Preparation of pH-sensitive core-shell organic corrosion inhibitor and its release behavior in simulated concrete pore solutions

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HIGHLIGHTS
• The core-shell organic corrosion inhibitor encapsulated with benzotriazole was prepared based on PEO-b-PS copolymers and dialysis method.
• The release process of BTA reserved in core-shell corrosion inhibitor presented strong pH-sensitivity in simulated concrete pore solutions.
• The size and morphology alterations of core-shell inhibitors determine their release mechanism in simulated concrete pore solutions.

GRAPHICAL ABSTRACT

ABSTRACT
In this paper, core-shell organic corrosion inhibitors (COCI) based on poly(ethylene oxide)-b-polystyrene (PEO-b-PS) copolymers were successfully prepared. The release process of benzotriazole (BTA) reserved in COCI was investigated by UV spectrophotometry in deionized water and simulated concrete pore (SCP) solutions with different pH values, and the size and morphology of COCI were determined by dynamic light scattering measurements and SEM combined with EDS before and after the release process. The release amount of BTA was slightly higher (9%) in deionized water with lower pH values, which was related to the higher protonation degree of oxygen groups in PEO moieties and less compact structure of COCI at lower pH environment. In SCP solutions, the pH sensitivity of BTA release process was more pronounced, evidenced by 5 times lower release amount of BTA in SCP solution with a pH value of 13, compared to SCP solutions with pH values lower than 11. The most plausible reason is that in SCP solution with a pH value of 13, the existence of Ca\textsuperscript{2+} and high alkaline environment are beneficial for the agglomeration of COCI and formation of Na-rich layer around COCI, hindering the diffusion rate and subsequently release process of the reserved BTA.

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1. Introduction
It is well known that corrosion of steel reinforcement in concrete is a major cause for concrete deterioration, leading to significant engineering damages and economic loss. In reinforced concrete, normally the
steel reinforcement is in a passive state due to the high alkaline concrete environment (pH = 12.6–13.5) [1,2]. However, corrosion of the reinforcement can be initiated by carbonation and chloride penetration. During the carbonation process, the pH value of the concrete pore solution can be reduced to below 11.5, resulting in de-passivation and uniform corrosion of the steel reinforcement [3,4]. Chloride causes pitting corrosion, and the local pH on the steel surface will drop to even 5 [5], resulting in severe corrosion propagation and damage. The accumulation of corrosion products (with a larger volume compared to steel reinforcement) will result in the cracking and spalling of concrete, further accelerating the corrosion rate of the reinforcing steel and possible rapid failure of reinforced concrete structures [6].

In order to mitigate the corrosion damage of reinforced concrete, several methods were proposed and developed, e.g. surface coatings for the steel [7], sealing and membranes for concrete surface [8,9], electrochemical protection [10] and corrosion inhibitors [11,12]. Due to the easy-operation and low cost, organic corrosion inhibitors (e.g. alkanolamines, amines and amine acid) were widely studied and applied for the corrosion protection of reinforced concrete [13]. Based on the application methods and mechanisms, organic corrosion inhibitors are divided into two types [13]: migration corrosion inhibitors, which are externally applied on concrete surface, penetrating though the concrete matrix and reaching the surface of steel reinforcement (for existing reinforced concrete structures); adsorbed corrosion inhibitors, which are added in fresh mixture during the concrete preparation (for new reinforced concrete structures). Normally, the admixed organic corrosion inhibitors can form a barrier layer by adsorbing on the steel surface, halting either the anodic reaction or cathodic reaction, thus preventing the corrosion damage of the steel reinforcement [14]. Although the admixed corrosion inhibitors are largely used to prevent chloride-induced corrosion in reinforced concrete structures, their interaction mechanisms with the passive film present on steel still requires deeper understanding [14]. Besides, the admixed organic corrosion inhibitors may influence the initial set [13,15] and present negative effect on the material properties of concrete: e.g. amine and ester corrosion inhibitors increased the transport coefficient of concrete, which was related to a shift of the pore size distribution to the large diameter direction [16]. The more porous microstructure and modified transport property will logically lead to a higher permeability and ions transport property, which is harmful for the durability of reinforced concrete. Further, corrosion is normally initiated at local sites on steel surface, leading to environmental alterations (pH drop and chloride increase) at these corrosion sites. However, normally used organic corrosion inhibitors are not able to identify the local sites for corrosion initiation, thus can’t targeted repair the corrosion damage at the first moment. Corrosion initiation of the steel reinforcement is accompanied with a pH drop from high pH value to low pH value. Therefore, if pH sensitive self-healing microcapsule materials (encapsulated with organic corrosion inhibitors) are used for the corrosion control of reinforced concrete, on one hand, before corrosion initiation, organic corrosion inhibitors are stably encapsulated in microcapsules in the high pH environment, thus their negative effect on the material properties of concrete can be mitigated; on the other hand, after corrosion initiation, the smart repair of corrosion damages can be achieved because the reserved corrosion inhibitors can be efficiently released due to the local pH drop at corrosion initiation sites (in fact such self-healing microcapsule materials (micro and nano-containers) based on pH-trigger mechanism have already been reported for the preparation of anticorrosion coatings [17–19]).

