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Nano ZnO/acrylic coating for antifouling applications

Abstract: Fouling causes huge material and economic costs in maintenance of mariculture, shipping, naval vessels, and seawater pipelines, etc. Prevention of biofouling is an important property expected of coatings in these fields. In the present work, we prepared nano ZnO/acrylic latex by mechanical mixing as well as by the *in situ* method. The effect of nanoparticles on the drying of coatings and their antimicrobial nature were investigated.

Keywords: acrylic latex; antifouling; coating; polymer.

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1 Introduction

Biofouling is found in almost all circumstances where water-based liquids are in contact with other materials. Industrially important examples include membrane systems, such as membrane bioreactors, reverse osmosis, spiral wound membranes, cooling water cycles of large industrial equipment and power stations, oil pipelines carrying oils with entrained water especially those carrying used oils, cutting oils, soluble oils, or hydraulic oils. The process of biological fouling is often grouped into two key growth stages: (a) microfouling – biofilm formation and bacterial adhesion, which include an initial accumulation of adsorbed organics, the settlement and growth of pioneering bacteria creating a biofilm matrix, (b) macrofouling – attachment of larger organisms, of which the main culprits are barnacles, mussels, polychaete worms, bryozoans, and seaweed. Together, these organisms form a fouling community. Microfouling or slime formation consists of four essential stages or steps undergone by exposed living or nonliving surfaces submerged in the sea-macromolecular adsorption, bacterial colonization, surface fouling by diatoms and protozoans, and establishment of unicellular and multicellular epibionts such as invertebrate larvae and algal propagules.

Antifouling is the process of removing the accumulation or preventing it. Generally, coatings with antifouling properties are used for controlling fouling. Reduced human or ecotoxicity, versatile antifouling activity, and economy are expected from these antifouling coatings. The use of toxic antifoulants on ship hulls has been a historic method of controlling fouling, but biocides such as lead, arsenic, mercury, and their organic derivatives have been banned due to the environmental risks that they posed. Tributyl tin (TBT)-based antifouling paints have been successfully used for over a long period of time to protect a ship's hull from biofouling. However, due to its high toxicity to marine organisms, the International Maritime Organization (IMO) adopted a resolution recommending governments to adopt measures to eliminate antifouling paint-containing TBT. The anticipation of these prohibitions reactivated the development of nontoxic, low surface energy coatings. The use of nanometal oxide coatings represents a promising approach for the development of nontoxic control technologies for antifouling [1–5]. Recently, James and Maureen [6] reviewed about the environmentally friendly marine coating. Advances in nanotechnology and polymer science, and the development of novel surface designs 'bioinspired' by nature, are expected to have a significant impact on the development of a new generation of environmentally friendly marine coatings.

In the present work, we synthesized nano ZnO, incorporated them into acrylic coatings, and investigated the antimicrobial nature of the coating. ZnO is an environmentally friendly material and has little toxicity. It is widely used as an active ingredient for dermatological application in creams, lotions, and ointments on account of its antibacterial properties.

2 Materials and methodology

2.1 Materials

Styrene (ST) monomer (at a purity of 99.8%), acrylic acid, methyl methacrylate (MMA) monomer (at a purity of 99.9%),

ethanol were of reagent grade and distilled before use. Zinc acetate, lithium hydroxide (LiOH), ammonium persulfate were from SD Fine Chemicals (Mumbai, Tamilnadu, India). The surfactant, polyoxyethylene nonylphenyl ether (OP-10) is from Sigma Aldrich (Milwaukee, USA). The chemicals used for the antimicrobial studies were also of reagent grade.

2.2 Synthesis of ZnO nanoparticles

ZnO nanoparticles were prepared from zinc acetate by distillation method [7]. A solution of zinc acetate, 0.1 M, in absolute ethanol was refluxed under distillation and stirred for 3 h at 80°C. The condensate was separated out, and the remaining hygroscopic product was mixed with 0.1-M LiOH prepared in 100 ml deionized water. The precipitate formed was separated out using a centrifugal machine at 2800 rpm followed by drying in the oven in oxygen atmosphere at 150°C.

2.3 Preparation of acrylic emulsion

Emulsion polymerization was carried out in a three-neck flask equipped with a stirrer, thermometer, and condenser. At first, nonionic surfactant (OP-10) was introduced into the flask along with deionized water. The monomers, ST, MMA, and acrylic acid (AA) were introduced into the system. Once the temperature reached 60°C, ammonium persulfate was slowly added. The system was kept under stirring, and the temperature was maintained constant for another 2 h to assure the completion of the reaction. The solid content of the emulsion was determined by the gravimetric method. For preparing the emulsion with ZnO by the *in situ* method, the nanoparticles were added to the reaction vessel along with the surfactants. Meanwhile, with mechanical mixing, the acrylic latex and the ZnO were constantly stirred at a high speed for 20 min. Before every testing, the emulsion was shaken for a fixed brief period.

