Improvement of the Tribological Properties and Corrosion Resistance of Epoxy–PTFE Composite Coating by Nanoparticle Modification

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Abstract: In order to meet the requirements of high corrosion resistance, wear resistance, and self-lubrication of composite coatings for marine applications, epoxy matrix composite coatings containing PTFE and TiO2 nanoparticles were prepared on the steel substrate. With silane coupling agent KH570 (\(\text{CH}_2=\text{C(CH}_3\text{)}\text{COOC}_2\text{H}_4\text{Si(OCH}_3)_3\)), titanium dioxide nanoparticles were modified, and organic functional groups were grafted on their surface to improve their dispersion and interface compatibility in the epoxy matrix. Then, the section morphology, tribological, and anticorrosion properties of prepared coatings, including pure epoxy, epoxy–PTFE, and the composite coating with unmodified and modified TiO2, respectively, were fully characterized by scanning electron microscopy, friction–abrasion testing machine, and an electrochemical workstation. The analytical results show that the modified TiO2 nanoparticles are able to improve the epoxy–PTFE composite coating’s mechanical properties of epoxy–PTFE composite coating including section toughness, hardness, and binding force. With the synergistic action of the friction reduction of PTFE and dispersion enhancement of TiO2 nanoparticles, the dry friction coefficient decreases by more than 73%. Simultaneously, modified titanium dioxide will not have much influence on the water contact angles of the coating. A larger water contact angle and uniform and compact microstructure make the composite coating incorporated modified TiO2 nanoparticles show excellent anti-corrosion ability, which has the minimum corrosion current density of 1.688 × 10−7 A·cm−2.

Keywords: composite coating; epoxy–PTFE; modified TiO2; tribological properties; corrosion resistance

1. Introduction

For the advantages of excellent friction, stable chemical property, and low cost [1–3], epoxy resin is one of the excellent polymer coating materials, which is widely applied in the metal protection, electronics, and medical equipment [4,5]. Especially, epoxy–PTFE composite coatings have low friction coefficient and anticorrosion ability as well as high temperature resistance [6]. Such coatings could increase the anticorrosion capacity of metals and the self-lubricity of bearings as well as modify the hydrophobic and ice-phobic properties for wind turbine blades [7–9].

However, due to the curing shrinkage and warpage deformation of epoxy, there are always a lot of micro-pores and cracks in the composite coating. Moreover, the low hardness of PTFE will also lead to the poor wear resistance of the epoxy–PTFE composite coating [10,11]. A viable solution is to add hard or inorganic particles, such as TiO2, CuO, CuF2, CuS, and Al2O3, which will improve the tribological properties of the coating [12–15].

Larsen et al. [14] obtained a composite coating containing CuO and PTFE by mixing CuO and PTFE with epoxy solution. The evidence shows that both CuO and PTFE particles are well dispersed in the epoxy. The incorporation of PTFE and CuO has a positive synergistic effect on the friction and wear properties when the content of CuO is in the range
of 0.1–0.4 vol.%. Hamad et al. [15] investigated the mechanical properties of toughened epoxy by utilizing two kinds of nanoparticles sizes of TiO₂ (17 and 50 nm) at different weight fractions (1%, 3%, 5%, and 10%). The results indicate that the addition of a small fraction of TiO₂ nanoparticles can bring an improvement in the mechanical properties of epoxy composite. Researchers also expect that the addition of some lubricating substances will have a good effect on the performance of the epoxy resin composite coating [16,17]. The tribological properties of epoxy composites were also studied by Chang et al. [18]. With different proportions of graphite, PTFE, short carbon fiber, and TiO₂ and their combinations as additions, the frictional coefficient, wear resistance, and contact temperature of composite coatings were tested in a dry sliding condition with different sliding velocities and contact pressures. Results show that TiO₂ works best in improving the wear resistance of epoxy.

