

Tensile Performance of Waterborne Epoxy Coating Immersed in Saline Solutions

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ABSTRACT

Organic coatings can greatly improve the resistant abilities against the migration of harmful species into concrete, resulting in the higher durability performances of concrete structures. Therefore, it is essential to assess the engineering performances of organic coatings in the service environments. In this work, the engineering performances and microstructure of a waterborne epoxy that can be used as a component of concrete's protective coatings were investigated. The waterborne epoxy samples were immersed in tap water, 5wt% NaCl solution and 5% Na₂SO₄ solution for 28 d. A direct tensile test equipped with microscopy was conducted to measure the tensile strength and failure process of the waterborne epoxy samples before and after the immersion actions. The physicochemical interactions between the environments and waterborne epoxy samples were investigated by X-ray photoelectron spectroscopy (XPS), and scanning electron microscope (SEM) with dispersive X-ray spectroscopy (EDS). Results show that the immersion actions had limited influences on the tensile performances of the waterborne epoxy, but altered the microstructure and chemical structure to certain extents. The findings of this work would deepen the understandings in environmental actions to organic coatings, enabling a more accurate assessment of service life of concrete with organic coatings.

1. INTRODUCTION

Concrete is a heterogeneous porous material containing weak phases, such as, pores and micro-cracks, that allow the migration of harmful species [1]. For reinforced concrete structure serving in harsh environments, the invasion of corrosive substances may unavoidably raise the corrosion damages. An ordinary way to enhance the corrosion resistances of a reinforced concrete structure is to provide more compacted cover concrete for promoting the resistances against species ingression [2]. Alternatively, use of organic coatings on concrete surface can be a flexible and effective option to increase durability of concrete structures [3]. The attachment of organic coatings on concrete surface can form a hydrophobic layer that acts as a physical barrier to prohibit the ingression of water, chloride ions and other corrosive substances from the external environments into the concrete [4].

Polymers may degrade when subjected to some weathering aging factors, such as ultraviolet (UV) radiation, oxygen, humidity, and temperature, so the protective performances are decreased. The aging failure of polymer coatings is mainly manifested in the appearance of chalking, blistering, cracking, holes and peeling given rise to photooxidation, thermo-oxidative and hydrolytic degradation [5]. In construction industry, epoxy resins are widely used

due to their excellent properties including good chemical resistance, low shrinkage and high adhesion to many substrates [6]. Therefore, the environmental weathering effects on the properties of epoxy resins have gained increasing interests. Feng et al. [7] pointed that salt precipitation can occur in pores or defects of epoxy coatings, causing the crystallization-assisted degradation. However, the mechanisms of crystallization-assisted material degradation remain still to be advanced.

In this work, a waterborne epoxy resin was selected to fabricate film samples, and immersed into tap water, 5%wt sodium chloride (NaCl) and 5%wt sodium sulfate (Na₂SO₄) solutions for 28 d. A direct micro tensile device was applied to measure the tensile behavior of the waterborne epoxy resin samples before and after the immersion actions. SEM and XPS techniques were used to evaluate the morphological and chemical changes.

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation and weathering test

An A-B type waterborne epoxy was purchased from Jiangsu Sanmu Group Co., Ltd., China. The component A is an epoxy emulsion SMW602 with excellent performance, while the component B SMW703 is an aliphatic amine water-based epoxy curing agent. These two components were mixed and thoroughly reacted with a weight ratio 100A:

15B at room temperature. Then free waterborne epoxy films were prepared, with an extender, on Teflon plates. The samples were kept in air for a week at room temperature for sufficient curing. After that, the waterborne epoxy films were detached from the Teflon plates and immersed in solutions for ageing. The coating thickness was measured with digimatic micrometer and the average film thicknesses were between 60 and 70 μm .

Three immersion actions were designed, i.e., tap water (TW), 5wt% NaCl solution and 5wt% Na₂SO₄ solution respectively. The immersion actions lasted for 28 d. The test procedure is shown in Figure 1.

