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Flame sprayed environmentally friendly high density polyethylene (HDPE)–capsaicin composite coatings for marine antifouling applications

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ABSTRACT

Marine biofouling has emerged as worldwide serious problems for artificial marine infrastructures. Among the measures taken so far to solve the abovementioned problems, construction of an antifouling layer has been proven to be effective in offering long-term antifouling performances. Antifouling based on the use of biocides is the most important method in modern maritime industries. While tributyltin (TBT)-based self-polishing coatings are being replaced by other biocide-releasing coatings, the environmental toxicity of these compounds is also under scrutiny. Therefore, there is a significant interest in developing non-toxic technologies. Green biocides can also be extracted from many types of organisms including terrestrial plants, sea creatures and bacteria. The capsaicin was extracted from chili pepper. In this study, flame sprayed high density polyethylene (HDPE)–capsaicin composite coatings were developed for marine antifouling applications. Capsaicin powder were fixed by polymer-based substrate and distributed evenly. Antifouling performances of the films were assessed by examining survival and colonization behaviors of *E. coli* and *Bacillus* sp. bacteria and *Phaeodactylum tricornutum*. Antifouling test indicated excellent antibacterial properties of HDPE–capsaicin composite coatings against both gram-negative *Escherichia coli* and gram-positive marine *Bacillus* sp. bacteria. Excellent antifouling performances against bacteria and algae of the thermal sprayed composite coatings give clear insight into their potential applications as environmentally friendly antifouling layers in the marine environment.

1. Introduction

Any surface immersed in seawater for year round is always suffered serious biological damage and fouling. Bio-fouling is caused by marine organisms, such as protein, bacteria, algae, or mollusks [1]. Antifouling is an essential issue for the maritime industries worldwide to prevent the growth of marine organisms on submerged surfaces. Among the measures taken so far to solve the abovementioned problems, construction of an antifouling layer has been proven to be effective in offering long-term antifouling performances [2]. Thermal spray was proven successful in large-scaled fabricating protective coatings for antifouling [3–6]. Biocides based coating is the most important method preventing biofoulings. As the most widely used anti-fouling agent, various metals and metalbased compounds have been applied for decades. Tributyltin (TBT) has been the most successful one in preventing biofoulings on artificial marine infrastructures. However, the very serious environmental issues and extensive damages to shellfish caused by the accumulation of TBT have attracted extensive attention from all over the world. While TBT-based self-polishing coatings are being replaced by other biocide-releasing coatings, the environmental toxicity of these compounds is also under scrutiny [7]. Recently, considerable effort has been made recently to develop low toxic and even nontoxic biocides [8,9], such as various natural products, inorganic nanoparticles, and ionic liquids. In recent years, capsaicin of chili peppers was reported as a natural nontoxic biocide agent for antifouling application [9–11]. The research work showed that capsaicin-mimic compounds possessed much more attractive properties than the current toxic antifoulants. Capsaicin is well known as a spicy vanilla amide alkaloid with broad-spectrum antimicrobial effect. As capsaicin can be extracted from hot peppers easily by organic solvent, the technique should be low-cost and widely used. This research aims to develop novel coating techniques for loading environmentally friendly biocides for marine antifouling applications. High density

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polyethylene (HDPE) is known for its large strength to density ratio and its excellent corrosion resistance in marine environment [12]. Capsaicin was selected as the natural antifoulants that are enwrapped and dispersed in the polymer matrix. Microstructural features and antifouling properties of high density polyethylene (HDPE)–capsaicin coatings were characterized. The antifouling performances were assessed by examining sterilizing rate of typical marine bacteria and diatom.

