Research Article

Synthesis, Characterization, and Performance Evaluation of Starch-Based Degradable Temporary Plugging Agent for Environmentally Friendly Drilling Fluid

Wuzhen Gong,1,2,3 Weian Huang,1,2,3 Jian Liu,4 Jiaqi Zhang,5 Ting Yv,1,2,3 Lin Jiang,1,2,3 and Zengbao Wang1,2,3

1Shandong Key Laboratory of Oilfield Chemistry, School of Petroleum Engineering, China University of Petroleum (East China), Qingdao 266580, China
2Key Laboratory of Unconventional Oil & Gas Development, China University of Petroleum (East China), Qingdao 266580, China
3School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, China
4China Petroleum Western Drilling Engineering Co., Ltd., Urumqi, XinJiang 830011, China
5CNPC Engineering Technology R&D Company Limited, Beijing 102206, China

Correspondence should be addressed to Weian Huang; masterhuang1997@163.com

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Reservoir protection in well drilling and well completion is one of the most significant challenges that have been connected with the quality of the temporary plugging zone and the recovery value of the reservoir permeability when the foreign water invaded into the reservoir copied with the temporary plugging agents. The regular temporary plugging agents are linked with high demand for the matching rate about the pore throat of formation, effect of a single, and poor environmental performance, etc. which markedly impact the operational efficiency. This work reports the synthesis and characteristic of starch-based degradable water-absorbent resin to protect the layer during drilling. Both degradable and excellent SDTA through introducing the nanometre calcium carbonate composites which used as the rigid core were synthesized, characterized, and revalued with standard methods. After purification, there were some groups including the carboxylic acid group, amide group, methyl group, and S=O which reflected the successful synthesis of the monomers. The composites displayed remarkable salt resistance and calcium resistance with 5% and 0.5% as well as thermal stability of 130°C and degradation rate of 50%, respectively. Results also demonstrated that SDTA composites could make the mud cake structure more compact and exhibit self-adaptive to the formation. The SEM images of mud cake treated SDTA revealed that the mechanism could be base on the collaborative action of the structure compact and holes plugging to form an impressive filter cake which could effectively avert the water molecules invasion into the reservoir. Hence, SDTA composites could be a suitable material as a degradable temporary plugging agent for well drilling and completion.

1. Introduction

Reservoir protection has been recognized as a major challenge in well drilling and well completion especially when the foreign fluid invaded into the reservoir [1, 2]. This has been linked with a series of adverse consequences while reservoir formations interact with the foreign fluid which eventually results in the solid-phase migration, clay expansion, and fluid incompatibility and ultimately gives rise to the decrease of near-well zone permeability and reservoir productivity [1–3]. Adequate efforts have been made through various methods to protect the oil and gas layer, one of which is screen temporary plugging technology. It is important for the performance of temporary plugging agents to select the temporary plugging materials. Water-absorbent resin is a kind of polymer with hydrophilic groups, which is associated with a three-dimensional network structure with a certain degree of crosslinking, can swell in contact with water but not dissolve, and exhibits variability and self-adaptability remarkably [4–8]. Strategic design of environmentally
benign and biodegradable water-absorbent resin is a prominent objective of the screen temporary plugging technology in well drilling and well completion. Miao et al. [9] prepared a kind of water-absorbent resin used as drilling plugging material, which was introduced by calcium carbonate to improve its strength and water absorbency. The elastic colloid was formed, which could squeeze deformation into the pores of the formation and promote clogging as well as demonstrate notable sealing effect after water absorption and resist the extrusion pressure of 0.3 MPa. Lai et al. [10] developed a water-absorbent resin with a double network structure, which was used for the drilling plugging agents that showed outstanding performance in resisting the pressure of 16.2 MPa and simultaneously in salt tolerance. Combining the acrylic acid with glass fiber and silane coupling agent, Niu et al. [11] investigated the composite plugging water-absorbent resin which could expand 250 times to resist pressure of 2 MPa in the 1–2 mm crack. Di et al. [12] designed a super water-absorbent resin plugging agent which can flexibly select the resin with various particle sizes for clogging in the light of the physical properties of the layers. Albeit, the synthetic polymeric compound has excellent properties such as good expansion and water plugging [13], but they show poor high thermal stability, degradation, and toxicity [14]. The starch-based water-absorbent resin as a crosslinked polymers connecting with a three-dimensional network structure has not only the starch degradability but also the thermal resistance and salt resistance of monomer [15]. This makes it to be integrated into diverse formations in industries such as agriculture, pharmaceuticals, foods, oil, and gas, [16]. Particularly, the starch-based water-absorbent resin had made certain progress in the profile control and water plugging in petroleum production and development. Ward et al. [17] prepared a starch-based tackifier which can be used for adjusting the flow model on the ground that many additives significantly affected fluid rheology and thixotropy and hindered their real-time drilling applications. Thomas et al. [18] studied the heat stability of starch copolymer which was designed as the plugging agent in the water base drilling fluid (WBDF). Lutfor et al. [19] made a super water-absorbent resin associating acrylic acid methyl ester with sago starch to compare the salt solutions under different valences. Wolff et al. [20] designed a degradable super water-absorbent resin bonding uncrosslinked nonionic polysaccharide polymer which can absorb tens of times of its own weight of seawater as well as be biodegraded by 98% after 28 days of injection into the bottom hole.