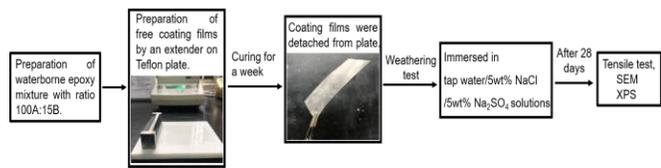


Figure 1. Schematic of testing procedure

2.2 Characterization

Tensile properties of the waterborne epoxy films were conducted by using a micro tensile test stage (Deben MICROTST), as shown in Figure 2. This device can be fixed in SEM chamber, hence microscopic failure process could be directly observed via SEM. Waterborne epoxy films were cut into the demensions of 16x8 mm² according to the size of the equipment. After both ends of the film were fixed with a secotone, tensile load accumulated at a contant speed of 2 mm/min. Three tensile tests for each waterborne epoxy film were conducted, and the average value was used to estimate tensile strength.

Scanning electro microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) was applied to obtain morphology characteristics of the samples before and after the weatherings.

X-ray photoelectron spectroscopy (XPS) with Al K α (hv=1486.6 eV) radiation in Thermo Scientific K- Alpha system was used to measure the atomic changes in the samples. The binding energy (BE) scale was regulated by setting the C1s transition at 284.80 eV.

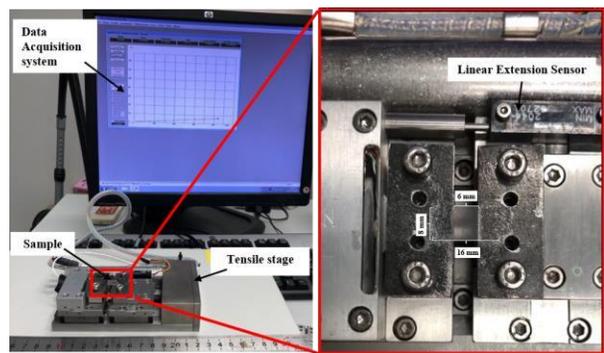


Figure 2. Experimental set up of tensile test

3. RESULTS AND DISCUSSION

3.1 Tensile behaviors

In this section, the immersion aging impact on tensile properties of the waterborne epoxy coating was investigated. Figure 3 presents the tensile process of a waterborne epoxy film after Na₂SO₄ solution immersion action observed by SEM and its stress- strain curve. The whole process can be divided into three part (see Figure 3(b)). In the early stage of loading (part A-B), the stress increases almost linearly, and as shown in Figure 3(a-1), during which the film had not been damaged. When loaded to point B, the stress reached its maximum, in where some microcracks began to appear (see Figure 3(a-2)). With continuous loading, these microcracks expanded and connected with each other (Figure 3(a-3)). During this time, the stress began to decrease, while the strain continued to increase (part B-C), and the film fractured when reached to the maximum strain.

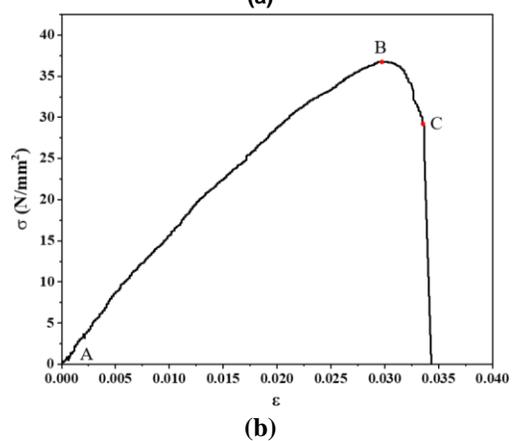
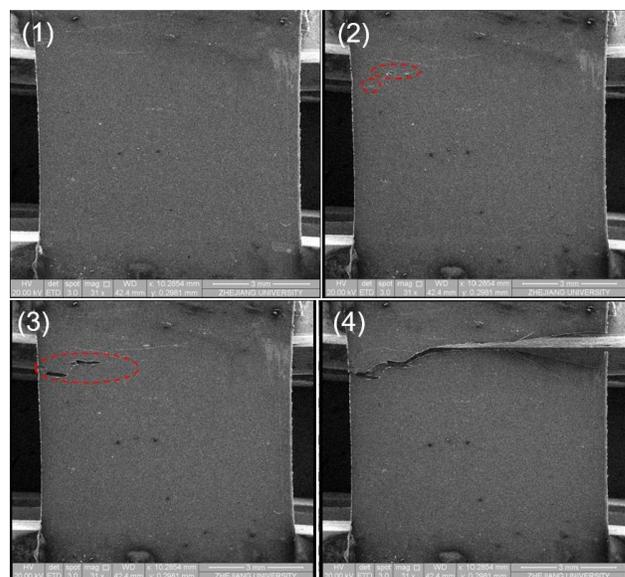


