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Inhibition and biodegradability performance of modified polyepoxysuccinic acid as a scale inhibitor against calcium carbonate

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ABSTRACT

Scaling by calcium carbonate precipitation is one of the major challenges in circulating cooling water systems, which are used to transfer an amount of waste heat in industrial productive process. Calcium carbonate scale decreases the efficiency of heat transfer equipment, hinders the normal heat transfer process, and even causes the equipment layoff. Polyepoxysuccinic acid (PESA) is an environmentally friendly scaling inhibitor. In order to enhance the performance of its scale inhibition on calcium carbonate, a modified and new PESA inhibitor, epoxysuccinic acid-oxalic acid-allypolyethoxy carboxylate polyethoxy carboxylate (PEM), which contained carboxylic acid and ether groups, was synthesized. The structure of PEM was characterized, and the optimal synthesis conditions were obtained by single-factor experiments. Its scale inhibition performance was estimated with static scale inhibition methods, and the biodegradability of PEM was studied with shaking-bottle incubating test. The results indicate that when monomer ratio (n_{ESA}:n_{APEM}) is 2:1, dosage of initiator is 6% and reaction temperature is 70°C. The polymer PEM exhibited more excellent scale inhibition property against $CaCO_3$ than PESA, and the comprehensive scale inhibition property of PEM is much better than the property of PESA. The scale inhibition efficiency of PEM against $CaCO_3$ was 95.60% when the dosage was 16 mg L^{-1}. PEM exhibited good biodegradability performance because degradation rates were more than 40% on day 10 and above 95% on day 28. The influence of PEM on formation of $CaCO_3$ was investigated using scanning electronic microscopy and X-ray powder diffraction. The inhibition mechanism reveals that PESA chain in PEM could react with Ca^{2+} or crystal nucleus of $CaCO_3$, affect the growth of $CaCO_3$ crystals, and then distort its crystal structure. Meanwhile, there are four elements, carbon (C), hydrogen (H), oxygen (O), and sodium (Na), in its structure, without phosphorous (P), nitrogen (N), and sulphur (S), which will lead to secondary pollution to water environment, indicating that PEM is an environment-friendly calcium scale inhibitor.

Keywords: Modified polyepoxysuccinic acid scale inhibitor; Biodegradation; Calcium carbonate scale inhibition; Scale inhibition mechanism

1. Introduction

Nowadays, with the increase of worldwide population, the development of industry and society, and the depletion of fresh water, the shortage of water resources is intensified. In order to resolve the contradiction, the utilization of circulating cooling water system is considered as an effective way to save water and alleviate the water resource crisis. At the same time, with the raising cycle of concentration, scale formation is a severe problem encountered in this system because cooling water contains scale forming ions, such as Ca^{2+}, Mg^{2+}, CO_3^{2-}, SO_4^{2-}, and HCO_3^- [1–3]. Among them, it is worth

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noting that one commonly available calcium scale is $CaCO_3$, which has certain thermodynamic property, that is, increase in water temperature decreases its solubility. Fouling and/or scaling deposition can have catastrophic effects on the equipment, such as declined heat exchange efficiency, increasing economical and operational costs, and the shortening of the service lifetime of the apparatus [4–6].

To retard or prevent scale formation in circulating cooling water system, the addition of chemical scale inhibitors is therefore of considerable interest [7,8]. Currently, according to the development time and their performance, scale inhibitors can mainly be classified into natural polymer inhibitors, phosphorous inhibitors, polycarboxylic acid inhibitors, and green degradable polymer inhibitors. Natural polymer inhibitors include lignin, tannin, starch, and sodium humate. They are costly, unstable, and liable to decomposition under high temperature and pressure conditions, although they possess the function of scale inhibition, anticorrosion, and dispersion [9,10]. Phosphorous inhibitors, such as diethylene triamine penta methylene phosphonic acid (DTPMP), amino trimethylene phosphonic acid (ATMP), and 2-phosphomobutane-1,2,4-tricarboxylic acid, are expert in preventing the deposition of calcium scales under the condition of high hardness, pH, and temperature with good chemical stability. However, under the influence of hydrolysis and/or decomposition, these inhibitors can easily lead to the formation of orthophosphate, which will react with calcium ions to form relatively insoluble calcium phosphate scales. Besides, polyphosphonates, when reverted to orthophosphates, are potential nutrients for algae when discharged with wastewater [11–14]. With good chelating ability and dispersability, polyacrylic acid (PAA) and polymaleic acid inhibitors are part of polycarboxylic acid inhibitors, which can also be safely used up to a high temperature and pH at a very low dosage level. Nevertheless, their disadvantages, such as low calcium tolerance and the formation of calcium micelles, become more and more obvious and limit their application range in the circulating cooling water system [15,16]. Green degradable polymer inhibitors, such as polyaspartic acid and polyepoxysuccinic acid (PESA), are environment friendly and have the merits of biodegradation, chelation, and dispersion, but most of them only contain one kind of functional groups, which results in its poor performance in high-temperature environments [17,18]. In conclusion, the exploitation of new type of multifunctional calcium scale inhibitors being environmentally friendly has important social and economic benefits.

PESA, a representative "green" scale inhibitor, has been widely used because of its nontoxicity, nonphosphorus, and biodegradability features [8]. In order to improve its comprehensive scale inhibition performance, chemical modification, such as introducing new functional groups into the side chain of PESA, is proven to be available [19,20,27].

In this study, a modified and new PESA inhibitor, epoxysuccinic acid-oxalic acid-allypolyethoxy carboxylate (ESA-co-APEM), which contained carboxylic acid and ether groups, was synthesized successfully. Polyethoxy carboxylate (PEM) was prepared with water as solvent and redox system of hypophosphorous and ammonium persulfate as initiator by the free-radical polymerization. This polymer inhibitor is environment friendly as there are no phosphorus elements in its molecular formula. The chemical structure was characterized by Fourier transform infrared (FTIR), ^1H nuclear magnetic resonance (^1H NMR), and ^{13}C NMR; the scale inhibition performance of the polymer was studied by the method of static scale inhibition test; the biodegradability of PEM was studied with shaking-bottle incubating test; and the scale crystals were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The synthesized PEM, polyethoxy calcium carbonate inhibitor, is a new type of fine chemical product with the merits of simple production, low costs, and low dosages. There are four elements, carbon (C), hydrogen (H), oxygen (O), and sodium (Na), in its structure, without phosphorous (P), nitrogen (N), and sulphur (S), which will lead to secondary pollution to water environment, indicating that PEM is an environment-friendly calcium scale inhibitor.

