

Development of high strength polyvinyl alcohol gel for water shutoff in carbonate reservoirs

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Abstract. To provide a high-strength, non-resin organic plugging agent for water shutoff in carbonate fracture and cave reservoirs, a high-strength gel was prepared with polyvinyl alcohol 1788 as gelant and p-phthalaldehyde as crosslinker in this study. By selecting latent acids rather than strong acid such as hydrochloric acid and sulfuric acid as catalysts, and by adding clay and sulphonated phenolic resin as stabilisers to the gelation, the drawbacks of short gelation time of polyvinyl alcohol and high dehydration rate of the formed gel soaking in brine were overcome. The evaluation results showed that the gellant composed of 7wt% polyvinyl alcohol, 4wt% clay, 0.3wt% aldehyde crosslinker, 0.25wt% latent acid, 1.5wt% sulphonated phenolic resin, and 0.3wt% hexamethylenetetramine had a gelation time of 2 h at 130 °C. The storage modulus of the gel was up to 2000 Pa, and the dehydration rate of the gel after soaking in synthetic brine for 30 days was less than 15%. Furthermore, the breakthrough pressure gradient in a slim tube with a diameter of 3mm reached 15 MPa / m, which indicated that the gel is a temperature and salinity resistant plugging agent with strong plugging ability.

Keywords: Water Plugging; Crosslinked polyvinyl alcohol; latent acid

1. Introduction

The Taher carbonate reservoir is a bottom water-rich reservoir [1,2]. The rising bottom water causes excessive water production with oilfield development [3]. Due to the high formation temperature (above 110 °C) and high salinity of formation water (Salt content 22×10^4 mg/L, calcium and magnesium ion content 2×10^4 mg/L), bottom water treatment is difficult. Recently, great progress has been reported about temperature-resistant and salinity-resistant gel composed of AM-AMPS copolymer with a molecular weight over 6 million [4,5]. Polymer gel is injected into formation first and then the formation is sealed with water glass gel to prevent the polymer gel from displacing. This treatment has a better water plugging effect. However, field trials found that after two rounds of water plugging, the well fluid production dropped significantly. It is supposed that the high concentration of water glass gel caused permanent damage to the formation. So a non-resin organic high-strength plugging system is required to replace the high-strength water glass gel. In this paper, a high-strength polymer gel with good stability in high-temperature and high-salinity environments was developed.

2. Experimental section

2.1 Materials

The materials used in the experiment include Polyvinyl alcohol 1788 (industrial product, Chengdu Huamao Co., Ltd.), para-phthalaldehyde (Shanghai Aladdin Reagent Co., Ltd.), clay (Dinglong Mining), sulphonated phenolic resin (industrial product, Davey Petroleum Technology Co., Ltd.), latent acid catalyst (industrial product, Qingdao Qucheng Technology Co., Ltd.).

2.2 Methods

The storage modulus of the gel was measured using a MCR-92 rheometer and the dehydration rate of the gel was calculated according to equation (1).

$$A = \frac{m_0 - m_i}{m_0} \times 100\% \quad (1)$$

Where: A is the dehydration rate of gel after high temperature heat treatment; m_0 is the initial mass of gel; m_i is the mass of different time periods of heat treatment.

3. Results and Discussion

3.1 Development of high-strength polyvinyl alcohol gel

3.1.1 Screening of cross-linkers

Aldehydes that can undergo acetal reactions with polyvinyl alcohol include formaldehyde, glyoxal, glutaraldehyde, terephthalaldehyde, and o-phthalaldehyde. Formaldehyde is highly toxic, and glyoxal and glutaraldehyde are easily volatile, and o-terephthalaldehyde and terephthalaldehyde have low volatility. Considering the low toxicity and slightly lower cost of terephthalaldehyde, this paper selected terephthalaldehyde as the cross-linking agent.