2. Experimental

Commercially available HDPE powder (Korea Petrochemical Ind. Co., Ltd) and capsaicin (Aladdin, 97%) was used as the starting feedstock. The starting HDPE feedstock powders were mechanically blended with capsaicin of 1.0 wt% and 2.0 wt%. The coatings were deposited by flame spray (CDS 8000, Castolin, Germany) on mild steel plates (MS, E235B, $20 \times 20 \times 2\ mm^3$). Prior to spraying, all the steel substrates were cleaned in turn by deionized water, alcohol and acetone and finally mechanically coarsened by sand blasting with alumina. For the flame spraying, acetylene was used as the fuel gas with flow rate of $1.5\ N\ m^3/h$ and working pressure of 0.1 MPa. Pressure and flow rate of oxygen were 0.7 MPa and $2.5\ N\ m^3/h$, respectively. Feed rate of the powder was set as 60 g/min. The spray distance from nozzle exit to substrate surface was 200 mm. Microstructure of the powder and the coatings was characterized by field emission scanning electron microscopy (FESEM, FEI Quanta FEG250, the Netherlands). Artificial seawater (ASW) was prepared according to ASTM D1141-98. Antifouling performances of the coatings were assessed by examining sterilizing rate of bacterial biofilm on their surfaces. Marine gram-positive *Bacillus* sp. (MCCC No. 1A00791) and gram-negative *Escherichia coli* (*E. coli*, ATCC 25922) were used in this study. *Bacillus* sp. and *E. coli* bacteria were cultured in 2216E (CM 0471) and LB media, respectively. The 2216E medium for culturing *Bacillus* sp. was prepared by dissolving 1 g yeast extract and 5 g peptone in 1000 ml ASW. The LB medium was prepared by dissolving 10 g NaCl, 5 g yeast extract and 10 g peptone in 1000 ml deionized water. The viability of bacteria growth was tested using the spread plate method. The diatom *Phaeodactylum tricornutum* was cultured in artificial sea water. The formation of the algae biofilm on different coating surfaces for 1 week was examined. After the fixation by 2.5% glutaraldehyde for 6 h, the specimens were characterized by confocal laser scanning microscopy (CLSM, TCS SP5, Leica, Germany). Bactericidal coefficient (extinguishing efficiency) of bacteria was determined by the standard plate counting approach.

3. Results and discussion

The commercially available capsaicin particles exhibit rod-like shape with the dimension of ~1 μm in diameter and 5–15 μm in length (Fig. 1a). The starting HDPE particles present an ellipsoidal shape, and their average diameter (d50 of the particle size distribution) is 85 μm (Fig. 1b). The route for making the HDPE–capsaicin coatings is schematically depicted in Fig. 1c. The coatings were fabricated by flame spraying. Dense microstructure for all the HDPE and HDPE–capsaicin coatings has been achieved (Fig. 2).

The capsaicin powders are fixed by polymeric matrix and uniformly distributed in the coating (Fig. 2b–f). Typical topographical view of the coating clearly suggests well melt state of the HDPE particles during the spraying, which is mainly responsible for the unidentifiable splats interfaces. It is noted that HDPE-based acts as binder entrapping capsaicin particles, which is promising since this special construction would facilitate constrained release of capsaicin elements into surrounding media for long-term functional services. The cross sectional morphologies of the coatings show the thickness of up to 150 μm, the composite coating present

