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Improvements of Nano-TiO_2 on the Long-Term Chloride Resistance of Concrete with Polymer Coatings

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Abstract: The long-term chloride resistance of concrete treated with nano-TiO_2-modified polymer coatings was studied. Three types of organic film-forming paints: polyurethane, epoxy resin, and chlorinated rubber were selected, and concrete specimens with nano-TiO_2-modified coatings were fabricated. Then, specimens were subjected to periodical ultraviolet-accelerated aging and subsequent Coulomb electric flux experiments. Nanomodified coatings before and after ultraviolet aging were observed through scanning electron microcopy. Results indicate that the nano-TiO_2 particles can effectively reduce the microdefects in coating films and alleviate damages due to aging. As a result, nano-TiO_2 can significantly reduce the Coulomb fluxes of coated concrete before and after coating aging, and the average reduction amplitudes reached 66% and 44%. That is, nano-TiO_2 can remarkably improve the long-term chloride resistance of coated concrete. In addition, we established the development models of the ultraviolet aging and chloride resistance of coated concrete according to an S-shaped curve.

Keywords: concrete; polymer coatings; nano-TiO_2; chloride resistance; aging

1. Introduction

The long-term performance of concrete structures in marine environments has always been a concern, and the application of polymer coatings is one of the effective measures to solve such a problem [1]. Polymer coatings can form consecutive dense films on concrete surfaces to prevent the invasion of external aggressive agents [2–5]. Using these coatings evidently improves the resistance of concrete against chloride ion penetration relative to common concrete surface treatments, such as hydrophobic impregnation or pore blocking [6,7]. However, polymer coatings often show poor resistance to aging [8–11]. Therefore, enhancing the long-term performance of organic polymer coatings has been an urgent task in concrete surface protective treatments.

Nanoparticles have been widely used in many fields, including food, medicine, pharmacy, chemical and biological testing, manufacturing, building materials, and coatings [12–25]. Zhang et al. [15], Bagherzadeh and Mahdavi [16], and Cheng et al. [17] indicated that nanomaterials can greatly improve the strength, toughness, ductility, impermeability, corrosion resistance, and wear resistance of polymer coatings for metal protection. Feng et al. [18] investigated the weather resistance of nanomaterials in latex paints and found that nano-TiO_2 particles absorb and scatter ultraviolet rays and thus inhibit aging. Xia et al. [19] studied the corrosion resistance of graphene/epoxy composite coatings under γ-ray irradiation. Their results showed that graphene acted as a radical scavenger and prevented damage by γ-ray irradiation.

Nanomaterials have also been used in concrete coatings for durability enhancement. Leung et al. [20], Woo et al. [21], and Scarfato et al. [22] showed that nanoclay in polymer paints substantially improves protection in concrete, especially against moisture permeation, chloride ion penetration, salt attack, surface water repellency, and color change. Liao et al. [23] and Li et al. [24] investigated the effect of adding nano-SiO_2 or nano-TiO_2 on the property of epoxy resin coatings and observed that the materials effectively improve the hydrophobicity of coated concrete. Li et al. [25] also conducted carbonation experiments on concrete with nano-SiO_2 modified polymer coatings after artificial and natural climate aging. They found that nano-SiO_2 modified polymer coatings can markedly enhance the long-term effectiveness of concrete carbonation resistance.

As shown above, nanomaterials may improve the long-term performance of polymer coatings. However, studies involving nanoparticles in polymer coatings for concrete protection remain limited, particularly studies about the quantitative effects of aging on the performance of coated concrete [1,26]. This study is part of the work that focuses on the influences of polymer coatings modified by nanomaterials on the long-term durability improvements of concrete. In this paper, nano-TiO_2 particles were added into polymer coatings, and the effects of the particles on the long-term chloride resistance of coated concrete before and after coating aging were investigated.

2. Experimental

2.1. Raw Materials

Concrete specimens were made from P·O42.5 ordinary Portland cement (Xuzhou Zhonglian Cement Plant, Xuzhou, China) as binder material, natural river sand with a fineness modulus of 2.5 as fine aggregate, crushed stone with a particle size of 5–20 mm as coarse aggregate, and ordinary tap water as mixing water. A polycarboxylate superplasticizer (Qingdao Hongxia Polymer Material Co., Ltd., Qingdao, China) was used as a water-reducing agent. The water/cement ratio was 0.6, and the detailed concrete mixture proportion was tap water:cement:river sand:crushed stone:water reducer = 210:350:737:1153:1.75 (kg/m^3). Three typical commercial paints: polyurethane (PU), epoxy resin (EP), and chlorinated rubber (CR) (Xuzhou Huili Anti-corrosion Technology Co. Ltd., Xuzhou, China), and nano-TiO_2 particles (Shanghai Yifu Industrial Co. Ltd., Shanghai, China) with white color and an average diameter of 15 nm were adopted.

