Bentonite–Acrylamide Hydrogels Prepared by the Nonmixing Method: Characterization and Properties

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ABSTRACT: A significant amount of research has been conducted on bentonite–acrylamide hydrogels. These gels are usually prepared by uniformly mixing bentonite with reactive monomers. Herein, a new preparation method of bentonite–acrylamide hydrogels has been proposed to cater to one novel application of bentonite–acrylamide hydrogels. In this method, bentonite–acrylamide hydrogel was obtained by pressing bentonite into a thin mud cake and extruding a mixed liquor of acrylamide, a cross-linking agent, an initiator, and water into the thin mud cake and then subjecting the system to water-bath curing. The effects of extrusion pressure, extrusion time, and acrylamide concentration on the tensile strength and elemental composition of bentonite–acrylamide hydrogel were investigated. The results show that the tensile strength of the bentonite–acrylamide hydrogel first increased and then tended to be stable with the further increase in extrusion pressure and extrusion time. As the concentration of acrylamide increased, the tensile strength of the bentonite–acrylamide hydrogel increased first and then decreased slightly. With the increase in extrusion pressure, extrusion time, and acrylamide concentration, the contents of C and N elements in the thin mud cake gradually increased and then tended to be stable, which reflects the state of the monomer entering the thin mud cake. In addition, the elemental composition of the bentonite–acrylamide hydrogel was analyzed via the scanning electron microscopy–energy dispersive X-ray spectrometry method, and it was found that the composition of the hydrogel was relatively uniform in the direction of mixed liquor extrusion.

1. INTRODUCTION

Hydrogels are typical functional polymer materials, and their internal three-dimensional network structure endows them with certain water absorption ability, excellent water retention ability, and a certain strength and water swelling capacity. Therefore, after being successfully developed in the 1960s, they have been widely used in various industries such as chemical, health, medicine, building materials, oil and gas field development, agriculture, and forestry.1–5

In particular, hydrogels are widely used in oil and gas field development. Herein, hydrogels are used as profile control and water shutoff agents to adjust the flow direction of the flooding water and drive more crude out to enhance oil recovery.6 They can also be used as a temporary plugging fluid to prevent the workover fluid in the well bore from leaking into the stratum during the workover process.7–12 The hydrogel can be used as an annulus sealant. In the production process of oil and gas wells, after an interlayer cross flow is formed in the annulus by the crack of the annulus cement ring, the hydrogel is squeezed into the channel to prevent the fluid flow from high-pressure formation to low-pressure formation through the channel. The

field applications indicate that the effective period of hydrogel sealing annular channeling is at least 2 years.13,14

This paper proposes a novel application of hydrogels in improving the sealing of cement sheath in oil and gas wells. The process of oil and gas well cementing operation is to insert a casing into the oil and gas well after drilling the oil and gas well hole and filling the cement slurry between the casing and the well wall.15 The oil and gas well cementing operation is aimed at sealing the stratum of different pressures by pumping cement slurry into the annulus between the casing and the stratum to prevent fluids in the high-pressure stratum from flowing into the low-pressure stratum through the well bore. The drilling fluid used in the drilling process contains much bentonite; after the oil and gas well cementing operation, a mud cake with a thickness of 2–5 mm often exists between the cement sheath and the wall of the oil well, wherein, the primary component of the mud cake is bentonite.16,17 During the
production of the oil and gas well, the mud cake gradually disappears due to dissolution and erosion of stratum water. After the mud cake disappears, the sealing ability of the cement sheath is seriously weakened. To prevent the erosion of the mud cake and ensuring the sealing ability of the cement sheath, the researchers have applied some measures to solidify the mud cake to a certain extent. However, the strength of the formed solidified mud cake is very low and easy to crack in the later production process, thereby forming a hydrocarbon channel. As bentonite can be used as a reaction raw material to enhance the performance of hydrogels, this paper proposes a technique of transforming the mud cake into hydrogels.

