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Sulfonation Modification of Guar Gum and Its Performance as a Fracturing Fluids Thickener

Yonggen Yi[1], Lanbing Wu[2, 3], Jie Zhang[2], Haiyang Wang[2], Xuan Xie[1], Chen Gang[2, 3*]

[1]Xi'an Changqing Chemical Group Co. Ltd, PetroChina Changqing Oilfield Co. Ltd, Xi'an, 710018, China
[2]Engineering Research Center of Oil and Gas Field Chemistry, Universities of Shaanxi Provence, Xi'an Shiyou University, Xi'an, 710065, China
[3]Shaanxi Province Key Laboratory of Environmental Pollution Control and Reservoir Protection Technology of Oilfields, Xi'an Shiyou University, Xi'an 710065, China
[*]*Corresponding author: e-mail:* gangchen@xsyu.edu.cn

To solve the contradiction between reducing water-insoluble content and maintaining high viscosity in the preparation of modified guar gum for oilfield fracturing fluid, in this work, sodium 3-chloro-2-hydroxypropylsulfonate was used as a modifier to prepare sulfonated guar gum. Orthogonal and single-factor extrapolation experiments were conducted to explore the effects of reaction conditions and the optimal process was determined as follows: reaction temperature of 26 °C, reaction time of 2.0 h, sodium hydroxide as a mass fraction of guar gum of 1.0%, and sodium 3-chloro-2-hydroxypropyl sulfonate dosage as a mass fraction of guar gum of 0.5%. Furtherly, the temperature stability, filtration property, and inhibition of formation clay of the sulfonated products were investigated. The results showed that the apparent viscosity of 0.6% solution of guar gum was increased by 33%, the water-insoluble content was decreased by 0.42%, and the temperature stability, filtration resistance, and clay inhibition were all improved. Especially, the viscosity of cross-linked sulfonated guar gum is 100% higher than that of unmodified guar gum. The structure of sulfonated guar gum was characterized and confirmed by infrared spectrum, DSC, thermogravimetric, and elemental analysis.

Keywords: Guar gum; sulfonation reaction; modification; fracturing fluids thickener; viscosity.

INTRODUCTION

With the increasingly strict requirements of the environment on the production of oil and gas fields, the application of natural products such as cellulose, lignin, and vegetable phenol in oil field production has attracted more and more attention. More and more researchers have modified natural products such as mountain yam[1], waste persimmon peel[2], Walnut peel[3], Carob gum[4], Konjac gum[5], Vegetable glue[6], lignin and its derivatives[7–11] to improve their properties and provide more efficient support for oil and gas field exploitation. Guar gum is a natural heteroglycan polymer, which is mainly composed of galactose and mannose[12, 13]. Due to its high solubility, high viscosity, and environmental friendliness, it has been used as a thickening agent for oilfield fracturing fluids for a long time[14, 15]. However, there are problems such as high water-insoluble substances, long time for dissolution, unstable viscosity, and susceptibility to microbial decomposition, which are not suitable for long-term use and preservation. This greatly limits its production and application in oilfield fracturing. From the perspective of molecular structure, the long molecular chain of guar gum exists in a spherical curl state, and most hydroxyl groups are wrapped by molecular chains. Due to Intermolecular force, intramolecular self-crosslinking occurs, that is, the molecular structure containing a large number of hydrophilic hydroxyl groups can not only promote the dissolution of guar gum, but also affect the swelling and hydration of guar gum. Therefore, it is necessary to chemically modify guar gum to improve its performance. To improve and enhance its performance, researchers have proposed various chemical modification methods, such as functional group derivation, and graft polymerization[16, 17]. For chemical modification methods, R. Lapasin conducted long-term research on hydroxypropyl guar gum and found that hydroxypropyl guar gum aqueous solution has better rheological and viscosity retention under continuous shear flow conditions[18]. Hydroxypropyl guar gum is currently the main product of thickeners used in oilfield fracturing fluids, with high viscosity and low water-insoluble substances. However, hydroxypropylation modification can lead to a decrease in the viscosity of guar gum compared to unmodified guar gum. Until now, they did not resolve the contradiction between reducing water-insoluble content and maintaining viscosity. G. Dodi used a method of introducing carboxymethyl groups into molecules and etherifying them to obtain carboxymethyl guar gum with a high swelling rate but did not explore the maintenance technique of its viscosity[19]. In this work, we use a highly hydrated modifier, sodium 3-chloro-2-hydroxypropylsulfonate, as a modifier to produce sulfonated guar gum with higher viscosity and lower water-insoluble content.

EXPERIMENTAL PART

Experimental material

Ethyl alcohol (AR 99.7%), sodium 3-chloro-2-hydroxypropyl sulfonate(AR), sodium hydroxide (AR), sodium tetraborate (AR), and acetic acid (AR) were purchased from Jincheng Comio Chemical Reagent Company. The guar gum powder is obtained from Changqing Chemical Group Company, the apparent viscosity of its aqueous solution is 78 mPa.s (0.6 wt%).

Preparation of sulfonated guar gum

Sulfonated guar gum was prepared by functional group derivative modification[20]. 3.6 wt% sodium hydroxide and 3.6 wt% sodium 3-chloro-2-hydroxypropylsulfonate and ethanol water solution (v(EtOH) : v(H_2O) = 3:1) were

