The Use of Environmental Scanning Electron Microscopy for Imaging the Microstructure of Gels for Profile Control and Water Shutoff Treatments

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ABSTRACT: The use of gel systems as profile control and water shutoff agents has become a wide practice in recent years for oil recovery applications. But few systematic studies have been carried out on the microstructure of gels. In this study, environmental scanning electron microscopy (ESEM) was employed to investigate the microstructure of gels in their natural state. It was directly observed that a three-dimensional network structure formed in chromium or zirconium crosslinked polymer gels is the same as organic/inorganic crosslinked gels. However, there is a dense flat structure in phenol resin crosslinked polymer gels or phenolic resin gels. The differences between the microstructures can be attributed to the different crosslinking sites and crosslinking density, and this affect the gel's stability at reservoir temperatures. In addition, this paper also introduced the crosslinking mechanism and macro-morphology of the bulk gels. It can contribute to a better understanding of the gel's microstructure. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39946.

INTRODUCTION

As oil reservoirs mature, water production increases. High water production has generated several issues, including lift expense, separation, pumping, filtering and reinjection, which greatly increase the exploitation cost. In addition, excess water production also increases corrosion, scale, and environmental pollution, which eventually results in well shut-in.[1,2] Therefore, reduction in water production of oil wells becomes an important emergency objective for mature oilfields.

Profile control and water shut off technologies are available for water production control in reservoir applications.[3–5] Profile control technology involves the injection of a plugging agent from water wells into high permeability channels or fractures. This technology is used to improve the water injection profile which makes the injected fluid flow through previously unswept low permeable zones and thus improves oil recovery. Water shutoff technology involves injecting a plugging agent from production wells to seal or selectively plug water production, which can directly reduce water production from productive wells. These two technologies can make the following water turn into the low-permeability layers and improve the swept volume. As a consequence, oil recovery is enhanced. Therefore, a good plugging agent is a key element in successful profile control and water shutoff treatments. Recent successful applications of crosslinked polymer gels for profile control and water shutoff treatments have emerged because of advantages of cost efficiency, controllable gelation time, and adjustable strength.

The most common gel systems used for profile control and water shutoff treatments are mainly composed of polyacrylamide (PAM) or acrylamide based polymers and inorganic or organic crosslinkers. These polymers typically have different degrees of hydrolysis charge densities and molecular weights, which can be crosslinked with inorganic or organic crosslinkers under different reservoir conditions. In general, the carboxylate groups of polymer chain react with multivalent cations and form crosslinks along the chain.[6] Chromium, aluminum, or zirconium are the most commonly used inorganic crosslinkers.[7–9] However, the gels produced through inorganic crosslinkers typically have lower thermal stability, resulting in over crosslinking or syneresis in high-temperature reservoirs.[10] The organic crosslinking reaction involves the formation of covalent bonds between amide groups of the polymer and the crosslinker, which usually forms a good stable gel in high-temperature

Table I. Chemical Analysis of the Brine

Ion composition	Ca^{2+}	Mg^{2+}	Na^+	Cl^-	SO_4^{2+}	HCO_3^-	Salinity
Concentration (mg/L)	31.86	8.46	161.46	243.24	46.98	0.08	492.08

reservoirs. Therefore, these polymer gels based inorganic or organic crosslinkers can be used in different temperature reservoirs according to their thermal stability.

Although the stability of these polymer based gels relates to their microstructure, relatively few systematic studies have been carried out. In previous studies, the gel's structure was inferred from the polymer's structure and reaction process. Recently, scanning electron microscopy (SEM) was used to investigate the microstructure of gel systems,[11] but samples were susceptible to damage during the freeze-drying and gold-coating process, resulting in inaccurate microstructures. To systematically investigate the microstructure of the gel systems without destroying them, environmental scanning electron microscopy (ESEM) was employed. The ESEM technique allows imaging of organic samples without conventional preparation techniques (such as freeze-drying and gold-coating) and permits examination of samples in their natural state (wet, hydrated, or uncoated).[12,13] It is an excellent way to accurately investigate the gel's microstructure without invasively damaging the network structure. ESEM was conducted to investigate the most commonly used gel systems in oilfield. The typical gel systems, including chromium crosslinked polymer gels, zirconium crosslinked polymer gels, phenolic resin crosslinked polymer gels, organic/inorganic crosslinked gels and phenolic resin gels, used in the research were prepared under different temperatures in our laboratory. Through this work, we expect the studies can contribute to a better understanding of the gel's microstructure.

