Application of Copolymeric Particulates for Oilwell In-depth Performance Control

Hongsheng Lu,[1,2,3] Zhiyu Huang,[2] Qaunsheng Chen,[1,3] Jian Wang,[4] Yujun Feng[1,5]

[1]*Center for Macromolecular Sciences, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan 610041, People's Republic of China*
[2]*Division of Applied Chemistry, College of Chemistry and Chemical Engineering, Southwest Petroleum University, Xindu, Sichuan 610500, People's Republic of China*
[3]*College of Chemistry and Chemical Engineering, Graduate University of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China*
[4]*Division for Enhanced Oil Recovery, College of Petroleum Engineering, Southwest Petroleum University, Xindu, Sichuan 610500, People's Republic of China*
[5]*State Key Laboratory of Oil/Gas Reservoir Geology and Exploitation Engineering, Southwest Petroleum University, Xindu, Sichuan 610500, People's Republic of China*

Received 27 December 2005; accepted 18 March 2006
DOI 10.1002/app.24885

ABSTRACT: The properties of two copolymeric particulates used for oilwell in-depth performance control were investigated systematically. The lab-scale studies showed that the average diameter of these particulates (E5 and G6) is 77.76 μm with the standard deviation of 2.16%. The two particulates exhibit good dilatability when immersed in 20 × 10^4 mg/L NaCl solution. Their capability of water retention (150 days) was 90% at 80°C. In addition, they exhibited good injectivity, driving performance and plug, and satisfied toughness index. The diffluence experiments confirmed that the coefficient of the profile modification were 85.7, 98.7, 86.1, and 98.1% when the permeability levels were 4.05 and 15.0, respectively. When using the two particulates, the average recovery ratio can reach 21%. The procedures mentioned earlier could be used as industry criteria to evaluate all kinds of particulate used as in-depth performance controllers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5330–5335, 2006

Key words: copolymeric particulate; in-depth performance control; salt tolerance; thermal stability

INTRODUCTION

During the middle or last period of oil exploration, many oil fields have taken measures to exploitation, including water flooding and polymer flooding.[1] In a serious heterogeneous reservoir, injected-water and polymer solution mainly flow into high-permeable layers.[2] This results in a lower sweeping efficiency, and a larger amount of residual oil remaining in the reservoir, which affects water injection and the implementation of polymer flooding. To solve this problem, many measures, especially chemical agents, were employed.

During the past 10 years, in-depth performance technology[3] has proved to be an effective way to increase oil production. This not only includes control of the unwanted water production (known as water shutoff), but also includes modification of differences between inner and outer layers and diversion of the flow direction of injected fluid (so-called profile modification).[4–7] In this process, a crosslinked polymer solution is injected into the deep production zone that then blocks high-permeable water channels.[2,8] As a result, water has to flow into the low-permeable zones, and oil recovery is enhanced.[9]

Nowadays, weak gel and colloidal dispersion gel[10,11] represent major in-depth performance controllers. However, these polymeric materials show drawbacks in terms of salt tolerance, temperature stability, and their small size.[7,12,13] Because of these, only low-permeable zones can be sealed, while little effect is found in high-permeable channels, especially in heavily waterflooded zones. At high temperatures, these polymeric materials could degrade and become smaller in size in concentrated salt solution, resulting in less effective in blocking high-permeable channels. For this reason, it is necessary to develop salt-tolerant, thermally stable materials that could effectively seal the big channels. It is well-known that water-absorbent resins are good swelling particulates.[14–21] However, normal water-absorbent resins do not show good salt-tolerance, thermal stability, elasticity, or toughness when they are fully swelled.[22] To obviate these problems, we developed copolymeric particulates as fluid diversion agents and reported their synthesis and bulk properties in a previous paper.[23]

Correspondence to: Y. Feng (yjfeng@cioc.ac.cn).
Contract grant sponsor: Opening fund, State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation Engineering, Southwest Petroleum University; contract grant number: PLN9911.

Contract grant sponsor: Opening fund, Key Laboratory of Sichuan Province, Southwest Petroleum University; contract grant number: SZS005.

