

Synthesis and characterization of modified sodium carboxymethyl cellulose and polyethylene glycol ester new copolymer as scale inhibitor

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ABSTRACT

A new scale inhibitor maleic anhydride-modified sodium carboxymethyl cellulose (CMCMA), acrylic acid (AA) and polyethylene glycol ester (PEGMA maleic anhydride-modified polyethylene glycol) were synthesized by aqueous solution free radical and evaluated as scale inhibitor against the growth of calcium carbonate (CaCO₃) scale through the static test experiments. When the reaction ratio is $m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA}) = 1:3:5$, the reaction condition is 80°C, the ratio of the initiator (ammonium persulfate) is 6%, the test temperature is 70°C, and the heat retention time is 8 h can get optimal scale inhibition results. The resistance rate of CaCO₃ scales up to 89%. The copolymer structure and CaCO₃ scale crystal were characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance (¹H-NMR) and scanning electron microscope. The performance of CaCO₃ scale crystallization and morphology data was found to be suitable for the conditions found in the cooling water system.

Keywords: Scale inhibitor; Calcium carbonate scale; Cooling water system

1. Introduction

Nowadays, water consumption has been increasing worldwide for economic reasons, urban development, population growth and area expansion. Besides, water pollution in industrial production and domestic use waste further aggravates the crisis of water shortage. The circulating cooling water system is an important way of decreasing industry water use. However, cooling water reused in 4–6 times can result in pipe surface scale fouling such as calcium carbonate (CaCO₃) and CaSO₄ and increasing costs [1–3]. To resolve the scale fouling accumulating on the heat exchange pipe surface in circulating cooling water systems, scale inhibitors used in this system is one of the most effective methods [4,5].

Many copolymer scale inhibitors with good CaCO₃ and CaSO₄ scale inhibition performance have been used in the market and in the literature, such as 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), polyamino polyether methylenephosphonate (PAPEMP), amino trimethylene phosphonic acid (ATMP), etc. However, the use of these inhibitors has recently been limited by environmental protection reasons [6–10]. Copolymer architecture and functional groups control the inhibition performance of the inhibitors. The most common functional groups are sulfonic acid and carboxylic acid groups. Currently, many kinds of literature about CaCO₃ scale inhibition have been carried out, but most of the inhibitors are contain phosphorus. Thus, it is of great significance to study environmentally friendly non-phosphorus scale inhibitors in CaCO₃ scale inhibition to the cooling water system [11–15].

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In this paper, our main aim was to synthesize and characterize new scale inhibitor carboxymethyl cellulose (CMCMA)-polyethylene glycol ester (PEGMA)-acrylic acid (AA) with a large number of carboxylic acid groups. The effects of reaction ratio, a ratio of the initiator on copolymer inhibition performance were studied in detail. This work provides great views into the application potentials of non-phosphorus green inhibitor in the cooling water system.

2. Experimental

2.1. Materials

CMC, MA, PEG200 ($n = 4$), AA were purchased from Aladdin Industrial Co., Ltd., Shanghai, China. All chemicals were of analytical grade and used directly without further treatment. Deionized water was used in all experiments. The Fourier transform infrared spectroscopy (FTIR) spectrum was obtained between 4,000–500 cm^{-1} from the powdered samples using a Fourier transform infrared spectrometer Vertex 80 (Bruker Company, Germany). PEGMA synthesis was according to literature [16]. Structures of CMCMA-PEGMA-AA were explored by a Bruker $^1\text{H-NMR}$ analyzer (AVANCE AV-500, Bruker, Switzerland) operating at 500 MHz and under room temperature, with dimethyl sulfoxide (DMSO) as the solvent.

