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Experimental Study, Characterization and Application of Starch-Graft-Acrylamide Gel for Plugging

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During underbalance drilling, completion and workover wells, plugging channeling, blocking preformation and plugging formation water are inevitable problems. Gel is one of the most effective and convenient method to solve the problem. In this study, modified starch gel is synthesized, investigated experimentally and improved for efficient oil and gas field applications. The gel slurry is composed of starch (3.6 wt.%), initiator (0.02 wt.%), acrylamide (14.4 wt.%), cross-linking agent (4.7 wt.%), all of the components are mixed together with water at pH 10 – 11 which viscosity is as low as 35 – 82 mPa.s and desired to form gel. Here the effects of the components, reaction temperature and pH on gelation time and gel viscosity are systematically investigated, and the results showed that the gelation can be controlled in a wide range 30 – 120 min efficiently by pH and initiator. Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM) are employed to study the molecular structure and microstructure of the gel, respectively. A compact three-dimensional network structure was formed in the gel, which contribute to a good adhesion. The gel has been successfully used in shale gas field which provides a reference for sealing other similar high formation pressure under unbalanced workover treatment.

Keywords: modified starch gel, plug, snubbing service, microstructure.

1. INTRODUCTION

Underbalanced drilling and completion are becoming increasing increasingly utilized worldwide as an alternative technique to conventional overbalanced operation to reduce invasive near wellbores formation damage problems in oil and gas producing formations [1 – 5]. The underbalanced drilling technology can also have been implemented in the workover treatment if the situation such as water flow into the well and lost circulation are encountered. Water flows into the well is one of the main problems encountered while drilling top holes of onshore and offshores wells and when the water breaking though in the gas wells in the later period of gas field development. Lost circulation which occurs when hydrostatic pressure of fluid column in the wellbore is higher than the formation pressure is another common problem in the drilling operations and is usually accompanied by wellbore stability problems which can even result in the lost of well.

All of the problems mentioned above are usually attempted to be solved by mechanical shutoff or chemical treatment of selective intervals. Mechanical-set packer is usually used as a method for low damage completion of injection or disposal wells, and permanent mechanical zonal isolation for horizontal wells must be installed in the well at the completion stage using external casing packers or sliding side-doors, it is high priced and appears easily sealed and lax circumstance as well, especially horizontal wells and multilateral wells have long interval lengths and irregular shape, which means that they frequently suffer problems of uneven production from certain sections of the wells, due to wellbore pressure losses or changes in geological and reservoir parameters [6]. However, chemical treatment such gel can be applied remedially. First, gel can be easily pumped into any location of the well and satisfy various irregular shape liking a cork. Second, after temporary isolation by gel plug, it will not take much time to wash it out. Furthermore, mechanical packer installation cost much more time and money than gel.

For the last few decades, gel has been widely used in the petroleum and natural gas industry for different purposes including water shutoff, gas shutoff, casing repairs, conformance and profile control, permeability modification, leak resistance and sealing, plugging lost circulation zones, consolidation of loose formations [7 – 12]. Nevertheless, there are no reports of the use of modified starches as packer in underbalanced drilling and completion. In this study, a modified starch gel is designed and synthesized for plugging in snubbing service. Starch consists of two types of molecules amylose (normally 20 – 30 %) and amylopectin (normally 70 – 80 %). Both consist of polymers of α-D-glucose unit in the $^4C_1$ conformation. For the last few decades, the chemical modification of starch by graft copolymerization have been investigated widely and various works have been reported

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on the grafting of acrylamide [13], acrylonitrile [14], acrylic acid [15], methacrylates [16] onto starch [17]. However, no systematic study has been done for the gelation performance and microstructure. So in this study, environmentally friendly gel system with facile preparation is developed with new gel features of high viscosity and adjustable gelation time for snubbing service. In addition, a gas field test was also conducted to confirm that using modified starch gel is an effective plugged slug for pressure control. Though the laboratory experiments and gas field test, the gel will also further promote the application of snubbing service in mature oil field and gas field.