On the other hand, in order to meet the requirements of a corrosive environment, the corrosion resistance of polymer coatings has received much interest recently. Shi et al. [19] reported two methods to improve the dispersing of nanoparticles in epoxy coatings, including silane treatment and preparing nano-oxide paste. Compared with nano-TiO₂ paste and silane-treated nano-SiO₂, the latter is better than the former in improving the corrosion resistance and hardness of epoxy. Fadl et al. [20] fabricated TiO₂ nanoparticles by a simple template-free sol-gel method and mixed them with poly-dimethylamino siloxane (PDMAS) to form a PDMAS/TiO₂ nanocomposite as a modifier for polyamine-cured epoxy coating. The corrosion resistance of PDMAS/TiO₂ epoxy coating versus unmodified epoxy was investigated by a salt spray accelerated corrosion test. The PDMAS/TiO₂ epoxy coating has better corrosion mitigation and a self-healing effect. Radoman et al. [21] obtained epoxy/TiO₂ nanocomposites by the incorporation of modified TiO₂ nanoparticles with gallic acid esters in epoxy. Due to the deoxidizing effect of modified TiO₂, the nanocomposites have better corrosion resistance than that of the pure epoxy. Therefore, it is possible to obtain better corrosion resistance of epoxy composite coating by incorporating and modifying nanoparticles.

From the perspective of comprehensive performance, TiO₂ nanoparticles were selected as the additive in this study. SiO₂ nanoparticles are mainly used to improve the mechanical properties and heat resistance of epoxy composites. Nano-zinc oxide has the characteristics of high activity, large specific surface area, easy agglomeration, and long dispersion time before preparation. Therefore, it is a difficult point to prepare nano-zinc oxide-modified epoxy resin. The surface of Al₂O₃ contains a large number of hydroxyl groups, which makes it difficult to evenly disperse in epoxy materials. On the contrary, TiO₂ nanoparticles not only have good chemical stability but also have excellent heat resistance and UV protection, so it is widely used in the fields of UV-resistant materials, packaging materials, and coatings. At the same time as rigid nanoparticles and its strong adhesion, TiO₂ is often used as a modified filler to improve the bending strength, tensile strength, and impact strength of epoxy resin. In the wear resistance test, TiO₂ nanoparticles can significantly improve the wear resistance of epoxy resin, because TiO₂ nanoparticles have a large specific surface area and a large contact surface with the substrate, which requires more external energy when sliding [22,23].

Overall, the current research shows that pure epoxy resin coating has good corrosion resistance, but the high friction coefficient and poor wear resistance could not meet the requirements for use under friction conditions. Adding PTFE can reduce the friction coefficient, but the hardness and wear resistance are still low. Generally, incorporating soft phase PTFE and hard phase TiO₂ is an effective way to improve the tribological performance of a coating. Nevertheless, due to agglomeration and the poor compatibility of nanoparticles in the coating, composite coatings that involve nanoparticles often show low corrosion resistance. In the paper, the research focused on the improvements of both the tribological property and corrosion resistance of epoxy composite coating. TiO₂ nanoparticles were modified by a silane-coupling agent to reduce their surface tension, avoid agglomeration, and improve the interfacial compatibility with epoxy firstly. Then, the influence of modified
2. Materials and Methods

2.1. Materials

The carbon steel SK85 was chosen as the substrate with dimensions of 30 × 12 × 1 mm³ and with the nominal composition as follows: 0.80%–0.90% C, ≤0.35% Si, ≤0.50% Mn, ≤0.03% P, ≤0.03% S, ≤0.20% Cr, ≤0.25% Ni, and ≤0.30% Cu. Epoxy resin (E44) with viscosity range from 40,000 to 45,000 mPa·s at 25 °C was purchased from Nanjing Star Synthetic Materials Co., LTD., Nanjing, China. TiO₂ nanoparticles with an average diameter of 40 nm were purchased from Shanghai Macklin Biochemical Co., LTD., Shanghai, China. The silane coupling agent KH570 (CH₂=C(CH₃) COOC₃H₆Si(OCH₃)₃, ≥99%, Silica Co., LTD., Nanjing, China) was used as a modifier. The ethanol (CH₃CH₂OH, ≥99.7%, Fuyu Fine Chemical Co., LTD., Tianjin, China) was used as a dispersant. The acetic acid (CH₃COOH, ≥99.8%, Sinopharm Group Chemical Reagent Co., LTD., Beijing China) was used to adjust the pH value of the solution. Additionally, all reagents were used without further purification.