Journal of Applied Polymer Science, Vol. 102, 5330–5335 (2006)

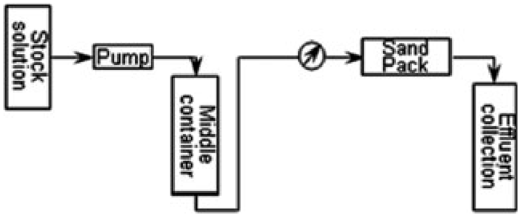

Figure 1 A typical schematic presentation of the coreflood setup.

In this article, the performance of the two copolymeric particulates based fluid diversion agents with test regard to granularity, mobility, sweep ability, salt tolerance, thermal stability, compatibility, and laboratory coreflood tests were discussed.

EXPERIMENTAL

Materials

The two particulates (E5, organic copolymeric particulate and G6, montmorillonite-containing composite copolymeric particulate) used in this work were synthesized as described previously.[23] Other inorganic chemicals and solvents (ethanol and methanol) were purchased from Beibei Reagent (Chongqing, China) and Shanghai. Crude oil (113.2 mPa s) was supplied by Zhongyuan Oil Field, Sinopec.

Granularity analysis

The two copolymeric particulates were washed with a mixed solvent (ethanol:methanol = 9:1) three times and dried under vacuum for 24 h at 30°C. Then, the particles were screened through different meshes and the residual content (m_i) was weighed. The average diameter d_a of the particles was calculated by the formula:

$$d_a = \sum_{i=1}^{k} m_i d_i \Big/ \sum_{i=1}^{k} m_i \tag{1}$$

where d_i refers to the size of the residual particles after screening.

TABLE I
Particle Size Distribution of Particulates (G6 and E5)

Mesh	Grain size (μm)	Weight (g)
20	833	0.021
40	430	0.028
60	276	0.039
80	210	0.053
100	149	0.68
120	125	0.98
140	105	1.42
160	96	2.89
180	83	4.17
200	74	3.01
250	62	1.96
270	53	0.64

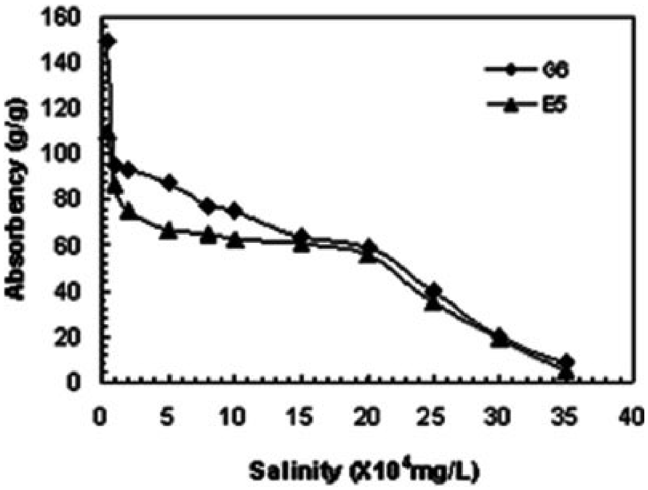

Figure 2 Absorbency of particulates plotted as a function of salinity.

Salt tolerance and thermal stability

One gram of dry copolymeric particulate was swelled completely in NaCl solutions at 25°C. The weight of the swelled gel was measured using the tea bag method.[24] Water absorbency of the particulate can be determined from

$$Q = (W_{\text{sp}} - W_p)/W_p \tag{2}$$

where W_{sp} and W_p represent the weight of swelled and dry particulates, respectively.

The abovementioned experiment was repeated at 30, 50, 70, and 80°C. After which, the gel was inserted into stainless steel cans with a sealed cups, and then the cans were inserted into a vacuum oven at 150°C for 200 days to examine the change in water absorbency.