Hence, the present study emphasized on the facile preparation of modified starch gel and the process parameters such as proportion of raw material, pH and salt will be investigated and optimized. The slurry is liquid when prepared initially which viscosity is as low as 35 – 82 mPa.s, then formed a gel after a given temperature and a period of time. The gelation time and viscosity are studied to determine the best application for modified starch gel. The objective of this study was therefore to investigate the synthesis of modified starch gel with high viscosity and controllable gelatinization time, which could permit the potential use of gel made of this polymer in enhanced oil recovery.

2. MATERIALS AND METHODS

2.1. Materials

Corn starch (reagent-grade, Aladdin Industrial Corporation) was used for graft polymerization. Acrylamide (AR, Sinopharm Chemical) as monomer and ammonium persulfate as initiator (AR, Sinopharm Chemical) were used without further purification. Cross-linking agent is a compound consisting of amino groups, secondary amino group and triazine ring (a purity of 99%, Aladdin Industrial Corporation) was used for cross-linking starch-g-AM. Sodium hydroxide (AR, Sinopharm Chemical) was used for adjusting pH value.

2.2. Preparation of modified starch gel

A definite amount of corn starch first dissolved in 80 mL of distilled water with stirring and heated within the temperature range of 80 ± 2 °C for 30 min in the constant temperature water bath pot. Initiators, monomers (AM), crosslinking agent and curing agent were added into the reaction. After all the agents mixed well, adjusted pH value by slow-adding particles of NaOH, then the reaction took place until completion to get a gel with high strength. The gelation time was recorded as the viscosity was increasing sharply.

2.3. Measurements and analysis

2.3.1. Viscosity measurements

AR2000ex rheometer (TA Instruments Ltd., Crawley, UK) with aluminum parallel plate geometry (40 mm diameter, 1 mm gap) was used to carry out the rheological measurements. The AR2000ex is a stress controlled rheometer equipped with a force rebalance transducer. Viscous properties of samples were measured through strain sweep tests carried out at 1 Hz. The temperature of the samples was controlled by using a water bath connected to the bottom plate. The temperature of the water was controlled by a Peltier system. Each sample was allowed to equilibrate for 2 min before the test carried out.

2.3.2. Fourier Transform Infrared Spectroscopy (FTIR)

The reaction product was washed with distilled water several times to remove any ungrafted molecules, monomer and base until the solution pH = 7. The washed product was dehydrated and precipitated with methanol and dried at 65 °C until the weight of the specimen was constant. Then the solid was crushed into fine powder. Fourier Transform Infrared Spectroscopy of the proceeded products using a KBr pellet were recorded on Avatar E.S.P. spectrometers, Nicolet Ltd, USA in the range of 4000-400 cm^{-1}.

2.3.3. Scanning electron microscopy (SEM)

The surface morphology and topography of corn starch and crosslinked starch-g-AM were evaluated by scanning electron microscope (JSM-6390lv, Jeol, Japan). Before examination, the samples were mounted onto stubs using double-sided dried adhesive carbon tape and vacuum coated with gold palladium film (thickness 2 nm) by sputter coater (Edward S-150, UK) to make them electrically conductive. Representative sections were photographed for evaluation.

3. RESULTS AND DISCUSSION

3.1. Effect of the initiator on the gel performance

Considering the process conditions and the cost of huge amount of applications in oil and gas field, ammonium persulfate (APS) was chosen as the initiator. In this experiment, the gel solution was composed of starch (3.6 wt.%), acrylamide (10.8 wt.%), cross-linking agent (4.7 wt.%), while initiator concentrations were varied from 0.002 % to 0.5 %, and the gel system was initiated at 80 °C. During the reaction APS could produce hydrogen sulfate free radical, while free radicals on the starch are not formed initially, they are produced through the chain transfer reaction with an existing free radical, meanwhile significant amounts of homopolymer and free copolymer are also formed by the reaction of initially formed radicals with monomer(s) before chain transfer to starch could occur [18]. Fig. 1 shows the effect of the initiator on gel properties.

