

I-3 The design of superhydrophobic coatings for concrete

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ABSTRACT: A method to produce hydrophobic and superhydrophobic concrete surfaces is reported. Concrete is normally a hydrophilic material and this parameter affects the durability of concrete structures and pavements. To carry out the above objective hydrophobic emulsions were prepared and applied on Portland cement mortar tiles. The polymethyl-hydrogen siloxane oil emulsion was enriched with metakaolin (MK) and silica fume (SF) to induce microroughness. Various emulsion types were investigated by using different mixing procedures, and single- and double-layer hydrophobic coatings were applied. The emulsions and coatings were characterized with optical microscope and scanning electron microscope (SEM), and wetting properties, including the water contact angle (CA) and roll-off angle were measured. The maximal CA measured was 156° for the specimen with PVA fibers treated with a MK based emulsion. Since water penetration is the main factor leading to concrete deterioration, the hydrophobic, over- and superhydrophobic water-repellent concrete have extended durability and, therefore, can have broad range of applications in civil and transportation infrastructure.

KEY-WORDS: Contact angle, hydrophobic concrete, superhydrophobicity, hierarchical roughness

INTRODUCTION

Fabrication of hydrophobic concrete is a very important task for many applications. Concrete, a mixture of Portland cement as binder, and water as well as aggregates as fillers, is a porous material with pores ranging in size from nanometers to millimeters. There are various pore types within the cement hydration products, including entrapped and entrained air voids up to a few millimeters in diameter, capillary pores in a range of a few micrometers in diameter and nanoscale gel pores. In most applications, concrete surface is subjected to external erosion, abrasion and environmental exposure to aggressive liquids, such as water, mineral solutions, oil, solvents, etc. When dry concrete comes into contact with a liquid such as water, most of the water is absorbed by the pores due to the capillary forces. The capillary forces are dependent on the surface tension of the liquid (typically water), its contact angle (CA) with the pore walls, and the radius of the pores [1], the durability (often affected by freeze-thaw exposure and sulfate attack) of concrete depends on its overall absorption and permeability to aqueous solutions. For example, freeze-thaw damage occurs when water in saturated concrete freezes due to temperature fluctuations, causing considerable stresses within the material. The cumulative effect of freeze-thaw cycles eventually cause expansion, cracking, scaling and crumbling of the concrete. It is therefore crucial to synthesize water-repellent concrete in order to increase its durability, and, in particular, to produce the ultra-durable concrete [2].

The apparent CA is the principal parameter which characterizes the wetting properties of the surface [3]. When the CA is greater than 90°, it indicates hydrophobicity, while a CA less than 90° shows hydrophilicity, which is the tendency of a surface to become wet or to absorb water, as shown in Fig. 1. The superhydrophobicity corresponds to an apparent CA between 150° and 180°. Furthermore, not only a high apparent CA but also a low hysteresis of contact angle is necessary for true superhydrophobicity [4-7]. The CA hysteresis is the difference between the advancing and receding CA and serves as a measure of adhesion between water and the solid substrate [8-11].

The surfaces that are not quite superhydrophobic but exhibit a high CA between 120° and 150° , which is above typical values for hydrophobic materials, are called “overhydrophobic.” Superhydrophobic hierarchical surfaces with roughness patterns imposed over larger roughness patterns (Fig. 2) have generated interest due to their potential application as self-cleaning surfaces as an example. These surfaces mimic the Lotus leaf surface, which is notorious for its superhydrophobicity and self-cleaning properties, the so-called Lotus effect. Mimicking living nature for engineering applications is called “biomimetics,” and here we apply a biomimetic approach to synthesize hydrophobic concrete [12-17].

