

Research on mariner growth prevention and anticorrosion tests of new type high toughness Resin/Steel/Copper alloy system

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Abstract. Multicomponent piping structure is common in ocean engineering material system. The new type of high toughness resin, marine steel and copper alloy as the main materials of the system is selected. The materials tests have been carried on in aging resistance, adhesion, water absorption, alternating temperature, salt spray resistance, weathering, electrochemical, antifouling and mariner growth prevention. The performances of the materials are analyzed by the quantitative results. The analysis shows that the high toughness resin coated on copper alloy materials and hull steel materials has good adhesion, water absorption, seawater resistance, alternating temperature resistance and salt spray resistance performances. Weathering performance meets the usage requirements of marine engineering. The electrochemical performance of the hull steel, copper alloy and high toughness resin materials is stable in seawater. High toughness resin/steel/copper alloy system has good anticorrosion, antifouling performance. The multicomponent piping system can satisfy the application in marine shipping requirements.

Keywords: high toughness; resin; multicomponent piping system; marine steel; copper alloy; antifouling; mariner growth prevention.

1 Introduction

Multicomponent piping structures are common in ocean engineering material system, widely used in vessels, drilling platforms and underwater facilities. Suitable material system selection is one of the highlights of marine materials research for a long time, as multicomponent piping system faces the multiple threats in the ocean, such as chemical/electrochemical corrosion [1], mariner growth [2, 3], sediment and so on. Especially in the condition of strong combination, the materials of multicomponent piping system need to have high toughness performance to maintain the stability of the structure in the complex ocean environment [4, 5]. Summing up, the material system of multicomponent piping structure [6] needs to meet the following main properties:

(1) seawater corrosion resistance; (2) antifouling performance; (3) potential corrosion performance; (4) anti-aging performance; (5) low water absorption performance; (6) The proper strength and toughness.

In this paper, a certain kind of material system with proper toughness, mariner growth prevention

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and anti-corrosion performances to fit the needs of ship navigation and the characteristics of ship hull irregular twisting is designed. The research on basic physical/chemical properties and antifouling/corrosion performance lab/practical tests of high toughness resin is done. The material system can be applied to be the components of the marine piping structure.

2 Material system selection

According to being applied outside ship hull, 945 marine steel is selected as the substrate material in the material system. The multicomponent piping functional materials, adhesive sealing compound material are screened out according to the substrates.

The principles of material system selection are as follows:

(1) Good molding process. (2) Good ability of anti-fouling, mariner growth prevention. (3) The electrochemical corrosion reaction is avoided to occur with the substrate material; (4) Good basic mechanics performance.

In this paper, the multicomponent piping alloy and adhesive sealing materials are selected and optimized based on the principles above.

2.1 Alternative materials

According to the requirements, this paper has carried on the preliminary investigation on the materials to select a suitable system for next study.

Table 1. Alternative materials list

Adhesive sealing material	Basic and physical chemical properties	Process performance	Piping system materials	Basic physical and chemical properties	Process performance
A two-component polyurethane materials	Shear strength ≥ 2.5 MPa, tensile strength (DIN 53504) ≥ 2.5 MPa, hardness (Shore A) 55 ~ 60, elongation at break $> 300\%$, water absorption $\leq 1\%$, good mariner growth prevention performance	Surface drying time (23°C , 50% relative humidity) 30 ~ 60 minutes, curing speed 4 mm / ~ 24 hours	945 hull steel	Poor mariner growth prevention performance	Homogenous with the substrates. Easy to weld. Bending forming is difficult.
A two-component epoxy materials	Shear strength ≥ 40 MPa, tensile strength (DIN 53504) ≥ 90 MPa, hardness (Shore A) 80 ~ 85, elongation at break $> 40\%$, water absorption $\leq 3\%$, poor mariner growth prevention performance	Surface dry time (23°C , 50% relative humidity) 30 ~ 60 minutes, curing speed 4 mm / ~ 24 hours	Copper alloy pipe	Good mariner growth prevention performance	Different from the substrates. Potential corrosion exists. Bending forming is easy.

Based on the properties illuminated in Table 1, the selected materials are as follows:

(1) In terms of resin adhesive sealing material, the two-component polyurethane has good performances of mariner growth prevention, elongation at break and toughness. The process performance is just about as epoxy's. Therefore, the two-component polyurethane is selected as the adhesive material in the subsequent experiments.

