

Accelerated Degradation of Coating-mortar Interface under UV Radiation in Presence of Water

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Abstract. *The application of organic coatings is one of the most effective and economic methods to protect concrete structures from deterioration. However, organic coatings are prone to degradation under aggressive environmental actions, so the protective function may loss. While ultraviolet (UV) aging is often blamed for the degradation of organic coatings, water may play a more important role on the interfacial adhesion between the coatings and the substrate. To uncover the effect of water on the degradation performance of coating-substrate system, mortar samples coated with water-borne epoxy resin (WER) were exposed to three assigned environments, i.e., UV radiation, UV/water immersion, and UV/dry-wet cycle, up to 60 days. The surface appearance, chemical structure, wettability, and surface micro-morphology of the aged WER coatings were characterized via image process analysis, attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR), static water contact angle, and scanning electronic microscopy (SEM). Results show that the UV/water immersion resulted in severest blistering on the WER-mortar interface, while the UV/wet-dry cycle caused the formation of micro-pinholes on the WER surface. In contrast, the UV radiation did not induce such severe aging. The data implied that water can accelerate the aging of WER-mortar system.*

Keywords: *Organic Coatings, Degradation, Water, UV, Cement Mortar, Interface.*

1 Introduction

Concrete is a heterogeneous porous material containing weak phases, such as, pores and micro-cracks, that allow the migration of harmful species (Zeng et al., 2021). As one of protective methods, organic polymer coatings are commonly used as the repairing and protective materials as they may compensate for the weakness of conventional cement-based materials (De Muynck et al., 2009, Al-Zahrani et al., 2003). Among the various types of organic polymers, epoxy resins are widely used as primer coating by virtue of their excellent properties including good chemical resistance, low shrinkage and high adhesion (Khotbehsara et al., 2020). The attachment of organic coatings on concrete surface can form a hydrophobic layer that acts as a physical barrier to prohibit the ingress of water, chloride ions and other corrosive substances from the external environments into the concrete (Pan et al., 2017, Sakr and Bassuoni, 2021).

Nevertheless, organic polymers may degrade when subjected to some weathering aging factors, such as ultraviolet (UV) radiation, oxygen, water, and temperature, so the protective performances are decreased (La Mantia et al., 2017). In the atmospheric environment, in addition to UV aging, water makes non-negligible contribution to the degradation of organic coatings in various forms such as immersion, rainfall and humidity etc (Jacques, 2000). Therefore, it is necessary to explore the effect of water on the degradation performance of organic coating as well as the interfacial bonding of coating-substrate.

In this work, cement mortar was used as substrate coated with waterborne epoxy resin

(WER), and exposed to UV radiation, UV/wet-dry cycle and UV/water immersion environments, up to 60 days. Water contact angle was used to evaluate the change of wettability. ATR-FTIR and SEM techniques were applied to monitor the morphological and chemical changes.

2 Materials and Methods

2.1 Materials

A Portland cement (PI 42.5 according to Chinese cement standard, identical to type I cement of ASTM C 150/C 150M) supplied by China Building Materials Academy Co., LTD was used in the present study. And A type of standard graded sand with the fineness of 2.6 was used as the fine aggregate.

Owing to the growing environmental pressure to minimize the application of solvent-based coatings, it has gradually become a trend to replace traditional coatings with new water-based coatings (Sun et al., 2020). Hence, an AB-type waterborne epoxy resin (WER, 881-WD02) was selected as coating provided by Avic New Material Co., LTD, and its density and volumetric solid content are 1.08 g/ml and 30% respectively. The component A is an epoxy resin latex, and the component B is a modified water-soluble aminated hardener. The WER coating (in a liquid form) was prepared by mixing the A and B components in 100:40 proportion by weight.

2.2 Sample Preparation and Accelerated Aging Exposure

Mortar specimens with a size of 70×70×70 mm³ were fabricated with a constant mass ratio of 1 : 2: 4 for water, cement, and sand. After demolding, mortars were kept at standard curing room (95±5% RH). At 28 d, mortars were removed from curing room and then cut into slices with a thickness of 7 mm for applying WER coating. The coating was applied uniformly to the surface of the specimens with a brush, and a controlled gravimetric method was used to ensure that all the coatings remained approximately the same thickness after hardening (around 100-150 μm). It took approximately 7 days for coating to completely hardening, after that, specimens were exposed into accelerated environments for aging.