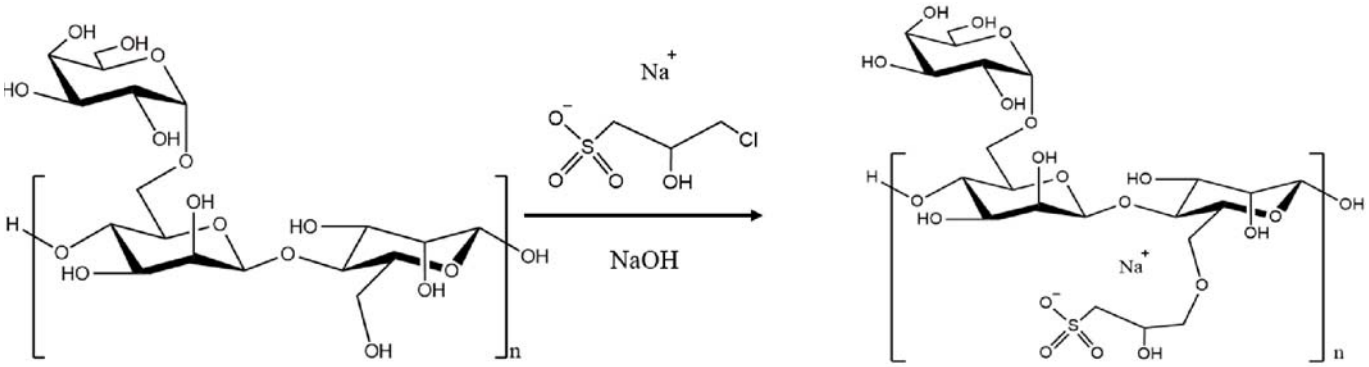

Figure 1. Synthesis of sulfonated guar gum

pre-prepared at first. 3.6 g guar gum powder and 40 mL ethanol-water (3:1) were added into a three-necked flask in turn, stirred for 30 min, until they were fully swollen. Keep the temperature constant, add sodium hydroxide solution and sulfonating agent solution in turn under constant stirring, and heat up to the set temperature and start timing. Cool the above mixture to room temperature, adjust the pH to neutral with acetic acid, filter under reduced pressure, wash twice with anhydrous ethanol, and dry the filter cake to constant weight in a constant temperature drying oven at 60 °C to obtain the modified product. The chemical reaction equation of this process is shown in Figure 1.

Apparent viscosity measurement

The apparent viscosity of sulfonated guar gum solution was determined by ZNN-D6S rotary viscometer (Qingdao Haitongda Special Instrument Company) according to SY/T 5764-2007 standard of petroleum and natural gas industry of the People's Republic of China.

Determination of water-insoluble content

According to the standard SY/T 5764-2007 of the petroleum and natural gas industry of the People's Republic of China, the gel solution with a mass concentration of 0.6% was prepared. SC-03 low-speed centrifuge (Anhui Zhongke Zhongjia Scientific Instrument Co., LTD.) was used to determine the content of water-insoluble content in the sulfonated guar gum solution, the data were processed according to Eq -1.

$$\eta = \frac{(m_3 - m_1)}{(m_2 - m_1) \times 0.6\% \times (1 - W)} \quad (1)$$

Here, η is water insoluble content expressed as a percentage; m_1 is the quality of centrifugal tubes (g); m_2 is the total mass of the centrifuge tube and the colloid (g); m_3 is the total mass of the centrifuge tube and water-insoluble content (g); W is the moisture content of glue sample, expressed as a percentage; 0.6% is the content of guar gum powder.

Crosslinking experiment

Crosslinking of sulfonated guar gum solution was evaluated according to SY/T 5764-2007, the standard of the petroleum and natural gas industry of the People's Republic of China.

Inhibition performance evaluation

According to SY/T 6335-1997, the oil and natural gas industry standard of the People's Republic of China, the adhesive solution with a mass concentration of 0.6% was prepared[21]. NP-1 dilatometer at normal temperature and pressure (Qingdao Haitongda Special Instrument Company) was used to test the inhibition performance of guar gum. Data processing is carried out in accordance with Eq -2.

$$S_r = \frac{R_0}{\Delta L} \times 100\% \quad (2)$$

Here, S_r is the linear expansion rate of bentonite; R_0 is the expansion amount of bentonite (mm); ΔL is the core height (mm).

Characterization of sulfonated guar gum

A Nicolet 5700 infrared spectrometer (Unobelium Industry Co., LTD) was used for infrared scanning under the experimental conditions of 4000–400 cm^{-1} scanning wave number to study the types and molecular structures of compounds TGA/DSC1 thermograms analyzer (Mettler Toledo, Switzerland) was used to study the thermal stability and components of the modified substances under the experimental conditions of heating rate of 15 °C/min, temperature space of RT~800 °C, atmospheric gas of N_2 and flow rate of 50.0 mL/min. DSC-822e differential scanning calorimeter (Mettler Toledo, Switzerland) was used to study the thermal transition temperature of modified substances under the experimental conditions of temperature rise rate of 10 °C/min, temperature space of 25~500 °C and atmospheric gas of N_2. The elements C, H, N and S of Guar gum and its modified products were analyzed with the element analyzer vario EL cube 6 (Elementar Instrument Company, Germany) at the heating rate of 3 °C/min and under the experimental conditions of air atmosphere and the main element composition and content of Guar gum and its modified products were studied.

RESULTS AND DISCUSSION

Orthogonal experiment study on sulfonation reaction process

Thro found through literature survey[18–19] that the preparation of modified guar gum usually involves several process parameters, such as reaction time, reaction temperature, and the amount of sulfonating agent; Combined with the investigation results of the relevant

range values of the influencing factors of modified guar gluing, the initial parameters of the synthesis factors were determined, and orthogonal experiments were intended to be used to design the experimental scheme. By using orthogonal experimental design, the influence of each parameter on product properties can be systematically investigated, the influence of parameter results can be understood more quickly and comprehensively, and the optimal parameter combination can be found, so as to realize the further optimization of production process[22]. Thus, a four-factor, three-level L9(3^4) orthogonal experiment table was designed to examine the effects of reaction temperature (A,℃), reaction time (B,h), NaOH addition (C,%), and sulfonation agent addition (D,%) on the apparent viscosity of the modified products[23]. The experiment results are shown in Table 1 and Table 2. By ANOVA, the order of influence of each factor on the apparent viscosity of the modified product is A > B > D > C. The optimized condition is $A_1B_1D_2C_1$.

Table 1. Preparation factors of sulfonated Guar gum

Factor	Level		
	1	2	3
Reaction temperature (A,℃)	30	50	70
Reaction time (B,h)	2.0	4.0	6.0
Addition of sulfonating agent (C,%)	0.1	0.5	1.0
NaOH dosage (D,%)	1.0	3.0	6.0

Here, K_i is the arithmetic mean of the test results obtained when the factor level number is i on any column (in the case where the apparent viscosity of the 0.6% solution is the evaluation criterion); k_i is the arithmetic mean of the test results obtained when the factor level number is i on any column (in the case where water-insoluble matter content is the evaluation criterion); R is the extreme deviation of the test results obtained at factor level number i on any column, R = max{K_1, K_2, K_3}-min{K_1, K_2, K_3} (in the case where the apparent viscosity of 0.6% solution is the evaluation criterion); r is the extreme deviation of the test results obtained when the factor level number is i on any column, r = max{k_1, k_2, k_3}-min{k_1, k_2, k_3} (in the case where water-insoluble matter content is the evaluation criterion).

