STUDY ON EFFECT OF NANOCOMPOSITE $AgCu/SiO_2$ ON THE PHYSICO-MECHANICAL PROPERTIES AND ANTI-CORROSION OF EPOXY COATING

NGHIÊN CỨU ẢNH HƯỞNG CỦA NANOCOMPOSITE $AgCu/SiO_2$ ĐẾN TÍNH CHẤT CƠ LÝ VÀ CHỐNG ĂN MÒN CỦA LỚP PHỦ EPOXY

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ABSTRACT

Among organic coatings, epoxy coating is an excellent material for corrosion prevention in structural metals in Vietnam's tropical marine climate conditions. This article presents some survey results of physico-mechanical properties and anticorrosion of epoxy coating which combined with nanocomposite $AgCu/SiO_2$. The physico-mechanical properties are determined according to international standards, corrosion resistance test of epoxy coating is carried out according to ISO 9227:2017. The survey result showed that, the epoxy coating combined with 1.0% $AgCu/SiO_2$ nanoparticles, adhesion increased by 13.4%, impact resistance increased by 9.1%, hardness of coating increased by 10.5%, abrasion resistance decreased by 20.0%, other properties have not changed much. After 720 hours of testing (30 test cycles), the epoxy coating combined with 1.0% $AgCu/SiO_2$ nanoparticles, the degree of blistering has reached S0, the degree of cracking - S1, the degree of flaking - S2, the degree of rusting - S0 and adhesion is reduced from 5.06 MPa down to 4.91MPa.

Keywords: *Epoxy resin YD-128, hardener G-5022, nanocomposite $AgCu/SiO_2$, anticorrosion, accelerated testing.*

TÓM TẮT

Trong các loại lớp phủ hữu cơ, lớp phủ epoxy là vật liệu chống ăn mòn tuyệt vời đối với kết cấu kim loại trong điều kiện khí hậu biển nhiệt đới Việt Nam. Bài báo trình bày một số kết quả khảo sát tính chất cơ lý và khả năng chống ăn mòn của màng sơn epoxy kết hợp nanocomposite $AgCu/SiO_2$. Các tính chất cơ lý của lớp sơn được xác định theo tiêu chuẩn quốc tế, thử nghiệm khả năng chống ăn mòn của lớp phủ epoxy được tiến hành theo tiêu chuẩn ISO 9227:2017. Kết quả khảo sát cho thấy, lớp phủ epoxy kết hợp với 1,0% nanocomposite $AgCu/SiO_2$ làm tăng độ bám dính lên 13,4%, độ bền va đập tăng 9,1%, độ cứng màng sơn tăng 10,5%, độ mài mòn giảm 20,0%, các tính chất khác thay đổi không nhiều. Sau 720 giờ thử nghiệm (30 chu kỳ), lớp phủ epoxy kết hợp 1,0% nanocomposite $AgCu/SiO_2$, độ phồng rộp đạt mức S0, độ rạn nứt - S1, độ bong tróc - S2, độ gỉ - S0 và độ bám dính giảm từ 5,06MPa xuống 4,91MPa.

Từ khóa: *Nhựa epoxy YD-128, chất đóng rắn G-5022, nanocomposite $AgCu/SiO_2$, chống ăn mòn, thử nghiệm gia tốc.*

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1. INTRODUCTION

Organic coatings are commonly used to protect metal and alloy surfaces against corrosion because they form a barrier layer and interfere with the diffusion of water towards the metal or alloy surfaces. These barrier properties are depended on the type of polymer matrix, the additives, the pigments, the solvent and the coating thickness [1].

Nowadays, epoxy resins are widely used in many different specialty structural applications. Because these resins have better adhesion to other substrates, good mechanical strength, good shear strength, lower curing shrinkage, better thermal stability and excellent tribological properties than some commonly used other resins. In addition, its chemical stability and good corrosion resistance makes it an outstanding material for the coating systems [2, 3, 4]. Because of the above good properties, epoxy coatings used in the marine industry are often exposed to the impact of seawater, one of the most harmful conditions affecting the properties of material structures [5].

