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Article

Application of Hydrothermal Carbon/Bentonite Composites in Improving the Thermal Stability, Filtration, and Lubrication of Water-Based Drilling Fluids

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Abstract

With the increasing harsh drilling environments encountered more frequently than ever before, developing environmental benign and multifunctional additives is essential to formulate high performance drilling fluid. Herein, hydrothermal carbon/bentonite composites (HCBCs) were prepared by hydrothermal carbonization reaction using soluble starch and sodium bentonite as raw materials. A systematic investigation was conducted into the effects of HCBC concentration on the rheological, filtration, and lubricating characteristics of xanthan gum, modified starch, and high-temperature polymer slurries. These properties were evaluated before and after exposure to hot rolling at different temperatures. The hydroxyl radical scavenging properties of HCBC was evaluated. Observation showed plentiful micro- and nano-sized carbon spheres deposited on the bentonite particles, endowing the bentonite better dispersion. HCBCs could maintain the water-based drilling fluids' rheological profile stable, decrease filtration loss and improve the lubrication with relatively low concentrations. The excellent properties were attributed to the highly efficient scavenging of free radicals and stabilization of bentonite particle dispersion.

Keywords: water-based drilling fluid; high temperature degradation; hydrothermal carbon/bentonite composites; radical scavenging; properties stability

1. Introduction

With the increasingly demand on resources, more and more complex formations such as deep and ultradeep reservoirs, unconventional shale oil and shale gas, and geothermal reservoirs are frequently encountered than ever before. To address these needs, a new generation of high-performance water-based drilling fluid is required—one that delivers better hole cleaning, enhanced wellbore stability, stable rheology, and low filtration under high-temperature conditions, behaving like the performance attributes and benefits of oil-based drilling fluids [1,2].

Water-based drilling fluid typically contain bentonite and polymers to impart the desired rheological and filtration properties [3]. The main component of bentonite is montmorillonite. Montmorillonite has a 2:1 layered crystal structure, composed of an aluminum-oxygen octahedral sheet sandwiched between two silicon-oxygen tetrahedral sheets, and contains exchangeable cations (such as Na⁺, K⁺, Ca²⁺, etc.). Many unit cells are stacked over each other and form layered structures [4]. Due to the isomorphic replacement of cations within the structure, the crystal surface of montmorillonite is negatively charged. Additionally, the fracturing of Al-O and Si-O result in the electrical properties of end surfaces [5]. When dispersed in aqueous environment, house of card

structures would be formed for montmorillonite particles via edge-face interactions. The colloidal behavior of bentonite clay is governed by several factors including surface charge nature, cation exchange capacity (CEC), concentration, particle size and shape, and density [6]. The dispersion of clay particles is a primary cause of water-based drilling fluid instability under high-temperature condition [7]. Previous study indicated that bentonite tend to flocculate at temperatures above 121 °C [8].

The colloidal stability of a bentonite dispersion can be improved by modifying its surface charge or by providing a steric barrier [3]. Various polymers have been employed during the past decades to impart different purposes. By adsorbing onto bentonite surfaces, polymers confer effective steric stabilization, preventing aggregation of the dispersed particles. Therefore, the rheology and filtration properties are improved. In addition, polymers can be used as lubricants, emulsifiers, drag reducers and show multi-functions [9]. There are generally natural polymers derivatives and synthetic polymers. When temperature exceed 150 °C, biopolymers undergo degradation through mechanisms including thermo-oxidative degradation, hydrolysis, and fragmentation, resulting in complete loss of function [10]. In terms of synthetic polymers, the carbon-carbon backbones endow improved thermal stability, however, thermal degradation still occurs due to oxidation and side-chain hydrolysis [1]. Once the polymers degrade, the colloidal stability of the bentonite dispersion would be lost rapidly. Therefore, developing new additives to improve the colloidal stability of bentonite dispersion under elevated temperatures is important and also a challenging task.

Except designing high temperature resistant polymers, such as star polymers, comb polymers, and dendritic polymers, combining the advantages of inorganic materials and organic materials to form a composite is also a desirable way. For example, an organic-inorganic composite for high-temperature, high-salt-resistant water-based drilling fluids was prepared by copolymerizing acrylamide (AM), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), diallyldimethylammonium chloride (DMAAC), and 4-acryloylmorpholine (ACMO) with laponite via aqueous radical polymerization. The water-based drilling fluid containing 2 wt% composite maintained excellent rheology and filtration properties even after hot rolling at 180 °C and contamination with 15 wt% NaCl [11]. In another study, Ahmed et al. prepared SiO₂/g-C₃N₄ hybrid and revealed that the hybrid nanoparticles can improve the thermal stability of drilling fluid, and reduce the filtration both before and after hot rolling at 225 °F [12]. A zwitterionic silica-based hybrid nanomaterial (ZSHNM) was designed with a dual-functional structure: a silicate core for thermal stability and a zwitterionic shell to improve filtration by complexing with cations and suppressing bentonite aggregation. The addition of 2 wt% ZSHNM enabled the water-based drilling fluid to maintain extraordinary filtration loss properties after being thermally aged at 240 °C [13].

Due to exceptional chemical, physical, mechanical, and thermal attributes, carbon nanomaterials have been paid more and more attention to improve the rheology, filtration, lubrication, and inhibition of drilling fluids drastically [12,14–16]. When bentonite and biomass are mixed together and exposed to a subcritical water, hydrothermal carbonization occurs and a composite materials of hydrothermal carbon spheres supported on montmorillonite could be obtained. Much oxygen-containing groups including hydroxyl, carboxyl, and carbonyl groups are anchored on the surface of the composites, which improves the dispersion stability of bentonite. Due to these particular properties, the composites have been widely used in the area of adsorption [17–19].

Herein, hydrothermal carbon bentonite composites (HCBCs) were designed and fabricated using low cost of soluble starch and sodium bentonite as the raw materials via one-step hydrothermal carbonization. FTIR analysis, TGA, XPS, SEM, TEM, and specific surface area were used to characterize the structure characteristic of HCBC. A systematic investigation was then conducted to assess the impact of HCBC on the water-based drilling fluid's key properties: rheology, filtration, and lubrication.

2. Materials and Methods

2.1. Materials

Sodium based bentonite was purchased from Shengli Oilfield Boyou Mud Technology Co., Ltd., with a montmorillonite content of 60%. Methyl violet (MV), hydrochloric acid, soluble starch, and anhydrous ethanol are both analytical grade reagents purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd. Xanthan gum (XC) was purchased from Ordos Zhongxuan Biochemical Co., Ltd. Modified starch was provided by China Oilfield Services Limited. HT, a high-temperature polymer fluid loss reducer, was provided by Chevron Philips Chemical Company.

