Experimental Study on Microbial Attachment Degree of New Polymer Nanomaterials on the Surface of Oil Field Development Platform Equipment

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Abstract. Nanomaterials have surface effects and quantum size effects, which can affect the structure and function of some biological macromolecules such as proteins and nucleic acid molecules. Nanomaterials were introduced into the development of Marine antifouling paint to solve the attachment problem of Marine fouling organisms. In this paper, the method of gene cloning was used to identify the early microbial species of oil field development platform equipment fouling. Finally, the antifouling effect of 13 kinds of nanomaterials and their combinations was tested by conventional PCR and real-time quantitative PCR. The experimental simulation shows that titanium nano polymer alloy coatings have obvious technical advantages in adhesion, impact resistance, coating hardness, wear resistance, high temperature resistance, high pressure resistance and chemical corrosion resistance.

Keywords: Nanomaterials; fouling microorganisms; 16SrRNA; real-time quantitative PCR.

1. Introduction

There are many toxic organisms in the water injection process, and sulfate reducing bacteria (SRB) is the main factor affecting the water injection process. Most of the SRBS that can cause metal erosion are Vibrio sulfate. The optimum growth environment is 20-40℃, the optimum pH is 7.0-7.5, and the sulfate conversion rate is as high as 94.3%. The suitable environment for sulfate-reducing bacteria existed in the reinjection water in this area, which promoted the rapid proliferation of sulfate-reducing bacteria and caused the rupture of oil casing, sewer and other facilities [1]. In addition, because sulfate-reducing bacteria (SRB) erosion of the material is very easy to cause formation obstruction, resulting in reduced permeability of the reservoir, which seriously restricts the effectiveness of oil recovery, so the use of anticorrosive coating for pipeline anticorrosion is an effective means.

At present, the most economical, effective and easy to implement measures to prevent and control microbial pollution in the Marine environment is to spray antifouling coating on ships, fish farming equipment or other carriers, which can effectively prevent the adsorption of pollutants in the Marine environment. At present, the existing antifouling coatings mainly include wear coating, soluble substrate coating, self-developed coating, etc. These coatings have strong anti-fouling performance, but their toxicity is relatively large, which will cause mutations of microorganisms in seawater, and then affect the Marine ecosystem, threatening people's life safety [2]. At present, the seawater antifouling coating widely used in the world has high toxicity, high toxicity of Cu and other defects, has been confirmed by some environmental protection agencies, and the main reason is the large number of applications of seawater antifouling coating. Due to environmental concerns and increasingly stringent environmental regulations, copper-based coatings are also facing the fate of being banned. Research shows that in the next 20 years, a green oil anti-pollution coating will replace the current oil anti-pollution coating.

In recent years, with the rapid development of nanotechnology, it is known that because of the small size of nano-materials, their properties and general substances have many differences, in a sense, they will have a destructive effect on the structure and function of some biological macromolecules, thus affecting the fouling organisms, especially the fouling microbial adhesion [3]. In addition, there have been some foreign nano substances that can play a good role in fouling, but these substances are only limited to a few substances such as nano silver, so it is completely ok to try to study their anti-fouling effect by using a variety of nano substances and their combination.

2. Develop new materials

2.1. Synthesis of nano-modified fluorinated polyaryl ether ketones

High temperature resistance, high pressure gas resistance and soil acid resistance of the coating are the three main requirements in the lining process of oil pipeline. These are three hard goals. In the process of development, a variety of traditional and new polymers at home and abroad have been selected to make membrane materials, such as: Epoxy resin, phenolic modified epoxy resin, silicone modified epoxy resin, furan modified phenolic resin, polyurethane resin, etc., to the latest polyurea, meta fluoride, tetrafluoride materials, etc., the coating materials produced are not up to the technical standards, no coating can be fully qualified. In the three-neck bottle equipped with mechanical stirring, thermometer, water separator and condensing tube, add the prescription amount of 3,5-(trifluoroethane) benzene hydroquinone, 4,4' -difluoro benzene, add slightly excess K2CO3 and a certain amount of cyclobutadiene and toluene, N2 gas, heated to 130 degrees Celsius, with toluene in 1.5~2 h will water out, Toluene is then released and heated to 220 degrees Celsius for another 3 hours. Finally, it is dehydrated under negative pressure and dried in a constant temperature drying oven. The desired polymerization product of light-yellow powder can be obtained [4]. An appropriate amount of nano-modifier is placed in a beaker, and then polymer fluorinated polarly ketone and TAZ-ND1 surfactants are added. They are mixed and stirred in a dispersion car. Exothermic reaction occurs during the process of dissolution. The result of total dissolution is a polymer resin containing fluoride ions.