The trend chart in Figure 2 is based on the arithmetic mean Ki of the test results obtained when the factor level number is i in either column of Table 2 (When the apparent viscosity of 0.6% solution is the evaluation criterion).

The trend chart in Figure 3 is based on the arithmetic mean ki of the test results obtained when factor level number is i in either column of Table 2 (In the case of water-insoluble content as the evaluation standard).

In general, the extremes of the columns are not equal, indicating that changes in the levels of the factors have different effects on the results of the test, A larger extreme difference indicates that a change in the value of the factor in that column within the test range will result in a numerically larger change in the test metrics, so the column with the largest extreme difference is the one in which the level of the factor has the greatest impact on the results of the test. As can be seen from Fig. 2 and Fig. 3, no matter whether the evaluation criterion is based on apparent viscosity or based on apparent viscosity of water-insoluble substances, the change of reaction temperature has the greatest extreme difference to the test results. Combined with Table 1 and Table 2, The optimal reaction conditions based on apparent viscosity evaluation are reaction temperature 30 °C, reaction time 2.0 h, dosage of sulfonating agent (mass fraction of sulfonating agent in guar gum) 0.5%, dosage of NaOH (mass fraction of NaOH in guar gum) 1%.

Single-factor study on sulfonation reaction

Orthogonal experiments are usually done to find the main parameters that have the most significant impact on the results and determine the best horizontal combination of them. Because in orthogonal experiment, each parameter usually only considers the level within a certain range, the single-factor epitaxy experiment can further optimize these main parameters and find the optimal process conditions[24]. Therefore, based on the orthogonal experiment results, the single-factor epitaxy experiment was further carried out to determine the influence of each factor on the modification results one by one, and to explore the optimal combination of conditions for the modification process of guar gum.

Table 2. Orthogonal experimental results and analysis

Number	A	B	C	D	Apparent viscosity of 0.6% solution / mPa·s	Water insoluble content /%	Crosslinking
1	30	2.0	0.1	1.0	92.3	13.05	pickable
2	30	4.0	0.5	3.0	77.8	7.02	pickable
3	30	6.0	1.0	6.0	46.4	13.90	pickable
4	50	2.0	0.5	6.0	99.1	20.54	pickable
5	50	4.0	1.0	1.0	8.9	5.80	unhanging
6	50	6.0	0.1	3.0	86.1	12.13	pickable
7	70	2.0	1.0	3.0	47.5	4.28	unhanging
8	70	4.0	0.1	6.0	8.9	4.46	unhanging
9	70	6.0	0.5	1.0	5.9	0.76	unhanging
K_1	72.2	79.6	62.4	35.7	Results of range analysis by apparent viscosity		
K_2	64.7	31.9	60.9	70.5			
K_3	20.8	46.1	34.3	51.5			
R	51.4	47.7	28.1	34.8			
k_1	11.32	12.62	9.88	6.54	Results of range analysis based on water-insoluble content		
k_2	12.82	5.76	9.44	7.81			
k_3	3.17	8.93	7.99	12.97			
r	9.65	6.86	1.89	6.43			

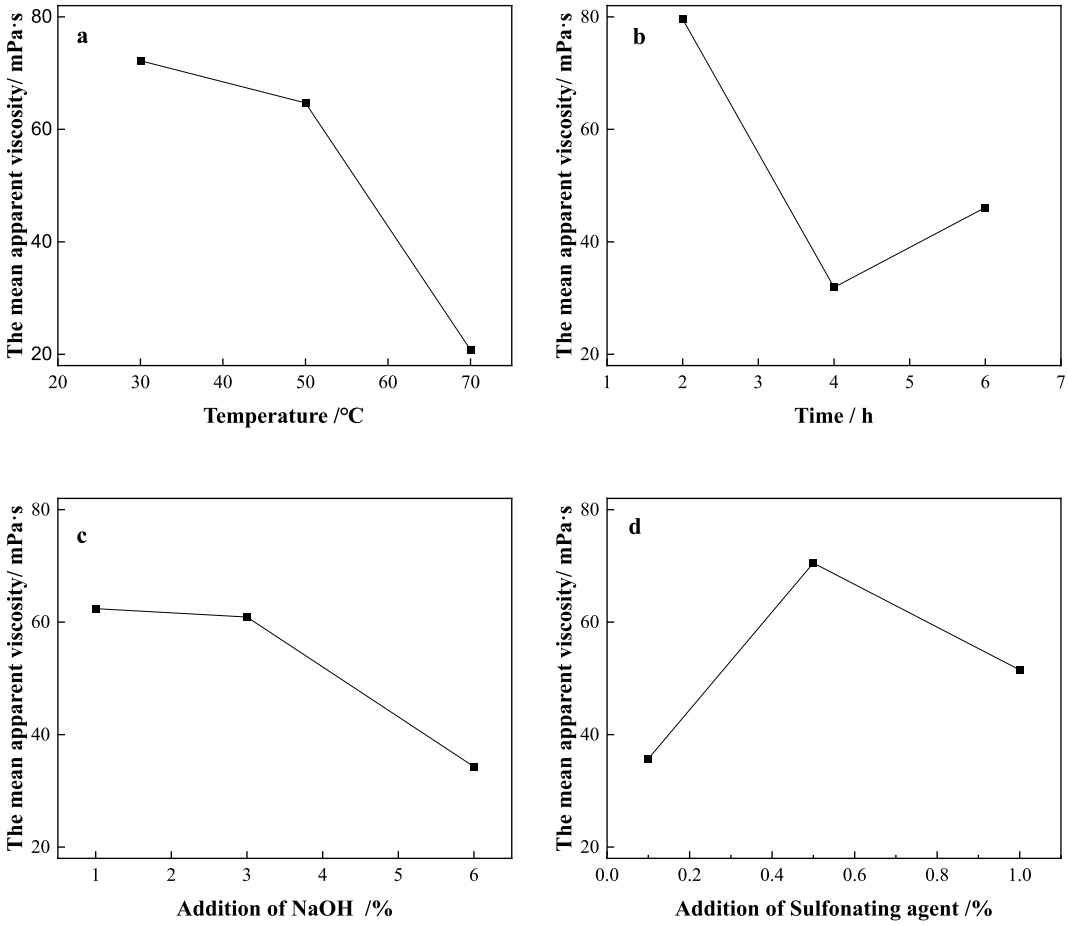

Figure 2. Main effect diagram of mean apparent viscosity: (a) The effect of reaction temperature; (b) The effect of reaction time; (c) The effect of NaOH dosage; (d)The effect of addition of sulfonating agent