2.4 Characterization

The synthesized samples were characterized for their phase purity by powder X-ray diffraction using BRUKER (Germany, D8 Advance diffractometer). The X-ray diffraction spectra were recorded using Cu-Kα radiation. The average crystalline size of the sample was estimated with the help of the Debye Scherrer equation using the diffraction intensity of all prominent lines.

$$crystalline\ size = \frac{0.9\,\lambda}{\beta\cos\theta}$$

where λ=X-ray wavelength, θ=Bragg's angle, β=FWHM (full width at half maximum) or integral breadth.

Fourier transform infrared spectra (FTIR) of the sample were carried out on a spectrometer (Nicolet Co., NEXUS, USA). The UV measurements were carried out using a HITACHI U – 2800 spectrophotometer in ethanol medium.

For antibacterial experiments, *Escherichia coli*, a Gram-negative bacterium, and *Staphylococcus aureus*, a Gram-positive bacterium, were selected. All disks and materials were sterilized in an autoclave before the experiments. Luria Bertani (LB) broth and nutrient agar were used as sources for culturing *E. coli* at 37°C on a rotary platform in an incubator. The antibacterial activity of ZnO was measured by paper disk diffusion assay in terms of minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC). The Petri plates used in the tests were prepared using a nutrient agar medium. The bacteria were sprayed evenly on top of the plates using a sterile glass rod. After allowing the bacteria to dry (within 5–10 min), test solutions of ZnO/acrylic emulsions of various concentrations (different particle sizes) were dropped. The zone of inhibition was measured after 48 h incubation.

To study the release profile of the nanoparticles from the acrylic coating, emulsion with nano ZnO and normal ZnO were coated on a tile and kept immersed in the beaker containing ethanol. Five milliliters of the solution is taken out every 24 h for 6 days, and the absorbance was noted. The quantitative determination of this release profile will be done by using UV spectrum.

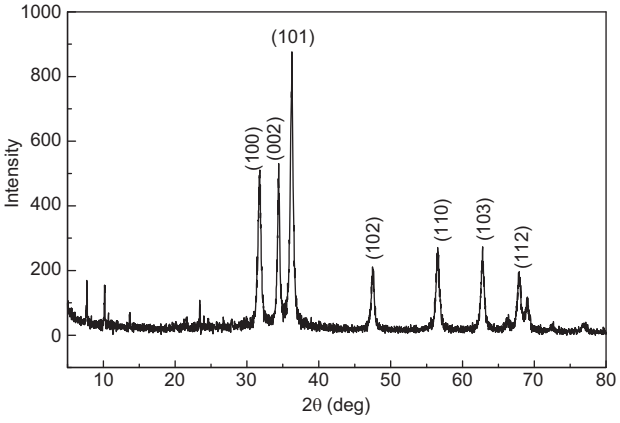

Figure 1 XRD pattern of nano ZnO.

Name of the bacteria	Zone of inhibition in diameter			
	In situ method		Mechanical method	
	Nano ZnO	Normal ZnO	Nano ZnO	Normal ZnO
Escherichia coli	8	13	8	9
Staphylococcus aureus	21	9	13	14

Table 1 Zone of inhibition of the emulsions.

3 Results and discussion

The XRD of the ZnO prepared are given in Figure 1. X-ray diffraction studies indicate that the materials synthesized are ZnO with wurtzite phase, and all the crystal structures agree with the reported JCPDS data (card no 36-1451). This shows that the product is of hexagonal lattice. The grain size was calculated using the Scherer equation and was found to be 19.44 nm.

The polymerization of the acrylic emulsion was done by introducing the monomers ST, MMA, AA into the system. The solid content of the emulsion was calculated and was found to be 43.45%. The nanofillers were

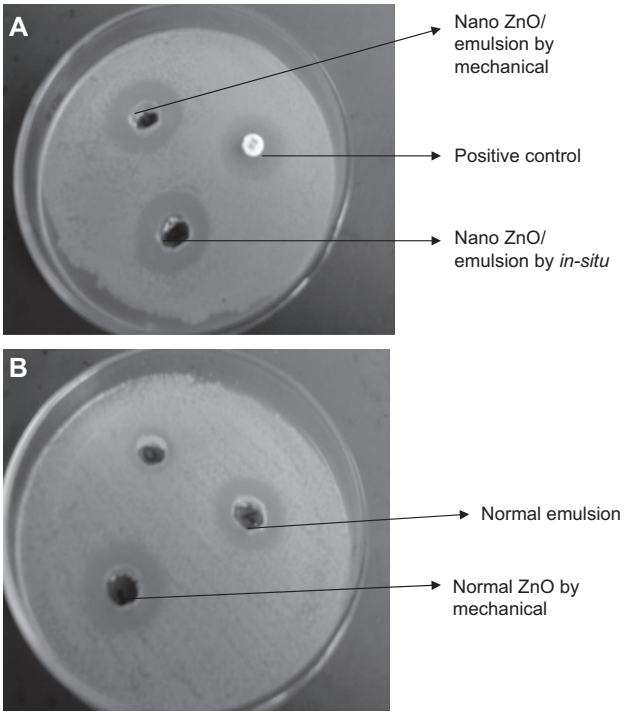

Figure 2 Images of *Escherichia coli* incubated (A) with nano ZnO/emulsion by mechanical and *in situ* method (B) with normal emulsion and by mechanical method with normal ZnO.

