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A novel polyacrylamide-based superabsorbent with temperature switch for steam breakthrough blockage

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ABSTRACT: A novel high-temperature resistant superabsorbent polymer (SAP) with a temperature switch to control its water absorbency was prepared through solution polymerization of acrylamide (AM), using *N*,*N*-methylenebisacrylamide (NMBA) and tetraallylammonium chloride (TAAC) as crosslinking agents. The SAPs were structurally characterized by Fourier transform infrared (FTIR) spectroscopy and energy dispersive X-ray spectroscopy (EDX). The factors that influence the water absorbency such as total crosslinker concentration, molar ratio of NMBA to TAAC and temperature were investigated. The SAP with optimized crosslinker concentration showed a swelling ratio less than 10 g/g at 25°C, and drastically enhanced water absorption capacity (190 g/g) at 300°C. The water absorption characteristics can be tuned by varying the temperature. Swelling experimental results combined with crosslinking density study and morphology observation by scanning electron microscopy (SEM) clearly demonstrated that the hydrolysis of amide bonds on NMBA played a critical role in creating these previously unreported SAPs, and that the use of TAAC with an appropriate amount rendered the SAPs high-temperature resistance. This kind of SAPs has high application potentials as plugging material for steam breakthrough and channeling in heavy oil reservoirs. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42067.

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INTRODUCTION

Nowadays thermal techniques such as cyclic steam stimulation (CSS), steam flooding and steam-assisted gravity drainage (SAGD) play a critical role in oil industry to enhance heavy oil recoveries.[1] However, after a certain period of steam injection, steam breakthrough becomes a common problem, which is preponderant for the vadose of steam, resulting in a narrow steam sweep area, poor heat efficiency and a reduction in ultimate oil recovery.[2,3] Thus, injection of plugging materials down to the problem formation is required to block breakthrough channelings.[4,5] Since the steam temperature is normally higher than 250°C, the blocking agents require high mechanical strength and high temperature resistance, which are different from those used for water shutoff and for profile modification purposes.[6–8] Several different types of plugging agents have been reported and applied in many steam injection reservoirs, including tannin foam,[9] phenolic resin,[10] fly ash, and superfine cement etc.[11] However, the use of phenolic resin as a plugging material suffers from its toxicity and it is too expensive for large scale applications. The disadvantage of the superfine cement is the permanent plug that may lead to permanent damage to the formation.

Bai *et al.* reported a preformed particle gel (PPG) as an economical gel blocking agent at temperature up to 150°C.[12] PPG is a kind of superabsorbent polymer (SAP), which can absorb and retain over a hundred times their weight in liquid even under certain pressure.[13] Traditional SAPs are primarily used as adsorbents for water and aqueous solution in many applications such as diapers, hygiene, agriculture, and horticulture products.[14] But, they cannot be used as steam breakthrough channeling plugging materials owing to their fast swelling time, low strength and poor thermal stability. Recently, a high temperature resistant SAP by using triallylammonium chloride as a crosslinker was developed in our group, but its fast swelling rate was unfavorable to industrial application. Fast swelling would impede the injection operation and lower the blocking efficiency.[15]

The aim of this work is to develop a high temperature resistant SAP with variable water absorbencies at different temperatures. The designed material should absorb little water at injection temperature in order to be pumped into the problem formation with working fluids, then it absorb the most part of water after prolonged exposure to steam injection temperature to become a rigid hydrogel. Here temperature serves as a switch to release the swelling ability of the SAP. The strategy and novelty of this work is to use two kinds of crosslinkers, namely *N*,*N*-methylenebisacrylamide (NMBA) and tetraallylammonium chloride (TAAC) for the preparation of SAP. NMBA is commonly used for the preparation of traditional SAPs.[16] The amide bonds in NMBA structure are not stable and tend to hydrolyze at high temperature (150°C).[17] Whereas TAAC does not contain any unstable bonds and shows high temperature stability. Thus NMBA is used to increase the crosslinking degree, which will result in a low swelling ratio at low temperature. As temperature increases, the amide bonds will be broken and crosslinking points from TAAC will remain. The decrease in overall crosslinking degree enhances the swelling ability of the SAP. Hence, investigations of the swelling characteristics, the effects of various parameters on the swelling properties, and the microstructure of the hydrogel were investigated.