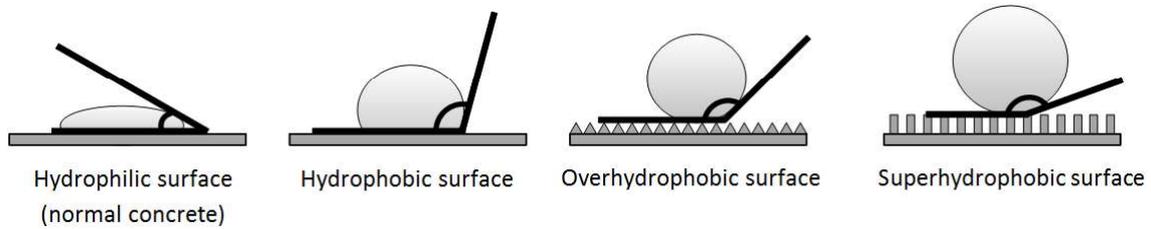


Fig.1. The hydrophilic ($0^\circ \leq \theta \leq 90^\circ$), hydrophobic ($90^\circ \leq \theta$), “over-hydrophobic” ($120^\circ \leq \theta < 150^\circ$) and superhydrophobic ($150^\circ \leq \theta \leq 180^\circ$) surfaces, where θ is the CA.

To generate hydrophobicity on porous materials (i.e. ceramics, concrete, etc.) it was proposed to use a siloxane based admixture containing hydrogen (e.g., polymethyl-hydrogen siloxane oil, PMHS) combined with small quantities of submicro- or nano-sized particles [1, 13]. Randomly distributed polyvinyl alcohol (PVA) fibers embedded in the porous material and emerging from the surface can be used to achieve superhydrophobicity (Fig. 2). When used for internal hydrophobization a modified PEHSO/PMHS admixture releases hydrogen and forms small ($10 - 100 \mu\text{m}$), uniform air bubbles which are evenly distributed through the concrete volume. The distribution of the air bubbles through hardened concrete can be precisely tailored by preparing the water-based PEHSO emulsion with a given droplet size. The combination of the submicro- or nanosized particles that provide the micro/nano roughness, and fibers that introduce a hierarchical structure plays an important role in forming superhydrophobic surfaces through the hardened concrete and so improves the durability potential of concrete. The application of such emulsions for hydrophobization of concrete surfaces is a very effective solution to control the durability [18-20].

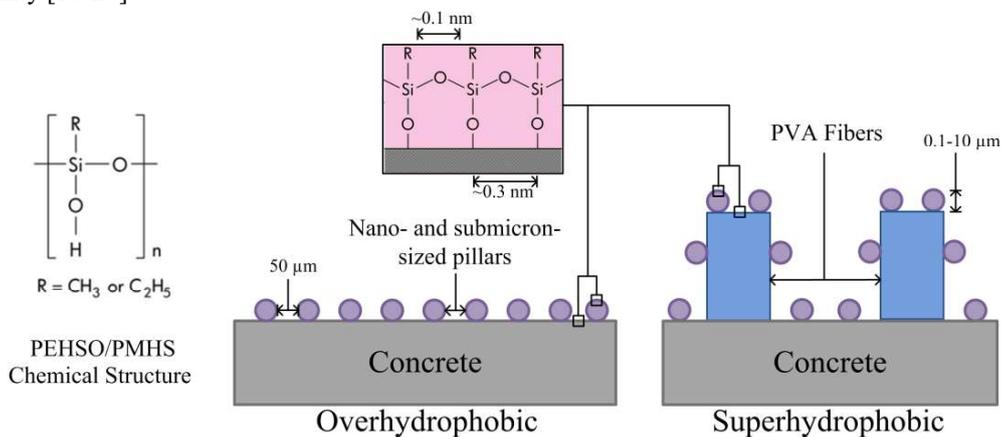


Fig. 2. Schematics of the proposed “overhydrophobic” and superhydrophobic concrete

MATERIALS AND PROCEDURES

Materials

For emulsion stabilization, water-soluble polyvinyl alcohol (PVA) was selected because of its nonionic character and perfect compatibility with concrete materials. A highly hydrolyzed (98%) PVA with molecular weight of 16,000 from Across Chemicals was used to reduce the tendency of foam formation. Deionized water (DI water) was used as the dispersion medium for the emulsions. Polymethyl-hydrogen siloxane oil, PMHS (XIAMETER MHX-1107) from Dow Corning with a specific gravity of 0.997 (at 25°C) and a viscosity of 30 cSt was used as hydrophobic agent. This product contains 85-100% of methylhydrogen siloxane as an active agent. Metakaolin

(MK) from Burgess Optipozz or silica fume (SF) from Elkem was added to the emulsions to induce the microroughness. The X-ray diffraction investigation (Fig. 3) was used to analyze the phases present within portland cement, MK and SF. Rough and flaky particles with sizes from 0.8 to 12 μm with a certain degree of agglomeration were found in metakaolin. Silica fume with spherical particles in sizes from 0.2 to 1 μm with a certain degree of agglomeration was used.