In recent years, self-healing microcapsules were investigated for the self-healing of cracks in cement-based materials and the release of the encapsulated healing agents was mainly triggered by the rupture of microcapsules caused by the physical force of cracking [20–22]. However, these self-healing microcapsules are not suitable for the corrosion control of reinforced concrete due to the lack of sensitivity to the environmental alterations (pH drop and chloride increase) caused by corrosion initiation. Therefore, the chemical self-healing materials were also investigated. Xiong et al. [23] prepared a novel capsule-based self-recovery system based on a silver alginate hydrogel. The results indicate that the capsules were entirely collapsed at a very low concentration of chloride ions (0.1 wt%), exhibiting a promising prospect for corrosion protection of reinforced concrete in marine environment. Besides the alteration of chloride concentration, the healing agents encapsulated in the capsules can also be triggered by pH variation. Wang et al. [24] prepared ethyl cellulose (EC)/calcium hydroxide microcapsules for the purpose of restoring the high alkaline environment to hinder the corrosion in cementitious materials. The results indicate that the prepared microcapsules was disintegrated in solutions with a pH value lower than 12 and the encapsulated calcium hydroxide was released to increase the pH value of the solution. Dong et al. [25] produced a type of chemical self-healing microcapsules, in which sodium monofluorophosphate was covered by polystyrene resin (PS). The release rate of sodium monofluorophosphate increased with the decrease of pH value in the simulated concrete pore solution: up to 90 days, the accumulative release amount of sodium monofluorophosphate was about 10% higher in simulated pore solution with a pH value of 7 than in simulated pore solution with a pH value of 13. However, the above prepared microcapsules may present negative effect on the material properties of concrete due to their particle sizes (about 2.5 mm and 500 μm in reference [23,24] respectively; in the range of about 680–770 μm in reference [25]). Further, there is still a large potential to improve the pH sensitivity of the self-healing materials.

In order to achieve the efficient self-healing effect on corrosion damage of reinforced concrete, there are some special requirements for the used self-healing materials: (1) high chemical stability of microcapsules in cement matrix (high alkaline environment), (2) successful encapsulation of healing agents in the microcapsules under high alkaline environment; (3) rapid release of the encapsulated healing agents after the environment alterations (pH drop or chloride increase) related to the corrosion initiation of reinforced concrete. Therefore, the release process of the healing agents reserved in the microcapsules under different pH values is very important.