2.2. TiO₂ Modification

In this study, titanium dioxide nanoparticles were selected as the strengthening particles, the average diameter of which are 40 nm. They were modified by the silane coupling agent KH570 (CH₂=C(CH₃) COOC₃H₆Si(OCH₃)₃) to graft organic functional groups on the surface of TiO₂ nanoparticles. The unique method is described as follows.

Ethanol was used as the dispersant, and the pH value was adjusted by acetic acid to 6. The silane coupling agent KH570 and TiO₂ nanoparticles were added into a certain volume of dispersed solutions at a mass ratio of 15:100. Firstly, the configured modified liquid was sonicated by ultrasonic liquid processors for 10 min. Then, it was disposed with a magnetic stirrer at 50 °C for 240 min with a speed of 300 r/min. Subsequently, the modified powder was washed with ethyl alcohol and deionized water three times to remove excess organosilane. Finally, collected precipitates were dried at 80 °C in a drying oven and stored in vials for further testing. The presence of organic phase on the modified TiO₂ nanoparticles surface was tested with the FT-IR spectrum (PerkinElmer Co., LTD., Shanghai, China).

2.3. Coating Preparation

Four kinds of coatings were prepared, including epoxy, epoxy–PTFE, epoxy–PTFE/TiO₂ (unmodified), and epoxy–PTFE/TiO₂ (modified). Carbon tool steel (SK85) and n-butanol are chosen for the matrix material and diluent, respectively, and phenolic amine resin (T13) was the curing agent for epoxy resin (E44). The mass ratio of T13/n-butanol/E44 was 1:2:4. The mass content of PTFE and TiO₂ was controlled at 15% and 2%, respectively. During the preparation process, after stirring the mixture thoroughly, it was ultrasonicated for 10 min to allow complete defoaming. Subsequently, the as-cleaned steel panels were immersed in the mixture solution adequately for 20 min, and we used a small mold to ensure that the thickness of the samples were uniform at 52 ± 3 µm. Then, the drying was carried out in an oven at 90 °C for 180 min. Finally, samples were successfully prepared for evaluating their surface morphology as well as mechanical and corrosion properties.

2.4. Coating Performance Testing

The performance test of coatings mainly includes the surface morphology, hardness, bonding force, tribological properties, and corrosion resistance. The section morphology of the coatings was characterized by scanning electron microscopy (SEM, FEI, Quanta200, OR, USA). Shore durometers (Petey Testing Instrument Co., LTD., Guangzhou, China) were used for testing the micro-hardness. The average micro-hardness value was acquired by averaging the results of six measurements. The binding force of the coatings—the average
results of two sets of measurements—was tested by pull-off tester (DeFelsko Co., LTD., Ogdensburg, NY, USA). The tribological properties of the coatings were examined by a friction-abrasion testing machine (SFT-2M, Zhongke-Kaihua, Lanzhou, China) at a load of 5.0 N and a stage rotated speed of 200 r/min. The friction counterparts were GCr15 steel balls with a diameter of 5.0 mm; the radius of the friction circle was set to 2 mm, the duration of each wear test was 10 min. Subsequently, the friction–wear behavior of the coatings was estimated by SEM. The corrosion resistance of the composite coatings was measured by an electrochemical workstation (CHI660B, Chenhua, Shanghai, China) after being soaked in 3.5% NaCl solution for 72 h. The samples were used as the working electrode, while a platinum sheet and a saturated calomel electrode (SCE) were the counter and the reference electrodes, respectively. The test frequency of electrochemical impedance spectroscopy (EIS) ranged from 1000 Hz down to 10 Hz, and the scanning voltage was 10 mV. The corrosion potential \( E_{\text{corr}} \) and corrosion current density \( i_{\text{corr}} \) were obtained from the potentiodynamic polarization curves. All corrosion tests were performed at room temperature.

