Research on Seawater Corrosion Resistance of Spray Polyurea Protective Coating

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Abstract. In this paper, the changes of mechanical properties and surface properties of QF-162 polyurea coating after soaking in seawater for 120 days were studied. The changes of internal chemical bonds before and after coating corrosion were observed with Fourier Transform infrared spectroscopy (FT-IR). The results of mechanical properties study showed that after soaking in seawater for 120 days, the tensile strength of QF-162 polyurea coating decreased by 4.23%, the elongation at break decreased by 7.10%. The hardness changed slightly and Shore A hardness decreased by 3.23%. Surface performance results showed that the contact angle of QF-162 polyurea coating decreased with the increase of soaking time, and the surface energy showed a trend of increase. After soaking 120 days, the contact angle of polyurea coating decreased by 6.08%, surface energy increased by 15.83%. FT-IR microscopic results showed that there was no obvious fracture phenomenon in the internal chemical bonds of QF-162 polyurea coating and the coating had good anti-corrosion to seawater soaking.

1. Introduction

At present, with the rapid development of marine engineering construction in China, more and more offshore buildings (such as cross-sea bridges, undersea tunnels) have appeared [1-2]. Affected by the bad marine environment, many marine buildings appeared corrosion and exfoliation, even collapse phenomenon [3-5]. The durability of building structures in marine environment had become the focus of attention of many experts and scholars [6-9]. Coating protection technology was a simple and effective method to protect concrete building structure. It was particularly important to study the performance of the marine environmental building structure protective coating, to grasp the variation rule of the performance of the protective coating in the marine environment, and to improve the service life of the building structure [10].

Polyurea was a new environment-friendly material which did not contain a catalyst, and its curing speed was fast. It could be sprayed on any surface, vertical plane and inclined plane. It had excellent corrosion and aging resistance. In this paper, the QF-162 polyurea coating developed by the institute of functional Materials of Qingdao University of Technology was selected to carry out the seawater corrosion resistance experiment, and the variation rule of the seawater corrosion resistance of the QF-162 polyurea coating after soaking in seawater for 120 days was discussed.

2. Experiment

2.1 Sample preparation
The polyurea material used in this paper was made by the laboratory of Qingdao University of Technology. It was coated with a thickness of about 2.0mm using PMC spraying equipment in the United States. The materials required for tensile test were cut into dumbbell shape by slicing machine.

2.2 Experimental equipment and test methods

Tensile testing: the slicer (MZ-4102) and universal testing machine (MZ-4000D1) used in the experiment are all provided by Jiangsu Ming Zhu experimental machinery co., LTD. According to GB/T 528-2009, the coating was cut into dumbbell shape for testing.

Hardness test: adopt the rubber and plastic bench measurement meter provided by Jiangsu Ming Zhu experimental machinery co., LTD. According to the provisions of GB/T 531.1-2008, after the superposition and leveling of three layers of samples, the measurement was carried out by using Shore hardness tester.

Contact angle test: the SDC-200 contact angle measuring instrument provided by Dongguan Sheng Ding Precision Instrument Co., Ltd., Using a syringe with a needle, a drop of ultrapure water droplet was placed on the surface of the sample to be tested, and stopped for a few seconds. The contact angle was measured within 30 seconds after the drop was stabilized. Finally, the arithmetic average of five points was chosen to represent the final result.

FT-IR test: the Fourier infrared spectrometer (Nicolet 8700) provided by American Thermo Nicolet Corporation, with a resolution of 4cm-1and a spectral range of 7800~350cm-1.

2.3 Experimental environment

The sea water pool on the roof of the No. 2 experimental building of Qingdao University of Technology was selected as the experimental site for seawater corrosion. According to the requirements of GB/T 1690-2010, the prepared samples were placed in the sea basin for soaking experiments, and the changes of mechanical properties (tensile strength, fracture elongation and Shore A hardness) and surface properties (contact angle and surface energy) were measured respectively when soaked for 30 days, 60 days and 120 days.

3. Results and discussion

3.1 Mechanical properties

Figure 1 showed the variation of tensile strength and elongation at break of QF-162 polyurea coating after soaking in seawater for 30 days, 60 days and 120 days respectively. The Shore A hardness of QF-162 polyurea coating after soaking in seawater for 120 days was shown in figure 2.

As can be seen from the curve in the figure 1, the tensile strength and elongation at break of polyurea coating generally showed a downward trend after being soaked in seawater for 120 days. After soaking for 120 days, the tensile strength decreased from 22.68MPa to 21.72MPa, decreased by 4.23%. The elongation at break reached 473.52% after 120 days, decreasing by 7.10%. The tensile strength and elongation at break of polyurea coating remained above 20MPa and 400% after soaking for 120d, respectively. This indicated that seawater had little influence on the tensile properties of QF-162 polyurea coating, and the coating had good elastic properties.
Figure 1. Variation curve of tensile properties of QF-162 polyurea coating after soaking in seawater for 120 days.

As can be seen from figure 2, after soaking in seawater for 120 days, the Shore A hardness of QF-162 polyurea coating generally showed a downward trend, but the change was not significant. After soaking for 120 days, the Shore A hardness of polyurea coating decreased by 3.23%, but remained around 90.

It can be seen from figure 1 and figure 2, seawater soaking corrosion had a certain effect on QF-162 polyurea coating. The polyurea coating had good anti-corrosion to seawater. After soaking in seawater for 120 days, the tensile strength remained above 20MPa. Shore A hardness remained around 90. The high tensile strength and hardness indicated that the molecular structure of polyurea coating was compact and no swelling damage occurs. The infiltration of the coating was further analyzed by studying the surface performance.