In this study, a novel type of core-shell organic corrosion inhibitors (COCI) was prepared based on poly (ethylene oxide)–b–polystyrene (PEO-b-PS) copolymers. Benzotriazole (BTA) and its derivatives were reported as effective corrosion inhibitors for steel reinforcement in simulated concrete pore solutions [6,26,27]. Compared to the traditional amine-based admixed organic inhibitors [13], BTA presented an excellent corrosion inhibition efficiency even at a low concentration (10⁻⁴ M) in the presence of 3.5 wt% chloride [28]. Therefore, BTA was used as the healing agent encapsulated in the prepared core-shell organic corrosion inhibitors. The release process of BTA reserved in COCI was investigated both in deionized water and simulated concrete pore (SCP) solutions with different pH values. The accumulative release amount of BTA reserved in COCI was evaluated by UV spectrophotometry; dynamic light scattering (DLS) measurements and scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS) were applied to characterize the size and morphology alterations of the prepared COCI after the release process.

2. Materials and methods

2.1. Materials

Methoxy poly (ethylene oxide) (PEO13,OH, Mn = 5000, Aldrich) was precipitated in cold methanol (−40 °C, Aladdin, 99.9%) to remove trace of H₂O, and dried under vacuum at 40 °C overnight. CuBr (Aldrich, 98%) was stirred over-night in glacial acetic acid (Aladdin, 99.5%), filtered and rinsed successively by acetic acid (Aladdin, 99%) and ether (Guangzhou, 99%) to remove trace of CuBr₂. Styrene (Aladdin, 99%), dichloromethane (DCM, Aladdin, 99%), triethylamine (Aladdin, 99.5%)
and anisole (Aladdin, 99%) was stirred overnight in calcium hydride (Aldrich, 97%) and distilled. N,N,N′,N″-pentamethyldiethylenetriamine (PMDETA, Aldrich, 98%), 2-bromoisobutyryl bromide (BIB, Aldrich, 98%), tetrahydrofuran (THF, Aladdin, 99%), alumina (Aladdin) and 1,4-dioxane (Aladdin, 99%) were used as received. Cellulose membrane bag (MWCO 12,000 g/mol, Aldrich) was pre-swollen prior to use, deionized water used was Milli-Q water (Milli Q, USA).

2.1.2. Preparation of core-shell organic corrosion inhibitors

The prepared PEO-b-PS diblock copolymers have amphiphilic forms, presenting hydrophilic PEO chain and hydrophobic PS chain [30]. Therefore, PEO-b-PS copolymers have self-assembly property and can form vesicles with PEO shell and PS core at the interface between organic solvent and water. As shown in Fig. 2, during the self-assembly process, organic corrosion inhibitor can be encapsulated in the vesicles to prepare the core-shell corrosion inhibitors. The core-shell corrosion inhibitors were prepared by dialysis method: PEO-b-PS copolymers (0.25 g) and benzotriazole (0.5 g) were dissolved in 1, 4-dioxane (200 ml), and the solution was sealed in a cellulose membrane bag. The dialysis bag was first dialyzed against 1 g/l BTA solution (to remove un-capsulated BTA remained in the solution) for another 12 h (deionized water was also replaced every 2 h). Finally, an opalescent COCl solution was obtained. The concentration of COCl was 0.5 g/l in the solution, and the zeta potential determined by DLS measurement (Malven Zetasizer Nano S, U.K.) was — 40.6 mV.

2.1.3. Preparation of simulated concrete pore solutions

The influence of pH on the release process of BTA reserved in COCl was investigated in deionized water and simulated concrete pore solutions (SCP). The pH value of the received deionized water was about 7, and the pH value of deionized water was increased to 9, 11 and 13 by 0.1 M NaOH solution respectively. The simulated pore solution in this study is used to investigate the influence of different ions (e.g. Ca²⁺, Na⁺, etc.) in concrete together with pH value on the release behavior of BTA. In order to simplify the environment for the investigation of release process of BTA, based on the reported study [14], SCP solution with a pH value of 13 was prepared by NaOH (0.06 M) and Ca(OH)₂ (saturated) in this study: the pH value of SCP solution was also adjusted to 11, 9 and 7 by using 32.5 wt% HNO₃ solution, respectively.

