C-2-1 Influences of organic film coatings incorporated with nano-SiO_2 on concrete carbonation resistance

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ABSTRACT: Coatings modified with nano-materials were prepared by incorporating 0.4, 1.2, and 2 wt.% nano-SiO_2 particles into three types of paint including polyurethane, chlorinated rubber, and epoxy resin. The influences of coatings with different nano-SiO_2 dosages on the carbonation resistance of coated concrete specimens were studied through accelerated carbonation, static contact angle, and scanning electron microscopy experiments. Results indicate that the incorporation of nano-SiO_2 can reduce the porosity and defects in coating film, and improve the carbonation resistance of coated concrete. However, the carbonation resistance of coated concrete decreases when the nano-SiO_2 dosage is beyond the optimal dosage of approximately 0.4 wt.%. The carbonation resistance of coated concrete exhibits a positive relation with its surface contact angle, and concrete with large contact angle corresponds to high carbonation resistance.

KEY-WORDS: Coating, nano-SiO_2, concrete, carbonation, contact angle.

INTRODUCTION

The carbonation of concrete is a major problem that leads to the corrosion of steel bars in concrete and the durability degradation of concrete structures. Applying organic film coatings on the surface of concrete is an economical and effective way to improve its carbonation resistance. The studies in [1–3] indicated that organic film coatings can significantly inhibit the diffusion of CO_2 into concrete, and then decrease the carbonation rate of concrete. The works in [4–6] also suggested that different coating categories or coating film thicknesses always correspond to different improvement effects on concrete carbonation resistance. However, organic film coatings are prone to aging, that is, the carbonation resistance improvements of organic coatings decreases gradually with the aging of coating.

Nano-material is a nanoscale material and is often used to improve the physical, mechanical, or durability properties of organic coating due to its ideal functions [7–13]. Liao et al. [10] investigated the property of waterborne epoxy resin nano-composite coatings, and drawn that the addition of nano-SiO_2 can effectively improve the mechanical property, durability, and thermal stability of coating. The experimental results of Scarfato et al. [11] indicated that two kinds of polymer resin incorporated with nanoclay can significantly improve the protection effectiveness on concrete unlike with the plain resins, especially in terms of liquid and vapor water barrier properties, salt attack resistance, surface water repellency, and color changes. Leung et al. [12] studied the improvement in barrier properties of epoxy and silane by incorporating nanosized organoclay. They concluded that, owing to the tortuous path effects produced by the incorporation of nanomaterials, the moisture diffusion coefficient of concrete coated with epoxy resin containing 3 wt.% nano-organoclay decreases by 90% compared with that of control coated specimens.

Furthermore, the resistance to Cl^- diffusion is significantly improved. However, opposite findings are also presented. Woo et al. [13] explored the barrier performance of silane/clay nanocomposites as a coating on concrete, and found that the addition of clay nanoparticles insignificantly contribute to the improvement in the barrier against moisture permeability or chloride ion penetration.

The literature review above indicates that the influence of organic coatings with nano-materials on the durability improvements of concrete has been extensively examined. However, the improvement effects of coating with nano-materials on concrete carbonation resistance have been rarely studied [14–15]. Although concrete with coatings exhibit high carbonation resistance [2–4], such barrier properties must be improved for structures under severe environments. This study is part of a work that focuses on the influences of coatings modified with nano-materials on the long-term durability improvements of concrete. The nano-SiO_2-modified epoxy resin, polyurethane, and chlorinated rubber coatings are prepared and used to study the improvement effects in organic film coatings with nano-SiO_2 on the carbonation resistance of concrete.