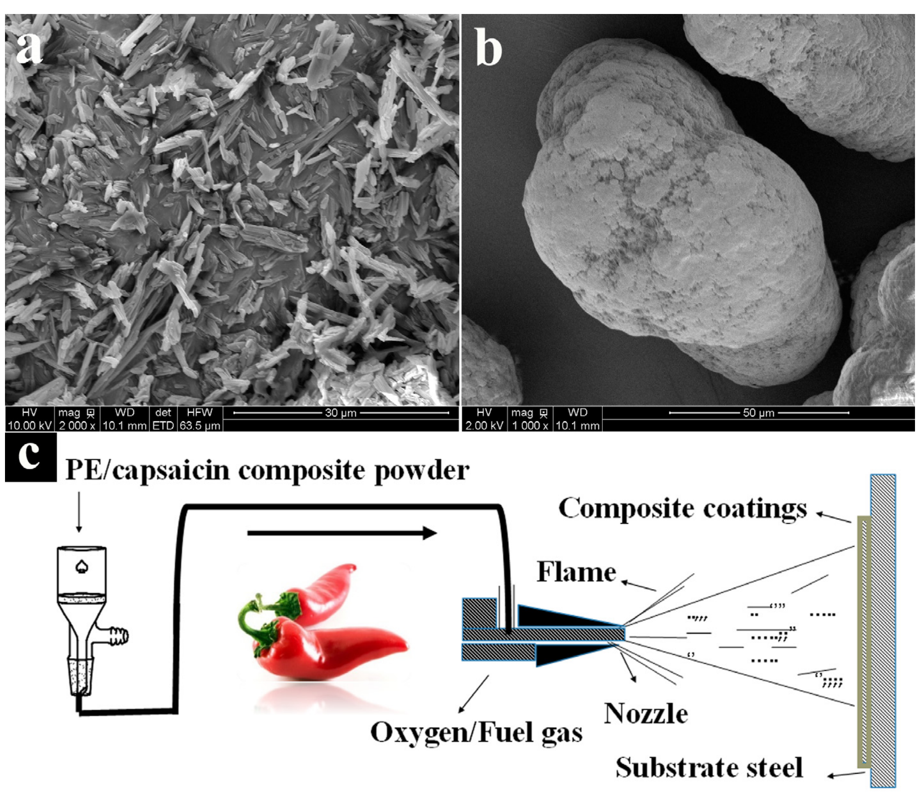

Fig. 1. Characteristics of the starting powder: (a) FESEM image of the starting capsaicin powder, (b) FESEM image of the starting HDPE powder, and (c) schematic depiction illustrating the fabrication route for the HDPE–capsaicin antifouling coatings deposited by flame spraying.

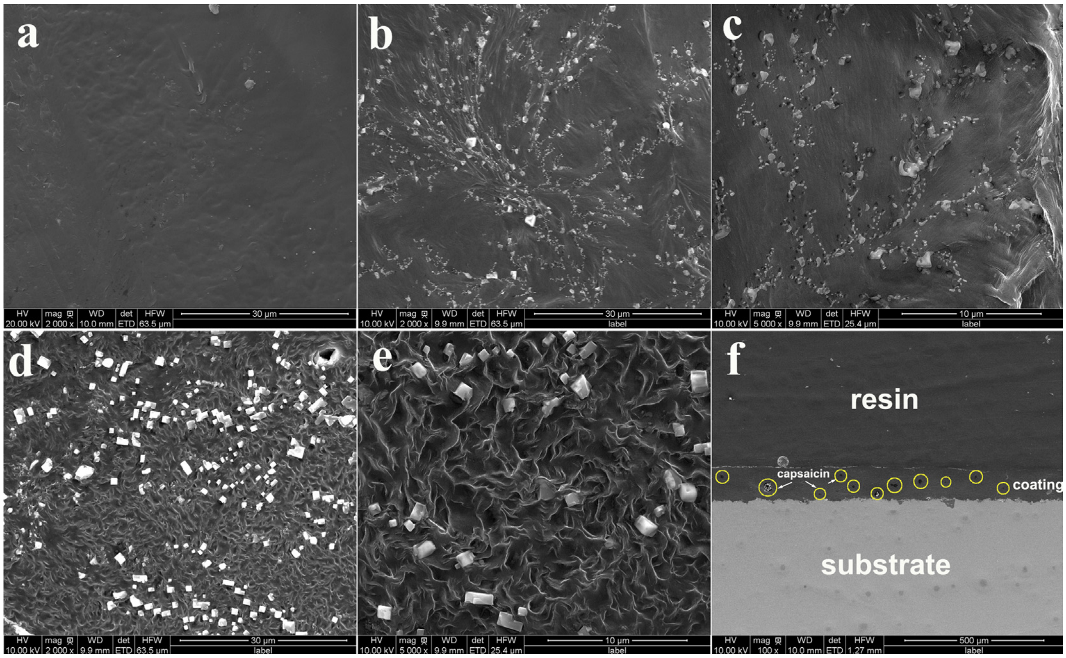

Fig. 2. FESEM surface views of the HDPE–capsaicin composite coatings, (a) the pure PE coating, (b) HDPE–1.0 wt% capsaicin composite coating, (c) enlarged view of (b), (d) HDPE–2.0 wt% capsaicin composite coating, and (e) enlarged view of (d), and (f) cross-sectional view of HDPE–2.0 wt% capsaicin composite coating.

good contact to the substrate (Fig. 2f). Furthermore, the dense structures have been achieved, and no marked flaws for instance microcracks or pores are noticed from either the surfaces or the cross-sections of the coating, presumably indicating feasibility of the flame spray for depositing HDPE–capsaicin composite coatings.