2.2. Preparation and Characterization of HCBCs

HCBC was synthesized via a hydrothermal method. Briefly, 4 g of soluble starch and 4 g of sodium bentonite were added to 80 mL of deionized water. The mixture was stirred at 10,000 rpm for 30 minutes and then subjected to a hydrothermal reaction in a 100 mL Teflon-lined kettle at 200 °C for 16 hours. After cooling to room temperature, the product was collected by centrifugation, alternately washed three times with deionized water and absolute ethanol, dried at 80 °C for 24 h, and finally ground and passed through a 100-mesh sieve (Figure 1).

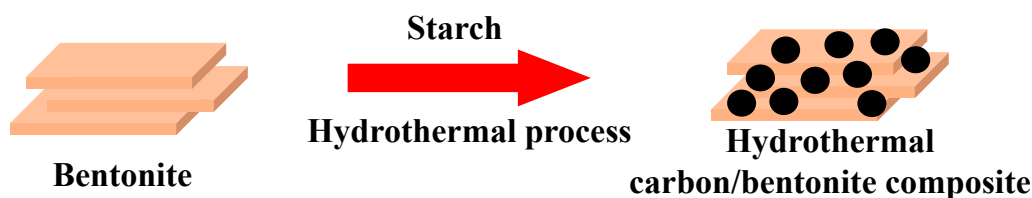


Figure 1. Scheme of hydrothermal reaction.

The functional groups on the surface of HCBC were investigated with a NEXUS Fourier transform infrared spectrometer. Thermal stability was evaluated employing a TGA5500 thermogravimetric analyzer, scanning from 35 to 1000 °C at 10 °C/min under a nitrogen atmosphere. The interlayer spacing of HCBC was measured using an X-ray diffractometer (X'Pert PRO MPD) under the conditions of 45 kV voltage, 40 mA current, a fixed slit width of 0.76 mm, Cu-K α radiation ($\lambda = 0.154$ nm), a scanning rate of 3.86°/min, a step size of 0.017° (2 θ), and a scanning range of 3-15°. The microstructure of HCBC was observed by field emission scanning electron microscopy (SU8010) and high-resolution transmission electron microscopy (FEI Tecnai G2 F20). The specific surface area was tested using an automatic specific surface area analyzer (Micromeritics APSP2460). The surface elements of HCBC were analyzed with a high-resolution X-ray photoelectron spectrometer (ESCALAB XI+), using Al K α radiation ($h\nu = 1486.6$ eV) during the test, and the binding energy was calibrated by the C1s line at 284.8 eV. The Zeta potential of HCBC suspension was measured using a multi-angle particle size and high-sensitivity Zeta potential analyzer (Omni). To determine the water adsorption capacity of HCBC, 1 g HCBC was put in a glass dish. Then the glass dish was placed in the middle position of a dryer where the bottom was filled with water. After sealing the dryer for a certain interval, the glass dish was quickly taken out and weighed. Then the glass dish with HCBC was put in the dryer and sealed again until the weight change reaching a balance.

2.3. Drilling Fluid Preparation and Properties Measurement

Sodium bentonite (16 g) was putted in 400 mL fresh water and mixed at 10,000 rpm for 20 min on a Hamilton Beach mixer. Then the suspension was sealed and incubated overnight to yield before use, which is also called bentonite slurry. Xanthan (XC) slurry was prepared by adding 0.8 g NaOH

and 0.8 g XC into the 400 mL bentonite slurry and stirring at 10,000 rpm for 20 min. The modified starch slurry and HT polymer slurry was prepared via a similar method, where both the dosage of modified starch and HT polymer are 4 g.

2.4. Hydroxyl Free Radicals Scavenging Experiment

Under the test conditions, MV exhibits its characteristic purple color. The highly reactive hydroxyl radicals generated via the Fenton reaction cause the discoloration of methyl violet, leading to a significant decrease in the maximum absorbance value. With the increase in the dosage of free radical scavenger, the color of the methyl violet solution gradually deepens, and the absorbance increases correspondingly. Therefore, the free radical scavenging efficiency can be indirectly detected [20,21]. First, 0.001 mol/L FeSO_4 solution, 2×10^{-4} mol/L MV solution, 0.1 mol/L Tris-HCl buffer, and 0.004 mol/L H_2O_2 solution were prepared. Then 0.4 mL of HCBC suspension, 0.4 mL of MV solution, 0.4 mL of FeSO_4 solution, 0.4 mL of H_2O_2 solution, and 0.4 mL of Tris-HCl buffer (pH=3.7) were sequentially added to a beaker. The total volume of the mixture was adjusted to 4 mL with deionized water. After allowing the reaction to proceed for 5 minutes, the solution was transferred to a cuvette. The absorbance was measured using a UV1750 ultraviolet-visible spectrophotometer (Shimadzu Corporation, Japan), and the hydroxyl radical scavenging rate was calculated based on the absorbance values obtained.

3. Results

3.1. Characterization of HCBCs

3.1.1. FT-IR

As shown in Figure 2, the infrared spectroscopy of bentonite exhibits characteristic absorption peaks at 3624 cm^{-1} (Al-OH stretching vibration), 3444 cm^{-1} (adsorbed water -OH stretching vibration), 1644 cm^{-1} (adsorbed water -OH bending vibration), 1032 cm^{-1} (Si-O-Si stretching vibration), 521 cm^{-1} (Si-O-Al bending vibration), and 464 cm^{-1} (Si-O-Si bending vibration) [22]. These characteristic peaks remain after the hydrothermal carbonization reaction, and new stretching vibration peaks of C=O and C=C appear at 1704 cm^{-1} and 1631 cm^{-1} , respectively. This indicates that soluble starch is deposited on the surface of bentonite, introducing oxygen-containing functional groups after hydrothermal carbonization [18].

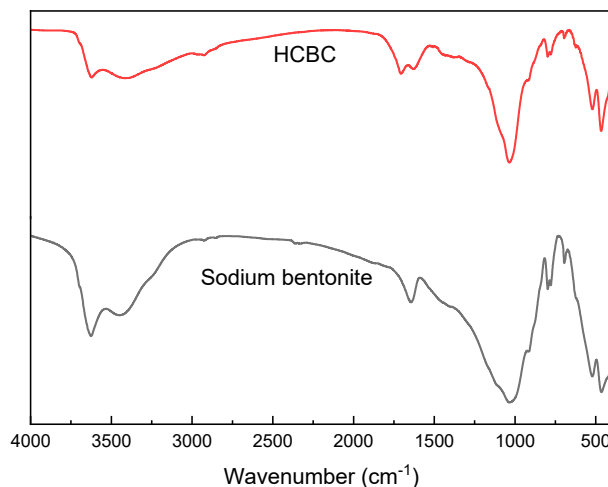


Figure 2. FTIR of sodium bentonite and HCBC.

