



2,3-Epoxy-2-methyl-1,4-naphthoquinone Microcapsule Emulsion: Preparation and Application in the Controlled-Release

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In this paper, 2,3-epoxy-2-methyl-1,4-naphthoquinone (ME) microcapsule emulsions were prepared and applied to preparation of a waterborne antifouling coating. Nano-particle size analyzer and TEM were used to characterize 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsules. The effects of core-shell initial weight ratio on the release rate of 2,3-epoxy-2-methyl-1,4-naphthoquinone and the antifouling property of the coating were studied. When the core-shell initial weight ratio of microcapsules was 1:7, the release rate of 2,3-epoxy-2-methyl-1,4-naphthoquinone from the coating was steady and the antifouling property of the coating was excellent.

Key Words: 2,3-Epoxy-2-methyl-1,4-Naphthoquinone, Microcapsule, Antifouling coating.

INTRODUCTION

Antifouling coatings are applied to ship hulls to prevent biological fouling which reduces ship maneuverability and raises propulsive fuel consumption¹⁻³. Based on the high-speed developing navigation and environmental concerns, the research of efficient, non-toxic antifouling coatings has become a priority for antifouling coating⁴. Long term efficiency of the coating is dependent on the effective antifoulant additive. 2,3-Epoxy-2-methyl-1,4-naphthoquinone (ME), as an environmental friendly effective antifoulant additive, shows excellent antibacterial activity and potential antifouling property⁵. The use of it as antifoulant additive is expected to be very important and have great potential application in the development of antifouling coating.

Prior to this work, numerous antifouling coatings were developed in which effective antifoulant additives were incorporated into suitable marine coating bases⁶. These coatings were then applied to underwater surfaces in an effort to limit the growth of marine organisms. However, uncontrolled release rate of antifoulant additives can cause the short service life of the coating. Thus, it has been a goal of the prior art work on antifouling coating to control the leaching rate of the antifoulant additives in order to prolong the useful life of the coating⁷. Microencapsulation has been used in this field to prolong the service life of the coating⁸. Until now, there are few reports that 2,3-epoxy-2-methyl-1,4-naphthoquinone as novel antifoulant additive was microencapsulated and used in waterborne antifouling coating. In this work, acrylic emulsion

was chosen as the shell material for 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsules because of its excellent film forming ability, chemical stability and solubility⁹. And, a totally non-toxic silicone-acrylic emulsion which was prepared according to previous research was used as coating film former¹⁰. The aim of this investigation was to control the release rate of 2,3-epoxy-2-methyl-1,4-naphthoquinone by regulating core-shell initial weight ratio of 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsules and so prolong the service life of this waterborne antifouling coating formulated with 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsule emulsion.

EXPERIMENTAL

2,3-Epoxy-2-methyl-1,4-naphthoquinone was purchased from Shenyang Research Institute of Chemical Industry. Iron oxide red, talcum powder and calcium carbonate were purchased from Lingshou Xinhui Mining Fiber Plant (Hebei, China). Nano-sized ZnO and nano-sized TiO₂ were purchased from Changzhou Maideng Rubber Plastics Chemical Co. Ltd. (Changzhou, China). Zinc pyrithione was purchased from Funan Chemical industrial Co. Ltd. (Quzhou, Hebei, China). Other chemicals were reagent grade and purchased from Shenyang No. 1 Chemical Reagent Factory (Liaoning, China). Silicone acrylate was homemade.

Preparation of 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsules and antifouling coatings: The recipes of 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsule were shown in Table-1. 2,3-Epoxy-2-methyl-1,4-naphthoquinone microcapsule emulsion was prepared through the

TABLE-1
Z-AVERAGE PARTICLE SIZE AND PDI OF
THE PREPARED MICROCAPSULES

Core-shell initial weight ratio	Z-Average particle size	PDI
1:5	447.4	0.176
1:7	338.4	0.034
1:9	318.6	0.058

following steps: 50 mL deionized water, 0.4 g SDS, 0.4 g OP-10 were added into a beaker and homogenized by emulsifying-machine for 3 min (rotation speed from 10000-19000 rpm), meanwhile 9.4 g 2,3-epoxy-2-methyl-1,4-naphthoquinone in 6 mL acetone was dropped into the beaker to form 2,3-epoxy-2-methyl-1,4-naphthoquinone emulsion. After the evaporation of acetone was complete, this 2,3-epoxy-2-methyl-1,4-naphthoquinone emulsion was poured into a four-neck flask equipped with an inlet for nitrogen, a mechanical stirrer, a dropping funnel and a reflux condenser. When the solution was heated to 80 °C, 20 % of the mixed monomers ($n_{\text{MMA}}:n_{\text{BA}}:n_{\text{AA}} = 26:35:40$) and 0.015 g KPS were added into the flask. Then, 0.060 g KPS was added into the four-neck flask 20 min later. After that, the remaining mixed monomers were added by dropping funnel. The emulsion polymerization was carried out at 90 °C for 1 h. After the mixture was cooled to room temperature, the pH was adjusted to 7-8 by ammonia.

