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Influences of modified nanoparticles on hydrophobicity of concrete with organic film coating

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HIGHLIGHTS

- Hydrophilic nanoparticles can be effectively modified into hydrophobic by KH-570.
- Nanoparticles can enhance contact angles and reduce water absorption of coated concrete.
- Water absorption of coated concrete is closely related with its contact angle.

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ABSTRACT

To study the influences of modified nanoparticles on hydrophobicity of concrete with organic film coating, nanocomposite organic film coatings were prepared with three types of organic polymer paints and two types of nanoparticles. Surface contact angles and water absorption of concrete coated with such coatings were tested. Fourier transform infrared spectrum experiment was also carried out to check modification effects on nanoparticles. Results indicated that hydrophilic nano-SiO_2 and nano-TiO_2 can be modified effectively to become hydrophobic by silane coupling agent KH-570. Incorporation of nanoparticles can enhance contact angles on coated concrete and reduce water absorption by increasing degree of surface roughness of coatings, whereas nano-SiO_2 is relatively more effective than nano-TiO_2 in modifying surface properties of coatings. However, a dosage limit exists for nanoparticles in coating, and observed improvements decreased when dosage reached beyond the limit.

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1. Introduction

Organic film coating is a type of paint with polymeric compounds as the main film-forming substances, thereby forming a dense film layer on the surface of substrate after hardening [1]. Therefore, when applied on concrete, organic film coatings can effectively prevent invasion of aggressive mediums from the outside and attain effective improvements on concrete durability. However, given sunlight, heat, water, salt, or alkaline pore solution, protection effects of coating on concrete usually decreases [2–5].

Hydrolysis resistance and impermeability of coatings are important indexes that are related to their long-term durability performance. Given the increase in water absorption of hardened coatings, chemical bonds in coatings are easily hydrolyzed and degraded into small molecules, eventually resulting in the decrease in protection capability. By contrast, penetration of corrosive ions in coatings and their reaction with substrate produce deleterious effects, resulting in coating failure. Increasing hydrophobicity of coatings is an important measure in improving their hydrolysis resistance and impermeability. To enhance hydrophobicity of coatings, the adopted method often involves changing polarity and reducing surface energy by incorporating materials with different polarities [6]. In this process, nanomaterials are often used [7].

Nanomaterials usually comprise ultrafine particles with a diameter of 1–100 nm. Previous studies have shown that the use of nanomaterials can significantly improve various performances of organic anticorrosive coatings [8–10]. However, owing to their very small particle size, large surface area, high surface activity, and poor stability, nanoparticles easily agglomerate [11,12]. Meanwhile, nanoparticles easily interact with water molecules in air and carry hydroxyl groups, rendering them with strong hydrophilic properties. Even dispersion of nanoparticles in organic medium presents difficulty, easily producing defects within polymeric film coatings [13,14].

Zhou et al. [9] found that with the incorporation of 1.5 wt% colloidal nanoparticles of TiO_2-SiO_2, the fabricated fluorocarbon/TiO_2-SiO_2 composite coatings exhibited a more stable hydrophilic-

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ity, superior self-cleaning and anti-aging performance. Ammar et al. [15] studied the influence of nano-SiO_2 on hydrophobicity and corrosion resistance of acrylic-silicone polymeric matrix. They discovered that coatings incorporated with 3 wt% nano-SiO_2 exhibited the highest contact angle of 97.3° and significant improvements in corrosion resistance. Bai et al. [16] investigated the influence of SiO_2 nanoparticles on hydrophobicity and carbonation resistance of concrete coated with polymer paints. They observed that coatings featured the highest surface contact angle and the best carbonation resistance when 1 wt% nano-SiO_2 was used. However, most current studies regarding application of nano-materials in coatings focused on metal substrates [7–9,15,17], and a few studies centered on concrete substrates [16]. Characteristics of concrete and metal substrates differ.

Concrete hydrophobicity is an important index that is closely related to concrete durability [7,16]. In this study, concrete was used as substrate material. Two types of nanoparticles and three types of organic polymer paints were selected to study the influence and improvement mechanism of modified nanoparticles on hydrophobicity of concrete with coatings.

2. Experimental

2.1. Raw materials

Two types of nanoparticles on the market, namely, nano-SiO_2 and nano-TiO_2, were selected; their average particle sizes were 30 and 15 nm according to the product description, respectively. Three types of organic polymer paints, namely, polyurethane (PO), epoxy resin (ER), and chlorinated rubber (CR), were employed. Silane coupling agent KH-570 was used as modifier for nanoparticles. Absolute ethyl alcohol (AE) and oxalic acid (OA) were used as hydrolysis materials for silane coupling agent KH-570. P·O42.5 ordinary Portland cement, natural river sand with fineness modulus of 2.5, crushed stones with particle size of 5–20 mm, ordinary tap water, and polycarboxylate superplasticizer were used as cementitious material, fine aggregate, coarse aggregate, mixing water, and admixture, respectively. The detailed mixture ratio of concrete was cement:sand:stones:water:plasticizer = 350:737:1153:210:1.75 (in kg/m^3).