2.2. Preparation of Specimens

Coated specimens can be fabricated in three steps: the fabrication of concrete specimens, the preparation of nano-TiO_2-modified paints, and the application of paints on concrete surfaces. Cylindrical specimens, 100 mm in diameter and 50 mm in height, were adopted. Concrete was mixed by a forced mixer and compacted with a flat plate vibrator. After demolding, the specimens were placed in a standard curing room (T = 20 ± 2 °C, $RH \geq 95\%$) for 28 days.

Nano-TiO_2 is an inorganic hydrophilic material, whereas polymer paints are organic hydrophobic materials. To enhance the dispersing effect of nanoparticles in polymer coatings, nano-TiO_2 particles were surface-modified with a KH570 silane coupling agent before they were applied into paints. Fixed dosages of 2.5 wt.%, 2 wt.%, and 1 wt.% nano-TiO_2 were added to the PU, EP, and CR paints, respectively. Then, nano-TiO_2-modified PU (PUT), EP (EPT), and CR (CRT) paints were obtained. The detailed operation information about the nanomodified polymer coatings can be found in a previous study [24].

After initial curing, concrete specimens were placed in an oven at 60 °C for 48 h, then taken out and cooled to room temperature. Prior to the application of the paints, the concrete surfaces were cleaned with sandpaper and moisture cloth. The nanomodified paints were then applied on the surfaces of the specimens with a wire rod applicator (Figure 1). The thickness of each coating film was controlled at approximately 30 μm so that the nanomaterials' protective effects against the penetration of chloride ions could be externalized, and the experimental time needed for the complete coating aging could be reduced. The coated specimens were placed indoors for 7 days until the subsequent experiments. In addition, uncoated specimens also remained for comparison.

Figure 1. Application of paints on a concrete surface using a wire rod applicator.

2.3. Experimental Methods

Coulomb flux is a common index reflecting the chloride resistance of concrete. A high Coulomb flux value usually corresponds with a low chloride resistance [27,28].

Given the influences of aging on the chloride resistance of coated concrete, ultraviolet-accelerated aging experiments were performed in an artificial climate chamber (Figure 2) equipped with two ultraviolet lamps of 400 W before the Coulomb experiment. The temperature in the artificial climate chamber was maintained at 60 °C, and the total duration plan was 36 days. Every 3 days of ultraviolet irradiation, partial specimens were removed and subjected to Coulomb electric flux experiments, which were based on Chinese standard (GB/T 50082-2009) [29]. The quantitative effects of ultraviolet irradiation on the aging of the coatings were determined. Specifically, the irradiation intensities in the artificial climate chamber were measured periodically with an LS123A ultraviolet radiation meter. Total irradiation for each specimen was calculated by combining irradiation intensity with irradiation time.

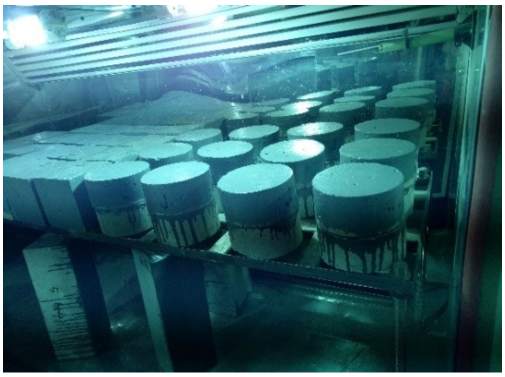

Figure 2. Ultraviolet aging of coated specimens in an artificial climate chamber.

Micromorphological changes in polymer coatings with and without nano-TiO_2 particles were observed through scanning electron microscopy (SEM) before and after the coatings were exposed to ultraviolet radiation. The coating film samples for SEM observation were peeled from coated specimens with a sharp knife, and the size was controlled at 5×5 mm^2.