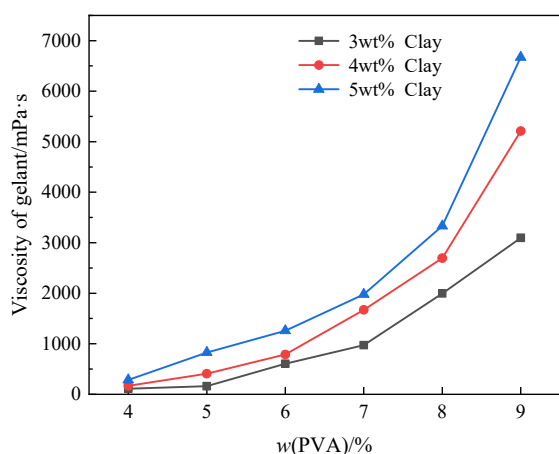


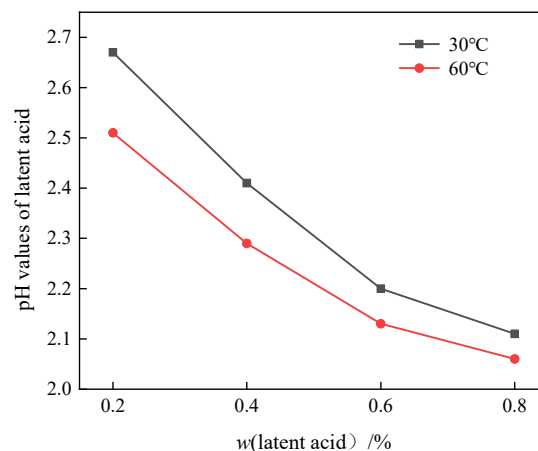
Fig. 1 Effect of polyvinyl alcohol and clay content on viscosity of gum-forming solution

Since the viscosity of the gellant increases with the polyvinyl alcohol content (as shown in Fig. 1). The viscosity of the gellant with 8wt% polyvinyl alcohol (also containing 0.2wt% crosslinker and 4wt% clay) up to 2696 mPa·s, which is close to the upper limit of the pumped fluid, so it is recommended that the amount of polyvinyl alcohol in the gellant is 4wt% to 8wt%. For terephthalaldehyde, the strength of the gel also increases with the amount of terephthalaldehyde. However, the over cross-linking reaction can reduce the hydrophilicity of the gel, and the dehydration rate of the gel in synthetic brine increases with terephthalaldehyde, so the amount of cross-linking agent is recommended to be 0.2wt% to 0.5wt%.

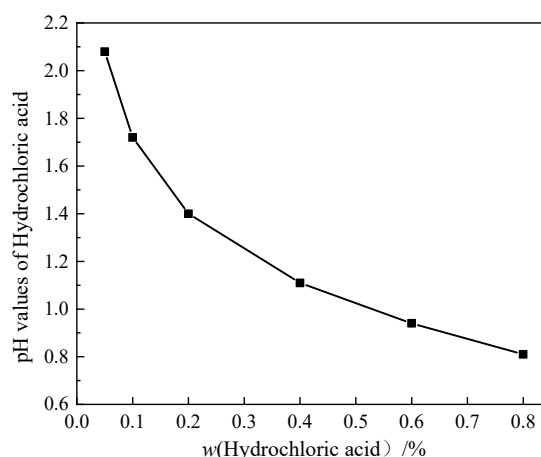
3.1.2 Screening of catalysts

To ensure the successful injection of plugging agent into the formation, the gellant should have a long gelation time. The above experiment used 0.2wt% mass fraction of hydrochloric acid as the catalyst, and the gelation time is shorter under high temperature, thus it is tricky to meet the construction injection requirements. To reduce the cross-linking rate of polyvinyl alcohol, latent acid is considered as the catalyst. Latent acid can be hydrolyzed in water to produce H^+ , thus delaying the acetal reaction.

The pH values of different concentrations of Latent acid and hydrochloric acid was shown in Fig. 2.



(a) pH values of latent acids



(b) pH values of hydrochloric acid

Fig. 2 pH values of different acid solutions

The gellant was formulated according to Table 1. The gelation time of the gel containing 4wt% clay, 7wt% polyvinyl alcohol, 0.3wt% crosslinker, and 0.2wt%-0.25wt% Latent acid of the catalyst can reach more than 2 h at 130°C, which can meet the requirement of near-well injection (more than 60 min).

Table 1 Formulation table for different catalyst contents

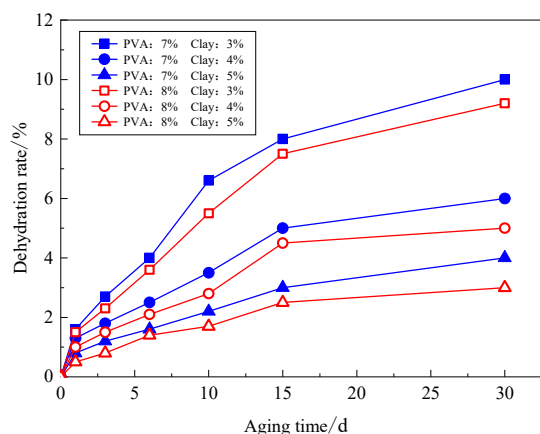
w(Clay)/%	w(PVA)/%	w(Crosslinker)/%	w(Latent acid)/%	Gelation time/h
4	7	0.3	0.20	4.0
4	7	0.3	0.25	2.5
4	7	0.3	0.30	1.5
4	7	0.3	0.35	1.0