It can be seen from Fig. 1 that, as the concentration of APS increased, the viscosity of gel increased first and then decreased. It benefited from the growth of the chain length, the acceleration of the polymerization reaction and the combination reaction between them will rise, so as the viscosity increasing. But redundant initiator concentration can lead to excessive free radicals. Based on steady-state theory and free radical polymerization reaction kinetics, when the trigger rate is too high, both the termination rate of the grafting reaction and the percentage of free polymers with short chain length will increase with increasing concentration of the initiator due to the fixed amount of monomer, which will result in the decreasing of viscosity and the decline of gelation time. The maximum of gel viscosity was about 2×10^6 mPa.s. According to the practice application, the reaction time was controlled for at least 30 min at 80 °C and for the viscosity, the higher the better, so in the present work, the concentration of APS was selected at 0.02 wt.%.

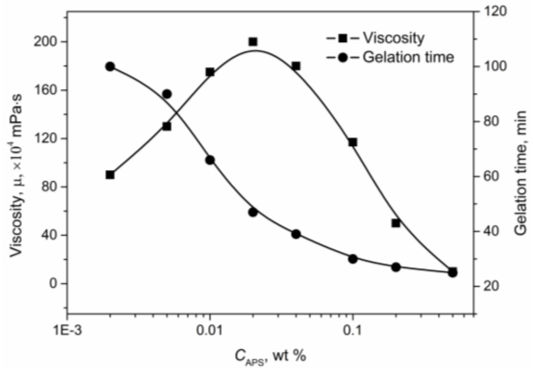

Fig. 1. The influence of the concentration of initiator

3.2. Effect of monomer-to-starch ratio on the gel performance

AM is selected for copolymerization monomer since it easily forms hydrogen-bonds with more water to be expected to obtain the copolymer with greater water absorption capacity so as to decrease syneresis and make sure stable performance at the condition of high temperature and high formation pressure. Different amount of monomer AM was added in the graft polymerization procession at 80 °C while starch (3.6 wt.%), initiator (0.02 wt.%) and cross-linking agent (4.7 wt.%) were added in the gel solution. The effect of AM-to-starch ratio on the performance of gel is presented in Fig. 2.

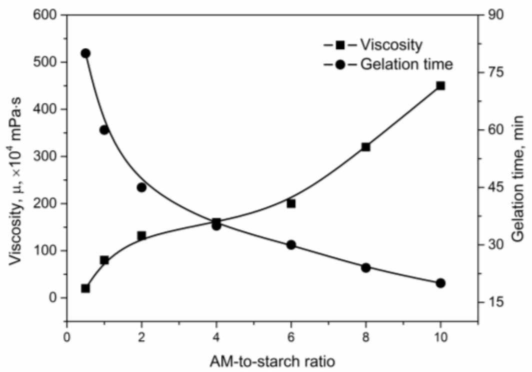

Fig. 2. Effect of AM-to-starch ratio on the gel performance

As can be seen from the Fig. 2., the gelation time was shortened and the viscosity of the gel increased as AM-to-starch ratio increased. As at a lower amount of AM, a small number of monomer can diffuse to graft onto the starch backbone, and the increasing of the monomer concentration was beneficial to graft polymer chain. On one hand, it was advantageous for monomers to spread to the active site of the long chain of starch, forming the graft copolymer and improving the efficiency of grafting. On the other hand, the graft copolymerization with a higher grafting efficiency gives the graft copolymer containing higher amount of hydrophilic chains with large length. Thus the viscosity increased due to the increasing amount of intramolecular and intermolecular hydrogen bonds. In addition, the viscosity also increased because the free water content is reduced [19].

Because hydroxyl group on the starch chain was used to graft copolymerization with AM, a proportion of AM to corn starch should not to too low. Moreover, considering the gelation time, viscosity and cost, the optimum ratio of AM to corn starch was controlled at 4:1.

3.3. Effect of pH on gel performance

In consideration of the acid-base properties of on-site water collection in the oilfield or gasfield, the effect of pH on gel was investigated here. The influence of selected pH 7 – 13 on the gel performance (starch (3.6 wt.%), initiator (0.02 wt.%), acrylamide (14.4 wt.%), cross-linking agent (4.7 wt.%), at 80 °C) is shown in Fig. 3.