Figure 3. (a) Diagram of tensile process of a film after 28-d Na₂ SO₄ immersion observed by SEM and its (b) stress-strain curve.

The stress-strain curves of all samples after 28-d immersion are displayed in Figure 4. By comparison, it can be found that the tensile fracture mode of all immersed samples is different from those of the fresh ones. For fresh films, the strain reached the maximum when the stress reached the maximum, and then the film fractured abruptly, which is a brittle fracture mode. However, for all films after 28 days of immersion, the form of the stress-strain curve is the same as that described in Figure 3(b). This result indicates that the plasticity of waterborne epoxy film increased slightly after being immersed in saline solution.

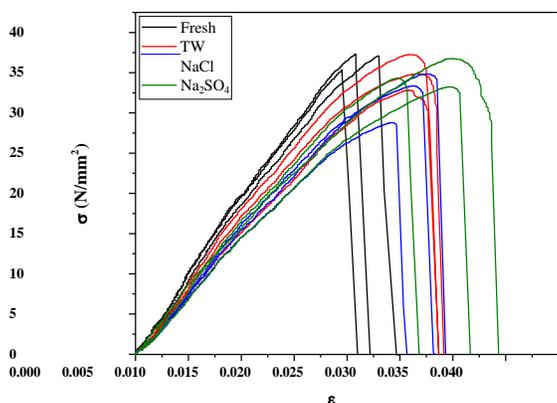


Figure 4. The stress-strain curves before and after 28-d immersion in three solutions.

In addition, the tensile strength results are summarized in Figure 5. It is interesting to find out that there is only slight change (increase or decrease) and no regular trend in tensile strength values in sample during the early stage of aging, it did not decrease as expected. This result maybe related to the enhancement of molecular cross-linking in the early aging period, and in this period, the effect of molecular cross-linking was greater than molecular bond rupture [8].

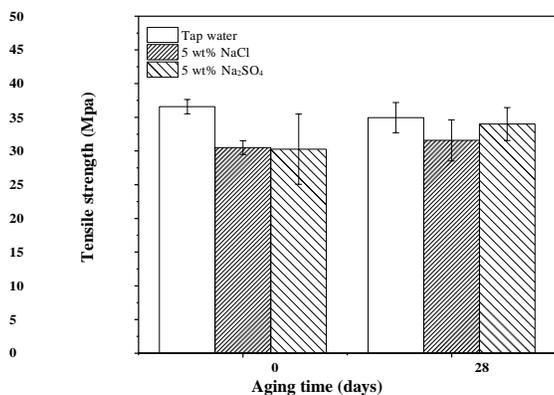
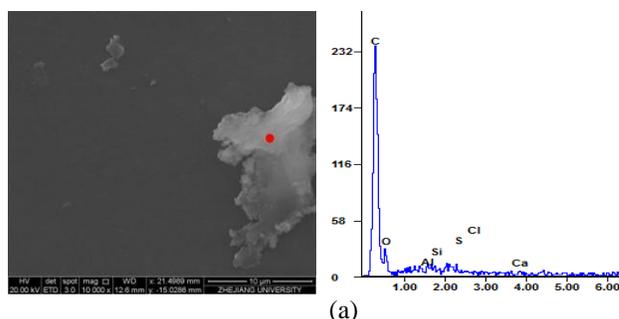