EXPERIMENTAL

Materials

AM, NMBA, TAAC, ammonium persulfate (APS) were analytical grade and purchased from Sinopharm and used as received. All solutions were prepared with distilled water.

Preparation of SAPs

The polymerization was carried out under nitrogen atmosphere in a four-necked flask equipped with a thermometer and a gas inlet at 55°C. Taken the sample with monomer concentration (weight percentage of AM in polymerization solution) of 30 wt %, TAAC to AM ratio of 1 mol %, NMBA to AM ratio of 1 mol %, APS to AM ratio of 0.1 mol % as a representative example, the detailed procedure is as follows: 28.4 g AM (0.4 mol) was dissolved in 50 g distilled water, then the solution was introduced into the flask. After being purged with nitrogen for 30 min to remove the dissolved oxygen, the solution was heated to 55°C in a water bath, then 0.854 g TAAC (4 mmol) (in 5 mL water), 0.616 g NMBA (4 mmol) (in 5 mL water), and 0.0912 g APS (0. 4 mmol) (in 5 mL water) were introduced into the monomer solution. The polymerization process was continued for 4 h. The resulting gel was extruded to thin strips, and dried to constant weight in a vacuum oven at 80°C, then milled through 30–50 mesh screen. In a similar way, a series of crosslinked polyacrylamides with varied crosslinker ratios were prepared.

Water Absorbency Measurement

The sample (0.2 g) was immersed in excessive distilled water at the temperature range from 25 to 300°C for different time. If not specified, the water absorbencies were equilibrium values, which were normally obtained in a swelling time of about 24 h. The measurement at temperature higher than 90°C was carried out in a JN-500B stainless steel pressure vessel (Qingdao Petroleum Instrument). The vessel was kept in a Muffle furnace set to desired temperature for certain period of time. After cooling to room temperature, the swollen gel was separated from unabsorbed water by filtering through a 100-mesh screen. The remaining gel was collected and weighed. The water absorbency of the sample (Q) was calculated based on the following equation:[18]

$$Q=(m_2-m_1)/m_1 \quad (1)$$

where m_1 and m_2 are the weights of the dry sample and the gel, respectively.

The Determination of Crosslinking Density

A series of solvents were prepared with methanol and distilled water by changing the volume ratio of them at 25°C. V_1 was the molar volume of mixed solvent. The swelling ratio Q was measured by immersing certain mass of SAP in different volume ratio of methanol-water solvent at 25°C and 300°C for 24 h. The following formula was obtained according to Flory-Huggins theory and correlative reference:[19]

$$D_2 V_1 Q^{5/3}=M_c\,(0.5-K_1 C) \quad (2)$$

where D_2 is the density of the SAP, C is the volume fraction of methanol in the methanol-water mixed solvent, K_1 is a proportional constant. M_c is the average molecular weight of the molecular chain between the two crosslinking points of the SAP. When $Y=D_2V_1Q^{5/3}$, the formula (2) can be replaced by the following equation:

$$Y=M_c\,(0.5-K_1 C) \quad (3)$$

The value of M_c can be calculated using the formula obtained from the linear relationship between Y and C. It has been well known that the crosslinking density is inversely proportional to the value of M_c.[20]

Characterization

Fourier transform infrared (FTIR) spectra were performed on a Thermo Nicolet NEXUS spectrophotometer in the range of 400–4000 cm^{-1} (KBr disk). Morphology of the dried samples was examined by a HITACHI S-4800 scanning electron microscope (SEM) and after coating with gold film. Energy dispersive X-ray spectroscopy (EDX) was recorded using an SEDX-500 (Shimadzu, Japan).