EXPERIMENTAL

Raw materials

Three typical commercial paints, namely, polyurethane (PO hereinafter), epoxy resin (EP hereinafter), and chlorinated rubber (CR hereinafter) (supplied by Xuzhou Huili Anti-corrosion Technology Co., Ltd), were adopted to prepare organic film coatings for concrete. Given the small size of nano-scale particles, nano-materials are prone to agglomeration and weakened effects [10-16]. A uniform dispersion of nano-SiO_2 particles in the paint was guaranteed by incorporating a nano-SiO_2 dispersed solution (supplied by Shenzhen Aili Chemical Co., Ltd) into the abovementioned paints at 1, 3, and 5 wt.% by the weight of paint used. This nano-SiO_2 dispersed solution was produced with propylene glycol methyl ether acetate as a solvent, and silane coupling agent as a modifier; in the solution, the concentration of nano-SiO_2 was 40 wt.% and the average particle size was 30 nm. Hence, the actual concentrations of nano-SiO_2 were 0.4, 1.2, and 2 wt.% by the weight of coating. P·O42.5 ordinary Portland cement, natural river sand with a fineness modulus of 2.5, crushed stone with a particle size of 5–20 mm, ordinary tap water, and a polycarboxylate superplasticizer were used as raw materials of concrete. The detailed mixture proportion of concrete used in this study was composed of cement: sand: stones: water: plasticizer = 350: 737: 1153: 210: 1.75 (in kg/m^3).

Fabrication of coated concrete specimens

The first procedure was the fabrication of concrete specimens. Concrete was mixed with a forced mixer, and the size of each specimen was 100 mm × 100 mm × 100 mm. Specimens were cured in molds at indoor environment and demolded 24 h after casting. Then, they were transferred into a standard curing room (T = 20 ± 2 °C, RH ⩾ 95 %) until the age of 28 days.

The second procedure was the synthesis of paints with nano-SiO_2. As double-component paint, EP was mixed with A and B components in the mass ratio of 5:1. PO was mixed with A and B components in the mass ratio of 6:1 following the instruction of the manufacturer. CR is a single-component paint; thus, CR was prepared by adding only 5%–10% diluent into paint; the resultant was mixed evenly. After the preparation of each neat paint, nano-SiO_2 dispersed solutions at 1, 3, and 5 wt.% by the mass of paint were added into the paint; the resultant was stirred evenly. A uniform dispersion of nano-SiO_2 particles in paint was ensured by ultrasonicating each nano-SiO_2/paint mixture with a disperser for around 15 min.

The final procedure was the application of paints on the surface of specimen. After the completion of curing, specimens were placed into an oven at 60 °C and dried for 48 h, followed by cooling down to room temperature. The surfaces of specimens were polished with sandpaper and cleaned with a damp cloth prior to the brushing of paint. The previous synthesized EP, PO, and CR paints were brushed on the surface of specimen at the dosages of 180, 150, and 150 g/m^2; the corresponding thicknesses of dry coating films were nearly 45, 29, and 34 μm. Blank specimens and specimens with coating without nano-SiO_2 were also fabricated for comparison. The coated specimens were cured at indoor environment for 7 days before the subsequent experiments.

Experimental methods and evaluation parameters

The accelerated carbonation experiments on specimens were conducted in accordance with Chinese national standard (GB/T50082-2009), in which the concentration of CO_2 was 20 ± 3%, the relative humidity was 70 ± 5%, and the temperature was 20 ± 2 °C. After 28 days of carbonation, each specimen was divided into two halves and then measured for carbonation depth with the use of 1 wt.% phenolphthalein ethanol solution. In evaluating the improvement effects of coating on concrete carbonation resistance, and η was defined as shown in Eq. (1).

$$\eta = \left(1 - \frac{x_c}{x_0}\right) \times 100\% \tag{1}$$

where x_c and x_0 are the carbonation depths of specimens with and without coating corresponding to the same carbonation time/mm.