Figure 5. Tensile strength of waterborne epoxy coating

3.2 Surface morphologies

Figure 6 shows the selected SEM images to demonstrate typical changes in surface morphology of the waterborne epoxy samples before and after three immersion actions. The fresh film was relatively smooth, and no obvious defects appeared (Figure 6(a)), telling its good completeness. A large debris was observed on the fresh film, probably owing to the insufficient mixing of the A and B components. With the increase of immersion time, surface morphology changed greatly. For the sample immersed in tap water, some small blisters uniformly distributed on the surface, while no obvious changes in element distribution was observed (Figure 6(b)). For the sample immersed in 5 wt% NaCl solution (Figure 6(c)), in addition to dense blisters on the surface, NaCl crystals nucleated somewhere and grew to salt flowers. Similar observation can also be found in [7]. For the sample immersed in 5 wt% Na₂SO₄ solution, some large Na₂SO₄ crystallization were observed and detected (Figure 6(d)). Blistering on the surface of an organic coating was widely reported for the material under immersion actions. Corrosive ions in water (such as OH⁻, Na⁺, Cl⁻, SO₄²⁻, etc.) can pass through the open channels and/or defects in the coating, then osmotic pressure will rise between the corrosive products and corrosive medium. Swelling occurs to local areas of the material, so blister takes place [9]. In NaCl solution, the salt concentration has a non-negligible effect on water uptake and polymer swelling, which can be attributed to the crystallization effect. In the immersion environment, NaCl solution can penetrate into the micropores or cracks of epoxy; as the water is progressively dried out, NaCl supersaturation begins to crystallize at these places [7]. In this paper, NaCl crystals filled and grow in blisters, resulting in the growth of these blisters.



(a)

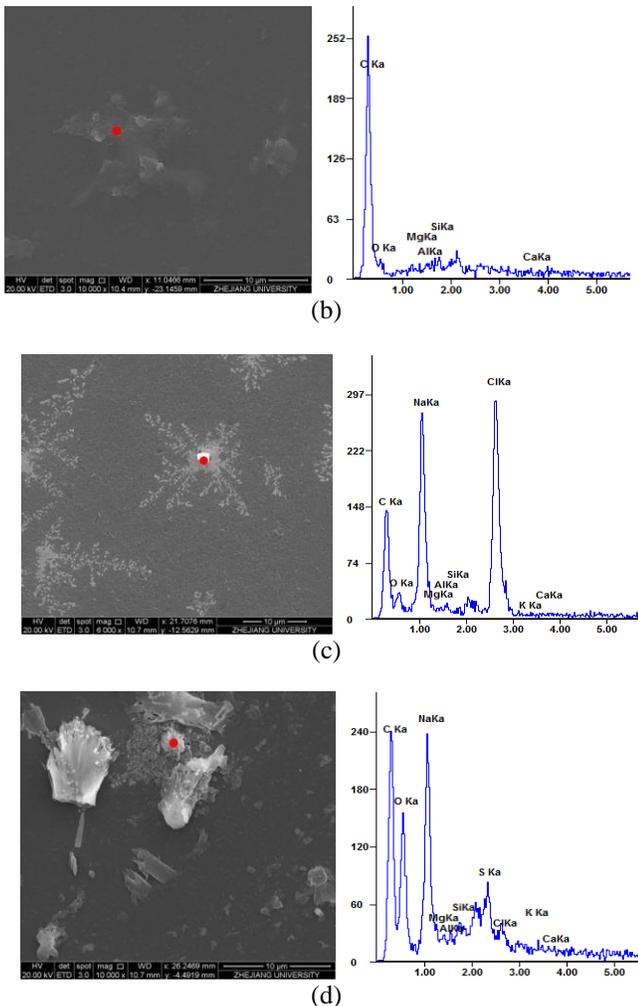


Figure 6. SEM-EDS images of the waterborne epoxy samples before and after 28-d immersion in three solutions: (a) fresh sample, (b) tap water, (c) 5 wt% NaCl solution, and (d) 5 wt% Na₂SO₄.

