DETERIORATION OF ORGANIC COATINGS ON CONCRETE UNDER ARTIFICIAL AGING

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Abstract

The deterioration of organic coatings on concrete is closely linked to the efficiency in the protection process of reinforced structures. In the present work, polyurea resin and epoxy resin, which are widely used engineering coatings, were selected to measure and compare the performance under artificial aging. Fourier Transform infrared spectroscopy, water contact angle and scanning electron microscope were used to determine the deterioration of coatings. X-ray fluorescence method was used to measure chloride content passing through the coatings, which represent the efficiency of protection. Test results demonstrate that both deterioration and resistance to corrosion are important in assessment of the organic coatings under aging.
Keywords: organic coating, concrete, artificial ageing, efficiency

1. INTRODUCTION

Reinforced concrete structures in harsh environments, such as hypersaline environments or circumstances with large difference in temperature or humidity, have already drawn special attention worldwide. The corrosion of steel materials, embedded in alkaline concrete with a passivation film, are considered as the significant part in structure failure. On the other hand, various durability improvements are proposed in order to prevent this essential position from the erosion outside.

Amelioration of reinforced structure can be divided into three main types focusing on different parts. First, fiber-reinforced polymer bars[1], epoxy coated reinforcement[2], or corrosion inhibitors[3] were adopted to enhance the quality of bars. Second, various methods were used in order to improve the performance of concrete, mainly aiming at a better hole

structure and enhanced compactness, including employing better raw materials or mineral admixtures, using high performance admixtures or other active control of properties of concrete[4]. Third, surface treatments including organic or inorganic coatings, hydrophobic impregnation or pore-blocking surface treatment are aiming at establishing a barrier resisting the corrosion[5]. Under comprehensive consideration of economy, construction convenience and repeatable implementation, organic coatings have great advantages in durability enhancement of situ reinforced concrete. Almusallam A. A. et al[6] showed that the chloride diffusion coefficient for polyurethane coated concrete was about 10 times smaller than uncoated concrete.

However, as mentioned in[7], the service life of organic coating is much shorter than that of structures. Organic materials are more vulnerable to severe environment including ultraviolet light irradiation, temperature variation, water invasion or other environmental factors. Also, decreased interface properties or more serious de-bonding will result in descending properties of coating efficiency. Many researches have focused on deterioration of organic coatings under different situations[8, 9, 10]. Researches are limited concentrating on the relations between different deterioration degree and efficiency.

In order to reflect the influence of deterioration under artificial aging on the protective performance, two kinds of organic coatings are used in this research. After being treated in artificial ageing environment, various changes of coatings including chemical structures and physical properties are measured and analyzed. Efficiency of resistance to chloride content, or called protective performance of organic coatings are also studied mainly focus on the resistance to chloride ions.

2. EXPERIMENTAL

2.1. Materials and mix proportions

Two kinds of commercial organic coatings were employed in this research, epoxy resin and polyurea resin produced by SOBUTE NEW MATERIALS CO.,LTD, and both of these types are widely used concrete coatings. Coatings were applied on the paste surface or the metal base for the convenience of different tests respectively. The water-to-cement ratio of paste samples is 0.35 and commercial PII.52.5 Portland cement, tap water and polycarboxylic acid type superplasticizer were used in the paste casting. Mix design was shown in Table 1. Paste samples of size 40mm×40mm×160mm were made to measure chloride content. After 28-days standard curing, paste samples were treated to surface dry condition and polished with sandpaper for coating. Metal base used in this paper were 10mm×10mm×1mm sized 304 stainless steel square plates, which were used to evaluate the self-structure changes of organic coatings. Coatings were applied to cleaned concrete or metal base by SZQ-400 film equipment and cured at 23 ± 1℃ and 40% relative humidity for 144h until weight constant.