To explore the role of water played during aging process, specimens were exposed to three assigned environments, i.e., UV radiation ($\lambda=340$ nm, $I=0.89$ W/(m²·nm)), UV/dry-wet cycle, and UV/full immersion (marked as UV, UV/cycle and UV/full, respectively). The UV exposure cycle consists of 8 h of UV irradiation at 60 °C followed by 4 h of condensation at 50 °C according to ASTM D4587 (International, 2019). And the specimens were collected periodically up to about 60 days.

2.3 Characterization

In order to study the chemical changes on the surface of aged coatings, FTIR was adopted using Thermo Scientific Nicolet iS10 with ATR mode. FTIR spectra were recorded in a range of 600 cm⁻¹ to 4000 cm⁻¹, with a resolution of 4 cm⁻¹.

Water contact angle analysis is used to assess the wettability of WER coatings. Water droplet around 5 μL was carefully applied on the surface of unaged and aged samples.

SEM test was applied for analysis of the microstructure of coatings before and after the aging. Experiments were carried out using a device of thermal field emission microscope (GeminiSEM

300) with an acceleration of voltage of 15 keV and spot size of 1.8.

3 Results and Discussion

3.1 Surface Appearance Changes

Figure 1 shows the surface appearance of coated mortars under different aging conditions after 60 days. Compared to the unaged samples (Figure 1a), no obvious changes were observed on the appearance of samples in UV (Figure 1b) and UV/cycle (Figure 1c). However, apparently, severe blistering occurred on the surface of samples in UV/full (Figure 1d). Moreover, it can be observed that the blistering led to the debonding at the coating-mortar interface, as shown in Figure 1e. The blistering on the surface may be related to the combined actions of the water inside of the coating and the water in the pores of mortar substrate. On the one hand, polymer coatings will be hydrolyzed in the immersion environment. The distribution and the state of water in the coating will change during the long-term water diffusion process, resulting in the physical structure changes of the coating (Bouvet et al., 2016). In addition, the water molecules may react with the polar functional groups, leading to the recombination of polymer chains and changing the chemical structure of the coating, resulting in swelling phenomenon (Bouvet et al., 2016, Yang et al., 2002). On the other hand, the water molecules in the pores of the mortar substrate were heated at a higher ambient temperature and generated thermal motion, which may result in an upward expansion act on the coating (Luo et al., 2023). Therefore, these two actions of water may lead to the debonding at the coating-mortar interface.

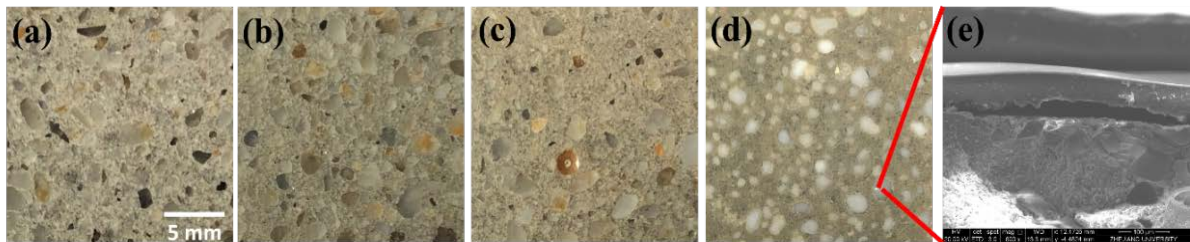


Figure 1. Appearance images of coated mortar surface before and after 60 days of aging: (a) unaged, (b) UV, (c) UV/cycle, (d) UV/full and (e) cross-sectional SEM image of blistering.

3.2 Surface Micro-morphology Analysis

Figure 2 displays the micro-morphology of WER coating surface before and after aging. The fresh sample was relatively smooth, and no obvious defects appeared (Figure 2a), telling its good completeness. For the samples exposed to just UV radiation (Figure 2b), micro-cracks were observed clearly on the coating surface. Similar observation can also be found in (Al-Turaif, 2013), referring it to as sliver cracks. However, with the presence of water, the coating surface morphology changed greatly. For samples exposed to UV/cycle condition (Figure 2c), numbers of micron-sized pinholes appeared on the coating surface, and severe area may lead to chalking phenomenon. For samples exposed to UV/full immersion condition (Figure 2d), a few of holes unevenly distributed on the coating surface, along with some salt crystallizations (ions from tap water).