2. Materials and methods

2.1. Reagents and instruments

Maleic anhydride (MA), hydrogen peroxide, sodium tungstate, calcium chloride, sodium bicarbonate, potassium hydrogen phosphate, disodium hydrogen phosphate, magnesium sulfate, ferric chloride, ammonia sulfate, and ammonium persulfate used were obtained from Zhongdong Chemical Reagent Co., Ltd. (Nanjing, Jiangsu, People's Republic of China). All the above chemicals were of analytical reagent grade without further purification. Distilled water was used in the whole experiments.

As the molecular weight (Mw) had a great impact on scale inhibition efficiency, gel permeation chromatography (GPC, calibrated with polyethylene glycol (PEG) standards) was used to detect the polymer's Mw. Water was used as the mobile phase, and the flow rate was 1.0 mL min^{-1}. The structure of synthesized ESA was analyzed by FTIR spectroscopy (VECTOR-22, Bruker Co., Germany), ^1H NMR, and ^{13}C NMR (AVANCE AV-500, Bruker, Switzerland). The structure of PEM polymer was characterized by the FTIR, ^1H NMR, and ^{13}C NMR. The morphological change of the $CaCO_3$ crystals on glass plates was recorded by using SEM (S-3400N, HITECH) and (XRD, Miniflex600).

2.2. Preparation of ESA, APEM, and PEM

The synthesis procedure of ESA is shown in Fig. 1. MA (9.8 g, 0.1 mol) was dissolved in a three-neck flask under alkaline conditions, and 20 mL of hydrogen peroxide was slowly added into it and reacted at 50°C for 1.5 h with magnetic stirring. Then, the solution was separated with ethyl alcohol and dried under nitrogen to 90°C.

Synthesis procedure of APEM is shown in Fig. 2. APEM was synthesized in our laboratory according to our previous

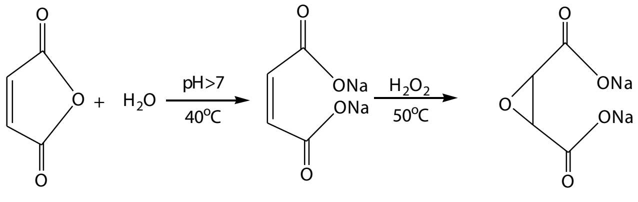


Fig. 1. Preparation of ESA.

studies [21]. Allyloxy polyethoxy ether (APEG) was carboxylate terminated using oxalic acid with a molar ratio of 1:1.

The synthesis procedure of PEM from ESA and APEM is shown in Fig. 3. ESA was copolymerized with APEM in aqueous medium. A 250 mL round-bottomed flask equipped with a mechanical stirrer, thermometer, and reflux condenser was charged with 30 mL DI water and a total of 0.1 mol ESA and then heated to the reaction temperature of 70°C over a period under nitrogen atmosphere. In mixed conditions, the initiator ammonium persulfate was dropped at a certain flow rate separately for about 1.5 h. Finally, the modified biodegradable polymer ESA-co-APEM was obtained, containing about 20.34% solid.

2.3. Inhibition performance against $CaCO_3$ scale

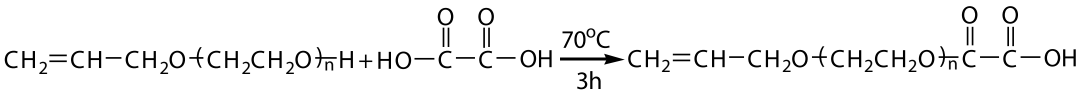
The inhibition performance of calcium carbonate using PEM was tested according to the national standard of People's Republic of China (GB/T16632-2008). The concentrations of Ca^{2+} and HCO_3^- in the system were 240 and 732 mg L^{-1}, respectively. The reaction was maintained at 80°C for 10 h with an amount of scale inhibitors. Then, they were cooled to room temperature. The remaining Ca^{2+} in the supernatant was titrated by ethylene diamine tetraacetic acid standard solution and compared with blank test. The inhibition efficiency η was defined as in Eq. (1):

$$\eta = \frac{\rho_1\left(Ca^{2+}\right) - \rho_2\left(Ca^{2+}\right)}{\rho_0\left(Ca^{2+}\right) - \rho_2\left(Ca^{2+}\right)} \times 100 \tag{1}$$

where $\rho_0(Ca^{2+})$ is the total concentration of Ca^{2+} (mg L^{-1}), $\rho_1(Ca^{2+})$ is the concentration of Ca^{2+} (mg L^{-1}) in the presence of the polymer inhibitor, $\rho_2(Ca^{2+})$ is the concentration of Ca^{2+} (mg L^{-1}) in the absence of the polymer inhibitor.

2.4. Biodegradability performance

The biodegradability of the copolymer PEM was studied with shaking-bottle incubating test according to the national standard of People's Republic of China (GB/T 15456-2008) and the method of Organisation for Economic Co-operation and Development [22]. Nutrient solutions were prepared ahead of time, including phosphate buffer, calcium chloride, magnesium sulfate, ferric chloride, and ammonia sulfate solutions. There were 30 mg L^{-1} copolymer PEM, about 10–20 mg L^{-1} permanganate indices (ρ(chemical oxygen demand (COD_{Mn})), certain amount of nutrient solutions, and inocula in tested materials, which were then cultured under the conditions of 30°C and 120 rpm vibration frequency in water-bathing constant temperature vibrator (DSHZ-300) for a period of 20–28 d. $\rho(COD_{Mn})$ was calculated and compared



$$CH_2{=}CH{-}CH_2O{+}CH_2CH_2O{+}_nH + HO{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH \xrightarrow[3h]{70^{\circ}C} CH_2{=}CH{-}CH_2O{+}CH_2CH_2O{+}_n\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH$$

Fig. 2. Preparation of APEM.