2.2. Coating Preparation

Nano organic titanium anti-corrosion coating: Its size is 120 mm x 60 mm x0.5 mm cold rolled steel and 100 mm x 120 mm carbon steel test rod, on the surface of the butyl ketone cleaning, drying, polishing with coarse sandpaper, and then in accordance with its used ratio, the paint A/B components are mixed, and fully stirred, use thinner to spray or brush [5]. The sample was used as a single coating, middle and surface respectively, and the sample rod was used as a composite coating. In the preparation process, the coating time of each coating is 12 hours, dried at room temperature, and anticorrosion test is carried out after one week. Ti Nano-Polymer alloy coating: During the preparation of the sample, the two base coatings were sprayed first and dried at 120℃ for 15 minutes, followed by the two surface coatings, which were dried at 220℃ for 20 minutes. For sample testing, the thickness of the dry film shall be more than 100 microns, and the physical and chemical properties of the sample shall be tested according to this specification. To prepare the test sticks, adjust the special diluent of the coating to 35-40 s (coated -4 cups), then soak the sticks once, hang them in a constant temperature oven, and heat them to 120-150 degrees for drying; Then soak and dry the coating again, heat to 280 degrees, and then directly dry for 15 minutes; The thickness of the test drying coatings shall be greater than or equal to 100 microns, and their physical and chemical properties shall be tested according to this specification.

2.3. Test procedure

According to the difference of sol components, the content of the coating in the coating is not the same, so it is necessary to select the appropriate sol components, so that the coating has better corrosion resistance and pollution resistance [6]. Through preparation of Nano-ZnO/TiO2 coating with a certain proportion, the impedance conductivity was measured, and the Nano-ZnO/TiO2 coating with high corrosion resistance and pollution resistance was screened out. The impedance admittance can be determined by a function of the Angle. The angular frequency function Y is calculated by the following formula

$$Y = Y_0 = \omega^n \left[cos\frac{n\pi}{2} + sin\frac{n\pi}{2} \right] \tag{1}$$

Where: Y_0 is the film resistance; ω refers to the argument Angle of the constant phase Angle element; n is the angular frequency. Impedance admittance value can be calculated by the following formula:

$$Z = \frac{1}{Y} = \omega^{-n} \left[cos\frac{n\pi}{2} - sin\frac{n\pi}{2} \right] \tag{2}$$

By calculating the impedance acceptances of different proportions of coatings, it can be obtained that the nano-zinc oxide composite titanium oxide Marine antifouling coating obtained by mixing titanium oxide sol and zinc oxide sol in the ratio of 4:6 has the best antifouling and antifouling performance, so it is used as the experimental coating [7]. In order to verify the antiseptic and antifouling performance of nano-zinc oxide composite titanium oxide Marine antifouling coating, traditional oxide coating was used as a comparison. The two coatings are applied to the same area of alloy material with the same thickness. The two coatings were observed to see whether the double arc feature appeared and the change of the surface state within 30 days.

2.4. Performance Test Results

Performance testing was carried out according to GB/T1723~1735, and the relevant enterprise standards of Q/QBT002-2008 "Nano organic titanium Special anticorrosive Coating (packaging)" and Q/QBT001-2008 "Special Anticorrosive Coating for Pipelines used in Oil and gas Wells" were formulated according to the testing data. In order to obtain samples of early fouling microbial liquid, samples need to be taken within a short time after the steel plate is put into the sea. Sampling method: remove the steel plate from the sea, with high temperature sterilization of distilled water will plate surface rinse clean, then use high temperature sterilization brush constantly washing plate surface, with pipette gun collection plate surface liquid is the sample we need, the sample back to the laboratory stored in the -80℃ refrigerator, so as to use for follow-up experiments.