3.1.2. XPS

From the full-spectrum analysis of bentonite and HCBC in Figure 3a, a C1s peak appears at a binding energy of 284.8 eV in HCBC, suggesting that the hydrothermal carbonization reaction increases the carbon content on the surface of bentonite. As shown in Figure 3b, the C1s peak is located at 284.8 eV, and its four fitted peaks at 284.8, 285.3, 286.8, and 288.2 eV correspond to aromatic groups or alkyl-substituted aromatic groups ($\text{R-C}_6\text{H}_5$), phenolic or ether groups ($\text{C}_6\text{H}_5\text{-O/C-O-C}$), carbonyl groups (R-C=O), and carboxyl, ester, or lactone groups (-O-C=O), respectively [23]. As shown in Figure 3c, the O1s peak is located at 531.7 eV, and its three fitted peaks at 531.1, 532.0, and 532.7 eV correspond to carbonyl groups (C=O), ester groups (C-O-C), and hydroxyl groups (-OH), respectively [24]. It can be seen that the surface of the composite formed after hydrothermal carbonization of bentonite contains abundant oxygen-containing functional groups.

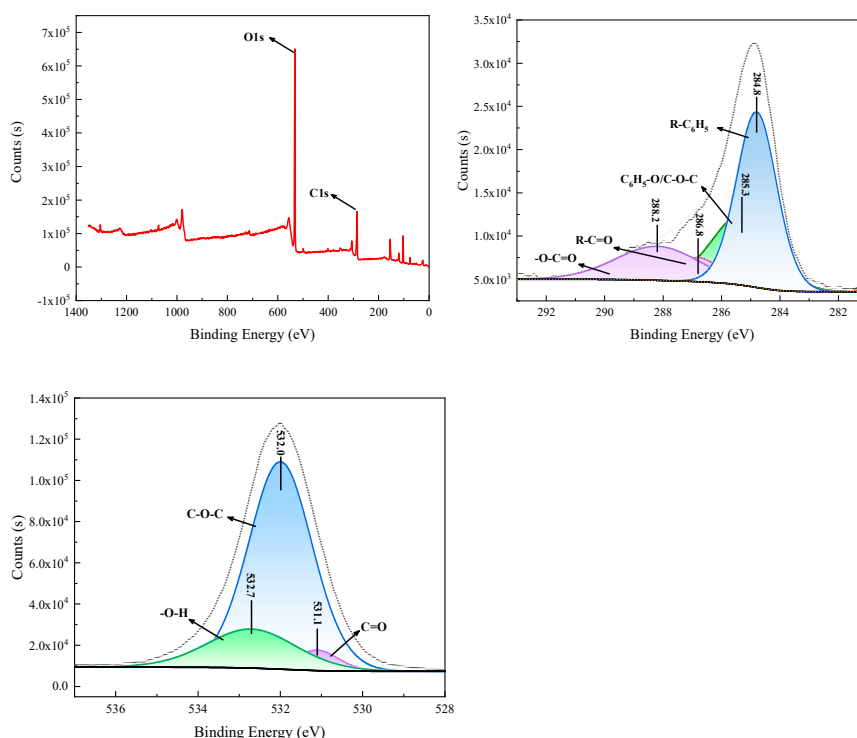


Figure 3. XPS spectra of HCBC: (a) survey spectrum, (b) C1s spectrum, (c) O1s spectrum.

3.1.3. XRD

Figure 4 shows the X-ray diffraction patterns of bentonite and HCBC. Compared with bentonite, new diffraction peaks did not appear in the X-ray diffraction pattern of HCBC, indicating the basic crystal structure of bentonite was not destroyed. According to the Bragg equation, the interlayer spacing of bentonite increased from 1.22 nm to 1.40 nm after the hydrothermal carbonization reaction. Water-soluble starch was adsorbed into the interlayer of montmorillonite through hydrogen bonds and other interactions, and carbon particles were formed at high temperatures through hydrothermal carbonization, which could increase the interlayer spacing. Combined with the SEM analysis, it can be known that the hydrothermal carbonization reaction not only occurred on the outer surface of bentonite but also in the interlayer of bentonite.

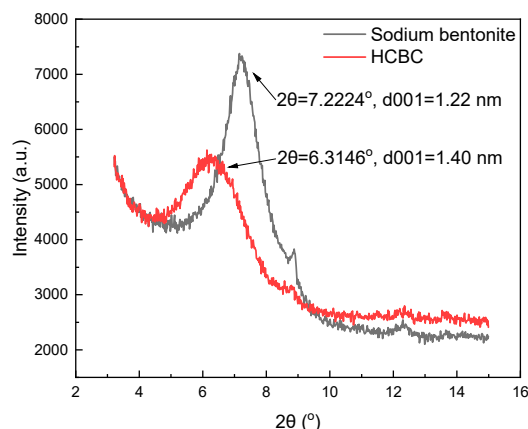


Figure 4. XRD of sodium bentonite and HCBC.

3.1.4. SEM and TEM

It can be seen from the SEM image in Figure 5a that bentonite has a typical plate-like structure. In HCBC, in addition to retaining some plate-like structure, a large number of nearly spherical and irregular nanoparticles can also be observed, some of which are embedded between the layers of bentonite, while others are in a free deposition state. In a high-temperature hydrothermal environment, starch and other sugar compounds first hydrolyze into low-molecular substances such as glucose, and then dehydrate to form intermediates such as 5-hydroxymethylfurfural. These intermediates undergo condensation or addition reactions to form poly-furan structures, and then undergo aromatization reactions to ultimately form hydrothermal carbon [25]. When bentonite is present, there are mainly two reaction pathways: a portion of the soluble starch is adsorbed on the surface of bentonite under the influence of hydrogen bonds and the polarity of the bentonite surface, and 5-hydroxymethylfurfural and other intermediates nucleate and grow on the active sites of the bentonite surface to form carbon particles. The growth of these carbon particles is restricted by bentonite, resulting in a smaller particle size, mainly at the nanoscale. Another portion of the soluble starch undergoes hydrothermal carbonization directly in the solution to form micrometer-sized carbon spheres, which deposit on the surface of bentonite [18]. Due to the different reaction pathways, the hydrothermal carbon between the layers of bentonite has a graphite-like structure, while the hydrothermal carbon on the surface of bentonite has an amorphous structure [26]. After the surface of bentonite is covered with micro-nano carbon spheres, the BET specific surface area decreases from 6.7379 m²/g to 2.8357 m²/g. It can also be seen from the TEM images in Figure 5c and 5d that a typical plate-like aggregation structure can be observed in the bentonite suspension, while in the HCBC suspension, not only a large number of nearly spherical nanoparticles deposited on the surface of the bentonite layers, but also hundreds of nanometer-sized or even micrometer-sized free particles could be observed.