3.1.3 Screening of stabilizers

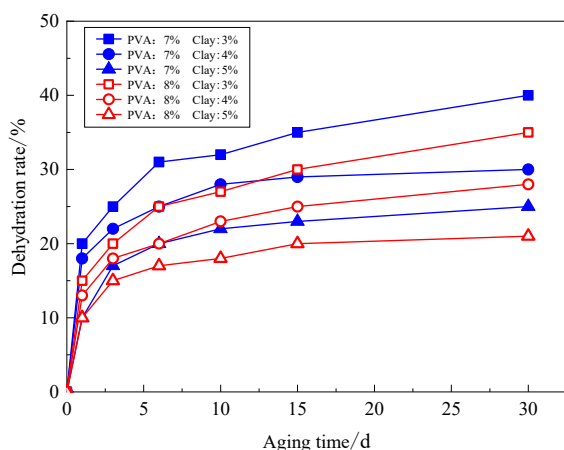
It is proposed to improve the stability of cross-linked polyvinyl alcohol by adding clay and introducing salt-resistant groups.

(1) Addition of clay. Clay is a material commonly used in hydrogels to improve the strength and water holding capacity. The cross-linked polyvinyl alcohols with different clay loading were prepared by fixing the amount of cross-linker at 0.3wt% and catalyst at 0.2wt%. The dehydration rates of these cross-linked polyvinyl alcohols aged in situ at 130 °C and immersed in synthetic brine with different aging times were shown in Fig. 3.

It can be seen that the dehydration rate of the cross-linked polyvinyl alcohol formed by adding clay to the gellant is significantly lower. The higher the content of clay and polyvinyl alcohol in the gellant, the lower the dehydration rate of cross-linked polyvinyl alcohol gel formed. Since the high viscosity (see Fig. 1) and the difficulty of pumping when the content of clay and polyvinyl alcohol in the gellant is too high, the amount of clay used is finally determined to be 4wt%.



(a) Aging in ampoules



(b) Aging in simulated formation brine

Fig. 3 Effect of clay on the stability of polyvinyl alcohol jelly

(2) Addition of sulfonated phenolic resin and hexamethylenetetramine. Whereas the good salt resistance of the sulfonated phenolic resin, the

temperature and salt resistance of the compound cross-linked polyvinyl alcohol is improved by adding sulfonated phenolic resin and hexamethylene tetramine.

Under the condition of the 6wt% polyvinyl alcohol, 4wt%clay, 0.3wt%cross-linker, 0.2wt%catalyst, less than 2wt% sulfonated phenolic resin loading and sulfonated phenolic resin to hexamethylenetetramine in a 5:1 mass ratio, The stability of the prepared cross-linked polymer in synthetic brine was shown in Table 2.

Table 2 Stability of cross-linked polymers immersed in simulated formation water with different sulfonated phenolic resins, hexamethylenetetramine and catalyst contents

Seri al nu mbe r	w (Hexamethylen etramine) /%	w (Sulf onated phenoli c resins) /%	Dehyd ration rate after 10 days of aging/ %	Dehyd ration rate after 30 days of aging/ %
1	0.1	0.5	15	20
2	0.2	1.0	12	18
3	0.3	1.5	9	13
4	0.4	2.0	8	11

As can be seen from Table 2, the dehydration rate of the produced particles under high temperature and high salt conditions decreased significantly with the increase of sulfonated phenolic resin and hexamethylenetetramine, indicating that the introduction of sulfonated phenolic resin and hexamethylenetetramine improved the temperature and salt resistance of the cross-linked polymers. After the cross-linked polymer gel particles with 1.5wt% or 2wt% sulfonated phenolic resin loading in synthetic water aged for 30 days, the dehydration rate of the two particles was close. Considering the production cost, the mass fraction of sulfonated phenolic resin could be determined as 1.5wt% and the mass fraction of hexamethylenetetramine as 0.3wt%.

