

Article

Organic–Inorganic Composite Antifouling Coatings with Complementary Bioactive Effects

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Abstract: Traditional antifouling coatings are toxic to marine life, which makes developing new environmentally friendly marine antifouling coatings imperative. Antifouling coatings that are nonadhesive and antimicrobial may provide an effective approach to achieving this goal. In this study, an organic–inorganic composite coating consisting of fluorinated polyurethane (FPU) and carboxymethyl chitosan–zinc oxide (CMC–ZnO) was prepared to achieve antifouling. The coating took advantage of the complementary bioactive effects of the low surface energy of FPU and the antimicrobial properties of CMC–ZnO. The coating showed good antifouling performance, with a survival rate for *Escherichia coli* of 3.15% and that for *Staphylococcus aureus* of 3.97% and an anti-protein adsorption rate of more than 90%. This study provides a simple method for preparing antifouling coatings using nonpolluting raw materials with minimal adverse effects on marine environments.

Keywords: antifouling; polyurethane; carboxymethyl chitosan–ZnO nanocomposite; complementary bioactive effects



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1. Introduction

Biofouling [1] involves the adsorption and accumulation of biological materials on the surface of materials. It may lead to equipment malfunctions in many fields that may cause serious economic losses and safety problems, which may jeopardize human life [2]. Two main strategies can be used to reduce biofilm formation: the use of non-adherent and bactericidal surfaces [3–6]. However, the functionality of a single surface is limited. Non-adhesive surfaces have limited antifouling properties due to the lack of external shear provided by water currents when left standing in the ocean [7], while the positive charge of antibacterial surfaces attracts the negative charge of the bacteria and thus facilitates bacterial adhesion [8]. Therefore, the antifouling effect of surfaces with both functions is more desirable. Non-adhesive surfaces inhibit initial microbial adherence [9], while bactericidal functions help kill adherent bacterial cells [10]. Ji et al. [11] prepared polyurethane (PU) coatings with synergistically enhanced antimicrobial mechanisms consisting of low surface free energy and bactericidal agents, which exhibited excellent antimicrobial properties and durability.

PU are widely used biomaterials due to their excellent mechanical properties and biocompatibility [12]. However, PUs have poor water resistance due to the hydrophilic –CH₂OH groups on the molecular chain. Hydrophobic structures can be introduced into

the molecular chain to enhance the water resistance of PUs. Currently, hydrophobic structures have two common types: fluorine and silicon chain segments [13]. However, silicone coatings are also susceptible to mechanical damage and have poor resistance to tearing and puncturing, which limits their application in marine antifouling [7]. Fluorinated PUs (FPU) show improved water resistance, weathering resistance, and mechanical properties [14–17]. Qiao Z. et al. [18] investigated the synthesis and antifouling activity of FPU and showed that FPUs with greater microphase separation showed excellent antifouling activity. However, pure FPU has a low adhesion strength to the substrate without a bonding layer and is prone to being damaged by external forces and falling off. Thus, researchers have conducted a series of improvements and optimizations on it. Among them, nanocomposites are a class of materials that offer advanced properties [19]. Nanoparticles in coating formulations can enhance various properties, including antifouling, mechanical and optical properties, and wettability [20]. Dimitrakellis et al. [21] showed that a low-surface-energy antifouling coating with a novel antimicrobial nano-filler could achieve the dual development of anti-bioadhesion and “active” antimicrobial properties. Metal nanoparticles and their oxides have unique morphological characteristics, size dependence, and self-cleaning properties. Thus, they are a good strategy for the development of environmentally friendly coatings that can effectively prevent pollution from marine activities. Zinc oxide is inexpensive, antimicrobial, non-toxic, and UV-blocking, which makes it a popular material for polymeric bio-nanocomposites [22]. However, due to the poor dispersion of zinc oxide, it tends to agglomerate in composites, which damages normal cells and weakens the overall antimicrobial effect [23]. Zinc oxide nanoparticles can be modified to prevent this phenomenon. S. Sanuja et al. [24] showed that chitosan–neem oil–zinc oxide nanocomposites had good mechanical strength, thermal stability, and antimicrobial activity. Chitosan shows strong antifungal properties [25,26]. The macromolecule of chitosan contains active hydroxyl and amino groups, which allow it to strongly chelate metal ions. However, chitosan forms an extremely poor water barrier. Compared with chitosan, carboxymethyl chitosan has superior biocompatibility, biodegradability [27], antioxidant properties [28], and antimicrobial properties [29,30].