Conventional hydrogels are formed by evenly mixing the raw materials, whereas the hydrogels in this paper were prepared via a two-step process (as shown in the Figure 1). In the first step, part of the reaction raw material (bentonite slurry) is pressed into a mud cake under a pressure difference. The second step is to press the remaining reaction materials (reactive monomer, cross-linking agent, initiator, water, etc.) into the mud cake and then curing at a predetermined temperature to form the gel. The hydrogel formation method in the paper is significantly different from the conventional hydrogel formation method. When the monomer, cross-linking agent, and initiator are determined, the properties of the hydrogel formed by our proposed method are related to the amount of the reactive monomer, the cross-linking agent, and the initiator in the mud cake. Due to the low permeability of the formed mud cake, which usually does not exceed $2 \times 10^{-9}$ Darcy, the aqueous solution containing the monomer, cross-linking agent, and initiator requires sufficient extrusion pressure and extrusion time to enter the mud cake.

Therefore, the effects of extrusion pressure and extrusion time on the properties of the pie bentonite–acrylamide hydrogel were investigated. Also, the elemental analysis of the bentonite–acrylamide hydrogel was carried out to determine the mechanism of the influence of extrusion pressure and extrusion time on the properties of the hydrogels. The research has a definite significance in expanding the application field and preparation methods of hydrogels.

2. RESULTS AND DISCUSSION

2.1. Effects of Extrusion Parameters on Hydrogel Properties. To explore the effects of the extrusion parameters on gel properties, the effects of extrusion pressure and extrusion time on the tensile strength and elastic modulus of the hydrogel were investigated. The extrusion pressure levels in the study were 0.75, 1.5, and 3 MPa, respectively, whereas the extrusion time levels were 10, 30, 45, 60, and 90 min. The experimental results are shown in Figures 2 and 3.

![Figure 1. Flow diagram of the preparation of the bentonite–acrylamide hydrogel by the nonmixing method.](image)

![Figure 2. Effect of extrusion time on the tensile strength of the hydrogel.](image)

As shown in Figure 2, when the extrusion pressures were 0.75, 1.5, and 3 MPa, the tensile strength of the hydrogel gradually increased as the extrusion time increased from 10 to 60 min. After the extrusion time exceeded 60 min, the tensile strength of the hydrogel did not change significantly. In

![Figure 3. Effect of extrusion time on the elastic modulus of the hydrogel.](image)
addition, the same effect of extrusion time and extrusion pressure on the elastic modulus is observed in Figure 3. The increase in the tensile strength and elastic modulus of the hydrogel was primarily caused by the increase in the effective content of the reaction materials in the mud cake and the increasingly denser network structure inside the hydrogel with the increase in extrusion time.

To understand the rule of reaction materials entering the mud cake with the increase in extrusion time, elemental analysis was performed on the hydrogels formed at different extrusion times, as shown in Figures 4−6. The contents of C element and N element increased first and changed slightly after 60 min as the extrusion times increased.

By comparing the change in the content of C and N and the tensile strength of hydrogel with time, it can be seen that the change in tensile strength of the hydrogel has a strong consistency with the change in the contents of C and N. In addition, as shown in Figure 6, the molar ratios of C/N were basically about 3, which is in good agreement with acrylamide (molecular formula: C3H5NO).

The effect of extrusion pressure on the tensile strength of the hydrogel can be observed in Figure 2. In summary, the extrusion pressure had no significant effect on the tensile strength of the hydrogel. As the extrusion pressure is relatively difficult to control in the site operation, a low sensitivity to the extrusion pressure is conducive for on-site construction. The extrusion pressure had no significant effect on the content of the C element and the N element in the hydrogel (see Figures 4 and 5). However, when the extrusion pressure was 0.75 MPa, the contents of the C element and the N element in the hydrogel were slightly higher than those at the extrusion pressures of 1.5 and 3 MPa. This may be because the mud cake became denser at the extrusion pressures of 1.5 and 3 MPa, and thus, it became more difficult for the solution containing the reaction raw material to enter the mud cake. Comparing the change in C element and N element and the change of hydrogel tensile strength with the extrusion pressure, there was no clear correlation between the tensile strength of the hydrogel and the content of C and N. This may be because the content differences of C and N elements were not clear under different extrusion pressures.

