



The fabrication and corrosion resistance of benzotriazole-loaded raspberry-like hollow polymeric microspheres



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ABSTRACT

This work presents a synthesis of submicron-sized raspberry-like hollow microspheres loaded with corrosion inhibitor (1*H*-benzotriazole (BTA)) through a multi-stage emulsion polymerization. The combination of hierarchical raspberry-like surface structure and loading of BTA makes the prepared microspheres have good corrosion resistance. When BTA-loaded raspberry-like hollow microspheres are embedded in a water-borne polyurethane film, the obtained composite film can protect the copper from corrosion both in acidic and alkaline corrosive solutions.

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1. Introduction

Copper and its alloy possess high strength, excellent electrical conductivity and favorable thermal conductivity. However, copper is prone to localized pitting corrosion in solution containing some anions such as sulfate, chloride ions [1,2]. Chromate conversion coatings have been historically applied as most effective corrosion protection technique. But it has been prohibited officially due to unfriendly character of poison and carcinogen. Thereby, many scientists turn their interest into finding alternatives to hexavalent chromium compounds so that a lot of inorganic compounds, such as cerium, molybdc acid, phosphoric acid and colloidal silica have been expected to effective alternatives for chromium compounds, as well as organic compounds [3–10]. For instance, 1*H*-benzotriazole (BTA) and its derivatives are found to act as effective corrosion inhibitor of metals, such as copper, mild steel, etc., due to generating complex compound [11–15].

On the other hand, to achieve the releasing of the inhibitor directly into damaged area occurred with environmental changes and long-term releasing of the inhibitor on demand, a feasible way is to add various inhibitors into a passive film, which can provide a physical barrier layer to prevent the metals from contacting with the corrosive environment [16–19]. For example, van Ooij et al. [17] introduced organic inhibitors of triazole and inorganic cerium salts into silane films. These inhibitors can be leached out, and thus a better corrosion protection of Al alloys (AA2024-T3) in a 0.5 M NaCl solution was achieved. However,

the passive film embedded inhibitor compounds sometimes cannot provide enough corrosion protection. In most cases, the release of organic inhibitors from the coating film has no stimuli-response to the external environment [19]. Therefore, if the solubility of inhibitors in the film is very high, the uncontrollable fast release of inhibitors can lead to blistering, and finally deteriorate the integrity of the coating [20,21].

Thus, recent work pays much attention to the encapsulation of the eco-friendly corrosion inhibitors into various nanocontainers prior to their straightforward addition into the passive film. These nanocontainers should be sensitive to environmental changes (e.g., mechanical damage, pH changes, and laser irradiation.) [22–30]. At the same time, it can avoid undesirable leakage of the inhibitor and the possibility of destroying barrier properties of the film. Hosseini et al. [31] prepared inhibitor-encapsulated SiO₂ or halloysite nanotubes coated by a poly(allylamine hydrochloride)/sodium poly(styrene sulfonate) shell formed through the layer-by-layer assembly. The control release rate of anti-corrosive agent can be tunable with the solution parameters (pH, temperature and stirring) to achieve the goal of smart protection. Borisova et al. [32] developed mesoporous silica nanoparticles with high surface area, narrow pore size distribution and large pore volume to load corrosion inhibitor BTA. They successfully embedded the mesoporous silica nanocontainer into the passive anti-corrosive SiO_x/ZrO_x film and improved the corrosion efficiency through the controlled release of BTA from silica nanocontainers. Recently, organic nanocontainers, such as polymeric nanocontainers, have been fabricated to encapsulate the anti-corrosive agents [33,34]. Zheludkevich et al. [35,36] introduced cationic Ce³⁺ into a chitosan layer. The complexation of Ce³⁺ with the amino groups of chitosan prevented the uncontrollable and fast leaching of Ce³⁺. These coatings were found to have improved active corrosion protection toward aluminum alloy 2024.

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Additionally, hybrid nanocontainers constituted by polymeric core and inorganic shell were also prepared to load active agents [24,25]. Shi et al. [37] used cage-like oil core/silica gel shell particles with opened and closed pores to load and release repairing agent and catalysts. The sol-gel film embedded with these particles had a certain self-repairing effect for AA2024 aluminum alloy surface.

Over the past years, there are some reports about the preparation of raspberry-like hollow microspheres [38–41]. For example, Cheng et al. prepared raspberry-like polystyrene/SiO₂ composite microspheres through the ethanol sol-gel processing of TEOS on polystyrene template particles. Then wettability gradient surfaces from superhydrophobic to superhydrophilic. The previous works in our group [42,43] also found that a hierarchical micro/nano surface structure of the raspberry-like particles is beneficial to improve the surface hydrophobic performance. Therefore, in this work, we design an anti-corrosive inhibitor, BTA, loaded raspberry-like hollow polymeric microsphere. This microsphere could not only prevent the unnecessary leakage of BTA, but also control the release of BTA according to the pH value of corrosive solution. The raspberry-like hollow polymeric microspheres were prepared by the multi-stage emulsion polymerization, and BTA is loaded during the formation process of the microspheres. Then the prepared polymeric microspheres are embedded into water-borne polyurethane (WPU) coatings to obtain an effective anti-corrosive protection layer for copper. Water-borne anti-corrosive polyurethane coatings, which are green materials, can be cured under low temperature, and possess oil resistance, seawater resistance, wear resistance, impact resistance, etc. [44] They not only have improved anti-corrosive performance, but also are pollution-free or less contaminative due to some factors such as environmental regulations. Corrosion resistance of metal could be accelerated by the combination of polyurethane coatings with nano-ZnO, conducting polymers or clay nanocomposites [45–47]. However, few reports involve the preparation of WPU coatings embedded with inhibitor-loaded organic nanoparticles, although organic nanoparticles are better compatible with WPU coatings compared with the inorganic nanoparticles [16]. In this manuscript, the anti-corrosive behavior of the WPU films embedded with BTA-loaded raspberry-like hollow polymeric microspheres would be discussed in detail.