(2) In terms of piping materials, 945 steel is lack of good mariner growth prevention performance, although it can be welded with the substrates without potential corrosion. Therefore, copper alloy pipes, which can be insulated from the substrates by adhesive resin, are used in the subsequent tests.

3 Experimental procedure

The specimens are prepared according to GB/T14522, GB 9274-1988, GB/T 5210-2006, GB/T 1462-2005, GJB 150.5-1986, GB/T 1771-2007, GB/T 14522-2008, JB/T 7901-1999, JB/T 8424-1996 to meet the requirement of aging performance test, water resistance test, adhesion test, water absorption test, temperature alternating test, salt spray and weathering resistance test, electrochemical test and natural seawater test.

The high toughness resin coating is brushed inside the 945 steel tank. Then the copper alloy pipe is fixed promptly. After 24-hour curing, the high toughness resin is continually poured into the steel tank with fixed distance between the pipe and the bottom of the tank. The components for the real sea tests are ready after another 24-hour curing.

4 Material performance test

4.1 Aging performance

In accordance with GB/T14522-2008[7], the resin specimens are prepared to determinate the change of hardness, tensile strength and elongation at break, as shown in Table 2.

Table 2. The influence of accelerated aging time on the properties

Serial number	Aging time, day	Tensile strength , MPa	Elongation at break, %	Hardness, Shore A
1	0	4.28	370	59.6
2	5	4.82	298	61
3	10	4.52	216	65.6
4	15	5.24	297	64.6
5	20	5.18	271	65.4

4.2 Seawater resistance

In accordance with GB/T14522-2008, the resin specimens are prepared to determinate the change of hardness, tensile strength and elongation at break in natural seawater, as shown in Table 3.

Table 3. The influence of immersed time in seawater on the properties

Serial number	Time in seawater, month	Water absorption, %	Tensile strength, MPa	Elongation at break, %	Hardness, Shore A
1	0	0	4.45	413	61
2	1	0.27	3.58	243	63
3	3	0.12	4.40	210	66
4	6	0.07	4.80	236	65
5	9	0.11	7.14	265	65
6	12	0.21	4.68	279	62

In accordance with GB 9274-1988 [8], hull steel material specimens coated with high toughness resin are immersed in Qingdao seawater of 40 °C for 1000 h, observed whether phenomena of color change, bubble, crack, warped surface or break off occur on specimens' surfaces. The morphology of the specimens before and after the test is shown in Figure 1.



Figure 1. The morphology of the high toughness resin specimens before and after the seawater test

4.3 Adhesion test

The piping alloy and hull steel material specimens coated with high toughness resin are immersed in Qingdao seawater at room temperature for 10, 20 and 30 days. In accordance with GB/T 5210-2006[9], the results of adhesion test are shown in Table 4.

Table 4. The results of the specimen adhesion tests after the seawater test for 10, 20 and 30 days

Serial number	Specimen	Adhesion force, MPa		
		10 days	20 days	30 days
1	Copper alloy specimen	1.95	1.98	1.94
2	Hull steel specimen	2.06	2.03	1.99

4.4 Water absorption test

In accordance with GB/T 1462-2005[10], hull steel specimens coated with high toughness resin are investigated by water absorption test. The specimens are put in 50 °C oven for 24 h, cooled to room temperature and weighed; then put in 23 °C distilled water for 24 h, weighed after removing surface moisture. The results are shown in Table 5.

Table 5. Water absorption test results

Serial number	weight before test, g	weight after test, g	Water absorption capacity, g	Average, g
1	119.743	119.786	0.043	0.045
2	121.262	121.307	0.045	
3	118.908	118.956	0.048	

4.5 Temperature alternating test

In accordance with GJB 150.5-1986[11], the piping alloy and hull steel material specimens coated with high toughness resin are tested in alternating temperature chamber under the conditions of -40 °C ~ 70 °C temperature alternating, 2h per cycle, 50 cycles.