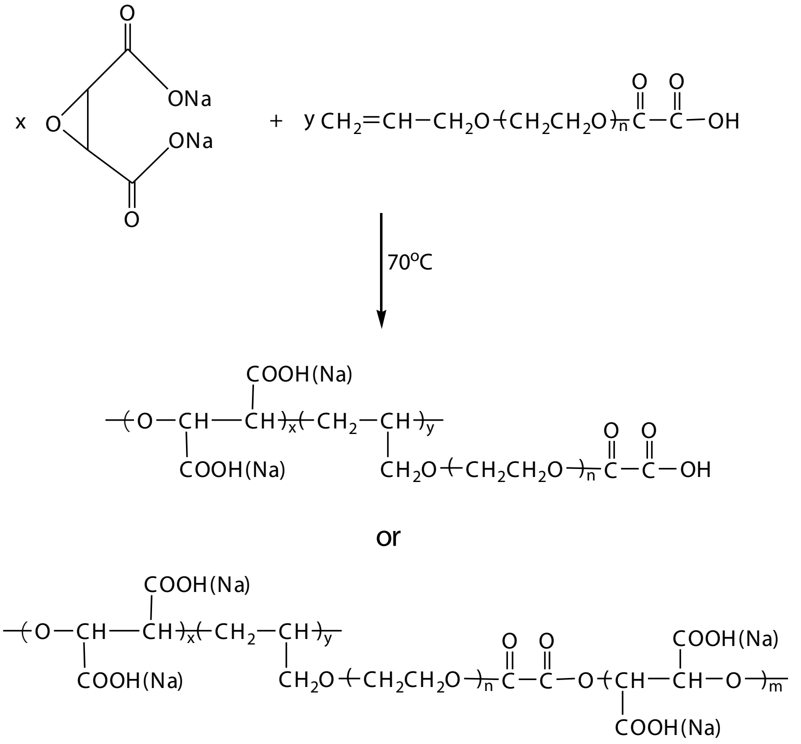


Fig. 3. Preparation of PEM.

with blank test, and then the degradation rate η_n was defined as in Eq. (2):

$$\eta_n(\%) = \left(1 - \frac{\rho\left(COD_{Mn}^{n}\right)}{\rho\left(COD_{Mn}^{0}\right)}\right) \times 100\% \tag{2}$$

where $\rho(COD^{n}_{Mn})$ and $\rho(COD^{0}_{Mn})$ are permanganate indices in *n* days and the initial value, respectively.

3. Results and discussion

3.1. Mw analysis of the PEM polymer

The results of GPC are listed in Table 1. APEM was a kind of ester monomer, its Mw was 320 g mol^{-1}, and the degree (*n*) was 6. As the final synthesized copolymer, PEM's Mw was 16,868 g mol^{-1}.

3.2. FTIR analysis of the PEM polymer

Fig. 4 shows the FTIR spectrum of ESA. It is seen from the curve that the absorption peak at 850 cm^{-1} is attributed to the deformation vibration of C–O–C (closed loop), the peak at 945 cm^{-1} is the symmetrical stretching vibration of C–O–C (closed loop), the absorption peak of 1,230 cm^{-1} is attributed to the asymmetric stretching vibration of C–O–C (closed loop), indicating the existence of a three-membered ring epoxy structure, the peak at 1,314 cm^{-1} is the bending vibration of C–H, the peak at 1,405 cm^{-1} is in plane bending vibration of O–H, the peak at 3,038 cm^{-1} is the stretching vibration of C–H (methenyl), and the peak at 3,348 cm^{-1} is the stretching vibration of O–H, demonstrating that it is ESA [23–25].

Table 1
Polymer's molecular weight

Product	Mw g^{-1} mol^{-1}
APEM (*n* = 6)	322
PEM (3% initiator)	16,868

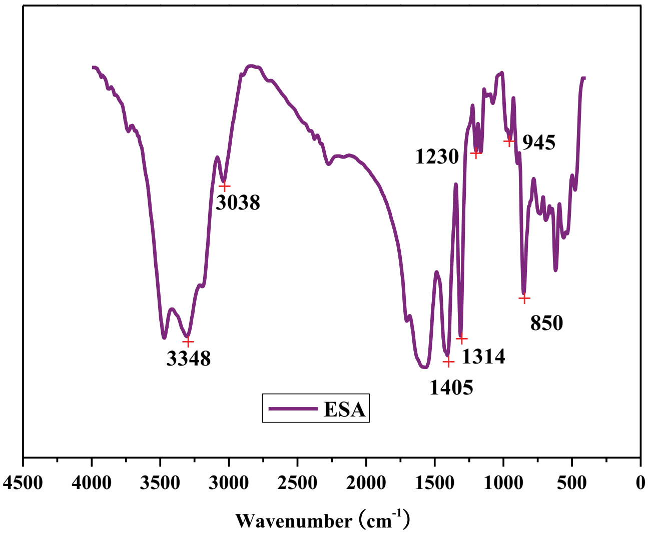


Fig. 4. FTIR spectra of ESA.

The FTIR spectra of APEM (a) and PEM (b) are shown in Fig. 5. The peak that appears at 1,638 cm^{-1} in curve (a) is for the C=C stretching vibration, while there are no peaks between 1,620 cm^{-1} and 1,680 cm^{-1} in curve (b). Meanwhile, the absorption peak at 1,128 cm^{-1} is the stretching vibration of cycle C–O–C bond, indicating that PEM has been successfully synthesized.

3.3. ^{1}H NMR and ^{13}C NMR spectrum of the PEM polymer

Fig. 6 is the spectrum of ^{13}C NMR of ESA in $(CD_3)_2SO$. It is seen from the ^{13}C NMR spectrum that peaks between 37.390 and 38.659 ppm are the solvent residual peak of $(CD_3)_2SO$, 130.481 ppm is assigned to C=C of the residual maleic anhydride, and 173.362 and 175.147 ppm are the signals of C=O. The peak at 55.268 ppm is attributed to C–O–C (closed loop), and in addition, there is no peak at 85.4 ppm, which is the adsorption peak of C–C. Thus, it can be inferred that ESA was synthesized successfully, and there was no by-product tartaric acid.

Fig. 7 shows the spectra of ^{1}H NMR of ESA, APEM, and PEM in $(CD_3)_2SO$. From the spectrum, we can obtain that peaks around 2.50 ppm are also assigned to the solvent residual peak of $(CD_3)_2SO$, and 3.327 ppm is attributed to C–H (three-membered ring) in curve (a). The chemical shifts in the region from 4 to 6 ppm are assigned to propenyl protons (CH_2=CH–CH_2–) in curve (b), while there are no peaks in this range in curve (c). In this case, the double bond absorption peaks completely disappear, revealing that the free-radical polymerization among ESA and APEM has occurred, which is corresponding to the results of FTIR analysis.

3.4. Effect of molar ratio of ESA and APEM on scale inhibition against $CaCO_3$

In order to obtain the optimum synthesis conditions of PEM copolymer, single-factor experiments were carried out.