Mortar tiles were prepared using: 1. a commercial Type I portland cement (PC) from Lafarge [21]. (the results of phase analysis by the X-ray diffraction of NPC are presented in Fig. 3); 2. ASTM C778-graded standard quartz sand with an average particle size of 425 μm ; 3. tap water; 4. Polyvinyl alcohol (PVA) fibers (RECS 15x12 mm Kuralon K-II) with a diameter of 15 dtex (0.04 mm) and length of 12 mm were added to achieve superhydrophobicity (these fibers had a Young's modulus of 40 GPa and a tensile strength of 1.6 GPa); 5. The high-range water-reducing admixture (PCE) was used to improve the workability of fiber based mortar (a commercially available polycarboxylate ether superplasticizer with a 31% solid concentration).

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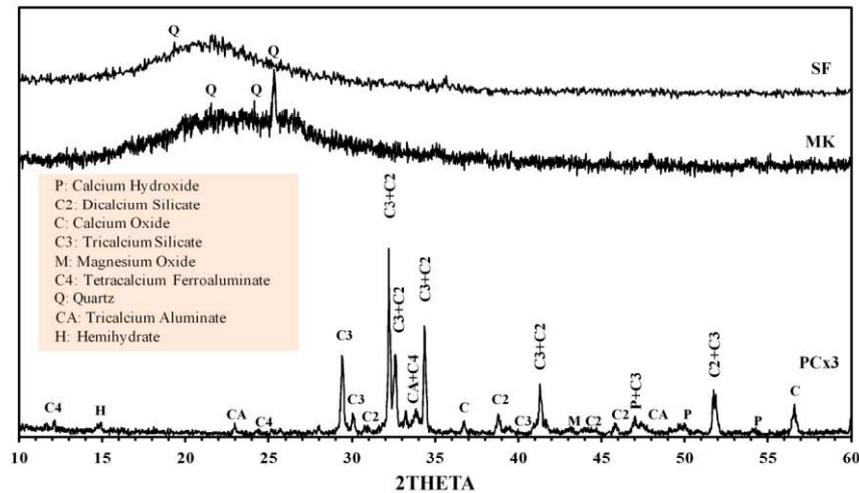


Fig.3. X-ray diffraction of SF (top), MK (middle) and PC (bottom).

Preparation of hydrophobic and superhydrophobic coatings

To prepare the emulsion, water was used as a dispersion medium, water-soluble PVA as a surfactant, and PMHS as the dispersed phase. Metakaolin or silica fume were used to stabilize and modify the emulsion using three different approaches [1]. Fig. 4 demonstrates the differences between the three emulsion types, “simple”, “shell” and “core”, tested. The concentration of surfactant and siloxane was kept constant at 2.5 and 25%, respectively, by weight of the emulsion. The water-soluble PVA swells quickly in water and then clumps together. To avoid clumping, it was gradually added to de-ionized water and stirred for 10 minutes at $23\pm 3^\circ\text{C}$, using a magnetic stirrer with a hot plate. Once a complete dissolution was achieved, temperature was increased to $95\pm 2.5^\circ\text{C}$, and kept constant for 40 minutes under stirring. The solution was allowed to cool in a water bath until a temperature of $23\pm 3^\circ\text{C}$ was reached. The mixing procedure of PHMS and metakaolin/silica fume in PVA solution is explained in Fig. 5. The proportions of metakaolin or silica fume to achieve “over-hydrophobic” and superhydrophobic surfaces were 0.5 and 5.0% by weight of emulsion, respectively. A high speed mixer (HSM, model L5M-A from Silverson) was used to prepare the emulsions. To stabilize the plain emulsions (without particles), a high speed/shear mixed at 10,000 rpm was used to produce the small droplet size. Medium speed (5000 rpm) was used only when particles were added. The emulsions were characterized by an optical microscope (Olympus BH-2) at 1000x magnification.