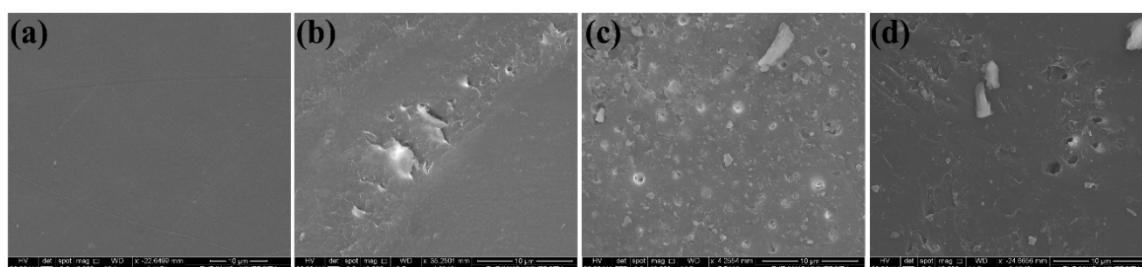


Figure 2. SEM images of WER coating surface before and after 60 days of aging: (a) unaged, (b) UV, (c) UV/cycle, and (d) UV/full.

3.3 Wettability Changes

Water contact angle (WCA) of coatings was measured to monitor the changes in wettability on coating surfaces after aging. Figure 3 shows the results of the WCA variations and the photographs of droplets on surface of samples under different condition after 60-d aging. As can be seen from the figure, compared to the unaged sample, water droplets spread out in a great degree. The average value of WCA decreased from 86.9° (unaged) to 65.3° (UV), 74.1° (UV/cycle) and 52.6° (UV/full), respectively, suggesting that three aging environments can lead to the significant increase in the hydrophilicity of WER coating.

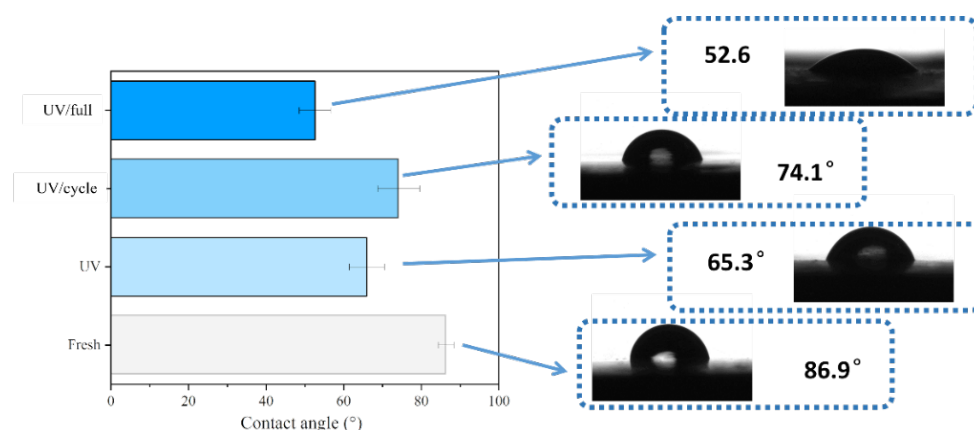


Figure 3. Results of WCA under different aging conditions before and after 60 days.

3.4 ATR-FTIR

FTIR spectroscopy was used to investigate the changes in chemical structure of WER coating before and after aging. Figure 4 exhibits the typical results of samples subjected to UV radiation for different aging time. For fresh WER coating, the stretching vibrations of C-H bonds from methylene groups, C=C bonds from aromatic rings and C-O bonds connected with benzene appeared at $2800\text{--}2950\text{ cm}^{-1}$, 1607 cm^{-1} and 1245 cm^{-1} , respectively. The broad peak centered at around 3362 cm^{-1} and the one in the range of $1000\text{--}1100\text{ cm}^{-1}$ were assigned to the stretching vibrations of O-H bonds and C-O-C linkages, respectively, as shown in Figure 4a. As increasing aging time, new peak around 1703 cm^{-1} appeared gradually, which was the carbonyl group in saturated aldehyde, ketone or acid (Figure 4b) (Wang et al., 2020). Moreover, after aging, the

peak of amide group gradually moved to a high wavenumber, and its intensity and width were also increased over time (Figure 4b), implying that hydroxyl, carbonyl and amide groups were more sensitive to UV radiation.