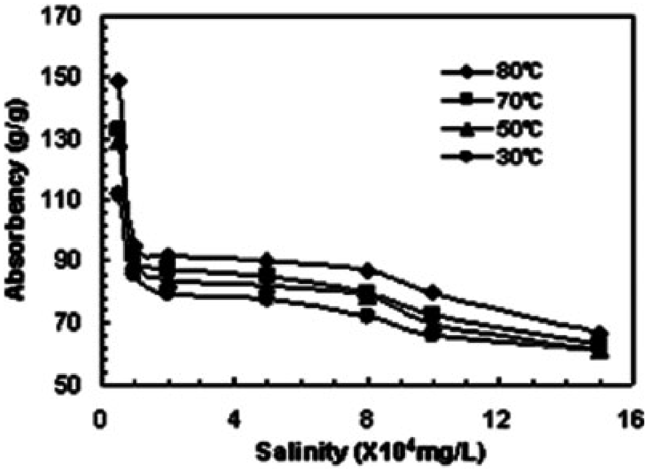

Figure 3 Particulate E5's absorbency versus salinity at different temperature.

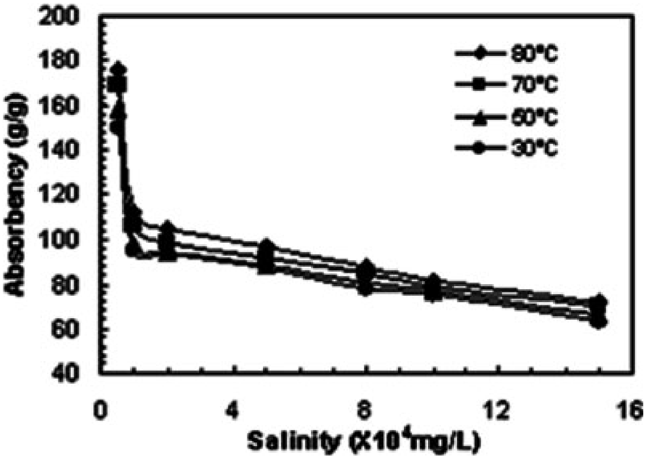

Figure 4 Particulate G6's absorbency versus salinity at different temperature.

Constringency of particulate in crude oil

Copolymeric particulate (0.5 g) was immersed into crude oil and then its weight was measured as a function of immersing time.

Coreflood experiments

To simulate the oil reservoir condition in oilfield, the copolymeric particles were suspended in a polymer solution and dispersed in the middle container of a coreflood device designed based on Smith's procedure (Fig. 1).[25] Pressure difference (ΔP_1) was recorded until no fluid flowed out. Then, the used fluid was put back into the middle container, the pressure difference (ΔP_2) was recorded when the above steps were repeated.[25]

A sand pack was made with water permeability of 2–20 μm^2, length of 4.0 cm, and cross-sectional area of 0.95 cm.^{2} Then, the particulate containing partially hydrolyzed polyacrylamide (HPAM) solution (100 mg/L) was poured into the middle container and was allowed to flood through the pack. The corresponding flux and the fluid pressure difference of the particulate containing HPAM solution were recorded.[25]

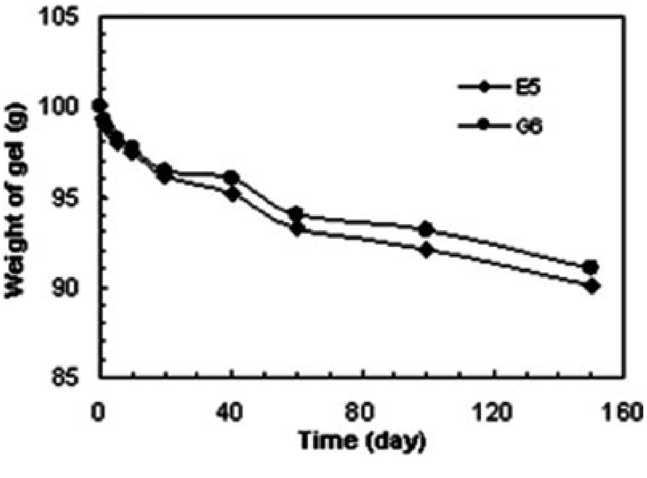

Figure 5 Water retention property of the particulates.

