The influence of ultra-fine glass fibers on the mechanical and anticorrosion properties of epoxy coatings

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Abstract

The effects of different contents of ultra-fine glass fiber on mechanical and anticorrosion properties of epoxy coatings have been investigated. The FTIR and SEM have been used to analyze the surface nature and microstructure of the coatings. Electrochemical impedance spectroscopy (EIS) and a salt spray test have also been used to characterize the contents of ultra-fine glass fibers on the impedances of the coatings. When 10%, 20%, 30% of ultra-fine glass fibers are added to the coatings, their hardness and adhesion increases by 67%, 67%, 200% and 21.6%, 39%, 40%, respectively, compared with the properties of the pure coating. But the anticorrosion properties of the coatings containing high ultra-fine glass fiber content decreased with respect to the pure coatings properties.

1. Introduction

The protection of ocean facilities, such as ports, bridges, is a systematic engineering and it includes many fields and factors. Corrosion occurs most seriously in the marine splash zone. This area always encounters the varying conditions of wet and dry environments and erosion by sea water. In order to protect the facilities, anticorrosion coatings, especially heavy duty anticorrosion coatings, must be used due to their favorable adhesion, long-acting and good anticorrosion properties. Epoxy resins have many excellent properties, such as high Young's modulus, tensile strength, thermal stability, as well as excellent adhesion to various substrates and good environmental resistance [1]. As a result, they are widely used in heavy duty anticorrosion coatings. However, the major disadvantages of pure epoxy resins are their brittleness and low fracture toughness [2].

Glass fibers have a higher modulus, higher toughness, lighter weight than traditional materials, so that they are widely used in many reinforcement situations, such as in polymer-fiber composites, ceramic-fiber composites and concrete-fiber composites [3–5]. Many researchers [6–16] have studied the influence of polymer–glass fiber composites where some glass fibers are used as the reinforcing materials. Glass fibers whose surface has been modified by first using a coupling agent and then mixing with the polymer can improve the composite impact resistance [17,18] and shear strength.

Previous studies have mainly focused on continuous glass fibers [19–21] or short glass fibers, their diameters lying between 14 and 19 μm and with a length between several millimeters to several meters. They are difficult to apply in a coating directly because of their length. In order to solve this question, ultra-fine glass fibers can be added to the coatings to take the place of the long or short glass fiber in the coating. They have smaller diameters and length, and are dispersed in the resin more easily and are easily applied than traditional long or short glass fibers. The ultra-fine glass fiber has lower price than whisker and so they can be used widely in coating industry. Research about the use of ultra-fine glass fibers in paints has not previously been reported. In the work reported in this paper we have studied coatings containing ultra fine glass fibers and their influence on the coating anticorrosion properties and mechanical properties. At the same time, the effect of adding some content of zinc powder in the coating as an anticorrosion pigment [22–27] to protect the iron substrate has also been investigated.

2. Experimental

2.1. Sample preparation

Fig. 1 shows an SEM micrograph of the zinc powder (Jiangsu Kechuang Metal Materials Co., Ltd., China) and of the ultra-fine glass fibers (Tianjin Junsheng Architecture Material Company, China). It can be seen from the Fig. 1 that the ultra-fine glass fibers were mostly of length 50–80 μm, with diameters 10 μm and the diameters of zinc powder was between 2 and 5 μm. Fig. 2 shows the result from XRD spectroscopy of the zinc powder and the ultra-fine glass fibers. It can be seen from the Fig. 2 that the ultra fine glass fiber is amorphous.
Fig. 1. (a) SEM micrograph of short ultra-fine glass fiber (b) SEM micrograph of Zn powder.

Table 1
The coatings containing different ultra-fine glass fiber content used in the experiments.

<table>
<thead>
<tr>
<th>Coating number</th>
<th>Zn (%)</th>
<th>Ultra-fine glass fiber (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>2#</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>3#</td>
<td>9</td>
<td>20</td>
</tr>
<tr>
<td>4#</td>
<td>9</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 2
Mechanical properties of the four coatings.