RESULTS AND DISCUSSION

Preparation of the SAPs

In this work, solution polymerization protocol was applied and APS was used as initiator for the preparation the SAPs. As a traditional technology, the polymerization of acrylic monomer using NMBA as a crosslinker leading to SAPs has been well documented in the Refs. [21–23]. Although examples of using TAAC as a crosslinker have also been found,[24,25] the related information about crosslinking mec

hanism is rare. Diallyammonium chloride (DMDAAC), which is analogues to TAAC but has only two allyl groups in molecular structure, has been reported to forms a five-membered ring during a microwave-assisted reversible addition fragmentation chain transfer (RAFT) polymerization.[26] In this work, it has been verified that under the same condition as in the preparation of SAP, the homopolymerization of DMDAAC also results in a linear five-membered ring structure. Therefore, it is reasonable to assume that TAAC builds two five-membered rings centered at the nitrogen atom during the polymerization process, as illustrated in Figure 1.

The FTIR spectra of AM, NMBA, TAAC, and the synthesized SAP with total crosslinker concentration 2 mol % (n_{NMBA}/

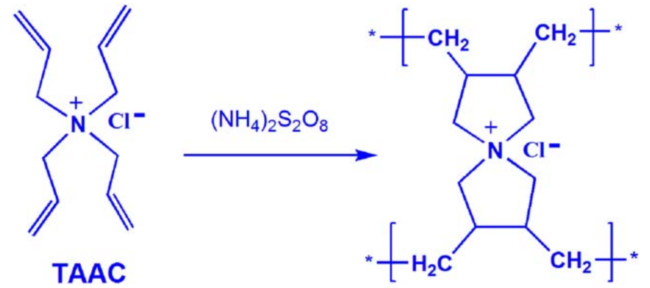

Figure 1. Proposed crosslinking mechanism for TAAC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$n_{TAAC} = 1$) are shown in Figure 2. The absorption bands at 2941 and 1462 cm^{-1} in Figure 2(d) are attributed to the —CH_2— group on the polymeric chain. The broad peaks centered at 1619 cm^{-1} are ascribed to the appearance of —C=O groups. To further identify the presence of the crosslinker units in the SAP networks, the chemical composition of the metal surface was measured by EDX. Figure 3 shows the EDX spectrum of sample. Characteristic peaks of chlorine are found. The presence of Cl in chemical composition confirms that the TAAC has been successfully mounted into the polymer. As for another crosslinker NMBA, although both FTIR and EDX cannot offer positive evidence, it is reasonable to believe that NMBA has also been incorporated in the polymer because it is analogues to AM in structure.

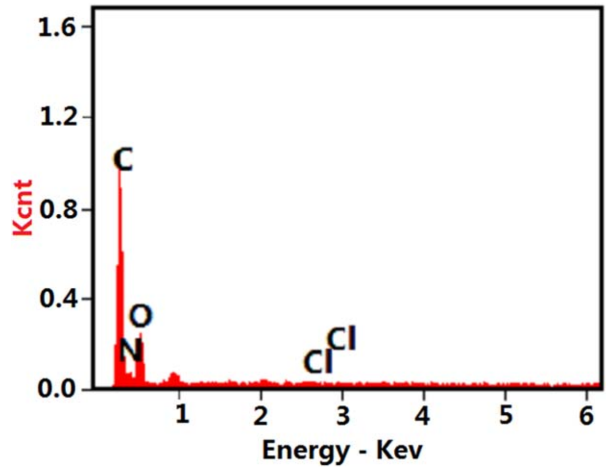

Figure 3. EDX spectrum of SAP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of the Hydrolysis of Acrylamide on Water Absorbency at Different Temperature

Swelling behavior of the SAP is influenced by many factors. Among them the structural characteristics of the polymer and the crosslinking density are the most important issues. In this work, AM is chosen as the monomer, other than the most commonly used partially neutralized acrylic acid as its fast swelling rate is not favored for our purpose. Further, to best control the swelling properties at different temperature, relatively large crosslinker concentration was dosed for the preparation of SAP. Unlike the poly(partially neutralized acrylic acid)-based SAP, the crosslinked polyacrylamide (PAM) itself doesn't have a polyelectrolyte structure. Its water-absorbing mechanism is based mainly on the hydrolysis of the $CONH_2$ groups on the polymer chains, which generate the COO^- groups that bestow the water-