The incorporation of nanomaterials changes the hydrophobicity of coating [13], a condition related with the carbonation resistance of concrete. The effects of nano-SiO_2 on the hydrophobicity of coating were determined by measuring the surface contact angle of each coated specimen by use of a USB digital microscope. The dispersion effect of nano-SiO_2 particles in coating and the micro-morphology changes of coating after the addition of nano-SiO_2 were obtained by observing partial coating samples with a S3000N scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Influences of nano-SiO_2 on carbonation depth of coated concrete

The carbonation depths of coated concrete specimens obtained by experiments are shown in Fig. 1. Compared with those of the control specimen, the concrete carbonation depths of coated specimens significantly decrease; the decrease magnitudes of carbonation depth for each coated specimen differ. From Eq. (1), the improvement indexes η of carbonation resistance for specimens coated with PU, EP, and CR coatings are obtained as 42.9%, 36.7%, and 28.2%, respectively; these results are consistent with those in [2] and [4]. Among the three investigated coatings, the ranking order of improvement effects on concrete carbonation resistance is PU coating > EP coating > CR coating. The differences in the improvement effectiveness of carbonation resistance for each coating can be attributed to the different film forming materials in various coatings. PO and EP coatings are double-component paints [10-12].

They can form a film through the crosslinking reactions of hardener agent and resin functional group, and makes the polymer molecules linked together to form a cubic structure. As a result, the membranes of the two types of coating are dense. On the contrary, CR is a single-component paint; thus, it forms the film through the evaporation of diluent and drying. During film formation, the molecular structures remain unchanged; the film is also hard, brittle, and less dense.

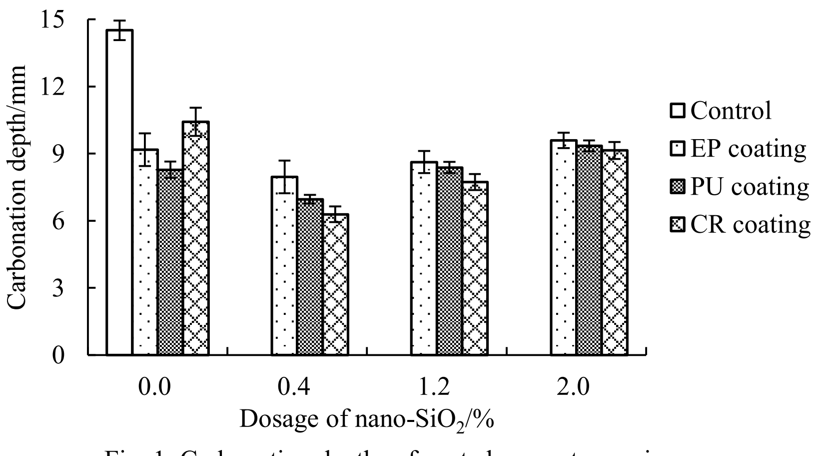


Fig. 1. Carbonation depths of coated concrete specimens

As shown in Fig. 1, the carbonation depths of coated specimens change after the incorporation of a certain nano-SiO_2 dosage into coating. When the nano-SiO_2 dosages are from 0.4 to 1.2 and 2 wt.%, the improvement indexes η for CR coating on concrete carbonation resistance are 57.9%, 48.2%, and 38.8%, respectively. Those for PO coating are 50.1%, 42.2% and 35.6%, and those for EP coating are 45.7%, 40.6%, and 34.5%. Therefore, the optimal dosage of nano-SiO_2 in the coating to improve the carbonation resistance of coated concrete is 0.4 wt.% [12]. When this dosage is exceeded, the carbonation resistance of coated concrete declines. In other words, the beneficial effects of nano-SiO_2 weakens when the dosage is extremely high.

When the nano-SiO_2 dosage is 0.4 wt.%, the improvement effect of nano-SiO_2 on carbonation resistance for concrete with CR coating is the best; the increase magnitude reaches approximately 29.7% unlike with the neat coating. By contrast, the increase magnitudes of PO and EP coatings are small at only around 8%. Therefore, the improvement effects of nano-SiO_2 on the carbonation resistance of concrete with various coatings differ.