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>1#</th>
<th>2#</th>
<th>3#</th>
<th>4#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (H)</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>Flexibility (mm)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Impact resistance (kg cm⁻¹)</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Adhesion (MPa)</td>
<td>5.1</td>
<td>6.2</td>
<td>7.1</td>
<td>7.2</td>
</tr>
</tbody>
</table>

The ultra-fine glass fibers were treated with a 4 mass% KH-570 (γ-methacryloxypropyl trimethoxy silane) silane coupling agent (Nanjing Shuguang Chemical Group Co., Ltd., China) ethanol solution, and dried in an oven at 80 °C for 10 h. The product was screened before use. The diglycidyl ether of bisphenol A resin, E-44 (epoxy equivalent 212–243 g/equiv, Jiangsu San-Mu Group. Co., Ltd., China) and diglycidyl ether of bisphenol F resin, DER 354 (epoxy equivalent 167–174 g/equiv, DOW. Co., Ltd., US) blended in a mass ratio of 85: 15 was selected as the matrix. The curing agent was KH-570 (γ-methacryloxypropyl trimethoxy silane)
Fig. 5. The process of the glass fiber modified by KH-570 coupling agent.

Fig. 6. SEM of the four coating cross sections.
NX-2003 (amine value 340 mg KOH/g, Cordolite Co., Ltd., US). The solvents were mixed with xylene, 1-butanol, cyclohexanone in a mass ratio of 7:2:1. The zinc powder and the short ultra-fine glass fibers which had been modified by KH-570 were added to the epoxy mixture, then dispersed using high shear dispersing machine at 1800 rpm for 30 min in order to obtain the paint. The contents of the ultra-fine glass fibers were 0%, 10%, 20%, 30% in the coatings and these are numbered 1#, 2#, 3#, 4# (Table 1). The matrix was blended with the curing agent in the required proportion before painting.

2.2. Mechanical properties test

The mechanical properties were measured using tinplates whose surface were painted with the test paint, and their dimension were 10 mm × 5 mm × 0.3 mm. The tinplate surface was polished with sand paper and then cleaned with ethanol. The coatings were painted by a thread applicator. The dry film thickness was 30 ± 3 μm. The adhesion force test sample was prepared by the Q235 mild steel with the dimension of 150 mm × 75 mm × 2 mm whose surface was blasted to Sa 2.5 (SIS055900-67) and then degreased with acetone before painting and the dry film thickness was 250 ± 25 μm. All the coatings were dried firstly at room temperature for 24 h at ambient temperature and then dried in an oven at 60 °C for 8 h after the coating surfaces had dried. The coating thickness was measured by magnetic thickness gauge (PosiTector 6000-FN, DeFelsko corporation, US). The adhesion forces were measured by the pull-off method using the adhesion tester (Model 3800, DeFelsko corporation, US). The hardness was measured by scratched hardness tester (Model 291, Erichsen Testing Equipment, Germany). The coating impact resistance and flexibility were measured by the QG-L impact testing machine and QTX-1 film elasticity tester respectively (Tianjin Jinke Materials Test Machine Company, China).

Fig. 8. Diagrams of equivalent electric circuits.

Fig. 7. SEM of the fracture surfaces of the four coatings.
2.3. Electrochemical impedance spectroscopy (EIS)

In the electrochemical impedance spectroscopy (EIS) experiments Q235 mild steel was used as the substrate with the dimensions of the panels being 5 mm × 5 mm × 3 mm. These panels were polished with sand paper and cleaned with ethanol in an ultrasonic bath before painting. The coatings were painted twice by a thread applicator and the coated drying interval is 12 h at ambient temperature. All the coatings were dried firstly at ambient temperature until the coating surface had dried and then dried in an oven at 60 °C for 8 h. The dry film thickness was 75 ± 5 μm. The test solution was 3.5% sodium chloride solution. The immersion area of the coated panel was 12.56 cm². Electrochemical impedance spectroscopy measurements were performed on a three electrode corrosion cell by an electrochemical impedance analyzer (Model 273A EG&G). A saturated calomel reference electrode (SCE) and platinum foil were used as reference and counter electrodes, respectively. The EIS spectra were collected in the range of 10 mHz to 10⁵ Hz using an AC signal of amplitude of 20 mV on open circuit at the rest potential. All measurements were carried out at ambient temperature (25 ± 2 °C). The experimental data were analyzed by using the commercial software package ZSimpWin 3.2.

2.4. Salt spray test

The substrate of the salt spray test was Q235 mild steel, and its dimension was 150 mm × 75 mm × 2 mm. The surfaces of the panels were blasted to Sa 2.5 (SIS055900-67) and then degreased with acetone before painting. The dry film thickness was 250 ± 25 μm. The coatings were air sprayed on the panels. The coatings were dried firstly for 24 h at ambient temperature and then 60 °C 8 h. Coated panels for salt spray test contained scribed and unscribed surfaces and the scribe width is 1 mm. Each type of coating was prepared for seven panels, there scribed surfaces, three unscribed surfaces, and one as the reference panel. A salt spray test as per ASTM B117 standard was carried out in a chamber. The coated panels were subjected to a continuous spray of neutral 5% NaCl solution at 35 °C. The panels were carefully observed and photos taken by digital camera (Canon IXUS 860 IS). The time for the formation of white rust and blisters was noted.