Interestingly, FESEM views from top surfaces of the coatings suggest completely different microstructural features for the coatings with/without addition of capsaicin. As noticed from the topographical views of the capsaicin-containing coatings, homogeneously dispersed small capsaicin crystallites in the size

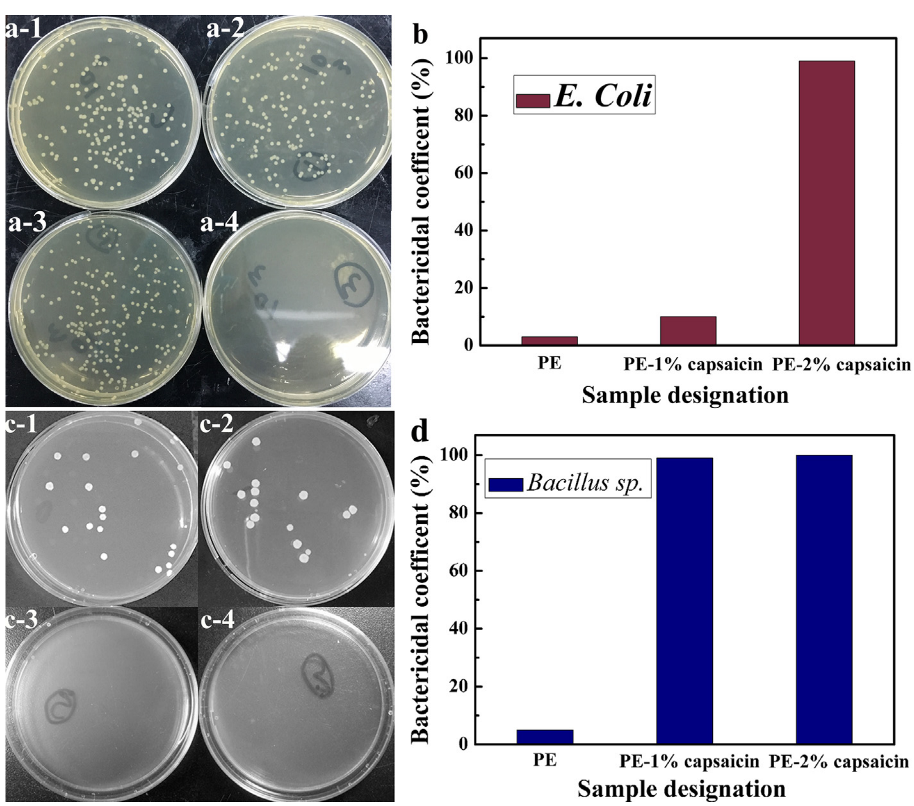

Fig. 3. Examination of (a) the viability of the bacteria *E. coli* growth, (b) sterilization results of the samples against *E. coli*, and the viability of the *Bacillus* sp. growth (c), and (d) sterilization results of the samples against *Bacillus* sp., -1: control, -2: pure PE coating, -3: PE–1.0 wt% capsaicin composite coatings, and -4: PE–2.0 wt% capsaicin composite coatings.

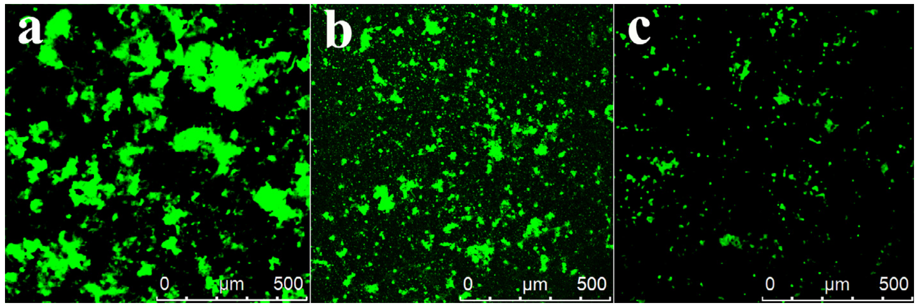

Fig. 4. SLCM images showing adhesion of *Phaeodactylum tricornutum* on HDPE and capsaicin loaded HDPE coatings after 1 week incubation.

of 1–3 μm are seen on the coating surfaces (Fig. 2b–e). Compared with the starting feedstock (Fig. 1a), the capsaicin in coatings show obvious changes in the morphology and grain size. This is not surprising since the coating deposition was operated at high temperature and the effect of capsaicin on the rheology and crystallization behavior of HDPE. Close surface examination shows the HDPE–2.0 wt% (or 1.6 vol%) capsaicin composite coatings exhibit rough surfaces (Fig. 2d and e). The surface roughness R_a of the composite coating (1.85 ± 0.20 μm) is higher than that of the HDPE coating (0.22 ± 0.02 μm). The melting temperature of the feedstock powders showed the values of 132.2 °C, 130.4 °C, and 127.6 °C for the pure HDPE powder, the HDPE–1.0 wt% capsaicin and the HDPE–2.0 wt% capsaicin composite powders respectively. The current flame spray processing, which involves melting and solidification of capsaicin and HDPE, together with the addition of capsaicin, has slightly altered the crystallization behavior of HDPE.