Here, we constructed FPU coatings with complementary bioactive effects against marine fouling. FPU was selected as the material to resist the adhesion of marine microorganisms. Carboxymethyl chitosan–zinc oxide (CMC–ZnO) was selected as an antimicrobial agent to inhibit microbial proliferation. Both antimicrobial and anti-adhesion work together to compensate for the lack of a single surface function. The prepared samples showed excellent antimicrobial effects and anti-protein adhesion. In addition, the film has good thermal stability and water resistance, which has a broad practical application prospect in marine antifouling and underwater engineering.

2. Experiments and Methods

2.1. Materials

Polyether diol (DL2000D) was purchased from Shandong Bluestar Dongda. Isophorone diisocyanate (IPDI, CAS: 4098-71-9), 1H,1H,2H,2H-perfluorooctanol (CAS: 647-42-7), carboxymethyl chitosan (CAS: 83512-85-0), and 1,4-butanediol (BDO, CAS: 110-63-4) were purchased from Macklin. Zinc sulfate heptahydrate (CAS: 7446-20-0) and sodium hydroxide (CAS: 1310-73-2) were purchased from the Guangzhou Chemical Reagent Factory. Dibutyltin dilaurate (DBTDL, CAS: 77-58-7) was purchased from Shanghai Aladdin Reagent Company Limited (Shanghai, China). N, N-Dimethylformamide (DMF, CAS: 68-12-2) was purchased from Xilong Science Co. (Shantou, China) Deionized water was made in-house in our laboratory.

Peptone and agar powder were purchased from Guangdong Hankai Biotechnology Co. (Chaozhou, China) Yeast powder was purchased from Thermo Fisher Scientific-CN (Shanghai, China). Sodium chloride was purchased from Guangdong Chemical Reagent Factory. *Escherichia coli* ATCC 11229 and *Staphylococcus aureus* ATCC 6538P were purchased from the Beijing Microbiological Culture Collection Center (BJMCC). Bovine serum protein

($\geq 98\%$) was purchased from Amresco, and phosphate-buffered saline (PBS) was purchased from Beijing Lanjike Technology Co., Ltd. (Beijing, China).

2.2. Synthesis of Carboxymethyl Chitosan-Zinc Oxide Composites (CMC-ZnO)

As shown in Figure 1a, CMC (3 g) was added to a beaker containing 500 mL distilled water and fully dissolved. Then, 15 g zinc sulfate was added and stirred for 30 min, followed by the addition of 4 g NaOH. The mixture was heated at 45 °C for 2 h, allowed to stand at 80 °C for 8 h, and finally taken out for filtration and freeze-dried for 24 h.