Figure 5 shows the chemical structure changes in the presence of water after 60-d aging. Compared to fresh coating, after aging 60 days, the FTIR spectra under different aging environment altered to some extent (Figure 5a). In addition to the change of hydroxyl groups, the change of amide groups affected by water was significant. As shown in Figure 5b, the amide peaks of UV and UV/ cycle were obvious and with relatively high intensity, while the amide peak of UV/full was very slight. These results indicated that the full immersion environment can weaken UV radiation to a certain extent.

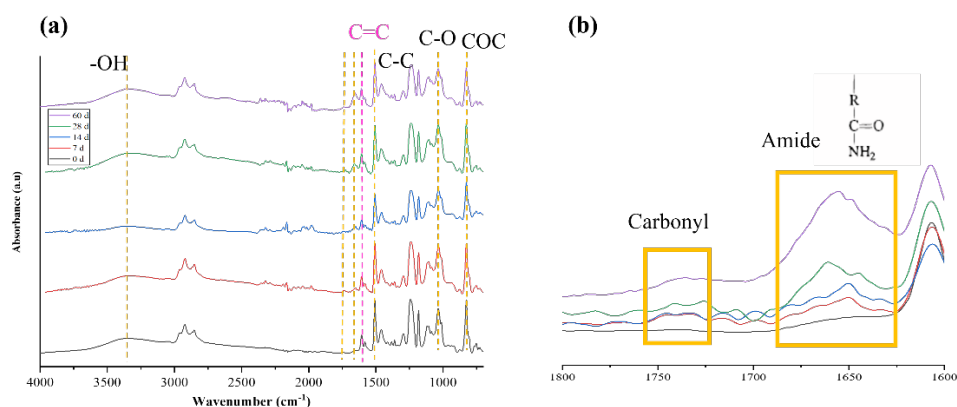


Figure 4. ATR-FTIR spectra of WER coating exposed to UV radiation for different aging time: (a) Full scale spectra and (b) enlargement region from 1800cm^{-1} to 1600cm^{-1}

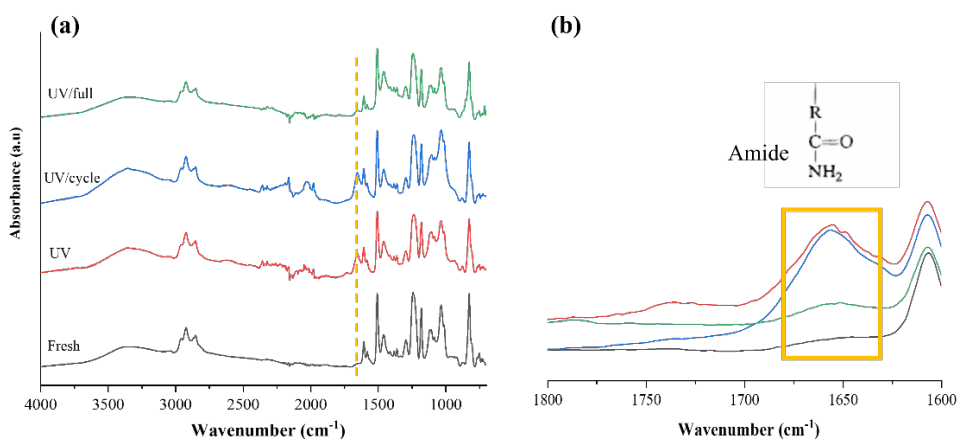


Figure 5. ATR-FTIR spectra of WER coating exposed to different aging conditions after 60 days: (a) Full scale spectra and (b) enlargement region from 1800cm^{-1} to 1600cm^{-1}

4 Conclusions

In this paper, the role of water played on degradation of WER coating-mortar system during UV radiation was studied. The surface appearance, wettability, micro-morphology and

chemical changes were comprehensively analyzed. The main conclusions can be drawn as follows:

- UV/water immersion caused the most severe blistering, resulting in debonding at coating-mortar interface and increase of the hydrophilicity of coating. The interfacial debonding was mainly attributed to the hydrolysis and swelling of water inside coating, meanwhile, the hydrothermal expansion action of water in pores of mortar substrate was another main reason. Additionally, the full immersion environment can weaken UV radiation to a certain extent.
- UV/ wet-dry cycle led to numbers of micron-sized pinholes on the coating surface, while just UV radiation did not induce such severe aging performance, implying that the wet-dry cycle environment may accelerate the aging of the WER coating.

Acknowledgements

The authors greatly thank the financial support from the National Natural Science Foundation of China (No. 52038004).

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