3.2 Surface performance
The change of contact angle and surface energy of QF-162 polyurea coating at 120 days was tested. It reflected the change of wettability of polyurea coating before and after seawater immersion. The experimental results were shown in figure 3.
Figure 3 showed the change of contact angle and surface energy of QF-162 polyurea coating with seawater soaking time. The experimental results showed that the contact angle of QF-162 polyurea coating decreased with the increase of soaking time, while the surface energy increased. This indicated that the wettability of polyurea coating increased with the increase of seawater soaking time. Before seawater soaking, the contact angle of polyurea coating was 82.76 ° and the surface energy was 57.80 N·m⁻¹. After soaking for 30 days, 60 days and 120 days, contact angle decreased by 2.31%, 3.49% and 6.08% respectively. The surface energy increases by 5.85% and 15.83% respectively at the above time points. The reason for the change in contact angle and surface energy of polyurea coating might be due to the uneven change of coating surface affected by corrosion ions in seawater. The corrosion ions directly contacted with the surface of the coating or infiltrate into the coating through micropores, which destroyed the coating and enhance the wettability of the coating. The change of coating internal structure would be further analyzed by FT-IR spectrum.

3.3 FT-IR analysis

The FT-IR spectra of QF-162 polyurea coating after soaking in seawater for 30 days, 60 days and 120 days were shown in figure 4. As can be seen from figure 4, near 3360cm⁻¹ was the N-H stretching vibration peak. The absorption peak was relatively strong, and it was a typical stretching vibration absorption peak of hydrogen bonding N-H. That means that N-H on the urea group was almost completely hydrogen bonded. Near 1530cm⁻¹ was the stretching vibration peak of C-N and N-R. Within the range of 2965–2870cm⁻¹ was the C-H stretching vibration peak. The characteristic peak of C=O was within the range of 1600–1700cm⁻¹. The 1100–1016cm⁻¹ range was the telescopic vibration peak of the C-O-C. The existence of the above characteristic peaks proved that the materials contain urea bonding -NHCONH-. The comparison of four curves a, b, c and d in figure 4 can be found, the FT-IR spectra of polyurea coating were basically consistent after being soaked for 30 days, 60 days and 120 days. It indicated that no chemical reactions such as chemical bonds breaking or redox occurring in the coating.

A combination of figure 1 and figure 4 can be found, QF-162 polyurea coating was soaked in seawater for 30 days, 60 days and 120 days, the tensile strength decreasing, the elongation at break decreasing slightly, and the hardness did not change much. But the internal structure of the material had not change in any form. That is, during the whole process of seawater immersion, the polyurea coating had not suffer any structural damage. It showed that seawater immersion corrosion had little effect on the internal structure of polyurea coating.

![Figure 4. FT-IR spectra of QF-162 polyurea coating before and after seawater soaking.](image-url)
4. Conclusion

It can be seen from the above experimental results, the QF-162 polyurea coating maintained good corrosion resistance in 120 days seawater immersion corrosion environment. Tensile strength and elongation at break showed a general downward trend. The tensile strength reached the lowest when soaked for 60 days, which was 21.72MPa. The elongation at break remained above 400% after soaking 120 days, indicating that the QF-162 polyurea coating had good elastic properties. FT-IR results showed that the internal structure of polyurea coating did not change. It showed that polyurea coating had excellent anti-corrosion.

References

[1] Itoh, Y., Gu, HS. Prediction of Aging Characteristics in Natural Rubber Bearings Used in Bridges [J]. Journal of Bridge Engineering.2009, 14 (2):122-128.

[2] H.S. Gu, Y. Itoh. Aging Behaviour of Natural Rubber and High Damping Rubber Materials Used in Bridge Rubber Bearings[J]. Advances in Structural Engineering.2010, 13(6): 1105-1113.

[3] Huang Weibo. Spray polyurea elastomer technology [M]. Chemical Industry Press.2005.

[4] Huang Weibo, Liu Xudong, Lv Ping, et al. Key Point Analysis of Beijing-Shanghai High Speed Railway Polyurea Protective Project [J]. Journal of Modern Paint and Finishing.2012,15(8): 11-15.

[5] Lv Ping, Shi Shifan, Xiang Jiayu, et al. Spray pure polyurea technology applied to improving the durability of concrete cross-sea bridge [J]. Journal of Concrete.2012, (8):119-121.

[6] Lv Ping, Li Zhigao, Zhang Jing. Anti-corrosion Behaviors of Polyurea Coating in Acid, Alkali and Salt Solution[J]. Journal of Corrosion and Protection.2011, 32(2):103-106.

[7] Huang Weibo, Hu Xiao, Xu Fei. Research progress of protection technologies for scour-abrasion resistance of hydraulic concrete [J]. Journal of Water Resources and Hydropower Engineering.2014, 45(2): 61-63.

[8] Huang Weibo, Xiang Jiayu, Liu Xudong. Polyurea Technology Applied to Post-earthquake Disasters for Defencing [J]. Journal of Earthquake Resistant Engineering and Retrofitting. 2012,34(2):115-118.

[9] Huang Weibo, Xiang Jiayu, Jiang Linlin, et al. Study on pure polyurea protective technology and applications of hydraulic engineering [J]Journal of New Building Materials.2012,39(4):7-9.

[10] Almusallam A A, Khan FM, Dulaijan SU, et al. Effectiveness of surf-face coatings in improving concrete durability[J].Cement and Concrete Composites.2003, 25 (4) : 473-481.