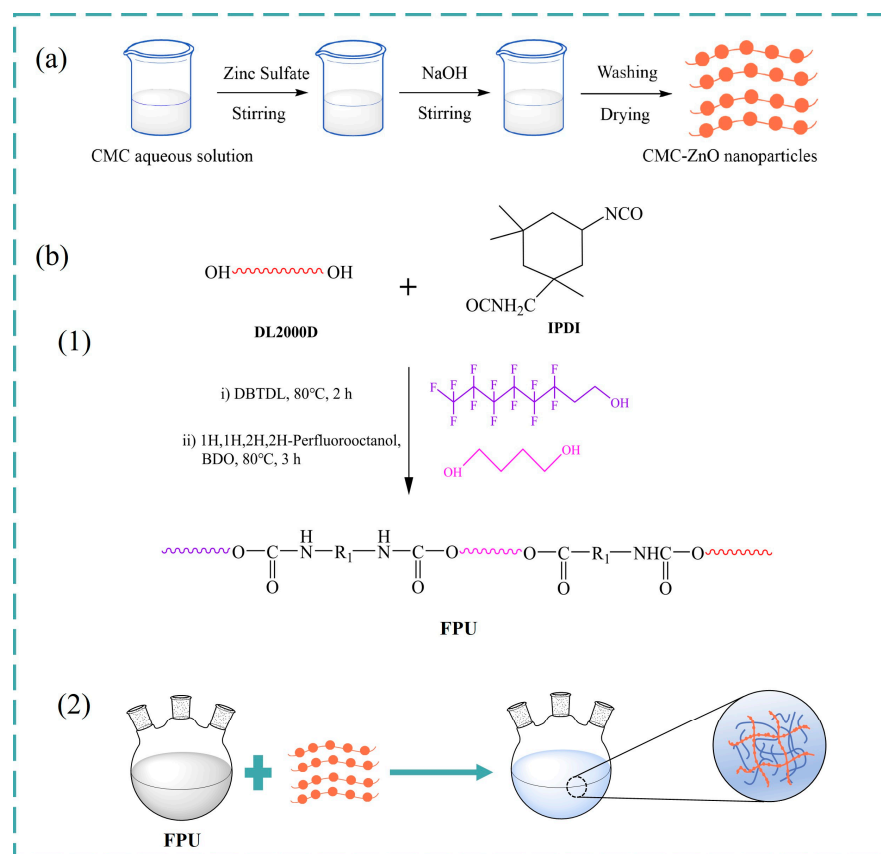


Figure 1. Synthetic route of (a) CMC-ZnO, (b) FPU and FPU/CMC-ZnO coatings.

2.3. Preparation of FPU Antifouling Coatings

The process basically consisted of two steps: (1) the preparation of polyurethane prepolymer and (2) the incorporation of CMC-ZnO via a chain extension and condensation reaction (Figure 1b).

Step 1: Preparation of polyurethane prepolymer. Before use, DL2000 was dried in a vacuum drying oven at 120 °C for 2 h. The condensation reaction was carried out at 80 °C using DL 2000 and IPDI at an NCO/OH ratio of 2:1 and 0.1% DBTDL as a catalyst for 2 h. 1H,1H,2H,2H-Perfluorooctanol was dissolved in DMF and then added (the molar ratio of perfluorooctanol-to-DMF was 1:1) to obtain the prepolymer.

Step 2: BDO was used as a small-molecule chain extender and was added to the system and then heated for 30 min at 60 °C. Finally, 0%, 5%, 10%, 15%, or 20% of CMC-ZnO and DMF were added to the prepolymer system and stirred well. Then, the reaction was continued for 3 h at 80 °C.

At the end of the reaction, the prepared composite coating was poured onto a tinplate sheet coated with a polyurethane topcoat, placed at room temperature for 24 h, and then dried in an oven at 60 °C for 24 h.

The above composite coatings were labeled as FPU, FPU-5, FPU-10, FPU-15, and FPU-20, respectively, depending on the CMC-ZnO content.

2.4. Characterization

2.4.1. Structural Characterization

FTIR scans were performed in the 4000–400 cm^{-1} range using a Frontier FTIR analyzer to determine structural features. The samples were prepared by the potassium bromide tableting technique. The crystalline properties of the materials were evaluated by a Rigaku SmartLab X-ray diffractometer using monochromatic Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), and the samples were recorded at diffraction angles between 10° and 80° (2θ). Samples were mounted on conductive gel on a sample stage and then sprayed with a thin layer of platinum and gold. An S-4800 scanning electron microscope was used to characterize the surface morphology of the samples.

2.4.2. Thermogravimetric Analysis (TGA)

Samples were thermally analyzed using a thermogravimetric analyzer (TG 209 F3) under a nitrogen atmosphere at a ramp rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in the range of 45–600 $^\circ\text{C}$.

2.4.3. Wettability of Composite Coatings

Contact Angle Test

The contact angle of deionized water on the surface of the coatings was measured using a Biolin Scientific optical contact angle meter with a test droplet of 5 μL , and the average values were obtained based on the values obtained at five different locations.

Water Absorption Test

Each coating specimen with an initial mass of m_1 was immersed in water for various times at room temperature and then removed and weighed after drying the water on the surface, and the weight was recorded as m_2 . Then, the water absorption rate was calculated by the following formula:

$$\eta = \frac{m_2 - m_1}{m_1} \times 100\%$$

2.4.4. Anti-Fouling Experiments with Composite Coatings

Antimicrobial Experiment

The antimicrobial properties of the polyurethane coatings against *Escherichia coli* and *Staphylococcus aureus* were evaluated by the plate counting method. First, polyurethane coatings (control, FPU, FPU-5, FPU-10, FPU-15, or FPU-20) were poured into a well plate, and 1 mL of the original bacterial solution was added to the well plate and placed in an incubator at 37 $^\circ\text{C}$. Then, 5 μL of the bacterial suspension was taken and diluted 1×10^{-9} times after 6 h. The target bacterial solution (200 μL) was quickly added to the Luria–Bertani solid medium, and then the whole Petri dish was gently coated with a sterile coating rod until there was no liquid flow. After 16–24 h of incubation in an incubator at 37 $^\circ\text{C}$, the number of colonies on the Petri dish was counted, and the antimicrobial rate of the coating was calculated. Blank solutions containing only *Staphylococcus aureus* and *Escherichia coli* were used to observe the normal growth of these bacteria on agar plates.