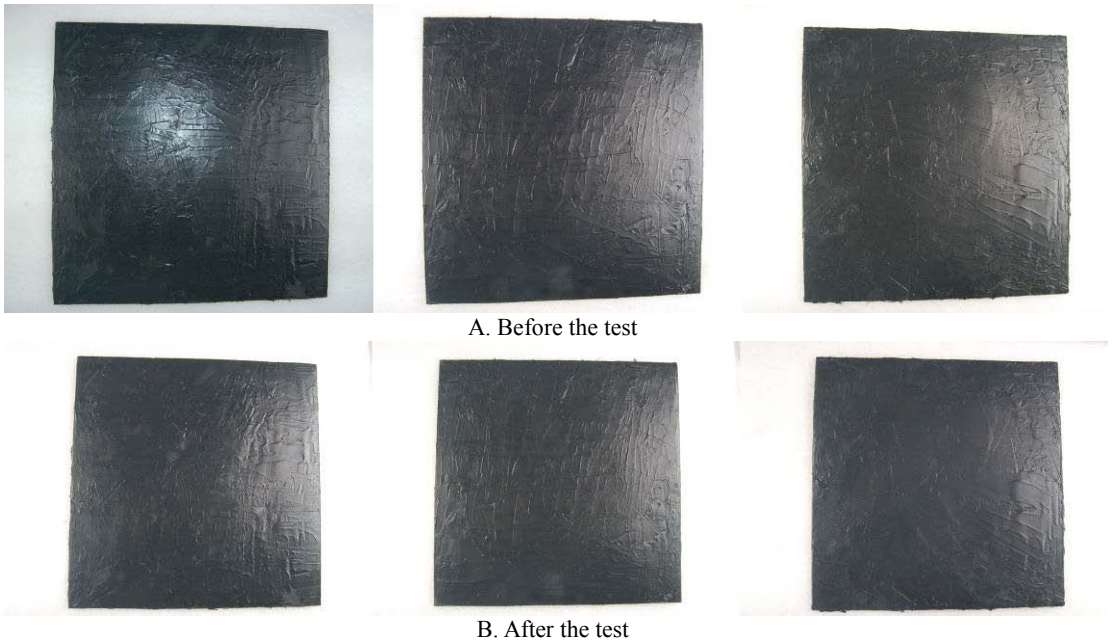


Figure 2. The morphology of the specimens before and after the temperature alternating test with copper alloy as the substrates

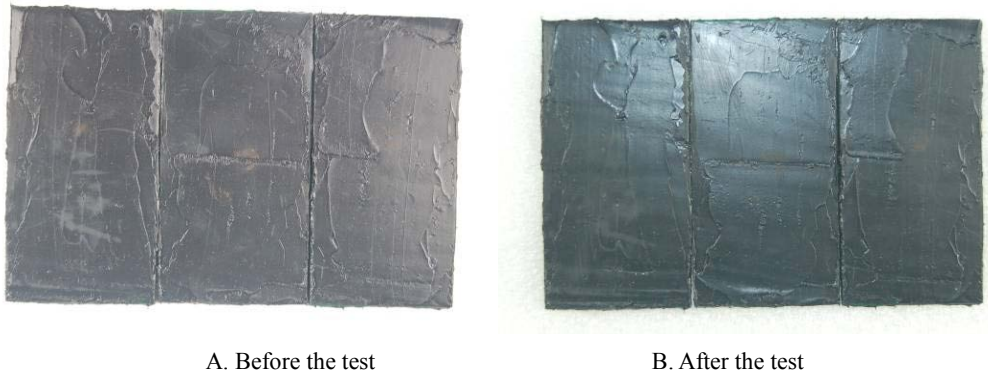


Figure 3. The morphology of the specimens before and after the temperature alternating test with hull steel as the substrates

4.6 Salt spray resistance

In accordance with GB/T 1771-2007[12], hull steel material specimens coated with high toughness resin are tested in salt spray chamber under the condition of 35°C, the test medium concentration of 50 g/L (prepared with distilled water and sodium chloride), spraying for 15 min and pause for 45 min, 1000 h, observed whether phenomena of color change, bubble, crack, warped surface or break off occur on specimens' surfaces.

