

Synthesis and Evaluation of a Composite Crosslinked Copolymer as a Particulate Fluid Diversion Agent

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ABSTRACT: To meet the needs for polymer particulates for the flooding of oil fields, a composite crosslinked copolymer of hydrophilic monomers [acrylamide (AM) and acrylic acid (AA)] and a hydrophobic monomer [methyl methacrylate (MMA)] was synthesized. In this study, we first added a rare-earth thermal stabilizer and inorganic montmorillonite (MMT) clay to the copolymer; this showed that the composite crosslinked copolymer exhibited good water-swelling performance at 200°C, with gel static grade

of 5, a toughness index of 1.1170, and a salinity limit of 250,000 mg/L. It also had better injection abilities. The AM/AA/MMA ratio was 4 : 1 : 0.03 w/w, the crosslinker additive content was 0.03 wt %, the thermal stabilizer additive content was 5 wt %, and the clay (MMT) additive content was 13 wt %. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4429–4433, 2006

Key words: composites; crosslinking; thermal properties

INTRODUCTION

With the development of modern society, more and more energy is being demanded, especially from petroleum. In the middle or last period of oil exploitation, many oil fields have taken measures toward exploration, including water flooding and polymer flooding.¹ In the serious heterogeneity reservoir, injected water and polymer solutions mainly flow into the high-permeability layers;² this results in a lower sweeping efficiency, and a large amount of residual oil remains in the reservoir, which affects water injection and the implementation of polymer flooding.

During the past 10 years, fluid diversion technology³ has proven to be an effective way to EOR, which is not only for enhancing oil recovery by profile modification or water shutoff to reduce water cut but also for modifying inner and outer layer differences.^{4–7} The major method is to inject a crosslinked polymer into deeper production zones and then block high-

permeability water channels.^{2,8} Then, the water has to flow into the low-permeability zones, and oil recovery is enhanced.⁹

At present, deep modification agents, such as weak gels and colloidal diffusion gels,^{10,11} have been developed, but they show defects in the aspects of salt tolerance and temperature stability, and their flow size is small;^{7,12,13} they cannot block the high-permeability zones, only the low-permeability zones, especially seriously water-flooded zones. So it would be useful for us to develop a salt-tolerant and thermally stable agent that could block the big channel. Water-absorbent resins are good swelling particulates, but a normal water-absorbent resin does not have good enough salt tolerance, thermal stability, elasticity, or toughness after full swelling.¹⁴ In this article, we discuss the performance with regard to mobility, driveability, salt tolerance, and thermal stability in reservoirs of our composite crosslinked copolymer after special disposal.

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EXPERIMENTAL

Materials

Some materials used in this study were purchased from Shanghai Chemical Reagent, Ltd. (Shanghai, China); these materials included acrylamide (AM),

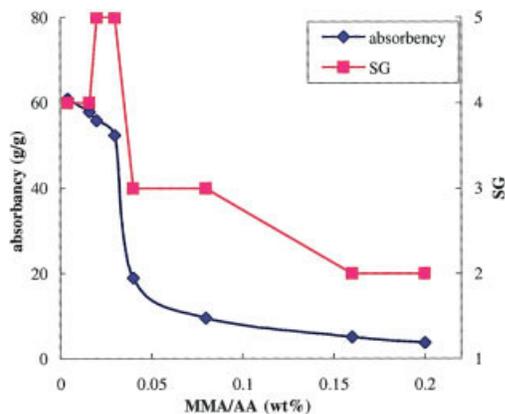


Figure 1 Absorbency and SG versus MMA/AA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

methyl methacrylate (MMA), acrylic acid (AA), 1-dodecaic acid, citric acid, oxalic acid, and phenylacetic acid. The inorganic compounds were purchased from Chongqing Beibei Reagent, Ltd. (Chongqing, China), these materials included potassium persulfate montmorillonite (MMT) clay, AlCl_3 , and sodium hydroxide (NaOH). Rare earth (RaCl_3) was purchased from China Baotong. AA, MMA, and AA were distilled under reduced pressure before use, and the other materials were used directly.