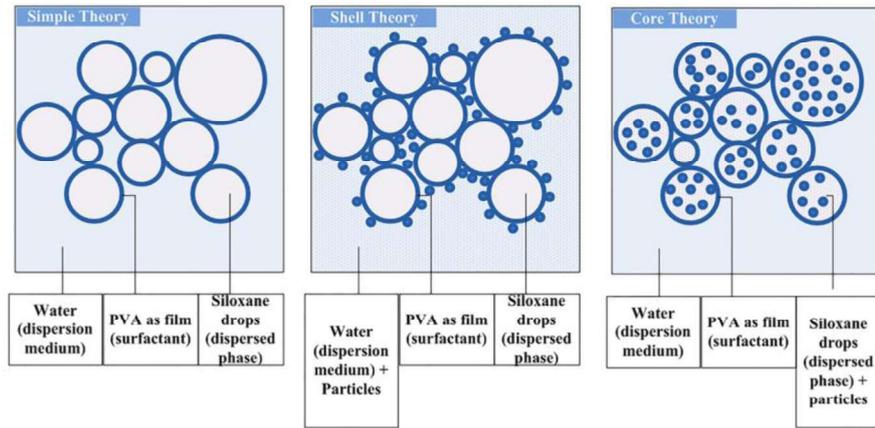


Fig 4. The explanation of simple, core and shell concepts used to design PMHS emulsions

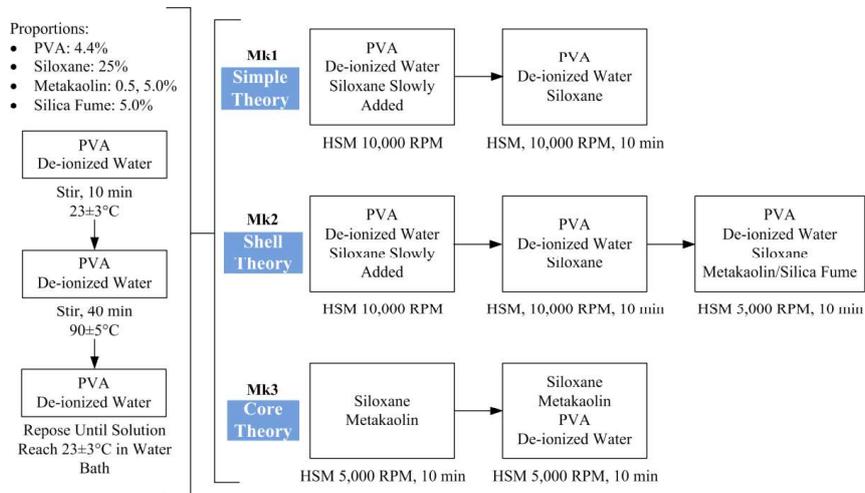


Fig.5. The procedure for preparing the PHMS emulsions

Sample tile preparation

Standard mortar (ASTM C109) [22] tiles of 10 × 10 × 5 mm were prepared for test on hydrophobicity using water to cement ratio (W/C) of 0.5 and sand to cement ratio (S/C) of 2.75. Tiles were cast and compacted using a vibrating table at 150 Hz for 20 seconds. Tiles were allowed to harden for 24 hours at 23±3 °C and at least 90% of relative humidity. After 24 hours, the tiles were demolded and their surface was roughened with a silicon carbide grinding paper with a grit of 60 for 1 minute in order to expose the fresh surface and sand aggregates. High porosity and scratches were revealed on the specimens after this procedure. A soft brush and water were used to remove any loose particles from the tile surface. The tiles were allowed to dry for 24 hours at 40±2 °C and subsequently exposed to room conditions for 24 hours. The tiles were then immersed into the PHMS emulsion for 20 seconds. Excess emulsion from the tiles was removed using a soft plastic spatula. Specimens were dried at a room temperature for 48 hours. This procedure was repeated when two coating layers were required.

For superhydrophobic tiles, the standard (ASTM C109) [22] mortar was produced with 1% (by volume of the total mix) of PVA fibers. Superplasticizer at a dosage of 0.1% (of solid content by weight of Portland cement) was used to provide the required workability level. After hardening, the surface of the tiles was roughened with a silicon carbide grinding paper with a grit of 60 for 30 seconds in order to expose the fresh surfaces, fibers and sand aggregates. Polished tiles were washed with tap water to remove any contamination from the surface. An ultrasound processor UIP1000hd was used at 50% of maximum power for 60 seconds to remove any loose particles from the surface of the tiles. Specimens were placed in an oven at 40 °C for 24 hours to remove any excess of water.

