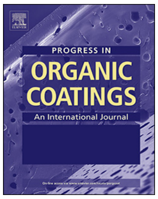
Progress in Organic Coatings 125 (2018) 48–60

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat



Development of water-repellent cement mortar using silane enriched with nanomaterials

Karthick Subbiah[a], Dong-Jin Park[a], Yun Su Lee[a], Saraswathy Velu[b], Han-Seung Lee[a,*], Hyun-O Jang[a], Hyun-Jun Choi[a]

[a] Department of Architectural Engineering, Hanyang University, 1271 Sa 3-dong, Sangrok-gu, Ansan 426-791, Republic of Korea
[b] Corrosion and Materials Protection Division, CSIR-Central Electrochemical Research Institute, Karaikudi, 630 006, Tamilnadu, India

ARTICLE INFO

Keywords:
Superhydrophobic surface
Cement mortar
Nanomaterials
Contact angle

ABSTRACT

The exposure of reinforced concrete structures to freezing temperatures during winters can create internal stresses and surface microcracks in concrete owing to tiny ice crystal formations in the pores of concrete structures. Thus, in the present study, superhydrophobic surfaces were created on concrete by spraying and admixing superhydrophobic materials, comprising 1H,1H,1H,2H-perfluorodecyltriethoxysilane (PFDTS) with nano TiO_2 and SiO_2 inclusions, with cement mortar. TiO_2 nanomaterials were synthesized using ginger (*Zingiber officinale*) as a bio-template. The PFDTS enriched with nanomaterials (PFDTS-NM) was admixed with cement mortar during casting and was spray-coated on the cement mortar surface after casting. The spray-coated and admixed cement mortar sample surfaces were characterized by XRD, SEM/EDAX, and UV–vis spectroscopy, and their water-repellent properties were evaluated by measuring the contact angles (CA) and conducting water absorption and freeze-thawing tests. The pore size distributions of the samples before and after freeze-thawing were evaluated by mercury intrusion porosimetry (MIP). The results confirm the presence of PFDTS with inclusions of rod-shaped TiO_2 nanoparticles on the concrete surface. Further, the CAs of normal, coated, and admixed cement mortar surfaces were found to be 45.5°, 162.3°, and 162.0°, respectively. The spray-coated and admixed concrete can be used to form superhydrophobic surfaces on concrete structures to reduce water absorption and increase the durability of cement mortar.

1. Introduction

Reinforced concrete structures play a significantrole in this world such as buildings, bridges, roads, power plants, and dams. Hence, it is compulsory that the concrete used should be durable. However, the durability of concrete structures is a significant problem in the construction industries during winters [1,2]. This is because reinforced concrete structures are typically hydrophilic and porous, and quickly absorb water and some aggressive ions through capillary pores [3,4]. The absorbed water molecules convert into ice crystals at freezing temperatures in the winter season, which results in an increase in the concrete's internal stress and creates microcracks on the concrete surface. Consequently, the durability of concrete reduces [5–8].

Some researcher have attempted to reduce the pores and capillary absorption of concrete by using filler materials such as rice husk ash, fly ash, silica fume (SF), slag, and other industrial waste fine products [9–14], which are added to the concrete mix and can reduce the capillary pores and decrease the speed of water penetration into the concrete structures. However, the use of filler materials is not effective for prevention of water absorption in concrete structures because although they fill the concrete pores, the concrete retains in hydrophilic nature. Hence, the concrete surface still absorbs water because of the hydration reaction between water and cement matrix [15], and the absorbed water molecules can easily form ice at freezing temperatures and reduce the durability of the concrete structure.