Zeze Armande Loraine Phalé et al [6] studied composite coating on base of geopolymer modification by 20 - 30% epoxy resin. The results showed that the shrinkage of epoxy resin-geopolymer was decreased compared to geopolymer after 56 days seawater soaking; as the epoxy resin content increased, the adhesive strength and chloride corrosion resistance were increased. The findings suggested that epoxy resin-geopolymer can provide promising alternative as anticorrosion coating in marine environment.

Tuan Anh Nguyen et al [7] studied the thermal and mechanical properties of epoxy coatings incorporated with nanoparticles (SiO_2, Fe_2O_3, TiO_2). The measurement results showed that TiO_2 nanoparticles increased the Tg value (from 58°C up to 170°C) and improved the impact strength of the epoxy coating. The incorporation of ZnO nanoparticles improved the best thermal stability and additives of Fe_2O_3 nanoparticles improved the adhesion of the epoxy coatings.

Mohammad Asif Alam et al [8] studied the effects of SiO_2 and ZnO nanoparticles on the mechanical and thermal properties of epoxy coatings. The results showed that the addition of 2% ZnO nanoparticles increased 33% hardness compared with the coatings without ZnO.

Xianming Shi et al [9] studied the effect of nanoparticles (SiO_2, Zn, Fe_2O_3 and halloysite clay) on the anticorrosion and mechanical properties of epoxy coating. The results showed that nanoparticles dispersed into epoxy resin matrix at a concentration of 1% by the total weight of epoxy resin and its hardener, and improved significantly the corrosion resistance of epoxy coating, with the halloysite clay and Fe_2O_3 nanoparticles being the best.

Romulo Pletsch et al [10] studied the efficiency of Ag/SiO_2 nanoparticles on the anticorrosion of epoxy coatings. The measurement results showed that addition of 0.5% w/w Ag/SiO_2 to the epoxy coating improved the efficiency of the anticorrosive coating compared to the epoxy coating without Ag/SiO_2 nanoparticles.

However, the effects of $AgCu/SiO_2$ nanoparticles on physico-mechanical properties have not been studied.

2. RESEARCH METHODS

2.1. Materials

Epoxy resin (YD-128X90) (Kukdo Chemical Co. Ltd., South Korea); hardener (G-5022X70) (Kukdo Chemical Co. Ltd., South Korea); nanocomposite $AgCu/SiO_2$ (size of the particles AgCu: < 100nm, size of the particles $AgCu/SiO_2$ < 10µm; Vietnam); xylene AR (Xilong, China); butyl acetate AR (Xilong, China); acetone AR (Xilong, China); steel plate Ct-3 (Vietnam); aluminum alloy plate (Vietnam).

Spray gun (Lanest, Japan); Ultrasonic cleaning Elma S10 (Germany); technical balance Ohaus PR2202/E (USA); analytical banlance (ACE-Germany); glass cup 100 ml (Schott-Duran, Germany); stirring rod (China).

2.2. Preparation for paint solution

Paint solution is composed of epoxy resin YD-128, hardener G-5022, $AgCu/SiO_2$ nanoparticles and solvents. Epoxy resin solution YD-128X90 and hardener solution G-5022X70 are prepared by ratio YD-128X90/ G-5022X70 = 1,0/1,3 (w/w) [11].

Studies and surveys have shown that the content of nanoparticles $AgCu/SiO_2$ in epoxy coating from 0.1% to 1.0% to achieve antibacterial, antifouling and economic efficiency [12, 13]. Survey ratio of $AgCu/SiO_2$ nanoparticles, epoxy resin YD-128 and hardener G-5022 is given in Table 1.

Table 1. Component of paint samples surveyed (w)

Sign of sample	Epoxy resin YD-128	Hardener G-5022	Nanocomposite $AgCu/SiO_2$
KT00	50.00	50.00	0.00
2KT01	49.95	49.95	0.10
2KT05	49.75	49.75	0.50
2KT10	49.50	49.50	1.00

Fabrication of paint solution sample 2KT10:

1.0g nanoparticles $AgCu/SiO_2$ dispersed into 20mL butyl acetate solvent in ultrasonic cleaning Elma S10. 49.5g epoxy resin solution YD-128 was slowly added to the above mixture, and continued to be dispersed by ultrasonic until a homogeneous mixture. 49.5g hardener G-5022 are mixed with the above mixture at room temperature until a homogenous solution. Solvent is added to achieve the appropriate viscosity for use with a paint spray gun to cover on the surface of steel plates Ct-3.