3. Experimental results

3.1. Experimental results of hanging plate

(1) As shown in Figure 1, the steel plate photos were taken 15 days and 43 days after the oil field hanging plate and the water depth was 1.3m. As can be seen from the figure, fifteen days after the hanging plate, the surface of the steel plate is only wet and sticky, and the surface attachment is not obvious; Forty-three days after the hanging plate, algae and other obvious attachments appeared on the surface of the plate [8]. This indicates that with the extension of hanging plate time, the propagation rate of fouling organisms on the surface of steel plate is accelerated, resulting in the obvious increase of attachments.

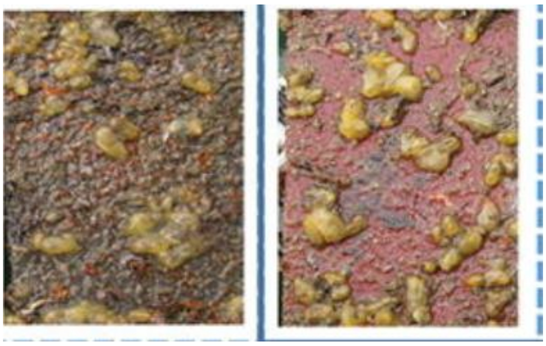

Figure 1. Microbial attachment of steel plate after 15 days and 43 days of oilfield hanging plate

3.2. Microbial attachment of nanomaterials

The carbon nanotube coating was divided into two concentrations, one was 0.2%, one was 4 ml of the base coating added 8 mg of carbon nanotube, one was 2%, adding 80 mg of the base liquid added 4 ml of the base coating. For paired nanotubes, choose 2% concentration, which is 80 mg nanotube 1+80 mg nanotube 2, plus 4 ml of substrate. Because the number of carbon nanotubes is large and the number of pairs is also large, we selected 26 carbon nanotubes from 77 carbon nanotubes as pairs for coating. The adhesion of bacteria can be seen on the nano substrate (Figure 2).

Figure 2. Antifouling effect of 0.2% concentration nanomaterials

But as the immersion continued, more electrolyte reached the interface, and at the interface, electrolyte and interface formed a "capacitance - resistance" mode, rather than a "dispersion" characteristic. So by the eighth day, the dispersive tail in Nyquist's spectrum had completely disappeared, replaced by a large electric arc that acted as a barrier, keeping the corrosive material away from the metal and preventing it from being eroded. However, it has also been shown that under these conditions, the interaction between metal ions and metal ions can lead to the migration of metal ions in metal ions and thus lead to the migration of metal ions. The impedance value of the coating is higher than before. This represents an increase in charge transfer resistance and a decrease in erosion rate. At this point, we can see an equivalent circuit.

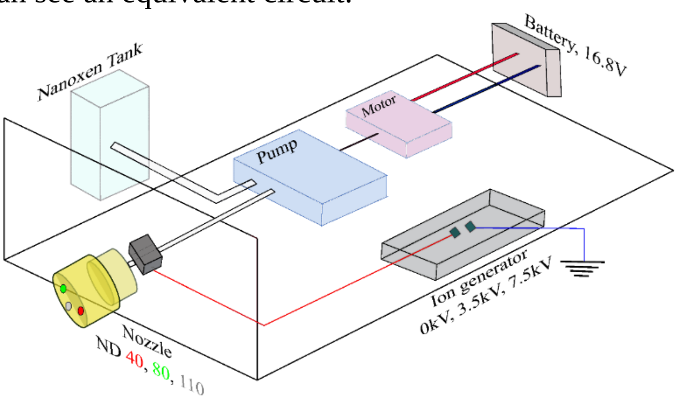

Figure 3. Simulated equivalent circuit diagram of acrylic polyurethane varnish soaked to day 8