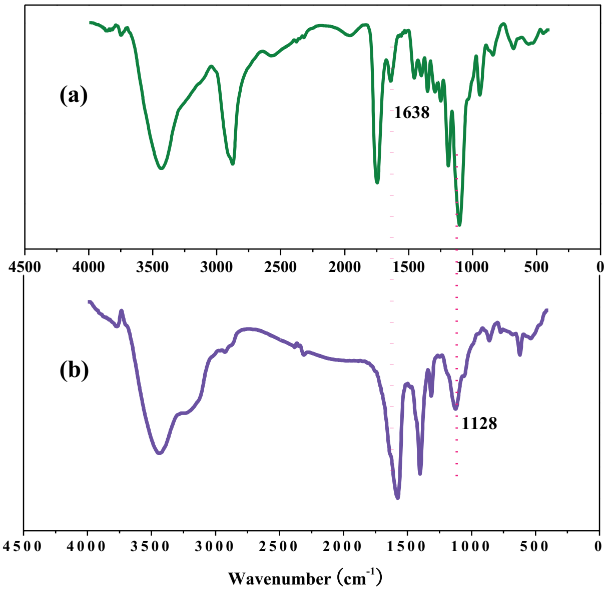


Fig. 5. FTIR spectra of (a) APEM, and (b) PEM.

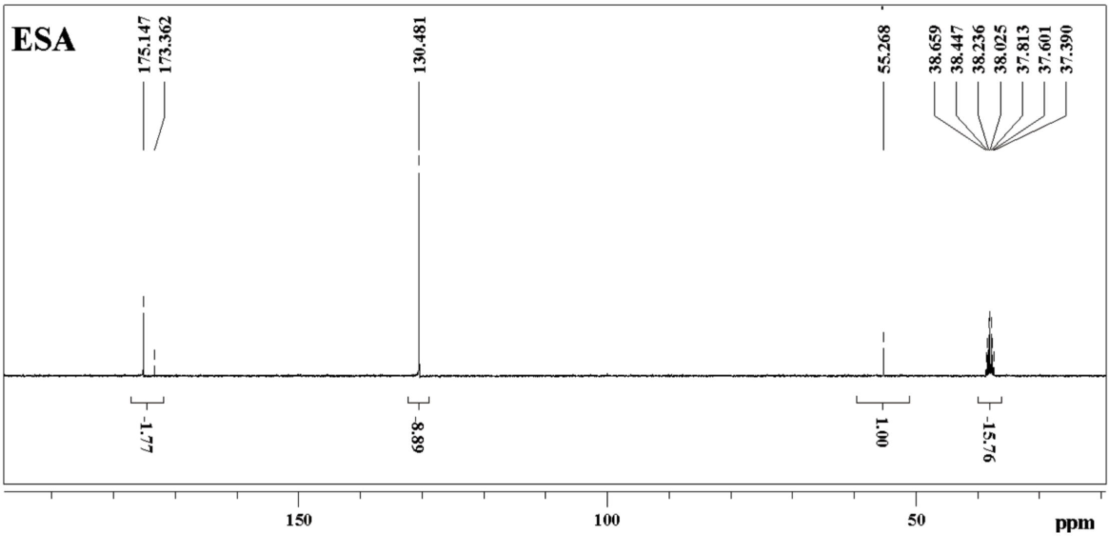


Fig. 6. The ^{13}C NMR spectra of ESA.

The effects of monomer molar ratio (n_{ESA}:n_{APEM}), the dosage of initiator (ammonium persulfate) (wt.%), and reaction temperature on the copolymer's scale inhibition efficiency were investigated.

The effect of molar ratio of ESA and APEM on inhibition efficiency of PEM against $CaCO_3$ scale is displayed in Fig. 8. According to the data, the polymers show poor antiscaling performance at 2 mgL^{-1} dosage, and there are sudden increases as the concentrations increase from 2 to 8 mg L^{-1}. In addition, the scale inhibition efficiency of PEM increases as the molar ratio of ESA and APEM is less than 2:1 and shows the best scale inhibition performance when the molar ratio is 2:1. However, the scale inhibition efficiency decreases as the molar ratio is greater than 2:1. At this best molar ratio, the maximum inhibition efficiency is 95.60% when the concentration of PEM is 16 mg L^{-1}. There is a fundamental reason that the molar ratio affects the number and distribution of functional groups and the molecular structure of PEM, which are responsible for scale inhibition performance.

3.5. *Effect of initiator dosage on PEM against $CaCO_3$ scale*

The Mw of PEM is one of the important factors that affect the scale inhibition, while initiator dosage can affect the Mw of PEM [17,26]. The result of the effect of initiator dosage on PEM against $CaCO_3$ scale is shown in Fig. 9, and the initiator dosage is 3%, 4%, 5%, 6%, 7%, 8%, and 9% of the total weight, respectively. It is observed that inhibition performance is better when the initiator dosage is 6%; inhibition performance is poor when the initiator dosage is more or less than 6%. The reason for this change is that the initiator dosage affects the number of free radicals produced in polymerization. The initiator dosage is too small to produce enough radicals, which leads to incomplete copolymerization, reduced complexing abilities for Ca^{2+}, and poor scale inhibition performance. However, when the initiator dosage is too large, too many free radicals are produced, which will make the polymerization rate too fast, the lengthy side chain too easy to curl up, the Mw of copolymer too small, and eventually lead to poor scale inhibition performance.

3.6. *Effect of reaction temperature on PEM against $CaCO_3$ scale*

Fig. 10 displays the effect of reaction temperature on PEM against $CaCO_3$ scale. The datum of Fig. 10 indicates that the scale inhibition efficiency increases when the reaction temperature is increased and reached a maximum at 70°C. However, the scale inhibition performance decreases when the reaction temperature is more than 70°C. It is because that reaction temperature affects the growth mode and speed of the copolymer chain. The low reaction temperature decreases the number of free radicals produced, while polymerization reaction is easy to occur in the position of far side chain groups in view of the steric effect. On the other hand, high reaction temperature leads to a large amount of free radicals, the reaction tends to take the polymerization approach of proximal side chain groups, and the polymerization rate is acute. There are coulomb electrostatic interactions between negatively charged carboxyl groups and positively charged calcium ions. When the distance between carboxyl groups of PEM matches with that between calcium ions of calcite surfaces, the adsorption interaction is extremely strong, retarding the further deposition of calcium carbonate on the crystal surfaces, leading to lattice distortion, and inhibiting growth of calcium carbonate crystals. As a result, too low or too high temperature is not beneficial to the formation of copolymer, in which the carboxyl groups have appropriate spatial distances [27].

This result demonstrates that the optimum conditions for PEM synthesis are the molar ratio of 2:1, polymerization temperature of 70°C, and initiator dosage of 6%.