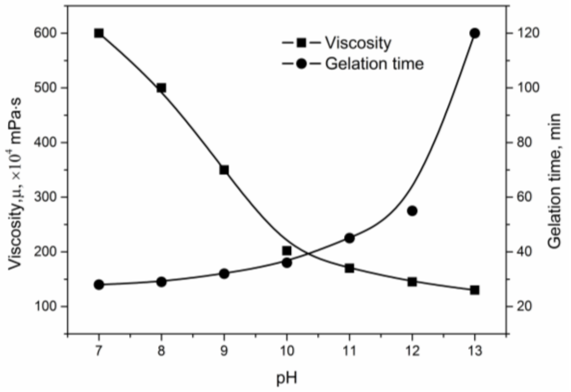

Fig. 3. Effect of pH on the gel performance

When the system was under alkaline condition, the viscosity of system decreased with the increasing of pH value while gelation time increases. With the increase of the amount of NaOH, large amount of $-CONH_2$ group are converted into -COOH or -COONa groups due to the hydrolysis reaction according to the Eq. 1.

$$R\text{-}CONH_2 + NaOH \rightarrow R\text{-}COONa + NH_3. \qquad (1)$$

R-COONa can be considered as a weak alkali, and there is a hydrolysis equilibrium shown as Eq. 2 [18, 20].

$$R\text{-}COONa + H_2O \leftrightarrow R\text{-}COOH + NaOH. \qquad (2)$$

The decrease of the amount of $-CONH_2$ could reduce the opportunity of reaction between -OH groups on starch and $-CONH_2$ group on acrylamide chain to take place, which lead in the extension of gelation time. At higher pH values, the concentration of anionic groups in the polymer network increases according to Eq. 1 and Eq. 2, so the electrostatic repulsion between the graft copolymer becomes stronger which will lower the crosslink density of gel, as a result the viscosity decreases and the gelation time was extended. Fortunately, it was obvious that the gelation time and viscosity can be controlled by pH adjusting, which give the gel a broader range of application. As a result, the optimal pH was selected 10 – 11.

3.4. Effect of reaction time on the viscosity

The onset time of gelation is an important parameter in understanding reaction mechanism in the network-formation system, because in the practical application it should leave enough time before the reaction takes place, that is make sure all the reactants will be pumped to the destination before gelatinization. In the published literatures, some determined the gelation time as the time that gel materials could be detected by solvent extraction [21 – 24], others defined it as the moment that the reaction solution lost its mobility in a tube at an upside-down position for 10 s [25 – 28]. In this work, the gelation time was determined by the sharp variation of complex viscosity of the reactant fluent during the polymerization. The relation between time and viscosity is studied shown in Fig. 4.

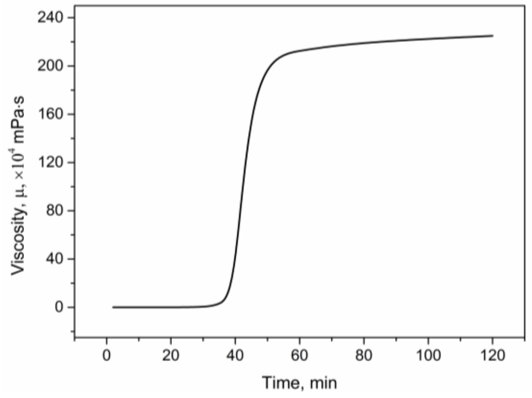

Fig. 4. Variation of viscosity during gelatinization

The curve depicted in Fig. 4 shows that under the conditions applied, the value of viscosity was very small about 40 ± 5 mPa.s and had remained constant for 38 min at the beginning of reaction, followed by an abrupt acceleration upon the network formation, after that the growth became gradually again for a long time. This phenomenon can be explained by slow initiation, fast propagation, fast termination and fast crosslinking [22 – 24]. In the reaction, corn starch and monomer AM were initiated slowly within a period of time at the early stage of grafting and polymerization. Then these short chains grew rapidly through propagation with vinyl groups in monomers. At a higher conversion, these chains combine one another though crosslinking to form huge networks resulting in an abrupt increase in viscosity. It is when the gel is formed that the viscosity will maintain a steady standard.