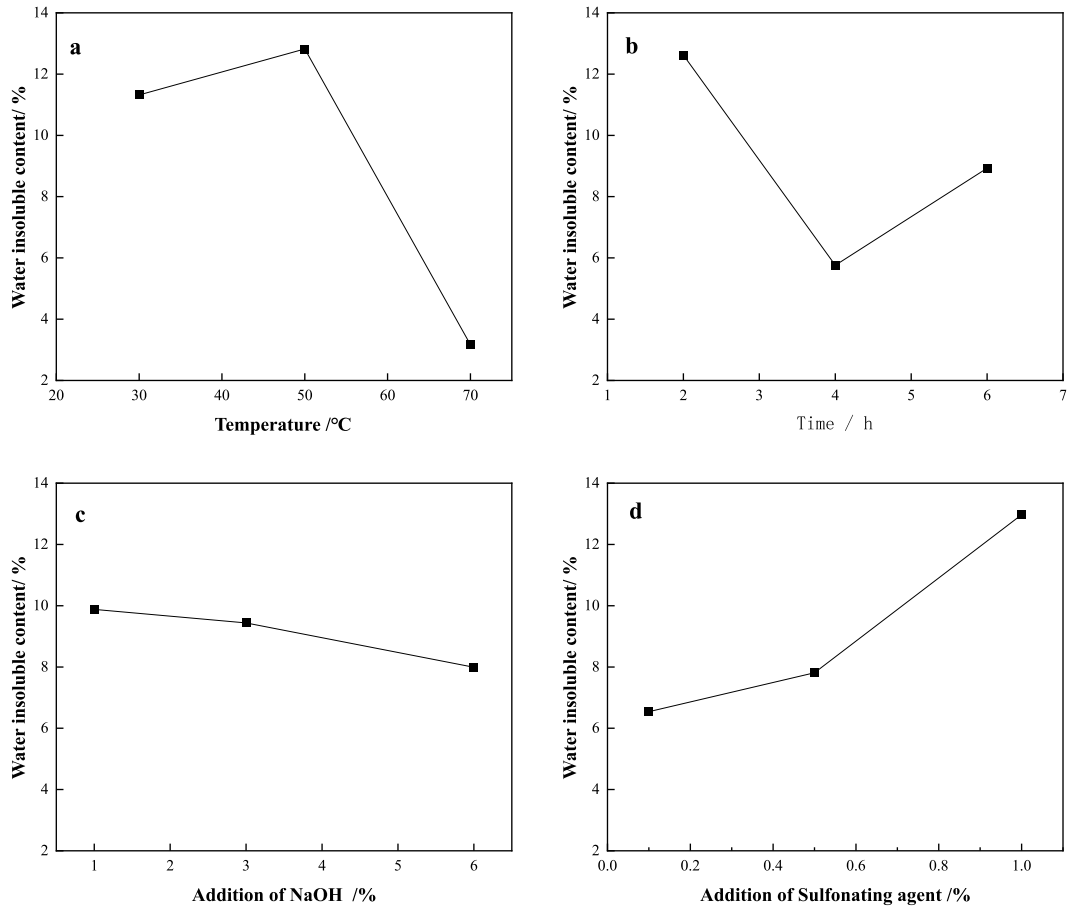

Figure 3. Main effect diagram of mean water-insoluble content: (a) The effect of reaction temperature; (b) The effect of reaction time; (c) The effect of NaOH dosage; (d) The effect of addition of sulfonating agent

Effect of temperature

Under the premise of fixing other factors unchanged, only the reaction temperature was changed to explore the influence of temperature on the result of guar gum sulfonation modification. By observing and analyzing the apparent viscosity mean main effect Fig. 2 we can get that: Around 30 °C, the temperature decreases while the viscosity increases conversely. On this basis, the temperature in the single-factor experiment is set as 22, 24, 26, 28, 30, 32, and 34 °C. The reaction time was 2.0 h, the amount of sodium hydroxide (mass fraction of sodium hydroxide in guar gum) was 1.0%, and the amount of sulfonating agent (mass fraction of sulfonating agent in guar gum) was 0.5%. The results of obtaining the viscosity and water-insoluble substances of the product are shown in Fig. 4.

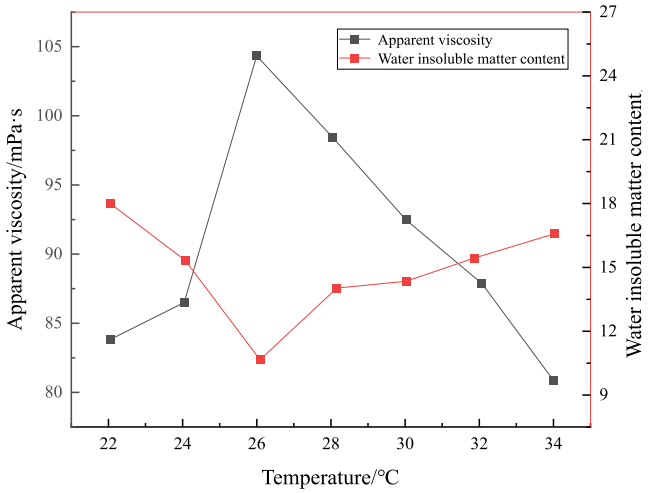

Figure 4. Effect of temperature on viscosity and water-insoluble content of sulfonated guar gum

The above figure shows that the apparent viscosity curve changes as follows: when the temperature ranges from 22 °C to 26 °C, the viscosity increases with the increase of temperature; The viscosity decreases with increasing temperature between 26 °C and 34 °C, and the viscosity reaches its maximum value when the temperature is 26 °C. Compared with 0.6% aqueous solution of Guar collagen powder, the viscosity increased from 78.4 mPa.s to 104.3 mPa.s, with an overall increase of 33%. While the water-insoluble content is as follows: as the temperature is between 22 °C and 26 °C, the water-insoluble content decreases with increasing temperature. In the range of 26 °C to 34 °C, the content of water-insoluble substance increases with the increase of temperature, and the insoluble substance content is the minimum under the reaction temperature of 26 °C. Compared with 0.6% solution of Guar collagen powder, the water-insoluble content was reduced by 0.63%.