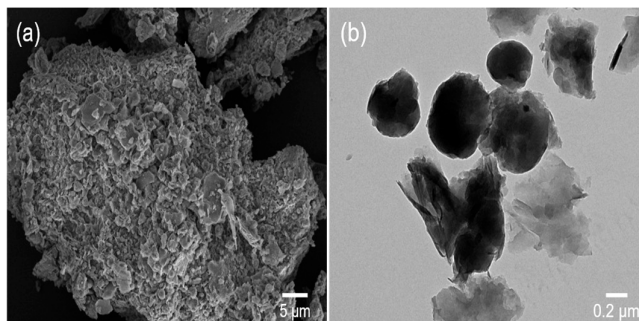


Figure 5. SEM (a) and TEM (b) images of HCBC.

3.1.5. TGA

As shown in Figure 6, for bentonite, the mass loss between 30 and 200°C mainly results from the removal of free water and bound water, and the mass loss between 400 and 600°C corresponds to the dehydroxylation reaction. When the temperature rises to 1000°C, the mass loss rate is 11.47%. For HCBC, starch molecules enter the interlayer of bentonite and undergo hydrothermal carbonization reactions, displacing some water molecules. Within the range of 30 to 200°C, the weight loss is lower than that of bentonite. After exceeding 350°C, HCBC begins to lose weight rapidly, and at this time, the carbon particles loaded on the surface of bentonite start to degrade. When the temperature rises to 1000°C, the mass loss rate is 24.28%. From this, it can be inferred that the content of hydrothermal carbon particles loaded on the surface of bentonite is approximately 12.81%.

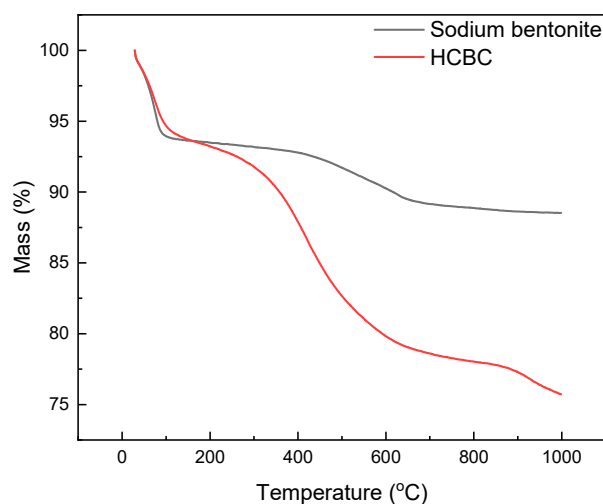


Figure 6. TGA curves of sodium bentonite and HCBC.

3.1.6. Particle Size Distribution and Water Adsorption

As depicted in Figure 7a, both sodium bentonite and HCBC exhibit multimodal distribution. The average particle size of sodium bentonite and HCBC is 5.434 μm and 0.811 μm respectively, indicating that after modification, the dispersion of bentonite particles is remarkably improved. This could also be verified by the zeta potential measurement results. The zeta potential of bentonite being -38.41 mV changes to -45.51 mV for HCBC. As shown in Figure 7b, for bentonite, the weight increases rapidly at the initial 2 hours, followed by a gradual increase. After about 56.5 hours, the weight increment is 33%, which corresponds to the amount of water adsorption. In terms of HCBC, the weight increases rapidly at the initial 1.3 hours, then increases with a much slower rate. After 56.5 hours, the weight increases only by 14%, much lower than that of bentonite. This indicates that the water affinity is decreased to some degree after modification with the hydrothermal carbon clusters on the bentonite surface.

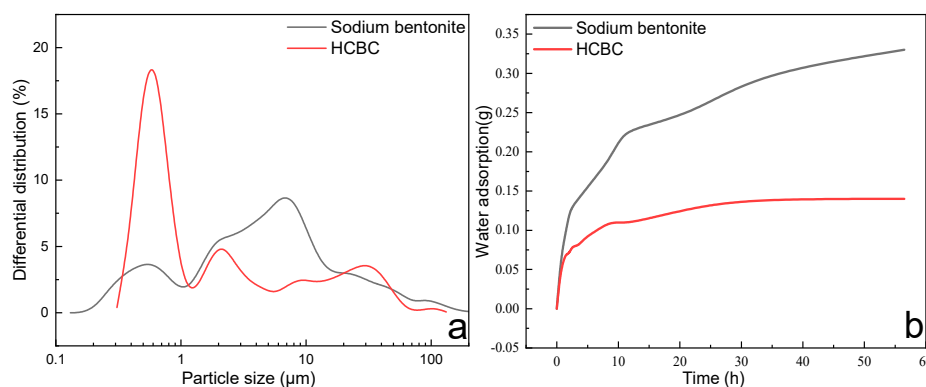
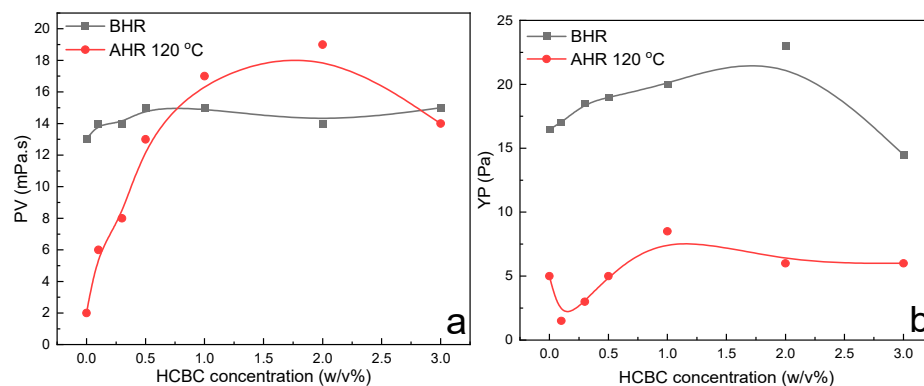


Figure 7. Particle size distribution (a) and water adsorption amount (b) as a function of time for bentonite and HCBC.

