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The effect of high voltage pulse electric field (HPEF) on attachment of diatom on graphene composite coating and carbon fiber composite coating in marine environment

Ke Chai[a], Yuying Sun[a], Jinyi Wu[a,b,*]

[a] Key Laboratory of Advanced Materials of Tropical Island Resources (Hainan University), Ministry of Education, Material and Chemical Engineering College, Hainan University, Haikou 570228, China

[b] Key Laboratory of Marine Environmental Corrosion and Bio-fouling, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

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ABSTRACT

With increasing restrictions of environmental regulations and safety concerns on the traditional poisonous coatings, it is highly desirable to develop a new green anti-biofouling method in marine environment. In this paper, graphene composite coating and carbon fiber (CF) composite coating connected with high voltage pulse electric field (HPEF) were developed to inhibit the attachment of diatoms. The polarizing microscopy showed that the attachment rates of *Thalassiosira* and *Navicula* reached the lowest levels which were 0.23 cells mm^{-2} and 6.06 cells mm^{-2} on the graphene composite coating, 0.38 cells mm^{-2} and 4.17 cells mm^{-2} on the CF composite coating, under the HPEF with 1 h duration, 23.15 kHz frequency, 0.5 duty cycle and 19 kV pulse amplitude. While the attachment rates of *Thalassiosira* and *Navicula* were 21.21 cells mm^{-2} and 61.89 cells mm^{-2} on the graphene composite coating, 22.75 cells mm^{-2} and 62 cells mm^{-2} on the CF composite coating, without HPEF. Scanning electron microscopy (SEM) revealed that HPEF disintegrated the diatom cells, which could underlie the considerable inhibition of the diatom attachment by the HPEF. Additionally, the hardness, flexibility and shock resistance tests indicated that graphene and CF could considerably increase the mechanical properties of epoxy resin coating. HPEF stimulation had no obvious effect on the mechanical properties of the composite coatings.

1. Introduction

Biofouling, a global problem, leads to significant material damage and pecuniary economic loss [1–3]. Especially, fouling microorganisms can accelerate corrosion of many metals [4–6]. In ocean environment, temporary or permanent adhesion of microalgae to surfaces, as well as the secretion of extracellular adhesives to form a matrix, both play important roles in the biological fouling process [7,8]. The adhesion of microalgae provides food for macro fouling halobios, for instance, barnacle, oyster etc. Hence, the inhibition of the adhesion of microalgae is critical for anti-biofouling. Most of algae do not tend to adhere on the surfaces, however, some diatoms are prone to, which need to be controlled. Over the past decades, a great variety of marine anti-fouling paints has been developed to protect matrix surfaces from being adhered by fouling organisms [9]. Nevertheless, these marine anti-fouling paints inherently have drawbacks such as the generation of secondary contaminants due to the use of poisonous chemicals or heavy metal ions. Thus, alternative strategies for marine antifouling are required.

With increasing restrictions of environmental regulations and safety concerns on the marine environment [10–12], pulsed electric field (PEF) is a promising tool for antifouling because it is environmentally friend. Actually, pulse electric field treatment is a common way to sterilize many materials. Electroporation of the cell membrane is considered as a main mechanism of the microorganism inactivation [13,14]. Depending on the electric field parameters, these pores across the cell membrane cause reversible or irreversible cell damage or cell death [15]. High voltage pulse electric field (HPEF) with short electric pulses even can destroy the cell membrane [16,17]. HPEF is widely applied in the field of food sterilization [18–20]. HPEF and other non-thermal technologies such as high intensity light pulses have been combined successfully to sterilize juice [20]. Nevertheless, to our knowledge, there is no published work on investigating the anti-biofouling effect of HPEF on coating.

In this work, we explored the influence of HPEF on the diatom attachment on the graphene composite coating and the carbon fiber (CF) composite coating by polarizing microscopy and scanning electron

* Corresponding author at: Key Laboratory of Advanced Materials of Tropical Island Resources (Hainan University), Ministry of Education, Material and Chemical Engineering College, Hainan University, Haikou 570228, China. Tel.: +86089866279122.
E-mail address: wujinyi1976@163.com (J. Wu).

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microscopy (SEM). In addition, we investigated the influence of the content of the two fillers, graphene and CF, and HPEF on the mechanical properties of the coatings by the hardness, flexibility and shock resistance tests.

2. Experimental

2.1. Material

Analytically pure $Na_2SiO_3{\cdot}9H_2O$, Vitamin B_1 and Vitamin B_{12} were purchased from Guangdong Huankai Microbial Sci. & Tech. Co., Ltd. (Guangdong, China). Epoxy resin anticorrosion paint was provided by Institute of Metal Research, Chinese Academy of Sciences (Shenyang, China). Short CF (5 mm) and graphene were commercially purchased.

2.2. Preparation of samples

Epoxy resin, mixed solvent, levelling agent and curing agent were dispersed at a low speed (500 rmp) to form epoxy resin anticorrosion paint. Then the graphene and the CF, which are conductive components, were slowly added to the epoxy resin anticorrosion paint respectively and dispersed at 1800 rmp for 20 min to form the composite paints with a high shear-dispersing machine. For the research about the influence of HPEF on the diatom attachment on the composite coatings, the same contents of the graphene and the CF were 0.3% in the composite paints. The composite paints were respectively brushed on the resin material plates with dimensions of 100 mm × 50 mm × 4 mm. The composite coatings were the conductive layers. After curing for 7 days at room temperature, the dry composite coatings were coated with the epoxy resin anticorrosion paint by brush. The coating was air dried for 7 days at room temperature. The epoxy resin anticorrosion coating was the insulating layer. For the research about the effect of the content of the two fillers and HPEF on the mechanical properties of the coatings, the same contents of the graphene and the CF were 0%, 0.1%, 0.3%, 0.5%, 0.7%, 0.9% and 1.0% in the composite paints, which were brushed on tinplates with dimensions of 120 mm × 50 mm × 0.3 mm. The coatings were air dried for 7 days at room temperature. The thickness of the coatings was in agreement with GB/T 12452.2-2008. All the samples were subsequently kept in a desiccator before the measurement.