At the 16th and 30th days, due to the significant decrease of the impedance of the coating, the surface of the coating/coating was eroded. Therefore, a series of erosion occurred on the surface of the coating/coating. Therefore, in the coating, the migration of oxygen became the main erosion link of the coating. The measured impedance spectrum has two-timed constants, and the first reactance arc on the 30-day spectrum has become very small, the paint resistance R p has been reduced to 106 ohms, the corrosive medium completely penetrates the paint system and reacts with the metal matrix, the paint has lost its protective ability. Good results were obtained when two Nyquist curves at 16 and 30 days were used for fitting.

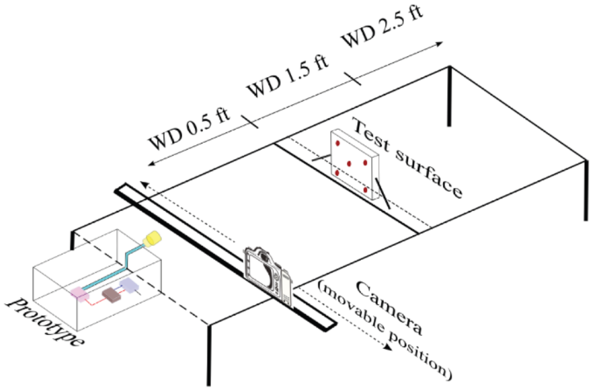

Figure 4. The equivalent circuit diagram of the impedance spectra of two time constants during the soaking of acrylic polyurethane varnish

At the initial stage of the coating, the capacitor capacity Cc of the coating increases and the capacitor impedance of the coating decreases due to the continuous penetration of the electrolyte into the coating. The main factor causing this phenomenon is the infiltration of electrolyte. Compared with those materials and holes in composite coatings, the resistance and dielectric constant of the electrolyte solution are relatively low, and its penetration will change the resistance and capacity of the coating (figure 5). In 3 days, four kinds of coating system of the low frequency impedance modulus values have found some change. The results show that when the concentration is 0.05% and 2%, the modulus of impedance decreases obviously in the low frequency range. However, all the four coatings showed a time-varying property, that is, the protection was still good in the initial impregnation stage.