3. Results and Discussions

3.1. The Modification of TiO\(_2\) Nanoparticles

The transmission FT-IR spectra of TiO\(_2\) nanoparticles with and without KH570 modification were compared, as shown in Figure 1. For unmodified TiO\(_2\) nanoparticles, the absorption band between 3400 and 3500 cm\(^{-1}\) corresponds to the hydroxyl group (–OH) due to the partial electron–hole pairs migration on the surface of TiO\(_2\) nanoparticles. The vibration absorption peak is situated in the wavenumber interval of 500–750 cm\(^{-1}\), which demonstrates the presence of Ti–O–Ti groups. However, the new absorption bands appear in the FT-IR spectrum of modified TiO\(_2\) nanoparticles in curve \( b \), and there are some characteristic absorption peaks of KH570 at 2917 cm\(^{-1}\) (–CH\(_3\)) and 1717 cm\(^{-1}\) (C=O), 1620 cm\(^{-1}\) (C=C), 500–750 cm\(^{-1}\) (Ti–O–Si), so it could be inferred that the organic functional group has been grafted onto the surface of TiO\(_2\) nanoparticles successfully.

![Figure 1. FT-IR results of unmodified TiO\(_2\) and modified TiO\(_2\).](image)

Figure 2 is the energy-dispersive spectrometer (EDS) pattern of the TiO\(_2\) nanoparticles before and after modification. The content of Si and C elements in Figure 2b is much higher than that in Figure 2a. The silane coupling agent molecule can be adsorbed on the surface of TiO\(_2\) nanoparticles by its hydrophilic end and can react with the surface –OH groups on TiO\(_2\) nanoparticles; therefore, the modified TiO\(_2\) nanoparticles contain Si and C elements from KH570(CH\(_2\)-C(CH\(_3\))COOC\(_6\)H\(_4\)Si(OCH\(_3\))\(_3\)). All these experimental results demonstrate that the organic functional group of KH570 was successfully grafted onto the surface of TiO\(_2\) nanoparticles.
The fractured surface of four kinds of coatings was exhibited by scanning electron microscopy (SEM), as shown in Figure 3. It can be seen that the fractured surface of epoxy is very smooth (Figure 3a) even at 5000 times magnification. With the addition of PTFE and TiO2 nanoparticles, the fractured surface of the composite coatings becomes much rougher than that of the pure epoxy coating. Furthermore, by comparing Figure 3b,c, it can be observed that there are still some flat areas and aggregated TiO2 nanoparticles on the cross-section of the coating with unmodified TiO2 nanoparticles (Figure 3c). However, with modified TiO2 nanoparticles, the composite coating fracture surfaces are much rougher (Figure 3d), which can be attributed to the dispersive distribution of TiO2 preventing crack propagation, and the excellent interfacial compatibility reducing the crack source. Generally, an increased section roughness means that the path at the crack tip is distorted, and the coating might absorb more section energy during the fracture process and possess better fracture toughness. Therefore, due to the grafting of organic functional groups adsorbed on the modified TiO2 nanoparticles surface, the toughness of the composite coating is improved [24,25].

Figure 2. The energy-dispersive spectrometer (EDS). (a) TiO2 (unmodify), (b) TiO2 (modify).