Capsaicin is a spicy vanilla amide alkaloid extracted from natural product namely peppers. To gain clear insight into effect of the addition of capsaicin on antifouling performance, the HDPE–pepper composite coatings were deposited by flame spray, and the sterilization was further examined. The effect of pepper on the antifouling of the composite coatings might be reflected by active components capsaicin. For comparation, it is observed that HDPE–50 wt% pepper composite coating has no effect on resisting *E. coli* and *Bacillus* sp. bacterial growth (data not shown). This is likely attributed to low quantities of capsaicin in hot pepper powder. Extinguishing efficiency of the bacteria was determined by the standard plate counting approach through triplicate experiments. The antifouling testing against survival of gram-negative *E. coli* and gram-positive *Bacillus* sp. shows encouraging antibacterial properties of the environmentally friendly biocides (Fig. 3). It is found that HDPE–capsaicin composite coatings are more resistant to bacterial growth than HDPE–hot pepper composite coatings. Moreover, higher capsaicin dosage in the coatings gives rise to more pronounced constrained growth. This is not surprising since continuous release of antifouling components from the composites. Obviously, after 48 h exposure, ~100% *E. coli* were killed by the HDPE–2.0 wt% (or 1.6 vol%) capsaicin composite coatings (Fig. 3a). In contrast, marine *Bacillus* sp. bacterial survival shows ~100% extinguishing efficiency on the HDPE–1.0 wt% (or 0.8 vol%) capsaicin composite coatings and HDPE–2.0 wt% (or 1.6 vol%) capsaicin composite coatings (Fig. 3b and c). It suggested that, comparing to *E. coli*, marine *Bacillus* sp. bacteria exhibit more damage as a result of the capsaicin-induced extinguishment. HDPE coating loading capsaicin biocide inhibits the growth of both gram-negative *E. coli* and gram-positive *Bacillus* sp., and its critical inhibitory concentrations are 2.0 wt% capsaicin in coatings. Mechanism of capsaicin in the growth inhibition to microbe cells could be that capsaicin enters to the cells and it functions as a toxic substance to membrane structure and/or as osmotic stress [10].

To gain clear insight into effect of the addition of biocide extracted from natural products on biofilm formation on the HDPE–capsaicin coatings, algae adhesion was further examined. During the formation of biofilm, the capsaicin containing composites perform better than the pure HDPE coating in resisting *Phaeodactylum tricornutum* adhesion (see Fig. 4). The of HDPE–2.0 wt% (or 1.6 vol%) capsaicin composite coating has powerful antifouling effect and removal rate as high as 90%. Both olvanil and the E-isomer of capsaicin are potent agonists of the vanilloid-1 receptor (TRPV1) which mediate some functions of zebra mussels, such as relaying information concerning pain and temperature sensations [13]. Consequently, for alga and mussel growth inhibition, capsaicin and other capsaicin-like compounds showed the promising activity for marine antifouling, but weakly toxic toward non-target organisms [13,14].

4. Conclusions

Novel HDPE–capsaicin composite coatings have been successfully fabricated by flame spraying. The content of capsaicin was tailored in a range up to 2.0 wt% (or 1.6 vol%). Dense microstructure for all the HDPE and HDPE–capsaicin coatings has been achieved. Capsaicin powder were fixed by polymer-based substrate and distributed evenly. The capsaicin in coatings showed obvious changes in the morphology and grain size compared with the starting feedstock. Capsaicin is a promising and an alternative biocide for marine antifouling application. The excellent antifouling performances against gram-negative *E. coli*, gram-positive *Bacillus* sp. and *Phaeodactylum tricornutum* provide exciting possibilities of extending the applications of the capsaicin-based coatings.

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