Anti-Protein Adsorption Experiment

Because the benzene rings of tyrosine and tryptophan residues in proteins contain conjugated double bonds, the protein solutions produced a distinct UV absorption peak at 275–280 nm. Therefore, the attachment of coated bovine serum protein (BSA) was evaluated by UV spectrophotometry according to the Beer-Lambert Law.

BSA was first prepared into standard solutions with different concentrations (0.1, 0.25, 0.5, 0.75, 1, and 1.25 g/L) using PBS solution. The absorbance of the standard solution at 278 nm was evaluated by UV spectrophotometry, and the standard curve was made with

absorbance as the y-axis and concentration as the x-axis (Figure 2). Before the test, the coating was immersed in a PBS solution for 3 h to prevent it from affecting the concentration of BSA due to water absorption. The liquid on the surface of the coating was wiped off, and the coating was placed in 1 mL of a 1 g/L BSA solution for 5 h. After reaching adsorption equilibrium, the absorbance of BSA at 278 nm was measured by UV spectrophotometry, and the concentration of BSA was measured against the standard curve to calculate the anti-protein adsorption rate of polyurethane coatings.

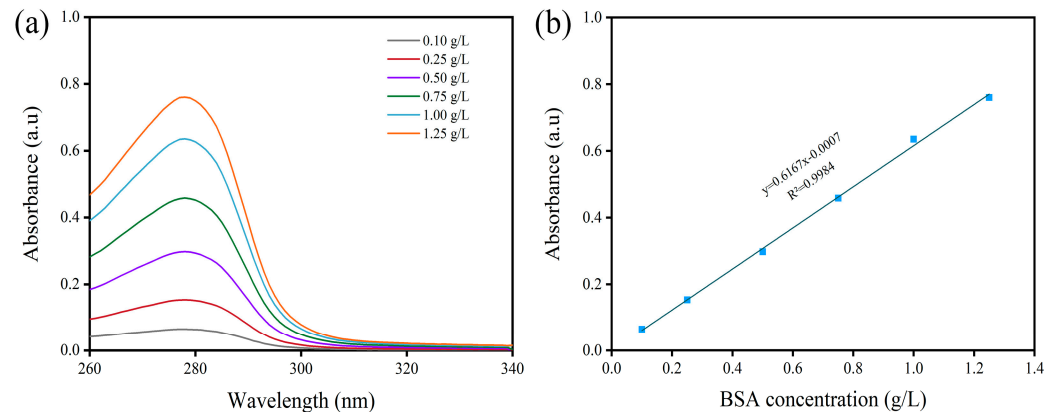


Figure 2. (a,b) Standard concentration versus absorbance curves of bovine serum albumin (BSA).

3. Results and Discussion

An antifouling coating with nonadhesive and antimicrobial complementary bioactive effects was constructed by a two-step process using DL2000D as the polyol, IPDI, 1H,1H,2H,2H-Perfluorooctanol, and CMC-ZnO as the raw materials. As a marine antifouling coating, the possible antifouling mechanism of this coating is shown in Figure 3.