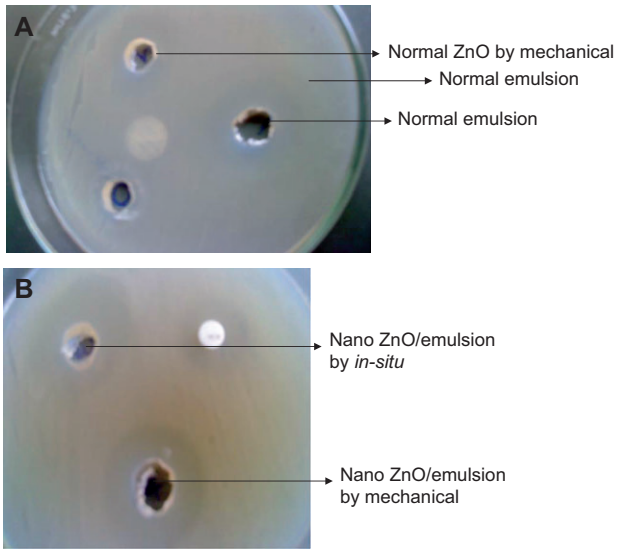

Figure 3 Images of *Staphylococcus aureus* incubated (A) with normal ZnO by mechanical method and normal emulsion (B) with nano ZnO/emulsion by mechanical and *in situ* method.

observed to have no influence on the drying of the coating. Similarly, the coatings prepared both via *in situ* as well as mechanical mixing also did not show any difference in drying rate. The coatings thus prepared were subjected to antimicrobial testing. The results are tabulated and given in Table 1. The photographs of the test specimens are given in Figures 2 and 3). The zone of inhibition in the case of *Escherichia coli* was observed to be 8 and 13 mm for emulsion with normal and nano ZnO prepared by the *in situ* method, respectively. For the emulsion prepared by mechanical mixing, the zone of inhibition was observed to be 8 and 9 mm for normal and nano ZnO, respectively. This indicates a better antimicrobial property for the emulsions

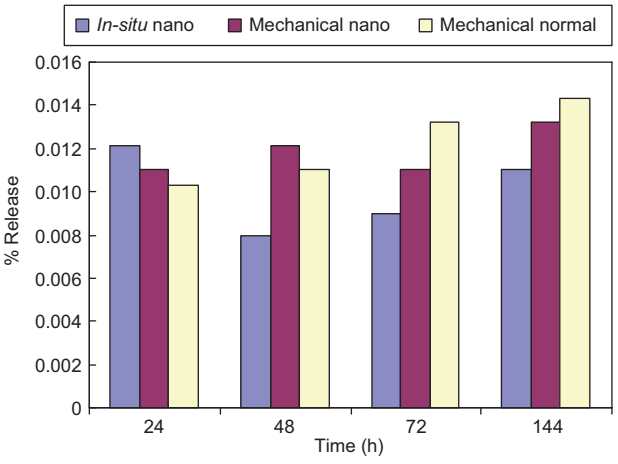

Figure 4 Release profile of emulsions prepared by *in situ* nano ZnO, mechanical nano ZnO and mechanical normal ZnO.

having nano ZnO compared to normal ZnO. At the same time, the emulsion was prepared by the *in situ* method. This may be due to a better and uniform dispersion of the filler in the matrix in the case of the *in situ* preparation. However, the zone of inhibition in the case of *Staphylococcus aureus* was observed to be 21 mm for the emulsion/nano ZnO prepared by the *in situ* method. Whereas the emulsion was prepared by mechanical mixing, the zone of inhibition was observed to be 13 and 14 mm for normal and nano ZnO. The nano ZnO/emulsion showed a better zone of inhibition compared to that of the emulsion with normal ZnO.

The release profile of the coatings is given in Figure 4. From the release profile study, we observed that the release of ZnO was found to be higher in the case of the emulsion prepared by the mechanical mixing method. The lower release rate in the case of the mechanically mixed emulsion is due to a stronger interaction between the polymer and the biocide. We concluded that the nano ZnO/emulsion showed a lesser release rate than the emulsion having normal ZnO.

4 Conclusion

The XRD of the ZnO prepared indicated that the materials synthesized are ZnO with wurtzite phase. The antimicrobial natures of the emulsion with and without ZnO were studied and were found to be higher for the emulsion with nano ZnO. From the release profile study, the release of ZnO is found to be higher in the case of mechanical mixing than that for the *in situ* prepared emulsion.

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