3. Results and Discussion

3.1. Coulomb Electric Flux of Coated Concrete after Ultraviolet Irradiation

Ultraviolet irradiation is usually one of the major influencing factors leading to polymer coating aging [18,25,30]. Figure 3 presents the Coulomb electric fluxes of coated concrete after ultraviolet-irradiation-induced aging and control concrete. Taking the control (uncoated concrete) as a criterion, it can be easily found that prior to ultraviolet aging, the application of polymer coatings reduced the Coulomb fluxes of concrete considerably, whereas the addition of nano-TiO_2 reduced the Coulomb fluxes further. The Coulomb fluxes of concrete specimens with CRT, EPT, and PUT coatings were reduced by 76.8%, 61.8%, and 60% relative to those of the specimens with CR, EP, and PU coatings, respectively, and the average reduction amplitude was 66.2%. Obviously, the addition of nano-TiO_2 improved the resistance of coated concrete against chloride attack.

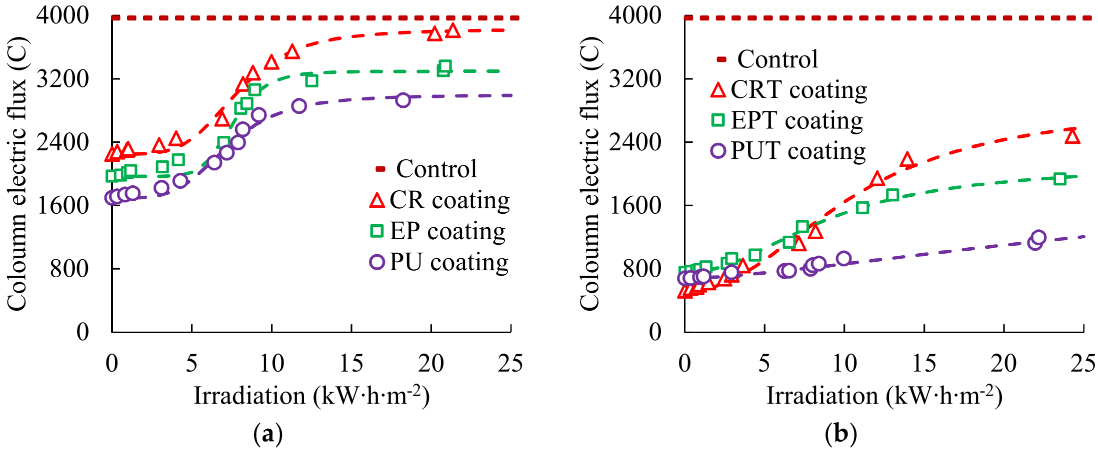

Figure 3. Development of Coulomb electric fluxes of coated concrete with ultraviolet irradiation. (**a**) Ordinary coatings; (**b**) Nano-TiO_2-modified coatings.

As shown in Figure 3, the Coulomb fluxes of the coated concrete specimens all increased gradually with ultraviolet irradiation and generally exhibited a sigmoid curve development mode [11]. This curve showed that the chloride resistance of coated concrete gradually decreased under ultraviolet aging. Notably, ordinary polymer coatings and the nano-TiO_2-modified coatings both aged during ultraviolet irradiation, although the rate of aging of the latter were obviously lower than that of the former because nano-TiO_2 inhibits the aging of polymer coatings [18]. At an ultraviolet irradiation of 25 kW·h·m^{-2}, the Coulomb fluxes of concrete specimens with CRT, EPT, and PUT coatings were reduced by 32.2%, 40.2%, and 59.7%, respectively, relative to those of concrete specimens with ordinary coatings, and the average reduction amplitude was 44%. Thus, nano-TiO_2 can substantially improve the resistance of coated concrete against chloride attack after ultraviolet aging, and the different coatings vary in improvement efficiency.

Furthermore, the rank of Coulomb fluxes of concrete with ordinary coatings did not change before and after ultraviolet aging, that is, the Coulomb value of concrete with CR coating remained the largest, followed by EP-coated concrete and PU-coated concrete. However, the rank of Coulomb values of concrete with nano-modified coatings changed after ultraviolet aging. The rank changed from EPT > PUT > CRT before aging to CRT > EPT > PUT after aging. The results show that different polymer coatings vary in terms of resistance to ultraviolet-induced aging. Generally speaking, the anti-aging performance of PU coating is the best, followed by EP coating and CR coating.