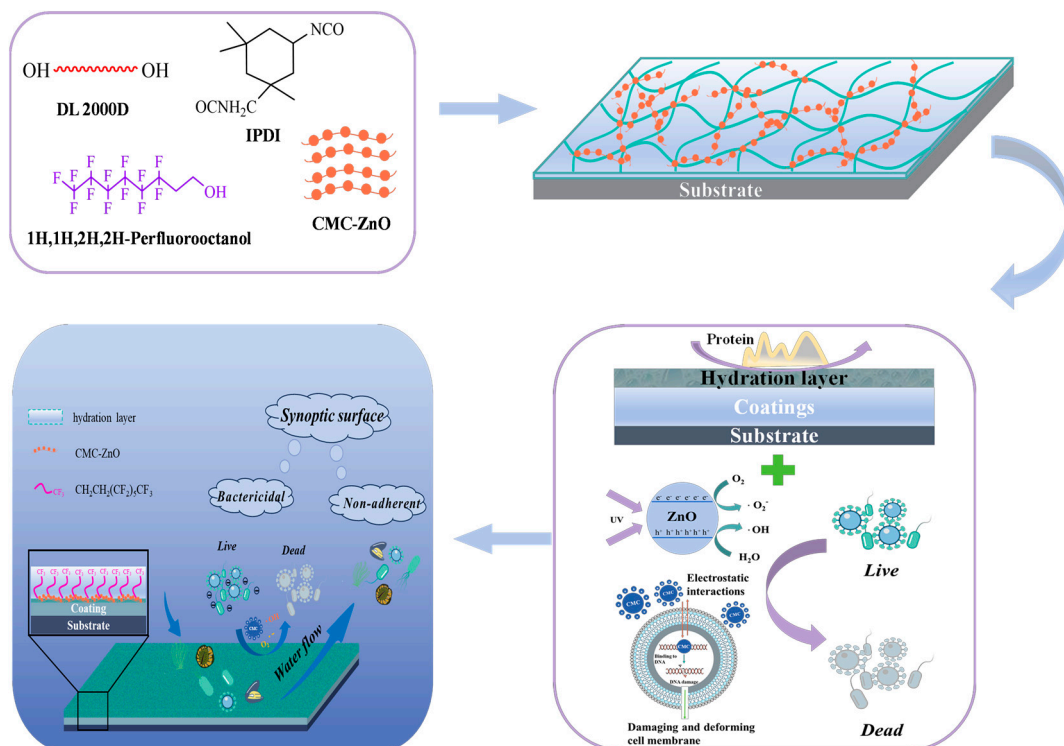


Figure 3. Scheme of the construction of the antifouling coatings and application mechanisms in seawater.

By introducing a fluorine side chain into the PU main chain, the surface energy of the coating is reduced to form a nonadhesive surface. The surface hydration in the doped CMC–ZnO is improved due to the presence of many –OH groups in the ZnO, which prevents the adhesion of bacteria. The antimicrobial effect may be induced by the CMC–ZnO, the hydroxyl radicals (–OH) produced by ZnO after absorbing ultraviolet light due to its excellent photocatalytic properties, and the reactive oxygen species, such as single-linear oxygen ($^1\text{O}_2$), can induce intracellular ROS production leading to death [31]. Since the phosphomuconic acid of the bacterial cell wall contains a large number of highly acidic phosphate groups, resulting in a negatively charged bacterial surface, chitosan alters the permeability of the cell membrane by electrostatic interactions between the protonated $-\text{NH}_3$ and the negative charges on the cell wall, thereby disrupting the bacterial structure and lysing the internal material [32]. Therefore, a greater positive charge on chitosan corresponds to its higher antimicrobial activity. Carboxymethyl chitosan has a higher positive charge density than chitosan. In this case, $-\text{COOH}$ may react with $-\text{NH}_3$ to increase its polycationic nature, which raises its antibacterial activity [33–35]. The non-adhesion and antimicrobial effects complement each other against biofouling. This complementary effect of bioactivities provides a new avenue for marine antifouling.

3.1. Characterizations of CMC–ZnO and Composite Coatings

Figure 4a shows an optical photograph of the prepared FPU and FPU/CMC–ZnO coatings. The FT-IR spectra of CMC and CMC–ZnO are shown in Figure 4b. In the CMC–ZnO spectrum, a distinct peak was observed at 471 cm^{-1} due to the chelation of Zn with CMC to form Zn–N bonds, which indicates the successful reaction of the composites. The peak at 3454 cm^{-1} represented –OH and –NH groups of CMC, and the peaks at 1612 and 1404 cm^{-1} represented the C=O stretching of CMC–ZnO, which was attributed to interactions between CMC and ZnO to form zinc carboxylate. The FT-IR spectra of the composite coatings are shown in Figure 4c. The stretching vibration peaks of C–F, $-\text{CF}_3$, and $-\text{CF}_2$ were observed at 661 , 823 , and 1249 cm^{-1} , respectively, which indicates that fluorine was introduced into the PU chains. Therefore, we successfully prepared CMC–ZnO and FPU. However, the characteristic peaks of zinc oxide were not observed because zinc oxide is an inorganic material that is IR-inactive.

Figure 4d shows the XRD patterns of CMC and CMC–ZnO. Comparison with the ZnO standard card shows that CMC–ZnO produces characteristic peaks that closely match those of the standard card. By contrast, only an amorphous halo at $2\theta = 20^\circ$ is observed for pure carboxymethyl chitosan. Figure 4e shows the XRD patterns of the CMC–ZnO/FPU coatings, where the characteristic peaks belonging to ZnO were also observed for FPU 5–20. Therefore, ZnO interacted with carboxymethyl chitosan to form carboxymethyl chitosan ZnO bio-nanocomposites, and the crystalline form of ZnO in the coatings did not change.

