of borate. The concentrations of guar, borate, and enzyme were the same in all of the preparations. The resulting gels were incubated on a table shaker at 150 rpm and 25°C, and samples were removed at intervals for viscosity measurement at a shear rate of 4.5 s^{-1}. Figure 4 shows the viscosity of the gelled guar containing pectinase entrapped by nanoparticles with different ratios of PEI : DS. Nanoparticles with pectinase added before the addition of DS (systems A′ and B′) showed later degradation times compared to the nanoparticles to which pectinase was added after the addition of DS (systems A and B).

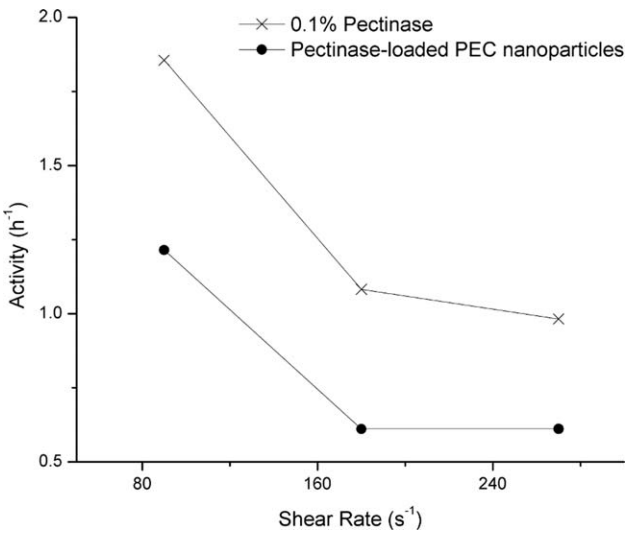

Figure 3 Comparison of effect of shear on the activity of the 0.1% pectinase solution and pectinase-loaded nanoparticles (PECNP system A) at 25°C and pH 8.8. Activity = $1/t_{1/2}$ of a 5000-ppm HPG solution.

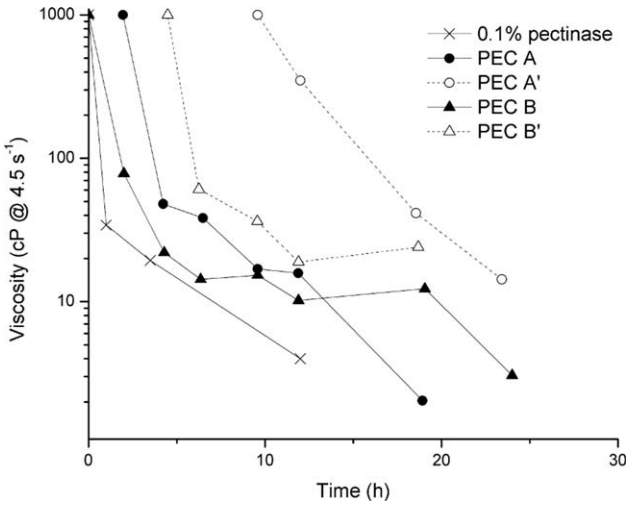

Figure 4 Viscosity of the borate-crosslinked guar gel mixed with 0.1% pectinase or pectinase-loaded PECNPs versus time at 25°C and pH 9. NB = Nota bene The viscometer was only able to measure the viscosity up to 1028 cP, so the graph indicates the latest measurement for which the viscosity exceeded this value.

Although viscosity is the most commonly measured property during field application, it is difficult to measure the viscosity of a gel. To further characterize the degradation process, a rheometric study was performed. Pectinase-loaded nanoparticles (final pectinase concentration = 0.02%) with 2 : 1 ratios of PEI to DS (systems A and A′) were mixed with a 5000-ppm HPG solution in 2% KCl. 2000 ppm borax was added to form crosslinked HPG. Gels were shaken on a table shaker at 150 rpm and 25°C; samples were removed at intervals, and viscoelastic moduli were measured with a Bohlin rheometer. A frequency sweep was performed at different times, and G'' and G' were plotted versus time for a

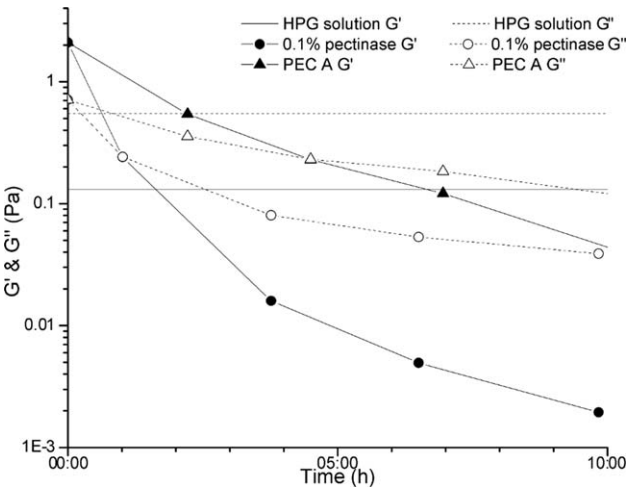

Figure 5 G' and G'' versus time for the HPG solution and gel degraded with either 0.1% pectinase or nanoparticle-entrapped pectinase (PECNP system A) at 25°C and pH 9.

frequency of 0.5 Hz (Fig. 5). Delays in the degradation of both moduli were observed. Both G' and G'' reached values lower than those of an equivalent HPG solution in 10 h; this indicated a significant delay in the activity of the enzyme. The point at which plots of G' and G'' crossed (i.e., the time at which G' became smaller than G'') was shifted toward longer times for the systems degraded with nanoparticles compared to the systems degraded with enzyme; this represented a delay in the transition from gel to solution. A faster decline of G' compared to G'' is typical for enzymatic degradation of guar solutions because the gel structure is attacked first, followed by the degradation of the guar back bone.[14]

The viscosity measurements (Fig. 4) showed that gels containing PECNPs reached the same viscosity values as those degraded with unentrapped pectinase given enough time. The decreasing rate of the viscoelastic moduli confirmed this result.