2.2. Evaluation of CMCMA-PEGMA-AA CaCO_3 scale inhibition performance

Inhibition performance of copolymer against CaCO_3 scale was evaluated using the static scale inhibition test based on [17]. An aqueous solution containing 732 mg/L HCO_3^- was prepared with NaHCO_3 , then add different concentrations of CMCMA-PEGMA-AA, and then add CaCl_2 aqueous solution in the colorimetric tube to make the solution Ca^{2+} was 240 mg/L (calculated as CaCO_3). Finally, the colorimetric tube was placed in a water bath at a temperature of 80°C for 10 h. A blank experiment was performed under the conditions at the same time. The filtrate was filtered after natural cooling, can get 25 mL filtrate, measured by the ethylenediaminetetraacetic acid (EDTA) standard solution (calcium-carboxylic acid indicator among this solution). The scale inhibition rate was represented by η and the calculation equation was as follows:

$$\eta = \frac{S_2 - S_1}{0.240 - S_1} \times 100\% \quad (1)$$

where S_2 - Ca^{2+} concentration in the test solution with scale inhibitor, g/L; S_1 - Ca^{2+} concentration in the test solution without scale inhibitor, g/L.

2.3. Preparation of CMCMA, CMCMA-PEGMA-AA

First, in a nitrogen atmosphere, 4.64 g of CMC into a three-necked flask, and add an appropriate amount of acetone to dissolve. The water bath switch was turned on, the temperature was adjusted to 60°C, and a three-necked flask equipped with CMC was placed in a magnetic stirrer under a nitrogen atmosphere for heat stirring. After 10 min 4.90 g MA was added into the flask over 1 h. After the addition was completed, the reaction was kept for 2 h at 60°C. When the reaction was completed, the solution was suction filtered, and the filtrate was left. The filtrate was then recovered and evaporated to dryness, finally, the target product CMCMA was successfully synthesized and stored at room temperature (Fig. 1).

0.3 g CMCMA was added into a three-necked flask, adjust the temperature to 70°C, and place a three-necked flask with CMCMA in a magnetic stirrer under a nitrogen atmosphere and weigh PEGMA 0.90 g and AA 1.50 g, respectively. Ammonium sulfate 0.08 g, and dissolved in a small amount of distilled water, added to a three-necked flask within 1 h, and then the temperature was raised to 80°C, and the reaction was kept for 2.5 h. After the reaction is completed, the solution is poured into a jar and sealed and labeled. CMCMA-PEGMA-AA can be obtained (Fig. 2). When $m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA}) = 1:3:5$, molecular weight (g/mol) of the CMCMA-PEGMA-AA was investigated through gel permeation chromatography (GPC-Waters-2410) and the result was 18856. The PEG200 ($n = 4$) was used in the synthesis procedure.

3. Results and discussion

3.1. FTIR and $^1\text{H-NMR}$ measurements

Fig. 3 shows the FTIR spectra of MA, CMC, CMCMA, AA, PEGMA and CMCMA-PEGMA-AA.

The synthesized CMCMA has an unsaturated double bond stretching vibration absorption peak at 1,645 cm^{-1} ; CMC has no double bond, so there is no absorption peak of the double bond; the unsaturated double bond stretching vibration absorption peak of MA ($-\text{C}=\text{C}-$) is 1,637 cm^{-1} . It can be seen that the absorption peak of the double bond is redshifted, and the redshift occurs just to show that the CMC and the MA are polymerized.

AA has a distinct unsaturated double bond stretching vibration absorption peak at 1,640 cm^{-1} , and the unsaturated double bond stretching vibration absorption peak of the synthesized PEGMA is 1,644 cm^{-1} . The unsaturated double bond stretching vibration absorption peak of the synthesized CMCMA is 1,645 cm^{-1} , and the peak of the synthesized final

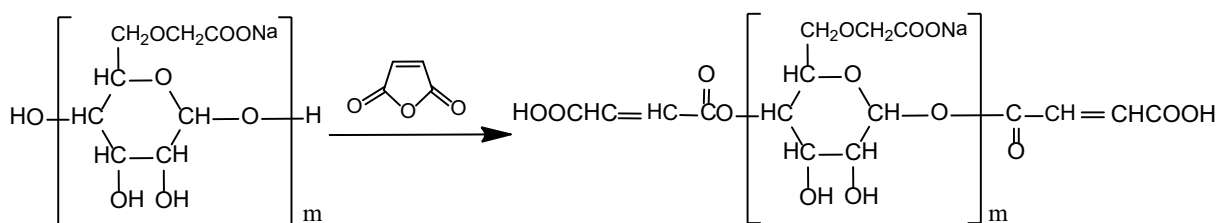


Fig. 1. Preparation of CMCMA.