Other paint solution samples (KT00, 2KT01 and 2KT05) are manufactured similarly to the above process.

2.3. Preparation for sample test

The surface of the steel plates Ct-3 is polished to a roughness of 0.5µm to 1.4µm.

The steel plates Ct-3 with size L x W x H = 150 x 75 x 2 mm were covered by coatings surveys for the tests of gloss value, hardness of coating, adhesion of coating, impact resistance and anticorrosion.

The steel plates Ct-3 with size L x W x H = 100 x 100 x 2mm were covered by coatings surveys for test of abrasion resistance on Taber device, using abrading wheel CS-17.

The aluminum alloy plates with size L x W x H = 150 x 10 x 0.2mm were covered by coating surveys for bending strength test.

The investigated paint samples were painted in 2 layers on the surface of the steel plate Ct-3, each layer was spaced at least 24 hours and allowed to dry at room temperature for 7 days. After this days the paint samples determined physico-mechanical and other properties. Each measurement was performed on 5 samples. Images of samples are illustrated in Figure 1.

Size of sample 100 x 75 x 2 mm

Size of sample 100 x 100 x 0.2

Size of sample 100 x 100 x 2

Figure 1. Image of samples

2.4. Test methods

Gloss value of coating is determined according to ISO 2813:2014, using a measuring angle of 60° on a 3-angle 20/60/85 gloss meter of Rhopoint [14].

Thickness of coatings is determined by using ultrasonic waves according to ISO 2808:2007 [15].

Hardness of coatings is determined by Persoz pendulum damping test according to ISO 01522:2006 [16].

Adhesion of paint coatings is determined by a pull-off test according to ISO 4624:2016, the diameter of dolly was 2 mm [17].

Impact resistance is determined by falling-weight test, large-area indenter according to ISO 6272-1:2011 [18].

Bending strength is determined by cylindrical mandrel according to ISO 1519:2011 [19].

Abrasion resistance is determined according to ISO D4060:2010 [20], on the Taber device, using abrading wheel CS-17, rotation speed of abrading wheel was 60 rounds/min. The abrasion resistance is calculated after 300 rounds.

Corrosion resistance test of coating is carried out according to ISO 9227:2017 with conditions solution: 5% sodium chloride, temperature: 35°C, spray speed NaCl 5%: 200mL/h [21].

3. RESULTS AND DISCUSSION

3.1. Investigation of physico-mechanical properties of coatings

Outstanding properties of epoxy materials are adhesion, impact resistance and abrasion resistance which is higher than the other materials by a reaction takes place between the oxirane cycle (epoxy group is in resin's structure YD-128) and the amide group (amide group is in hardener's structure G-5022). This reaction produces no by-products H_2O, CO_2,...), so epoxy material without pores, high stability,...

In this study has surveyed some physico-mechanical properties of epoxy coating with $AgCu/SiO_2$ nanoparticles. There are gloss value, adhesion value, impact resistance and adrasion resistance. The results are summarized in Table 2.

Table 2. Some physico-mechanical properties of coatings

Sign of sample	Gloss values, GU	Adhesion values, MPa	Impact resistance, kg.cm	Abrasion resistance, mg
KT00	110.50 ± 0.24	4.46 ± 0.09	110 ± 1	0.025 ± 0.001
2KT01	110.50 ± 0.36	4.70 ± 0.04	110 ± 1	0.023 ± 0.001
2KT05	111.20 ± 0.28	4.89 ± 0.03	120 ± 1	0.022 ± 0.001
2KT10	111.20 ± 0.20	5.06 ± 0.07	120 ± 1	0.020 ± 0.001

The results in Table 2 showed that, with a small content $AgCu/SiO_2$ (0.1%), gloss has no change. However, if this content $AgCu/SiO_2$ was 0.5% or 1.0%, the gloss value increases up to 0.6%.

When the epoxy coating combined with 0.1%, 0.5% and 1.0% $AgCu/SiO_2$ nanoparticles, the adhesion of coating into the surface steel Ct-3 increased respectively to 5.4%, 9.6% and 13.4%. The impact strength has not change compared to the original coating if the epoxy coating combined with 0.1% $AgCu/SiO_2$ nanoparticles. However, with 0.5% and 1.0% $AgCu/SiO_2$ nanoparticles, impact strength increased by 9.1%.