3.7. *Effect of PEM concentration on scale inhibition against $CaCO_3$*

The effect of PEM concentrations on scale inhibition efficiency against $CaCO_3$ was compared with that of other

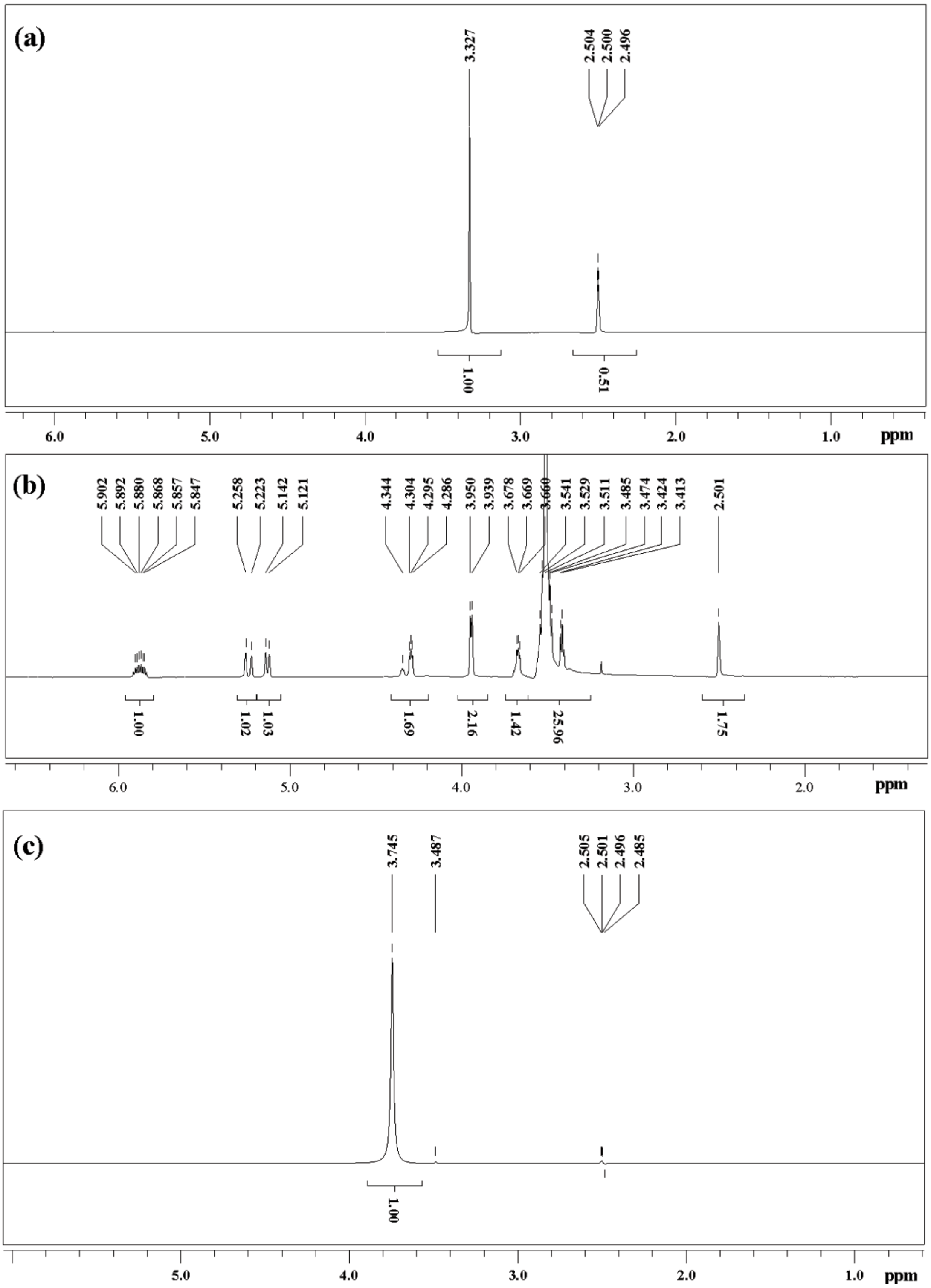


Fig. 7. The ^{1}H NMR spectra of (a) ESA, (b) APEM, and (c) PEM.

scale inhibitors, as shown in Fig. 11. It is seen that the PEM inhibitor has very good scale inhibition function and shows much better inhibition performance against $CaCO_3$ than DTPMP, ATMP, PESA, and PAA. As is apparent from Fig. 11, the scale inhibition efficiency against $CaCO_3$ increased with the rising of PEM concentration and beyond 10 mg L^{-1} the inhibition efficiency kept nearly constant with further rising of the concentration of PEM inhibitor. The scale inhibition efficiency of PEM inhibitor reached the value of 89.60% at the concentration of 8 mgL^{-1}. Compared with PEM,

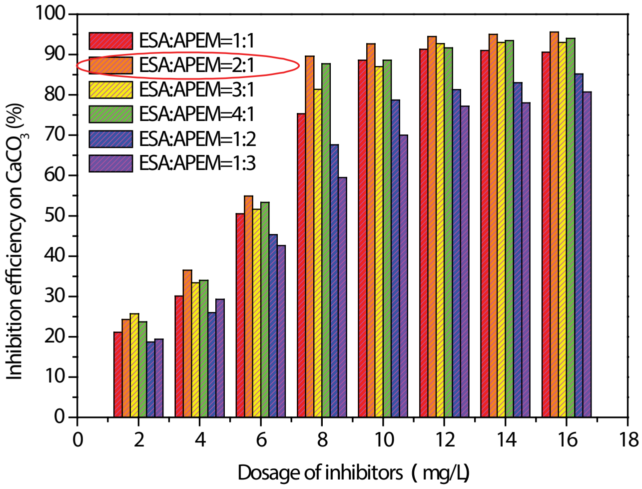


Fig. 8. Effect of molar ratio of ESA and APEM on scale inhibition against $CaCO_3$.