The viscosity is related to how easy the solution of reactants will be pumped to the destination in the pre-determined length of time. In the field application, the smaller the primary viscosity is, the better it is. Hence, it is desired not bigger than 300 mPa.s, because under high pressure the fluid with high viscosity is difficult to pump into the wellbore. Under the reaction condition shown in Fig. 4., the pumping process should have been finished within 38 min to avoid the gelatinization taking place. The optimum gelation time at different temperature could be obtained through the adjustment of pH as well as the amount of initiator.

3.5. Effect of salt on gel performance

In the consideration of application condition, the evaluation of effect of salt, especially divalent metal ions, on gel performance was carried out. The gel solution was prepared with high concentration of Mg^{2+} and Ca^{2+}, as high as 10000 ppm, respectively, and the viscosities were shown in Fig. 5.

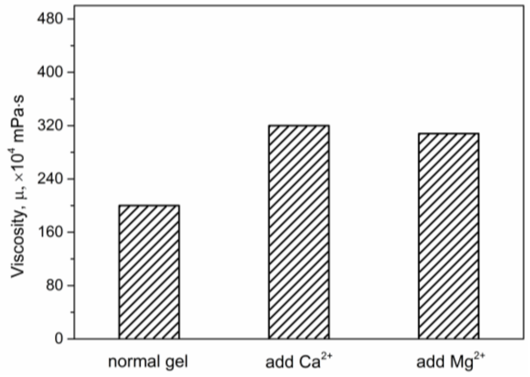

Fig. 5. Effect of Ca^{2+} and Mg^{2+} on viscosity of gel

Compared with the empty sample, the viscosity of gel increases with addition of ions in the solution. This phenomenon can be explained from two aspects. Firstly, the presence of ions in the solution could counteracts the mutual repulsion of the original ion in the network itself though the intramolecular and intermolecular complex formations ability of carboxamide and carboxylate groups [29, 30]. Secondly, the divalent ion is able to neutralize the charges which could weaken the electrostatic repulsion between charged groups inside the gel. Consequently, the excellent gelling properties are obtained under the condition of high salinity, which can be due to enhancement of the crosslink density of the network.

3.6. FT-IR spectra of the polymers

The infrared spectra of the compounds under investigation were recorded in the 4000 – 500 cm^{-1} region with KBr pellets. The functional groups of starch and crosslinked St-*g*-AM were characterized by FTIR as shown in Fig. 6.

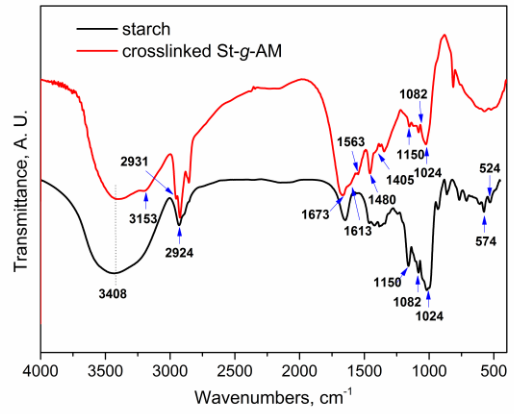

Fig. 6. FTIR spectra of corn starch and crosslinked St-g-AM

FTIR spectra of starch and crosslinked St-g-AM give all the characteristic absorption bands of corn starch (3408 cm^{-1} (s, broad); 2924 cm^{-1} (m)); 1150, 1082 and 1024 cm^{-1} (s) for O-H, C-H and C-O stretching, respectively) [19, 31]. After the reaction the absorption peak at 574 and 524 cm^{-1} attributed to -OH group on starch become smaller, this indicated that the OH groups on starch are converted during the reaction. The absorption bands at 3153, 1673 and 1613 cm^{-1} attributed to the -CONH$_2$ group on the acrylamide also change during the reaction and a absorption peak at 1405 cm^{-1} attributed to -CO$_2$ group appeared [18]. The IR spectrum of acrylamide grafted starch showed distinctive and characteristic absorption bands around (3500 – 3545 cm^{-1}) for ν (NH$_2$) and (2931 cm^{-1}) for stretching band for methylene group [32, 33]. All these bands mentioned above indicated the presence of the polyacrylamide chains grafted on starch.