2.3. Culture of algae

The two diatoms, *Navicula* and *Thalassiosira*, were provided by Ocean College, Hainan University, China. They were cultured in simplified seawater-based culture medium, namely f/2 medium [21,22], at 18 °C for 7 days under the controlled illumination (100 μmol photons $m^{-2}s^{-1}$ provided by cool-white fluorescent lamps with a 16 h: 8 h light: dark cycle). When the concentrations of the diatoms reached 1.0×10^6 CFU (colony-forming units)/mL, the culture solutions were used to the attachment experiment, which was carried out in triplicate.

2.4. High voltage pulse electric field treatment

HPEF treatment was performed on a HPEF equipment (Ding Tong DMC-200, Dalian, China). The apparatus generated square waveform pulse. The maximum output voltage and frequency were 40 kV and 80 kHz, respectively. The two electrodes were clamped to the both ends of the composite coatings of the attachment sample plates along the length direction. Before HPEF treatment, 10 mL of the diatom culture solutions were transferred to the insulating layer surfaces of the attachment sample plates (Fig. 1). The treatment parameters varied in duty cycle, pulse frequency and voltage, respectively.

The HPEF treatment was carried on for 1 h per day for 4 days at room-temperature under the above controlled illumination. Then the coating surface was washed 3 times with distilled water to remove the unattached diatoms away. The coating surface was observed using polarizing microscope (Nikon eclipse LV100POL). Ten different views were randomly selected to count the diatoms in every view.

The diatom attachment rates were calculated using the following Eq. (1).

$$R = C/S \times 100\% \quad (1)$$

Where R is the diatom attachment rate, C is the average number of the diatoms in ten different views, S is the area of a view.

The cell morphology of the diatoms on the coating surface was assessed by a scanning electron microscope (SEM) (Hitachi Model S-4800, Tokyo, Japan).

2.5. Test of mechanical properties of the coatings

The mechanical properties of the composite coatings were investigated using QTX film elasticity tester (Tianjin, China), QCJ paint film impact tester (Changzhou, China) and pencil hardness tester (Tianjin, China), according to GB/T1731-1993, GB/T 1732-1993 and GB/T 6239-2006, respectively. The test was carried out in triplicate.

3. Results

3.1. The effect of the HPEF on the diatom attachment on the coatings

3.1.1. The effect of the HPEF on the Thalassiosira attachment on the coatings

The attachment experiment results showed that the three HPEF treatment parameters considerably influenced the *Thalassiosira* attachment rates on the two composite coatings (Fig. 2). The attachment rates were 21.21 cells mm^{-2} and 22.75 cells mm^{-2} on the graphene composite coating and the CF composite coating without HPEF treatment (Fig. 2a). The attachment rates decreased considerably with the increasing of voltage under 0.5 duty cycle and 23.15 kHz frequency, when voltage was less than or equal to 15 kV (Fig. 2a). However, the attachment rates decreased slightly when voltage exceeded 15 kV (Fig. 2a). They decreased to 0.23 cells mm^{-2} and 0.38 cells mm^{-2} on the graphene composite coating and the CF composite coating at 19 kV (Fig. 2a). When voltage was 15 kV and duty cycle was 0.5, the attachment rates decreased with increasing of frequency and achieved the lowest levels at 23.15 kHz (Fig. 2b). Then they increased slightly when frequency was greater than 23.15 kHz (Fig. 2b). The large decreases of the attachment rates were detected between 15.06 kHz and 17.86 kHz and between 15.06 kHz and 23.15 kHz (Fig. 2b). The attachment rates decreased considerably from 0.1 to 0.3 duty cycle and 0.3–0.5 duty cycle under 15 kV voltage and 23.15 kHz frequency (Fig. 2c). When duty cycle was greater than 0.5, the attachment rates increased slightly (Fig. 2c).

3.1.2. The effect of the HPEF on the Navicula attachment on the coatings

Similarly, the HPEF treatment parameters had considerable influence on the *Navicula* attachment rates on the two composite coatings (Fig. 3). Under 23.15 kHz frequency and 0.5 duty cycle, the attachment rates of *Navicula* decreased considerably from 0 to 11 kV voltage, 11–13 kV voltage and 13–15 kV voltage (Fig. 3a). Above 15 kV voltage, the attachment rates decreased slightly (Fig. 3a). The attachment rates reached 6.06 cells mm^{-2} and 4.17 cells mm^{-2} on the graphene composite coating and the CF composite coating at 19 kV voltage, which were considerably lower than 61.89 cells mm^{-2} and 62 cells mm^{-2} on the coatings at 0 kV voltage (Fig. 3a). The attachment rates decreased considerably with increasing of frequency and achieved the lowest levels at 23.15 kHz frequency under 0.5 duty cycle and 15 kV voltage (Fig. 3b). Then they increased slightly when frequency was greater than 23.15 kHz (Fig. 3b). When voltage and frequency were 15 kV and 23.15 kHz, the attachment rates decreased considerably with increasing