Influences of nano-SiO_2 on hydrophobicity of coating

The contact angle changes of each coating with different nano-SiO_2 dosages are shown in Fig. 2. The surface contact angle of each coated specimen increases significantly compared with that of the control specimen. Given that concrete is a hydrophilic material, the surface contact angle of the control specimen is around 38°. After the application of PO, EP, and CR coatings, the contact angles increase to 84.6°, 80.5°, and 82.1°, respectively. The average increase in the contact angles is approximately 44.4°, and the surfaces of specimens are nearly close to hydrophobicity after the application of coating. In other words, organic film coating presents very good improvement effects on concrete hydrophobicity.

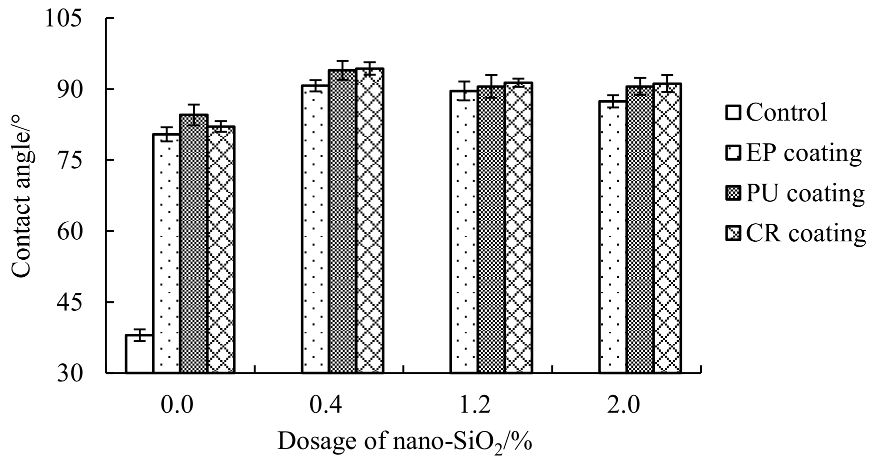


Fig. 2. Contact angles of coated concrete specimens

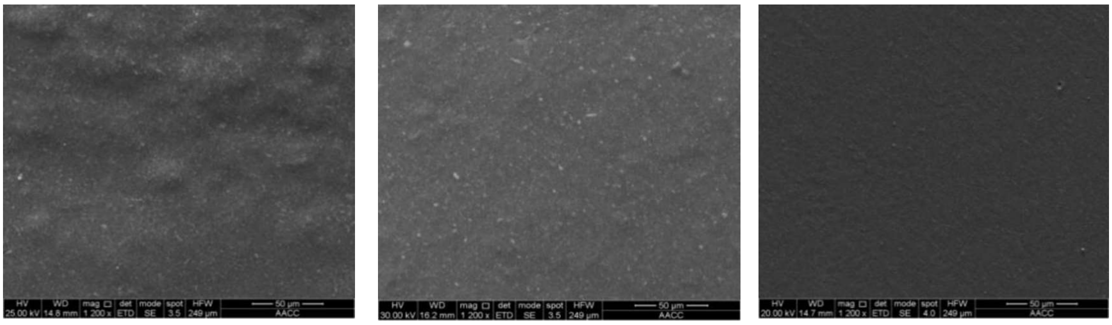
Notably, the surface contact angle of each coated specimen increases first and then decreases with the increase in nano-SiO_2 dosage. At the nano-SiO_2 dosage of 0.4 wt.%, all surface contact angles reach the maximum value. In particular, the contact angles on the surfaces of CR, PO, and EP coatings are 94.4°, 93°, and 91°, respectively. From the contact angle of CR coating with 0.4 wt.% nano-SiO_2, the coating surface is found to have obvious hydrophobicity. In other words, nano-SiO_2 further increases the hydrophobicity of organic film coating. Such findings are in line with those obtained by Woo et al. [13]. However, with the further increase in nano-SiO_2 dosage, the contact angle of each coating decreases. An optimum dosage of nano-SiO_2 exists for coating to improve hydrophobicity.