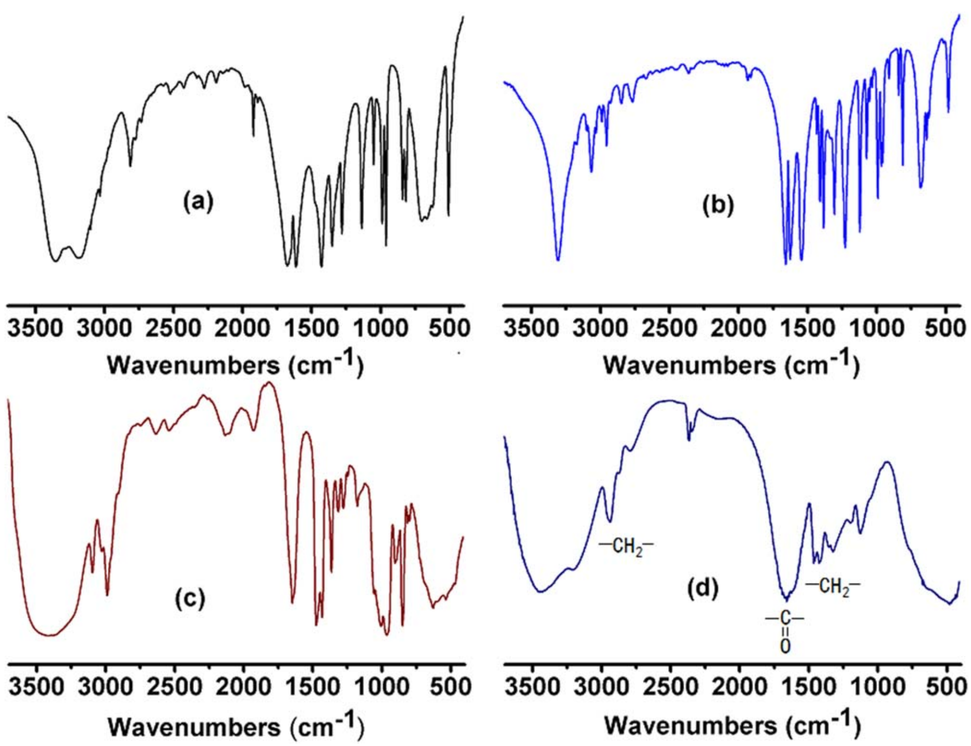

Figure 2. FTIR spectra of (a) AM, (b) NMBA, (c) TAAC, and (d) SAP. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

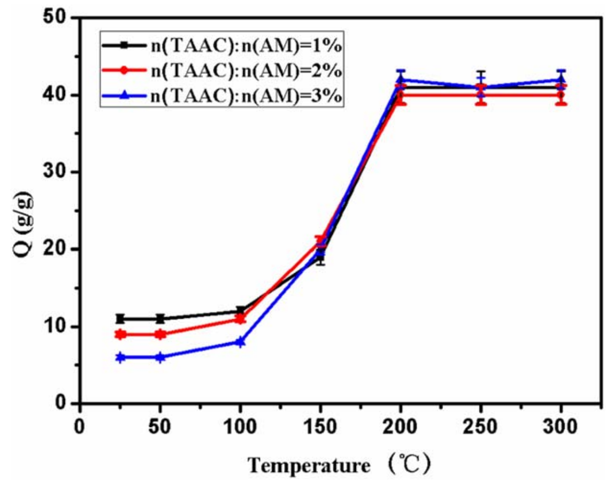

Figure 4. Effect of the hydrolysis of acrylamide on water absorbency at different temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorbing capacity on the material. The hydrolysis degree of the crosslinked PAM is strongly influenced by temperature. Figure 4 shows the effect of the temperature on swelling ratios of the polymer materials. Three samples with different TAAC concentration (1–3 mol %) after the water absorption for 12 h show similar profiles with increasing temperature. Before 100°C, sample with higher TAAC concentration shows lower swelling ratio at the same temperature, indicating that higher crosslinker concentration will shorten the distance between two neighbor crosslinking points, thus decrease the water absorbency. Owing to high level of crosslinking, the changes are very little. This change caused by increased crosslinker concentration become even unnoticeable above 100°C, as hydrolysis of amide groups turns out to be the main factor influencing the swelling ratio.