The antifouling coatings were formulated by spreading 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsule emulsions or 9.4 g unencapsulated 2,3-epoxy-2-methyl-1,4-naphthoquinone, 1 g iron oxide red, 1 g calcium carbonate, 2 g talcum powder, 4 g nano-sized ZnO, 1 g nano-sized TiO₂ and 1 g zinc pyrithione into 120 g silicone-acrylic emulsion. The grinding time is 2 h. The coatings were applied by means of air spray to tin panels (0.28 mm thickness, 50 mm × 120 mm), which had been primed with epoxy-polyamide amine coatings under specified procedures. These panels were dried at 20 °C for 3 days prior to the measurements. The film thickness was $85 \pm 5 \mu\text{m}$.

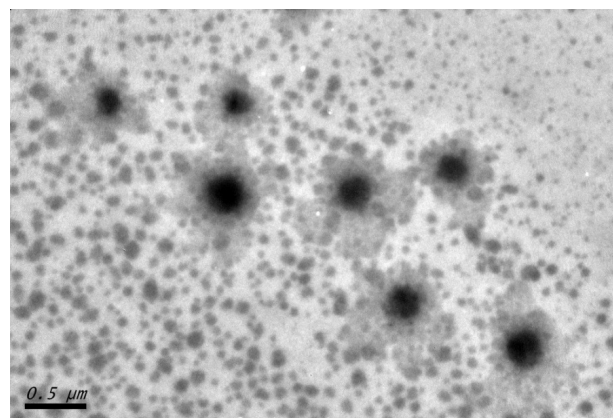
Analytical techniques: Z-Average particle size of the prepared 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsules was measured using nano-particle size analyzer (Zetasizer nano series Nano-ZS90). Transmission electron microscopy (TEM) micrograph of the 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsule particles was taken with Tecnai G220S-Twin transmission electron microscope. The capsules were coloured by phosphotungstic acid for visualization of the microcapsules.

2,3-Epoxy-2-methyl-1,4-naphthoquinone release tests were performed in artificial sea water¹¹. The coated panels were placed in a beaker containing 1 L of seawater, which was changed daily. Each water volume was extracted with 100 mL of hexane which was then concentrated to 5 mL. The concentration of 2,3-epoxy-2-methyl-1,4-naphthoquinone in hexane was determined quantitatively by using ultraviolet-visible spectrophotometer (HP8453).

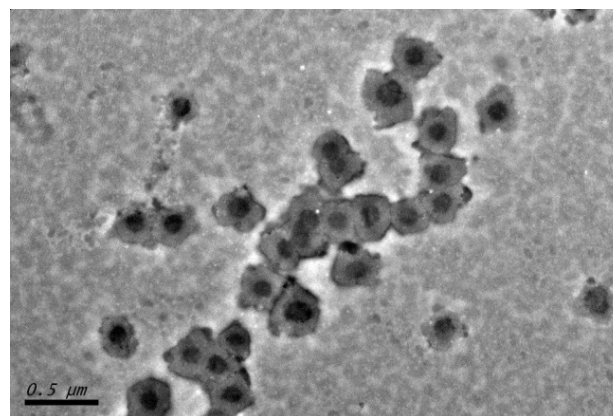
Panel exposure was done in the East China Sea, outside Dalian, China during June to September 2010. The cumulative coverage on panels was monitored according to the Standard Test Method for Testing Antifouling Panels in Shallow Submergence (ASTM D 3623-78a, 2004)¹².

