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Full Length Article

Induced superhydrophobic and antimicrobial character of zinc metal modified ceramic wall tile surfaces

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ABSTRACT

Hydrophobic surfaces are also known to have antimicrobial effect by restricting the adherence of microorganisms. However, ceramic products are produced by high temperature processes resulting in a hydrophilic surface. In this study, an industrial ceramic wall tile glaze composition was modified by the inclusion of metallic zinc powder in the glaze suspension applied on the pre-sintered wall tile bodies by spraying. The glazed tiles were gloss fired at industrially applicable peak temperatures ranging from 980 °C to 1100 °C. The fired tile surfaces were coated with a commercial fluoropolymer avoiding water absorption. The surfaces were characterized with SEM, EDS, XRD techniques, roughness, sessile water drop contact angle, surface energy measurements, and standard antimicrobial tests. The surface hydrophobicity and the antimicrobial activity results were compared with that of unmodified, uncoated gloss fired wall tiles. A superhydrophobic contact angle of 150° was achieved at 1000 °C peak temperature due to the formation of micro-structured nanocrystalline zinc oxide granules providing a specific surface topography. At higher peak temperatures the hydrophobicity was lost as the specific granular surface topography deteriorated with the conversion of zinc oxide granules to the ubiquitous willemite crystals embedded in the glassy matrix. The antimicrobial efficacy also correlated with the hydrophobic character.

1. Introduction

Hydrophobic surfaces are defined as having sessile water drop contact angle greater than 90°, while surfaces with contact angles larger than 150° are rendered as superhydrophobic. The surface chemistry and morphology are the major factors determining hydrophobicity [1–6]. The Young's model states that a smooth solid surface with a lower free energy has a higher sessile liquid drop contact angle since any isolated system changes to achieve a minimum free energy. Whether a smooth surface is hydrophilic or hydrophobic depends on the solid-liquid and solid-air interfacial energies [7]. In order to explain the phenomena related to rough surfaces Wenzel [8] and Cassie-Baxter [9] basic models are employed. Wenzel model states that the contact between a rough solid surface and a liquid is uninterrupted, and the increased surface area of the solid due to roughness causes a chemically hydrophilic surface to have a further decreased contact angle, while on a chemically hydrophobic surface the contact angle rises above that of the smooth surface. However, Cassie-Baxter model assumes air pockets to be trapped between the rough solid surface and the liquid, and a chemically hydrophilic surface may become hydrophobic and vice versa depending on the solid-air, liquid-air interfacial energies. The superhydrophobicity is a required property especially for keeping the surfaces free of wetting, and thus avoiding contamination by water based slurries, suspensions, and solutions. These types of surfaces are also classified as self-cleaning due to the difference in advancing and receding contact angles [10–14].

Hydrophobic surfaces are also known to have non-migrating antimicrobial character by restricting the adherence of microorganisms on the surface [15]. Since the inhibiting effect is not due to the consumption of any antimicrobial agent, and is only physical, advantageously any immunity development is not possible [16,17]. Nevertheless, antibacterial ceramic tile surfaces with a biocidal antimicrobial molecular barrier coating were developed as an alternative to hydrophobic surfaces [18]. Antimicrobial floor and wall coating materials in clinical, industrial and household spaces,

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Table 1
Sessile water drop/ceramic surface contact angles, and ceramic surface free energies.

Tile surface type/Heat treatment peak temperature and duration	Industrial glaze contact angle	Industrial glaze + polymer coating contact angle	Zn modified glaze contact angle	Zn modified glaze + polymer coating contact angle	Zn modified glaze + polymer coating overall SFE (γ_{sg})
980 °C, 5 min	∼40°	∼70°	125° → absorbed	125°–135°	11.3 mJ/m^2
1000 °C, 5 min	<30°	∼70°	130° → absorbed	145°–150°	5.40 mJ/m^2
1050 °C, 5 min	<30°	∼70°	55° → absorbed	115°–120°	16.0 mJ/m^2
1100 °C, 5 min	<30°	∼70°	50° → absorbed	90°–95°	29.7 mJ/m^2
1050 °C, 60 min	<30°	∼70°	50° → absorbed	85°–90°	34.2 mJ/m^2
1100 °C, 30 min	<30°	∼70°	50° → absorbed	80°–85°	41.3 mJ/m^2

Table 2
Surface roughness parameters.

Tile surface type/Heat treatment peak temperature and duration	Industrial glaze surface roughness		Zn modified glaze surface roughness	
	Ra (μm)	Rz (μm)	Ra (μm)	Rz (μm)
980 °C, 5 min	–	–	450	2200
1000 °C, 5 min	2.6	18	540	2900
1050 °C, 5 min	–	–	370	2000
1100 °C, 5 min	–	–	70	300
1050 °C, 60 min	–	–	60	270
1100 °C, 30 min	–	–	40	220

especially on wettable surfaces is demanding, with a potential to reduce the hospital infections and various dermatome risks [19].