Syntheses of the crosslinker SW1 and thermal stabilizer SW2

A 100-mL beaker equipped with a constant-temperature water bath and a stirrer was charged into a certain amount of AlCl_3 , NaOH, and water. The mixture was stirred until no white sedimentation existed and then charged it into the required amount of citric acid, oxalic acid, and phenylacetic acid. The solution was kept at 70°C for 4 h. After the reaction, the solution was cooled and dried, and then, the crosslinker SW1 was obtained. A 200-mL beaker equipped with a constant-temperature water bath and a stirrer was charged into certain amount of 1-dodecaic acid and deionized water. NaOH (50 wt %) was added into the solution to adjust the pH. Next, RaCl_3 (45 wt %) solution was dropped into the beaker; the temperature was increased and maintained at 90°C for another 6 h. The product was filtered at a high temperature and size-reduced; then, the thermal stabilizer (SW2) was obtained.^{15,16}

Preparation of the particulate fluid diversion agent

A 200-mL beaker equipped with a constant-temperature water bath and a stirrer was charged into AM, MMA, AA, potassium persulfate, (MMT), SW1, SW2, and Span80, of which the total concentration was 30

wt %. The mixture was stirred, and polymerization was set at 50°C for 3 h; the product was then dried in a vacuum oven at 120°C for 1 day and ground into powders with size around 20 mesh.

Evaluation of the particulate fluid diversion agent

We took 1 g of dry copolymer, swelled it completely, and used the tea bag method to weigh the gel. We then measured the static grade (SG); there are five SGs: 1 = rigid gel; 2 = elastic gel; 3 = low elastic and mobile gel; 4 = moderate elastic and mobile gel; and 5 = high elastic and mobile gel. We put the gel into a vacuum oven at 200°C for 200 days and observed the changes in absorbency and gel strength. We put 1 g of the copolymer into solutions with different contents of NaCl; we then weighed the completely swelled gel after removing the free water.¹⁷ We made a polymer solution of a certain content to suspend the fluid diversion agent and designed a device based on Smith's¹⁸ procedure; we let some copolymer disperse in the polymer solution in the middle container, turned on the power, and recorded the pressure difference (ΔP_1) until no fluid flowed out. We then put the used fluid into the middle container again, repeated the steps, and recorded the pressure difference (ΔP_2).¹⁸ Copolymer (0.5 g) was introduced into crude oil and then weighed when the copolymer was dipped in crude oil at intervals. Sand pipes were made with a permeability of $2\text{--}20\ \mu\text{m}^2$, a length of 4.0 cm, a cross-sectional area of $0.95\ \text{cm}^2$; we then made the agent (200 mesh) in the HPAM solution (100 mg/L) in the middle container flood through pipe and recorded the flux and the fluid pressure difference.¹⁸

RESULTS AND DISCUSSION

Effect of the monomer mass ratio on the properties of copolymer

At a specific reaction temperature, we chose the optimum amount of MMA amount with a certain amount

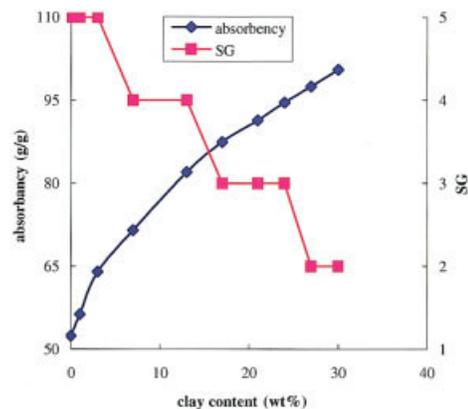


Figure 2 Absorbency and SG versus clay content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

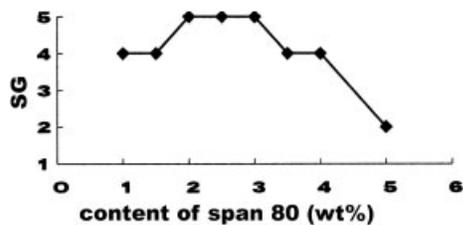


Figure 3 Content of span80 versus SG.

of crosslinker (1.5 wt %), initiator (2 wt %), and ratio (4 : 1) of AM/AA (Fig. 1).