At present, the studies about the starch-based super water-absorbent resin both at home and abroad were almost product developments, and the basic theoretical researches were weak. There are now no reports on the systematic and in-depth achievements of starch-based water-absorbent resin used for the temporary plugging agent, especially no reports on the degradation of starch-based resins by organic/inorganic/nanomaterials blending. Therefore, to modify the starch water-absorbent resin and introduce nanometre calcium carbonate as the rigid core to improve its performance comprehensively will be a great idea to prepare a degradable plugging agent for effective and efficient reservoir protection. Herein, we designed starch-based degradable temporary plugging agent (SDTA) that could serve as an excellent WBDF additive in oil and gas drilling operations. Their mode of action could be premised on the synergetic effort of the structure compact and the plugging ability that could allow prevention of foreign fluid from engrossing into the reservoir.

2. Experimental

2.1. Materials. Corn starch, acrylamide (AM), and acrylic acid (AA) were obtained from Aladdin Chemistry Co., Ltd. (China). Sodium persulfate (SPS), N,N'-methylene diacrylamide (MBA), and sodium hydroxide were provided by Sinopharm Chemical Reagent Co., Ltd. (China). Nano calcium carbonate, unidirectional pressure sealant DF-1, water soluble temporary plugging agent FC-9, and oil soluble temporary plugging agent TJ-1 were purchased from Shanghai Yuanjiang Chemical Co., Ltd. (China). All the chemicals utilized are of analytical grades.

2.2. Synthesis of SDTA. The starch-based degradable temporary plugging agent was prepared through the graft copolymerization. The total reactant concentration of starch and grafted monomer (AA, AM, and salt resistance monomers) was 10%. The mole ratio of monomer to starch is 4: 1, and the mole ratio of the monomers in the composites is 1: 2: 1 of AA, AM, and salt resistance. The graft copolymerization was initiated finally by the introduction of 0.5% SPS as initiator and 0.7% MBA as crosslinking agent in the neutral pH condition. This was followed by the gelatinization for 30 min at 50 °C and then continual reaction for 3 h at °C. Thereafter, a specified amount of starch was dissolved in water and gelatinized under nitrogen inert atmosphere for 30 min to get rid of the dissolved oxygen in the mixtures at room temperature. On the other hand, the initiator was added, prepriming for 15 min, and then the monomers and crosslinkers, respectively, dissolved in water were added successively in the reaction of 3 h at 70°C. The composites mixed with acetone were transferred in the Soxhlet extractor for 10 h to purify. This was then washed with ethanol, dried at ≈70°C, and pulverized into a fine powder to obtain starch-based water-absorbent resin. This was followed by combining the synthesized starch-based water-absorbent resin with 15% and 500 mesh nanometer calcium carbonate (additive) and sodium stearate (activator). After completion of the reactions, the composites were dissolved in acetone. The solution was coped with Soxhlet extractor which was then retrieved by filtration by ethanol and dried for 10 h at 70°C under vacuum. The materials were then crushed and sifted to get the starch-based degradable temporary plugging agent (SDTA).

