Scholars Bulletin *(Chemical Engineering)*
An Official Publication of "Scholars Middle East Publishers", ISSN 2412-9771 (Print)
Dubai, United Arab Emirates ISSN 2412-897X (Online)
Website: http://scholarsbulletin.com/

The Investigation of the Effects of Various Low Temperature Processing Organic Materials on the Ceramic Wall Tile Surface Morphology

Selçuk Özcan*
Department of Chemical and Process Engineering, Bilecik Şeyh Edebali University, Bilecik, Turkey

***Corresponding author**
Selçuk Özcan

Article History
Received: 13.12.2017
Accepted: 21.12.2017
Published: 30.12.2017

DOI:
10.21276/sb.2017.3.12.12

Abstract: It would be required to impart hydrophobic and hence antimicrobial property to inherently hydrophilic ceramic wall tiles in order to reduce health risks. For this purpose an industrially applicable ceramic wall tile opaque glaze was modified by the addition of the various organic materials. The organic matter included in the industrial glazes most probably acted as agents leaving pores behind and changing the liquefaction temperature of the glaze on the pore borders, and forming protruding microscale surface structures by burning and gasifying out during gloss firing. The optimum temperature range for gloss firing of the modified industrial opaque wall tile glaze was determined as 960-980°C by thermal microscope measurements and TG analysis. The SEM images of the surfaces revealed microscaled surface morphologies which might be potentially instrumental in the hydrophobic surface formation due to the trapped air gaps between the tile surface and the sessile water drops in accord with Cassie-Baxter model. The surface topography obtained in this way by polyvinyl butyrate and modifications provided hydrophobic contact angles.
Keywords: Wall tile, low melting organic solids, ceramic glaze, hydrophobicity, contact angle, Cassie-Baxter theory.

INTRODUCTION

Hydrophobic surfaces are also known to have antimicrobial effect, and hence ceramic wall tiles with a hydrophobic surface would possess properties that are required of wall coating materials in clinical, industrial and domestic spaces, especially on wettable surfaces reducing the potential health risks [1-3]. However, ceramic wall tiles are inherently hydrophilic due to high temperature processing resulting in a glassy surface [4].

The hydrophobic character of smooth surfaces depends on the surface chemistry, that is, the solid-liquid and solid-air interfacial energies as described by Young's model [5]. A smooth surface is hydrophilic when $\gamma_{sl} < \gamma_{sg}$ and hydrophobic when $\gamma_{sl} > \gamma_{sg}$. On the other hand, the phenomenon related to rough surfaces is successfully explained by Wenzel and/or Cassie-Baxter models. The Wenzel model accounts for the increase in the surface area of an uninterrupted rough surface rendering an increase in either hydrophobicity or hydrophilicity of an already chemically hydrophobic or hydrophilic surface, respectively [6]. The Cassie-Baxter model states the effect of entrapped air pockets between a rough solid surface and a contact liquid [7]. Depending on the solid-air and liquid-air interfacial energies a chemically hydrophilic surface may turn into a hydrophobic surface, and vice versa. A chemically hydrophilic surface can become hydrophobic or superhydrophobic due to surface morphology when $\gamma_{lg} > \gamma_{sg}$ [8]. The wettability of liquids of the ceramic materials was studied [9] and superhydrophobic ceramic surfaces were manufactured without any potential of application in the conventional ceramic wall tile production lines [10-15]. A few recent studies specifically addressed the production of hydrophobic and antimicrobial ceramic tiles in conventional ceramic tile production lines with surface modification and/or coating [8, 16, 17].

In this study, in an attempt to impart a hydrophobic surface topography to commercial wall tiles, their surface texture was modified with the inclusion of organic materials in an industrially applicable glaze. The materials used for modification were polyvinyl butyrate, wax, polymethyl methacrylate, waste paper cellulose, corn starch, and carboxymethyl cellulose all of which were low temperature fuming (burning) or melting materials. It was aimed to form a specific surface texture during the gloss firing of the glazed ceramic tiles, which in turn, would cause the surfaces to become hydrophobic due to the surface topography as described by Cassie-Baxter theory. The method is adaptable for the conventional production lines with an additional firing cycle.

