Transparent superhydrophobic coating application to the interlocking clay block for the microbial growth mitigation

O Nimittrakoolchai1*, M Suwan1 and S Supothina1,2
1National Metal and Materials Technology Center, National Science and Technology Development Agency (NSTDA), 114 Thailand Science Park, Phahonyothin Rd., Klong Luang, Pathum Thani 12120, Thailand
*E-mail: sitthis@mtec.or.th

Abstract. Interlocking clay block is of widespread use in many countries due to its less labor-intensive design. The block comprises of considerable amount of pore structures; therefore water can easily penetrate into it causing deterioration by natural weathering as well as the growth of microbes on its surface. In this present work, a transparent, superhydrophobic coating was applied onto the block’s surface to prevent water absorption. The coating which is a poly(methyl hydrogensiloxane) base containing fumed SiO2 nanoparticle was designed to possess surface topographic feature similar to that of the lotus leaf. After coating the block with the superhydrophobic compound, its water absorption decreased from 11.5 to 4.8% and porosity substantially decreased from 22.5 to 9.2%, while bulk and apparent densities did not change. Accelerated weathering test revealed that the coating had good stability. The coated samples exhibited growth inhibition of algae.

1. Introduction
An interlocking clay block is widely employed in buildings and other artefacts essentially due to its simplicity and less labor-intensive of construction as no mortar is required for joining as in the case of a conventional clay brick [1]. The block can be fabricated in a variety of shapes and designs simply by changing the mold of a pressing machine. Nowadays, the interlocking clay block has been utilized not only for structural purpose but also for decoration and gardening purposes which require natural-like appearance. In the tropical zone, there is plenty of raw material called ‘laterite’ or ‘red earth’ which is one of fine starting materials for production of the interlocking clay block. As the laterite’s color is red, the block made from this material has natural appearance which, for a certain artefact, do not require painting.

The interlocking clay block is typically fabricated by uniaxial dry pressing of the feed consisting of red earth, sand and cement after which it is dried in open air for a few days. Since most of raw materials are coarse grains and there is no heat treatment for densification, the finished block comprises of both micro- and nanopores, which can draw significant amount of water into it, causing a rapid deterioration by natural weathering. In addition, when utilized in humid environment it is observed that microbes such as lichen and algae can grow rapidly, especially, during a rainy season because of high moisture content at the block’s surface, leading to a loss of aesthetic appearance as a result of such biological fouling. This is a major drawback that can limit the utilization of the block in humid environment. To protect the material from natural weathering and more importantly to reduce the biological fouling, the surface must be coated with a protective layer that inhibits water penetration. The most common protective coating is partially fluorinated polymeric compounds containing acrylic,
urethane or silicone resin. For instance, it was found that perfluoropolyethers provide a very satisfactory protecting performance and compatibility with the stone heritage [2]. An influence of side-chain fluorination on the performance of acrylic-based copolymers has been investigated for stone protection. The presence of fluorine was found to increase water repellency, thus providing protective efficiency [3]. Similarly, siloxane branches of a polydimethylsiloxane-grafted polymer can enhance hydrophobic property [4]. A fluoropolymer has also been utilized to coat glazed tiles to enhance water repellency and to reduce soil attachment, thus providing a better cleanability [5]. Environmental friendly, solvent-free hybrid organic-inorganic methacrylic-based coatings have been introduced with a performance in terms of hydrophobicity and color change comparable to those of the commercial products [6]. Recently, oligoamide grafted with perfluoropolyether blocks which are environmental friendly has been synthesized. This coating material can be used as a protective coating for low porous stone materials such as stone artworks [7]. For large porous stones, it has been reported that coating application performed by brushing resulted in better water-repellent property due to the formation of a superficial film compared to capillary absorption [8]. In order to evaluate their protective performance, weathering stability of waterproof polymers have been evaluated under artificial weathering. It was found that all the polymers under investigation underwent irreversible modifications with reduction of their conservative properties, color change and impossibility of their complete removal [9]. The coatings of these compounds usually provide water contact angle in a range of 110-140 degrees, and some of them have glossy or darken appearance which may be undesirable for certain artefacts especially those requiring natural appearance.