2.3. Characterization. FTIR spectrum of SDTA and starch were obtained using Fourier Transform infrared spectrometer (NEXUS FT-IR). About 2 mg pellet starch and SDTA screened through 200 mesh were prepared from 200 mg potassium bromide.

Morphologies of the SDTA particles of 2 mm diameter were observing under the scanning electron microscope (SEM) EVO-15/LS. Thermogravimetric analysis (TGA)
analyzer (HTG-1) was used to evaluate the thermal stability of the starch and SDTA under a nitrogen atmosphere at 25–900°C.

2.4. Performance Evaluation

2.4.1. Water Absorbency Evaluation of SDTA in Drilling Muds. The 4% Na-bentonite slurry was prepared in the water absorbency experiment. Its formulation was 4% bentonite, 0.2%–0.4% NaOH, and 0.2%–0.3% Na₂CO₃. The slurry was vigorously stirred on a magnetic stirrer for 30 min with the same increment amount for five successive Na-bentonite added. Starch-based water-absorbent resin with 20% calcium carbonate content was selected, and particle sizes of which are 100-200 mesh and 40-100 mesh. 1% SDTA was added to 4% base muds. The system was stirred for 2 h to test water absorbency evaluation of SDTA under various particle sizes that distribute. This was transferred into different concentrations of NaCl solution (2%, 6%, 10%, 15%) and CaCl₂ (0.1%, 0.3%, 0.5%, 0.7%, 0.9%), respectively, to measure the water absorption ratio. This was put into solutions with varying pH values to try out its water absorption ratio under pH of 5, 6, 7, 8, 9, 10, and 11, which adjusted by hydrochloric acid and sodium hydroxide. Then, this was added to deionized water to measure its water absorption rate and water absorption ratio at different temperatures.

2.4.2. Plugging Property of SDTA. In this study, approximately 15% SDTA crushed and sieved in 100 mesh sizes...
was added to 120 mL fresh water to carry out the filtration test of sand bed under different pressures after 2 h of sufficient water absorption. The sand particle size is 40-100 mesh, and the addition amount is 300 g in this experiment.

2.4.3. Thermal Stability of SDTA in Drilling Muds. 1.5% SDTA was put into 4% Na-bentonite slurry. After that, it was hot rolled in the hot roller oven for 16 h at 120°C, 130°C, and 140°C, respectively. Upon completion, the system was allowed to cool to the room temperature. Then, the Fanna 50SL rotational rheometer was used to measure the rheological properties such as apparent viscosity (AP), plastic viscosity (PV), and yield point (YP) at room temperature using the following equations:

\[
\begin{align*}
\text{AV} &= \frac{\theta_{600}}{2}, \\
\text{PV} &= \theta_{600} - \theta_{300}, \\
\text{YP} &= 0.511(2\theta_{300} - \theta_{600}).
\end{align*}
\]

![Figure 3: TGA of (a) starch and (b) SDTA.](image-url)
D10 = 1.798 μm
D50 = 10.08 μm
D90 = 53.88 μm

**Figure 4:** Particle size distribution of 4% bentonite-based slurry.

D10 = 65.22 μm
D50 = 252.4 μm
D90 = 614.6 μm

**Figure 5:** Particle size distribution of 100-200 mesh water absorbent in 4% bentonite-based slurry.
D10 = 14.50 μm
D50 = 125.2 μm
D90 = 431.5 μm

Figure 6: Particle size distribution of 200 mesh above water absorbent in 4% bentonite-based slurry.