Ceramic coating products are produced by heat treatment for sintering and vitrification, and the vitrified matrix of the surface is inevitably hydrophilic due its water attracting chemistry [20]. Imparting a hydrophobic character on a gloss fired ceramic surface depends on the formation of nano or micro patterned surface topography by the nano or micro sized granular structures on the glazed or full body ceramic tile surfaces. In nature there are a number of examples of superhydrophobic plant or animal shell surfaces due to surface topography rather than surface chemistry such as the lotus flower leaves and the snail shell [21,22].

The wettability of diverse liquids of many different surfaces was also studied extensively [23,24] and superhydrophobic surfaces including alumina ceramics, silica hybrid films, and titania coatings on float glass were constructed by a number of methods such as thermal spray, laser texturing, vapor-fed aerosol flame synthesis, and sol-gel route methods [25–27]. None of these methods have the potential of application in the conventional ceramic wall tile production lines.

Zinc oxide nanoparticles are known to exhibit antibacterial activity that depends on the localized interaction of ZnO in terms of increased membrane permeability, direct endocytosis of nanoparticles, and the uptake of dissolved zinc ions, interfering with the intracellular metabolism. The effect of ZnO particle size, concentration, morphology, porosity, defects, and particle surface modifications on the bacterial and fungal inhibition were extensively studied [28–31]. The applications can be topical or systemic, however, the inconvenience of the diffusion and consumption of the migrating bactericidal component for ceramic coating materials necessitates to develop hydrophobic and hence non-migrating bactericidal or bacteriostatic ceramic tile surfaces.

In this study, body fired ceramic wall tiles were coated with industrially applicable glazes modified with the inclusion of metallic zinc powder, which is suitable for gloss firing in the already existing conventional wall tile production lines. The effects of the formation of micro-structured zinc oxide (ZnO), and willemite ($2ZnO.SiO_2$) crystals on the gloss fired tile surface topography and/or chemistry as the peak gloss firing temperature and duration was changed, which in turn affecting the hydrophobicity and antibacterial character, were determined.

2. Materials and methods

2.1. Ceramic tile coating and sintering

The green ceramic wall tile bodies were fired in an industrial ceramic furnace (roller, open hearth) of 90 m long for a firing cycle of 28 min with the firing zone maximum temperature of 1140 °C. The body fired wall tiles were coated with a modified glaze by pressurized air spraying. The glaze was modified with the addition of metallic zinc powder into an industrially applicable glaze composition prior to aqueous milling. The glaze composition was prepared as 30% frit (boric acid 15%, alumina 3%, quartz 27%, potassium feldspar 35%, potassium nitrate 2%, calcite 15%, magnezite 3%, 3 ppt sodium carboxymethyl cellulose, 1.5 ppt sodium tripolyphosphate), 5% china clay, and 65% metallic Zn powder, all percentages being by weight for the rest of the document. The metallic zinc powder was obtained from the manufacturer Hepsen Kimya Ltd., Bilecik, Turkey, under the brand name of "Zinc Powder Blue" with the technical specifications as follows. The particles under 32 μm was 99.1%, total zinc content was 97%, metallic zinc content was 94%, Pb content was 0.03%, and Fe content was 0.15%. The modified glaze was prepared in ceramic jar jet mills rotated at 120 rpm for 20 min with a milling load of alumina balls and in water medium with 35% water and 65% dry matter. The glaze slurry was sieved through 45 μm. The coated tiles were fired in a laboratory muffle kiln at the maximum temperatures of 980 °C (5 min), 1000 °C (5 min), 1050 °C (5 min, and 60 min), 1100 °C (5 min, and 30 min) with a heating rate of 30 °C/min below 500 °C and 5 °C/min above 500 °C. Some of the sintered tiles were further processed by spray coating with a commercial polymeric composition of 10% fluoropolymer, 60% alkoxysilane and 30% ethanol, under the trade name ECC-4000, and curing at 120 °C for 10 min in order to avoid water absorption and to enhance the hydrophobic character. The sprayed quantity was approximately 250 g/m^2.

2.2. Tile surface characterization

The contact angle and surface free energy (SFE) measurements were carried out by drop shape analyzer (Kruss, DSA-25), using water and diiodomethane as liquids of known surface tensions (ST) in air. The SFE calculations were done according to Young's equation (Eq. (1)) and a two-component model developed by Fowkes [32],

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