MATERIALS AND METHODS

Materials
Nonionic PAM with a degree of hydrolysis 3.31% and average molecular weight of 9,650,000 g/mol was provided by Yuguang, China. Anionic polymer with a degree of hydrolysis of 24.38% and average molecular weight of 12,000,000 g/mol was provided by Fanghua, China. The crosslinkers, including phenolic resin, chromium acetate and inorganic chromium, were purchased from Fanghua, China. Zirconium acetate as a crosslinker was purchased from Zibo, China. The brine salinity used in all experiments was 492.08 mg/L. Chemical analyses of the brine are given in Table I.

Preparation of Gels
Gelant solution was prepared by mixing polymer solution and crosslinker at room temperature. The polymer solution was first diluted to the required concentration using the brine. Then, the crosslinker was slowly dropped into the polymer solution and stirred to produce a uniform gelant solution. Then, the gelation solution (25 mL in volume) was injected into an ampoule through tygon tubing leaving about one-third of the ampoule volume as headspace, and the ampoule was sealed at neck. In this study, the crosslinking reaction was initiated by heating the

gelant solution at different temperatures in an oven (UN 260, Memmert Company, Germany).

Characterization Methods
ESEM (Quanta 200 FEG, FEI Company Hillsboro, OR) was employed to characterize the gelation microstructure. When the gel had formed in the ampoule, a drop of gel was directly placed on a covered ESEM grid. Pressure and temperature were initially set at 313 Pa to 455 Pa and 0°C, respectively. Determinations were conducted at accelerating voltage of 15 kV and working distance from 5 mm to 10 mm.

RESULTS AND DISCUSSION

Chromium Crosslinked Polymer Gels
The gel based on chromium crosslinkers has been widely used to control water production due to its high success rate and relatively low cost.[14,15] Inorganic chromium, such as $K_2Cr_2O_7$ and $Na_2Cr_2O_7$, are generally used at the initial stage for profile control and water shutoff treatments. Some aspects of the crosslinking reaction of the polymer/inorganic chromium system were reported in previous studies.[16] Only a brief summary is presented in this section. Chromium (VI) ions are strong oxidizing agents and are readily reduced to chromium (III) by a reducing agent. Then the ions and water molecules can form $[Cr(H_2O)_4]^{3+}$ due to complexation. As the reaction proceeds, a further hydrolysis reaction and hydroxyl bridge reaction results in the formation of the Cr (III)-ligand of the multi-core hydroxyl bridge. So, the carboxylate group ($-COO^-$) from the polymer is converted to the Cr (III)-ligand of the multi-core hydroxyl bridge by the crosslinking reaction, resulting in the formation of a uniform porous mesh-like network structure, with pores sizes ranging from 0.5 μm to 2.5 μm [Figure 1(b–d)]. Surrounding the pores [Figure 1(d)], chain bunch structures appear as a continuous network several micrometers-thick. This three-dimensional network structure with high density is convenient for water to incorporate into the mesh structures, which enhances the stability of gel systems during oil well treatment. Figure 1(a) shows the chromium crosslinked polymer gels prepared at 60°C. The gel system (formulation: 0.3% anionic polymer + 0.6% chromium acetate) is shown in Figure 1(b–d).