Figure 7: SDTA absorbency test with different particle sizes.
2.4.4. Salt Resistance of SDTA. The salt resistance study was carried out on 4% Na-bentonite slurry added to 1.5% SDTA under the different NaCl contents of 2%, 4%, 6%, 8%, and 10% as well as the varying CaCl₂ content of 0.1%, 0.3%, 0.5%, 0.7%, and 0.9%, respectively, to test each rheological properties and filtration amount.

2.4.5. Degradability of SDTA. PVC (polyvinyl chloride) was a nonbiodegradable material, while PVC powder was soluble in tetrahydrofuran. 10 g of PVC pulverized into a fine powder was dissolved into 40 mL tetrahydrofuran and 10 g of SDTA crushed and sieved in 40-100 mesh sizes, which was added to the mixed solution slowly. Then, it was poured into a flat glass plate after stirring even. Upon completion, the system was allowed to dry at 40°C to prepare the PVC sheet which was cut into 1×1 cm block weighed. An appropriate amount of fresh soil was transferred into a jar, and the prepared samples were buried in the soil placed in a thermostatic chamber at 30°C and 100°C with and without air, respectively. One of samples was taken out after 30 d, 60 d, and 90 d and was rinsed with ethanol. After removing impurities, the sample was washed several times with distilled water and dried to constant weight. Then, the degradation rate X was calculated as

\[
X = \frac{(1 - c)m_0 - (m_1 - m_0c)}{(1 - c)m_0} \times 100\%
\]

where \(X\) is the degradation rate, %; \(m_0\) is the initial weight of the sample, g; \(m_1\) is the sample weight degraded, g; and \(c\) is the quality percentage of PVC, %.

2.4.6. Environmental Protection Property Evaluation. Chemical oxygen demand (COD) was accomplished in accordance with the China’s standard GB11914 Determination of Chemical Oxygen Demand of Water-dichromate Method for measuring the amount of a reducing substance in a water sample that needs to be oxidized. The biochemical oxygen demand (BOD) test was obtained using Model 880 digital BOD5 tester. Environmental protection property evaluation criterial is that biodegradability is good during BOD5/COD more than 45%, middle more than 30% and less than 45%, and difficult less than 30%.

### Table 1: Particle size distribution of SDTA with different particle sizes.

| Particle size | >20 mesh | 20-40 mesh | 40-100 mesh | 100-200 mesh | <200 mesh |
|---------------|----------|------------|-------------|--------------|----------|
| Median particle size D₅₀/μm | 772.2 | 570.6 | 521.4 | 249.4 | 118.8 |

Figure 8: Water absorption of SDTA in NaCl and CaCl₂ solution.

\[ \text{NaCl} \quad \text{CaCl}_2 \]
3. Results and Discussion

3.1. Synthesis of SDTA. FTIR spectra of starch and SDTA are shown in Figure 1. As shown in the spectra for the starch, the peak at 3424 cm\(^{-1}\) is due to the O-H stretch of stretching vibration. The C-H bending vibration appears at 2929 cm\(^{-1}\) and 928 cm\(^{-1}\), while the peaks at 1159 cm\(^{-1}\) and 1080 cm\(^{-1}\) are characteristic features of C-O-C stretching vibration and C-O skeleton vibration, respectively. The SDTA spectrum has a weak O-H stretching vibration absorption peak at 3424 cm\(^{-1}\). The -COONa characteristic peak is seen at 1654 cm\(^{-1}\). It also shows that the vibration absorption peak at 1452 cm\(^{-1}\) is attributed to -O-C-O- symmetric and asymmetric indicating starch grafts with acrylic acid. The bending vibration peak of NH\(_2\) and the absorption peak of CH\(_4\) can be observed at 1540 cm\(^{-1}\) and 2929 cm\(^{-1}\), respectively, which

![Figure 9: Water absorption of SDTA at different pH values](image9.png)

![Figure 10: Water absorption of SDTA at different temperatures.](image10.png)
demonstrate acrylamide band starch. The special absorption peak of S=O is shown at 1202 cm\(^{-1}\), which manifests that salt-resistant monomers are grafted with starch. Therefore, the FTIR reflects the successful synthesis of SDTA of the monomers in both composites.