RESULTS AND DISCUSSION

Characterization of coatings

The droplet sizes and the dispersion of metakaolin in the emulsions are shown in Fig. 6. Emulsion Mk1 (Fig. 6a) is mainly characterized by uniform droplets of approximately 2 μm with few inclusions of larger droplets (<20 μm). Emulsion Mk2 (Fig. 6b) shows well-distributed droplets with sizes ranging from 3 to 30 μm . Particles of metakaolin were found on droplet boundaries. Emulsion Mk3 (Fig. 6c) is represented by well-distributed droplets with sizes from 2 to 5 μm with some inclusions of larger droplets (<40 μm). In this emulsion, the metakaolin particles were found to be embedded within the droplets.

These three emulsions successfully represent the proposed concepts detailed in Fig. 4. The speed selected allows the formation of an emulsion with small droplets (Fig 6a), which is one of the key parameter for the stability of the emulsion. Due to its hydrophilic surface, metakaolin/silica fume particles increase the coalescence of the emulsion during the mixing procedure, acting as an attraction force that combines the smallest droplets observed in Fig. 6(a), into bigger droplets observed in Fig. 6(b). Contrary to Mk2 emulsions, encapsulated particles of metakaolin in the oil-phase of Mk3 emulsion (Fig. 6c), prevented the droplets from coalescence.

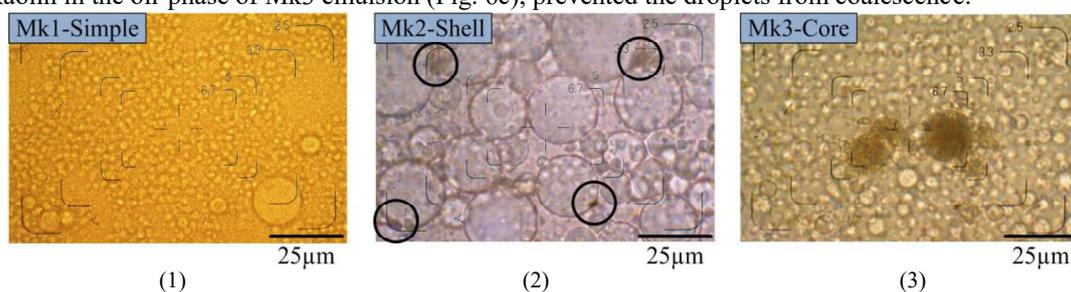


Fig.6. Emulsion images taken by optical microscope at 1000x magnification for: (a) Mk1; (b) Mk2; and (c) Mk3; with metakaolin particles.

The morphology of two-layer superhydrophobic coatings was analyzed by SEM technique (Fig. 7) in order to understand the effects of emulsion type and surface treatment. The coatings on these specimens are directly related to the method that was used to produce the emulsions. Irregular surface structure is produced by collapsed bubbles with the size of 3 to 13 μm and by smaller bubbles of 1 to 2.5 μm as observed for Mk1 coating (Fig. 7a). The collapsed bubbles are dominant in the Mk1 sample, and it can be concluded that the simple emulsion had no capability of preserving the bubble structure on a surface resulting in the appearance of “moon craters”. The Mk2 coating (Fig. 7b) appears to mimic the relief of the surface, leaving a uniform foam free self-assembled particle coating with a “lump” size of 0.5 to 8 μm . At higher magnification (Fig. 7d), the Mk2 surface reveals the bubble formation of the coating due to the first coating application. With the second application of Mk2 emulsion covers the voids left by the irregularities of the tile surface and partially cover the bubbles and particles (Fig. 7d). The Mk3-core emulsion with incorporated particles allows the formation of “intact” bubbles reinforced by MK particles as a coating structure. Bubbles of 0.5 to 22 μm remained on the surface of the specimens, and some collapsed bubbles of 1 to 19 μm can be observed on these coatings (Fig. 7c).