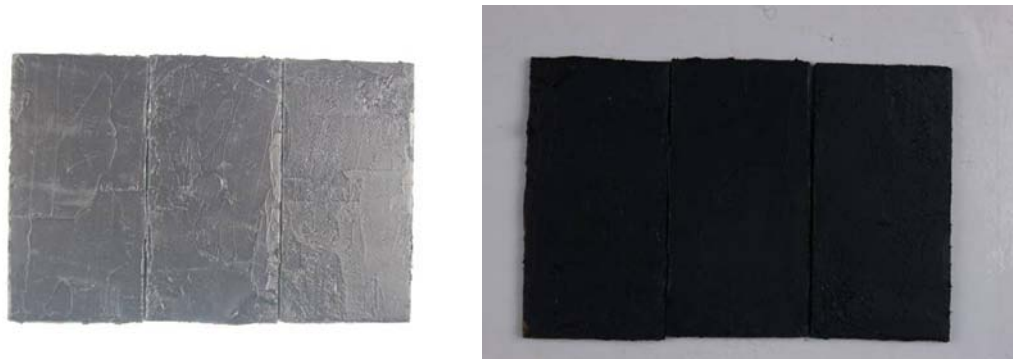


Figure 4. The morphology of the high toughness resin specimens before and after the salt spray test

4.7 Weathering resistance

In accordance with GB/T 14522-2008and GB/T 528-2009[13], the specimens are tested in ultraviolet aging chamber (Test time 20 d, 5 d as a test cycle. The light phase at 60 °C for 8h, the condensing stage at 50 °C for 4 h per cycle). The hardness and tensile strength are tested at the end of each cycle and the test data are shown in Table 6.

Table 6. High toughness resin weathering test data

Serial number	Test time, day	Hardness, shore hardness	tensile strength, MPa
1	0	60	465
2	5	61	312
3	10	66	260
4	15	65	242
5	20	65	180

4.8 Electrochemical test

In accordance with JB/T 7901-1999 [14], copper alloy piping material and hull steel specimens coated with high toughness resin are immersed in Qingdao seawater. The potentials among piping materials/resin, hull steel/resin are measured every day. The reference electrodes are saturated calomel electrode. Test results are shown in Figure 5.

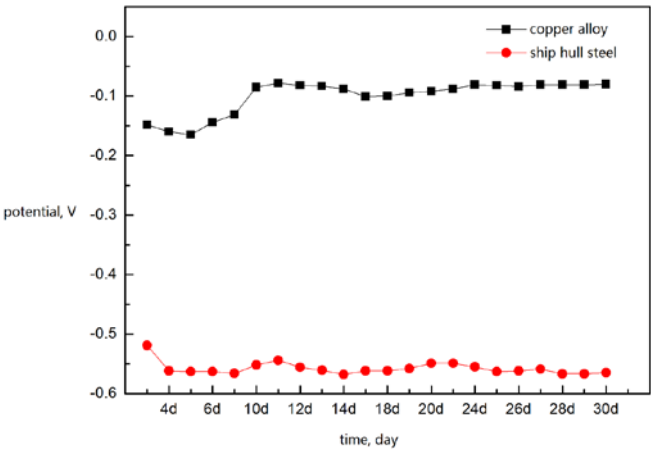


Figure 5. The electrochemical test data of copper alloy piping material and hull steel specimens coated with high toughness resin

4.9 Test in natural seawater

In accordance with JB/T 8424-1996[15], copper alloy piping material and hull steel specimens coated with high toughness resin are respectively hang in full immersion zone, tidal range zone and splash zone for test. The test period is 12 months. The morphology of the copper alloy piping material and hull steel specimens coated with high toughness resin 12 months later is shown in Figure 6.