3.2. Microstructural Characterization. Figure 2 represents the SEM image of the surface of SDTA. This represents that SDTA has a rough surface and holes which are evenly distributed. Since many gullies of different depths and multilayer honeycombs existing, it could firmly absorb water molecules on its surface, which is also the structurally internal cause of the excellent water-absorbent performance of starch super water-absorbent resin products.

3.3. The TGA Results. The high-temperature tolerance of plugging agents is recognized vital to their efficiency during the drilling process as a consequence of a high temperature as a rule experience in well bore. The TGA displaying the thermal stability of starch and SDTA is displayed in Figures 3(a) and 3(b). In Starch of Figure 3(a), about 10% weight loss was experienced as the temperature rises to 275°C from room temperature. The loss at this stage could be owing to moisture evaporation. A further decrease gradually accounted for 60% up to a temperature of 375°C. The starch materials started going through decomposition at this stage. The last part of the graph shows further decomposition of the starch over 375°C to around 600°C. And there is no obviously discern weight reduction until 730°C that is reached. Eventually, about 15% residue was still present.

In contrast, in the TGA graphical representation of SDTA (Figures 3(b) and 3(a)), steady reduction of SDTA’s weight could be observed from room temperature to 200°C. This might be the response of the water molecule volatilization that forms the SDTA with 5% declination in weight. Above this temperature to 380°C or so, apparent weight diminish is clearly shown as a result of rapid decomposition, and there are around 40% reduction. The last part of the graph shows further decomposition of the starch over 380°C to around 735°C. When heating was continued to 900°C, it resulted in weight loss by occasion of the fracture

| Condition | AV/MPa·s | PV/MPa·s | YP/pa | G10''/pa | G10'/pa | API/mL | HTHP/mL |
|-----------|---------|---------|-------|---------|--------|--------|---------|
| Before aging | 58 | 37 | 21 | 5.5 | 9 | 4.4 | / |
| 120°C/16h | 64 | 40 | 24 | 5.5 | 10 | 4 | 13.6 |
| 130°C/16h | 61 | 38 | 23 | 6 | 9.5 | 4 | 13.2 |
| 140°C/16h | 10.5 | 10 | 0.5 | 0.25 | 0.5 | 8 | 31.4 |

Table 3: Test of sand bed compressive strength of SDTA in bentonite slurry.

| Sand mesh | 1 | 2 | 3 | 4 |
|-----------|---|---|---|---|
| <20 mesh | 2 min penetration | Rapid penetration | Rapid penetration | Rapid penetration |
| 20-40 mesh | 30 min no penetration | 25 min penetration, filtration loss 4.1 mL | 22 min penetration, filtration loss 9.1 mL | 16 min penetration, filtration loss 16.7 mL |
| 40-60 mesh | 30 min no penetration | 30 min no penetration | 28 min penetration, filtration loss 1.2 mL | 26 min penetration, filtration loss 5.2 mL |
| 60-80 mesh | 30 min no penetration | 30 min no penetration | 30 min no penetration | 30 min no penetration |
| 80-100 mesh | 30 min no penetration | 30 min no penetration | 30 min no penetration | 30 min no penetration |
| 100-200 mesh | 30 min no penetration | 30 min no penetration | 30 min no penetration | 30 min no penetration |
| >200 mesh | 30 min no penetration | 30 min no penetration | 30 min no penetration | 30 min no penetration |

Table 2: Test of compressive strength of bentonite slurry with SDTA.