Table 1: Concrete mix design

Mix components	Water	Cement	Water reducer
Weight (kg/m^3)	156	450	2

2.2. Artificial aging process

Accelerated aging tests for coatings samples were carried out by using a home-made ageing box shown in Fig.1, in which irradiation intensity in different parts has been tested to be uniformly distributed. In order to avoid rapid temperature changing, spray humidification was employed in the condensation system rather than direct water cooling. Remote status monitoring and remote control are available for this ageing box. The ageing process included 4 hours of UVB lamp irradiation and 4 hours of condensation. Irradiation wavelength concentrated at 340nm with average radiation intensity was 12 W/m^2. During the weathering process, the temperature increased from room temperature (RT) to 49℃ in the irradiation stage and decreased to RT in the condensation stage periodically.

Figure 1: The home-made ageing box

2.3. Performance assessment

A series of tests were carried out to characterize the degradation process of organic coatings during aging and test can be divided into three parts: chemical changes, physical changes and efficiency changes.

To determine the chemical changes over aging, Fourier Transform infrared spectroscopy (FTIR) was conducted using Thermo Scientific Nicolet iS10 under Attenuated Total Refraction (ATR) mode. Pieces of coatings around 1 cm2 were used and FTIR spectra were recorded in a range of 400 cm^{-1} to 4000cm^{-1}, with 4 cm^{-1} as scanning resolution.

Hydrophilicity of the coating surfaces was tested by observing the wettability of the methyl

blue aqueous solution on coatings. Nikon D7200 N1406 with a 25mm f/2.8 2.5-5X Ultra-Macro lens was adopted to take photographs. Then water contact angles were measured according to these photographs.

The morphology of both surface and cross-section of coatings was observed using FEI Quanta 3D scanning electron microscope (SEM). Samples less than 1cm^2 were cleaned by compressed clean air and sprayed gold particles on observed side with. It is worth mentioning that cross-section samples were made by dip organic coatings into liquid nitrogen and broken with tweezers. This step of sampling was to obtain natural fracture cross-sections.

In order to evaluate the efficiency of coatings, paste samples which applied coatings (all other surfaces are sealed using epoxy resin) were immersed into 10wt% sodium chloride solution for 960 hours. After immersion, coatings were removed and powders were obtained by milling the paste samples (within 1mm). X-ray fluorescence method was used to measure chloride content in paste samples by using ThermoFisher ARL Perform X 4200.

3. RESULTS AND DISCUSSION

3.1. Deterioration

3.1.1. Chemical structure changes

Figure 2 shows the FTIR of coatings before and after aging. From Fig. 2, chemical structures were nearly unchanged in polyurea resin before and after aging. This suggest that polyurea has kept its stability of functional groups under ultraviolet aging. As shown in Fig. 2, it is illustrated that the transmittance around 3300cm-1 of epoxy resin becomes border and lower after aging 1440 hours, which represents the increased hydroxyl group. During the aging process, epoxy resin shows a worse chemical stability than polyurea resin and then a worse resistance.