The reason is that with the increase of temperature, the irregular Thermal motion of molecules intensifies and the molecular chain can be further stretched and expanded, which will promote the contact opportunity of active hydroxyl with catalyst and sulfonation agent to increase, thus promoting the occurrence of reaction, and the macroscopic performance increases viscosity. Further increase in temperature will lead to partial cross-linking of molecular chains, hinder effective contact between reaction materials, and inhibit the occurrence of reaction modification. Based on the above results, the optimal reaction temperature was 26 °C.

Effect of reaction time

Based on the temperature determined above, other factors were fixed, and the reaction time was changed to continue to explore the influence of these factors on the results of sulfonation modification of guar gum. As can be seen from Fig. 2, the optimal reaction time is 2.0 h, so the reaction time in the single-factor experiment is set as 1.5, 2.0, 2.5, 3.0, and 3.5 h. When the temperature is 26 °C, the amount of sodium hydroxide (mass fraction of sodium hydroxide in guar gum) is 1.0%, and the amount of sulfonating agent (mass fraction of sulfonating agent in guar gum) is 0.5%, the results of viscosity and water-insoluble content obtained are shown in Fig. 5.

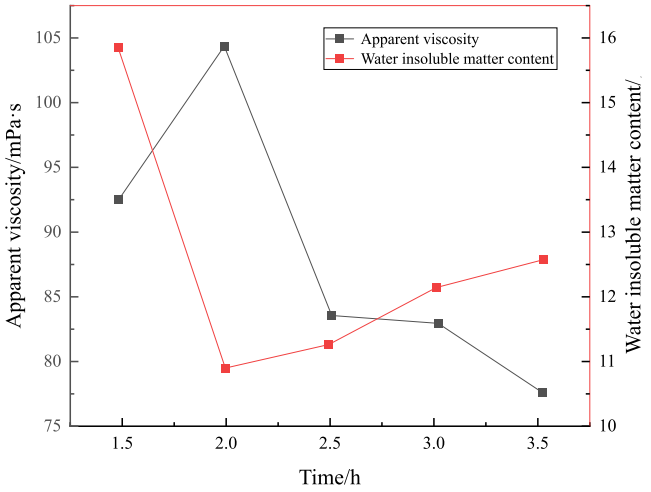

Figure 5. Effect of time on viscosity and water-insoluble content of sulfonated guar gum

The above figure shows that the apparent viscosity curve changes as follows: when the time range is between 1.0 h and 2.0 h, the viscosity increases with the increase of time; Between 2.0 h and 3.5 h, the viscosity decreases with increasing time. When the reaction time is 2.0 h, the apparent viscosity reaches maximum value. Compared with 0.6% aqueous solution of Guar collagen powder, the viscosity increased from 78.4 mPa·s to 104.4 mPa·s, with an overall increase of 33.2%. Accordingly, the variation of the water-insoluble content curve is as follows: the water-insoluble content decreases with increasing time between 1.0 h and 2.0 h. When the reaction time was 2.0 h~3.5 h, the water-insoluble content increased with increasing time. When the reaction time was 2.0 h, the content of water-insoluble content reached the minimum value. Compared with 0.6% solution of Guar collagen powder, the water-insoluble content was reduced by 0.39%. Although this is a multiphase reaction, the reaction speed is still relatively fast, indicating that the sufficient swelling of guar gum powder in the early stage plays an important role. It can be seen that a long reaction time is not conducive to increasing viscosity and reducing insoluble content, possibly due to excessive crosslinking. Therefore, the optimal reaction time was determined to be 2.0 h.

Effect of the amount of sodium 3-chloro-2-hydroxypropylsulfonate

Based on the temperature and time determined above, the amount of sodium hydroxide was fixed, and only the amount of sulfonating agent was changed. As can be seen from the trend chart of the influence of sulfonating agent dosage on guar gum viscosity in Fig. 2, the optimal value of sulfonating agent dosage is 0.5%. Therefore, the amount of sulfonating agent is set as 0.2, 0.4, 0.5, 0.6, and 0.8% in the single factor test. The temperature was 26 °C, the reaction time was 2 h, and the amount of sodium hydroxide (mass fraction of sodium hydroxide in guar gum) was 1.0%, the response results of viscosity and water-insoluble content are shown in Fig. 6.

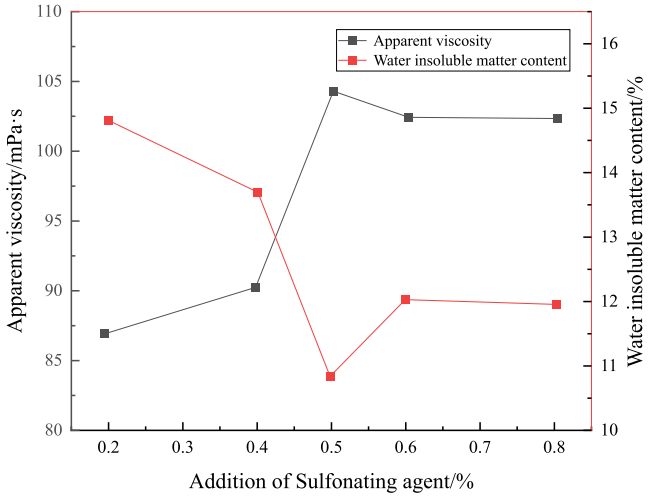

Figure 6. Effect of sulfonation agent dosage on viscosity and water-insoluble content of sulfonated guar gum

The above graph shows the variation of the apparent viscosity curve as follows viscosity increases with the increase of sulfonating agent dosage in the range of 0.2% to 0.5%. Between 0.5% and 0.8%, the viscosity decreases with the increase of sulfonating agent dosage, and the maximum viscosity is achieved when the dosage of sulfonating agent is 0.5%. Compared with 0.6% aqueous solution of Guar collagen powder, the viscosity increased from 78.4 mPa·s to 104.3 mPa·s, with an overall increase of 33%. Correspondingly, the curve of water-insoluble content varies from 0.2% to 0.5%, and the water-insoluble content decreases with increasing sulfonating agent dosage. Between 0.5%~0.8%, the content of water-insoluble increases with the increase of sulfonating agent dosage, when the dosage of sulfonating agent is 0.5%, the water-insoluble content obtains the minimum value. Compared with 0.6% solution of Guar collagen powder, the water-insoluble content was reduced by 0.45%. The reason is that with the passage of time, the degree of material participating in the reaction increases, as the viscosity increases and the insoluble substance decreases, the excessively long molecular chain will be involved in the side chain, hindering the reaction of the active hydroxyl group in the side chain. On the contrary, the part exposed to lye will be hydrolyzed, and the viscosity of sulfonated products will show a downward trend. Therefore, Therefore, the optimal mass percentage of sulfonating agents in gur gum is 0.5%.