| Content/% | 1 | 2 | 3 | 4 |
|-----------|---|---|---|---|
| 0.5 | 30 min no penetration | 30 min no penetration | 28 min penetration, filtration loss 2.4 mL | 17 min penetration, filtration loss 16.5 mL |
| 1 | 30 min no penetration | 30 min no penetration | 27 min penetration, filtration loss 2.2 mL | 30 min no penetration |
| 1.5 | 30 min no penetration | 30 min no penetration | 30 min no penetration | 30 min no penetration |
| 2 | 30 min no penetration | 30 min no penetration | 30 min no penetration | 30 min no penetration |
of the graft side chain. Eventually, approximately 40% residue was still present. Hence, SDTA showed better thermal stability than starch.

3.4. Performance Evaluation of SDTA

3.4.1. Water Absorbency of ADTA

(1) Absorbency of Different Particle Sizes. The absorbency of different particle sizes is presented in Figures 4–6. In the 4% base muds, it could be observed that the median grain diameter of the solid phase was 10.08 μm. The SDTA median grain diameter of 100-200 mesh sizes, above which was 125.2 μm, was 252.4 μm. The SDTA had a larger particle size, comparing with solid phase sizes in the 4% based muds, distribution range of which was from tens of microns to hundreds of microns. And the results showed that the larger the particle size of SDTA was, the larger the particle size after expansion in the muds was.

Table 5: Anti-NaCl performance test of SDTA in bentonite slurry.

| Content | AV/MPa·s | PV/MPa·s | YP/MPa·s | G10''/pa | G10'/pa | API/mL |
|---------|----------|----------|----------|-----------|----------|--------|
| 0       | 27       | 21       | 6        | 2         | 3        | 4.2    |
| 2%      | 29       | 23       | 6        | 2.5       | 4        | 4.2    |
| 4%      | 25       | 20       | 5        | 1.5       | 3        | 4.8    |
| 6%      | 23       | 18       | 5        | 1.5       | 2.5      | 5.8    |
| 8%      | 14       | 11       | 3        | 0.5       | 1        | 9.6    |
| 10%     | 15       | 11       | 4        | 1         | 2        | 9.8    |

Table 6: Anti-CaCl₂ performance test of SDTA in bentonite slurry.

| Content | AV/MPa·s | PV/MPa·s | YP/MPa·s | G10''/pa | G10'/pa | API/mL |
|---------|----------|----------|----------|-----------|----------|--------|
| 0       | 27       | 21       | 6        | 2         | 3        | 4.2    |
| 0.1%    | 24       | 19       | 5        | 1         | 2.5      | 5      |
| 0.3%    | 20       | 16       | 4        | 1.5       | 2.5      | 6.6    |
| 0.5%    | 17.5     | 14       | 3.5      | 0.5       | 1        | 8.2    |
| 0.7%    | 9.5      | 9        | 0.5      | 0.5       | 1        | 13.4   |
| 0.9%    | 6        | 5        | 1        | 0         | 0.5      | 15.8   |

Figure 11: Rate of degradation of SDTA under different conditions.
The result of the SDTA absorbency test with different particle sizes is shown in Figure 7. It could be observed that the water absorbency ratio of SDTA increased steadily with time and basically reached the swelling equilibrium at 80 min. For SDTA with different particle sizes, the smaller the particle size was, the more enough the contact with an aqueous solution will be, and the faster the equilibrium will be reached. When equilibrium was reached, the water absorbency ratio of SDTA with different particle sizes differed little.

As presented in Table 1, the median particle size after absorbing was greater than 500 μm when the SDTA particle size was greater than 100 mesh. This indicates that large particle size was not conducive to the adjustment of drilling fluid rheology, and it was not easy to pass through the vibrating screen, affecting the reuse.