3.2. Properties Evaluation

3.2.1. Xanthan Slurries

The variation of rheological parameters including PV and YP, filtration loss, and extreme pressure lubrication coefficient of XC slurries as a function of HCBC concentration before and after hot rolling at 120 °C is presented in Figure 8. Before hot rolling, the rheological parameters such as PV and YP, as well as filtration loss changed slightly with the increasing concentration of HCBC, indicating that HCBC imposes little influence on the rheological and filtration properties of XC slurries. After hot rolling at 120 °C, the degradation of XC resulted in remarkable decrease in PV and YP for the control slurry, while the addition of HCBC can restore the PV to that of before hot rolling, and increase the YP to some extent. Meanwhile, both the filtration loss and lubrication coefficient decreased obviously along with the addition of HCBC. A reduction of 55.4% and 30.3% was observed respectively, for the filtration loss and lubrication coefficient at 2 w/v% HCBC. As depicted in Figure 9, after hot rolling, the AV retention rate was only 23.7% for the XC slurries, indicating severe degradation of XC. However, it recovered to over 50% when the concentration of HCBC was above 0.5%. Howard et al. (2015) stated that the fluids maintaining 50% of their viscosity after hot rolling for 16 hours can be defined to be thermal stability [27]. Therefore, the addition of HCBC improves the thermal stability of XC slurries effectively. Overall, the XC slurries having HCBC maintain stable viscosity, low filtration loss, and low lubrication coefficient after hot rolling.



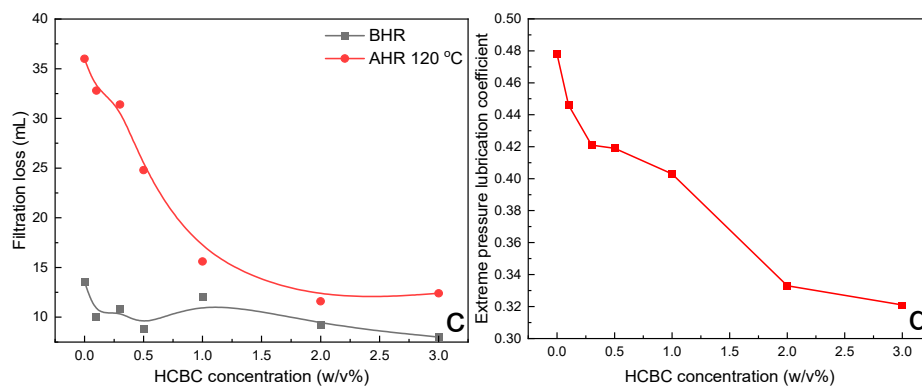


Figure 8. Variation of rheological, filtration, and lubrication properties of XC slurry as a function of HCBC concentration before and after hot rolling at 120 °C.

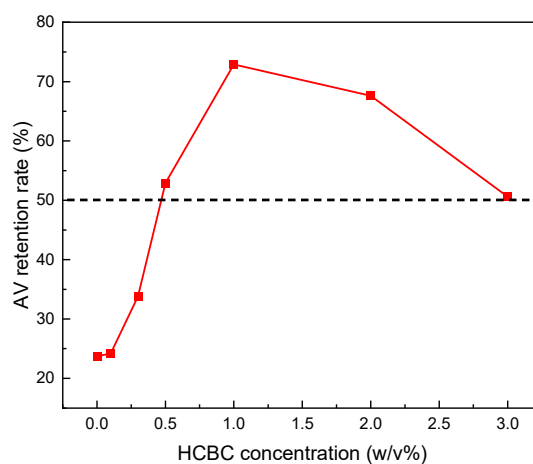


Figure 9. Variation of AV retention rate as a function of HCBC concentration for the XC slurry after hot rolling at 120 °C.

3.2.2. Modified Starch Slurries

The variation of rheological parameters including PV and YP, filtration loss, and extreme pressure lubrication coefficient of modified starch slurries as a function of HCBC concentration before and after hot rolling at 150 °C is presented in Figure 10. Regarding the rheological parameters, the PV exhibited an increasing trend along with the addition of HCBC for the case of before hot rolling and after hot rolling, whereas, the YP generally increased before hot rolling but decreased slightly after hot rolling along with the addition of HCBC. In terms of filtration and lubrication, they exhibited a similar pattern of change as XC slurries. When 3 w/v% HCBC was employed, the filtration loss and lubrication coefficient was reduced by 67.2% and 20.5%, respectively. For the AV retention rate, as shown in Figure 11, it increased at low concentration of HCBC while decreased slightly at relatively high concentration of HCBC. Nevertheless, for all the concentrations of HCBC, the AV retention rate is higher than 50%, indicating the thermal stability after thermal treatment.

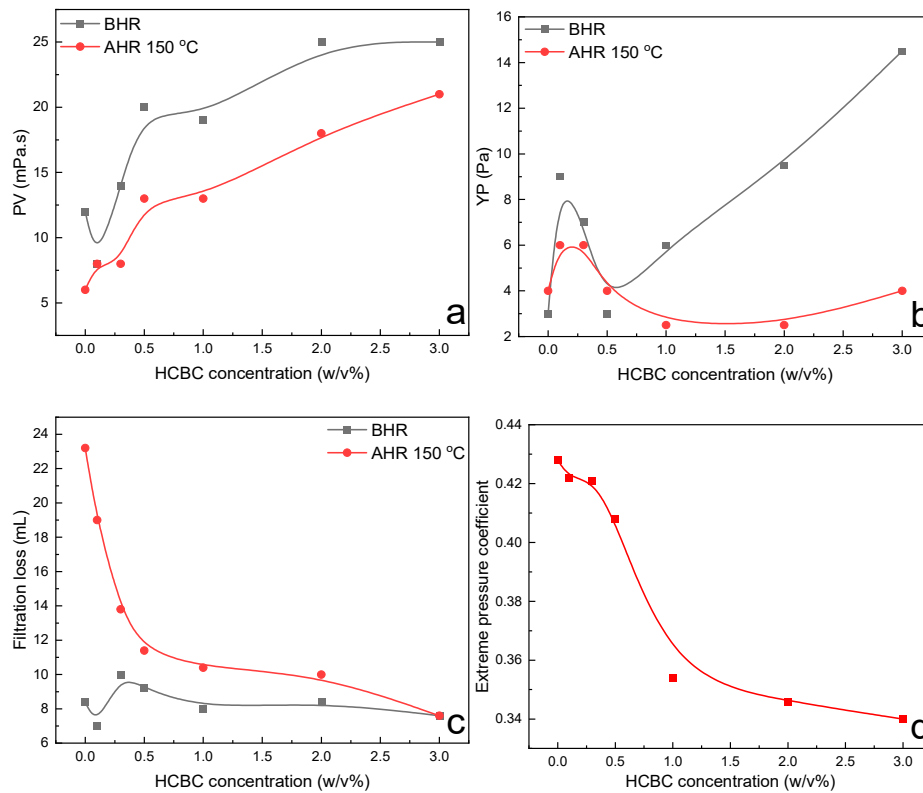


Figure 10. Variation of rheological, filtration, and lubrication properties of modified starch slurry as a function of HCBC concentration before and after hot rolling at 150 °C.