To understand the effect of droplet size in the emulsion on the irregularities of hydrophobic surface coating, the maximum and minimum diameters of droplet size and intact or collapsed bubbles were determined. Emulsion droplets and intact or collapsed bubbles were considered of spherical shape. The effect of the droplet size of the emulsion on surface irregularities is shown in Fig. 8. As a general trend, the bigger the droplet size is, the bigger the diameter of the bubble. Collapsed surface structure (Mk1-Simple) requires a small increment in the droplet size so as to increase the surface irregularities. Therefore, to produce small “moon craters”, a higher speed during the emulsion production is required. Bigger intact bubbles (Mk3-Core) can be attained with larger emulsion droplet size (>30 μm). However, intact bubble structure is difficult to achieve, since larger droplets result in unstable emulsions. Here, the addition of particles increases the stability of emulsions and reinforces the bubbles.

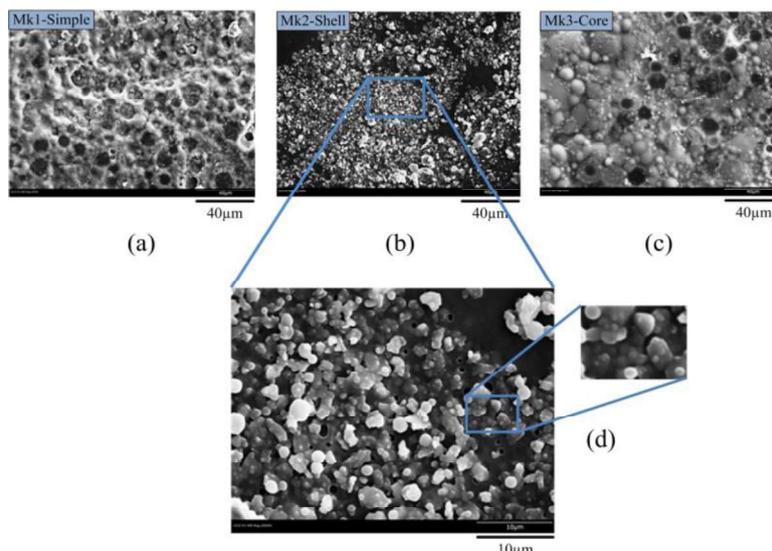


Fig.7. SEM images of superhydrophobic coatings at 500x magnification for: a) Mk1; b) Mk2; c) Mk3; and d) Mk2 at 2000x magnification.

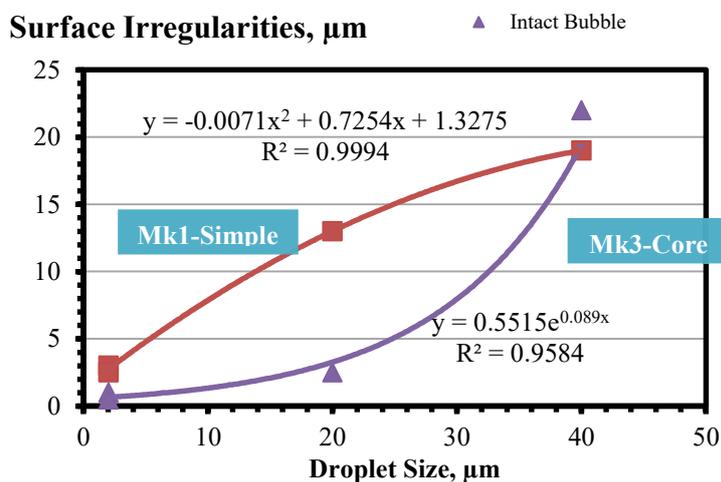


Fig.8. The effect of the droplet size on the irregularity of the coatings.

Contact angle measurement

The wetting properties of the tiles were examined by measuring the water CA using the Ramé-Hart Goniometer model 250. At least three, 5µl water droplets were placed at different points on each sample. The siloxane based emulsion with 0.5% of metakaolin was used to achieve hydrophobicity. The values of water CAs as well as the images of water droplets on different hydrophobic coatings are shown in Fig. 9. It was found that the CAs of all coated specimens increased by more than 120% vs. the reference material. The application of a second coating did not improve the performance of Mk1 and Mk3. Apparently, the hydrophobic first coat of Mk1 and Mk3 did not allow the deposition of a second coat. A remarkable performance of self-assembled Mk2 was observed, not only on single-coated specimens (with CA of 3 times better vs. the reference) but also for double-coated specimens (CA of 3.5 times the reference). Metakaolin particles, located at the boundaries of the droplets, acted as support for the second coating, providing the surface a microroughness and increasing the hydrophobicity to the “over-hydrophobic” range.