Effect of the amount of sodium hydroxide

Based on the above-determined reaction temperature, reaction time, and amount of sulfonating agent, the amount of sodium hydroxide was varied to explore the effect of sodium hydroxide on the sulfonation modification of guar gum. As can be seen from the trend chart of the influence of base addition on Guar adhesive viscosity in Fig. 2, the optimal amount of sodium hydroxide is 1.0%. Therefore, the value of mass fraction of sodium hydroxide is set as 0.1, 0.5, 1, 1.5, and 2.0% in the single factor test. When the temperature is 26 °C, the reaction time is 2 h, and the dosage of sulfonating agent (mass fraction of sulfonating agent in guar gum) is 0.5%, the obtained results of viscosity and water-insoluble content are shown in Fig. 7.

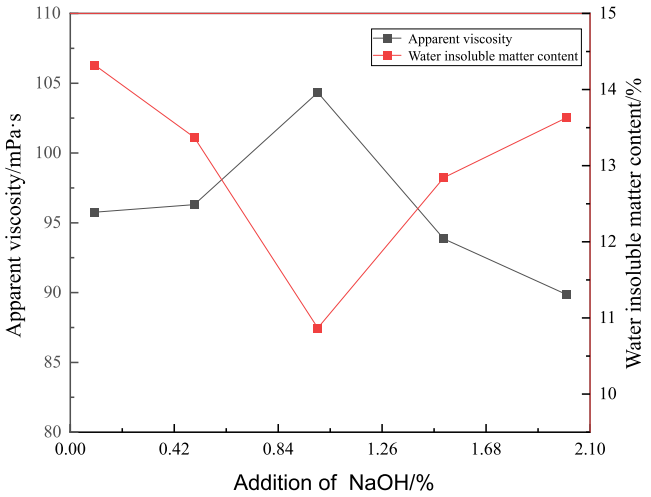

Figure 7. Effect of NaOH dosage on viscosity and water-insoluble content of sulfonated guar gum

Figure 7 shows that the apparent viscosity curve changes as follows: when the amount of NaOH ranges from 0.1% to 1.0%, the viscosity increases with the increase of the amount of NaOH. Between 1.0% and 2.0%, the viscosity decreased with increasing the amount of NaOH, and reached the maximum value when the amount of NaOH was 1.0%. Compared with 0.6% aqueous solution of Guar collagen powder, the viscosity increased from 78.4 mPa·s to 104.3 mPa·s, with an overall increase of 33%. Accordingly, the curve of water-insoluble content varied from 0.1% to 1.0%, and the water-insoluble content decreased with increasing the amount of NaOH. In the range of 1.0% to 2.0%, the content of water-insoluble content increased with the increase of the amount of NaOH. When the amount of NaOH was 1.0%, the content of water-insoluble content reached the minimum value. Compared with 0.6% solution of Guar collagen powder, the water-insoluble content was reduced by 0.42%. The reason may be that as the amount of catalyst increases, the catalytic effect becomes more significant and promotes the reaction in a positive direction, while excessive NaOH can lead to the hydrolysis of long polymer chains, resulting in a decrease in viscosity.

Considering various factors, the optimal sulfonation process parameters were obtained as follows: temperature 26 °C, time 2.0 h, sodium hydroxide dosage 1.0%, sulfonation dose 0.5%, viscose viscosity of the optimized product was 104.3 mPa·s, water-insoluble content was

10.87%. Compared with the modification method of hydroxypropyl gumelon gum proposed by C. Wang, we ensured that the water-insoluble content was greatly reduced and the viscosity was increased as well[25].

Performance as a fracturing fluid thickener

To further explore the effects of structural changes on the properties of sulfonated guar gum, the effectiveness of guar gum and sulfonated products as fracturing fluid thickeners was fully evaluated.

Temperature resistance

Prepare fracturing fluid with concentration of 0.3%, add 0.02% $Na_2B_4O_7$ solution and cross-link it to form a gel. The experimental temperature is RT~60 °C, and the HAAKE MARS60 complex fluid-specific tester (Germany Haaker Company) was used, which is a two-column design with the size W×D×H (mm) of 600×600×89[26]. The shear rate is set to be constant at 170 s^{-1} until the required experimental temperature is reached. The relationship between temperature and corresponding viscosity is regarded as a temperature resistance indicator for fracturing fluid thickening agents. Under these conditions, the temperature stability of guar gum and sulfonated products was evaluated, and the results are shown in Fig. 8.

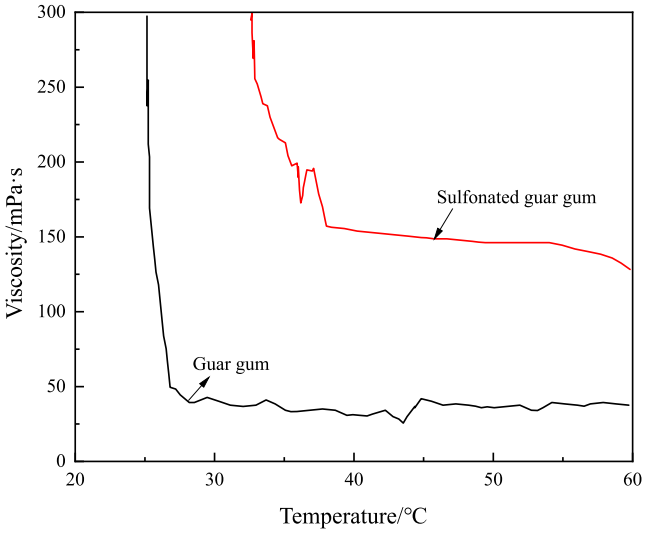

Figure 8. Viscosity-temperature relationship of guar gum and sulfonated guar gum solution

From the above figure, it can be seen that both cross-linked guar gum and sulfonated guar gum liquids have high viscosity at low temperatures, and their viscosity decreases significantly with increasing temperature but the degree of decrease is different between the two. As the temperature reaches 60 °C, the viscosity of cross-linked sulfonated guar gum remains at 122 mPa·s, while the viscosity of cross-linked unmodified guar gum is only 60 mPa·s, which means the viscosity of cross-linked sulfonated guar gum is 100% higher than that of the unmodified guar gum. It can be seen that the viscosity and the temperature stability of sulfonated guar gum have been significantly improved. The possible reason is that the extension and entanglement of polyhydroxy polymers in solution form their viscosity, but as the temperature increases, the extension of the polymer chain is inhibited and contracts, leading to a macroscopic decrease in viscosity. The addition of sulfonic acid groups as strong polar anionic groups maintains a significant repulsive force between polymer segments, allowing them to remain in an extended state at higher temperatures, demonstrating high-temperature stability.