2.5. Measurement

X-ray diffraction (XRD) patterns were obtained by using a DMAX/2400 (Rigaku Denki) instrument equipped with Ni filtered Cu-Kα radiation (40 KV, 100 mA). The infrared spectra were recorded with a Nicolet 560 FTIR spectrometer in a KBr medium at ambient temperature in the scanning range of 400 cm⁻¹ to 4000 cm⁻¹. The morphologies of the composites were analyzed using an ESEM XL30 FEG. The samples were sputtered with gold before observation using a voltage of 10 KV.

3. Results and discussion

3.1. FTIR studies

The ultra-fine glass fibers give peaks at 2946 cm⁻¹, 2838 cm⁻¹, 1720 cm⁻¹, 1650 cm⁻¹, 1095 cm⁻¹ which they do not have before the treatment. The peaks at 2946 cm⁻¹, 2838 cm⁻¹ are the –CH₃ and the –CH₂–C–H stretching vibrations, respectively. The peaks at 1720 cm⁻¹, 1650 cm⁻¹, 1095 cm⁻¹ are attributed to the C=O, C=C and Si–O stretching vibrations, respectively. These results indicate...
that the coupling agent has reacted with the fibers to form chemical bonds and the ultra-fine glass fiber surface was covered coupling agent KH570. The chemical name of the coupling agent KH-570 is γ-methacryloxypropyl trimethoxy silane and its structure is shown in Fig. 4. The hydrolysis of the KH-570 coupling agent and it reacted with the ultra-fine glass fiber are shown in Fig. 5. The KH-570 coupling agent hydrolyzed first and got the silanol, and then the silanol reacted with the hydroxy on the surface of the glass fiber forming a thin film on the surface of the glass fiber. Alkyl group of the coupling agent has compatibility with the resin and so the glass fiber can combine with epoxy resin tightly processed by silane coupling agent.

3.2. Mechanical properties

The mechanical properties of the four coatings are listed in Table 2. It can be seen from the Table 2 that the hardness and adhesion increased with increasing ultra-fine glass fibers content. The hardness and adhesion of the 2#, 3#, 4# coatings increased by 67%, 67%, 200% and by 21.6%, 39%, 40% compared to the 1# coating, respectively. But the flexibility and the impact resistance do not change. It is concluded that glass fibers can improve the hardness and adhesion of coatings due to the glass fiber can act as the skeleton function in the coating and the rigid glass fiber can improve the coating hardness. When the fiber content is increased, there are more layered fibers in the coating and the glass fiber paralleled with the substrate which is shown in Fig. 6. The surface of the glass fibers is modified by the coupling agent and they can react with the epoxy resin which improves the chemical bonding between the fiber surface and the resin. This gives an improvement to the interfacial strength and the hydrothermal resistance of the surface [28]. The fibers in the coating can induce stress relaxation, eliminate stress propagation and residual stresses and reduce any internal stresses [29]. The ultra-fine glass fibers can transform and absorb energy which prevents crack propagation and grownup when the coating is subjected to an external stress and it will result in the improvement of the coating flexibility. The improvement of the coating flexibility will lead to improve the cohesion between the coating and substrate finally. And this is the reason that the ultra-fine glass fibers can improve coating flexibility and adhesion and reduce brittleness at the same time. So adding some content of glass fiber to the coating can improve the polymer’s cohesive strength and its mechanical properties.