2. Experimental

2.1. Materials

The monomers, styrene (St), methyl methacrylate (MMA), butyl acrylate (BA) and methyl acrylic acid (MAA) (from Shanghai Chemical Reagents Co. Ltd) were purified by vacuum distillation before use. Potassium persulfate (KPS) was recrystallized from distilled water. 1*H*-Benzotriazole (BTA) (99.8%), sodium hydroxide (NaOH) and sodium dodecyl sulfate (SDS) were supplied by Shanghai Chemical Reagents Co. Ltd. Poly(tetramethylene ether) glycol (PTMG2000; M_n = 2000), 1,4-butanediol (BDO), 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) and bis(hydroxymethyl) butyric acid were supplied by Shanghai Yuanfeng Chemical Co. Ltd. Tungstophosphoric acid (TPA) was purchased from Shanghai Jiaye Biotechnology Co. Ltd. Triethylamine (TEA, ≥99.9%), copper foil (99.9%, Bi < 0.1 wt.%, Sb < 0.2 wt.%, Ca < 0.2 wt.%, Cd < 0.2 wt.%, Cl < 0.1 wt.%, Cr < 0.2 wt.%) were

purchased from Shanghai Chemical Reagents Co. Ltd. Double-distilled and deionized (DDI) water was used in all experiments.

2.2. Preparation of BTA-loaded raspberry-like hollow polymeric microspheres

The fabrication of hollow particles with a rough polymer shell surface via a multi-stage seeded emulsion polymerization has been reported in the literature [48]. The process involves synthesizing a structured particle with a carboxylated polymer core, followed by forming an outer polymer shell during neutralizing of the carboxylated core with a base. In this work, raspberry-like hollow polymeric microspheres encapsulated with BTA were prepared after altering some experiment conditions of the reported multi-stage seeded emulsion polymerization, as illustrated in Fig. 1 [49]. The recipe of each step is listed in Table 1. Unless specified otherwise, emulsion polymerization was carried out in a four-necked flask equipped with a condenser, a stirrer and a gas inlet. The flask was placed in an oil bath. A thermometer was inserted in the reaction medium in order to monitor the reaction temperature.

A: Preparation of the seed latex

The monomer mixture (BA, 0.23 g, MMA, 0.10 g, and MAA, 0.04 g) was mixed with water (15 mL) containing KPS (0.02 g) and SDS (0.02 g, 4.0 mM L⁻¹) in a 100 mL four-necked flask. The flask was placed in an oil bath of 85 °C. The system was stirred mechanically in a nitrogen atmosphere. The reaction lasted for 24 h to obtain the seed latex.

B: Preparation of the primary Core-1

Firstly, water (20 mL) containing KPS (0.02 g) and SDS (0.05 g) was added into the above seed latex. Then, a monomer mixture (BA, 0.20 g, MMA, 2.83 g, MAA, 1.40 g) was dropped gradually into the reaction system within 50 min. The polymerization was carried out at 85 °C for 6 h to form copolymer latex, here named as Core-1.

C: Loading BTA into Core-1

The as-synthesized Core 1 latex (5 g) was mixed with 40 g of aqueous BTA solution (3% BTA, w/w) in a 250 mL four-necked flask at 85 °C. The mixture was stirred for 2.5 h.

D: Encapsulation of BTA—preparation of Core-2

KPS (0.04 g) was added into BTA-loaded Core-1 latex in a 100 mL four-necked flask at 85 °C. Then a monomer mixture (MMA, 4.10 g, BA, 0.33 g, MAA, 0.15 g) was gradually added within 50 min. The polymerization was carried out for 8 h. The product was named as Core-2 latex and abbreviated as Poly(MMA-co-MAA-co-BA) since the polymer core is made by the copolymerization of three (methyl) acrylate monomers, i.e., MMA, MAA and BA.

E: Formation of a polystyrene (PS) shell coated on Core-2, i.e., raspberry-like hollow polymeric microspheres

The as-synthesized core-2 latex (10 g) was dispersed into water (20 mL) containing 0.02 g of KPS. After feeding St for 10 min (feeding rate: 0.03 g/min), the pH value of the latex was raised to 10 by adding the aqueous solution of NaOH (10 wt.%). Then the remaining monomer was added into the reactive system for 40 min. The total amount of St monomer was 1.50 g. The polymerization reaction

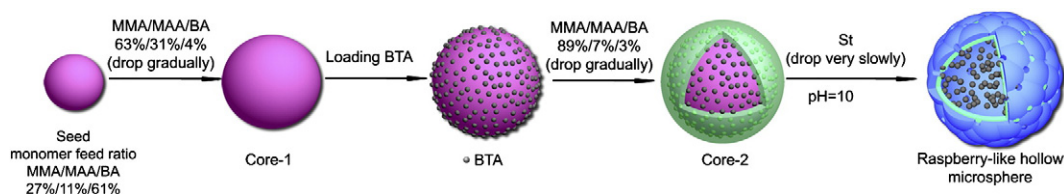


Fig. 1. Schematic illustration for the preparation of raspberry-like hollow polymeric microspheres loaded with BTA.

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