2.2. Methods

2.2.1. Copolymers characterization

Nuclear magnetic resonance (NMR) was used to determine the molecular structure of the prepared PEO-b-PS copolymers. ¹H NMR spectra measurements were conducted by a Bruker AVANCE III 400 (Switzerland) spectrometer, operating at 250 MHz, using deuterated chloroform (CDCl₃-d) as solvent and tetramethylsilane (TMS) as an internal standard (the temperature was 25 °C). The number-average degree of PS polymerization was calculated by comparing the peak integral assigned to PEO protons (4H, —O—CH₂—CH₂—) at 3.64 ppm to aromatic PS protons (5H, —Ph) at 6.2—7.2 ppm.

The average molecular weight (Mₘ) and polydispersity index (PDI, Mₙ/Mₘ) were determined by gel permeation chromatography (GPC) adopting an Agilent 1200 series GPC system equipped with an LC quant pump, PL gel 5 mm 500 Å, 10,000 Å, and 100,000 Å columns in series and RI detector. The column system was calibrated with a set of...
monodisperse polystyrene standard using THF as mobile phase with a flow rate of 1.0 ml/min at 30 °C.

The encapsulated amount of BTA in COCI was determined by UV–vis spectrophotometry (HEXIOS Gamma & Delta, USA) at 265 nm. 0.3 ml COCI solution was dissolved in 10 ml 1, 4-dioxane solvent. The concentration of BTA was calculated according to a standard curve of pure BTA/1, 4-dioxane solution (the influence of PEO-b-PS copolymers on the light absorption of BTA is negligible at 265 nm). The encapsulated amount was defined as the weight of encapsulated BTA weight per unit weight of PEO-b-PS copolymers used for the preparation of COCI.

2.2.2. Release process of BTA reserved in COCI
The release profile of BTA reserved in COCI in deionized water and SCP solutions with different pH values were investigated by using dialysis bags at room temperature. The dialysis bag containing 3 ml COCI solution was immersed in 120 ml deionized water/SCP solution (pH = 7, 9, 11 and 13 respectively) with stirring at 110 rpm. At different time intervals, 3 ml ($V_e$) deionized water/SCP solution was collected and BTA concentration in the solution was determined by UV–vis spectrophotometry (HEXIOS Gamma & Delta, USA) at 265 nm. The accumulative release amount ($E_r$, mg/l) was calculated by Eq. (1) as follows:

$$E_r = \left( V_e \sum_{1}^{n} C_i + V_0 C_f \right)$$

where, $V_0$ (ml) is the total volume of the release media ($V_0 = 123$ ml); $V_e$ (ml) is the volume of solution collected for the measurement of BTA concentration at each time interval ($V_e = 3$ ml); $C_i$ (mg/ml) is the concentration of BTA at the $i$th time interval; $C_f$ (mg/ml) is the concentration of BTA for the final sample. There were 3 replicates in SCP solution with different pH values.

2.3. Size and morphology alteration of COCI during the release process
The size distribution of COCI before and after the release process in deionized water/SCP solutions with different pH values was determined by dynamic light scattering (DLS) with a Malvern Zetasizer Nano S. The measurements were conducted in a 1.0 ml quartz cuvette, using a diode laser of 800 nm and the scattering angle was fixed at 90°.

The morphology of COCI before and after the release process were investigated by scanning electron microscopy (SEM, EVO18, Germany) combined with energy dispersive spectroscopy (EDS, Merlin Compact VP, England). SEM images were obtained with an accelerating voltage of 10 kV and magnification of 20,000×.