Fig. 7 shows SEM images of the fracture surface of the four coatings by the pull-off method. The texture of the 1# coating fracture surface was smooth which characterizes brittle fracture. When the coating has higher glass fiber content, the fracture surface shows a plastic fracture character. The 2# coating fracture surface shows plastic fracture character: the surface is not smooth and there are many dimples on the fracture surface. Fig. 7 (1#), (4#) shows that the fracture surface of the coating with 30% ultra-fine glass fiber illustrates the obviously plastic property compare to the coating has none ultra-fine glass fiber. There are a lot of dimples distributed on the fracture surface of 4# coating. It was can be seen from the Fig. 7 that the coating flexibility was increased with high content of the ultra-fine glass fiber. Only added 10% ultra-fine glass fiber can improve the coating flexibility.
3.3. Electrochemical impedance spectroscopy (EIS) studies

3.3.1. Equivalent circuits

The equivalent electric circuit (EEC) models shown in Fig. 8(a) and (b) have been used to analyze the impedance data and are adequate for interpreting the spectra for 1#, 2#, 3# and 4# during their immersion time. $R_s$ is the solution resistance, $R_t$ and $C_t$ denote the coating resistance and the coating capacitance, respectively. $C_d$ and $R_d$ are the double-layer capacitance and charge transfer resistance, respectively [30].

During the whole immersion stage of 1# coating and the initial immersion stage of 2#, 3#, 4# coatings, the coatings act as barrier layers and their EEC are composed of a coating resistance, $R_t$, in parallel with a pure capacitance, $C_t$, i.e. The equivalent circuit shown in Fig. 8(a) can be used to fit the experimental data.

After time has elapsed, the size of the capacitive loop decreases, which indicates the continuous absorption of water into the coating body. The coating model is in series with a solution resistance ($R_s$), and a coating resistance ($R_t$) in parallel with a pure capacitance ($C_t$) and a charge transfer resistance ($R_d$) in parallel with the double-layer capacitance ($C_d$). The electrochemical process at the metal interface (Faradic reaction) is composed of the double-layer capacitance ($C_d$) in parallel with a charge transfer resistance ($R_d$). This indicates that water and oxygen might arrive at the metal interface through the coating, and thereby the electrochemical reaction sites are generated at the metal/electrolyte interface. The equivalent circuit shown in Fig. 8(b) can be used to fit the data for the 2#, 3# and 4# coating systems at intermediate immersion times.

3.3.2. Evolution of the impedance spectra with immersion time

Fig. 9 shows impedance spectra of the four different coatings at different immersion times. All of the four coatings act as a barrier initially and so their impedance modulus |$Z$| reaches $10^{10} \Omega \text{cm}^2$. But with the elapse of time, water and electrolyte penetrate gradually into the coating and cause the coating resistance to decrease gradually. In all four coatings, the impedance modulus |$Z$| of the 1# coating remained at $10^9 \Omega \text{cm}^2$, while the |$Z$| value of 4# and 3# coatings decreased most seriously with their values reducing from the initial $10^{10} \Omega \text{cm}^2$ to $10^7 \Omega \text{cm}^2$ after 75 days immersion. The impedance modulus |$Z$| of 2# decreased from the $10^7 \Omega \text{cm}^2$ to $10^3 \Omega \text{cm}^2$. These results reveal that the high glass fiber content can cause deterioration in the coating anticorrosion property, despite the improvement in the mechanical properties of the coatings. For the four coatings, the phase angle diagram of 1# remains almost horizontal which indicates that there is only one time constant during the immersion, the coating acts as a capacitor and has a good barrier ability for the substrate. While the phase angle of the other three coatings decreased with immersion time, they present two time constants. The 2# coating resistance also remained at $10^7 \Omega \text{cm}^2$ and has a better anticorrosion ability than 3# and 4# coatings, though its phase angle decreased.

Fig. 10 shows Nyquist diagrams for the four coatings. Fig. 10(a) is for 1# coating, its impedance changed a little and there is only one time constant: it gives good protection to the metal. Fig. 10(b)–(d) are for the 2#, 3#, 4# coatings, respectively. With increasing immersion time, they all showed two time constants. This illustrates that the electrolyte solution has become saturated in the three coatings and that the solution has reached the coating/metal interface and that corrosion has occurred. The short glass fiber content is different in the four coatings, the higher content leading to lower protection for the metal. So the impedance of the 1# coating is higher than for the other three coatings. The higher pigment content enhances the defects of the coating. When the coating has been submerged in the electrolyte solution for a long time, these micro-defects can easily come into effect and the channels let the electrolyte solution penetrate from the coating to the metal surface and lead to the metal corrosion. The mechanism of the zinc rich coating is the corrosion product of zinc is difficult dissolve to water and it can block the channel which water can penetrated to the substrate and then erode the substrate. But in 2#, 3#, 4# coatings, they have only 5% (PVC) zinc powder and it corrosion product can not block all the channels. The higher ultra-fine glass fiber, the higher micro-defects are in the coating. Once the water penetrates through the surface of the coating, it will more easily get to the interface of coating/substrate along the micro-defect. In order to get the better result, the content of the ultra-fine glass fiber and the zinc powder must be adjusted or else choose other anticorrosion pigment take the place of zinc powder in the coating.