3.2. Service Life Prediction for Coatings after Ultraviolet Irradiation

As the development of Coulomb fluxes of coated concrete with ultraviolet irradiation in Figure 3 is highly consistent with an S-shaped curve, a logistic growth model (Equation (1)) [11,31] for sigmoid curves can be used to make a nonlinear regression analysis, and the obtained equations of Coulomb fluxes of coated concrete with ultraviolet aging are listed in Table 1. Meanwhile, the fitting curves are shown in Figure 3 as dashed lines. The fitting effects were excellent, and even the minimum confidence coefficient R^2 reached 0.975.

$$y = \mathrm{a} + \frac{\mathrm{b} - \mathrm{a}}{1 + \left(\frac{x}{\mathrm{c}}\right)^{\mathrm{d}}} \tag{1}$$

where y is the Coulomb values of coated concrete (C); x is the ultraviolet irradiation subjected by concrete coating (kW·h·m^{-2}); a, b, c, and d is constant, and all are greater than zero.

Table 1. Fitting equations of coated concrete with ultraviolet aging.

Item	Fitting Equations	R^2
Chlorinated rubber (CR) coating	$y = 3824 - \frac{1575}{1+\left(\frac{x}{7.88}\right)^{4.34}}$	0.987
Epoxy resin (EP) coating	$y = 3295 - \frac{1327}{1+\left(\frac{x}{7.55}\right)^{7.68}}$	0.975
Polyurethane (PU) coating	$y = 2997 - \frac{1300}{1+\left(\frac{x}{7.24}\right)^{4.16}}$	0.979
Nano-TiO_2-modified chlorinated rubber (CRT) coating	$y = 2887 - \frac{2365}{1+\left(\frac{x}{10.47}\right)^{2.21}}$	0.983
Nano-TiO_2-modified epoxy resin (EPT) coating	$y = 2115 - \frac{1363}{1+\left(\frac{x}{9.05}\right)^{2.09}}$	0.989
Nano-TiO_2-modified PU (PUT) coating	$y = 2113 - \frac{1435}{1+\left(\frac{x}{35.9}\right)^{1.5}}$	0.988

The development of an S-shaped curve can be divided into three stages: initial stage, middle stage, and later stage. In the initial stage, the curve develops slowly; in the middle stage, the curve increases sharply; and in the later stage, the curve develops slowly again until it becomes constant. These stages agree well with the aging process of polymer coatings under ultraviolet irradiation. The detailed physical mechanisms are as follows: in the initial stage, the aging rates of polymer coatings exhibit a slow growth, which reflects the gradual degradation of resistance to chloride attack; in the middle stage, the aging rates of polymer coatings increase rapidly, and this rapid increase reflects the quick degradation of resistance to chloride attack; in the last stage, the aging rates of polymer coatings recover slow growth again, which suggests that coatings' degradation has been fully developed, and the chloride resistance tends to be stable.

According to Equation (1), when x is zero, the value of y is b; as x approaches infinity, the limit of y is a. The physical meanings of "b" and "a" here represent the Coulomb fluxes of coated concrete before and after complete aging, respectively. Theoretically, the time needed for coatings' complete aging is infinite, which is meaningless in engineering practice. In this paper, a value of 95% a is set as a criterion to forecast coatings' service lives [11,25]. Taking an average daily irradiance of 0.13 kw·h·m^{-2} in Jiangsu province, China as an example [32], the effective service lives of the CR, EP, PU, CRT, EPT, and PUT coatings adopted in this paper were 95.6, 74.9, 90.9, 277.4, 227.6, and 1494.5 days, respectively. The service lives of the nano-TiO_2-modified coatings considerably improved relative to those of ordinary coatings. The service lives of the CRT, EPT, and PUT coatings improved 1.9, 2.0, and 15.4 times, respectively. Thus, nano-TiO_2 plays a significant role in inhibiting ultraviolet-induced aging and extending the service lives of the coatings.

Ultraviolet radiation is one of the factors that deteriorate polymer coatings [8–10,30]. Thus, simple ultraviolet irradiation cannot completely destroy polymer coatings. After ultraviolet aging, the resistance of the coatings to chloride attack was not completely lost, and residual chloride resistance varied among the different coatings. Overall, the PU coating showed the best performance, followed by the EP and CR coatings.