3.2 Evaluation of high-strength polyvinyl alcohol gel

3.2.1 Evaluation of high-temperature stability

Firstly, 100 g synthetic formation brine was added to the homemade high-temperature tank. Secondly, 50 g gellant was slowly injected. Then, the tank was sealed and de-oxygenation with nitrogen. Lastly, placed the sealed tank in an oven at 130 °C for aging. The dehydration rate and storage modulus of the gel were measured at different heat treatment times to evaluate the long-term stability of the gel under high temperature and high salt conditions. The results are shown in Figure 4 and Fig. 5.



Fig. 4 Diagram of the state of gel at different times of heat treatment

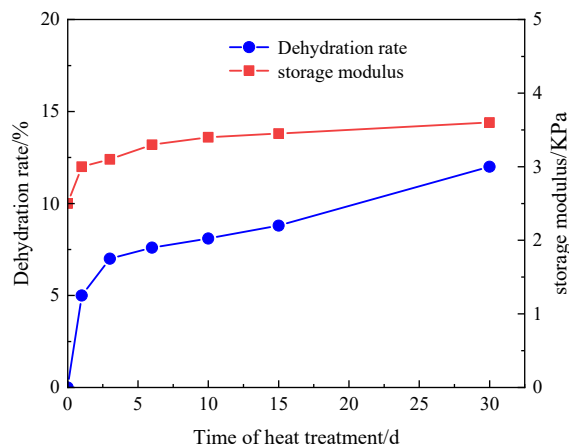


Fig. 5 Effect of heat treatment time on the dehydration rate and storage modulus of gel

The gel is formed in the upper area of the tank and the gel can still keep its shape intact after 30 days under high temperature and high salinity conditions. After 30 days of heat treatment, the storage modulus of the cross-linked polyvinyl alcohol is over 2000 Pa (much greater than the storage modulus of general strong gel) and dehydration rate is less than 15%, exhibiting as a stable high strength gel.

3.2.2 Sealing ability test of high strength cross-linked polyvinyl alcohol

In this paper, we used a slim steel tube with a diameter of 3 mm to simulate fractures and then compared the plugging capacity of two gels which composed of 7wt% polyvinyl alcohol, 4wt% clay, 0.3wt% aldehyde cross-linker, 0.25wt% latent acid, and 1.5wt% sulfonated phenolic resin, 0.3wt% hexamethylenetetramine and 1.0wt% AM-AMPS, 0.2wt% hydroquinone, 0.2wt% hexamethylenetetramine respectively. The former was formulated with tap water and the latter was formulated with synthetic brine. Both of two were aging at 130 °C for 5 days, and then the breakthrough pressure was measured at room temperature with a water injection rate of 64 m/d, and the results are shown in Fig. 6.

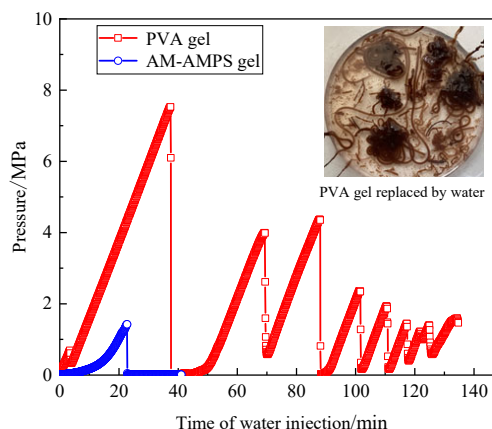


Fig. 6 Breakthrough pressure of AM-AMPS gel and PVA gel in a fine tube

It can be seen that the breakthrough pressure of cross-linked polyvinyl alcohol can reach 15 MPa/m, which is far higher than the general temperature and salt resistant gel. In addition, after the cross-linked polyvinyl alcohol was breached, the polymer in the slim tube can also reform a blockage, resulting in repeated fluctuations in injection pressure over time.

4. Conclusion

Using latent acid as a catalyst can substantially prolong the gelation time of polyvinyl alcohol and terephthalaldehyde; Adding a certain amount of clay and sulfonated phenolic resin when preparing cross-linked polyvinyl alcohol can improve the stability of the gel system in synthetic brine; The gel composed of 7wt% polyvinyl alcohol, 4wt% clay, 0.3wt% aldehyde cross-linker, 0.25wt% latent acid, 1.5wt% sulfonated phenolic resin and 0.3wt% hexamethylenetetramine has a gelation time of 2 h at 130 °C, and a storage modulus of 2000 Pa, a dehydration rate less than 15% after 30 days of immersion in synthetic brine, and a breakthrough pressure gradient in the simulated slim tube of 3 mm diameter up to 15 MPa/ m.

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