As shown in Fig. 6, the distinct bands at 1563 and 1480 cm^{-1} (C=N vibrations of the s-triazine ring) and there is an absorption indicative of a secondary amine at 1588 cm^{-1} in the fingerprint region confirm the successful incorporation of triazine units provided by the crosslinker into the network [34, 35].

3.7. Surface morphology of the gel

The surface morphology, structure of the starch and the representative crosslinked st-*g*-AM were studied by scanning electron microscopy (SEM) as shown in Fig. 7.

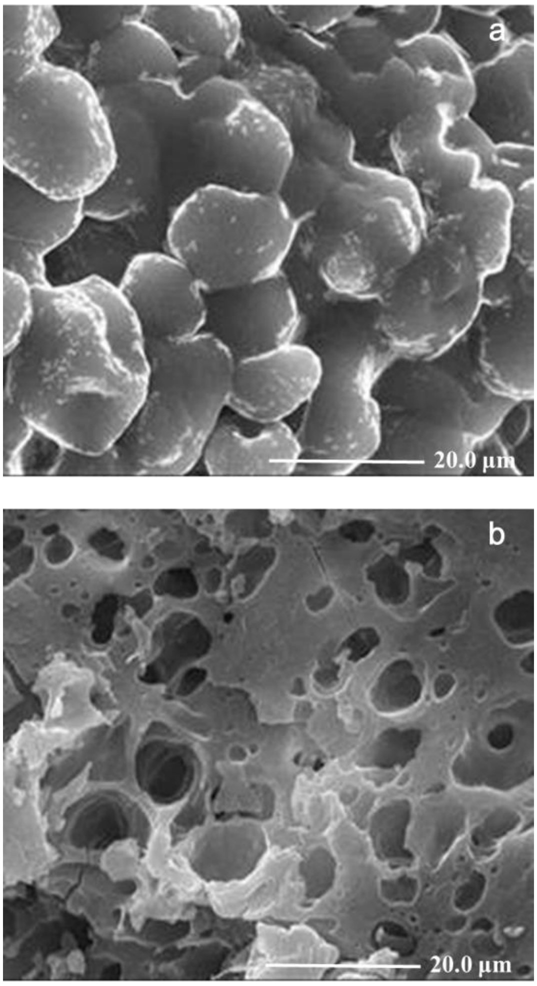

Fig. 7. SEM photographs: a – corn starch; b – crosslinked starch-g-AM: 80 °C, pH 10, AM-to-starch ratio 4, APS 0.02%

Fig. 7 a shows that the corn starch particles have a smooth and approximately spherical surface before grafting and crosslinking reaction, while after the reaction almost all of the starch particles were disrupted and formed many cavities inside the gel shown in Fig. 7 b. This phenomenon can also be explained through FTIR spectra of starch and crosslinked st-*g*-AM. The change of the characteristic peaks of -C-O-C- and nearly disappearance of -OH groups absorption peak could prove the degradation of starch particles; as a result, the spheres was not found in Fig. 7 b. Besides, the porosity can be explained by Eq. 1 that the hydrolysis reaction of amide groups that produced NH$_3$ under the alkaline condition, this gaseous product diffusion out of the product favor the formation of pores. This porosity is expected to enhance adhesive property of the crosslinked starch-g-AM gel, since, as is well known, the topography, the surface charge and interconnected pores are insuring good adhesion [36]. Fig. 7 b also shows the crosslinked polymer have a continuous and dense 3D structure which can contribute to the high elasticity of the gel. Fig. 8 is a schematic illustration to show the network.