The injection of higher enzyme concentrations has the potential to break fracturing fluids and their filter cakes more efficiently.[1–3,6] Breakers are required to break the fracturing fluid and formed filter cakes, typically in a 6–24 h period of time, depending on the size of the fracturing job and the depth of the reservoir. However, if efficient fracturing and proppant transport are to be achieved, premature degradation of the fracturing fluids during the injection time must be avoided. Reversible trapping of enzymes in PECNPs by a combination of transient electrostatic binding and steric interactions (electrosteric interactions)[10,15] delays the activity of the enzyme. This may allow the injection of higher enzyme concentrations.

In summary, polyelectrolyte nanoparticles made with a PEI : DS ratio of 2 : 1 (systems A and A′) showed good EEs for pectinase. They were stable over time and did not degrade with shear in the range studied. The size and EE of the nanoparticles were not strongly correlated with preparation shear. Viscometric assays were performed on the diluted nanoparticles, diluted supernatants, and equivalent concentrations of enzyme. EE was calculated after we measured the activity of the supernatant. SDS-PAGE was applied to measure the concentration of free pectinase in the supernatant. The EE values measured with viscometric assay were consistent with the SDS-PAGE data. The viscosity of the gelled guar was monitored under a 4.5-s^{-1} shear rate in the presence of enzyme-loaded nanoparticles. Nanoparticles with a 2 : 1 ratio of PEI to DS (systems A and A′) showed the best controlled release of enzyme over time.

CONCLUSIONS

Nanoparticle-entrapped pectinase was able to completely break borate-crosslinked guar and HPG gels, with the breaking being delayed significantly compared to unentrapped enzymes at the same concentration. The nanoparticles exhibited high enzyme EE and were largely insensitive to the shear forces likely to be encountered in the field. The delayed release of the enzyme allowed the loaded particles to be mixed with the gelant before gelation occurred. This, along with the small size of the particles, indicated that the enzyme was distributed homogeneously through the gel, which may have resulted in a more complete breakage of the gel and, hence, a higher posttreatment hydraulic fracture conductivity.[16] The polyelectrolyte complex (PEC) entrapment of gel-breaking enzymes shows promise for improvements in the performance of hydraulic fracturing treatments in conventional oil and gas reservoirs, but further investigation of enzymes with different pH values and temperature optima is required to identify the range of conditions in which the method may be applied.

References

1. Economides, M. J.; Nolte, K. G. Reservoir Stimulation; Wiley: New York, 2000; Vol. 2.
2. Ayoub, J. A.; Hutchins, R. E.; Van der Bas, F.; Cobianco, S.; Emiliani, C. N.; Glover, M.; Kohler, M.; Marino, S.; Nitters, G.; Norman, D.; Turk, G. Presented at the Society of Petroleum Engineers International Symposium and Exhibition on Formation Damage Control, Lafayette, LA, February 2006.
3. Ayoub, J. A.; Hutchins, R. E.; Van der Bas, F.; Cobianco, S.; Emiliani, C. N.; Glover, M.; Kohler, M.; Marino, S.; Nitters, G.; Norman, D.; Turk, G. Presented at the Society of Petroleum Engineers Annual Technical Conference and Exhibition, San Antonio, TX, September 2006.
4. Palisch, T. T.; Vincent, M. C.; Handren, P. J. Presented at the Society of Petroleum Engineers Annual Technical Conference and Exhibition, Denver, Colorado, September 2008.
5. Laramay, S. B.; Norman, L. R.; Carathers, B. K. Presented at the Society of Petroleum Engineers Permian Basin Oil and Gas Recovery Conference, Midland, TX, 1992.
6. Barati, R.; Hutchins, R. D.; Friedel, T.; Ayoub, J. A.; Dessinges, M.; England, K. W. Society of Petroleum Engineers Journal of Production and Operations, 2009, Vol. 2, Issue 24, 336-345.
7. Tiyaboonchai, W.; Woiszwillo, J.; Sims, R. C.; Middaugh, C. R. Int J Pharm 2003, 225, 139.
8. Berkland, C.; Cordova, M.; Liang, J.-T.; Willhite, G. P. (to University of Kansas). U.S. Pat. WO 2008/030758 A1 (2008).
9. Cordova, M.; Cheng, M.; Trejo, J.; Johnson, S. J.; Willhite, G. P.; Liang, J.-T.; Berkland, C. Macromolecules 2008, 41, 4398.
10. Koetz, J.; Kosmella, S. Polyelectrolytes and Nanoparticles; Springer: New York, 2007.
11. Bell, T. A.; Etchells, J. L.Botanical Gazette 1958, 119, 192.
12. Anonymous. Coomassie Plus—The Better Bradford™ Assay Kit Instructions, Thermo Fisher Scientific Inc.: Rockford, IL
13. Tayal, A.; Kelly, R. M.; Khan, S. A. Macromolecules 1999, 32, 294.
14. Cheng, Y.; Prud'homme, R. K. Biomacromolecules 2000, 1, 782.
15. Hartig, S. M.; Greene, R. R.; Dikov, M. M.; Prokop, A.; Davidson, J. M.Pharm Res 2007, 24, 2353.
16. Palisch, T.; Duenckel, R.; Bazan, L.; Heidt, H. J.; Turk, G. Presented at the Society of Petroleum Engineers Hydraulic Fracturing Technology Conference, College Station, TX, 2007.