The thermal stability of the coatings was characterized by extrapolating the starting point of the TG curve. Figure 4f shows the TGA curves of FPU and FPU/CMC–ZnO coatings. The coatings underwent a two-step weight loss. The first step ($271\text{--}360^\circ\text{C}$) was attributed to the cleavage of hard chain segments such as carbamate bonds. The second step ($360\text{--}400^\circ\text{C}$) is due to the thermal degradation of soft chain segments, such as polyether bonds, and a small part of the residue was due to zinc oxide. FPU/CMC–ZnO coatings showed greater thermal stability than FPU because interactions between CMC and ZnO restricted the mobility of the polymer chains and increased the degree of cross-linking within the FPU system. This condition restricted the free movement of the molecular chain segments. As a result, higher temperatures were required to decompose the system, which improved its thermal stability.

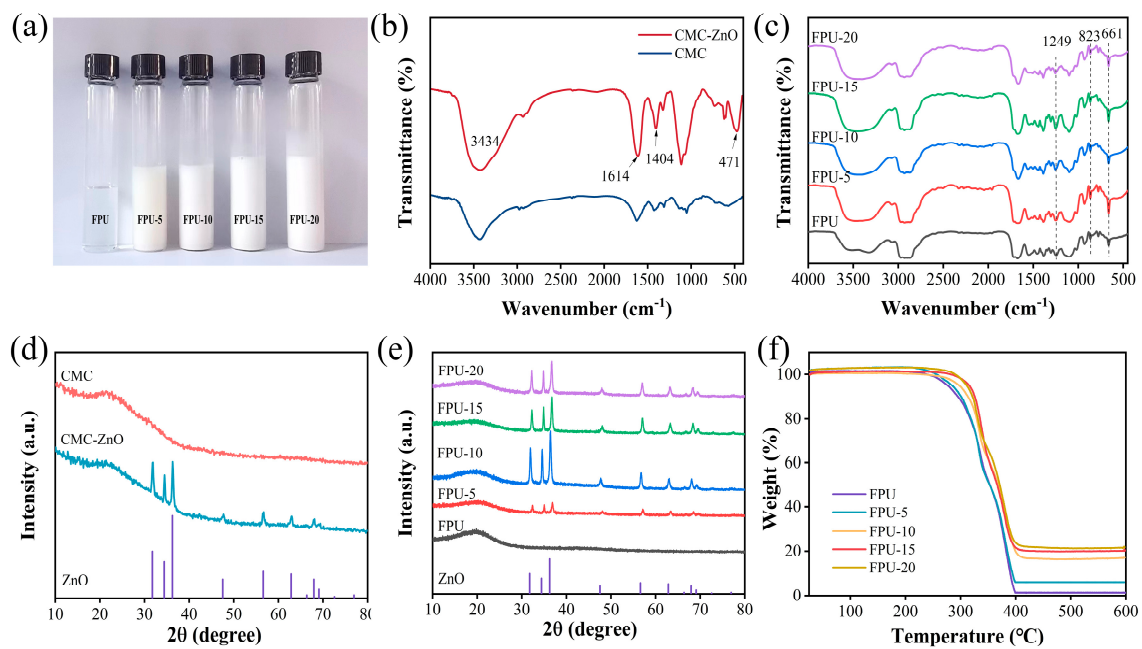


Figure 4. Preparation of FPU and FPU/CMC-ZnO. (a) Optical images of coatings. (b) Infrared spectra of CMC and CMC-ZnO. (c) Infrared spectra of FPU and FPU/CMC-ZnO composite. (d) XRD spectra of CMC and CMC-ZnO. (e) XRD spectra of FPU and FPU/CMC-ZnO composite.

3.2. Wettability of Composite Coatings

The nanocomposite coatings were tested for water contact angle (WCA) and water absorption capacity to assess the wettability of the coating. The WCA of FPU and FPU/CMC-ZnO coatings are shown in Figure 5a. The water contact angle of FPU was 82°, while the water contact angle of FPU/CMC-ZnO was overall smaller than that of FPU, with a minimum of 69°. However, the contact angle of FPU-20 was 71°, which was larger than that of FPU-15. This difference may be due to the decrease in porosity and pore clogging caused by too much doping. The water absorption of FPU and FPU/CMC-ZnO composites is shown in Figure 5b. The water absorption of FPU was 3.703%, which was increased by doping with CMC-ZnO and further increased with the rise in doping up to 6.910%. The SEM images in Figure 5c,d confirm the speculation that the porosity of FPU-20 was lower than that of FPU-15. The filler was captured on the membrane surface, which increased the total solid content. Thus, the doping of CMC-ZnO increased the hydrophilicity of the coating, which improved the surface hydration. The layer of water molecules tightly bound to the surface of the film may act as a physical and energetic barrier to bacterial adhesion. This condition may further reduce organic contamination and lower cleaning costs.