In this present work, a very thin super water-repellent coating (water contact angle ≥ 150 degrees) with high transparency was applied onto the interlocking clay block to minimize water penetration as well as reduce moisture absorption. The coating’s transparency provided the advantage that the coated block preserved its naturally aesthetic appearance. The coating comprising of a siloxane compound, fluorosilane and oxide nanoparticle was designed by mimicking surface feature of a lotus leaf that exhibited a “lotus effect” [10,11]. Physical and chemical properties of the blocks such as chemical composition, apparent porosity, water absorption, bulk and apparent densities of the bare and coated blocks were also measured. Growth inhibition of microbes was evaluated according to the ASTM standard, as well as by means of natural weathering test. In addition, stability of the coating on glass substrate was evaluated by subjecting to an accelerated weathering test. Surface topography and transparency of the coating on the glass substrate were also characterized.

2. Experimental procedure

2.1. Fabrication of interlocking clay blocks
The interlocking clay blocks of 10 cm x 10 cm x 10 cm in size were fabricated by pressing of raw material in a steel mold. The raw material consisting of 52 wt.% red earth, 31 wt.% sand, 11 wt.% cement and 6 wt.% water was mixed thoroughly, fed into the mold and pressed at 2.0-2.3 MPa using a hand-operated hydraulic machine. Finally, the resulting interlocking blocks were dried in open air for at least 5 days.

2.2. Transparent superhydrophobic coating
To reduce water absorption, the blocks were coated with a water-repellent coating as follows. The coating solution was prepared by dissolving 1 g of poly(methyl hydrosiloxane) (PMHS, Dow corning®) in hexane followed by an addition of 0.05 ml of 100 ppm Pt-catalyst which was prepared by dissolving platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Aldrich) in hexane. Then, 0.025 g of a fumed SiO₂ (Aerosil 200, JJ Degussa) nanoparticles, and 4.95 ml of trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane (CF₃(CF₂)₃CH₂CH₂SiCl₃, 97%, Aldrich) solution prepared by dissolving 0.4 ml of the fluorosilane in 2-propanol were added respectively into the PMHS solution under a continuous stirring. The resulting mixture was stirred at room temperature for at least 10 min. The water-repellent coating was applied onto the interlocking blocks by hand painting with special
attention on the amount of the coating precursor applied. The coated blocks were dried at room temperature for 15 min before they were re-coated for 2 more times to obtain uniform coating.

2.3. Characterizations

**Physical property analysis of the clay block:** A specific surface area (SSA) of the block was measured by means of nitrogen adsorption using an Autosorb-1 (Quantachrome). Surface morphology was observed by using a field-emission scanning electron microscope (FE-SEM, JSM 6301F). Apparent porosity (\( \%P \)), water absorption (\( \%A \)), bulk density (\( \rho_b \)) and apparent density (\( \rho_a \)) were measured by means of water displacement according to the standard test method (ASTM C67-03a) as follows. The block was cut into 2 cm x 2 cm x 2 cm pieces and dried in an oven at 110\(^\circ\)C for 24 h. After cooling to room temperature in a desiccator, the weight of the oven-dried specimen was measured. Then, the specimen was immersed in a beaker filled with de-ionized water maintained at 24± 1\(^\circ\)C for 24 h, and the specimen’s weight when it was submerged in water was measured. After submersion in water, surface water was wiped off with a damp cloth and the specimen was weighed again. The apparent porosity, water absorption, bulk density and apparent density were calculated from the equations below:

\[
\%P = \frac{W_{ws} - W_D}{W_{ws} - W_{ss}} \times 100, \\
\%A = \frac{W_{ws} - W_D}{W_D} \times 100, \\
\rho_b = \frac{W_D \cdot \rho_L}{W_{ws} - W_{ss}}, \\
\rho_a = \frac{W_D \cdot \rho_L}{W_D - W_{ss}},
\]

where \( W_{ws} \) is the weight of water-saturated specimen, \( W_D \) is the weight of oven-dried specimen, \( W_{ss} \) is the weight of water-saturated specimen when it is submerged in water, and \( \rho_L \) is the density of water.