RESULTS AND DISCUSSION

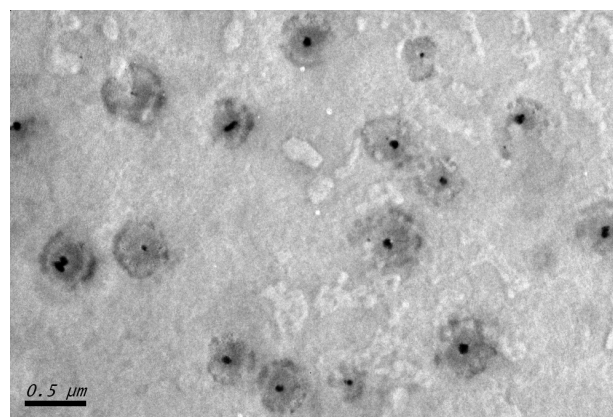
Characterization of the prepared 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsules: Fig. 1 shows the TEM images of the microcapsules. Based on the different electron penetrability, core phase and shell phase of the microcapsule particles were observed. Dark center (core phase) and light edge (shell phase) were 2,3-epoxy-2-methyl-1,4-naphthoquinone and acrylic resin, respectively. It was obvious that 2,3-epoxy-2-methyl-1,4-naphthoquinone was micro-encapsulated.



(a)



(b)



(c)

Fig. 1. TEM images of the microcapsules prepared at core-shell initial weight ratios of (a) 1:5, (b) 1:7 and (c) 1:9

The important factor which influences the application possibilities of capsules in paints is the diameters as well as wall thickness of microcapsules. The observed emulsion size (Fig. 1) is consistent with the result obtained by nano-particle size analyzer (Table-1). The diameters of microcapsules increase with the enhancement of initial weight ratio of core-shell material (Table-1). The main reason is that the size of core droplet in emulsion is larger when the initial weight ratio of core-shell is higher and the other processing parameters are kept constant. As Fig. 1, the TEM pictures show and confirm the shell thicknesses increase owing to the decrease of core-shell initial weight ratio.

Optimizing core-shell initial weight ratio of 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsule: The main character of microcapsule is that the release rate of core material can be controlled by adjusting the thickness of the shell material. To get an optimal thickness of shell, the core-shell initial weight ratio is considered to be the most important factor. Generally, the higher the core-shell weight ratio is, the thinner the shell of the microcapsule is and the faster the core material releases. Thus, in this paper, three types of 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsule emulsion with different core-shell weight ratio (1:5, 1:7, 1:9) were prepared and they were applied to formulate coatings (coating A, B and C, respectively). To get a clear comparison, coating D was formulated directly using unencapsulated 2,3-epoxy-2-methyl-1,4-naphthoquinone.

Fig. 2 showed the effect of core-shell initial weight ratio on the release rate of 2,3-epoxy-2-methyl-1,4-naphthoquinone. And Fig. 3 summarized the panel photos taken after the coated panels were immersed in seawater. Fig. 2 showed that the release of 2,3-epoxy-2-methyl-1,4-naphthoquinone from coating D prepared with unencapsulated 2,3-epoxy-2-methyl-1,4-naphthoquinone was more unstable and much faster than the others. This release mode will cause two problems: one is that 2,3-epoxy-2-methyl-1,4-naphthoquinone will be released completely to sea water in a short time and another is that there are many micro-holes in the coating film which increases the chance of biofouling. The antifouling performance of coating D shown in Fig. 3D confirmed that many marine organisms had attached on the panel after 3 months. By contrast, the releases of 2,3-epoxy-2-methyl-1,4-naphthoquinone from coating A, B and C showed much steadier in Fig. 2. The results also indicated that the release amount of 2,3-epoxy-2-methyl-1,4-naphthoquinone increased with increasing the core-shell initial weight ratio in the first 2 months. When the core-shell initial weight ratio was 1:5, the shell of the microcapsules was the thinnest and it can be seen that the release of 2,3-epoxy-2-methyl-1,4-naphthoquinone was too fast during the first 2 months and then decreased in the third month (Fig. 2A), this caused that the antifouling performance of coating A also decreased after 3 months (Fig. 3A). On the other hand, the shell of microcapsules with core-shell initial weight ratio of 1:9 was the thickest. It was difficult for 2,3-epoxy-2-methyl-1,4-naphthoquinone to release from such thick shell and the release amount was very small (Fig. 2C), which directly resulted in the poor antifouling properties of the coating C exhibited in Fig. 3C.