The changes in coating resistance, $R_c$, and capacitance, $C_c$, of the four coatings are shown in Fig. 11. As can be seen from Fig. 11, $R_c$ for the 2#, 3#, 4# coatings decreases with time except that the 1# coating remains at $10^7 \Omega \text{cm}^2$ during the course of immersion. The $R_c$ of the 4# coating reduces more quickly than the other three coatings, and its value is $10^6 \Omega \text{cm}^2$. This means that the electrolyte has reached the coating/metal interface and that corrosion has occurred. At this moment, there is an electrochemical reaction at the interface between the coating and the metal, so that the coating protection capability becomes weak. The $R_c$ of 1# coating remained at $10^7 \Omega \text{cm}^2$ for the whole immersion time which indicates that the electrolyte had not penetrated the coating and that the barrier property of the coating is good.

3.4. Salt spray test

The salt spray tests of the four coatings were carried out for 75 days. Records were kept at intervals by digital camera. Seven pan-
Fig. 12. Morphologies of four coatings after exposure for 75 days. (a) 1# coating; (b) 2# coating; (c) 3# coating; (c) 4# coating.
els for each type of coating were prepared, three are scribed with a cross on the surface, the width of scribing lines being 1 mm. The other three panels were not scribed and the seventh panel was used to compare the panels which were exposed in the salt spraying cabinet. A white corrosion product appeared on the 4# coating surface after exposure for only 10 days, while nothing occurred with three coatings. The scribed areas were full of rust for the four coatings but did not extend. After an exposure for 35 days, the scribed areas of all the coatings had extended but to different extents. The 4# coating was corroded most seriously, its surface is covered by the white anticorrosion products. The rust on the 4# coating extended seriously and reached 4 mm in some places with an average width of between 2 and 3 mm. While the rust trace of the other three coatings extended slightly and their surfaces did not show the white zinc anticorrosion products. Fig. 12 shows the morphologies of the four coatings exposed in salt spraying cabinet for 75 days. After salt spraying test had lasted for 35 days, the 4# coating loses the protection ability for the substrate basically. After salt spraying test had lasted for 75 days, the 4# coating surface is full of white zinc corrosion products, and the 3# showed some white zinc corrosion products, while the other two coatings showed nothing. The scribed areas on all four coatings had extended, the average width for the 1#, 2#, 3# are between 1 and 2 mm and in some places reached 3 mm, while the average width for the 4# coating had extended greater than 2 mm and in some places had reached 5 mm. A strange phenomenon was observed in the scribed areas where some blisters were found adjacent to the scribed area while the most heavily corroded 4# coating did not have blisters. The blisters only emerged on the 1#, 2#, 3# coating surfaces, which may accord with the adhesion of the four coatings. When the content of the glass fibers is increased in the coating, there are more micro-defects in the coating which will easily lead to the coating lost protection ability. The results of salt spray tests are accordance with the EIS results.

Fig. 13 shows SEM micrographs for the four coatings after 75 days exposure in the salt spray test. Many changes are observed between the original samples and the samples which endured the salt spray test. Some blisters appeared on the surfaces of the 1# and 2# coatings, while the original samples showed nothing. EDX analysis confirmed that...
the white blisters on the coating surface were the zinc powder oxidation product. The coating surfaces of the 1# and 2# also basically remained in good condition, though some blisters, which are zinc powder, were found on the samples which were corroded by the sodium chloride solution. The amount of corrosion product on the 4# coating surface is highest. It is mainly because that 4# coating has the highest pigment content in the four coatings and this causes many defects in the coating. During the salt spray test, the zinc powder was easily corroded by the sodium chloride solution. Fig. 14 shows the EDX of the 4# coating after 75 days exposure in the salt spray test. From the EDX spectra, the zinc powder has been oxidized during the salt spraying test.

4. Conclusion

The hardness and adhesion of the coating will be improved when the coating containing high content of ultra-fine glass fiber. But when the ultra-fine glass fiber content improves, the anticorrosion of the coating will be decreased. When the coating has more than 10% ultra-fine glass fiber, its anticorrosion property will decrease, though it has good mechanical properties. The next step work is going to adjust the content of the ultra-fine glass fiber and the zinc powder in the coating or else choose other anticorrosion pigment substitute zinc powder in order to improve the coating anticorrosion property.

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