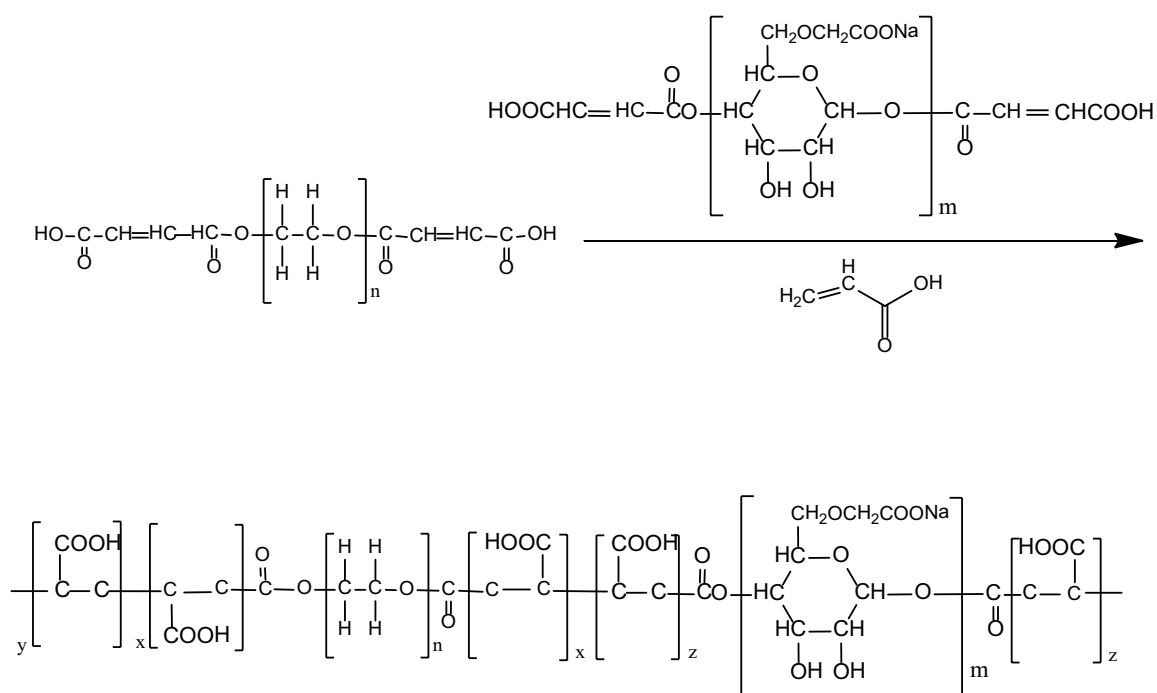


Fig. 2. Preparation of CMCMA-PEGMA-AA.

product CMCMA-PEGMA-AA at $1,640\text{--}1,645\text{ cm}^{-1}$ has disappeared, and only the carbonyl peak of $1,740\text{ cm}^{-1}$ is still present.

$^1\text{H-NMR}$ spectra for CMCMA-PEGMA-AA were shown in Fig. 4. When $m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA}) = 1:3:5$, $4.10\text{--}6.00\text{ ppm}$ ($-\text{C}=\text{C}-$) in this figure can be found double bond absorption peaks nearly disappeared off the CMCMA-PEGMA-AA. This reveals that free radical polymerization among CMCMA-PEGMA and AA has happened. It is evident that the targeted CMCMA-PEGMA-AA is obtained in our experiment.

3.2. Influence of the ratio of different monomer on CaCO_3 inhibition efficiency

To determine the Influence of the ratio of different monomer on CaCO_3 inhibition efficiency, the dosages of CMCMA, PEGMA and AA were adjusted at the initiator ammonium persulfate accounted for 6% of the total monomer mass and with reaction, the temperature was 80°C for 2.5 h. The results of the experiments are shown in Fig. 5.