2.2. Effect of the Concentration of Reaction Raw Materials on the Hydrogel. To understand the effect of concentration of reaction raw material on the hydrogel, the effect of concentrations of different reaction raw materials on the tensile strength of the hydrogel was studied. The specific concentration level of reaction raw materials is presented in Table 1. In this section, the extrusion pressure was 1.5 MPa and the extrusion time was 90 min. The tensile strengths of the hydrogel at different concentrations of the acrylamide monomer are shown in Figure 7.

As shown in Figure 7, when the acrylamide concentrations were 10 and 20%, no gelation reactions occurred; thus, the tensile strength of the gel was zero. As the acrylamide concentration exceeded 25%, the tensile strength of the gel could surpass 0.243 MPa. The gel had the highest tensile strength at the acrylamide concentration of 30%. As the acrylamide concentration further increased above 35%, the tensile strength of the hydrogel decreased to a certain extent.

To determine the effect of acrylamide concentration on the tensile strength, the mass fractions of C and N in the hydrogel at different acrylamide concentrations were analyzed using an elemental analyzer. As shown in Figure 8, with an increase in the acrylamide monomer, the mass fractions of C and N elements presented a trend of gradual increase. When the concentrations of acrylamide were 10 and 20%, the low concentrations of the reaction raw material in the mud cake might be the reason for no polymerization reaction. When the concentrations of acrylamide were 10 and 20%, the low concentrations of the reaction raw material in the mud cake might be the reason for no polymerization reaction. When the concentration of acrylamide was more than 25%, the reaction material concentration in the mud cake was high enough to undergo polymerization reaction, thus forming a hydrogel. With a further increase in the acrylamide concentration above 35%, the excessive content of cross-linking agent in the mud...
cake and excessive cross-linking point might have led to a certain decrease in the tensile strength of the hydrogel.25

2.3. Microstructure Characterization of the Hydrogel.

The samples of bentonite, AM, MBA, hydrogel without initiator, and hydrogel with initiator were analyzed by infrared spectra. The results are shown in Figure 9. The characteristic peak of C=O obtained from the samples of AM, MBA, and hydrogel without initiator appeared at 1614 cm\(^{-1}\). The characteristic peak of C=O disappeared in the sample of hydrogel with initiator which attributes to the polymerization reaction of AM or AM and MBA. The peak at 3626 cm\(^{-1}\) was attributed to the hydroxyl of the bentonite, and it disappeared in the sample of hydrogel with initiator.26 The peaks of primary amine of AM and secondary amine of MBA could be found at 3345 and 3300 cm\(^{-1}\) respectively, and they could not be found in the hydrogel with or without initiator, which may be attributed to the combination with bentonite.5,27

As the hydrogels prepared in this paper were not prepared by uniform mixing but rather by first preparing the clay mud cake and then squeezing the monomers, initiator, and other materials, the hydrogels prepared by this method may not be homogeneous in the longitudinal direction. Therefore, the elemental composition in the longitudinal direction of the gel was investigated via scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS). To characterize the change in the longitudinal composition of the hydrogel, three rectangular regions of 1, 2, and 3 were sequentially selected from the top to the bottom of the hydrogel. The elemental compositions of the three regions are displayed in Figure 10a. There was no significant difference in the elemental composition of the three regions (see Figure 10), indicating that there was no significant difference in the longitudinal direction of the formed hydrogel. After the resolution being increased as shown in Figure 10b,c, no pore existed in the hydrogel but wrinkles could be found on the surface, which may be generated by extrusion during squeezing of the active materials. Figure 11 shows the TEM image of the hydrogel, wherein the distribution of bentonite is relatively uniform.

### Table 1. Ingredients of an Aqueous Solution of the Reaction Raw Materials

| Sample | AM/\%(BWOW) | MBA/\%(BWOW) | Ammonium persulfate/\%(BWOW) |
|--------|-------------|--------------|-------------------------------|
| 1      | 10          | 0.3          | 0.04                          |
| 2      | 20          | 0.6          | 0.08                          |
| 3      | 30          | 0.9          | 0.12                          |
| 4      | 40          | 1.2          | 0.16                          |

Figure 7. Tensile strength of the hydrogel at different acrylamide concentrations.