Filtration of cross-linked guar gum

The guar gum and sulfonated guar gum solution with a mass concentration of 0.3% were prepared, and the gel was cross-linked with $Na_2B_4O_7$[27]. The filtration properties of the two gels were evaluated at 40, 60, and 80 °C respectively under the pressure of 3.5 MPa, and the results are shown in Table 3.

From Table 3, it can be seen that at the three test temperatures, the initial filtration loss, filtration coefficient, and filtration rate of sulfonated guar gum were lower than those of guar gum. The filtration rates at each temperature decreased by 34.23, 28.75, and 23.33%, respectively, indicating that the reduced filtration ability of sulfonated modified guar gum was improved compared to unmodified guar gum. This is because strong hydrophilic anionic groups are added to the sulfonation products, enhancing the repulsive force between polymer segments and making the polymer chains more extended. This conformation can improve the effectiveness with $Na_2B_4O_7$, enhance the density of the spatial network structure forming gel, and the water molecules are more firmly locked in the three-dimensional structure, thus reducing the filtering amount. As the temperature increases, the difference between the two gels gradually decreases. The reason is that high temperature destroys the cross-linking structure of gel, which makes the difference between the two filtration properties gradually reduce and become consistent.

Inhibition against clay swelling

During the fracturing operation, the contact between the fracturing fluid and the formation clay may lead to the hydration of the clay, leading to the expansion and dispersion of small particles. These particles may migrate with the fluid and cause damage to the formation[28–29]. The linear swelling test is the traditional method for evaluating the inhibitory capacity of inhibitors. For the sulfonated guar-modified system as well as the unmodified system, the ability of the two systems to inhibit

Table 3. Filtration performance evaluation results

Temperature /°C	Samples	Initial filtration loss /$m^3 \cdot m^{-2}$	Filtration coefficient /$m \cdot min^{-½}$	Filtration rate /$m \cdot min^{-1}$
40	Guar gum + $Na_2B_4O_7$	4.60×10^{-1}	8.00×10^{-4}	1.20×10^{-4}
	Sulfonated guar gum + $Na_2B_4O_7$	2.45×10^{-2}	5.00×10^{-4}	7.90×10^{-5}
60	Guar gum + $Na_2B_4O_7$	4.90×10^{-1}	1.00×10^{-3}	1.60×10^{-4}
	Sulfonated guar gum + $Na_2B_4O_7$	3.76×10^{-1}	7.23×10^{-4}	1.14×10^{-4}
80	Guar gum + $Na_2B_4O_7$	3.37×10^{-1}	1.14×10^{-3}	1.80×10^{-4}
	Sulfonated guar gum + $Na_2B_4O_7$	3.28×10^{-1}	8.75×10^{-4}	1.38×10^{-4}

the hydrological swelling of the clay can be visualized by comparing the linear expansion of the core in clear water with the two systems. Therefore, linear swelling experiments were carried out at 30 °C and atmospheric pressure to evaluate the inhibition performance of the two systems on the formation clays, and the results are shown in Figure 9.

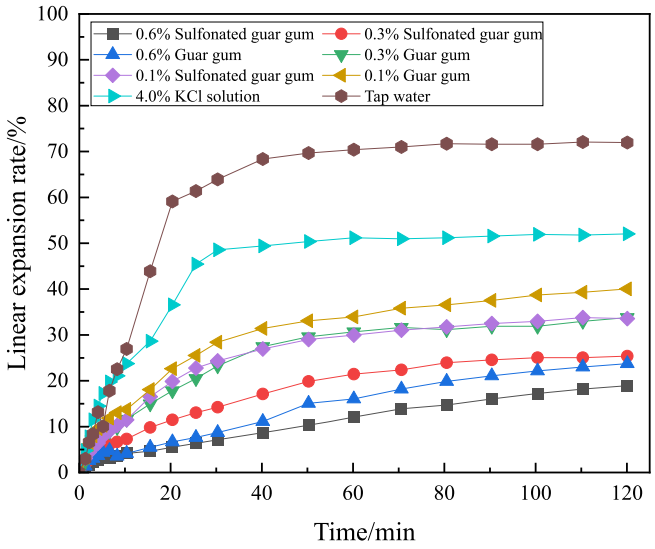

Figure 9. Hydration expansion of clay in guar gum and sulfonated guar gum solutions

From Figure 9, it can be seen that different concentrations of guar gum and sulfonated products have better inhibitory effects on clay than 4.0% KCl solution. With the increase of the concentration of guar gum and sulfonated gel solution, the inhibition of the solution on formation clay is enhanced, and the effect is best when the concentration is 0.6%. In contrast, the inhibitory effect of sulfonated guar gum (linear expansion rate of 19.7%) is better than that of unmodified guar gum of the same concentration (linear expansion rate of 23.6%), indicating that the inhibitory effect of guar gum on formation clay has been strengthened after sulfonation modification.

Characterization of sulfonated guar gum

Infrared Spectroscopy (IR)

The structure of guar gum and sulfonated guar gum was characterized by the infrared spectrometer. Figure 10 shows that the peak of wave number around 3384 cm^{-1} is the -OH stretching vibration on Guar gum, the peak of wave number around 2924 cm^{-1} is the C-H stretching vibration of $-CH_2$ in sugar unit, and the wave number around 1657 cm^{-1} is the ring vibration of galactose/mannose[30]. The wave numbers around 1195 cm^{-1} and 617 cm^{-1} show characteristic absorption peaks, which are sulfur-oxygen double bond (S=O) and carbon-sulfur bond (S-C), respectively, indicating the successful introduction of the sulfonic acid group $-SO_3H$, which confirms the modification[31].