The swelling ratios increase with temperature significantly between 100 to 200°C, corresponding to an increasing hydrolysis stage of the amide groups. Regardless the crosslinker concentration, the water absorbency of the material is predominantly controlled by the hydrolysis reaction. Above 200°C, the hydrolysis reaches an equilibrium the swelling ratios show roughly the same value of 40 g/g. Namely, the increased swelling ratio caused by hydrolysis of amide groups is almost fixed at about 30 g/g. Besides, the TAAC-crosslinked PAM is rather stable at high temperature. The hydrogel well maintained its shape at 300°C.

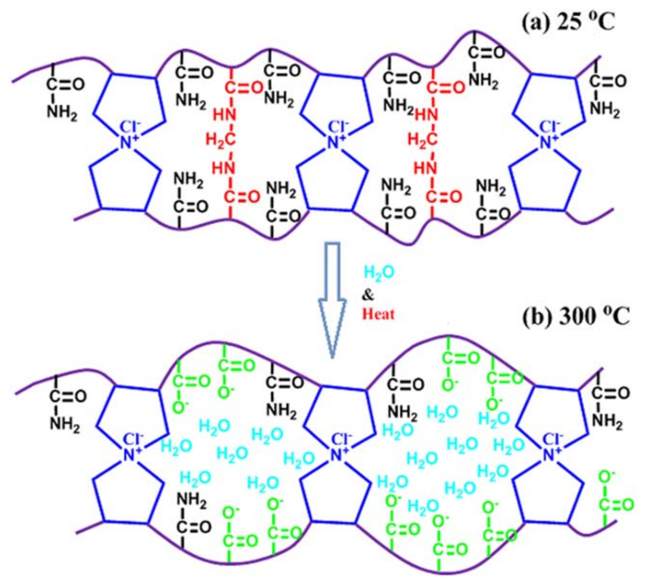

Figure 6. Structural changes in the network at (a) 25°C and (b) 300°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

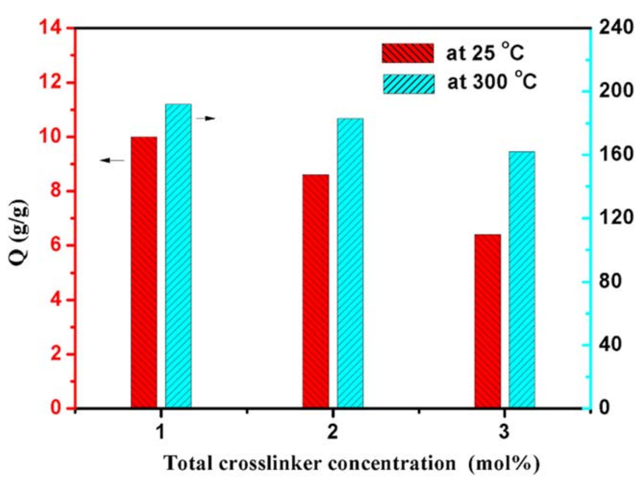

Figure 5. Effect of total concentration of composite crosslink agents on water absorbency. n_{NMBA}:n_{TAAC}=1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of Crosslinker Concentration on Water Absorbency

Crosslinker plays an important role on water absorbency.[27–29] Three SAP samples were prepared using the combination of TAAC and NMBA as crosslinking agents, while keeping the molar ratio of TAAC to NMBA constant (1 : 1). The effects of the total concentration of NMBA and TAAC on water absorbency at 25 and 300°C were comparatively investigated. As shown in Figure 5, the water absorbency decreases with the increase of crosslinker concentration both at 25 and 300°C. This results can be explained by the fact that higher crosslinking density decreases the free space between the polymer chains and consequently the resulted highly crosslinked rigid structure can neither be expanded nor hold a large quantity of water.[30]

The swelling ratios increase dramatically at 300°C, compared with those at 25°C. At low temperature, the amide bonds on