However, chromium (VI) which is more toxic than chromium (III) cannot meet the current environmental regulations.[17] So chromium (III) acetate was used instead of inorganic chromium. Generally, the Cr(III)/HPAM based gel systems can be crosslinked in several hours at high temperatures (>80°C), which reduce the propagation of chromium ions into the formation. Furthermore, if the gelation between the polymer and chromium acetate is processed at high temperature, it will result in expulsion of water from the gel structure and syneresis of the gels. Therefore, the chromium based gel systems are usually
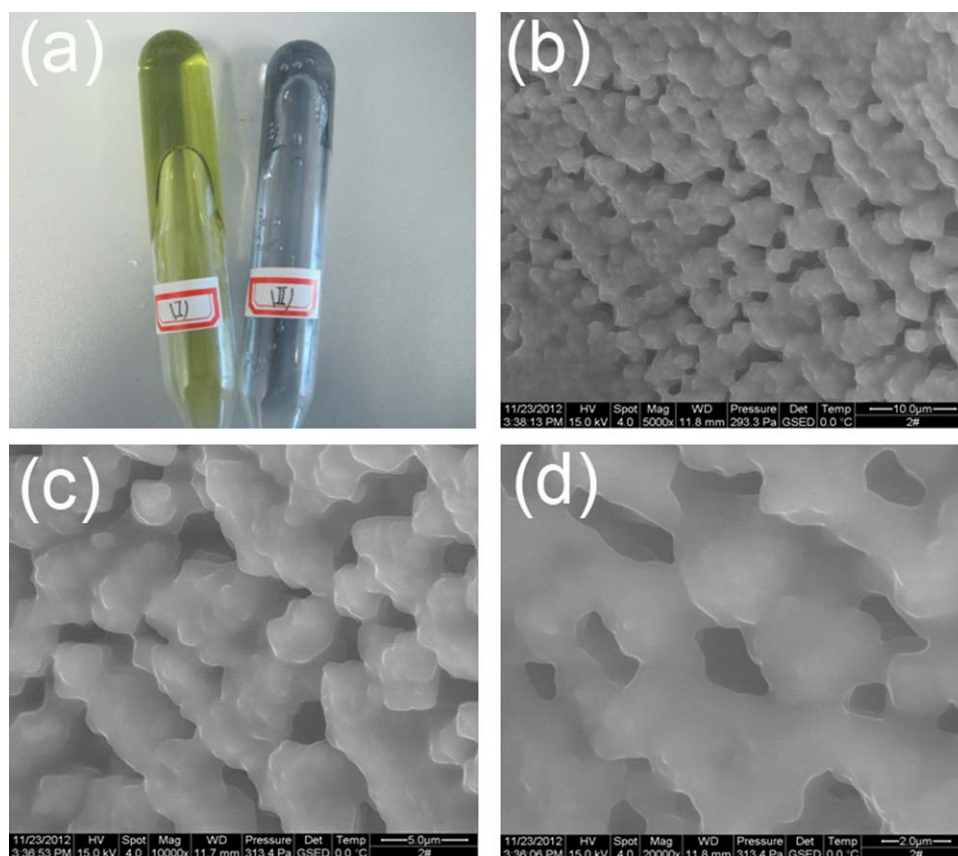
Figure 1. ESEM images of chromium crosslinked polymer gels. (aI): 0.3% anionic polymer + 0.1% Na_2SO_3 + 0.2% $Na_2Cr_2O_7$; (aII): 0.3% anionic polymer + 0.6% chromium acetate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

used for near-wellbore treatments in lower temperature reservoirs.[18]

Zirconium Crosslinked Polymer Gels

Zirconium crosslinked polymer gel is another broad application of gels for profile control and water shutoff in mature reservoirs. Generally, $ZrOCl_2$ or zirconium acetate is used as the crosslinker to produce good stable gels to control water production. However, the crosslinking reaction between the polymer and $ZrOCl_2$ is completed within only 15–45 s, thereby bringing difficulties for in-depth placement into reservoir formations.[19] In addition, the crosslinking reaction is only processed under acidic conditions (pH value: 2–4),[20] which also brings well bore corrosion. To overcome these issues of the short gelation time and reaction condition, a polymer gel based on zirconium acetate has been proposed.[21] In this gel system, the optimum pH value for gel formation is 7.49. Further study shows that the gelation time can be controlled within 26 h to 240 h by varying the nonionic PAM or zirconium acetate concentration at 28°C. But the initial gelation time of gel systems (0.4% nonionic PAM and 1.0% zirconium acetate) is 71 h at 28°C and sharply decreases to 2 h at 110°C. Moreover, the zirconium crosslinked polymer gels exhibit long-term stability at low temperature (28°C) while resulting in syneresis of the gels at 110°C after 1 month. So this gel system is recommended to be used in low temperature reservoirs. Figure 2 shows the macrostructure and

microstructure of zirconium gels (formulation: 0.6% polymer + 1.6% zirconium acetate).