(2) Absorbency in Salt Solution. As presented in Figure 8, the water absorbency ratio of SDTA decreased with the increase of NaCl and CaCl₂ salt solution concentration. It drastically declined in 6% NaCl solution and 0.5% CaCl₂, indicating that water absorption showed a positive correlation with the higher valence state of ions in salt solution. Hence, high-valence ions of Ca²⁺ and Mg²⁺ compound with COO⁻ can form a molecular complex to increase the crosslinking degree of temporary plugging agent and limit the swelling of resin.

(3) Absorbency under Different pH Values. The results of the water absorption of SDTA at different pH values are shown in Figure 9. As can be seen, the water absorbency ratio of SDTA was smaller when the pH value was 11 than other conditions, which was due to the drop of osmotic pressure resulted from the increase of metal ion concentration in the solution. Therefore, SDTA can be used in pH 5-11 environment.

(4) Absorbency under Different Temperatures. In Figure 10, the higher the temperature was, the faster the equilibrium speed will be reached. And the water absorbency ratio was lower during the water absorbency balance with the increase of the temperature. Although the water absorbency ratio dropped, the decreasing range was not big. In their equilibrium stage, the water absorbency ratio dropped from

| Samples              | COD/g·mL⁻¹ | BOD5/g·mL⁻¹ | BOD5/COD | Biodegradability     |
|----------------------|------------|-------------|----------|----------------------|
| Ultra-fine calcium carbonate | 21.3       | 30.30       | 142.31%  | Easy to biodegrade   |
| DF-1                 | 108.6      | 17.1        | 15.7%    | Difficult to biodegrade |
| FC-9                 | 1847.4     | 0.22        | 0.01%    | Difficult to biodegrade |
| TJ-1                 | 3882.2     | 0.72        | 0.02%    | Difficult to biodegrade |

| Core number | Length/cm | Diameter/cm | Porosity Rd/% |
|-------------|-----------|-------------|---------------|
| 1           | 2.92      | 2.51        | 12.84%        |
| 2           | 3.37      | 2.5         | 11.96%        |
| 3           | 2.81      | 2.5         | 17.45%        |
126 g·g⁻¹ to 92 g·g⁻¹ when the temperature rose from 20°C to 100°C.

3.4.2. Plugging Property. Table 2 shows that the sealing effect was drastically improved with the increase of the resin content. The sand bed test suffered from the hasty penetration rate and large filtration under 4 MPa during less than 1% SDTA. However, in greater than 1%, the drilling fluid cannot penetrate the sand bed and can resist the pressure of 4 MPa.

As presented in Table 3, the SDTA can promote the sealing effect with large particle size. At a pressure of 4 MPa, the sand bed could be penetrated by the bentonite slurry at a faster speed with a large filtration loss in less than 60 mesh sizes of STDA up which there was no penetration and pressure resistance of 4 MPa.

3.4.3. Temperature Resistance. It could be observed that SDTA had excellent performance before and after aging at 130°C with only 13.2 mL of filtration loss at high temperature and high pressure (shown in Table 4). However, the viscosity and shear stress dramatically diminished, and the water loss increased after aging at 140°C, demonstrating that the temperature resistance of SDTA was complete denaturation. Hence, its thermal stability was 130°C.

3.4.4. Salt Resistance. The change in properties of drilling muds was small with lower than 6% NaCl (shown in Tables 5 and 6). However, the rheological properties of AV and PV dramatically decrease, and the medium pressure water loss increased by 1 time from 4.2 mL. Therefore, SDTA can resist to 6% NaCl.

Meanwhile, the rheological properties of AV, PV, and YP also inclined with the increase of the CaCl₂ content. The API filtration loss increased from 4.2 mL to 13.4 mL as the CaCl₂ content added to 0.7%. Hence, SDTA properties were poor in the environment with the CaCl₂ content greater than 0.7%.

3.4.5. Degradability. Figure 11 shows that the degradation rate of SDTA in the soil can reach more than 50% under the temperature of 30°C and 100°C. The degradation rate was relatively high, and the air had little impact on the degradation rate of SDTA in the soil, which had more to do with the temperature.