2.2. Modification of nanoparticles

Surface modification is essential to dispersing inorganic nanoparticles uniformly and stably within organic resin coatings. The detailed modification steps are as follows [11]:

Initially, 40 ml mixed solution of AE and deionized water (volume ratio 3:1) and 3 g nanoparticles were poured into a beaker. The solution was dispersed by an ultrasonic dispersion instrument for 30 min. After preparation of OA solution with a pH of 3.5 and silane coupling agent KH-570 by a mass ratio 20 wt% of nanoparticles, the OA solution, KH-570, and AE were mixed following a mass ratio of 1:1:9 and stirred for 1 h using a magnetic stirrer. Then, the obtained solution was added to the previous beaker, and the mixture was stirred for 15 min at a constant temperature of 75 °C before stirring for 45 min at room temperature using a magnetic stirrer. Next, modified nanoparticles were obtained by centrifugation from the previous emulsion using a centrifuge at a speed of 10000 r/min. To remove the silane coupling agent adsorbed physically on the surface of nanoparticles, nanoparticles were cleaned for 10 min by ultrasonic cleaner with deionized water and AE. Eventually, surface-modified nanoparticles were achieved after freeze-drying for 6 h.

To check the modification effects, the modified nanoparticles were sampled and analyzed by a Fourier transform infrared (FTIR) spectrometer, which is developed based on the principle of Fourier transform after interference of infrared light. The spectral range and the highest resolution of the FTIR spectrometer used are 4000–400 cm^{-1} and 2.0 cm^{-1}, respectively.

2.3. Fabrication of coated concrete specimens

First, concrete specimens comprising 100 mm (diameter) × 50 mm (height) cylinders were fabricated. Specimens were cured at normal indoor conditions with room temperature of about 25 °C and demolded 24 h after casting and transferred to a standard curing room (T = 20 ± 2 °C, RH ≥ 95%) until the age of 28 days. Second, nanocomposite organic polymer paint was prepared. According to the mass ratio of corresponding paint matrix from 0 wt% to 4 wt% at every 0.5 wt% interval, each type of modified nanoparticle was weighed and dissolved in a diluent. Then, nanoparticles were introduced into the relevant PO, EP, or CR paints. Then, nanoparticles were dispersed by ultrasonic dispersion instrument for 10 min. Finally, coatings were applied on concrete specimens. After drying in an oven at 60 °C for 48 h, concrete specimen surfaces were polished with sandpaper and cleaned with a damp cloth. Then, the prepared nanocomposite paints were applied on specimen surfaces using a wire rod coater.

A high magnification digital microscope was used to measure the thickness of dry film coatings. As shown in Fig. 1, thickness of dry film coatings approximated 30 μm. After painting, specimens were kept indoors and dried for 7 days before the below experiments.

2.4. Contact angle experiments

Surface contact angle θ on a material is an important parameter for evaluating its hydrophobicity or hydrophilicity [18]. In general, 90° is considered a critical value. A material is defined as hydrophilic when $\theta \leq 90°$, but it is hydrophobic when $\theta > 90°$. A material with a larger contact angle usually features stronger hydrophobicity.

In this work, surface contact angles of coated concrete specimens were measured by using a method of half-angle algorithm [19]. In the test, water droplets were extremely small. Thus, deformation of droplets caused by gravity can be neglected, and a droplet can be regarded as part of a sphere. Therefore, contact angle θ can be calculated by Formula (1):

$$Tan\left(\frac{\theta}{2}\right) = \frac{2h}{d}, \tag{1}$$

where h is the height of droplets, and d corresponds to the diameter of the bottom circle of a spherical droplet.

2.5. Water absorption experiment

Water absorption is an important index for evaluating hydrophilicity of materials, and it can also be used to assess hydrophobicity. In general, lower water absorption of a material indicates stronger hydrophobicity and vice versa. Based on previous experimental results on contact angle, each type of coated concrete specimen with maximum contact angle was selected. Specimens with coatings incorporated with 0 wt% nano-SiO_2 or nano-TiO_2 were also selected and taken as blank specimens for comparison. After immersion in a water tank for 30 days, water absorption ratios of specimens were tested using a moisture meter JT-C50. If only the moisture meter was placed on the surface of coated concrete, the water content of it can be obtained instantaneously.

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