Figure 3. SEM images of section morphology of different coatings. (a) Unmixed epoxy, (b) epoxy-PTFE, (c) epoxy-PTFE/TiO2(unmodify), (d) epoxy-PTFE/TiO2(modify).
3.2. Hardness

Figure 4 shows the hardness values of different coatings. It indicates that the hardness of epoxy–PTFE–TiO$_2$ (modify), epoxy, epoxy–PTFE–TiO$_2$ (unmodify), and epoxy–PTFE coatings are arranged from high to low. The soft particles of PTFE improve the lubricity of the coating but also reduce its hardness. In contrast, modified hard TiO$_2$ nanoparticles can enhance the hardness of epoxy–PTFE composite coating better than unmodified hard TiO$_2$ nanoparticles. This is due to the modified TiO$_2$ nanoparticles dispersing more evenly in the coating, which has a dispersion strengthening effect in the coating.

![Figure 4. Hardness of different coatings.](image)

3.3. Interfacial Adhesion

The interface bonding adhesion strength of different coatings is given in Figure 5. As Figure 5 shows, PTFE enhances the interfacial adhesion of epoxy coatings from 1.43 to 2.30 MPa. On the other hand, with the addition of modified TiO$_2$ nanoparticles, the bonding strength value of the composite coating reaches 2.70 MPa, which is higher than that of the coating containing unmodified TiO$_2$ nanoparticles. We interpreted that the introduction of organic functional groups on the surface of TiO$_2$ nanoparticles resulted in the formation of hydrogen bonds and Si–O bonds between the TiO$_2$ nanoparticles and the coating. The modified TiO$_2$ nanoparticles have a strong interfacial adhesion with the surrounding particles, and the van der Waals force attraction becomes stronger; therefore, the epoxy–PTFE–TiO$_2$ (modify) composite coating has the highest interfacial adhesion value. This corresponds to the improvement in section roughness and the hardness of the coating.

![Figure 5. The results of interfacial adhesion.](image)
3.4. Tribological Properties

Figure 6 shows the friction coefficient curves of different coatings versus the sliding time. As shown in Figure 6, with the addition of PTFE to epoxy, the friction coefficient decreases from 0.6 to about 0.16. Furthermore, compared to curve C of adding unmodified TiO$_2$ nanoparticles, the friction coefficient of the composite coating is less than 0.10 after adding modified TiO$_2$ nanoparticles, as shown in curve D.

![Friction coefficients of different coatings.](image)

The SEM images of the worn surfaces are shown in Figure 7. After adding PTFE, the wear track width of the epoxy coating decreases from 634.21 µm (Figure 7a) to 321.56 µm (Figure 7b). Furthermore, with the addition of unmodified TiO$_2$ nanoparticles (Figure 7c), the width of the wear track narrows to 274.51 µm. With modified TiO$_2$ nanoparticles, the wear track becomes much smoother and narrower (Figure 7d). On the other hand, there are many micropores on the worn surface of epoxy, which indicates that the epoxy coating itself is not densification. When PTFE is incorporated, there are no obvious micropores. The PTFE with self-lubricating property spreads on the wear surface (as shown in curve A and curve B), reduces the friction coefficient, and brings a much smoother worn track (Figure 7b). When unmodified TiO$_2$ nanoparticles were added into the coating, particle agglomeration results in some micropores emerging on the worn surface (Figure 7c). However, there are seldom obvious micropores on the worn surface with modified TiO$_2$ nanoparticles (Figure 7d). Obviously, when modified TiO$_2$ nanoparticles coexist in the composite coating, uniformly dispersed nanoparticles and excellent interfacial compatibility lead to the narrowest and smoothest wear track. The composite coating D has the most excellent wear resistance.