3.3. Micromorphologies of Coatings before and after Ultraviolet Irradiation

The microstructure of a material is often the basis of macroperformance [28,33]. Figures 4 and 5 present the SEM images of the ordinary and nano-TiO_2 modified coatings before and after ultraviolet aging. As expected, polymer paints generally formed smooth, consecutive, and dense films after hardening. However, the coating films differ in quality. Generally, the PU coating had the best film quality (Figure 4e); the CR coating had the worst, presenting a considerable number of micropores on its surface (Figure 4a); and the EP coating presented a few silk-like cracks on its surface (Figure 4c). After the addition of nano-TiO_2 particles, the micropores in the CR coating and the silk-like cracks in the EP coating disappeared. The qualities of the CR and EP coatings markedly improved (Figure 5a,c). By contrast, the PU coating showed no obvious change (Figure 5e). The improvement of coating quality after nano-TiO_2 addition is similar to that observed in coatings complemented with nano-SiO_2 [25,34]. Moreover, the film quality of each coating agrees well with its chloride resistance. Thus, the addition of nano-TiO_2 particles in polymer coatings can fill the micropores and reduce the microscopic defects in coating films, and thus improve the resistance of the coatings to chloride attack.

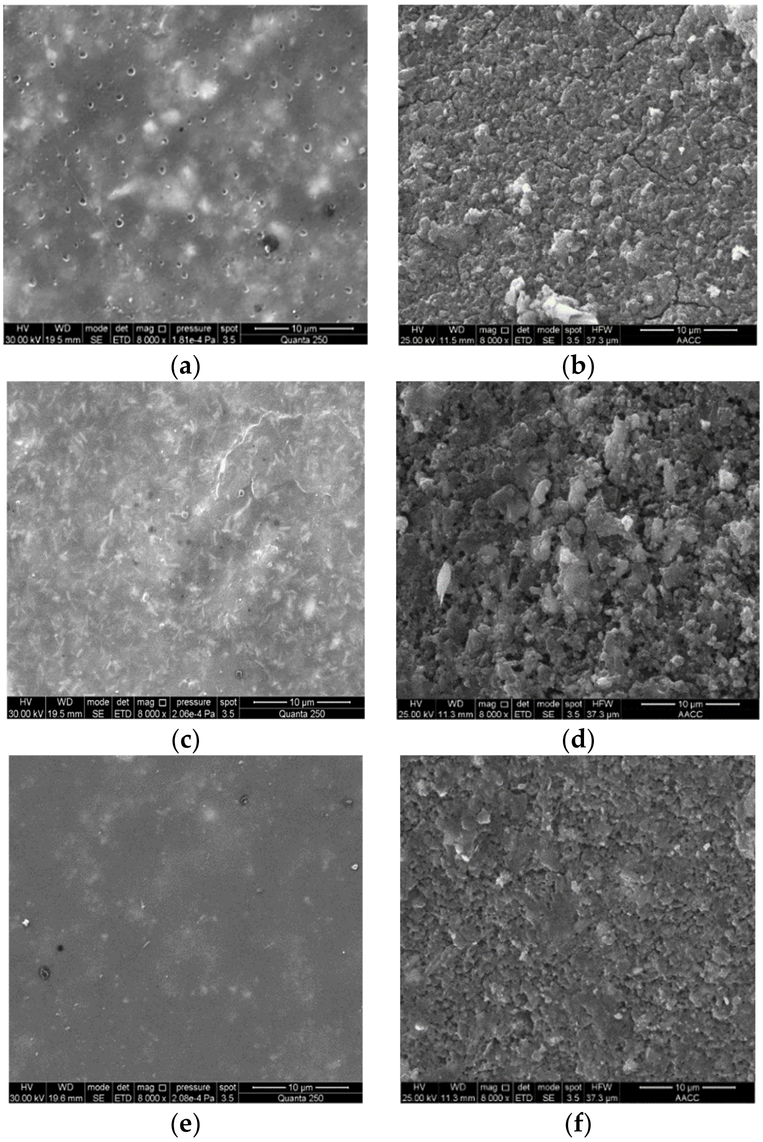

Figure 4. Scanning electron microscopy (SEM) pictures of ordinary coatings before and after ultraviolet irradiation. (**a**) Before aging (CR); (**b**) after aging (CR); (**c**) before aging (EP); (**d**) after aging (EP); (**e**) before aging (PU); (**f**) after aging (PU).