As a hydrophobic monomer, MMA could cause the copolymer to be undissolved in water at high temperatures; MMA has a superior tendency toward thermal stability and chemical inertia. It could keep these inherent properties. With increasing MMA content, the absorbency declined, the ratio of MMA/AA went over 0.03, and the gel strength increased toward a rigid gel. This could be explained by the fact that with more MMA in the copolymer, more of the physical crosslinker point existed as formed by the joint of the hydrophobic part. When the MMA/AA ratio was less than 0.03, with increasing MMA content, the absorbency declined, and the gel elasticity increased, which showed that the lower the MMA content was, the crisper the gel was.

Effect of the clay content (Fig. 2)

Because of the addition of the clay, an inorganic-organic mixed particulate was formed whose net structure had a high stability. With increasing clay content, the water-absorbed ratio increased, but when the value was beyond 2 wt %, there was a change, although not distinct. An impurity existed because of the clay, which affected the increase in molecular weight (the larger amount of initiator in this reaction could also justify the problem) and made the copolymer become crisp. Therefore, a content of 13 wt % was the optimum amount to balance the tenacity and lower cost.

Effect of the flexibilizer

Figure 3 shows that the effect of the flexibilizer on the gel strength was not obvious when the span80 content was

TABLE I
Effect of Thermal Stabilizer Content on Thermal Stability of Swelled Gel

	SW2 (wt %)							
	0	1	2	3	4	5	6	7
Temperature (°C)	120	160	160	180	180	200	200	200

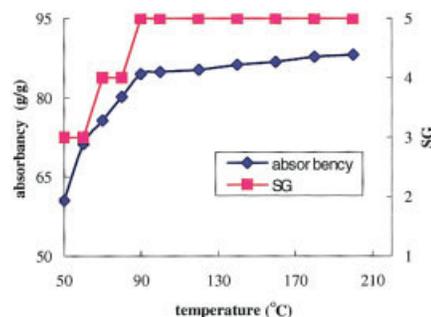


Figure 4 Absorbency and gel strength versus temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

less than 2 wt % and the gel strength was best when the content of span80 was 2–5 wt %. However, when the content was beyond 3 wt %, as an impurity, it became a chain-transfer agent that made the macromolecular end deactivate and terminate and influenced the growth of molecular weight, and the swelled gel strength declined.

Effect of the thermal stabilizer

As noted in Table I, the thermal stabilizer improved with increasing thermal stabilizer, which illustrates that it played an important role in the copolymer. The main reason was that thermal stabilizer could delay the degradation of the copolymer at high temperatures. The agent did not work well in the swelling gel if the content did not reach 5 wt %.

Basic properties of the composite copolymer

Temperature stability of the copolymer

Figure 4 shows that the composite copolymer had good swelling behaviors in the aqueous salt solution without degradation and that the absorbency upgraded with increasing temperature up to 200°C, which means that the composite copolymer could bear a high temperature up to 200°C. At the same time, MMA and the thermal stabilizer enhanced the thermal stability of the copolymer. In addition, the elasticity

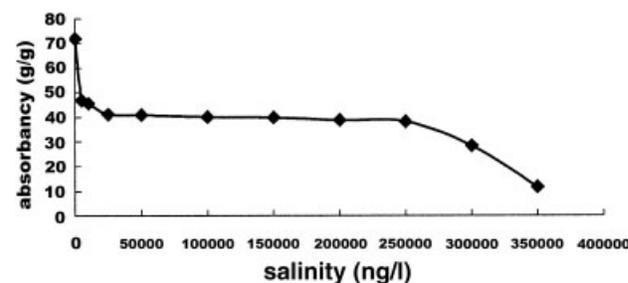


Figure 5 Swelling behavior of the composite copolymer at different salinities.

TABLE II
Influence of Polymer Content on Pressure Difference and Toughness Index

Content of polymer (mg/L)	ΔP_1	ΔP_2	f_{tay}
100	0.030	0.024	1.250
150	0.050	0.046	1.087
200	0.060	0.050	1.200
300	0.080	0.070	1.143

Average f_{tay} value = 1.170.

became better and better with increasing temperature. So it flowed easily during the injection period and could flow into the pore efficiently. The probable reason for this was that the copolymer was not crosslinking mainly between inner molecules. On one hand, the moving unit obtained more energy to restrain the potential energy barrier; on other hand, the polymer volume increased when the temperature rose, and the moving unit had much space to transfer. As a result, it accelerated the relaxation, and the gel strength became better.