Figure 2(a) shows a colorless gel produced by nonionic PAM reacting with $ZrOCl_2$ or zirconium crosslinkers. According to the gel strength code method,[22] it can be considered as a strong gel since the gels are slightly deformable but not flowing [Figure 2(a,b)] shows a three-dimensional network structure of zirconium gel through the ESEM imaging procedure. In the structure, the carboxylate group ($-COO^-$) from the polymer is converted to a Zr(IV) complexation by a crosslinking reaction, incorporating hydrophilic groups into the chain, which forms a three-dimensional network. Furthermore, an obvious "skeletal structure" of the bulk gels is formed [Figure 2(d)]. The gel systems have a uniformly porous mesh-like network structure with pore sizes ranging from several micrometers up to approximately 10 μm [Figure 2(c)]. This structure with numerous small pores may result in lower syneresis and greater water holding capacity, and thus promotes the stability of the gel systems during well treatment.[23]

Phenolic Resin Crosslinked Polymer Gels

The short gelation time and limited stability of the chromium or zirconium crosslinked polymer gel constrains their broad application in high-temperature reservoirs. Other problems with these systems include excessive hydrolysis and syneresis due to additional crosslinking with calcium and magnesium ions
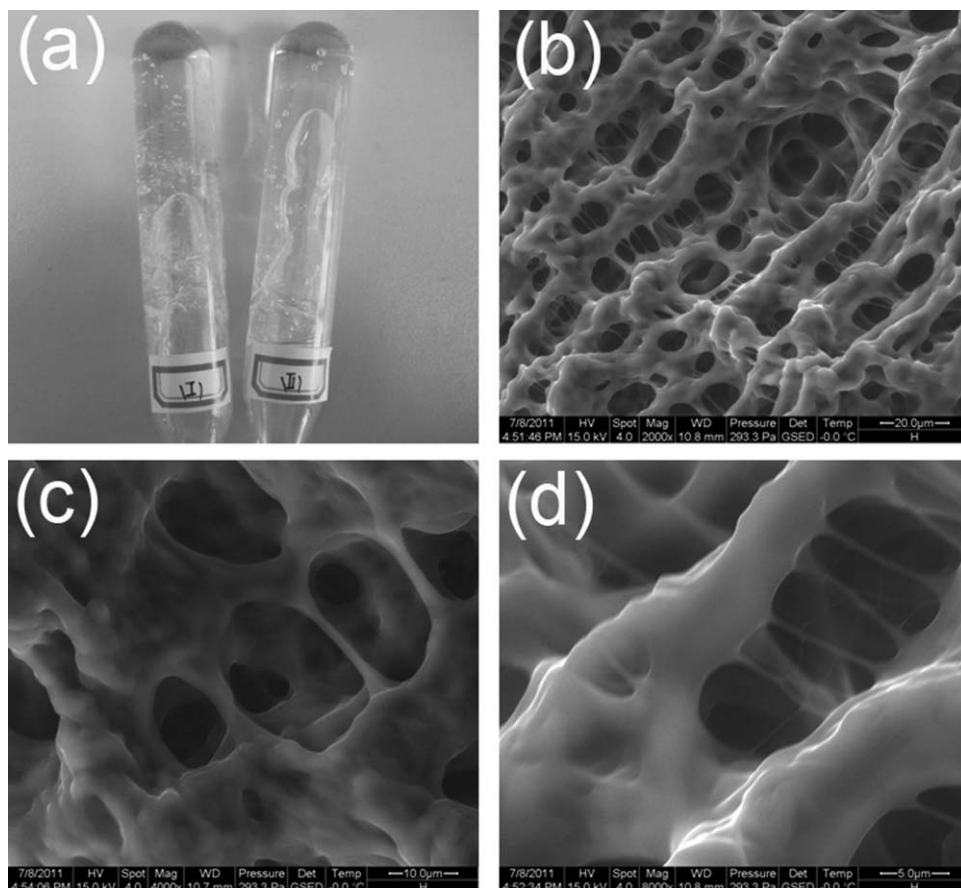
Figure 2. ESEM images of zirconium crosslinked polymer gels (aI): 0.6% nonionic PAM + 1.6% zirconium acetate; (aII): 0.6% nonionic PAM + 0.035% $ZrOCl_2$+ 0.02% pH modifier.