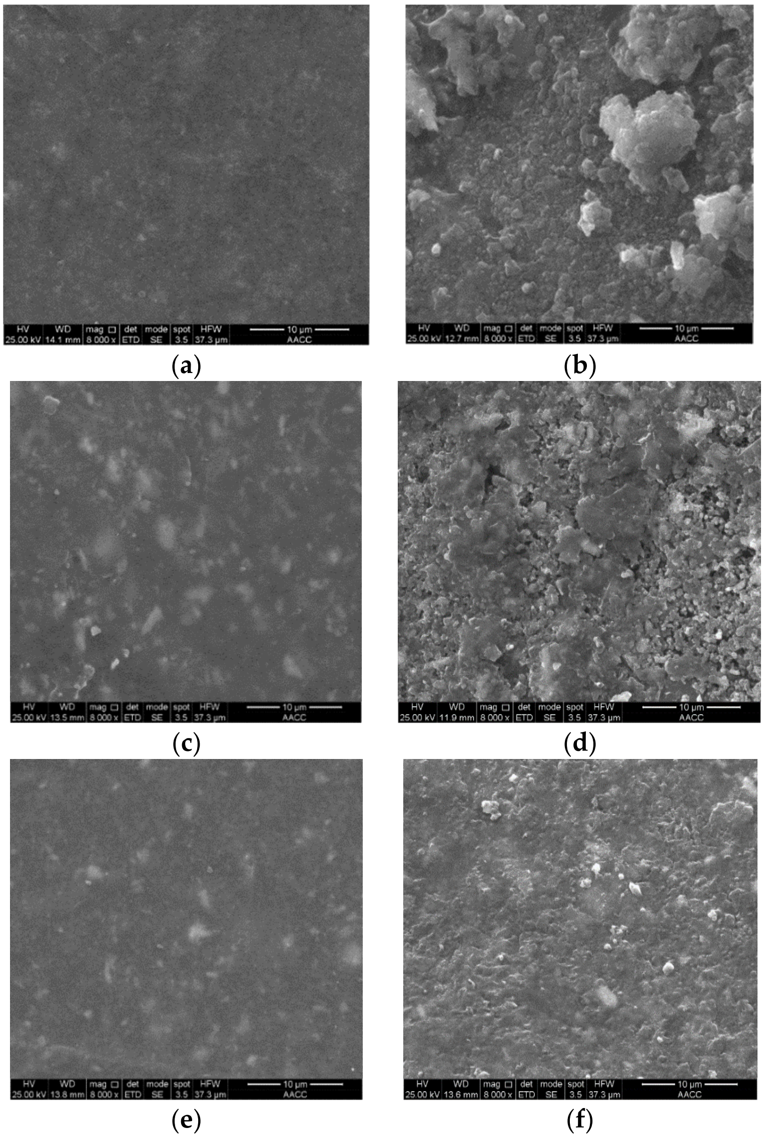

Figure 5. SEM pictures of nano-TiO_2 modified coatings before and after ultraviolet radiation. (**a**) Before aging (CRT); (**b**) after aging (CRT); (**c**) before aging (EPT); (**d**) after aging (EPT); (**e**) before aging (PUT); (**f**) after aging (PUT).

From further observation, it can be seen that each coating has been considerably deteriorated after ultraviolet irradiation. Generally, the surfaces of the coatings became rough and granulated and presented an increase in the number of micropores and some microcracks. These changes gradually decreased the resistance of each coating against chloride ion attack. Meanwhile, the coatings differed in micromorphology. Granulation in the EP coating was severe (Figure 4d), and the microcracks in the CR coating were obvious (Figure 4b). Meanwhile, the PU coating showed minimal deterioration (Figure 4f).

After the incorporation of nano-TiO_2, coating aging still occurred, although the damages were substantially alleviated. The microcracks in the CR coating (Figure 5b) and the obvious granulation in the EP coating (Figure 5d) were effectively alleviated, and the density of the PU coating was enhanced (Figure 5f). Thus, nano-TiO_2 can effectively reduce the extent of damage caused by ultraviolet-induced aging in polymer coatings and improve the resistance of coated concrete against chloride ion attack. This finding is consistent with previous findings [15,18,23,25].

4. Conclusions

Based on experimental studies and analysis, some conclusions were drawn:

- Nano-TiO_2 can reduce microdefects in coating films and remarkably enhance the chloride resistance of coated concrete. Prior to coating aging, nano-TiO_2 can increase the chloride resistance of concrete with CR, EP, and PU coatings by 76.8%, 61.8%, and 60%, respectively;
- Nano-TiO_2 can effectively alleviate ultraviolet-induced damages on polymer coatings and thus evidently enhances the chloride resistance of coated concrete after ultraviolet radiation. After ultraviolet aging, nano-TiO_2 can reduce the Coulomb fluxes of concrete with CR, EP, and PU coatings by 32.2%, 40.2%, and 59.7%, respectively;
- Based on an S-shaped curve, models depicting the resistance of coated concrete to ultraviolet aging and chloride ions were established and used to predict the service lifetime. The results showed that nano-TiO_2 considerably extends the service lifetimes of polymer coatings.

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