3.3 Chemical changes

XPS was used to investigate the molecular structure of the waterborne epoxy after the immersions. Figure 7 shows the full survey spectra of different samples, where the characteristic atomic percentages and the atomic ratios are summarized in Table 1. In all samples, three obvious peaks were detected at 285.3 eV (C1s), 532.7 eV (O1s), and 399.8 eV (N1s). After 28-d immersion, the relative content of C decreased obviously, while those of O and N increased substantially. As expected, Na and Cl were detected for the sample after the NaCl solution immersion, and Na and S were probed in the sample at the Na₂SO₄ solution immersion. The O/C and N/C ratios increased from 0.163 and 0.018 to 0.249 and 0.051, respectively, for the tap water aging, to 0.211 and 0.029 for the NaCl solution aging, and to 0.239 and 0.029 for the Na₂SO₄ solution aging. The increase of O/C and N/C ratios indicated that the progressive polymerization with time and depolymerization with the immersion actions. The increase of O/C

ratio might be related to the following reasons: (1) Corrosive ions (such as OH⁻, and SO₄²⁻), H₂O and O₂ diffuse into the coating through the micropores and defects [9]; (2) Etheric linkage (-C-O-C-) contained in epoxy coating that is sensitive to water will hydrolyze to form hydroxyl groups or hydroxymethyl [10]. Note that the increase of N/C ratio is relatively subtle, because the element “N” comes from the epoxy curing agent, thus the changes in this ratio is mainly related to the cross-linking reaction of the epoxy during the curing process. And as for sample in tap water, part of the increase in “N” may also come from impurities in water.

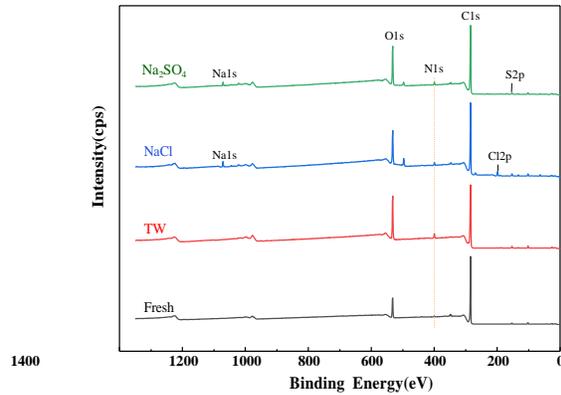


Figure 7. XPS full spectrum analysis before and after 28-d immersion in three solutions: (a) fresh sample, (b) tap water, (c) 5 wt% NaCl solution, and (d) 5 wt% Na₂SO₄.

Table 1. Atomic percentages of epoxy surfaces before and after 28-d immersion actions

Sample	Atomic Percentage/%					Atomic Ratio	
	C1s	O1s	N1s	Na Cl2p	S 2p	O/C	N/C
Fresh	84.63	13.82	1.55	-	-	0.163	0.018
TW	76.9	19.18	3.92	-	-	0.249	0.051
NaCl	78.01	16.45	2.28	1.27	1.99	0.211	0.029
Na ₂ SO ₄	77.74	18.56	2.28	0.8	-	0.239	0.029

Elaborate analysis on the C1s spectrum was performed in Thermo Avantage software to specify the changes in chemical group of C. Figure 8(a-d) presents the C1s spectra of all samples between 292 and 282 eV and the deconvolution curves. As shown in Figure 8, four main peaks to the C1s spectra at the binding energy of 289.1 eV, 288.2 eV, 286.3 eV, and 284.8 eV were resolved, corresponding to carboxyl (COO), carbonyl (C=O), hydroxyl (C-O), and aliphatic (C-H/C-C) carbon, respectively [11]. Analysis revealed that the aliphatic carbon group (85%) was dominative in the waterborne epoxy sample, while the hydroxyl group (11.99%), carbonyl (1.33%) and carboxyl (1.88%)

groups occupied limited contents. After the immersion actions, the percentages of C-C/C-H, C-O and C=O content changed greatly. As shown in Figure 8(c) and Figure 8(d), the NaCl and Na₂SO₄ immersion actions reduces the C-C content to 78.91% and 73.97%, but raised the C-O content to 15.55% and 13.45%, and the C=O content increased to 3.01% and 9.7%, respectively. The tap water immersion showed the similar trends in these chemical groups, and the extents were enhanced (Figure 8(b)). Results of Figure 3 suggested that the chemical structure of the waterborne epoxy coating has changed under the immersion actions.