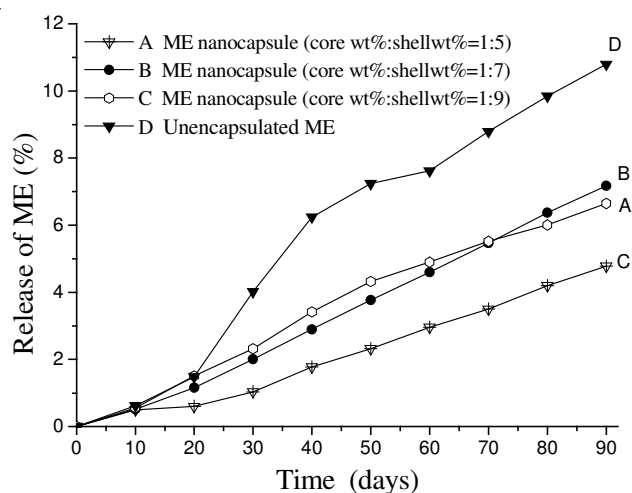


Fig. 2. Cumulative amount of the released 2,3-epoxy-2-methyl-1,4-naphthoquinone (ME) versus time

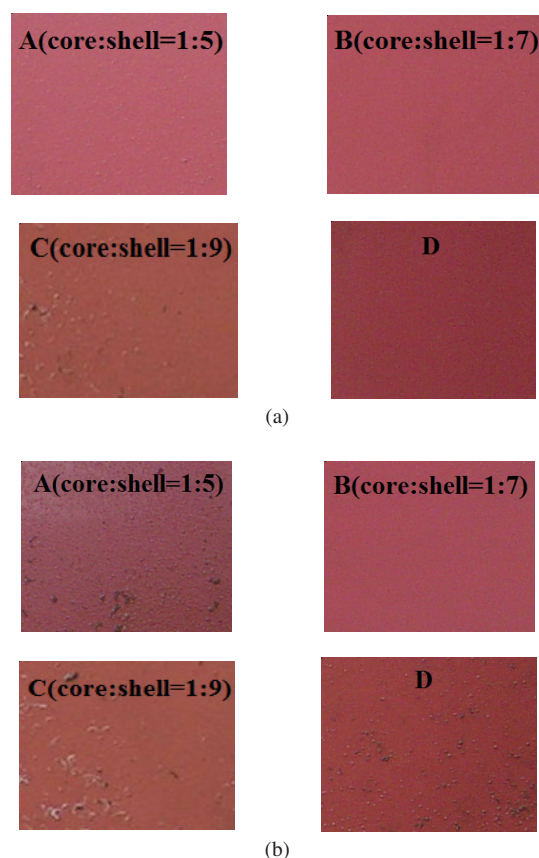


Fig. 3. Panel photos, (a) panel photos taken after immersion in seawater for two months, (b) panel photos taken after immersion in seawater for three months

By contrast, coating B was the best-performing one among the 4 coatings, there was nearly no biological fouling appearing on the panel after 3 months (Fig. 3B). This can be attributed to the suitable core-shell initial weight ratio of 1:7 which made release of 2,3-epoxy-2-methyl-1,4-naphthoquinone from coating B was much steadier than from the other coatings. 2,3-Epoxy-2-methyl-1,4-naphthoquinone microcapsules made from such core-shell initial weight ratio not only ensure the release of 2,3-epoxy-2-methyl-1,4-naphthoquinone was steady, but also made release amount of 2,3-epoxy-2-methyl-

1,4-naphthoquinone was enough to prevent biofouling. Moreover, release amount of 2,3-epoxy-2-methyl-1,4-naphthoquinone from coating B showed near linear relationship to time (Fig. 1B). Thus, with this 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsule emulsion and the waterborn, non-toxic silicone-acrylic emulsion used, a long-acting, high-performance and environmental friendly antifouling coating was successfully prepared.

Conclusion

In this work, 2,3-epoxy-2-methyl-1,4-naphthoquinone (ME) microcapsule emulsion was successfully prepared and applied to the waterborne antifouling coating. The stability of the release rates of 2,3-epoxy-2-methyl-1,4-naphthoquinone from the coatings in the laboratory assays was shown to be highly dependent on core-shell initial weight ratios. The stable release rate of 2,3-epoxy-2-methyl-1,4-naphthoquinone from coating can be achieved by applying 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsule with core-shell initial weight ratio of 1:7 and the release profile was nearly a zero-order release. Furthermore the antifouling efficiency of coating prepared using such 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsule was also excellent during the period of seawater immersion of 3 months (ASTM D 3623). This work demon-

strates the potential of the application of 2,3-epoxy-2-methyl-1,4-naphthoquinone microcapsule to the commercial exploitation and utilization in the field of antifouling coatings.

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