Abrasion resistance of epoxy coating is raised very little when the epoxy coating combined with 0.1% and 0.5% $AgCu/SiO_2$ nanoparticles, abrasion resistance decreased respectively by 8.0% and 12.0%. However, the abrasion resistance of the coating is significantly improved with combination 1.0% $AgCu/SiO_2$ nanoparticles which decreased by 20.0%.

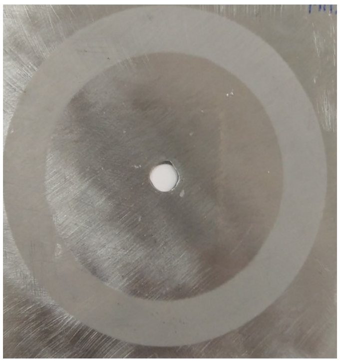
The mechanical and physical properties were improved, it can be explained through the chemical structure of epoxy resin, which combined with $AgCu/SiO_2$ nanoparticles to produce high gloss, good adhesion, high impact strength and excellent adrasion resistrance of coating film as follows: With ordinary solids, if their content is increased in the composition of the paint film, the gloss value decreases, but $AgCu/SiO_2$ nanoparticles (with the nano size) should easily disperse into the matrix phase to create a high density structure. In addition, copper metal also participates in bonding with the hydroxyl group in the chemical structure of epoxy resin to create a more stable polymer material structure [22]. Besides, metal nanoparticles with high hardness have increased the abrasion resistance of coating film. Therefore, the physico-mechanical properties of epoxy coating are enhanced when it is combined with $AgCu/SiO_2$ nanoparticles.

3.2. Investigation of other properties of coatings

In addition to the physico-mechanical properties above, some other properties of coating has surveyed according to the standards at the laboratory system Vilas 938. There are thickness of coating, hardness of coating and bending strength. Results are shown in the Table 3.

a) After pull-off test

b) After impact resistance test



c) After abrasion resistance test

Figure 2. Morphology images of coatings after tests

Table 3. Some other physico-mechanical properties of coatings

Sign of sample	Thickness of coating, µm	Hardness of coating	Bending strength, mm
KT00	41.20 ± 0.88	0.526 ± 0.008	1.00 ± 0.05
2KT01	38.90 ± 0.13	0.530 ± 0.003	1.00 ± 0.05
2KT05	41.80 ± 0.25	0.559 ± 0.002	1.00 ± 0.05
2KT10	40.60 ± 0.31	0.581 ± 0.005	1.00 ± 0.05

The results in Table 3 have shown that epoxy paint with additives $AgCu/SiO_2$ nanoparticles which didn't have much changed on the bending strength. However, the hardness of coating has increased by 10.5% when this coating is combined with 1.0% $AgCu/SiO_2$ nanoparticles.

Images of some samples after measuring and determining mechanical properties are illustrated in Figure 2.

3.3. Evaluation of anticorrosion

Coatings play an important role in protecting against corrosion for steel structures in tropical marine climate, so salt spay testing for survey paint samples is highly practical.

The surface of panel test is evaluated for the following criteria: degree of blistering (ISO 4628-2:2016) [23], degree of rusting (ISO 4628-3:2016) [24], degree of cracking (ISO 4628-4:2016) [25], degree of flaking (ISO 4628-5:2016) [26], adhesion of coating (ISO 4624:2016) [27]. The surface evaluation of the test samples showed that,