Comparing Fig. 1 with Fig. 2 shows that the carbonation resistance of coated concrete specimens is positively related to their surface contact angles. Large contact angle corresponds to high carbonation resistance of coated concrete, and vice versa. For example, when the nano-SiO_2 dosages are from 0 wt.% to 2 wt.%, the contact angles of coated concrete exhibit the same development with the carbonation resistance of the corresponding coated concrete. Specifically, at the nano-SiO_2 dosage of 0.4 wt.%, the ranking order of the contact angles of the three coatings are CR > PO > EP. This ranking is consistent with that for their carbonation resistance. The results suggest that the carbonation resistance of coated specimen can be predicted from its hydrophobicity, and coated concrete with high hydrophobicity presents high carbonation resistance.

Microstructure of nano-SiO_2-modified coating

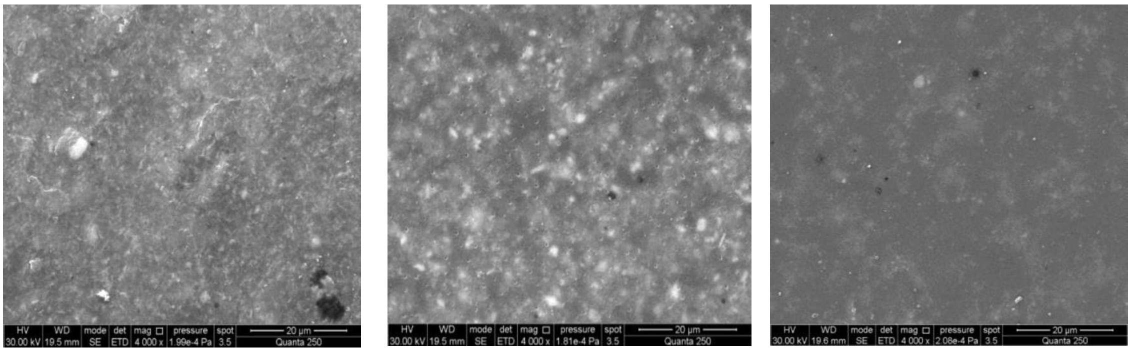
The SEM micrographs of the three coatings incorporated with 0.4 wt.% nano-SiO_2 are shown in Fig. 3. Meanwhile the SEM micrographs of the same coatings without nano-SiO_2 in [2] for comparison are shown in Fig. 4.

More or less micro-pores and defects are clearly found in each coating prior to the incorporation of nano-SiO_2 (Fig. 4). In particular, the quality of PO coating is the best, whereas that of CR coating is the worst. This finding is consistent with that for the carbonation resistance of coated concrete prior to the incorporation of nano-SiO_2.



a) Epoxy resin b) Chlorinated rubber c) Polyurethane

Fig. 3. SEM images of coatings incorporated with 0.4 wt.% nano-SiO_2



a) Epoxy resin b) Chlorinated rubber c) Polyurethane

Fig. 4. SEM images of coatings without nano-SiO_2 [2]

After the addition of nano-SiO_2 particles, the surface of each coating becomes dense. Given the high surface energy and filling effects of nano-SiO_2, these particles can effectively improve the micro-structure in a coating film, and reduce the porosity and defects in it [10-13]. Nano-SiO_2 can especially fill the micro-pores formed by the evaporation of the diluent in CR coating. Accordingly, a dense coating film is formed, thereby inhibiting the penetration of CO_2 into coating. However, with the increase in the nano-SiO_2 dosage, the carbonation resistance of coated concrete decreases. This condition may be due to the agglomeration phenomenon of nano-SiO_2 particles.