3. Results and discussion

3.1. Characterization of the synthesized PEO-b-PS copolymers and prepared core-shell organic corrosion inhibitors

The chemical structures of the obtained macroinitiator PEO-Br (spectra A) and PEO-b-PS diblock copolymers (spectra B) were characterized by $^1$H NMR, as shown in Fig. 3. For $^1$H NMR spectrum of PEO-Br, the signals at 3.65 (a), 4.32 (b) and 1.92 (c) ppm were ascribed to $\text{-OCH}_2\text{-CH}_2\text{-}$, $\text{-OCH}_3$ and $\text{-CCH}_3$. Further, the integral area ratio of the signals b and c was 1:3, indicating that PEO$_{113}$OH was completely esterified to form macroinitiator PEO-Br. For $^1$H NMR spectrum of PEO-b-PS copolymers, the signals at 3.65 (a) and 6.2–7.2 (d, e) ppm were ascribed to $\text{-OCH}_2\text{-CH}_2\text{-}$ and $\text{-Ph}$ respectively. Because the proton ratio of $\text{-OCH}_2\text{-CH}_2\text{-}$ and $\text{-Ph}$ was 12.95 (the chain length of PEO-OH used in this study is known as 113), the molecular formula of the prepared copolymers was PEO$_{113}$-b-PS$_{1171}$.

The GPC curve of the prepared PEO-b-PS copolymers is presented in Fig. 4. GPC result showed that the determined molecular weight was 93,561 (determined by the elution time), and the distribution of molecular weight $M_w:M_n$ was 1.25. Generally, it is considered that $M_w:M_n < 1.3$ is a narrow molecular weight distribution for copolymers [31]. Therefore, the GPC result combined with NMR indicates that PEO$_{113}$-b-PS$_{1171}$ copolymers were successfully synthesized through ATRP technique, and the synthesized copolymers can be used for the subsequent preparation of core-shell organic corrosion inhibitors.

The morphology and size of the prepared COCI are presented in Fig. 5 and Fig. 6, respectively. The SEM image showed that the prepared COCI...
presented a spherical morphology and the average diameter determined by DLS was about 250 nm. Further, EDS results (embedded in Fig. 5) indicated that the main chemical compositions of the prepared COCI included C, N and O; the existence of N proved that BTA was successfully encapsulated in the prepared COCI by dialysis method. The concentration of encapsulated BTA is 1.05 mg/ml in COCI solution, as determined by UV–vis spectrophotometry. Because the concentration of PEO-b-PS copolymers in COCI solution was 0.5 mg/ml, the encapsulated amount of BTA in COCI was 2.10 mg/mg.

3.2. Release process of BTA in deionized water with different pH values

3.2.1. Release amount of BTA from COCI in deionized water

The release amount of BTA reserved in COCI in deionized water with different pH values is shown in Fig. 7. It is observed that the release rate of BTA was influenced by the pH value of deionized water: in deionized water with higher pH values (11 and 13), the accumulative release amount of BTA was about 2.80 mg up to 7 days; in deionized water with lower pH values (pH = 7 and 9), the release rate of BTA was accelerated, and the accumulative release amount was about 3.05 mg after 7 days, which was about 96.86% of the encapsulated BTA amount (3.15 mg in 3 ml COCI solution, the dash line in Fig. 7) in COCI. The accumulative release amount in deionized water with lower pH values (pH = 7 and 9) was about 9% higher compared to that with pH values of 11 and 13 up to 7 days.

3.2.2. Related release mechanism in deionized water

The release of BTA reserved in COCI is a very complex process, including diffusion, erosion controlled release or a combination of these mechanisms [32]. Based on the reported studies [33,34], a normally used comprehensive semi-empirical equation (established by Ritger and Peppas, as shown in Eq. (2)) was applied in this study to analyse the release mechanism of BTA from COCI.

\[
\log \left( \frac{M_t}{M_\infty} \right) = n \log t + \log k
\]  

where, \(M_t\) and \(M_\infty\) (mg) are the absolute accumulative amount of BTA released at time t (hour) and infinite time (\(M_\infty\) was approximately considered as the encapsulated amount of BTA), respectively; k is a constant incorporating structural and geometric characteristics of COCI; n is the release exponent indicating the release mechanism. For spherical particles, the value of n is equal to 0.43 for Fickian diffusion and 0.85 for swelling-controlled mechanism; n < 0.43 is corresponding to the combination of diffusion and erosion control; 0.43 < n < 0.85 is due to anomalous transport mechanism [35–37].