As seen in this figure, when $m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA}) = 1:3:5$, the scale inhibition efficiency was reaching 89% (highest in this figure) for preventing CaCO_3 . This phenomenon could be attributed to the amount of carboxylic group which affects the inhibition of scale growth by CMCMA-PEGMA-AA. When $m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA}) = 1:3:3$ the inhibition efficiency is lower than 1:3:5 can be got from this figure. However, the more carboxylic group the better is not entirely correct. The scale inhibition effect is the lowest with $m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA}) = 1:3:10$. When there is no acrylic acid in the scale inhibitor, $m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA}) = 1:0:0$ and $0:1:0$ inhibition effect is relatively

poor, probably because there are fewer carboxyl groups that chelating calcium ions. The ratio of different monomer has a great influence on the scale inhibition of the copolymer. The developed copolymer in this paper with the carboxyl group, CMC and water-soluble PEG segment structure can exhibit a stronger chelating effect with calcium ion. The inhibitory performance is deeply affected by the main functional groups such as the carboxyl group and the water-soluble PEG segment. When the content of acrylic acid is low cause the chelating calcium ion functional group (carboxyl group) provided by the whole copolymer is limited, although the water-soluble PEG segment is more, resulting in low scale inhibition performance; furthermore, when the ratio of calcium ion functional group (carboxyl group) increasing, although the polymer can provide a large amount of chelating groups but the water-soluble PEG segment is too small, so that the formed CMCMA-PEGMA-AA- Ca^{2+} has low solubility, and the scale inhibition efficiency not very well. In addition, it is clear that CMCMA-PEGMA-AA exhibits an obvious “threshold effect” in preventing the CaCO_3 scale. The rate of calcium carbonate inhibition remains basically the same and reaches a maximum after 11 mg/L. Therefore, in the use of CMCMA-PEGMA-AA, the choice of 11 mg/L is appropriate.

3.3. Influence of different initiator on CaCO_3 inhibition efficiency

To determine the Influence of the different initiators on CaCO_3 inhibition efficiency, keeping the monomer ratio $m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA}) = 1:3:5$, the dosages of ammonium persulfate was adjusted and with reaction, the temperature was 80°C for 2.5 h. The results of the experiments are shown in Fig. 6.