Summing up, the friction coefficient of the composite coatings with PTFE is significantly improved because of the formation of PTFE lubricating transfer film on the wear surface. However, the wear resistance of a soft epoxy–PTFE composite coating is still weakened. With PTFE and TiO$_2$ coexisting in the epoxy–PTFE/TiO$_2$ (unmodify) composite coating, the combination of soft phase particles and hard phase particles leads to a higher wear resistance. In contrast, a relatively good interfacial compatibility brought by the modified TiO$_2$ nanoparticles decreases the furrow and adhesive effects, which leads to a lower friction coefficient, much smoother worn surface, and much higher wear resistance. Meanwhile, the addition of PTFE and TiO$_2$ nanoparticles may affect the mechanical properties, and the good interfacial compatibility of modified TiO$_2$ nanoparticles may improve the mechanical stability of the coating, which may also affect the tribological properties. As described by Homaeiaghohar et al., the uniform distribution of functionalized graphite nanofilaments can improve the mechanical stability of nanocomposite hydrogels, and the addition of tricalcium phosphate can affect the mechanical properties of
the polyethylene [26,27]. All in all, the synergistic action of the friction reduction of PTFE and dispersion enhancement of modified TiO$_2$ nanoparticles of PTFE makes the epoxy–PTFE/TiO$_2$ (modify) composite coating show excellent friction reduction and anti-wear performance.

**Figure 7.** Wear scar morphology of different coatings. (a) unmixed epoxy, (b) epoxy–PTFE, (c) epoxy–PTFE/TiO$_2$ (unmodify), (d) epoxy–PTFE/TiO$_2$ (modify).

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The water contact angle of coatings was measured for evaluating their hydrophobic property, as shown in Figure 8. The water contact angles of the pure epoxy coating and epoxy/PTFE composite coating are 74.81° and 100.90°, respectively, which indicates that PTFE can improve the hydrophobic property of the coating. With the further addition of TiO$_2$ nanoparticles to the epoxy–PTFE coating, due to the presence of hydroxyl groups on the surface of TiO$_2$ nanoparticles, the water contact angle of the composite coating is reduced greatly to 56.84°, which is manifested as hydrophilic. The small contact angle of coating C will result in the worst corrosion resistance. In contrast, with adding the modified TiO$_2$ nanoparticles instead of unmodified TiO$_2$, the water contact angle of the composite coating approaches that of the pure epoxy coating, and the hydrophilicity of the coating decreased greatly. However, due to the steric hindrance effect, the hydroxyl groups on the surface of TiO$_2$ are not fully replaced by organic functional groups and still have a certain hydrophilicity.
3.5. Anti-Corrosion Properties

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![Water contact angles of four kinds of coatings](image)

Figure 8. Water contact angles of four kinds of coatings.

When PTFE as hydrophobic particles were added to the epoxy coating, the water contact angle rose to 100.90°, showing hydrophobicity. Due to the presence of hydrophilic hydroxyl groups on the surface of TiO$_2$, the extremely poor interfacial compatibility between TiO$_2$ and epoxy coatings, resulting in easy agglomeration of TiO$_2$. Therefore, as shown in Figure 3c, there are still some flat areas on the cross-section of the coating, and the water contact angle of epoxy–PTFE/TiO$_2$ (modified) drops to 56.84° and shows hydrophilicity. Due to the influence of steric hindrance, part of the hydroxyl groups on the modified TiO$_2$ surface is replaced with organic functional groups. The interface compatibility between TiO$_2$ nanoparticles and the epoxy coating is enhanced, and the coating surface becomes rougher, as shown in Figure 3d. The water contact angle of the composite coating approaches that of the pure epoxy coating, while the hydrophilicity of the coating decreases greatly. All in all, the increase of the contact angle is beneficial to improve the corrosion resistance of the coating.

3.5.2. Potentiodynamic Polarization

The potentiodynamic polarization curves of different coatings are shown in Figure 9, and Table 1 exhibits the corrosion current density ($i_{corr}$) and corrosion potential ($E_{corr}$). Experimental results indicate that the corrosion current density decreases and the corrosion potential of the coating increases with the addition of PTFE.
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![Figure 9. Potentiodynamic polarization curves of different coatings.](image)

**Table 1. Potentiodynamic polarization parameters of different coatings.**

| Coatings                  | Corrosion Current Density ($A \cdot cm^{-2}$) | Corrosion Potential (V) |
|---------------------------|---------------------------------------------|------------------------|
| epoxy                     | $5.727 \times 10^{-7}$                      | -0.564                 |
| epoxy–PTFE                | $3.702 \times 10^{-7}$                      | -0.528                 |
| epoxy–PTFE/TiO$_2$ (unmodify) | $8.725 \times 10^{-7}$                      | -0.614                 |
| epoxy–PTFE/TiO$_2$ (modify) | $1.688 \times 10^{-7}$                      | -0.503                 |