Fig. 8 shows the experimental data and fitted curves for the release process of BTA in deionized water with different pH values, and the fitting parameters, including the release exponent n and rate constant k, are presented in Table 1. It is observed in Fig. 8 that the release process of BTA in deionized water was divided into two stages: the first stage was between 0 and 4 h, and the second stage was from 4 to 168 h.

<table>
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<tr>
<th>Elements</th>
<th>% Mass</th>
<th>%Atomic</th>
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<tr>
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<td>86.44</td>
<td>88.69</td>
</tr>
<tr>
<td>N</td>
<td>9.36</td>
<td>8.23</td>
</tr>
<tr>
<td>O</td>
<td>3.78</td>
<td>2.91</td>
</tr>
<tr>
<td>Na</td>
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<td>0.07</td>
</tr>
<tr>
<td>Ca</td>
<td>0.29</td>
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Good linearity was obtained for the two stages. In the first stage, n values in deionized water were all < 0.43, indicating that the release of BTA during the first 4 h was related to the combination of Fickian diffusion and erosion control. However, the n values in deionized water with pH values below 9 was lower, compared to deionized water with pH values above 11, suggesting that more severe erosion caused by the low pH environment presented a more significant effect on the release behavior of BTA. In the second stage, all n values were much lower than 0.43, indicating that COCI structures began to degrade and the erosion of COCI played a more important role on the release behavior of BTA. During the release process, the k values were larger in deionized water with pH values of 7 and 9, compared to deionized water with pH values of 11 and 13, indicating that the release rate of BTA was accelerated by decreasing the pH value of deionized water. It was reported that for self-healing anticorrosion coatings, pH alteration caused a reduced permeability of the polymer shell, leading to the rapid release of the encapsulated corrosion inhibitors [17,18]. Therefore, in this study, the possible reason for the higher release amount of BTA in deionized water with low pH values is related to the higher protonation degree of oxygen groups in PEO moieties under lower pH environment [38], leading to a larger repulsion force among PEO groups, thus less compact structure and higher permeability of COCI.

The above results indicate that the release process of BTA is sensitive to pH alterations in deionized water and a lower pH value is beneficial for the release of BTA. However, the pH sensitivity is still not very pronounced (only 9% difference in deionized water with different pH values). Concrete is a much more complex system, and different ions (e.g., Ca\(^{2+}\), Na\(^+\), etc.) may also influence the release rate of BTA in COCI. Therefore, the release process of BTA in simulated concrete pore solutions with different pH values was also investigated in this study and will be discussed further below.

### 3.3. Release process of BTA in simulated concrete pore solutions with different pH values

#### 3.3.1. Release amount of BTA from COCI in simulated concrete pore solution

The release amount of BTA in SCP solutions with different pH values is shown in Fig. 9. In SCP solution with a pH value of 13, the accumulative release amount of BTA was only about 0.5 mg up to 3 days. However, in SCP solutions with lower pH values (pH = 7, 9 and 11), the accumulative release amount of BTA was in the range of 2.5–2.8 mg, which means most of the encapsulated BTA (3.15 mg) was released, and the release amount was 5 times higher than the release amount of BTA in SCP solution with a pH value of 13.

In order to confirm the more pronounced pH sensitivity of COCI, after immersed in SCP solution with a pH value of 13 for 3 days, the dialysis bag was then immersed in SCP solution with a pH value of 7 for further investigation, and the result is shown in Fig. 10.

Immediately after the dialysis bag was immersed in SCP solution with a pH value of 7, BTA reserved in COCI was rapidly released: only after 30 min, a huge amount (1.9 mg) of BTA was released into SCP solution. This is consistent with the data shown in Fig. 9. The results indicate that the release process of BTA was very sensitive to the pH alteration in simulated concrete pore solution: when the pH value of SCP solution was 13, BTA can be stably encapsulated in COCI; when the pH value of SCP solution dropped to below 11, the release rate of BTA was dramatically accelerated.