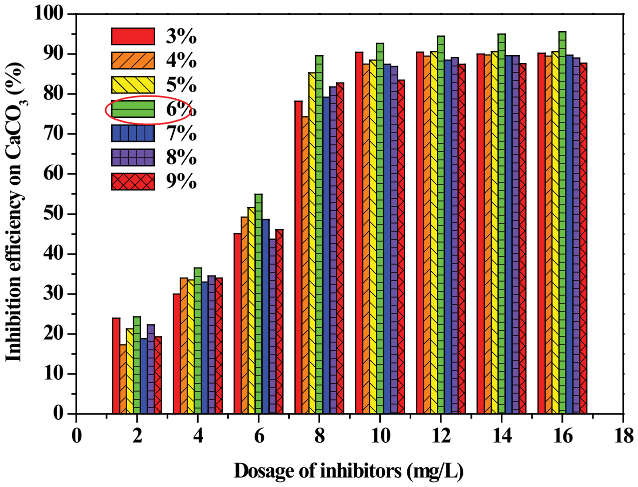


Fig. 9. Effect of initiator dosage on PEM against $CaCO_3$.

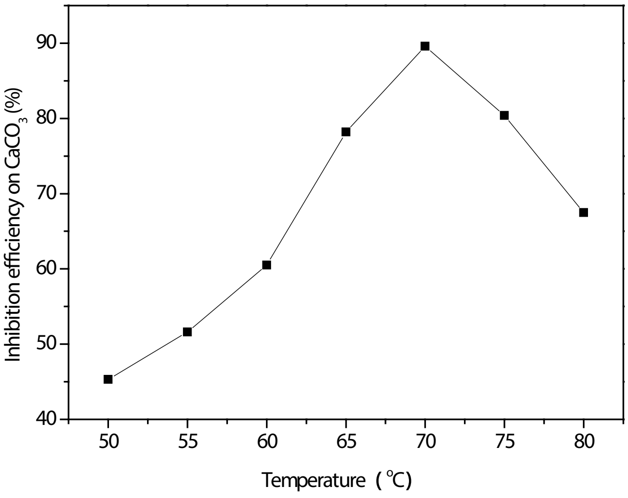


Fig. 10. Effect of reaction temperature on PEM against $CaCO_3$.

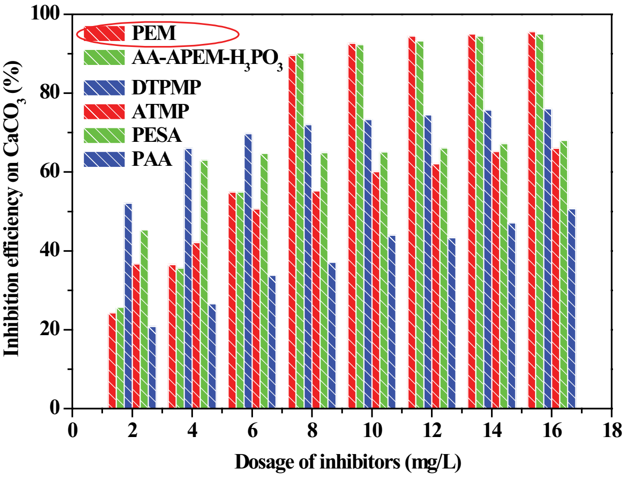


Fig. 11. Effect of PEM concentration on scale inhibition against $CaCO_3$.

AA-APEM-H_3PO_3 also has superior ability on the inhibition of $CaCO_3$ deposits, with 90.16% inhibition at a level of 8 mgL^{-1}, whereas it contains phosphorus in the molecule, which is harmful to the environment.

3.8. Influence of solution property on calcium carbonate inhibition

Solution properties have a great influence on the precipitation of calcium carbonate [28]. In order to optimize parameters of the circulating water process on an industrial scale, we investigated the effect of the solution parameters on calcium carbonate inhibition of PEM. The results are shown in Fig. 12 as follows.

Fig. 12(a) shows that scale inhibition efficiency is affected by the concentration of Ca^{2+}. The concentration of Ca^{2+} is in the range of 120–720 mg L^{-1}, the concentration of antiscalant is 10 mg L^{-1}, the temperature is 80°C, the heating time is 10 h, and pH value is 9. With the concentration of Ca^{2+} rising, the scale inhibition efficiency decreases. When increasing the concentration of Ca^{2+} from 120 to 720 mg L^{-1}, the inhibitory power decreases from 93.55% to 45.82%. This trend of scale inhibition is easy to understand that the hardness of the water is an essential factor on scale inhibition test. What should be emphasized is that the $CaCO_3$ inhibition efficiency is still higher than 40% even when the hardness value is 720 mg L^{-1}.

The effect of solution temperature on scale inhibition efficiency against $CaCO_3$ was researched in Fig. 12(b). The concentration of Ca^{2+} is 240 mg L^{-1}, the concentration of antiscalant is 10 mg L^{-1}, the temperature is in the range of 65°C–95°C, the heating time is 10 h, and pH value is 9. It is shown that temperature affects the formation of scale. The scale inhibition efficiency of PEM against $CaCO_3$ decreased with the rise of heating temperature. It can be attributed that the solubility of calcium carbonate crystal in water decreases and the scale formation rate increases with the increase of temperature.

Solution pH value is another factor affecting scale inhibition efficiency against $CaCO_3$ and the data are shown in Fig. 12(c). The concentration of Ca^{2+} is 240 mg L^{-1}, the concentration of antiscalant is 10 mg L^{-1}, the temperature is