present in high salinity brines. So a gel system based on a polymer and phenolic resin crosslinker has been introduced.[24,25] The polymers used for the gel systems can be homopolymer, copolymer, or terpolymer containing acrylamide.[26] Depending on the phenolic resin crosslinker and polymer composition, the gel systems exhibit excellent stability in high temperature and salinity reservoir conditions. In addition, the gelation delays are also relatively long, ranging from several days to a week or more over a broad temperature range (60–100°C),[27] which is not only suitable for near-wellbore applications but also deep formation treatments. They can be good candidates for some high-temperature and salinity applications.

The general mechanism involved in this phenolic resin crosslinked polymer gel formation is the same, the only difference is the rate of gelation. As previously reported, the crosslinking mechanism involves hydroxymethylation of the amide groups ($-CONH_2$) and multiple alkylation ($-CH_2OH$) of the phenolic ring.[28] During the gelation process, the amide groups of the polymer provide crosslinking sites reacting with multiple alkylation of the phenolic ring at high temperature, then forming the gel systems (Figure 3). It can be seen that the gel systems are yellow viscoelastic liquids [Figure 3(a)]. When the gel is formed, it can bridge across the pore throats and restrict the flow of water, thus reducing the permeability of reservoir cores. Figure 3(c–d) shows the microstructure of bulk gel (formulation: 0.4%

nonionic PAM + 1.2% phenolic resin). It can be seen that in this case gels are composed of a uniform continuous convex structure [Figure 3(b–d)]. As shown in the images, there are many spherical protrusions distributed over its surface, which contribute to water conservation during the gelation process. The compact structure would probably have minimum syneresis and great water holding capacity, thus increasing the thermal stability of the gel.

Further analysis from ESEM images shows that the microstructures between chromium or zirconium crosslinked polymer gels and phenolic resin crosslinked polymer gels are significantly different. The structure of the phenolic resin crosslinked polymer gels is denser than that of chromium or zirconium crosslinked polymer gels. The differences between these gel systems may be attributed to the crosslinking site and crosslinking density, thus affecting the scope for application in different reservoir conditions.[29]