CONCLUSIONS

On the basis of the experimental results and analysis, the following conclusions are obtained:

1. The incorporation of nano-SiO_2 can improve the carbonation resistance of coated concrete, and the optimal dosage is around 0.4 wt.%. When the nano-SiO_2 dosage is more than 0.4 wt.%, the improvement effect on each coating decreases.

2. The improvement effects of the same nano-SiO_2 dosage on the carbonation resistance of different coated concretes differ. For the three investigated coatings, the ranking order of improvement effects is CR > EP > PU coating.

3. Nano-SiO_2 can improve the hydrophobicity of coating, and the carbonation resistance of coated concrete is positively related to its surface contact angle. Coated concrete with large contact angle corresponds to high carbonation resistance.

4. Micro-pores and defects in coating can be filled or reduced by incorporating an appropriate nano-SiO_2 dosage. Consequently, a dense coating film can be obtained, which is beneficial to increase the carbonation resistance of coated concrete.

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REFERENCES

[1] LI, W. H., A. H. Wang, J. Yu. *Coating protection of concrete structures*. Modern Paint & Finishing 10(2007):26–29. (in Chinese)

[2] J. Z. CHEN. *Quantitative evaluation of the improvement in the carbonation resistance of concrete with organic film coating*. Highway 4 (2016):191–196. (in Chinese)

[3] X. Y. ALMUSALLAM, et al. *Effectiveness of surface coatings in improving concrete durability*. Cement and Concrete Composite 25 (2003):473–481.

[4] G. LI., et al. *Time dependence of carbonation resistance of concrete with organic film coatings*. Constr. Build. Mater. 114 (2016):269–275.

[5] M. K. MORADLLO, M. SHEKARCHI, 2012. *Time-dependent performance of concrete surface coatings in tidal zone of marine environment*. Constr. Build. Mater. 30 (2012) :198–205.

[6] S. SADATI, M. AREZOUMANDI, M. SHEKARCHI. *Long-term performance of concrete surface coatings in soil exposure of marine environments*. Constr. Build. Mater. 94 (2015):656–663.

[7] L. L. ZHENG, Q. MA, M. H. ZHU, et al *Progress in preparation and application of nano-silica modified polyurethane*. Chemical Engineering & Equipment 6 (2015):203–205. (in Chinese)

[8] L. M. CHIACCHIARELLI, et al. *The relationship between nanosilica dispersion degree and the tensile properties of polyurethane nanocomposites*. Colloid and Polymer Science 291(2013):1–9.

[9] SENSES, E., P. AKCORA. *An interface-driven stiffening mechanism in polymer nanocomposites*. Macromolecules 46(2013):1868–1874.

[10] LIAO, L. M., Z. Li, T. Wei, et al. *Synthesis and property of waterborne epoxy nano-composite coatings*. Construction Quality 32(2014):9–13. (in Chinese)

[11] P. SCARFATO, et al. *Preparation and evaluation of polymer/clay nanocomposite surface treatments for concrete durability enhancement*. Cement and Concrete Composite 34(2012):297–305.

[12] LEUNG, C. K. Y., H. G. Zhu, J. K. Kim, et al. *Use of polymer/organoclay nanocomposite surface treatment as water/ion barrier for concrete*. Journal of Materials in Civil Engineering 20(2008): 484–492.

[13] R. S. C.WOO, et al. *Barrier performance of silane-clay nanocomposite coatings on concrete structure*. Composites Science and Technology 68(2008):2828–2836.

[14] X. Y. PAN, Z. G. SHI, C. J. SHI, et al. *A review on concrete surface treatment Part 1: Types and mechanisms*. Constr. Build. Mater. 132(2017):578–590.

[15] X. Y. PAN, Z. G. SHI, C. J. SHI, et al. *A review on surface treatment for concrete Part 2: Performance*. Constr. Build. Mater. 133(2017): 81–90.

[16] F. SANCHEZ, K. SOBOLEV. *Nanotechnology in concrete – A review*. Constr. Build. Mater. 24 (2010): 2060–2071.