**Characterization of the coating:** Surface morphology of the uncoated and coated blocks was observed by using a field-emission scanning electron microscope (FE-SEM, JSM 6301F). Surface topography, transparency of the coating deposited onto the glass slide were characterized by using an atomic force microscopy (AFM, SPA 400) performed in a non-contact mode and a UV-Vis-NIR spectrophotometer (Perkin-Elmer Lambda 900), respectively. Thickness of the coating was determined by making a scratch on the sample, and then the z-height AFM scan was performed.

**Accelerated weathering and algae inhibition tests:** The accelerated weathering test was performed in a Ci3000 Xenon Weather-Ometer (Atlas Material Testing Solutions) following the ASTM standard (G 155-04a) by using the following operating condition: Xenon arc lamp irradiation: 0.35 W/m·nm at 340 nm; black panel temperature: 63\(^\circ\)C; relative humidity: 50%. The specimens were mounted on the holders which were placed on the specimen rack. The testing was conducted for a total time span of 325 h during which the specimens were taken out for water contact angle measurement every 50 or 100 h interval. Growth inhibition of algae was tested following the ASTM D5589-97 standard.

3. Results and discussion

3.1. Physical analysis of the clay block

Physical properties of the uncoated and coated blocks are summarized in table 1. Since the block did not subject to high-temperature treatment, the uncoated block consists of high porosity of 22.50\%, and low bulk and apparent densities of 2.53 and 1.96, respectively, leading to high water absorption of 11.50\%. The specific surface area is 23.80 m\(^2\)g\(^{-1}\).
Table 1. Physical properties of the uncoated and coated blocks.

| Properties          | Uncoated blocks | Coated blocks |
|---------------------|-----------------|---------------|
| SSA (m²g⁻¹)         | 23.80           | 20.84         |
| %P                  | 22.50           | 9.20          |
| %A                  | 11.50           | 4.80          |
| ρₐ (gcm⁻³)          | 1.96            | 1.92          |
| ρₖ (gcm⁻³)          | 2.53            | 2.11          |

3.2. Surface treatment with transparent, superhydrophobic coating

Most of the coating precursor was easily absorbed into the pores of the blocks during the first painting, and was drawn at a lesser extent during the subsequent painting cycles. After the block surface was modified with a water-repellent coating, the water absorption decreased from 11.50 to 4.80% and the porosity substantially decreased from 22.50 to 9.20%, while the bulk and apparent densities did not change. This result indicated that the water-repellent coating did not form a continuous film on the block surface, but part of it penetrated into the block and wetted the pores. It was anticipated that the extent of water absorption of the coated block in a condition of use would be much lower since water will form spherical droplet on its surface and roll off on a vertical surface very easily.

Surface morphology analysis of the uncoated and coated blocks (figure 1) revealed that surface of the coated block was still porous and there was merely continuous coating observed. Both the coated and uncoated blocks had similar surface morphology, indicating that the coating was very thin and most of the water-repellent compound penetrated into the pores and wetted the pore’s interior. Wetting of the pore’s interior by the water-repellent compound would prevent water absorption by the capillary force exerted by the pore structure. Thickness of the coating determined by performing z-height AFM scan was only 0.27±0.08 µ. This hand-painted coating was less uniform compared to the coating on a glass slide performed by using a dip coater.