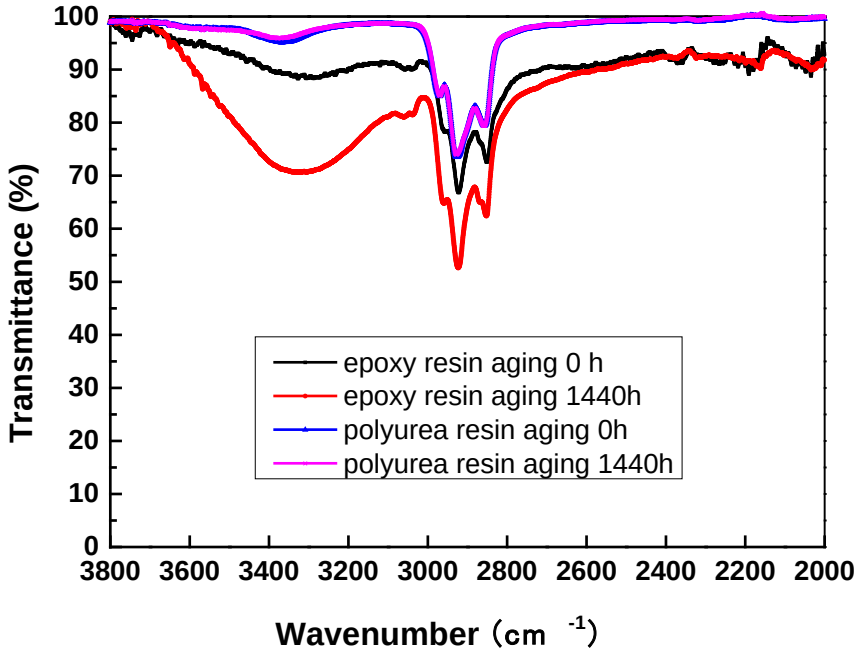


Figure 2: ATR-FTIR measurements in transmittance of coatings over aging

Table 2: Water contact angle of coatings over aging

	Aging 0h	Aging 1440h
Polyurea resin	80.1°	50.2°
Epoxy resin	53.6°	17.1°

3.1.2. Hydrophilicity test

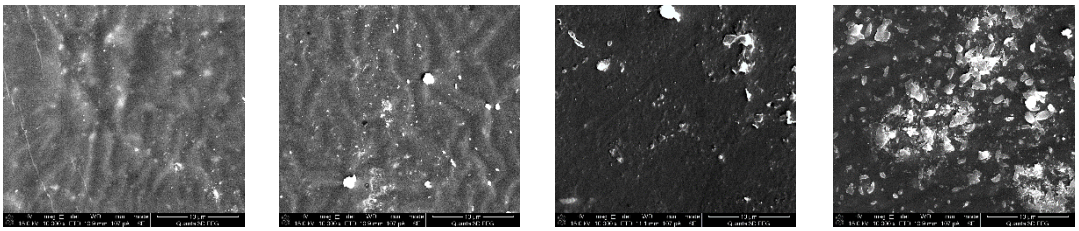
Table 2 shows the water contact angle of coatings before and after aging. The water contact angle of both polyurea coatings and epoxy resin coatings decreased after aging 1440 hours. This demonstrates that the hydrophobicity of coating decreased and water will enter into coatings easier. The hydrophobicity of epoxy resin decreased quicker, which can be associated with the worse chemical stability (increased polar functional groups) observed by FTIR.

3.1.3. Scanning electron microscope

Figure 3. shows the SEM morphology pictures of coating surface exposed to UV agin environment. It can be observed that after 1440 hours aging, defects appear obviously and the surface of epoxy resin turns to be rougher with some chalking phenomenon. The vulnerable surface of epoxy resin is consistent with its fragile chemical structure.

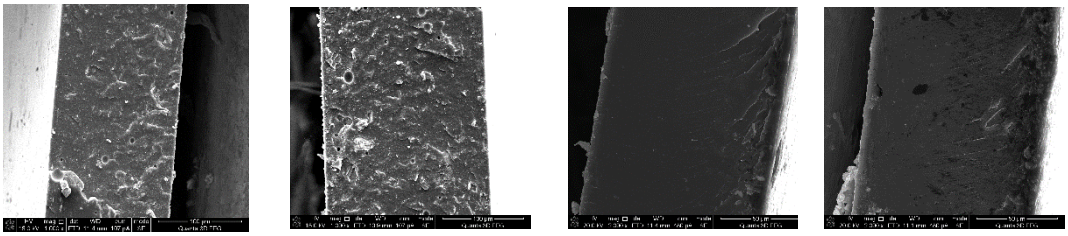
On the opposite situation, there is no obvious change of polyurea resin over aging under the SEM shown in Fig. 3 (b).

Figure 4. demonstrates the morphology pictures of cross-section of coatings. The same as the surface observation, polyurea resin keeps its stability before and after aging while deterioration occurs in epoxy resin. Defects are obvious in the epoxy resin, especially at the exposed side of the epoxy coating (right side in Fig. 4(d)), which may resulting in poor corrosion-resisting performance.



(a) 0 hours aged (b) 1440 hours aged (c) 0 hours aged (d) 1440 hours aged

Figure 3: SEM images of coating surface
(a)(b): Polyurea resin; (c)(d): Epoxy resin



(a) 0 hours aged (b) 1440 hours aged (c) 0 hours aged (d) 1440 hours aged

Figure 4: SEM images of coating cross-section
(a)(b): Polyurea resin; (c)(d): Epoxy resin

3.2. Chloride resistance

Table 3 shows the chloride content in paste near the surface. It is obvious that coatings (whether aging or not) can reduce the chloride content significantly. Polyurea resin exhibits worse after aging which is different from the performance in the deterioration characterize. This can be explained by the weak-interface between polyurea and samples. On the other side, the slight decreases of chloride content in aged epoxy resin sample may associate with the radical recombination[11].