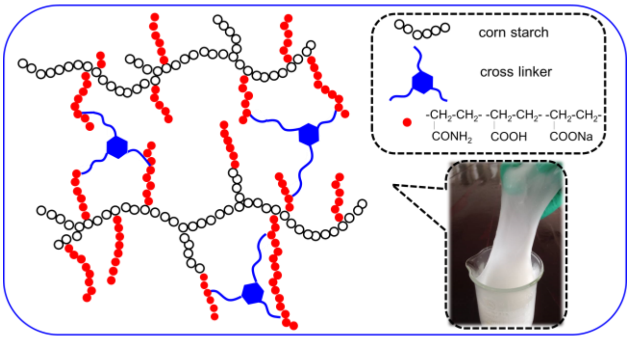

Fig. 8. Schematic illustration of the crosslinked starch-g-AM and the modified starch gel for the inserted picture

3.8. Field application

The gel as a packer was successfully applied in the shale gas field of China. The horizontal well named Longye 1HF as a production well has operated for nearly 10 years and was found that the phenomenon of bottom water coning was very serious in April 2017 as shown in Fig. 9, so the coiled tubing had to be pull out from the well to resume production through casing.

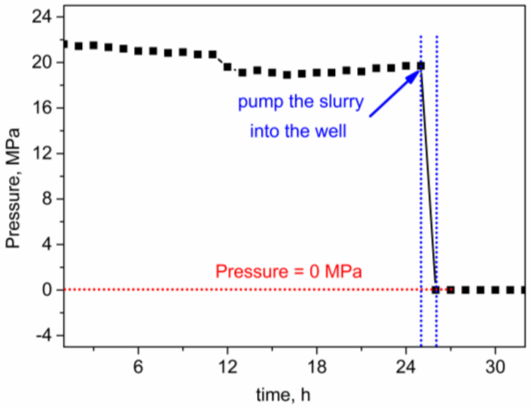

Fig. 9. The wellhead pressure curve of Longye 1HF

During the treatment process, about 1 m^3 ahead fluid and 0.5 m^3 of gel solution were injected into coiled tubing at a depth of about of 3500 m and 3000 m, and then the well was shut off for about 1h waiting for the gel to be fully formed. After this, the tubing pressure directly changed to zero (Fig. 9) and the tubbing was safely and successfully pulled out from the well. The wellhead pressure of zero was continuously observed for 3 days which indicated the gel presents a stable and reliable performance. The result proves that the gel plug as a packer slug was an effective treatment for snubbing service.

4. CONCLUSIONS

The novel gel with high viscosity composed by crosslinked starch-*g*-AM was synthesized by modifying grafted copolymerization of corn starch and AM, and the preparation conditions and synthesis techniques were discussed. The conclusions presented are as follows.

1. The dominant factor that effects the gel viscosity is the concentration of monomers, so dosage of AM could be changed to meet the needs of filed application.
2. The main factor that effects the gelling time is pH value, which could be adjusted to control time and suit the field operation need, the adjusted gelation time ensures that the gel solution enters the destination before becoming an unmovable plug, moreover the high gel viscosity gives the gel enough strength to plug high pressure. Above all, the optimal pH was selected 10 – 11.
3. The slurry is liquid when prepared initially which viscosity is as low as 35 – 82 mPa.s and the formula of gel is simple, various components and pH value could be confirmed easily before pumping into the wellbore, then formed a gel at a given temperature and a period of time.
4. Salt addition can compact the density of the network structure through screening of the charges, causing a significant lift in viscosity and confirming the involvement of electrostatic interactions.
5. The morphology of gel was observed by SEM, and it was found that the porosity and dense continuous phase could contribute to the high viscosity and elasticity, respectively.

These gels represent an important step towards the design and application of physical gels for oilfield and gasfield, since initiator, pH and ionic strength sensitivity of structure could be used to insure secure application conditions. Moreover, they are of interest as gelling agents with high viscosity and time controllable property which opens an important door to the study of this kind of environmental and easily pumped gels aimed to be used as smart plug for well completion engineering and in other applications in the field of oil and gas exploitation.

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