3.3. Anti-Fouling Experiments with Composite Coatings

We conducted bacterial culture experiments on FPU and FPU/CMC-ZnO composite coatings and counted the number of surface colonies by the bacterial plate counting method to verify the antimicrobial properties of the coatings. The antimicrobial optics of FPU/CMC-ZnO composite coatings against *E. coli* and *S. aureus* are shown in Figure 6a. The control group grew many bacterial colonies on agar plates. The growth of colonies of FPU became less compared with the control group, but the antibacterial effect was still unsatisfactory. By contrast, fewer bacteria grew on the FPU/CMC-ZnO composite coatings. Specifically, FPU-15 and FPU-20 had nearly no bacterial growth on the agar plates, which indicates that most of the bacteria were killed. The survival rate of bacteria on different coatings in Figure 6a was statistically calculated by Image J software 1.54i 03, and the results are shown in Figure 6b. The antimicrobial effect of the coatings increased with the rise in CMC-ZnO

content. The survival rate of *E. coli* decreased from 34.81% to 3.14%, and that of *S. aureus* decreased from 42.73% to 2.53%.

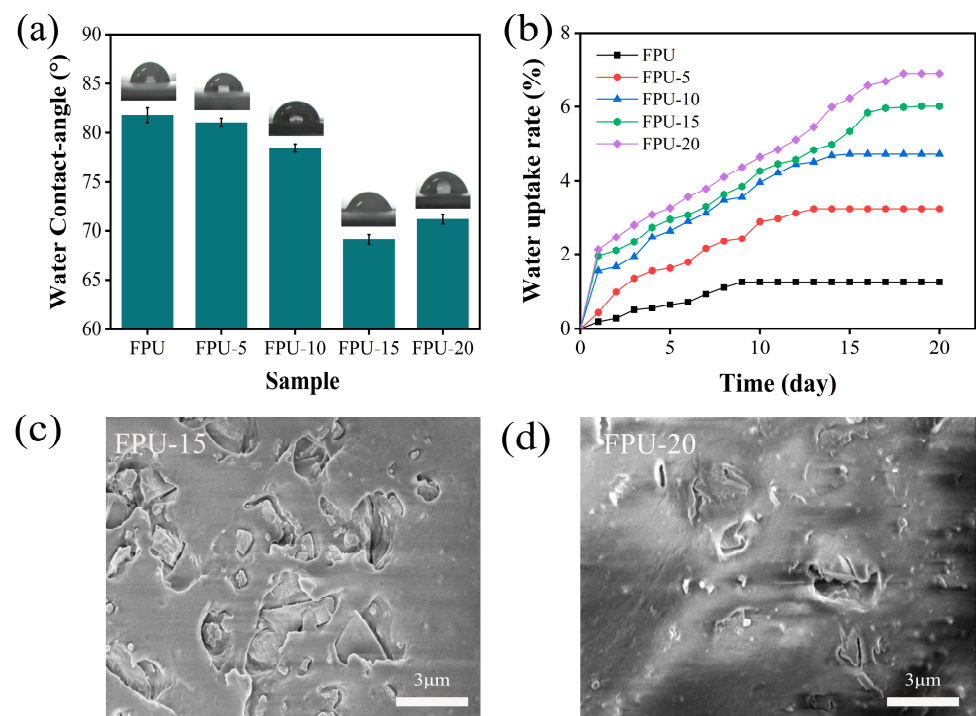


Figure 5. Wettability studies of FPU and FPU/CMC-ZnO composites. (a) water contact angle. (b) water absorption. (c) SEM images of FPU-15, and (d) SEM images of FPU-20.