Several methods have been adopted to enhance the durability of reinforced concrete structures, including surface treatment of concrete with epoxy coating, rubber coating, or water sealant coatings [16–18]. Silane-based compounds are generally used as water-repellent coatings on the concrete surface [19,20]. Some authors have also reported the formation of a superhydrophobic surface on concrete by using silane-based compounds functionalized with filler materials such as nano-silica, silica fume (SF) metakaolin (MK), rice husk ash, and fibers [21–23]. For example, Vivan et al. [21] reported that an emulsion enriched with polymethyl-hydrogen siloxane oil as a hydrophobic agent, and filler materials such as MK or SF can induce microroughness and

---

[*] Corresponding author.
E-mail address: ercleehs@hanyang.ac.kr (H.-S. Lee).

https://doi.org/10.1016/j.porgcoat.2018.08.021
Received 25 May 2018; Received in revised form 1 August 2018; Accepted 20 August 2018
0300-9440/

polyvinyl alcohol (PVA) fibers can create a hierarchical surface. Furthermore, Husni et al. [24] reported that a rice husk ash-incorporated silane coating creates a water-repellent surface on concrete. This surface coating technique is generally used to protect concrete from water diffusion through capillary pores. However, the surface coating becomes more vulnerable under UV radiation [25,26]. To overcome this issue, TiO_2 has been introduced by several groups for increasing the stability of coatings under UV radiations [25]. Besides, the use of TiO_2 nanomaterials has numerous advantages in various environmental applications such as wastewater treatment, solar cell photoinduced hydrophobic coatings with a self-cleaning surface, and antibacterial coatings [27–37] owing to its low cost, high stability under UV irradiation, and suitability for large-scale applications [38–41]. Further, the photocatalytic and hydrophobic properties were produced by using organic polymers functionalized with a hybrid sol of TiO_2 and SiO_2 nanoparticles, which is suitable for inhibition of water diffusion [42–45] and UV shielding [26]. However, unfortunately, cracks appear on the coated concrete surface by mechanical friction, which can significantly reduce the protection against water diffusion.

On the other hand, some researchers achieved internal hydrophobicity of concrete by using silane-based compounds admixed with concrete during casting [23,46,47]. They reported that the admixed cement mortar demonstrated internal hydrophobicity and water-repellent property [23]. Moreover, even when cracks formed on the concrete surface, the internal hydrophobic agent prevented the ingress of water into the concrete [47,48]. Based on this concept, in the present study, a superhydrophobic surface was created on cement mortar by using two methods: coating the cement mortar surface and admixing during casting. The coating emulsion was prepared by using 1H,1H,1H,2H-perfluorodecyl-triethoxysilane (PFDTS) enriched with synthesized TiO_2 and SiO_2 nanomaterials and was spray coated on the cement mortar surface (SCCM). The admixed cement mortar (ACM) was prepared by the addition of PFDTS and the synthesized TiO_2 and SiO_2 nanomaterials during casting. Further, in recent studies, the size and shape of nanomaterials have been changed by a bio-template synthesis method, wherein the bio-template effectively controls the morphology and particle size during the preparation of nanomaterials [49,50]. The size and shape controlled nanomaterials have attracted extensive attention owing to their unique properties, high surface area, and potential applications [51,52]. The TiO_2 nanoparticles were synthesized by using ginger (*Zingiber officinale*) as a bio-template and were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM)/EDS. Then, the PFDTS enriched with TiO_2 and SiO_2 nanomaterials was spray coated on the cement mortar surface (SCCM) and PFDTS, SiO_2, and TiO_2 were admixed with cement mortar (ACM) during casting. The fabricated SCCM and ACM were characterized by XRD, SEM, XPS, and UV spectroscopy, and their water repellent properties were evaluated by measuring the contact angle (CA) and water absorption properties, and by freeze-thawing tests. The results were compared with those of PFDTS and nanomaterial-free normal cement mortar (NCM).

2. Experimental details

2.1. Materials used

PFDTS and titanium isopropoxide were purchased from Sigma Aldrich. Sodium hydroxide (NaOH) and ethanol were purchased from SRL Chem. All the chemicals were of analytical grade and used without further purification.