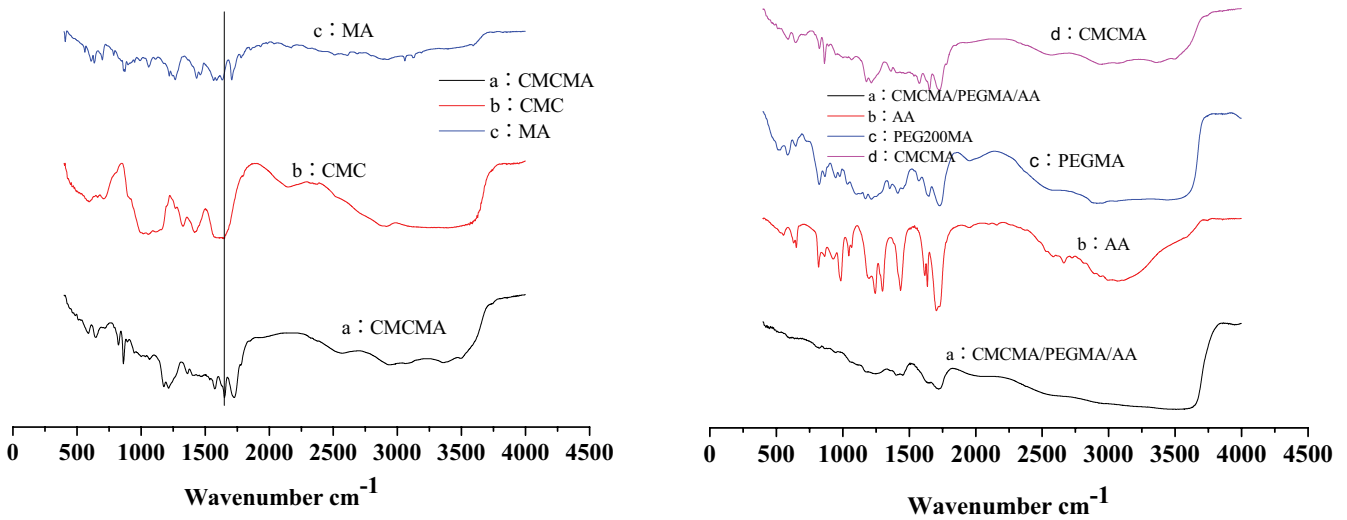


Fig. 3. FTIR spectra of MA, CMC, CMCMA, AA, PEGMA and CMCMA-PEGMA-AA.

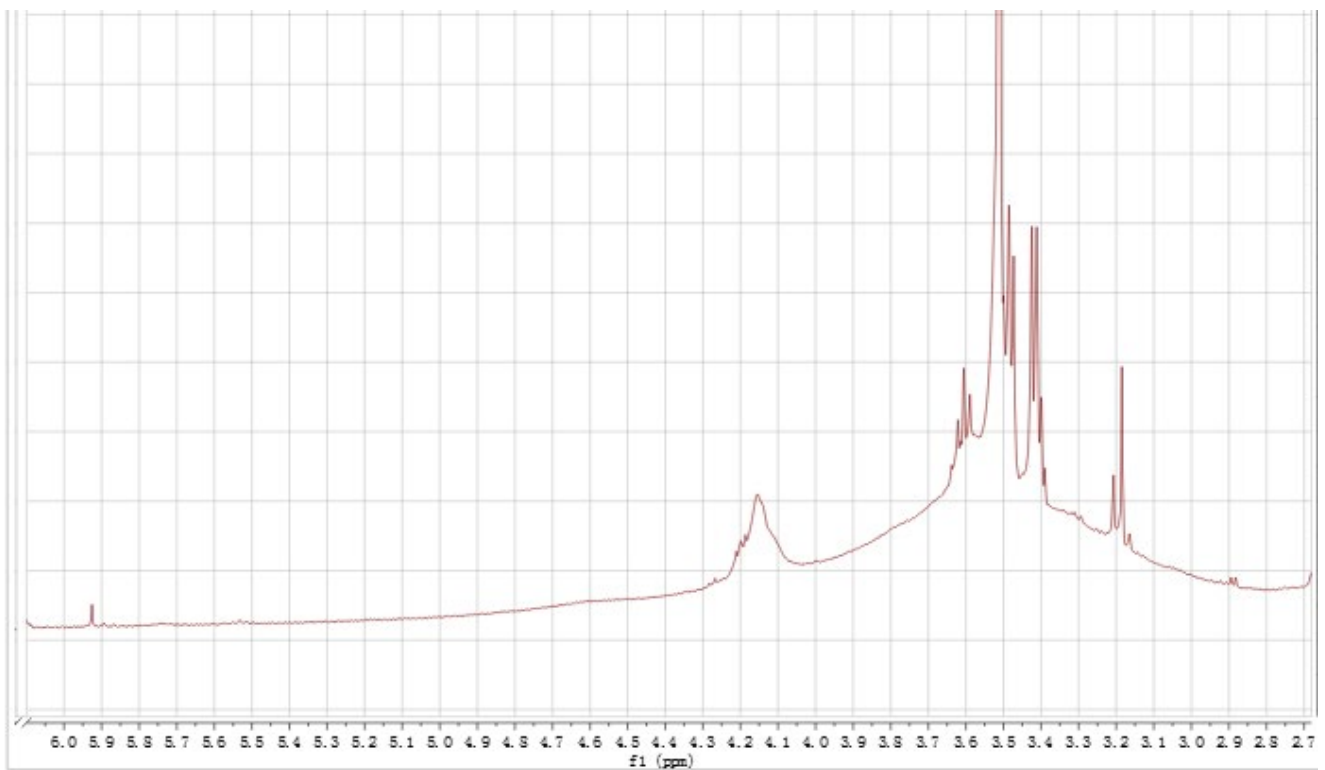


Fig. 4. $^1\text{H-NMR}$ spectra of CMCMA-PEGMA-AA.