Table 3: The chloride content in paste surface tested by XRF

Paste	No coating	Epoxy	Epoxy	Polyurea	Polyurea
samples		resin (0h)	resin(960h)	resin (0h)	resin(960h)
The chloride content (wt%)	3.580	0.127	0.117	0.017	0.369

4. CONCLUSIONS

In this study, deterioration and efficiency of coatings under artificial aging is being studied. Two kinds of coatings including epoxy resin and polyurea resin were used in order to make comparison. Under the aging process consisting ultraviolet irradiation, thermal-cycle and wet-dry-cycle, the rate of degradation of polyurea resin is slower than epoxy resin, indicating that polyurea resin is more suitable for top layer coating. However, in the chloride resistance test, aged polyurea resin exhibits poor resistance to chloride. While combining the results of deterioration and protective performance experiments, both sides should be taken into consideration in evaluation the coatings under aging on concrete surface.

REFERENCES

[1] Hollaway, L. C., A review of the present and future utilisation of FRP composites in the civil infrastructure with reference to their important in-service properties. *Construction and Building Materials* **2010,** *24* (12), 2419-2445.

[2] Kondratova, Ş. E. T. W. B. I. L., Accelerated testing of plain and epoxy-coated reinforcement in simulated seawater and chloride solutions. *Cement and Concrete Composites* **2001,** *31* (6), 861-867.

[3] Ormellese, M.; Berra, M.; Bolzoni, F.; Pastore, T., Corrosion inhibitors for chlorides induced corrosion in reinforced concrete structures. *Cement and Concrete Research* **2006,** *36* (3), 536-547.

[4] De Schutter, G.; Lesage, K., Active control of properties of concrete: a (p)review. *Mater Struct* **2018,** *51* (5), 123.

[5] Pan, X.; Shi, Z.; Shi, C.; Ling, T.-C.; Li, N., A review on concrete surface treatment Part I: Types and mechanisms. *Construction and Building Materials* **2017,** *132*, 578-590.

[6] Almusallam, A. A.; Khan, F. M.; Dulaijan, S. U.; Al-Amoudi, O. S. B., Effectiveness of surface coatings in improving concrete durability. *Cement and Concrete Composites* **2003,** *25* (4-5), 473-481.

[7] Rodrigues, M. P. M. C.; Costa, M. R. N.; Mendes, A. M.; Marques, M. I. E., Effectiveness of surface coatings to protect reinforced concrete in marine environments. *Materials and Structures* **2000,** *33* (234), 618-626.

[8] Bhargava, S.; Kubota, M.; Lewis, R. D.; Advani, S. G.; Prasad, A. K.; Deitzel, J. M., Ultraviolet, water, and thermal aging studies of a waterborne polyurethane elastomer-based high reflectivity coating. *Progress in Organic Coatings* **2015,** *79*, 75-82.

[9] Gheno, G.; Ganzerla, R.; Bortoluzzi, M.; Paganica, R., Accelerated weathering degradation

behaviour of polyester thermosetting powder coatings. *Progress in Organic Coatings* **2016,** *101*, 90-99.

[10] Yang, X. F.; Li, J.; Croll, S. G.; Tallman, D. E.; Bierwagen, G. P., Degradation of low gloss polyurethane aircraft coatings under UV and prohesion alternating exposures. *Polymer Degradation and Stability* **2003,** *80* (1), 51-58.

[11] Liu, F.; Yin, M.; Xiong, B.; Zheng, F.; Mao, W.; Chen, Z.; He, C.; Zhao, X.; Fang, P., Evolution of microstructure of epoxy coating during UV degradation progress studied by slow positron annihilation spectroscopy and electrochemical impedance spectroscopy. *Electrochimica Acta* **2014,** *133*, 283-293.