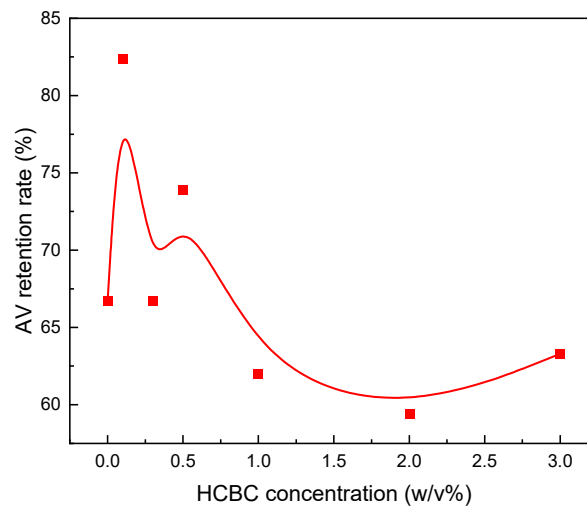


Figure 11. Variation of AV retention rate as a function of HCBC concentration for the modified starch slurry after hot rolling at 150 °C.

3.2.3. HT Polymer Slurries

The variation of rheological parameters including PV and YP, filtration loss, and extreme pressure lubrication coefficient of HT polymer slurries as a function of HCBC concentration before and after hot rolling at 200 °C is presented in Figure 12. Since HCBC are microparticles, the incorporation of HCBC increases the friction between the liquid and solid phase, as well as the friction between solid and solid phase, resulting in the increase of PV to some extent before hot rolling. The

oxygen-containing functional groups in HCBC probably promoted the formation of network structures among bentonite particles, HT polymers, and HCBC through hydrogen bonding. The YP increased obviously at 3.0 w/v% HCBC before hot rolling. After hot rolling at 200 °C, both PV and YP for the control slurries decreased to near zero, indicating that the slurries suffering from severe degradation under such harsh conditions. However, the addition of HCBC with much low concentration of 0.3 w/v% can maintain the PV and YP value approaching to that of before hot rolling. As shown in Figure 13, the AV retention rate was even higher than 100% when the concentration of HCBC above 0.5 w/v%, indicating excellent thermal stability effect. For filtration loss and lubrication, the addition of 2 w/v% HCBC resulted in decrease by 70.4% and 77.5%, respectively after hot rolling at 200 °C.

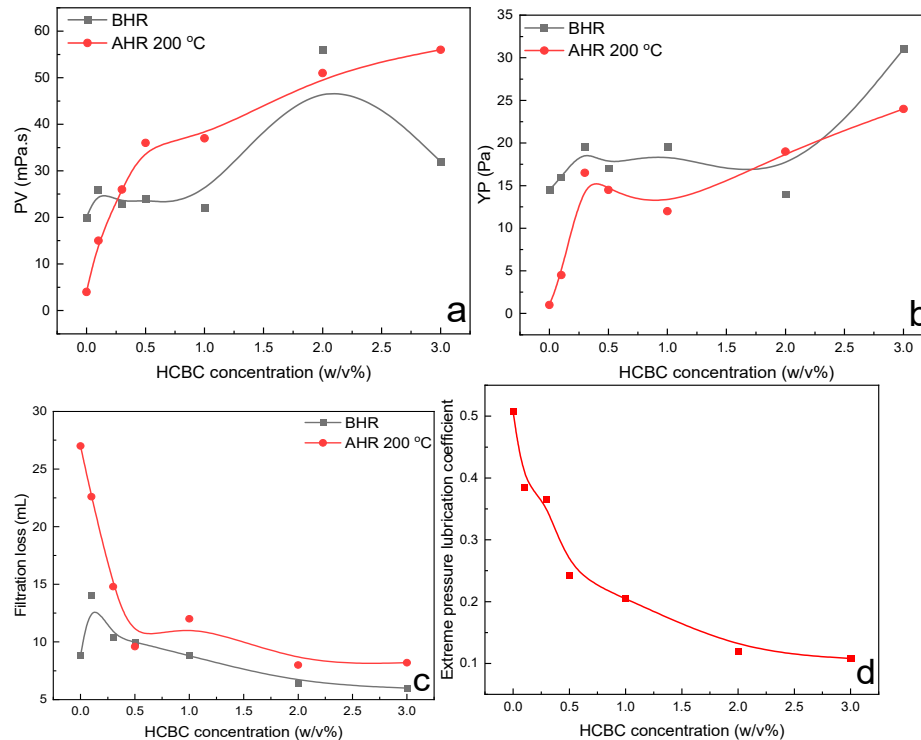


Figure 12. Variation of rheological, filtration, and lubrication properties of HT polymer slurry as a function of HCBC concentration before and after hot rolling at 200 °C.

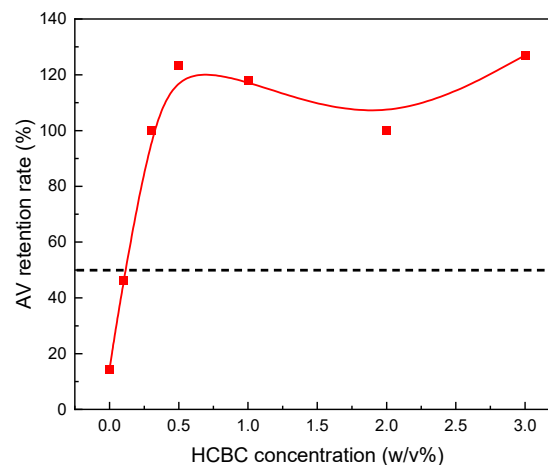


Figure 13. Variation of AV retention rate as a function of HCBC concentration for the HT polymer slurry after hot rolling at 200 °C.

3.2.4. Free Radical Scavenging

The variation of hydroxyl radical scavenging rate with HCBC concentration was calculated based on the change in maximum absorbance, as shown in Figure 14. At an extremely low concentration of 0.025 mg/mL, HCBC achieves a scavenging rate of 5.39%. Thereafter, the scavenging rate generally shows an upward trend with increasing concentration. When the concentration reaches 0.625 mg/mL, the scavenging rate can reach 67.35%, indicating that HCBC effectively blocks the reaction between hydroxyl radicals and methyl violet, indicating that it exhibits a scavenging effect on hydroxyl radicals. After the radicals generated through chain initiation are scavenged, the radical chain propagation reaction is interrupted, preventing subsequent oxidation reactions. This can effectively avoid the attack and damage of free radicals on polymer molecular chains.