It can be seen from Fig. 6 that the inhibition efficiency of different initiator shows a declining trend with the order followed $6\% > 3\% > 8\% > 10\%$ when the amount of ammonium persulfate is 6% of the total mass of the monomer, the rate of calcium carbonate inhibition is the highest, close to 88%. The reduction in the inhibition efficiency might be ascribed when the initiator is too small, the copolymer reaction is incomplete, and the monomer residue is too much,

resulting in low scale inhibition rate; but too much initiator cause too fast polymerization rate will make the scale inhibition effect is not good. The CMCMA-PEGMA-AA calcium carbonate scale with different initiator doses increased significantly with the increase of water treatment agent concentration as the dosage is <11 mg/L. It also can be seen that calcium carbonate inhibition efficiency did not increase, approach maximum value when the water treatment agent

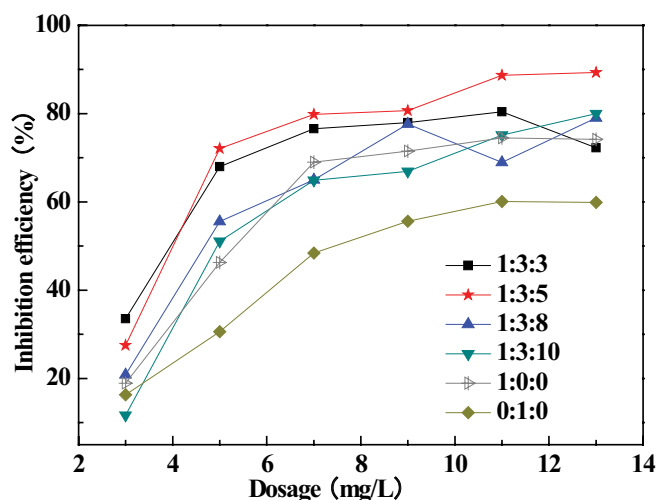


Fig. 5. Effect of the ratio of different monomer ($m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA})$) on CaCO_3 inhibition efficiency.

concentration reached 11 mg/L. Therefore, CMCMA-PEGMA-AA exhibits an excellent ability to inhibit calcium carbonate scale at 6% is appropriate.

3.4. Influence of different test pH on CaCO_3 inhibition efficiency

To determine the Influence of the different pH on CaCO_3 inhibition efficiency, keeping the monomer ratio $m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA}) = 1:3:5$, the initiator ammonium persulfate accounted for 6% of the total monomer mass and with reaction, the temperature was 80°C for 2.5 h. Change pH in the static scale inhibition test. The results of the experiments are shown in Fig. 7.

It can be seen from the experimental results that as the pH value increases, the CaCO_3 scale inhibition efficiency decreases. This may be because the solubility of calcium carbonate in the acidic solution is much greater than that in the alkaline solution and cause the solubility of CaCO_3 to decrease. When the pH is 9, the scale inhibition efficiency is less than 40%. The scale inhibition efficiency is higher with the pH is lower. Therefore, control of bicarbonate-calcium ion water to resolve calcium carbonate precipitation, and is more favorable for the scale inhibition efficiency in lower pH cooling water system.