Figure 8. Elemental mass fractions of the hydrogel at different acrylamide concentrations.

Figure 9. FTIR of hydrogel with initiator, hydrogel without initiator, AM, MBA, and bentonite.

Figure 10. SEM images and EDS results of the hydrogel.
3. CONCLUSIONS
A novel preparation method for bentonite–acrylamide hydrogels has been proposed in this paper. Bentonite–acrylamide hydrogels were obtained by first pressing the mixture of bentonite and water into a thin mud cake using the drilling fluid high-temperature and high-pressure water loss meter, extruding a mixture of water, acrylamide, a cross-linking agent, and an initiator into the thin mud cake and then subjecting it to water-bath curing. The effects of various factors on the properties of the novel bentonite–acrylamide hydrogels were studied, and the hydrogels were characterized by elemental analysis and SEM−EDS. The following conclusions are drawn:

1. With the increase in extrusion pressure and extrusion time, the tensile strength and elastic modulus of the bentonite–acrylamide hydrogel increased first and then tended to be stable. In combination with the elemental analysis, this may be because, with the extension of extrusion pressure and extrusion time, the entering of effective components such as reactive monomers in the clay mud cake was gradually increased.

2. As the concentration of acrylamide increased, the tensile strength of the bentonite–acrylamide hydrogel increased first and then decreased slightly. The gel had the highest tensile strength at the acrylamide concentration of 30%. The increase in the tensile strength of the bentonite–acrylamide hydrogel was due to the increase in the concentration of the acrylamide reaction monomer. The late reduction of tensile strength of the bentonite–acrylamide hydrogel may be because as the concentration of acrylamide and the content of the cross-linking agent increased, the excessively formed cross-linking points led to a decrease in the tensile strength.

3. The elemental composition of the bentonite–acrylamide hydrogel in the longitudinal direction was analyzed via the SEM−EDS method, and it was found that the components of the hydrogel were relatively uniform in the longitudinal direction. Moreover, there was a large amount of reaction monomers at the end of solution injection and few reaction monomers at the end of solution flow did not occur. In addition, the TEM image shows that the distribution of bentonite in the hydrogel is relatively uniform.

4. EXPERIMENTS

4.1. Materials. Sodium bentonite (industrial grade, Weifang Huajing Bentonite Co., Ltd.) was the clay used to prepare the mud cake. Acrylamide (AM), N,N-methylenebisacrylamide (MBA), sodium hydroxide, ammonium persulfate, and sodium carbonate were all of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd.

4.2. Preparation of the Pie Bentonite–Acrylamide Hydrogel by the Nonmixing Method. 4.2.1. Preparation of the Mud Cake. A certain amount of bentonite and water were poured into a slurry cup in a high-speed mixer, stirred at 10,000 rpm for 20 min and then hydrated at room temperature for 24 h. Then, 200 mL of clay slurry was poured into a GGS42-2A drilling fluid high-temperature and high-pressure water loss meter (manufactured by Qingdao Chuangmeng Instrument Co., Ltd.) and filtered at a pressure difference of 0.75 MPa for 90 min, forming a mud cake in the process.

4.2.2. Preparation of the Pie Bentonite–Acrylamide Hydrogel. Acrylamide, N,N-methylenebisacrylamide, and ammonium persulfate were added to distilled water in a certain ratio and stirred at high speed for 15 min to prepare a reaction solution.

The composition of the reaction solution was: distilled water 100% (by weight on water, BWOW) + acrylamide 30% (BWOW) + N,N-methylenebisacrylamide 0.9% (BWOW) + ammonium persulfate 0.12% (BWOW). After the mud cake was prepared, the excess clay slurry in the water loss meter cup was poured out and the integrity of the mud cake should be ensured. Then, the prepared reaction solution was reintroduced into the slurry cup with the mud cake. Using high-pressure nitrogen, the reaction solution was extruded into the mud cake at the predetermined extrusion pressure and extrusion time. After the extrusion of the reaction solution was complete, the excess reaction solution was poured out of the slurry cup. Finally, the mud cake with the reaction solution was taken out (as shown in Figure 12), sealed in a sealing bag, and placed in a water bath at 55 °C for 5 h to prepare the bentonite–acrylamide hydrogel (as shown in the Figures 13 and 14).