![Fig. 7. Release profiles of BTA in deionized water with different pH values.](image)

![Fig. 8. Plots of log (Mt/M∞) against log t for BTA released from COCI in deionized water with different pH value.](image)

<table>
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<tr>
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<th>k1</th>
<th>R1²</th>
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<th>k2</th>
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<td>0.977</td>
<td>0.135</td>
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</table>

**Table 1** Release exponent (n) and rate constant (k) for COCI in deionized water with different pH values.

![Fig. 9. Release profiles of BTA in SCP solution with different pH values.](image)
3.3.2. Related release mechanism in simulated pore solution

Similarly, the experimental data of the release amount in SCP solutions were fitted by Eq. (2), as shown in Fig. 11, and the fitting parameters, including the release exponent n and rate constant k, are presented in Table 2. The release process of BTA in SCP solutions was fitted in one stage, which was different from two stages in deionized water (as shown in Fig. 8 and Table 1). Further, in SCP solutions with a pH value lower than 11, most of the reserved BTA was released during the first 30 min; in SCP solution with a pH value of 13, the release amount of BTA was kept at a low level during the whole release process. Therefore, the related release mechanism in SCP solutions should be different from that in deionized water.

In order to further discuss the related release mechanism, the size and morphology alterations of COCI during the release process were also investigated. The size distribution of COCI before and after immersed in deionized water and SCP solutions with different pH values is presented in Fig. 12. After immersed in deionized water with different pH values, the average diameter of COCI was almost identical (Fig. 12 (a)), compared to the prepared COCI, indicating that the pH value of deionized water presented no obvious influence on the particle size of COCI. After immersed in SCP solutions with pH values lower than 11 (Fig. 12 (b)), there was also no significant size alteration of COCI; however, after immersed in SCP solution with a pH value of 13, the average diameter of COCI increased to about 500 nm. Similarly, after immersed in SCP solution with a pH value of 13 for 3 days, the dialysis bag was then immersed in SCP solution with a pH value of 7. After 30 min, the average diameter of COCI reduced to about 300 nm. The results indicate that in SCP solution, the size of COCI increased in a high alkaline environment (pH > 11).

In order to further explain this phenomenon, the morphology of COCI after immersed in SCP solutions with different pH values was also investigated in this study, as shown in Fig. 13. It is clear from Fig. 13 (a), (b) and (c) that after immersed in SCP solution with low pH values (pH = 7, 9 and 11) for 3 days, COCI maintained the spherical morphology. However, after immersed in SCP solution with a pH value of 13 for 3 days, the spherical morphology of COCI was not observed (Fig. 13 (d)); after the sample was then immersed in SCP solution with a pH value of 7 for only 30 min (Fig. 13 (e)), COCI resumed the spherical morphology.

C, Na and Ca amount of COCI in SCP solutions with different pH values determined by EDS analysis results are presented in Fig. 14. When immersed in SCP solution with a pH value of 13, C content was significantly lower and Na content was significantly higher, compared to other specimens. Further, after the sample was then immersed in SCP solution with a pH value of 7 for only 30 min, the content of C and Na resumed to the similar level of the specimens in SCP solutions with lower pH values. The result indicates that a Na-rich film may be formed around the surface of COCI in the high alkaline environment (with a pH value higher than 11), and this film is the possible reason for the increased diameter of COCI after immersed in SCP solution with a pH value of 13.