TABLE II
Toughness Index of Particulate E5

Content of polymer (mg/L)	ΔP_1 (MPa)	ΔP_2 (MPa)	f_{tay}	Average value
100	0.029	0.25	1.16	
150	0.048	0.045	1.06	
200	0.060	0.051	1.17	1.12
250	0.071	0.063	1.12	
300	0.082	0.074	1.10	

The composite sand packs (two plugs) were made with materials with different water permeability. The NaCl (1 wt %) solution was injected into the sand packs at a flow rate of 10 mL/h and the two samples of the sand packs' effluents were collected. About 5.0 pore volume (PV) of this suspension of particulate was injected into the sand packs. Then, the NaCl (1 wt %) solution was flooded through the sand packs with an injection rate of 10 mL/h. Two samples of the sand packs' effluents were collected.

Two steps were used to study the oil recovery ratio: first, the sand pack saturated with oil was flooded with water till the effluent was completely injected with water, and then the relationship between injected water PV and the recovery ratio was examined; second, the sand pack saturated with oil was flooded with water till the effluent contained 90% of water, and then the particulate solution was injected, followed by water flooding till the effluent was completely injected with water. Finally, the curves of recovery ratio versus PV of injected fluid were drawn to check the influence of particulate on recovery ratio.[26]

RESULTS AND DISSCUSION

Granularity of copolymeric particulates

Table I gives the experimental data of the particle distribution of the composite particulates E5 and G6, both of which were prepared by the same manner. On the basis of Table I and the formula 1 in the experimental section, the average diameter and standard deviation of both particulates were calculated to be 77.76 μm and 2.16%, respectively. It also shows that the distribution follows Gaussian distribution. This enables the particles to flow more easily into deep zones of the reservoir.

TABLE III
Toughness Index of Particulate G6

Content of polymer (mg/L)	ΔP_1 (MPa)	ΔP_2 (MPa)	f_{tay}	Average value
100	0.031	0.025	1.24	
150	0.051	0.044	1.15	
200	0.062	0.052	1.19	1.18
250	0.073	0.061	1.19	
300	0.084	0.0720	1.16	

TABLE IV
Constringency of Particulates in Crude Oil

Time	Weight of E5 (g)	Weight of G6 (g)
0	0.35	0.35
1 h	1.02	1.03
2 h	1.96	2.01
3 h	2.57	2.64
5 h	3.68	3.81
12 h	3.07	3.12
24 h	2.64	2.61
4 days	1.93	1.89
8 days	1.89	1.86
16 days	1.9	1.86

Effect of salinity on the property of particulates

Figure 2 compares the effect of salinity on the water absorbency of the two copolymeric particulates. The curves can be divided into three areas: the first part where the absorbency drops drastically from 150 g/g to 90 g/g as salinity increases; the second part where absorbency decreases gradually as salinity increases; and the third part (salinity: 20×10^4 to 35×10^4 mg/L) where further increasing the salinity results in a drastic drop in absorbency. It is important to note that the absorbency of G6 containing montmorillonite clay is a little better than E5's. It also shows that two kinds of particulate exhibited good salt tolerance with the salinity below 20×10^4 mg/L.

Effect of temperature on the property of particulates

Figures 3 and 4 indicate that the two copolymeric particulates retained their swelling behavior well in the aqueous salt solution without degradation and the water absorbency improved with the increasing temperature, showing their thermal stability within the measured temperature range (30–80°C). In addition, the elasticity becomes better and better as the temperature increases. Thus, it flows easily into pores during the injection period. It is obvious that the increase in the absorbency of composite particulate (G6) was smaller than that of the organic particulate (E5). This may be explained by the fact that the hydratability of montmorillonite clay was not high in concentrated NaCl solutions.