Organic/Inorganic Crosslinked Gels
As temperature (>100°C) increases, the difficulties in meeting the requirement of profile control or water shutoff agents increase. For example, the instability and dehydration in conventional gel systems usually lead to treatment failure within a very short time. Therefore, selection of stable gel systems for profile control and water shutoff treatments is a key technology
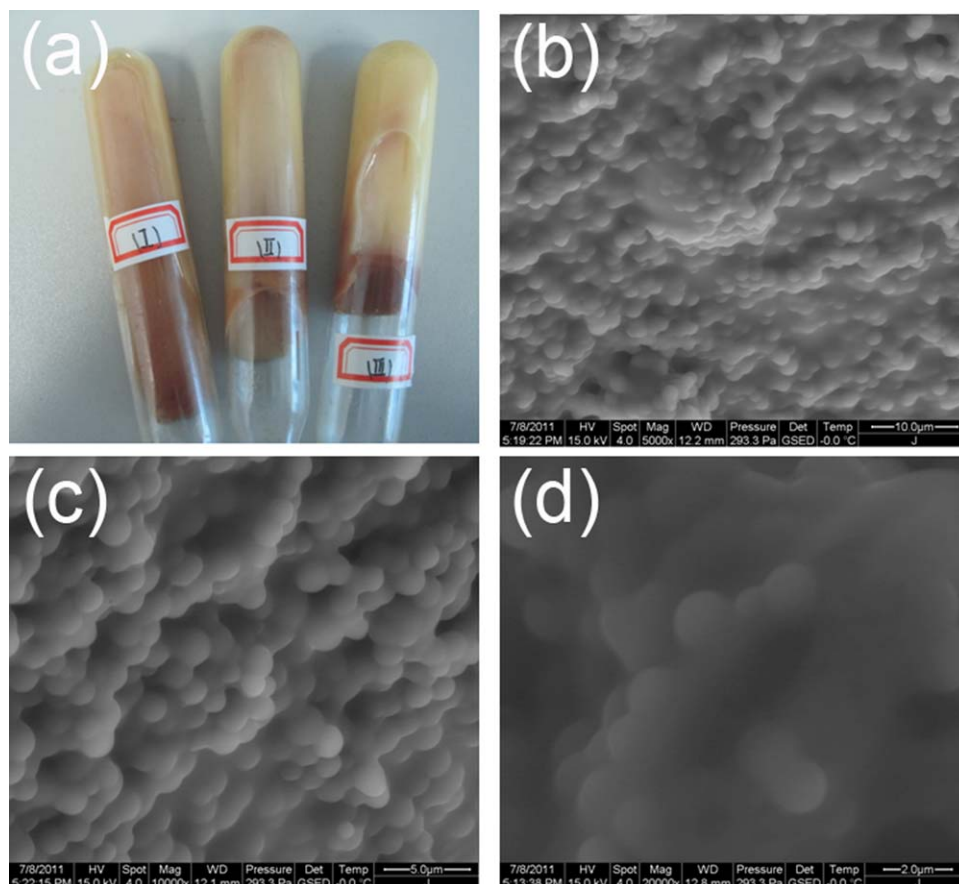
Figure 3. ESEM images of phenolic resin crosslinked polymer gels (aI): 0.4% nonionic PAM + 1.2% phenolic resin; (aII): 0.6% nonionic PAM + 1.2% phenolic resin; (aIII): 0.8% nonionic PAM + 1.2% phenolic resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in high-temperature reservoirs. Recently, an organic/inorganic crosslinked gel with an organic resin, water soluble silicide, a stabilizer for high-temperature reservoirs has been introduced by our group.[30] In our study, this gel systems was stable for more than 3 months without any dehydration at 130°C. Differential scanning calorimetry (DSC) studies show that the gel systems can be used for water production control at 155°C in oilfields. Figure 4 shows organic/inorganic crosslinked gels prepared at 130°C.

As shown in Figure 4(a), the surface of organic/inorganic crosslinked gels do not deform upon inversion of the ampoule. It suggests that the gel systems are strong enough to provide a large flow resistance in the high permeability zones during water flooding, resulting in injection water into the previously unswept, low-permeability zones. Figure 4(b–d) shows the microstructure of organic/inorganic crosslinked gels (formulation: 5.0% organic resin + 3.0% water soluble silicide + 0.2% stabilizer). It can be observed that a compact three-dimensional network is formed in the gel systems through ESEM imaging. Although there are many meshes in the network structure, the structure of organic/inorganic crosslinked gels is significantly different from the zirconium crosslinked polymer gels. The meshes in the organic/inorganic crosslinked gel systems are connected by a short and thick chain, which give the gel systems

good water retention capacity, thus improving the thermal stability of gel systems in high-temperature reservoirs. The thermal stability of gel systems are related to the bond energy. During the crosslinking procedure, the Si—O bonds are introduced into the gel systems. The average bond energy of the Si—O bond (about 422.5 kJ/mol) is higher than those of the C—O bond (about 344.4 kJ/mol) and C—C bond (about 331.0 kJ/mol). Therefore, it is not easy to break the bond. As a result, the organic/inorganic crosslinked gel systems will retain long-term thermal stability in high-temperatures reservoirs.