3.5. Scanning electron microscope (SEM) and X-ray diffraction (XRD) results of CaCO_3 crystals

The morphology of calcium carbonate formed under conditions of different water treatment agents was studied using an SEM. The results are shown in Fig. 8. Fig. 8a illustrates that the crystal form of calcium carbonate is a cube, and the surface of the crystal form is relatively smooth and complete of the water treatment agent content of 0 mg/L. Compared with Fig. 8a, it can be clearly seen that the crystal form of the cube has begun to be destroyed when the water treatment agent content is 2 mg/L (Fig. 8b). As shown in Fig. 8c, it is clear that the crystal form of calcium carbonate is broken, but it can be roughly recognized as a cube (5 mg/L); when

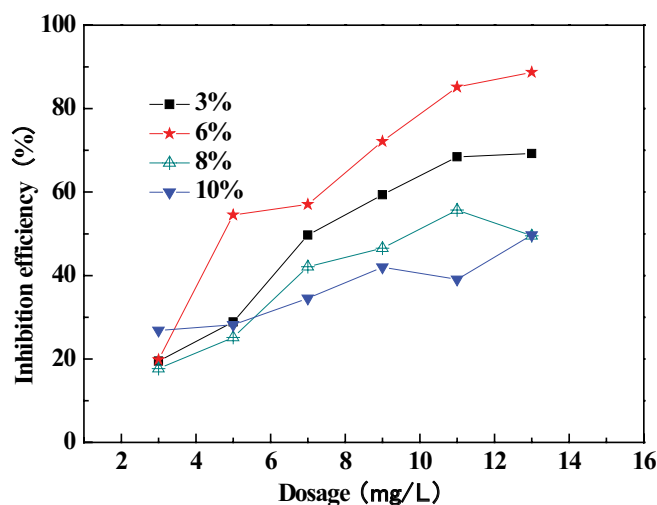


Fig. 6. Effect of different initiators on CaCO_3 inhibition efficiency.

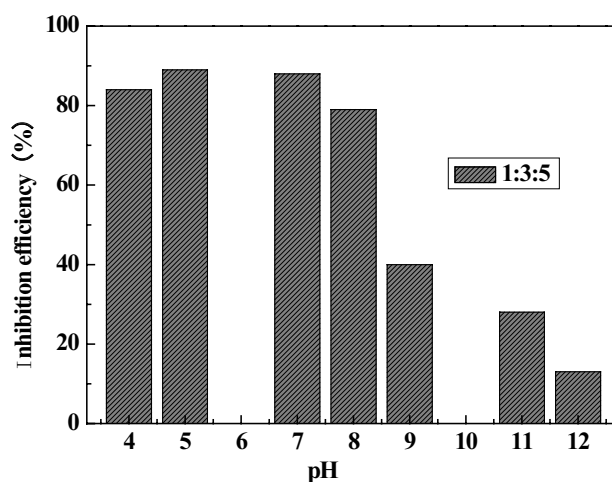


Fig. 7. Effect of different pH on CaCO_3 inhibition efficiency.

the water treatment agent content of Fig. 8d is 10 mg/L, it is difficult to see what the original crystal form is, indicating that the calcium carbonate is destroyed completely at this time. Furthermore, we can get the more dosage is, the stronger the influence is on calcium carbonate crystal morphology and size. In this case, the calcium scale is not easily formed, even if there is a little bit of calcium carbonate scale, and it is easy to be washed away by water flow. As can be seen from the SEM figure, the water treatment agent significantly changes the morphology of the calcium carbonate, making it lose and incomplete.

XRD analysis with the presence and absence of CMCMA-PEGMA-AA are illustrated in Fig. 9. The major peaks at C102, C100, C113 are attributed to calcite crystal form, and the peaks V110, V112, V114 belong to unsteady-state vaterite crystal form [18–20]. As we know, the vaterite crystal form is easy to disperse in cooling water and be washed away by the water. From the XRD results we can get copolymer can alter the structure of calcium carbonate. Scanning electron