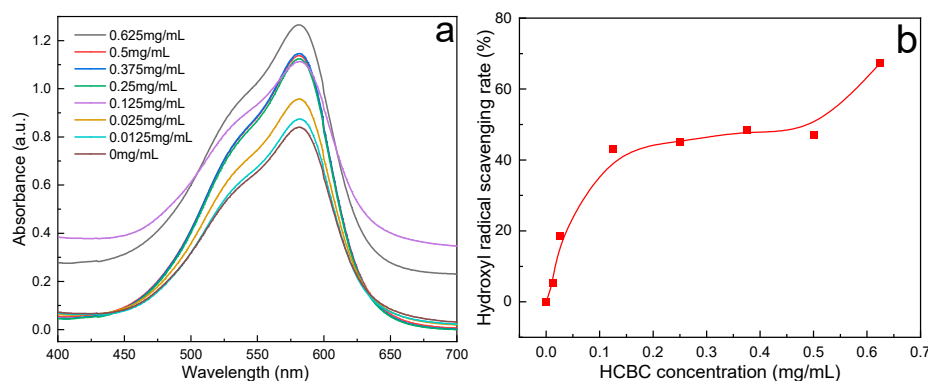


Figure 14. Hydroxyl radical scavenging as a function of HCBC concentration: (a) absorbance, (b) hydroxyl radical scavenging rate.

3.2.5. Filtration Loss

The LTLP filtration loss and HTHP filtration loss of bentonite slurry treated with various filtration reducers are illustrated in Figure 15. Before hot rolling, the addition of HCBC decreased the LTLP filtration loss from 20 mL to 17.2 mL, exhibiting a limited effectiveness, whereas the HT polymer could decrease the filtration loss from 20 mL to 10 mL, better than HCBC. After hot rolling at 220 °C, due to the degradation of HT polymer, the fluid having HT polymer lost filtration control with a high filtration loss of 37 mL. The combination of HCBC and HT polymer exhibited much lower filtration loss, indicating a synergistic effect. As shown in Figure 13b, after hot rolling, the dehydration of bentonite resulted in aggregation of clay particles, which corresponded to the quite high HTHP (200 °C/3.5 MPa) filtration loss of 640 mL. The degradation of HT polymer also caused the HTHP filtration loss uncontrollable, and the HTHP filtration loss reached 620 mL. The combination of 1 w/v% HT polymer and 1 w/v% bentonite decreased the HTHP filtration loss to a very limited degree. However, the HTHP filtration loss was significantly decreased to 180 mL in the presence of 1 w/v% HCBC, and further decreased to 84 mL when 1 w/v% HCBC and 1 w/v% HT polymer are both used. Both the LTLP filtration loss and HTHP filtration loss indicated that HCBC can effectively decrease the filtration loss of bentonite slurry and has a synergistic effect with HT polymer.

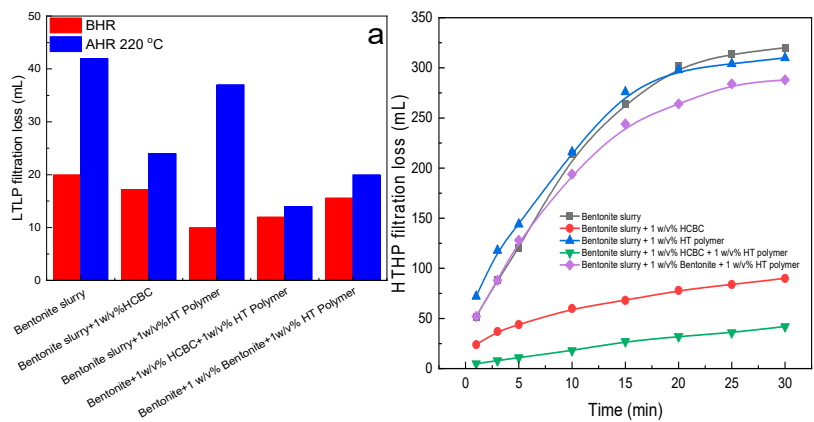


Figure 15. The LTPP filtration loss and HTHP filtration loss of bentonite slurry in the presence of various filtration reducers before and after hot rolling at 220 °C.

The SEM images of filter cake formed by bentonite slurry with and without HCBC before and after hot rolling are shown in Figure 16. Before hot rolling, the clay particles are fully hydrated and dispersed, and the particles are mainly connected by end to surface to form a typical honeycomb structure. Due to the thick hydration film, the edges of clay particles are relatively rounded after rapid freezing and freeze-drying with liquid nitrogen. After hot rolling at 220 °C, as shown in Figure 16b, due to the high-temperature dehydration effect, the repulsive force of the hydration film decreases, and the clay particles form larger sheet-like structures through surface to surface connections. The filtration channels significantly increase and the filtration loss significantly increases.

After adding HCBCs, as shown in Figure 16c, the oxygen-containing functional groups on the surface of HCBCs interact with clay particles before hot rolling, causing the clay particles to stick together and form sheets, which to some extent reduces the filtration area. As shown in Figure 16d, after hot rolling at 220 °C, the clay particles in the filter cake added with HCBCs also underwent agglomeration due to high-temperature dehydration. However, HCBCs enhanced the repulsive force between clay particles, and the agglomeration effect was significantly weakened compared to the filter cake without HCBCs. In addition, regardless of before and after hot rolling, a large number of micro and nano carbon spheres can be observed to be filled into the filter cake after adding HCBCs, which is beneficial for improving particle stacking efficiency and forming a dense mud cake.