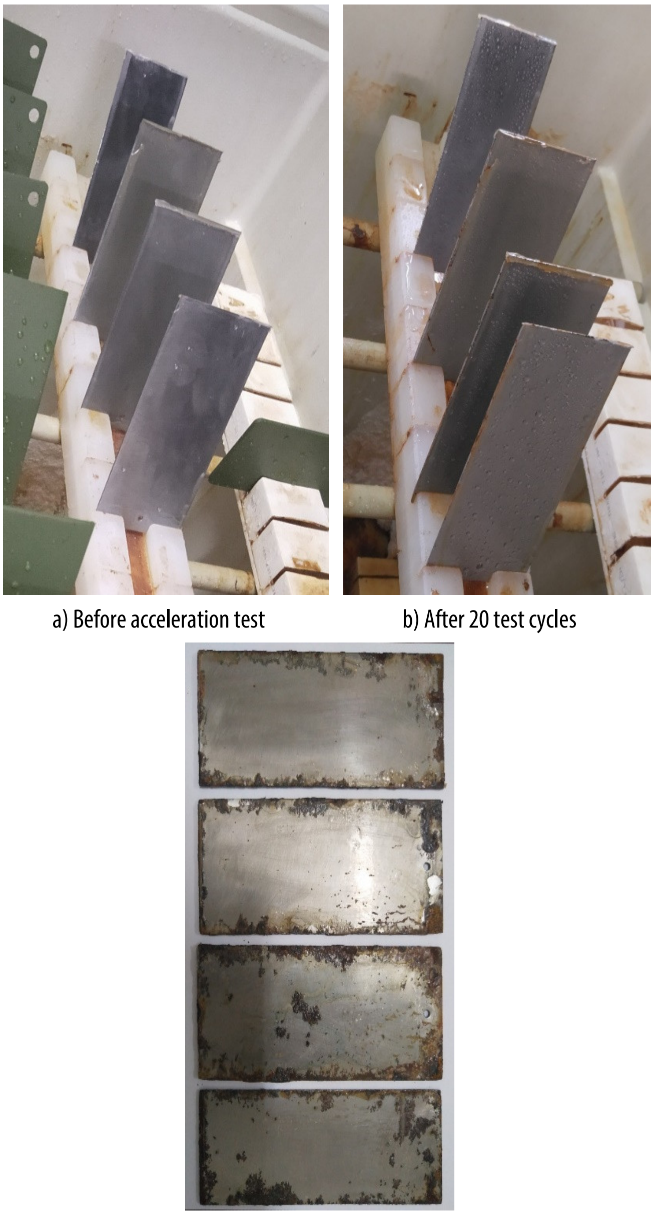
1) After 20 test cycles (equivalent to 480 hours): The paint film surface has not been blistered, cracked, flaked and rusted.

2) After 30 test cycles (equivalent to 720 hours): The paint film surface has changed. The blistering, rusting, cracking and flaking of the paint film decreased significantly when the $AgCu/SiO_2$ nanoparticles content increased in the paint film composition. With the coating using 1.0% nanoparticles, these parameters have not changed or changed very little. Adhesion was slightly degraded after 30 test cycles, which has shown that epoxy paint using 1.0% $AgCu/SiO_2$ nanoparticles has very good corrosion resistance and seawater resistance. The evaluation results are summarized in Table 4.

Table 4. Evaluation results after 30 test cycles (720h)

Sign of sample	Degree of blistering	Degree of rusting	Degree of cracking	Degree of flaking	Adhesion of coating, MPa
KT00	S5	Ri 5	S2	S2	4.21
2KT01	S5	Ri 4	S2	S2	4.45
2KT05	S2	Ri 1	S2	S2	4.66
2KT10	S0	Ri 0	S1	S2	4.91

Surface images of paint samples tested for spray salt acceleration are illustrated in Figure 3.



a) Before acceleration test b) After 20 test cycles

c) After 30 test cycles

Figure 3. Morphology images of test samples

4. CONCLUSION

Regarding physico-mechanical properties of epoxy coatings with additives AgCu/SiO_2 nanoparticles, the survey results showed that, with 1.0% AgCu/SiO_2 nanoparticles in the composition of epoxy coating, the physico-mechanical properties of epoxy coating were significantly improved (adhesion increased by 13.4%, impact resistance increased by 9.1%, hardness of coating increased by 10.5%, abrasion resistance decreased by 20.0%), and the economic efficiency of the AgCu/SiO_2 nanoparticles was used as additives in a epoxy coating is suitable. Besides, the corrosion resistance in salt water environment of epoxy coating is also improved. This results suggested the application of epoxy coatings with AgCu/SiO_2 particles used in exploitation conditions in marine, island and coastal climates, contributing to supplementing the data of physical and mechanical properties and anticorrosion of epoxy coating combined with AgCu/SiO_2 nanoparticles.

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THÔNG TIN TÁC GIẢ

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