Considering the present work is the first part of ongoing investigations, the possible mechanisms related to the pH sensitivity of the prepared COCI in SCP solutions are hypothesized as follows. It was reported that Ca\(^{2+}\) ions can crossbridge copolymer molecules to form larger agglomerates [39,40]. Further, in SCP solution with a pH value of 13, a less protonation of oxygen groups in PEO moieties can lead to a smaller repulsion force among PEO groups and thus smaller repulsion force among the prepared COCI. The combination of the above two effect results in the agglomeration of COCI in SCP solution with a pH value of 13 (the average diameter of COCI increasing from about 250 nm (Fig. 12 (b), pH = 7, 9, 11) to about 500 nm (Fig. 12 (b), pH = 13)), retarding the release of BTA reserved in COCI. Moreover, because the prepared COCI presents a negative zeta potential (−40.6 mV), positively charged Ca\(^{2+}\) and Na\(^{+}\) ions in pore solution may be adsorbed on the surface of COCI leading to a local high Ca\(^{2+}\) and Na\(^{+}\) concentration. The local high ion concentration combined with the agglomeration of COCI caused by Ca\(^{2+}\) and high alkaline environment, might be beneficial for the formation of a Na-rich film on COCI surface in SCP solution with a high pH value (pH = 13). The formed Na-rich film is stable and can also hinder the diffusion of BTA reserved in COCI. Therefore, in SCP solution with a pH value of 13, due to the agglomeration of COCI and formation of Na-rich film, the release rate of BTA is very slow and BTA can be stably reserved in COCI. However, in SCP solutions with lower pH values (pH = 7, 9, 11), the agglomeration of COCI is not pronounced due to the more protonation of oxygen groups in PEO moieties, and the Na-rich film also becomes unstable and dissolves under low pH conditions. Therefore, the reserved BTA was rapidly released into SCP solution (Fig. 9). It needs to be mentioned that the above relevant conditions. Therefore, the reserved BTA was rapidly released into SCP solution with a pH value of 13 for 3 days. The formation of Na-rich film is stable and can also hinder the diffusion of BTA reserved in COCI. Therefore, in SCP solution with a pH value of 13, due to the agglomeration of COCI and formation of Na-rich film, the release rate of BTA is very slow and BTA can be stably reserved in COCI. 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mechanisms are mainly based on the derived experiment results and reported literatures. The exact mechanisms are still to be clarified by further experimental evidences on the physical/chemical reactions between the core-shell corrosion inhibitors and different environment, e.g. isothermal titration calorimeter characterization on the crossbridge between Ca\(^{2+}\) and copolymer molecules, potentiometric titration investigation on the protonation degree of oxygen groups in PEO moieties in SCP solution with different pH values and TEM and AFM observations of the Na-rich film formed on COCI surface. The above investigations will be involved in a future work. However, the high pH sensitivity of the release process of BTA in simulated concrete pore solution is clear and well supported by the experimental results in this paper.

Based on the pH threshold value for corrosion initiation (pH $< 11.5$ [3,4]), and the above experiment results, after corrosion of the steel reinforcement was initiated (pH $< 11.5$), the release rate of BTA was significantly accelerated in simulated concrete pore solution and a large proportion of BTA reserved in COCI was released (Fig. 9). The released BTA can possibly halted corrosion propagation, leading to an increased corrosion resistance of the steel reinforcement. Therefore, the prepared core-shell organic corrosion inhibitors in this study can be potentially used for the spontaneous corrosion protection in reinforced concrete due to its controlled release behavior in SCP solutions. The influence of COCI on the corrosion performance of reinforced concrete is not in the scope of this paper and will be reported elsewhere.

4. Conclusions

The release behavior of the prepared novel core-shell corrosion inhibitors in deionized water and simulated concrete pore solutions with different pH values was reported in this study. The core-shell organic corrosion inhibitor encapsulated with BTA was successfully prepared based on PEO-b-PS copolymers by using dialysis method, and the encapsulation capacity was 2.1 mg/mg. The release process of BTA in deionized water was sensitive to the pH alterations and the release amount of BTA was slightly higher (9%) in deionized water with lower pH values, which was related to the higher protonation degree of COCI before and after immersed in deionized water (a) and SCP solutions (b) with different pH values.

![Fig. 12. Size distribution of COCI before and after immersed in deionized water (a) and SCP solutions (b) with different pH values.](image)

![Fig. 13. The morphology of COCI after immersed in SCP solutions with different pH values.](image)
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