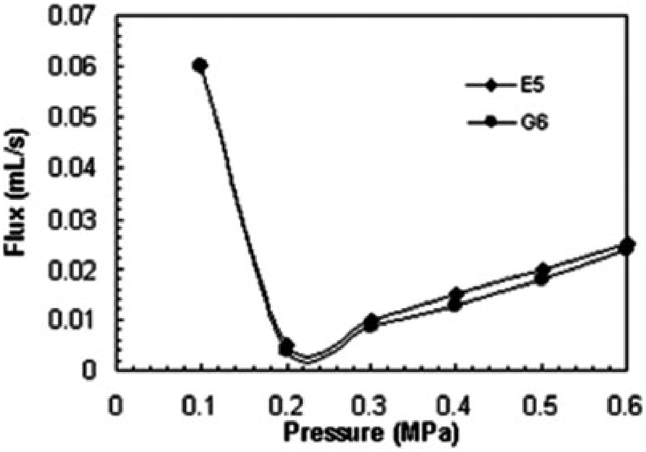

Figure 6 Flux versus pressure for two particulates.

Figure 5 shows that as time prolongs, the two particulates' weight gradually drops, and the particulates' rate of water retention was much higher than 90%, indicating that the two particulates are good performance controllers in view of their good water retaining capacity, especially for G6. The probable reason was that in the micronetwork of G6, the interaction between montmorillonite clays and polymer networks gives additional protection of the composite particulate and the hydrophilic groups in montmorillonite clays help to absorb more water.[23]

Evaluation of gel toughness

According to Smith method,[25] the toughness index is the ratio of the pressure difference and the flux when the water-absorbed grains (content 0.5%, 200 mesh, 20 mL) are screened twice. Namely,

$$f_{\text{tay}} = (\Delta P_1/\Delta Q_1)/(\Delta P_2/\Delta Q_2) \quad (3)$$

When $\Delta Q_1 = \Delta Q_2$, then $f_{\text{tay}} = \Delta P_1/\Delta P_2$, where f_{tay} is a dimensionless constant and surpasses 1, the larger the f_{tay} is, the more crisp the gel is. If its value approaches 1, in the extreme, the gel will show the best toughness. Then, the gel will have better tensile strength and compression strength properties, and will not be apt to disintegrate.

TABLE V
The Modifying Effect of E5 in Sand Packs with Different Permeability

Permeability (μm^2)	Permeability level	The ratio of imbibing		Profile modification ability (%)
		Before modification	After modification	
13.37 3.02	4.30	76/29	28/75	85.7
15.32 1.02	15.01	86/16	12/94	97.8

TABLE VI
Modifying Effect of G6 in the Packs with Different Permeability

Permeability (μm^2)	Permeability level	The ratio of imbibing		Profile modification ability (%)
		Before modification	After modification	
13.37 3.02	4.30	76/29	22/74	86.1
15.32 1.02	15.01	86/16	10/98	98.1

As shown in Tables II and III, the toughness index shows that both of the particulates exhibited better flexibility and could flow into pores in deep reservoir without being brittle.

Constringency of particulate in crude oil

As noted in Table IV, the two kinds of particulates exhibit good constringency properties in crude oil; from the beginning up to 12 h, the volume increased, and after that, it began to shrink. On the 8th day, the weight was only 0.55 g. On the 10th day, gel weight was 0.27 g. This shows that the constringency of the composite copolymer was good.

Gel-injection properties

As shown in Figure 6, the two particulate grains did not flow into the pore and the flux was larger at the low pressure (0.1 MPa). With increasing pressure, grains began to flow into the pore, and the flux declined sharply. As pressure continued to rise, the flux began to increase, which revealed that the grain was beginning to deform and flow into deep zones. When the pressure reached a certain value, the flux tended to be steady. It also showed that the deformability of E5 is somehow better than that of G6.

Profile modification ability

The profile modification ability could be depicted by the following equation:

$$f = (Q_{hb}/Q_{lb} - Q_{ha}/Q_{la})/(Q_{hb}/Q_{lb}) \times 100\% \quad (4)$$

where Q_{hb} and Q_{ha} are the bibulous volumes (mL) of the high-permeable sand packs before and after modification, Q_{lb} and Q_{la} are the bibulous volume (mL) of the low-permeable sand packs before and after modification respectively.

As noted in Tables V and VI, the water absorbency of sand packs did change after modification. If the permeability-level was larger, the effect of modification was much obvious. This proved that the in-depth performance controller exhibited good selectivity, especially for G6. This could be explained by the fact that montmorillonite clay was hydrophilic.