4.3. Mechanical Properties of the Hydrogel. The obtained pie hydrogel was cut into a strip of 22 mm in length and 6 mm in width. The maximum tensile force at break was measured by a ZQ-990A electric tensile testing machine (range: 2000 N, resolution: 0.01 N) produced by Dongguan Zhicai Precision Instrument Co., Ltd. The maximum tensile force at break was divided by the cross-sectional area of its original end face to obtain tensile strength, and the slope of the stress−strain plot formed when the tensile strength was tested was the modulus of the hydrogel.

4.4. Elemental Analysis of the Hydrogel. To understand the composition of the pie hydrogel under different extrusion times and pressures, the organic elements in the...
hydrogel were analyzed using a Vario ELIII CHNS/O elemental analyzer manufactured by Elementar, Germany. To eliminate the interference of the organic elements in the clay on the test results, the content of organic elements in the clay were first tested and then the contents of organic elements in the bentonite–acrylamide hydrogel at different extrusion pressures and different extrusion times were tested. The difference of the organic element content after and before the extrusion of the reaction materials was the increase in the organic elements in the mud cake due to the introduction of reactive monomers and cross-linking agents under the action of extrusion.

4.5. Fourier Transform Infrared (FTIR) Spectra of the Hydrogel. To understand the changing situation of the reactive materials, Fourier transform infrared (FTIR) spectra of the samples were recorded using a Thermo Fisher Nicolet 6700 FTIR spectrophotometer. The samples used to do FTIR analysis contains bentonite, AM, MBA, hydrogel without initiator, and hydrogel with initiator. Hydrogel without initiator means when the hydrogel was made, AM, MBA, and bentonite, except ammonium persulfate were included in the reaction materials.

4.6. SEM and EDS Analysis of the Hydrogel. To further understand the structural characteristics of the pie bentonite–acrylamide hydrogel formed by the nonmixing method, a Japanese Hitachi S-4800 scanning electron microscope combined with an EDAX XM2-60S spectrometer was used to analyze the elemental distribution in three regions (plane 1, plane 2, and plane 3) in the longitudinal section of the hydrogel (see Figure 15).

**Figure 12.** Mud cake (diameter = 5.36 cm, thickness = 1.9 mm) extruded with the reaction solution (Photograph courtesy of "Yao Lu". Copyright 2019.).

**Figure 13.** Formed pie hydrogels (diameter = 5.36 cm, thickness = 1.9 mm) in the original state (Photograph courtesy of "Yao Lu". Copyright 2019.).

**Figure 14.** Formed pie hydrogels in the stretched state (Photograph courtesy of "Yao Lu". Copyright 2019.).

**Figure 15.** Schematic diagram of the hydrogel analyzed by EDS.

**REFERENCES**

(1) Zhang, X.; Liu, T.; Yan, J.; et al. Multiple-Responsive Dendronized Hyperbranched Polymers. *ACS Omega* 2019, 4, 7667–7674.

(2) Zareie, C.; Bahramian, A. R.; Sefti, M. V.; et al. Network-gel strength relationship and performance improvement of polyacrylamide hydrogel using nano-silica; with regards to application in oil wells conditions. *J. Mol. Liq.* 2019, 278, 512–520.

(3) Singha, N. R.; Arnab, D.; Manas, M.; et al. In Situ Attachment of Acrylamido Sulfonic Acid-Based Monomer in Terpolymer Hydrogel Optimized by Response Surface Methodology for Individual and/or
Simultaneous Removal(s) of M(III) and Cationic Dyes. ACS Omega 2019, 4, 1763–1780.

(4) Madhushree, M.; Manas, M.; Arnab, D.; et al. Carbohydrate and collagen-based doubly-grafted interpenetrating terpolymer hydrogel via N–H activated in situ allocation of monomer for superadsorption of Pb(II), Hg(II), dyes, vitamin-C, and p-nitrophenol. J. Hazard. Mater. 2019, 369, 746–762.