Table I. The Swelling Parameters of SAP at 25°C and 300°C

C	V_1 (mL)	*Q* 25°C	*Y* 25°C	*Q′* 300°C	*Y′* 300°C
0.1	19.0	9.8	1346	157	136,231
0.2	20.2	9.0	1240	137	116,448
0.3	21.3	8.2	1119	118	95,662
0.4	22.8	7.3	989	100	77,106
0.5	24.4	6.2	805	86	64,749

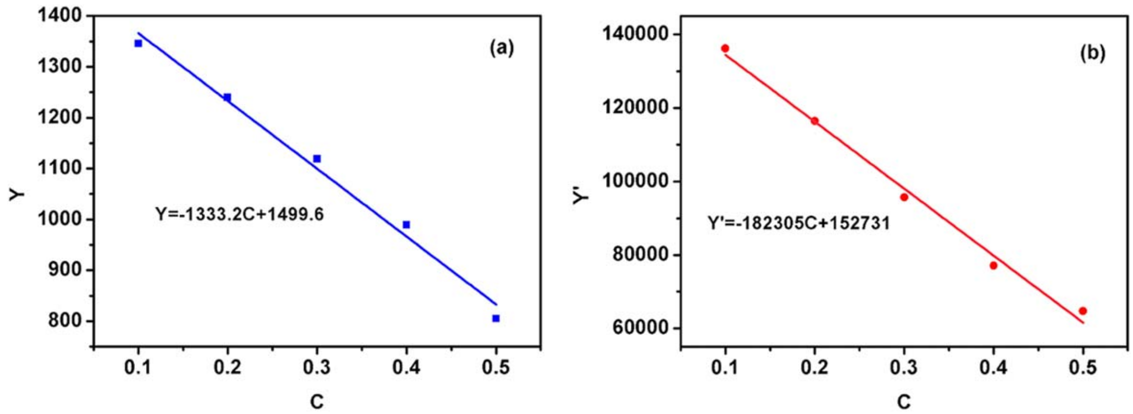

Figure 7. The fitting curves between Y and C (a) 25°C and (b) 300°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the NMBA moiety of the polymer networks were stable. The materials absorbed only a small amount of water owing to high crosslinking degree, whereas at 300°C, the crosslinked amide bonds were broken through hydrolysis, which decreased the crosslinking density. Thus the swelling ratios increased. With regard to the optimum total crosslinker concentration, 2 mol % seems to be the best choice in considering the swelling ratios both at 25 and 300°C along with the cost.

The structural change in the network from 25 to 300°C is illustrated in Figure 6 (crosslinking point by NMBA and TAAC together was not present for clarity).

As discussed earlier, the hydrolysis of amide groups in the polymer main chains could also contribute to the increase of the swelling ratio by about 30 g/g, when the temperature was increased from 25 to 300°C. In addition, it is worth mentioning that not only the cross linkages by NMBA itself also those by NMBA and TAAC together would collapse due to the hydrolysis of amide bonds. This in effect decreased the TAAC concentration. Consequently, the swelling ratios at 300°C are much greater than 40 g/g.

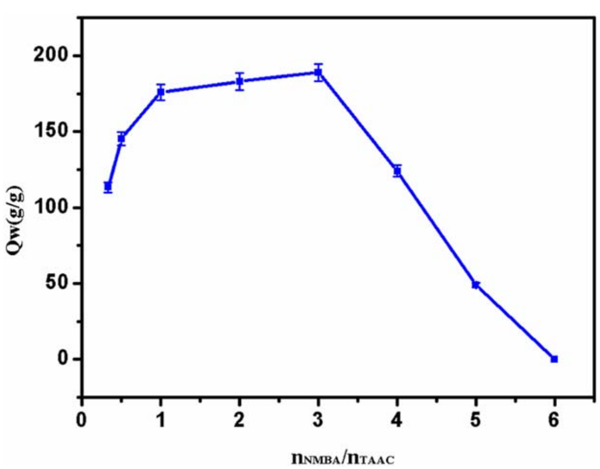

Figure 8. Effect of the molar ratio of NMBA to TAAC on water absorbency at 300°C. $(n_{NMBA}+n_{TAAC})/n_{AM}=2\%$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To prove the change of crosslinking density with varying temperature, the crosslinking densities of the sample with total crosslinker molar ratio 1% ($n_{NMBA}/n_{TAAC}=1$) were evaluated. The swelling ratio at 300°C was measured after cooling the hydrogel to 25°C, therefore molar volume of mixed solvent V_1 was the same. Considering that the hydrolysis of amide groups on polymer chain causes approximate 30 g/g increase in swelling ratio, which has no relation to the crosslinking density, this part should be taken out from the measured swelling ratios. The experimental results are shown in Table I ($D_2=1.5776$ g/cm^3).