3.4.6. Environmental Protection Property. From Table 7, it could be observed that the ultra-fine calcium carbonate exhibited favorable biodegradability to protect the environment, while DF-1, FC-9, and TJ-1 were difficult to be biodegradable and not environmentally benign.

3.5. Action Mechanism of SDTA

3.5.1. SEM Analysis of Mud Cake. The surface of mud cake was investigated with SEM. Figure 12(a) represents the SEM image of the bentonite-based mud cake. It shows a rough surface and obvious pores. The coarse and pore surface of the mud cake were effectively plugged by forming a thin film using SDTA which were deformable particles after absorbing water (Figure 12(b)). As a result, it can improve the quality of mud cake and the sealing effect of formation and prevent the reservoir from being polluted by foreign fluid.
3.5.2. Self-Adaptivity of SDTA for Different Permeability Formations

(1) Permeability Recovery Values. As shown in Table 8, the SDTA exhibited remarkable plugging performance for cores under different permeability. The permeability of contaminated cores under the initial permeability test pressure difference was 0. The recovery value of core permeability of varying permeability was greater than 85%. And the recovery value of core permeability of low permeability and small porosity was above 90%. They reflected the prominent self-adaptability of SDTA as a temporary plugging agent to the formation.

(2) Return Pressures. The recovery value of core permeability increased with the increase of the return pressures is displayed in Figure 13, which can reach more than 85% for 1# and 2# cores under 0.4 MPa, while for 3# core under 0.6 MPa. This is attributed to the lower permeability recovery which is not enough to destroy the dissolution zone even under the condition of small return pressures. A further damage will be done gradually in the plugging zone when the return pressures reached the critical value. The permeability recovery value rapidly rose, so as to achieve an essential plugging removal effect. The critical pressure value of 3# core at the end of the analysis is larger than that of 1# and 2# cores, which is owing to the 3# core with higher permeability promoting the temporary plugging agent into the deeper formations which need greater return pressure to break the plugging zone. The test results of the relationship between the core return pressure and permeability of high permeability and low permeability showed that the starch-based temporary plugging agent had strong self-adaptability to the pore structure of the formation, good blocking effect, small return pressure, and significantly less than the pressure drop of reservoir mining and can realize backflow and plugging.

4. Conclusions

The potential of the starch-based degradable temporary plugging agent (SDTA) associating with nanometer calcium carbonate used as the rigid core was investigated. This material exhibited outstanding performance to plug the formations by forming a thin film. The composites display superb thermal stability which is 130°C. About 40% residue was still present for SDTA compared to that of 15% for starch. The high-valence ions Ca^{2+} and Mg^{2+} linked with COO- could produce a molecular complex to promote the crosslinking degree of temporary plugging agent and conserve the swelling of resin. The environment of the pH value of 5-11 is the optimal pH condition. The pressure resistance using SDTA of more than 60 mesh sizes can reach 4 MPa without penetration. The percentage salt resistance was 0.6% for NaCl and 0.7% CaCl_2 solution. Approximately 55% degradation rate was recorded for SDTA after 90 d with air at 100°C. The value of BOD5/COD was 142.31% indicating that the biodegradability of this material was remarkable. The 4% bentonite slurry treated by SDTA revealed the formation of a thin film which is ascribed to the SDTA after absorbing water forming deformable particles to effectively seal the formation and prevent the reservoir from being polluted by foreign fluid. Overall, the SDTA composite could act as temporary plugging agent. This study gives an environmentally benign insight to synthesize a biodegradable material for oil and gas exploration and development.

Nomenclature

AR: Analytically pure
CP: Chemically pure
AV: Apparent viscosity
PV: Plastic viscosity
YP: Yield point
X: degradation rate, %
\(m_{i0}\): the initial weight of the sample, g
\(m_i\): the sample weight degraded, g
c: the quality percentage of Polyvinyl chloride, %.

Data Availability

The data are in the tables.

Conflicts of Interest

The authors declare no conflict of interest.

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