Phenolic Resin Gels

Steam flooding is the most widely used techniques for oil recovery in heavy oil reservoirs.[31] However, a steam channel is formed after a long term of steam flooding, which results in a lower volumetric sweep efficiency and thereby decreases the oil recovery. Therefore, some treatments, including injection of foaming agents, such as inorganic particles and gels, have been developed to reduce the steam channeling. But the foaming agents and common gels are instable at steam temperatures of 200–300°C. They will thus degrade and lose their plugging capability within a few days. In addition, injection of inorganic particles into deep formations is difficult and the particles are only utilized very near the well bore. To overcome the instability and injection difficulties of the plugging agents, phenolic resin
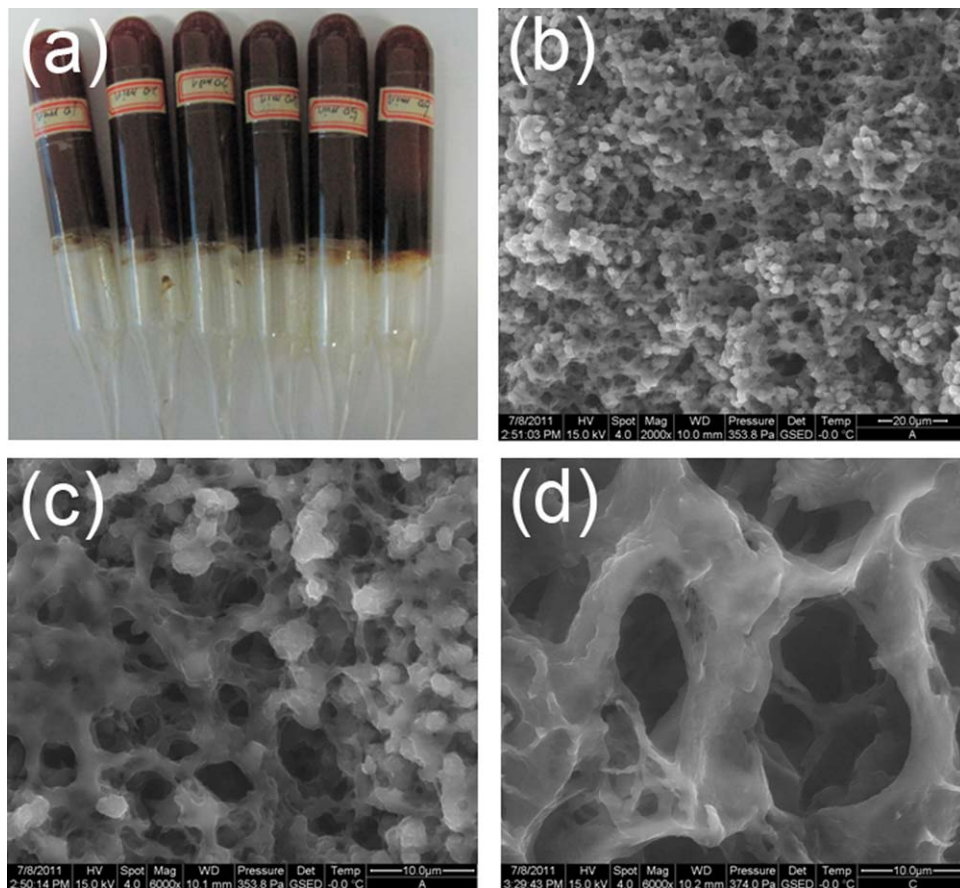
Figure 4. ESEM images of organic/inorganic crosslinked gels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
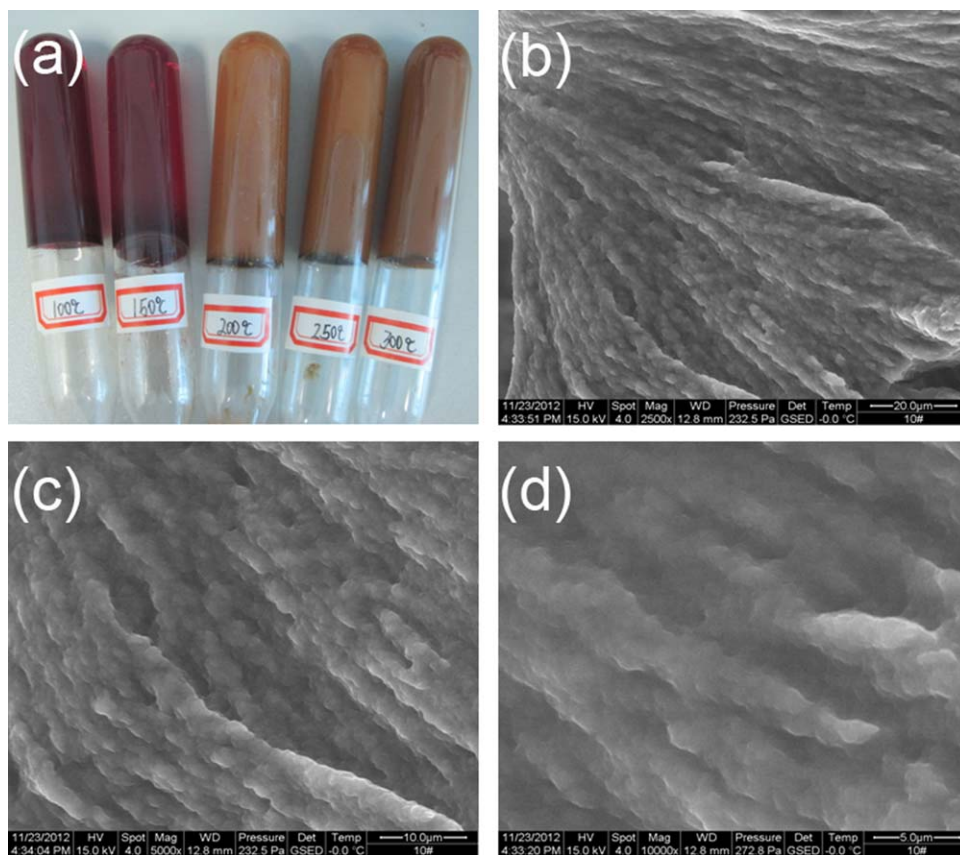