2.2. Preparation of bio-template from ginger (Zingiber officinale)

TiO_2 nanomaterials were synthesized using ginger (*Zingiber officinale*) as a bio-template. Soil particles and other impurities on the ginger surface were removed using distilled water. The outer layer of ginger was removed using a sterile knife and the ginger was cut into small slices (approximately, 1–2 *mm* thickness). The sliced ginger were dispersed in 500 *mL* of distilled water and boiled at $100 \pm 5^{\circ}C$ for 2 *h*. The entire bio-ingredient contents of ginger were removed by boiling, and the ginger slices were separated from water using a Whatman No. 1 filter paper. The collected ginger slices were immersed in 20 *mL* of ethanol solution for 1 *h*, and the bio-template was air dried at ambient condition.

2.3. Synthesis of TiO_2 nanomaterials by bio-template method

A typical synthesis of TiO_2 nanomaterials is as follows: the treated ginger slices as a bio-template were immersed in 50 *mL* of 0.1 *M* titanium isopropoxide solution under stirring for 12 *h* at room temperature. During this process, the Ti^{4+} ions occupy the pores in the ginger bio-template and provide platform for the adsorption of Ti^{4+} ions on the bio-template surface. After 12 *h*, the Ti^{4+} ions integrated with the bio-template were collected and transferred to another clean beaker. Then, 50 *mL* of 0.01 *M* NaOH solution was added slowly into the beaker, and the resulting mixture was stirred at $60 \pm 5^{\circ}C$ for 2 *h*. A white precipitate appeared within the bio-template of ginger. The bio-template was then heated for 1 *h* at $300 \pm 5^{\circ}C$, at which the bio-template completely burned. The collected powder sample was washed with distilled water to removal excess sodium ions and gently air-dried. Further, this sample was calcined at $700 \pm 5^{\circ}C$ for 3 *h* to obtain a white powder. The schematic diagram of the synthesis method is given in Fig. 1.

2.4. Synthesis of nano-SiO_2

Nano-SiO_2 was synthesized from rice husk ash by the precipitation method and the synthesis procedure and characterization details are reported in our earlier publication [53].

2.5. Characterization of nano-TiO_2

The synthesized nano-TiO_2 was characterized by XRD using a computer-controlled XRD system (JEOL, JPX-8030) with Cu-K_α radiation ($\lambda = 1.54059$ Å) generated at 40 *kV* and 20 *A* to record the XRD patterns. The diffraction peaks were identified using the ‘peak search’ and ‘search match’ programs in the software (PA Analytical, X’pert High score plus). Particles were dispersed in Milli-Q water and deposited onto a carbon tape to determine the particle size and morphology by SEM.

2.6. Fabrication of water-repellent cement mortar

2.6.1. Water-repellent material coating on cement mortar surface

In this study, ordinary Portland cement (OPC) of Type 1 with a specific gravity of 3.16 was used. The chemical composition of OPC is provided in Table 1. River sand, passing through 250-*μm* sieves with a specific gravity of 2.60, was used as fine aggregates. The concrete specimens were cast in a cubical mold with dimensions of $50 \times 50 \times 50$ mm using 1:1 ratio of cement and fine aggregate containing 0.45% water/cement ratio (w/c). After 24 *h*, the cement mortar specimens were demoulded and cured for 28 days in distilled water. After curing, the cement mortar specimens were removed from the water medium and gently air-dried at ambient temperatures. Thereafter, these specimens were coated with water-repellent materials in optimal conditions.

The superhydrophobic (water-repellent) coating emulsion was prepared by the following facial steps: equal weights of nano-TiO_2 and nano-SiO_2 (1.5 *g* each) were added into 50 *mL* of PFDTS/ethanol mixture (1:50 by volume) [24]. The water-repellent solution was enriched with PFDTS, which acted as a water-repellent, nano-SiO_2 to induce surface micro-roughness [54], and TiO_2 to induce UV resistance [26].