Copper alloy pipe material as substrates

Hull steel material as substrates

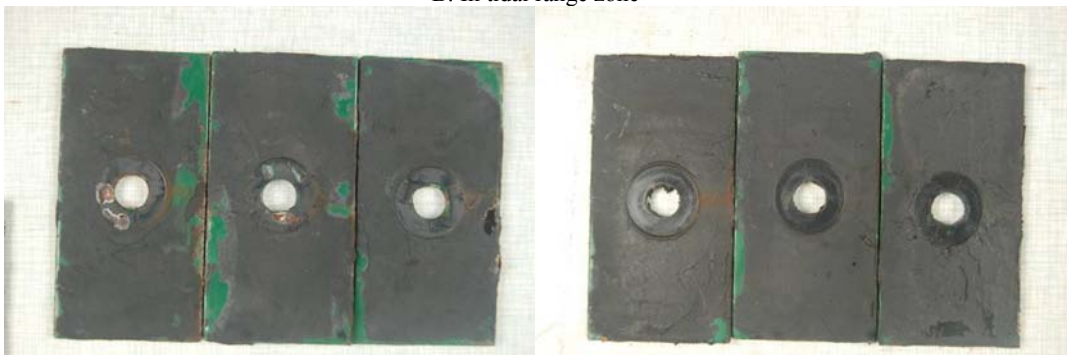
A. In full immersion zone



Copper alloy pipe material as substrates

Hull steel material as substrates

B. In tidal range zone



Copper alloy pipe material as substrates

Hull steel material as substrates

C. In splash zone

Figure 6. The morphology of the specimens tested in natural seawater after 12 months

4.10 Mariner growth prevention test in natural seawater

The components made of 945 hull steel, copper alloy pipe and high toughness resin are placed in full immersion zones of Qingdao, Zhoushan and Sanya seawater for 12 months.

The morphology of the components after the test is shown in Figure 7, 8 and 9.



Figure 7. The morphology of the component in Qingdao seawater after 12 months



Figure 8. The morphology of the component in Zhoushan seawater after 12 months



Figure 9. The morphology of the component in Sanya seawater after 12 months

5 Material performance analysis

In the resin aging performance test study, Table 2 shows the aging performance remains stable with aging time. At the start of the aging, the hardness and tensile strength increased, elongation decreased. The performances tend to constant values, satisfying the requirement.

The phenomena of color change, bubble, crack, warped surface or break off doesn't occur on the specimens' surfaces after the seawater absorption tests. In Table 3, the seawater absorption rates show

little changes (less than 0.5%) while the specimens are dipped in the seawater, although the test performance data exist some random fluctuations. The tensile strength, elongation at break and hardness fluctuate within permit ranges. The basic performances of the specimens maintain stable after one year's seawater immersion, satisfying the requirements.

Copper alloy and hull steel specimens coated with high toughness have steady adhesion performance in the test cycle shown in Table 4. The failure type is cohesion failure of high toughness resin.

The water absorption test shows that the high toughness resin has an extremely low absorption rate, satisfying the requirement of stable performance in seawater.

In alternating temperature test, the high toughness resin coated on the copper alloy and hull steel doesn't show obvious changes on the surface, as shown in Figure 2, 3.

After the salt spray test, the specimens' surfaces doesn't show obvious change, such as color change, bubble, crack, warped surface or break off, as shown in Figure 4.

The data in table 6 show that the hardness of high toughness resin specimens increases, while the tensile strength decreases along with the increase of the test time in weathering tests. This shows that the resin material in weathering test has certain aging problem. But during a minor repair cycle, the resin's performance remains stable under the waterline to avoid direct sunlight, satisfying the requirements of weathering.

The data in Figure 5 show that the potentials of the copper alloy and hull steel coated with high toughness resin in seawater are basically stable in electrochemical tests after 30 days. The potential of the copper alloy specimen coated with high toughness resin is about -0.08 V, while the one of the hull steel specimen coated with high toughness resin is about -0.56 V. The test results show that the high toughness resin has good insulation performance, which can prevent the hull steel and copper alloy pipe in seawater from electrochemical corrosion.

The morphology of figure 6 shows that a small amount of sea creatures grow on the components in Qingdao seawater after 12 months. There are nearly no sea creatures but only a small amount of sediment on the components in Zhoushan seawater after 12 months. A large amount of sea creatures grow on the anticorrosive coating part of the components but relatively less creatures grow on the surface of the resin in Sanya seawater after 12 months.

6 Conclusion

Multicomponent piping structure material system is designed according to the consideration of chemical/electrochemical corrosion, sediment/sea creature's growth and the characteristics of its structural rigidity and toughness.

Through the tests, it can be seen that the high toughness resin coated on copper alloy materials and hull steel materials has good adhesion, water absorption, seawater resistance, alternating temperature resistance and salt spray resistance performances. Weathering performance meets the usage requirements of marine engineering. The electrochemical performance of the hull steel, copper alloy and high toughness resin materials is stable in seawater. High toughness resin/steel/copper alloy system has good anticorrosion, antifouling performance. The multicomponent piping system can satisfy the application in marine shipping requirements.

Compared with the previous systems, the material system in this paper can well satisfy the requirements of the piping structure outside ship hull, and has a good application prospect.

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