Figure 5. ESEM images of phenolic resin gels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gels have been introduced for water control in heavy oil reservoirs. Generally, the oilfield use phenolic resins which are polycondensation products of phenols and formaldehyde, which can be crosslinked at reservoir temperature of 70–300°C. Moreover, the viscosity of 15% phenolic resin solution is only 1.1 mPa·s at 30°C, which allows the phenolic resin solution to enter the previous steam channel and crosslink in the deep formation. Figure 5 shows the macrostructure and microstructure of phenolic resin gels prepared at 250°C (formulation: 15% phenolic resin).

From Figure 5(a), it can be seen that the formed phenolic resin gels are rigid gels according to the gel strength code method.[22] In this research, the gelation time can vary from 3 days to 2 h when the temperature is increased from 70°C to 300°C. As the phenolic resin gels are formed in deep formations, they can build a resistance to flow within the steam channel, thus diverting injected steam into high oil saturation banks in the reservoir and improving steam sweep efficiency. Figure 5(b–d) shows the microstructure of phenolic resin gels. Compared with chromium or zirconium crosslinked polymer gels, the structure of phenolic resin gels is relatively compact and dense. The surface appears rougher and uniform with many protrusions. During the polycondensation process, the ring hydrogens in the para- and both ortho-positions relative to the hydroxyl group can react with formaldehyde, and then form a relatively rigid network. The compact and dense structure has a great hydration capability which contributes to reduction in water diffusivity and improves the stability of the gel systems.

CONCLUSIONS

In this work, ESEM technique is proved to be excellent in investigation on the microstructure of gel systems. ESEM images of the gels have shown that all samples' microstructures are close to their natural hydrated state. It directly shows that a three-dimensional network structure or a dense flat structure is formed in different gel systems. The main differences between gel's microstructure can be attributed to the different crosslinking sites whereas the crosslinking densities can lead to different reaction rates and gel strengths, and thus affect the gel's stability at reservoir temperatures. We expect this research can contribute to a better understanding of the gel system used in oilfields.

ACKNOWLEDGMENTS

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