Evolution of enhance oil recovery

As noted in Tables VII and VIII, the crude oil recovery ratio increased with modification. It was obvious that the recovery ratio of each sand pack with different permeability increased at the same rate as the average recovery ratio. The in-depth performance controller exhibited good selectivity owing to the largest recovery ratio of the high-permeability sand packs. As far as the two kinds of particulates were concerned, there was not much difference in the capability of enhance oil recovery. Considering the economic value, the composite particulate (G6) would be the better choice. Besides, Figure 7 also indicates that the coefficient of utilization of water increased with modification after the injection of about 4.0 PV, and the average recovery ratio was 17% after the injection about 15.0 PV; this also confirmed the capability of G6's modification.

CONCLUSIONS

In this paper, the properties of the two copolymeric particulates (E5 and G6) were systematically investi-

TABLE VII
Recovery Ratio with Modification

			CWE (90%)		CWE (100%)			
SPN	PW (μm^2)	VSO (mL)	VCO (mL)	ORR (%)	VCO (mL)	ORR (%)	*M* (%)	AM (%)
E51	1.264	31.42	15.88	50.54	23.51	74.82	24.28	21.31
E52	0.694	19.31	9.01	46.66	12.67	65.61	18.95	
G61	1.206	29.87	13.68	45.79	21.36	71.50	25.71	
G62	0.662	15.76	6.39	40.54	8.96	56.85	16.31	

SPN, sand packs number; PW, permeability of water; VSO, volume of saturated oil; VCO, volume of collected oil; ORR, oil recovery ratio; M, multiple; AM, average multiple; CWE, content of water of the effluent.

TABLE VIII
Recovery Ratio without Modification[a]

			CWE (90%)		CWE (100%)			
SPN	PW (μm^2)	VSO (mL)	VCO (mL)	ORR (%)	VCO (mL)	ORR (%)	*M* (%)	AM (%)
E53	1.318	36.14	18.01	49.83	21.08	58.33	8.50	6.90
E54	0.712	21.64	10.26	47.41	11.71	54.11	6.70	
G63	1.287	33.87	15.94	47.06	17.96	53.03	5.97	
G64	0.656	14.31	6.21	43.39	7.13	49.83	6.44	

[a] The meanings of the abbreviated symbol are the same as those in Table 7.

gated. They had average diameters of 77.76 μm and showed good salt tolerance with the salinity up to 250,000 mg/L, and E5 was somewhat superior to G6. The water absorbency of the two particulates increases with increasing the temperature of salt solutions. Their ability to retain water was above 90% at 150°C for 200 days. It was obvious that by using clay and rare earth stabilizers, G6 was better than E5. Both E5 and G6 have good toughness with the toughness index of 1.12 and 1.18, respectively. Their good constringency ensures them to exhibit selectivity to flowing into would-be-modified zones of the deep reservoir. They also exhibited better injection capability. The profile-modifying ability overrun 85%, for high-much permeability-level even above 95%. Upon modification, the oil recovery ratio has elevated drastically, especially when modified with G6. Modified copolymer particulate used for the in-depth performance controller is promising in deep profile control. The above-mentioned procedures could be adopted as industry criteria to evaluate all kinds of particulate used as in-depth performance controller.

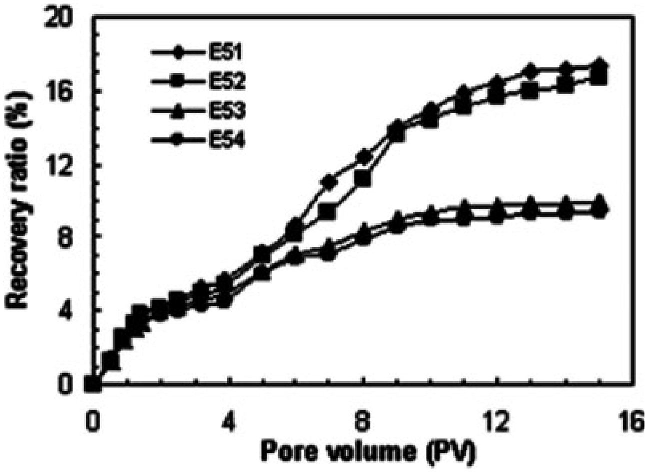

Figure 7 Injected PV versus recovery ratio.