Differential Scanning Calorimeter(DSC)

The thermal transition temperature of guar gum and sulfonated products was studied by DSC-822e differential scanning calorimeter[32]. Figure 11 shows that there are obvious endothermic peaks in both curves near 130 °C,

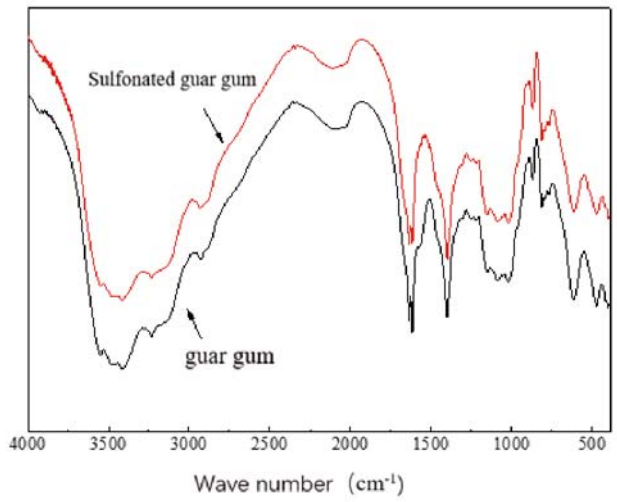

Figure 10. Infrared spectra of Guar gum and sulfonated products

and the endothermic temperature of sulfonated guar gum is lower, indicating a decrease in phase transition temperature after modification. The reason may be that the introduction of sulfonic acid groups enhances the extensibility of polymer chains, leading to a decrease in intermolecular and intramolecular hydrogen bond density, and thus a decrease in phase transition temperature.

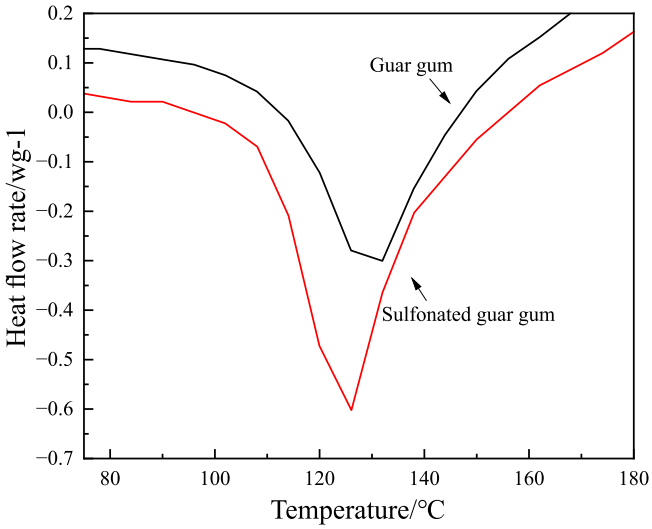

Figure 11. DSC of guar gum and sulfonated guar gum

Thermogravimetry Analysis (TGA)

A thermogravimetric analyzer was used to study the thermal stability and components of Guar gum and sulfonated products. Fig. 12 shows that the thermal decomposition process of guar gum is mainly divided into three steps. In the first step (T≤140 °C), the mass reduction is due to solvent evaporation. The weight loss rate of sulfonated guar gum around 100 °C is higher than that of the unmodified sample because the sulfonated guar gum powder is more loose, it adsorbs more water or ethanol. In the second step (230 °C≤T≤350 °C), the mass reduction of guar gum is due to decomposition or dehydration. In the third step (T > 350 °C), carbonization occurs, leading to a mass loss[33].

Elemental analysis

The elemental analyses of C, H, N, and S of guar gum and sulfonated products were conducted on an elemen-

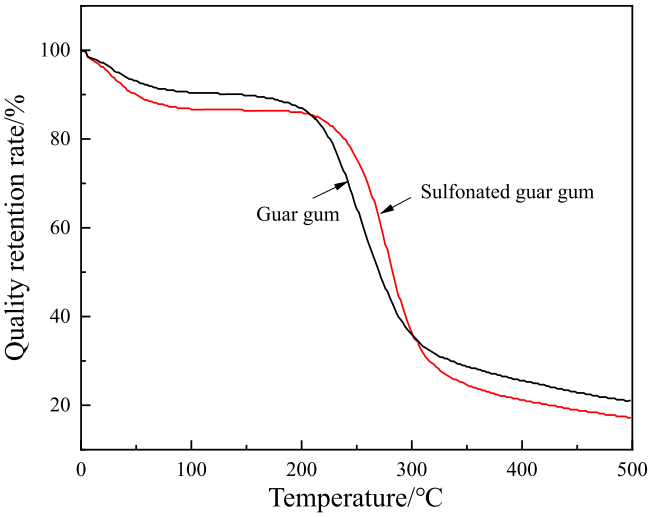

Figure 12. Thermogravigram of guar gum and sulfonated guar gum

tal analyzer, and the analyses and calculated results are shown in Table 4. From Table 4, it can be obtained that the change in the content of element N is not significant because it is mainly present in impurities such as water-insoluble content, and no element N was introduced into the system during the modification reaction, while the content of element C decreased by 1.580% and the content of element S increased by 0.142% because the presence of sulfonating agent introduced the element sulfur, which strongly indicates the successful introduction of the corresponding sulfonic group into the main chain of guar gum[34].

Table 4. Elemental analysis results

Samples	Elemental content /%				
	N	C	H	S	Others
Guar gum	0.520	39.600	5.946	0.630	53.304
Sulfonated guar gum	0.500	38.020	5.396	0.772	55.312

CONCLUSION

To develop high-performance guar gum derivatives, sulfonated guar gum was prepared using sodium 3-chloro-2-hydroxypropylsulfonate as a modifier. The optimum modification conditions of sulfonated guar gum were studied. Under the conditions of reaction temperature 26 °C, reaction time 2.0 h, mass fraction of 1.0% sodium hydroxide and 0.5% sodium 3-chloro-2-hydroxypropylsulfonate (mass ratio of guar gum), the apparent viscosity of 0.6% sulfonated guar gum aqueous solution was 33% higher than that of original guar gum powder and the water-insoluble content was reduced by 0.42%. Further performance evaluation shows that sulfonattion significantly reduces the content of water-insoluble substances in guar gum, increases the viscosity of guar gum, enhances the temperature resistance, and reduces the filtration capacity of the cross-linked guar gum. IR, DSC, TGA, and EA all match well with the structure of sulfonated guar gum, indicating that good sulfonated products have been prepared. This work provides a reference for research in related fields and can expand the application of guar gum products in oilfield development.

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