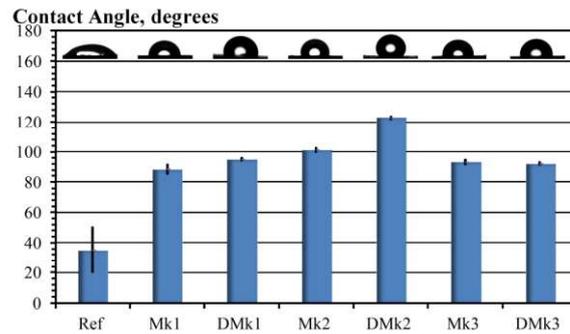


Fig.9. The contact angle of specimens with single (Mk)- and double (DMk)- coatings.

The specimens with randomly distributed PVA fibers emerging from the surface were coated with the siloxane based emulsion Mk2 with 0.5 and 5.0% of metakaolin (Mk2-MK-0.5 and Mk2-MK-5, respectively) and 5.0% of silica fume. Coated surfaces were compared with an uncoated tile. With the use of PVA fibers, the CA of Mk2 specimen was enhanced from 101.3 to 128.2 degrees (Mk2-MK-0.5), as demonstrated by Fig. 10. In this way, PVA fibers can be used to increase the hydrophobic effect by over 26% (over plain tiles). The combination of the sub-micrometer-sized particles which provide the micro- and nano-roughness, and fibers which introduce a hierarchical structure enable the superhydrophobic effect to be achieved as observed on specimens with 5.0% of particles. The use of a higher volume of particles enables the further increase of CA. The superhydrophobic behavior was confirmed by the roll-off angle tests, in which specimens with higher CA had lower roll-off angle (Fig. 10). In this way, the use of exposed fiber surfaces and emulsions with high volumes of particles (5% of silica fume or metakaolin) can induce the superhydrophobic performance.

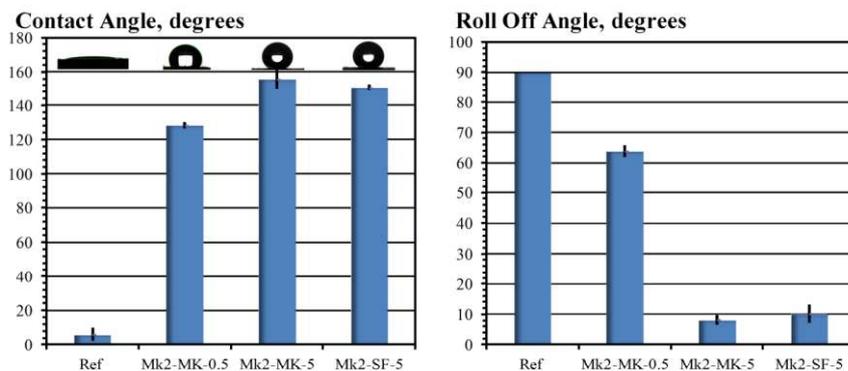


Fig.10. The contact and roll off angle of specimens with PVA fibers randomly distributed on the surface and coated with siloxane based emulsions.

CONCLUSIONS

The technology of hydrophobic emulsions and their application on Portland cement mortar tiles were investigated. The effect of dual scale roughness of concrete surface on CA was analyzed. The introduction of hierarchical roughness and chemical modification of the surface can be beneficial for the design of bioinspired superhydrophobic concrete.

The proposed emulsion types were successfully achieved by using different mixing procedures. Water wetting of mortar tile surfaces was investigated experimentally. Due to their hierarchical surfaces and hydrophobization the PVA fiber mortar tiles coated with the Mk2-MK-5 solution had the highest water-repellency reaching the superhydrophobic state with water contact angle of > 150 degrees and the roll-off angle of < 10 degrees. Therefore, an innovative method to produce “over-hydrophobic” water-repellent concrete with water CAs reaching superhydrophobicity values and low roll-off angles was developed and implemented. Water-repellent concrete can have many important applications in construction and civil engineering due to durability enhancement.

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