Due to the high hydrophilicity of TiO$_2$ nanoparticles, the containing corrosive medium of water molecules is more likely to penetrate the coating, get in the substrate, and reduce the corrosion resistance of the coating thereby. As shown in Figure 9, after adding unmodified TiO$_2$ nanoparticles into the epoxy–PTFE coating, the corrosion current density of the coating increases, and the corrosion potential decreases. In contrast, after adding the modified TiO$_2$ nanoparticles, the composite coating of epoxy–PTFE–TiO$_2$ (modified) has the minimum corrosion current density of $1.688 \times 10^{-7}$ A cm$^{-2}$, and the corrosion potential increases to some extent ($-0.503$ V). In comparison, the corrosion resistance of the coating before the titanium dioxide modification is the worst. It can be speculated that the modified TiO$_2$ nanoparticles have better interfacial compatibility with epoxy, which prevents the immersion of corrosive media and thus improves the corrosion resistance of the epoxy–PTFE coating.

3.5.3. Electrochemical Impedance Spectroscopy

Figure 10 shows the test data of the electrochemical impedance spectroscopy (EIS). As can be seen from the results in Figure 10a,b, with PTFE and unmodified TiO$_2$ nanoparticles involved in the coating, the arc radius in the Nyquist figure and the impedance value of the low-frequency region in the Bode figure are very small; therefore, the addition of unmodified TiO$_2$ nanoparticles will reduce the corrosion resistance of the epoxy–PTFE coating. On the contrary, after adding modified TiO$_2$ nanoparticles into the epoxy–PTFE coating, both the arc radius in the Nyquist figure and the impedance value of low frequency in the Bode figure are larger, and the corrosion resistance of the epoxy–PTFE coating is greatly improved. The analysis results are consistent with the Tafel curve test results. Obviously, the poor corrosion resistance of coating C has been effectively addressed by the modification treatment of TiO$_2$ nanoparticles.
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Figure 10. Electrochemical impedance of the coatings. (a) Nyquist, (b) Bode.

4. Conclusions
In order to meet the requirements of high corrosion resistance, wear resistance, and self-lubricating property of composite coatings for marine applications, the epoxy composite coatings containing PTFE and TiO$_2$ nanoparticles were prepared in this research. Through the modification treatment of TiO$_2$, the compactness of the coating is increased and the hydrophilicity is decreased, which leads to excellent tribological properties and corrosion resistance. The specific conclusions are as follows:

- Modifying the surface of TiO$_2$ nanoparticles grafted with organic functional groups can enhance their dispersion and further improve the interface compatibility with the epoxy matrix. Simultaneously, the bonding force between the coating and the matrix is increased. Compared with pure epoxy, epoxy–PTFE, and the composite coating with unmodified TiO$_2$, the epoxy–PTFE–TiO$_2$ composite coating with modified TiO$_2$ has the lowest friction coefficient and the most excellent wear resistance.

- With the incorporation of modified TiO$_2$ nanoparticles, the hydrophilicity of the epoxy–PTFE composite coating decreases significantly, which is beneficial to improve the corrosion resistance of the composite coating. Simultaneously, modified TiO$_2$ nanoparticles improve the interface compatibility and densification of the composite coating. There are very few micropores in the coating, so it is difficult for the water molecules containing corrosive media to penetrate the coating and get into the matrix. The composite coating including modified TiO$_2$ nanoparticles possesses better corrosion resistance than that of the coating with unmodified TiO$_2$. By the modification treatment of TiO$_2$ nanoparticles, the poor corrosion resistance of an epoxy–PTFE–TiO$_2$ composite coating has been effectively addressed.

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