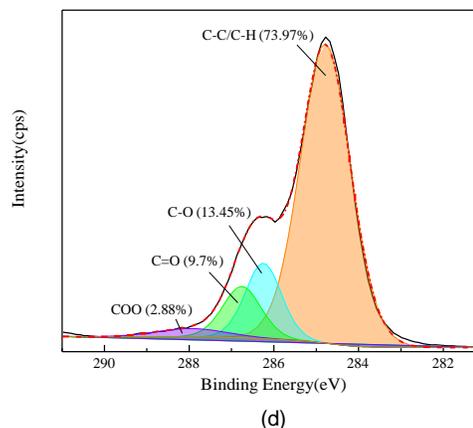
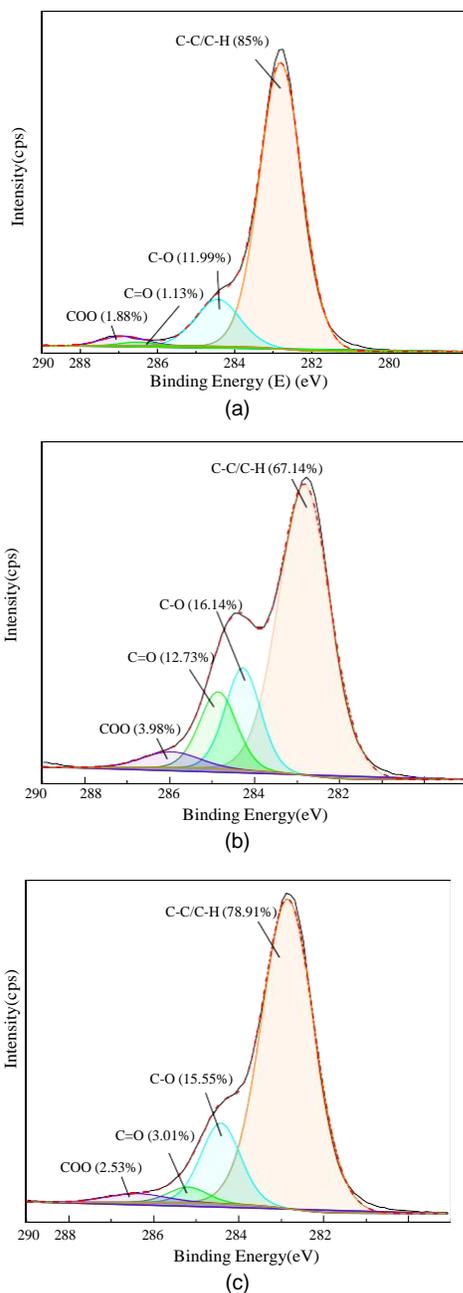


Figure 8. Deconvolution of C1s spectra of all samples: (a) fresh, (b) immersed in tap water, (c) immersed in 5 wt% NaCl solution, and (d) immersed in 5 wt% Na₂SO₄ solution.

4. CONCLUSION

In this paper, the tensile behaviors of a waterborne epoxy coating film immersed in tap water, chloride solution and sulfate solution were studied. After immersion, the coating film has gained a little plasticity. However, the immersion actions would not decrease the tensile strength of the waterborne epoxy samples. SEM observations indicated the blisters of all samples after immersion. Moreover, salt crystallization took place on the samples immersed in NaCl and Na₂SO₄ solutions. XPS evidenced the significant changes in chemical groups when the waterborne epoxy samples experienced 28-d immersion actions. Further rigorous investigations on the longterm engineering performances of epoxy coatings after immersion actions are required.

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