References

1. Datta-Gupta, A.; Vasco, D. W. Presented at the SPE Annual Technical Conference and Exhibition, Dallas, TX, Oct. 1995; Paper SPE 30589.
2. Dawe, R. A.; Zhang, Y. J Petrol Sci Eng 1994, 12, 113.
3. Seright, R. S. Improved techniques for fluid diversion in oil recovery processes, Report DOE/BC/14480-10. Washington, DC: US Department of Engineering; 1995; pp 1, 147.
4. Feltcher, A. J. P. J Petrol Sci Eng 1992, 7, 33.
5. Gallus, J. P.; Pye, D. S. J Petrol Technol 1969, 4, 497.
6. Fielding, R. C., Jr. Presented at the Ninth Society of Petroleum Engineers/Department of Energy on Improve Oil Recovery, Tulsa, OK, April 1994; Paper SPE 27773.
7. Seright, R. S. Presented at the SPE Rocky Mountain Regional Meeting, Gillette, WY, May 1999; Paper SPE 55628.
8. Liang, J.; Sun, H.; Seright, R. S. Soc Petrol Eng Reservoir Eng 1995, 11, 282.
9. Gallu, J. P.; Pye, D. S. Presented at the AIME (American Institute of Mining, Metallurgical, and Petroleum Engineers) Meeting, Tokyo, May 1972; Paper SPE 3811.
10. Mack, J. C.; Smith, J. E. Presented at Ninth Society of Petroleum Engineers/Department of Energy on Improve Oil Recovery, Tulsa, OK, April 1994; Paper SPE 27780.
11. Lane, R. H.; Sanders, G. S. Presented at the Society of Petroleum Engineers Production Operations Symposium, Tulsa, OK, April 1995; Paper SPE29475.
12. Midha, V.; Willhite, G. P. Presented at the 10th Society of Petroleum Engineers/Department of Energy Symposium on Improve Oil Recovery, Tulsa, OK, April 1996; Paper SPE/DOE 35450.
13. Abdo, M. K.; Chung, H. S. Presented at the Society of Petroleum Engineers Enhanced Oil Recovery Symposium, Tulsa, OK, April 1984; Paper SPE/DOE 12642.
14. Li, A.; Wang, A. J Appl Polym Sci 2004, 92, 1596.
15. Zhang, J.; Sun, M.; Zhang, L.; Xie, X. J Appl Polym Sci 2003, 90, 1851.
16. Kang, H.; Xie, J. J Appl Polym Sci 2003, 88, 494.
17. Raju, K. M.; Raju, M. P. J Appl Polym Sci 2002, 85, 1795.
18. Lee, W.-F.; Huang, Y.-L. J Appl Polym Sci 2001, 81, 1827.
19. Lee, W.-F.; Huang, Y.-L. J Appl Polym Sci 2001, 79, 1665.
20. Raju, M. P.; Raju, K. M. J Appl Polym Sci 2001, 80, 2635.
21. Lim, D.-W.; Yoon, K.-J.; Ko, S.-W. J Appl Polym Sci 2000, 78, 2525.
22. Houchin, L. R.; Dunla, P. D.; Hudson, L. M.; Begnaud, P. C. Presented at the Society of Petroleum Engineers Annual Technical Conference and Exhibition, New Orleans, Oct. 1986; Paper SPE 15547.
23. Lu, H.; Huang, Z.; Ma, Y.; Li, P.; Feng, Y. J Appl Polym Sci 2006, 100, 4429.
24. Wang, G.; Li, M. J Appl Polym Sci 1997, 65, 789.
25. Seright, R. S. Presented at the SPE Rocky Mountain Regional Meeting, Gillette, WY, May 1999; Paper SPE 55631.
26. Nars-El-Din, H. A.; Taylor, K. C. J Petrol Sci Eng 2005, 48, 141.