Salt tolerance of the composite copolymer

As shown in Figure 5, the salinity had great influence on the swelling behavior. The curve in Figure 5 can be divided into three parts. In the first area, the salinity ranges from 0 to 10,000 mg/L, and the absorbency declines sharply from 71.9 to 45.6 g/g with increasing salinity. In the second area, the salinity ranges from 10,000 to 250,000 mg/L, and there is no obvious change in the absorbency of the copolymer. In the third area, the salinity ranges from 250,000 to 350,000 mg/L, and the absorbency declines slowly. This shows that the composite copolymer had broad applicability in the salt solution.

Evaluation of gel toughness

According to Smith's¹⁸ method, the toughness index is the ratio of the pressure difference and the flux (ΔQ_1 and ΔQ_2) when the water-absorbed grains (content = 0.5%, 200 mesh, and 20 mL) are screened twice:

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

$$\text{let } \Delta Q_1 = \Delta Q_2, \text{ then } f_{\text{tay}} = \Delta P_1 / \Delta P_2$$

TABLE III
Constringency of Composite Polymer in Crude Oil

	Time											
	0	1 h	2 h	3 h	6 h	12 h	24 h	2 days	4 days	8 days	12 days	16 days
Weight of the sample (g)	0.05	1.35	1.46	1.58	1.76	2.03	1.94	1.32	0.92	0.55	0.42	0.27

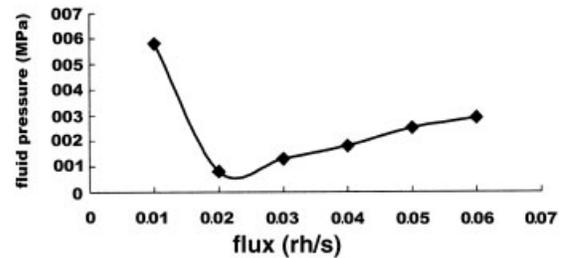


Figure 6 Flux versus fluid pressure.

When $\Delta Q_1 = \Delta Q_2$, $f_{\text{tay}} = \Delta P_1 / \Delta P_2$, where f_{tay} is a dimensionless constant and surpasses 1; the larger 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.

As shown in Table II, the toughness index showed that this composite copolymer exhibited better flexibility and could flow into pores in the deep reservoir without being brittle.

Composite copolymer constringency in crude oil

As shown in Table III, the composite copolymer exhibited good constringency properties in crude oil; from the beginning 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, the gel weight was 0.27 g. This shows that the constringency of the composite copolymer was good.

Gel-injection properties (Fig. 6)

At a pressure of 0.01 MPa, grains did not flow into the pore, and the flux was large. With increasing pressure, the grains began to flow into the pore, and the flux declined sharply. If the pressure went up, the flux increased, which revealed that the grain began to deform and flow into deep zones. When it reached a certain value, the pressure tended to be steady.

CONCLUSIONS

In this work, the effects of the self-made crosslinker SW1 and rare-earth stabilizer SW2 on the properties of

the copolymer were good, and this kicked off the luxury of normal crosslinker. The rare-earth stabilizer was first introduced into water-swelling crosslinked copolymer, and at low amounts, it enhanced the thermal stability, which proved that when it came to the thermal stability of copolyacrylamide, the rare-earth stabilizer showed better performance. After the clay was introduced into copolymer, the absorbency increased, and the inorganic-organic mixed grain tended to be rigid, which showed that the gel strength could be changed under composite action. The crosslinked particulate fluid diversion agent synthesized in this study exhibited superior properties of salt tolerance and thermal stability, and it behaved better at high temperatures than at room temperature. The optimum synthesis conditions follow: AM/AA/MMA ratio = 4 : 1 : 0.03 w/w; crosslinker = 1.5 wt %; clay = 13 wt %; span80 = 3 wt %; thermal stabilizer = 5 wt %; reaction temperature = 45°C. The fluid diversion agent could exist at 200°C, and the limiting salinity of salt tolerance was 250,000 mg/L; the gel SG was 5, the average value of the toughness index was 1.1170, and it had better injection capability. Above all, the composite copolymer as a particulate fluid diversion agent is promising for applications in deep profile control, and further discussion of practical applications will be done in future articles.

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