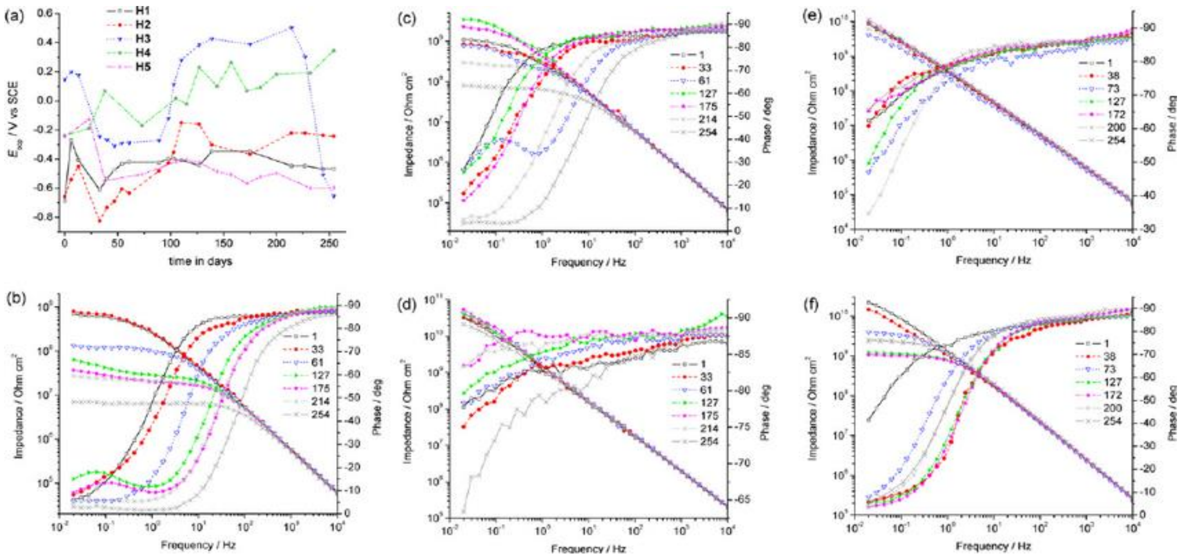

Figure 5. Bode spectra of nano-coating at different soaking times

At day 16, the most significant change was that the bath presented two different time constant peaks when the bath concentration was 2%, and the bath transited from high too high in the low frequency region to the middle frequency region. During this process, the slope of the curve increases and spreads downward in the high frequency region. At the point where the two contact, there is shedding. The study shows that the coating at 2% concentration has poor barrier and protection effect on the corrosive substances, and the corrosive substances enter the metal materials through the coating, forming the electrochemical reaction interface between the metal materials and the metal materials. At the same time, due to the impregnation in the coating, the porosity in the coating increases, which is conducive to the transfer of corrosive substances in the coating. At 30 days, because of the large number of micropores in the coating, the 2% composition of the coating, so that the original concentration of the coating gradually reduced, at the same time because of the substrate erosion reaction rate accelerated, so that the interface between the coating and the coating produced a new diffusion layer. The physical meanings of each electrochemical parameter are shown in FIG. 4, only the position of Warburg changes correspondingly due to the appearance of the diffusion layer. At this point, 0.5 percent of the coating is in the final stage, and 1 percent of the coating is in the middle stage. But in the initial phase, the 0.5% paint still showed good protection. The results showed that the corrosion resistance of 0.5% nano coatings was the best among the four coatings.

3.3. Adhesion to microorganisms

Ct value refers to the number of cycles passed by the luminous signal in each reaction tube to reach a set domain value. The experimental results show that the Ct value is linearly correlated with the logarithm of the number of copies of the initial template, and the more copies of the initial template, the lower the Ct value. The larger the Ct value, the smaller the number of copies of the initial template, that is, the larger the inhibition effect of the nano-substance on bacteria 4. As can be seen from Figure 1, Ct values corresponding to this test group are all larger than those of the control group. By inference, the number of initial template copies of normal control samples was more than that of test samples, indicating that both samples showed certain antibacterial effects.

Table 1. Mean Ct values and standard errors of three parallel experiments

Template number	First batch of experimental Ct values	Ct values of the second batch of experiments	Ct values of the third batch of experiments	Average value	Standard deviation
1	25.62	25.29	25.25	25.39	0.999
2	25.58	25.04	25.09	25.24	0.680
3	25.53	25.05	25.5	25.36	0.769
4	25.3	25.89	25.24	25.48	0.646
5	25.08	25.82	25.48	25.46	0.272
6	25.41	25.68	25.44	25.51	0.742
7	25.95	25.73	25.57	25.75	0.530
8	25.47	25.91	25.37	25.58	0.079
9	25.17	25.4	25.28	25.28	0.046
10	25.86	25.22	25.01	25.36	0.783
11	25.73	25.2	25.95	25.63	0.299

4. Conclusion

The Ti based nano polymer coating is developed for the corrosion protection and protection of drilling pipeline in oil drilling. It is used in oil drilling tools, drill pipe, pipe and casing. However, according to the comprehensive performance of the coating, it can be further expanded in the application of protective coating in aerospace, automobile manufacturing, electronic and electrical, medical and food processing, and also has a wide range of applications, and its development potential is great. A new type of room temperature curing heavy anticorrosive coating has been developed. It not only has non-toxic, anti-penetration, anti-aging, electrostatic conductivity, anti-stray current and other characteristics, but also has excellent physical and mechanical properties and excellent chemical erosion resistance. The product has good high temperature resistance and good high temperature resistance, and has high temperature resistance, high temperature resistance, high temperature resistance and other advantages, can be widely used in a variety of anti-corrosion, anti-corrosion, anti-corrosion and other aspects.

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