(5) Singh, N. R.; Dutta, A.; Mahapatra, M.; et al. Guar Gum-Grafted Terpolymer Hydrogels for Ligand-Selective Individual and Synergistic Adsorption: Effect of Comonomer Composition. ACS Omega 2018, 3, 472–494.

(6) Tessarolli, F. G. C.; Souza, S. T. S.; Gomes, A. S.; et al. Influence of polymer structure on the gelation kinetics and gel strength of acrylamide-based copolymers, bentonite and polyethylenimine systems for conformance control of oil reservoirs. J. Appl. Polym. Sci. 2019, 136, No. 47556.

(7) Jia, H.; Chen, H.; Guo, S. Fluid loss control mechanism of using polymer gel pill based on multi-crosslinking during overbalanced well workover and completion. Fuel 2017, 210, 207–216.

(8) Jia, H.; Chen, H. Using DSC technique to investigate the non-isothermal gelation kinetics of the multi-crosslinked Chromium acetate (Cr 3+)-Polyethyleneimine (PEI)-Polymer gel sealant. J. Pet. Sci. Eng. 2018, 165, 105–113.

(9) Jia, H.; Chen, H. The Potential of Using Cr/Salt-Tolerant Polymer Gel for Well Workover in Low-Temperature Reservoir: Laboratory Investigation and Pilot Test. SPE Prod. Oper. 2018, 33, 569–582.

(10) Jia, H.; Yang, X. Y. Environmental and strength-enhanced nanosilica-based composite gel for well temporary plugging in high-temperature reservoirs. Asia-Pac. J. Chem. Eng. 2018, 14, No. e2270.

(11) Jia, H.; Zhao, J. Z.; Jin, F. Y.; et al. New Insights into the Gelation Behavior of Polyethyleneimine Cross-Linking Partially Hydrolyzed Polycrylamide Gels. Ind. Eng. Chem. Res. 2012, 51, 12155–12166.

(12) Jia, H.; Pu, W. F.; Zhao, J. Z.; Liao, R. Experimental Investigation of the Novel Phenol-Formaldehyde Cross-Linking HPAM Gel System: Based on the Secondary Cross-Linking Method of Organic Cross-Linkers and Its Gelation Performance Study after Flowing through Porous Media. Energy Fuels 2011, 25, 727–736.

(13) Damasena, E.; Flew, S.; Ravichandran, N.; et al. In Novel Approach to Repairing Cement Channeling Between Two Reservoir Sand Bodies with Differential Pressure Gradient, International Petroleum Technology Conference, 2016.

(14) Vasquez, J. J.; Curtice, R. In A Porosity-Fill Sealant for Water and Gas Shutoff: Case Histories and Lessons Learned after more than 1000 Well Interventions, SPE European Formation Damage Conference & Exhibition, 2013.

(15) Chen, D.; Guo, J.; Xia, X.; et al. Abnormal gelation phenomenon of Class G oil well cement incorporating polycarboxylic additives and its counter measures. Constr. Build. Mater. 2017, 149, 279–288.

(16) Huang, X.; Lv, K.; Sun, J.; et al. Enhancement of Thermal Stability of Drilling Fluid Using Laponite Nanoparticles under Extreme Temperature Conditions. Mater. Lett. 2019, 248, 146–149.

(17) Ladva, H. K. J.; Craster, B. S.; Jones, T. G. J.; et al. The Cement-to-Formation Interface in Zonal Isolation. SPE Drill. Complet. 2005, 20, 186–197.

(18) Opedal, N.; Todorovic, J.; Torsæter, M.; et al. Filter Cake Behavior during Leakage at the Cement-Rock Interface in Wellsbores; American Rock Mechanics Association, 2015.

(19) Hao, H.; Gu, J.; Huang, J.; et al. Comparative study on cementation-cement-mudcake interface with and without mudcake-solidification-agents application in oil and gas wells. J. Pet. Sci. Eng. 2016, 147, 143–153.

(20) Heydari, A.; Sheibani, H. Fabrication of poly (β-cyclodextrin-co-citric acid)/bentonite clay nanocomposite hydrogel: thermal and absorption properties. RSC Adv. 2015, 5, 82438–82449.