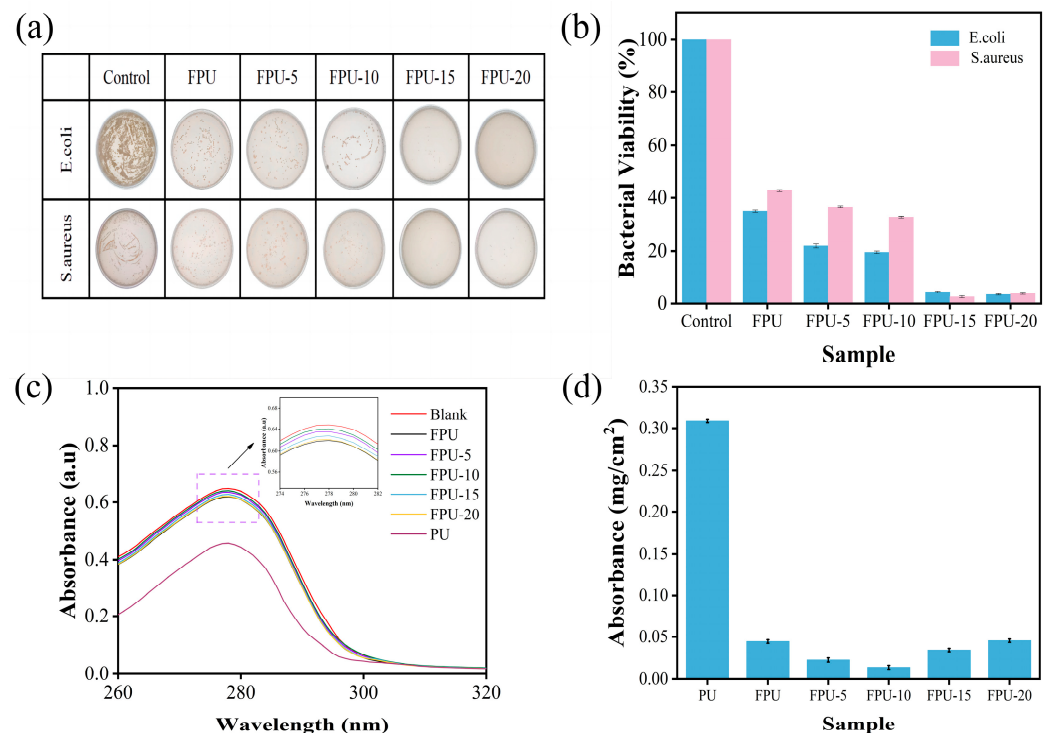


Figure 6. Anti-fouling properties of the coatings. (a) Plate counting experiments for *Escherichia coli* and *Staphylococcus aureus*. (b) Bacterial survival. (c) Assessment of anti-protein adsorption of coatings by UV spectrophotometry. (d) Results of quantitative absorbance-concentration testing.

The antimicrobial results proved that the antimicrobial effect of the complementary coatings was due to CMC–ZnO. We performed anti-protein adsorption tests on PU, FPU, and FPU/CMC–ZnO composite coatings to verify that the non-adhesion effect was due to the introduction of fluorine atoms into the system. Figure 6c shows the curve of bovine serum albumin concentration versus UV absorbance. The standard curve was used to derive the anti-protein adsorption rate of each coating per square centimeter, and the results are shown in Figure 6d. The protein adsorption values of FPU were all below 0.05 mg/cm², and the anti-protein adsorption rates were all greater than 90%. On the contrary, the protein adsorption of PU was 0.310 mg/cm², and the adsorption of bovine serum protein was significantly increased. The difference between the CMC–ZnO-doped and undoped coatings was insignificant. This result confirms that the anti-protein adsorption property is not caused by CMC–ZnO but by the addition of fluorine atoms to the coating. The results of antifouling experiments confirm that the composite coating prepared has non-adhesion and antimicrobial properties, and the two complement each other's deficiencies to improve the effect of anti-biofouling.

4. Conclusions

In summary, we have successfully constructed an antifouling coating with complementary bioactive effects on marine fouling that is both non-adhesive and antimicrobial. The coating has excellent anti-adhesion effects on proteins due to the properties of elemental fluorine. The antimicrobial effect of CMC–ZnO results in the remarkable inhibitory ability of the coating against marine microorganisms. These two effects work together to make up for the lack of a single function and enhance the anti-biofouling effect of the coating. Antifouling experiments show that the coating has good resistance to the adhesion and proliferation of marine microorganisms. It obtains survival rates as low as 3.14% for *E. coli* and 2.53% for *S. aureus*, and it exhibits an anti-protein adsorption rate higher than 90%. The coating also has good thermal stability and wettability. Considering its good performance, ease of preparation, and harmlessness, the technology can be applied to scenarios such as ships and underwater equipment.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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