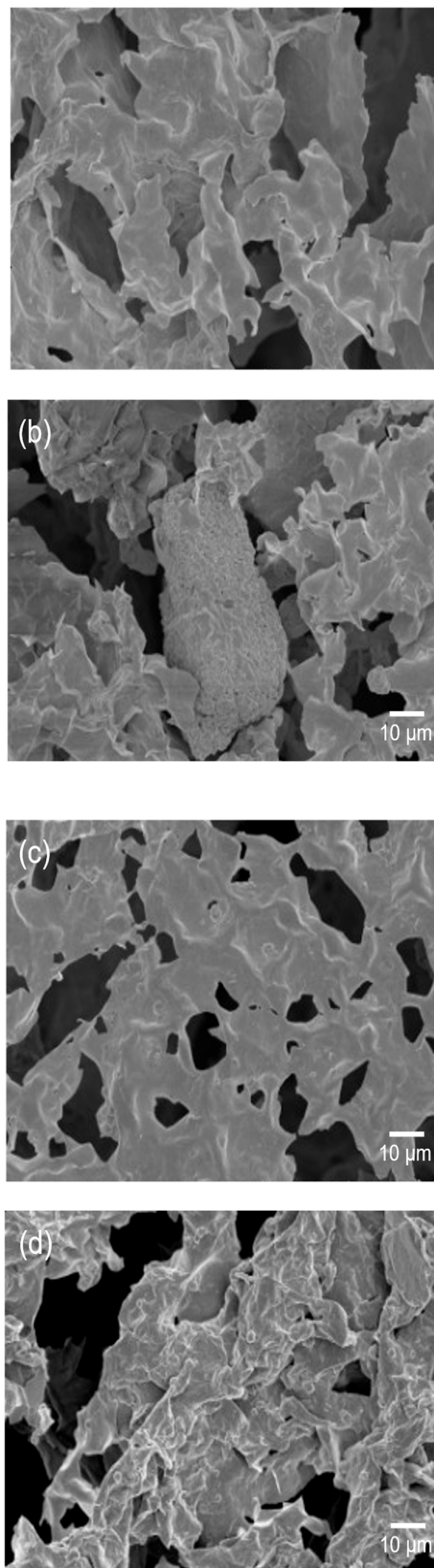


Figure 16. SEM images of filter cake: (a) bentonite slurry before hot rolling, (b) bentonite slurry after hot rolling at 220 °C, (c) bentonite slurry in the presence of HCBC before hot rolling, (d) bentonite slurry in the presence of HCBC after hot rolling at 220 °C.

3.3. High Temperature Stabilizing and Filtration Control Mechanism

When starch is dissolved in water under subcritical conditions, it first hydrolyze into low molecular weight mono saccharides such as glucose, and then dehydrate to form intermediates such as 5-hydroxymethylfurfural. The intermediates undergo condensation or addition reactions to form polyfuran structures, which are then subjected to aromatization reactions to ultimately generate hydrothermal carbon.

When bentonite is present, there are mainly two reaction pathways: a portion of soluble starch is adsorbed on the surface of bentonite under hydrogen bonding and polarity induction. Intermediates such as 5-hydroxymethylfurfural nucleate and grow at the active sites on the surface of bentonite to form carbon particles. The growth of this part of carbon particles is limited by bentonite, therefore, their particle size is relatively small, mainly at the nanoscale. For the other part of soluble starch which are dissolved in the aqueous solution, they can directly form micrometer sized carbon spheres through hydrothermal carbonization. These carbon spheres can deposit on the surface of bentonite.

The anchoring or depositing of hydrothermal carbon spheres on the surface of bentonite brings abundant oxygen-containing groups such as hydroxyl, carbonyl, and carboxyl groups. On the one hand, the hydroxyl groups tend to act as H-atom donors to unstable free radical molecules [28]. On the other hand, compounds with long conjugated C=C chains are usually great free radical scavengers. For graphene, carbon nanotubes, and fullerene, the radical addition to sp^2 carbon network plays an important role [29]. By analogy, there are plentiful sp^2 conjugated C=C chains in the core of hydrothermal carbon spheres. The spin across the conjugated graphemic backbone is delocalized, which forms free radical adducts and results in the decrease of free radical quantities [30,31]. The combination of hydrogen donating by surface hydroxyl groups and formation adducts by the core sp^2 C=C carbon contributed to the free scavenging effect, which in turn prevents the thermal oxidative degradation of polymers. Therefore, the thermal stability of water-based drilling fluid is significantly enhanced.

Regarding to filtration loss, due to the abundant oxygen groups on HCBC, on the one hand, the addition of HCBC promotes the dispersibility of clay particles. On the other hand, the partially free nano carbon spheres in HCBC increase the content of submicron particles in the system. Therefore, the addition of HCBC leads to a decrease in the average particle size of the suspension, and forms a reasonable gradation with bentonite particles, making it easier to form a dense filter cake and thus reducing filtration loss. At the same time, clay particles also undergo agglomeration due to high-temperature dehydration, but HCBC enhances the repulsion between clay particles, and the agglomeration is significantly weakened. In addition, regardless of before and after hot rolling, a large number of micro and nano carbon spheres are observed to be filled into the filter cake after adding HCBC, which is beneficial for improving particle packing efficiency and forming a dense filter cake.

4. Conclusions

In this study, hydrothermal carbon/bentonite composites (HCBCs) were prepared by hydrothermal carbonization reaction using soluble starch and sodium bentonite as raw materials. The interlayer spacing of bentonite increased from 1.22 nm to 1.40 nm after the hydrothermal carbonization reaction. There are plentiful micro and nano sized carbon spheres deposited on the surface of bentonite, the oxygenated groups on the carbon sphere surface improve the dispersion stability of bentonite particles.

HCBCs exhibit limited effect on the rheology of xanthan slurries, modified starch slurries, and high temperature resistant polymer slurries. However, after dynamical thermal aging, the presence of HCBCs could effectively improve the apparent viscosity retention, reduce the filtration loss and enhance the lubrication of the slurries.

The high efficiency in free radical scavenging contributes to excellent thermal stability of water-based drilling fluids. The surface of HCBC has abundant oxygen-containing functional groups, which improve the dispersion stability of clay particles at ultra-high temperatures through electrostatic repulsion and other mechanisms. The relatively small particle size of HCBC and the formation of free micro nano carbon spheres through hydrothermal reactions are beneficial for improving the solid-phase particle size distribution of drilling fluids and enhancing the quality of mud cakes. The above comprehensive effects make HCBC exhibit excellent ultra-high temperature filtration performance.

The raw materials used in the preparation of HCBC are widely sourced, and the preparation process is green and environmentally friendly. The multifunction of HCBC shows great potential in developing high performance water-based drilling fluids. This study also opens a new way to design and develop multifunctional and environmentally friendly additives for drilling fluids.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AV	Apparent viscosity
FTIR	Fourier Transform infrared spectroscopy
HCBCs	Hydrothermal carbon/bentonite composites
HT	High-temperature
HTHP	High-temperature and High-pressure
LTLP	Low-temperature and Low-pressure
MV	Methyl violet
PV	Plastic viscosity
SEM	Scanning Electron Microscope
TEM	Transmission electron microscope
TGA	Thermogravimetry Analysis
XC	Xanthan gum
XPS	X-ray photoelectron spectroscopy
YP	Yield point

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