![Figure 1](image_url)

**Figure 1.** SEM images of (a) uncoated block and (b) coated block.

Surface topography analysis of the water-repellent coating on the glass slide (figure 2) revealed that the surface was roughened, and had surface roughness of 95.7±5 nm which was much higher than surface roughness of bare glass slide (3.6±0.3 nm). The film consisted of sub-micrometer-sized protrusions created by SiO₂ agglomerates which consisted of many nanosized SiO₂ primary particles. The SiO₂ nanoparticle was added as a surface roughness enhancer to improve degree of hydrophobicity as described by Wenzel’s and Cassie-Baxter’s models [12,13]. This surface had water contact angle of 160.2±1.0 degrees, exhibiting a superhydrophobic property. With no addition of the
SiO$_2$ nanoparticle, the contact angle of only 103.9±0.4 degrees was obtained.

Figure 2. AFM images of the water-repellent coating on a glass slide.

Figure 3 shows SEM images of the superhydrophobic films on the glass slide. For the film without the addition of SiO$_2$ oxide filler (figure 3(a)), the surface is observed as a flat surface comprising of sub-micrometer to micrometer white spots. It is believed that these white spots took place during the drying step which resulted in rapid evaporation of the solvents employed. It is clearly seen that the film containing the SiO$_2$ filler (figure 3(b)) composed of the SiO$_2$ particles covering most of the surface. These particles formed loose agglomerates as seen in the inserted image. It was anticipated that the coating on the block would have more or less similar topographic feature to the coating on the glass slide. The transmittance of the coating (figure 4) was in a range of 60-80% in a visible region. Although, the transmittance of the modified glass was lower than that of the bare glass, the film was sufficiently transparent which can be employed as a water-repellent coating on the clay block without altering its aesthetic appearance.

Figure 5 shows photographs of the uncoated and coated blocks after water was dropped on their surfaces. The water was instantly drawn by the uncoated block. In contrast, it formed a droplet on the surface of the coated block, and rolled off when the block was tilted. The coated block had water contact angle of 151.4±2.1 degrees. This water-repellent property is similar to that observed at the surface of many plant leaves and insects [10,11,14]

Figure 3. SEM images of the coating on glass slide (a) without addition of SiO$_2$ particle, and (b) with addition of SiO$_2$ particle.
3.3. Accelerated weathering and algae inhibition tests

The result of accelerated weathering test (figure 6) clearly indicated that the coating was stable as the water contact angle remained virtually unchanged after accelerated weathering exposure of 325 h which is comparable to actual weathering exposure for ~7 weeks. For the samples subjected to algae inhibition test (figure 7), it is clear that green algae can grow on the uncoated sample but cannot grow on the coated sample due to no moisture absorbed on its surface. In addition, the samples were subjected to outdoor weathering test by placing them in the garden. It is clearly observed after a rainfall that the coated blocks were in their original light brown color, while the uncoated blocks were dark brown because they absorbed water. The green algae and lichen grew on the uncoated blocks within 1-2 months turning their brown appearance to green. According to the result after 6 months of the field test which was at the end of the rainy season, only small amount of green bio-organisms was observed on the coated blocks in the lowest row which was in contact with the ground and had been occasionally flooded. After the field test, the blocks coated with the superhydrophobic coating can preserve their original appearance. It is very obvious from this field test that the coating was efficient for growth inhibition of the algae.
Figure 6. Accelerated weathering test of the coating on glass.

Figure 7. Photographs of uncoated sample (left) and coated sample (right) after algae growth inhibition test.

4. Conclusions
The growth of bio-organisms such as algae on the interlocking clay blocks can be mitigated by coating their surface with the superhydrophobic coating having surface property similar to that of the lotus leaf. The water absorption and porosity of the coated blocks substantially reduced while the bulk and apparent densities did not change. Thick layer of green algae can grow on the uncoated blocks but cannot grow on the blocks coated with the superhydrophobic coating. The coating was of sufficient transparency, preserving natural appearance of the blocks. The accelerated weathering test also revealed that the coating had good stability. It is feasible to apply the superhydrophobic coating on other construction materials or artefacts to obtain a similar effect.

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