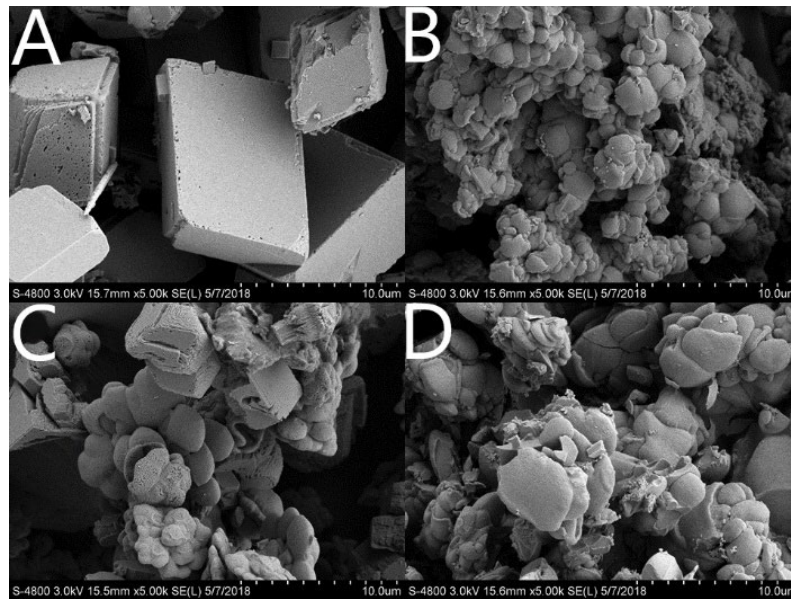


Fig. 8. SEM pictures of CaCO_3 with different concentration CMCMA-PEGMA-AA: (a) 0, (b) 2, (c) 5, and (d) 10 mg/L.

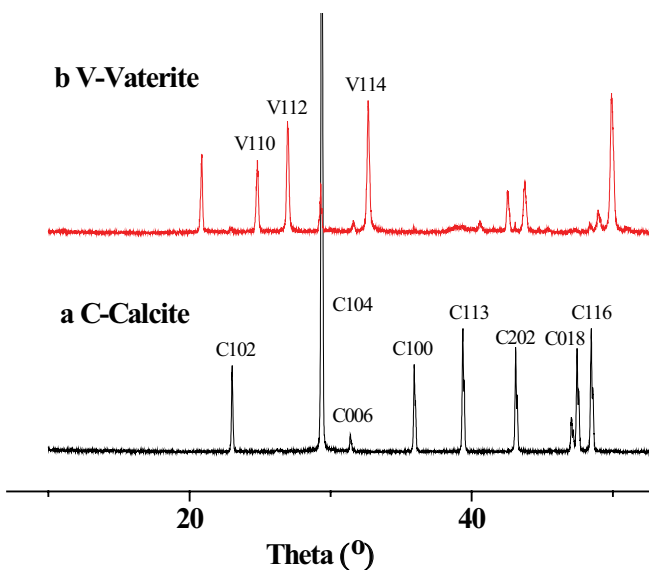


Fig. 9. XRD analysis of CaCO_3 crystals with the absence of CMCMA-PEGMA-AA (a) 0 and (b) 10 mg/L.

micrographs of calcium carbonate can also be seen that the calcium carbonate crystals are not only severely damaged, but also the crystal form changes.

4. Conclusions

PEGMA was obtained by modifying polyethylene glycol with maleic anhydride, which was subjected to free radical polymerization with maleic anhydride-modified sodium CMCMA and AA as monomers, and was initiated by ammonium persulfate. The optimum conditions for preparation the CMCMA-PEGMA-AA were $m(\text{CMCMA}):m(\text{PEGMA}):m(\text{AA}) = 1:3:5$, the amount of ammonium persulfate is 6% of the total mass of the monomer, the reaction temperature

is 80°C , and the heat reaction time is 8 h. Under the optimum conditions, the rate of calcium carbonate inhibition reached 89% when the dosage was 11 mg/L. The structure of the copolymer CMCMA-PEGMA-AA was characterized by FTIR. The effects of the different monomer ratios, pH (static scale inhibition test) and initiator dosage of the synthesized water treatment agent were investigated on the rate of calcium carbonate scale inhibition. The XRD and SEM analysis of calcium carbonate scale showed that the water treatment agent not only changes the morphology of the calcium carbonate but also changes the crystal form, making it difficult for the calcium carbonate scale to adhere to the wall of the circulating water pipe. The next work will focus on the use of the water treatment agent under different water quality conditions. In addition, the scale inhibitor does not contain phosphorus and was an excellent scale inhibitor.

Acknowledgments

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