Taken C as x-axis, Y or Y' as y-axis, the curves were shown in Figure 7. The calculated M_c for the SAP at 25°C and 300°C is 3.0×10^3, 3.1×10^5, respectively. As the crosslinking density is inversely proportional to the value of M_c, the crosslinking density at 300°C is much lower than that at 25°C. This testifies that the cross linkages from NMBA in the hydrogel network structure were broken at 300°C.

Effect of the Molar Ratio of NMBA to TAAC on Water Absorbency at 300°C

To study the effect of molar ratio of NMBA to TAAC on water absorbency at 300°C, a series SAP samples with same total crosslinker concentration but various n_{NMBA}/n_{TAAC} were tested. As shown in Figure 8, the water absorbencies rise at first and then decrease with increase in the molar ratio of NMBA to TAAC. When n_{NMBA}/n_{TAAC} is <1, with the increase of NMBA and the corresponding decrease of TAAC, the crosslinking

Table II. The Swelling Ratios of SAPs at 300°C

	n_{NMBA}/n_{TAAC}				
C	1 : 3	1 : 2	1 : 1	2 : 1	3 : 1
0.1	79	109	151	156	162
0.2	71	94	131	136	147
0.3	63	79	113	119	131
0.4	52	69	96	100	108
0.5	46	60	80	85	93
M_c	9.9×10^4	1.6×10^5	2.9×10^5	3.0×10^5	3.3×10^5

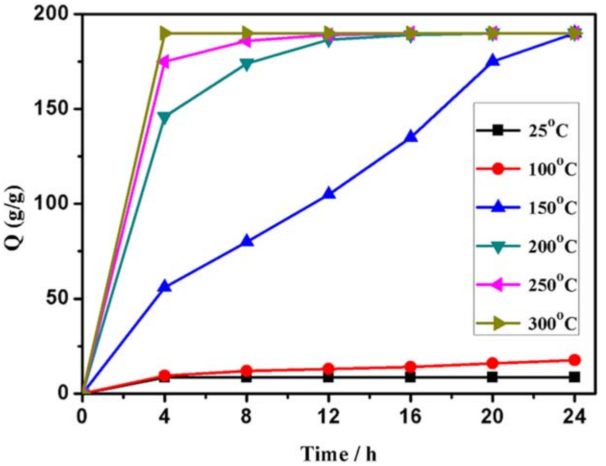

Figure 9. Water absorbency at different temperature $(n_{NMBA}+n_{TAAC})/n_{AM}=2\%$; $n_{NMBA}/n_{TAAC}=2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

points related to NMBA could be destroyed by hydrolysis of amide bonds, resulting in a decreased crosslinking density. The thus released free space in the network structure absorbs more water and the swelling ratios increase. However, when n_{NMBA}/n_{TAAC} is >3, excessive NMBA is added and more crosslinked amide bonds are broken at 300°C. With less TAAC remaining, the crosslinkages from TAAC may be not sufficient to maintain an effective network structure for water absorbency. The swelling ratios decrease accordingly. Further, the swelling ratio becomes zero as the molar ratio of NMBA to TAAC reaches 6 : 1, meaning that the gel becomes totally soluble in water at 300°C. Interestingly, there is a slow increase from 183 to 195 g/g, indicating that the swelling ratio is insensitive to the change of crosslinker composition in the range of $n_{NMBA}/n_{TAAC}=1$–3. This broad region centered at $n_{NMBA}/n_{TAAC}=2$ in crosslinker ratio would greatly facilitate the preparation for the SAP.