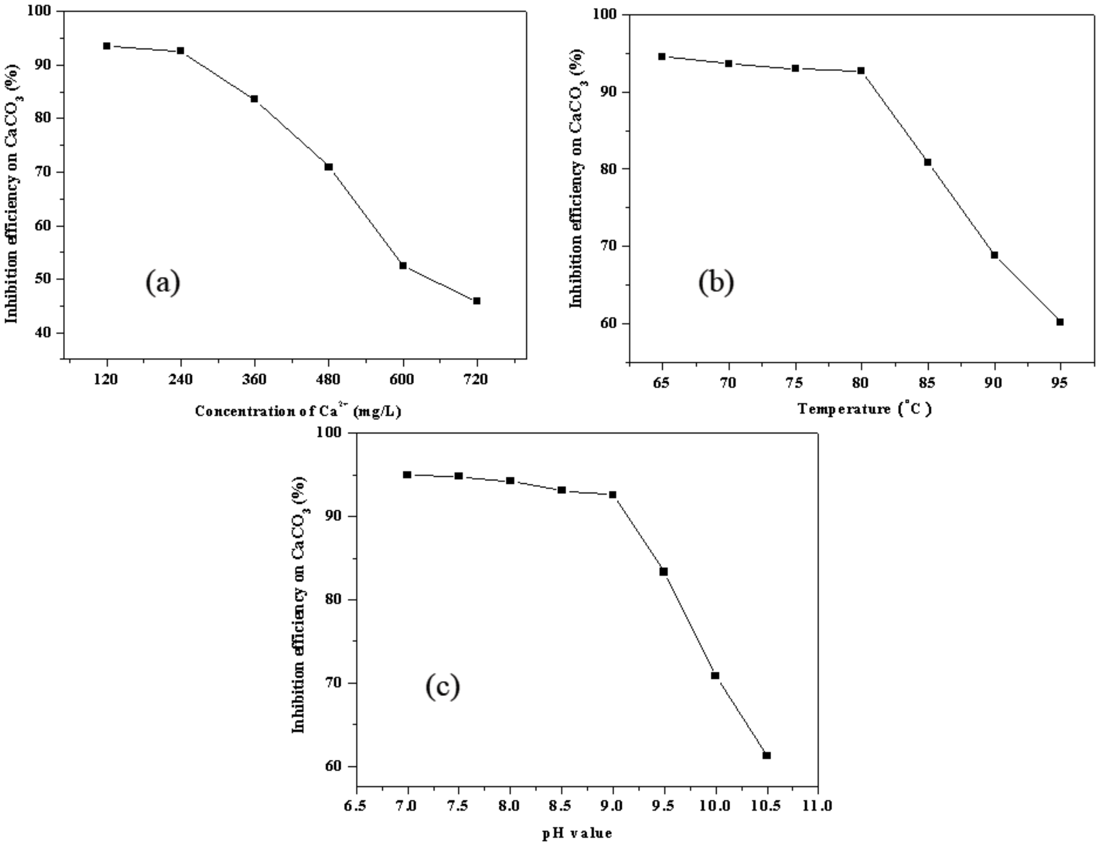


Fig. 12. Calcium carbonate inhibition at a level of 10 mg L^{-1} PEM as a function of Ca^{2+} concentration (a), temperature (b), and pH value (c).

80°C, the heating time is 10 h, and the pH value is in the range of 7–10.5. As illustrated from Fig. 12(c), calcium carbonate inhibitory power drops from 95% to 61% with the increase of pH values, which indicates that the scale inhibition efficiency is influenced greatly by the solution pH. It is known that the increase of pH will lead to the decrease of H^+, and then break up the equilibrium between Ca^{2+} and CO_3^{2-} and promote the formation of calcium carbonate precipitate.

3.9. Effect of PEM concentration on biodegradability

According to the literature [29], the biodegradability evaluation standards are listed in Table. 2 and the biodegradability results of PEM are given in Table. 3 at different inhibitor dosages. The results indicate that PEM is easily degradable because all rates are more than 40% on day 10 and above 95% on day 28, while the degradation rate is nearly 100% on day 20 at a dosage of 40 mg L^{-1}. This means the scale inhibitor will be thoroughly degraded as time goes on, being friendly to water environment. In addition, the degradation rate of PEM increases with added days, but there is no regularity with increasing dosages.

3.10. SEM images of $CaCO_3$ crystal

The $CaCO_3$ scale deposits were observed by means of an SEM. As shown in Fig. 13, $CaCO_3$ deposits show calcite structure with regular shape and glossy surface, without PEM (Figs. 13(a) and (b)). On the other hand, when PEM was added to the solution, the shapes of $CaCO_3$ deposits are irregular and the crystalline grain tends to be finer (Figs. 13(c) and (d)), and as the inhibitor was absorbed at the crystal surface, the crystal growth habits of $CaCO_3$ are blocked by

Table 2
The evaluation standards for biodegradability

Degradation rate	Performance
$\eta_{10} > 10\%$ or $\eta_{28} > 60\%$	Easily degradable
$\eta_{10} > 10\%$ or $\eta_{28} < 60\%$	Degradable
$\eta_{10} < 10\%$ or $\eta_{28} < 10\%$	Difficultly degradable

Table 3
The results of the biodegradability of PEM

Dosage (mg L^{-1}) Degradation rate	η_4	η_{10}	η_{16}	η_{20}	η_{28}
10	30.65	48.32	71.50	98.30	98.00
20	36.68	50.14	73.41	95.62	96.10
30	32.64	45.88	78.65	98.08	98.54
40	32.86	53.51	75.14	99.50	99.50

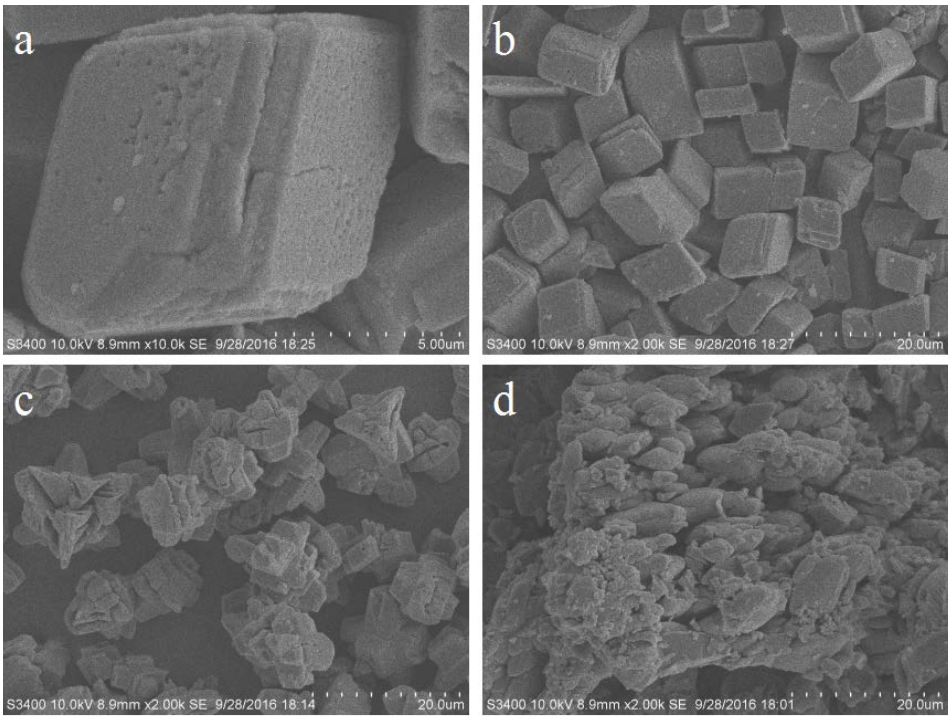


Fig. 13. SEM images of $CaCO_3$ (a, b) without PEM, $CaCO_3$ (c) with 3 mg L^{-1} of PEM, and $CaCO_3$ (d) with 8 mg L^{-1} of PEM ($\rho(Ca^{2+})$ = 240 mg L^{-1}, $\rho(HCO_3^-)$ = 732 mg L^{-1} (as $CaCO_3$), 10 h reaction at 80°C).

the PEM, which result in the crystal distortion. This change can make hard scale transforming into soft dirt that is easily washed away by water at certain water scouring velocity or temperature.

3.11. XRD analysis

XRD spectra of $CaCO_3$ crystals are shown in Fig. 14. We can see the diffraction peaks of 23.10°, 29.46°, 31.47°, 36.17°, 39.26°, 43.86°, 48.56°, and 50.23° in the spectrum (a), which are characteristic peaks of calcite. These results indicate that in the absence of PEM, the main crystal form of calcium carbonate precipitate is calcite [30]. In spectrum (b), diffraction peaks of 21.00°, 24.88°, 27.05°, 32.72°, 43.85°, and 50.03°, corresponding to vaterite [31], are very strong, which demonstrates that vaterite is the main crystal form in the presence of PEM. The change of crystal forms declares that PEM contributes to distortion of $CaCO_3$ crystals [32].

3.12. Inhibition mechanism toward $CaCO_3$ scale

PEM is a structurally well-defined biblock copolymer, depicted in Fig. 15; one block is PESA and the other is PEG segments. It is well known that PESA chain in PEM could react with Ca^{2+} or crystal nucleus of $CaCO_3$ and then affect the growth of $CaCO_3$ crystals. Both PESA and PEG (marked with black ribbons in Fig. 15) segments are hydrophilic blocks and exist randomly in water [33]. When polymer solutions are added into the cooling water system, carboxyl groups in PEM matrix can recognize and encapsulate or react with positively charged calcium ions. Encapsulation or interaction between Ca^{2+} and carboxyl groups leads to the spontaneous formation of PEM-Ca complexes (Encapsulation zone). Therefore, nucleation and crystal growth processes are retarded, the tenacity of the scale is weakened, and its crystal structure is distorted [15]. At the same time, water-compatible PEG segments have a very strong hydrophilicity and thus increase its solubility in water (highly dissolved solid particle zone). As a consequence, the aggregation of $CaCO_3$ solid particles is blocked.

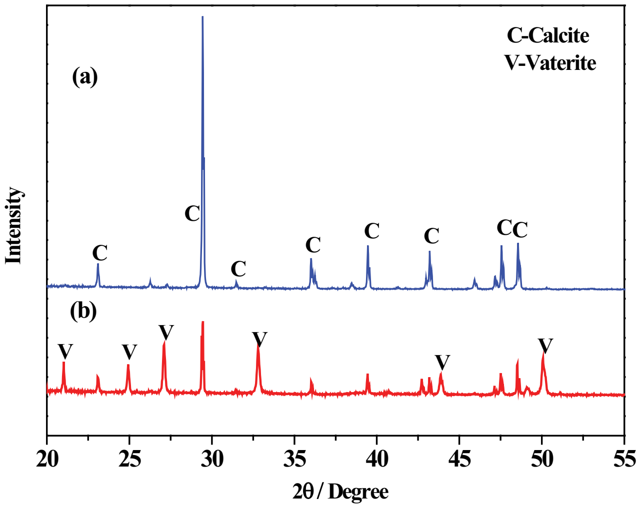


Fig. 14. XRD analysis of $CaCO_3$ (a) without PEM and $CaCO_3$ (b) with 5 mg L^{-1} of PEM ($\rho(Ca^{2+})$ = 240 mg L^{-1}, $\rho(HCO_3^-)$ = 732 mg L^{-1} (as $CaCO_3$), 10 h reaction at 80°C).

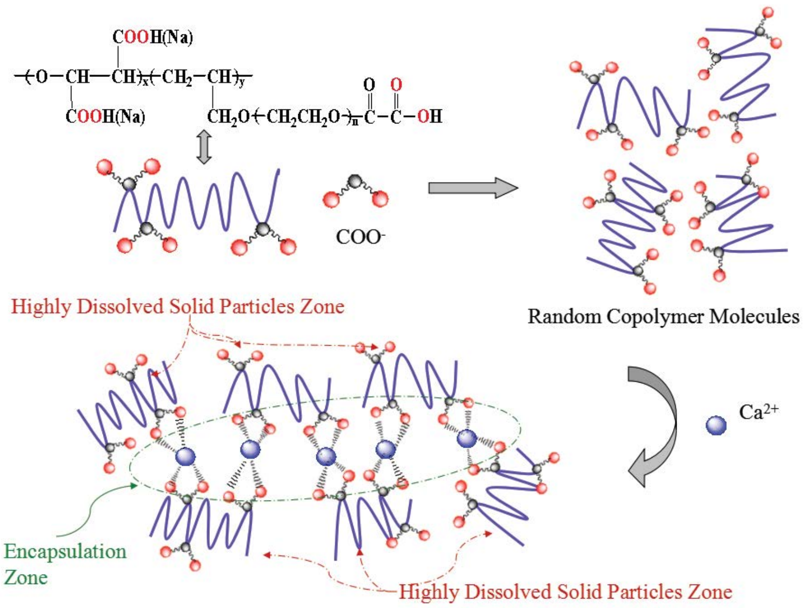


Fig. 15. The interaction between calcium ions (or $CaCO_3$ crystals) and PEM.

4. Conclusions

This study investigated the effect of a copolymer on the calcium carbonate inhibition. Monomer ESA was prepared from MA, APEM was produced from APEG and oxalic acid by carboxylic acid functionalization method, and modified PESA copolymer (PEM) was synthesized. Structures of ESA, APEM, and PEM were identified by FTIR, ^{1}H NMR, and ^{13}C NMR. The optimum synthetic conditions for PEM are the molar ratio of ESA and APEM which is 2:1, initiator dosage of 6%, polymerization temperature of 70°C, and reaction time of 3 h. PEM has good scale inhibition on $CaCO_3$. The dosage of copolymer has a strong effect on the formation of calcium carbonate precipitation. It can be concluded that the order of preventing the precipitation from flask tests is PEM > AA-APEM-H_3PO_3 > DTPMP > PESA > ATMP > PAA. The inhibition efficiency is 95.60% for $CaCO_3$ with inhibitor concentration of 16 mg L^{-1}. These better performances were partially attributed to PEM simultaneously possessing hydroxyl and carboxylic functional groups, thus increasing the chelating ability of the Ca^{2+} and then increasing the solubility of Ca scale. Meanwhile, PEM had good degradation ability and could degrade after discharge.

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