Besides, M_c values for the SAPs with different ratios of NMBA to TAAC ranging from 1 : 3 to 3 : 1 were measured. As shown in Table II, with the decrease of TAAC, the value of M_c increase, indicating that the crosslink density decrease. The results are also consistent with those measured in water at 300°C.

Swelling Kinetics at Different Temperature in Distilled Water

SAP sample with total crosslinker concentration of 2 mol % $(n_{NMBA}/n_{TAAC}=2)$ was used for swelling kinetic study. The swelling ratios at different temperature in distilled water are collected in Figure 9. At above 200°C, the swelling ratios increase rapidly, reaching equilibrium absorbency (190 g/g) within 8–16 h. This may be attributable to the fast hydrolysis of the amide bonds both on the polymer main chains and on the crosslinking points. The swelling ratio increases gradually at 150°C, indicating a steady hydrolysis of the amide bonds at this temperature. Owing to the completely hydrolysis reaction after 24 h, the final swelling ratio can also be close to 190 g/g. As expected, the swelling ratio increases very slowly at 100°C and shows no obvious change at 25°C after a minor increase in the very beginning stage. Here these results found are satisfactory, when the SAP is applied to field use, the slow and minor water absorbency would enable the plugging agent to be pumped into the problem zone, and the subsequent heating by the formation or by injected steam would switch its swelling capability on, so that the materials start to absorb water and expand in volume to block the steam breakthrough channels.

Surface Morphology of Hydrogels

SEM micrographs of SAPs $((n_{NMBA}+n_{TAAC})/n_{AM}=2$ mol %; $n_{NMBA}/n_{TAAC}=2)$ after absorption at different temperature are displayed in Figure 10 [(a) 25°C and (b) 300°C], respectively. The surface of the gel at 25°C is tense and rough whereas hydrogel at 300°C shows a more open porous channel structure with thicker pore wall than the former. The average pore size of the hydrogel treated at 300°C is more than double of that at 25°C. This is well consistent with that observed in their swelling behaviors. These results can explain why the swelling ratio of SAP at 300°C is much bigger than that at 25°C, from the view of microstructure. Meanwhile, the SEM observations also prove that the design of SAP with a temperature switch was successfully realized.

CONCLUSIONS

The combination of NMBA and TAAC crosslinkers in the polymerization of acrylamide has been shown to create a novel SAP material with a temperature switch to control its water absorbencies. The swelling experiments and microstructure characterization have shown that these new SAPs containing an appropriate amount of crosslinkers offer slow and minor water absorbency at 25°C but a significantly increased water absorption capacities with excellent thermal stability at 300°C. It has been demonstrated by crosslinking density and morphology

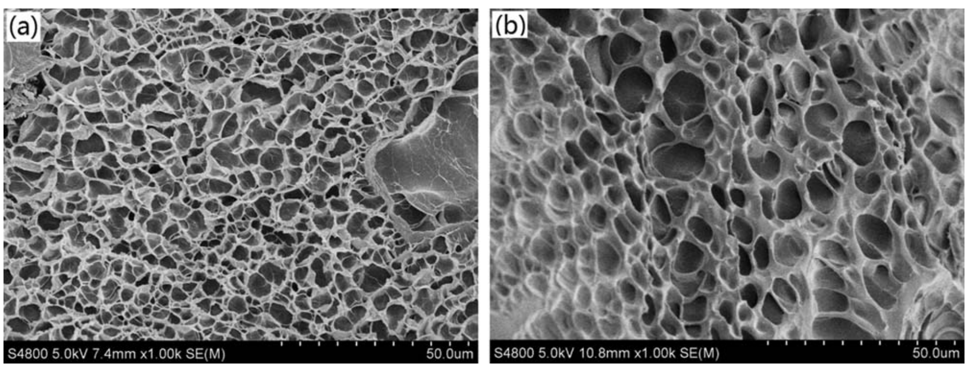

Figure 10. SEM images of SAPs after absorption at different temperature (a) 25°C and (b) 300°C.

studies that the hydrolysis of amide bonds played a critical role in creating these previously unreported SAP. This kind of SAPs meet the requirements for application as a cost-effective plugging material in steam stimulated reservoirs to solve the steam breakthrough problems, and thus have high industrial application potentials.

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