MATERIALS AND METHODS

Ceramic Tile Coating and Gloss Firing

The body firing of the green ceramic wall tiles was performed in an industrial ceramic furnace (roller, open hearth) at the maximum temperature of 1140°C. An industrially applicable wall tile glaze to be spray coated on the body fired wall tiles, was modified with the addition of a number of low temperature burning organic materials, namely, polyvinyl butyrate (PVB), wax, polymethyl methacrylate (PMMA), waste paper cellulose, corn starch, and carboxymethyl cellulose (CMC). The industrial wall tile glaze comprised 30% frit (boric acid 15%, alumina 3%, quartz 27%, potassium feldspar 35%, potassium nitrate 2%, calcite 15%, magnesite 3%, 3 ppt sodium carboxymethyl cellulose, 1.5 ppt sodium tripolyphosphate), 5% china clay, and 65% organic matter. The modified glaze composition was homogenized and DE agglomerated by aqueous milling with 35% water and 65% dry matter in ceramic jar jet mills rotated at 120 rpm for 20 min, followed by sieving through 45 µm sieve. The pre-sintered tiles were glaze coated with pressurized air spraying to a thickness of 150 µm. The coated tiles were fired in a laboratory muffle kiln at the maximum temperatures of 980°C for 30 min.

Characterization

The particle size distribution of the unmodified glaze was determined by laser diffractometer Malvern Mastersizer Hydro 2000s. The thermogravimetric (TG) analyses were performed by Setaram, Labsys Evo simultaneous thermal analysis system. The thermal microscope measurements were carried out with Misura Hsm Heating Microscope.

The contact angle (CA) measurements of the sessile water drop on the tile surfaces were carried out by drop shape analyzer (Kruss, DSA-25). The surface roughness measurements were performed by Mitutoyo SJ-301 surface roughness tester in the roughness profile mode with curve correction by Gaussian filter in accord with JIS B0601-2001 as the arithmetic mean deviation of the troughs and crests from the mean line of the roughness profile (Ra). The microstructure of the tile surfaces was examined by SEM-EDX (Zeiss, Supra 40 VP, with high voltage 10.0 kV, work distance 10.2–13.2 mm).

The experimental procedure is summarized in Figure 1.

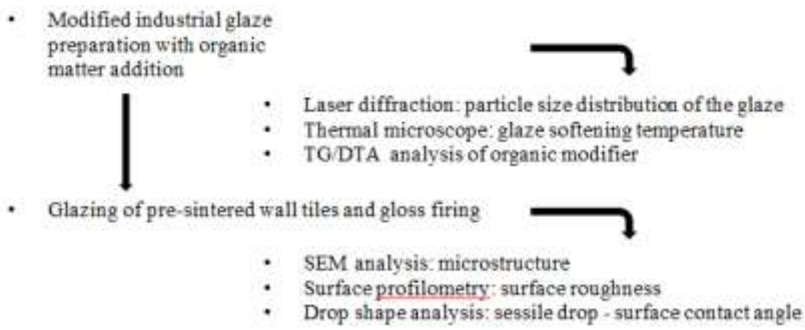

Fig-1: Experimental procedure

RESULTS AND DISCUSSION

In an effort to impart hydrophobic surface property to commercial ceramic wall tiles an industrially applicable opaque glaze was modified with the incorporation of various low temperature burning organic materials bringing about particular surface morphologies. The particle size distribution of the glaze to be modified is given in Figure 2. The distribution as determined by laser diffraction was broad with the most probable size of 3 µm typical of industrial glazes. As shown in Figure 3, the thermal microscope imaging revealed the softening temperature of the glaze as 1060°C. Importantly the onset of sintering was at 870°C, and 960-980°C temperature range was high enough for the formation of just the sufficient quantity of the liquid phase for vitrification without significant shape deformation, that is, the glaze did not spread by flowing.

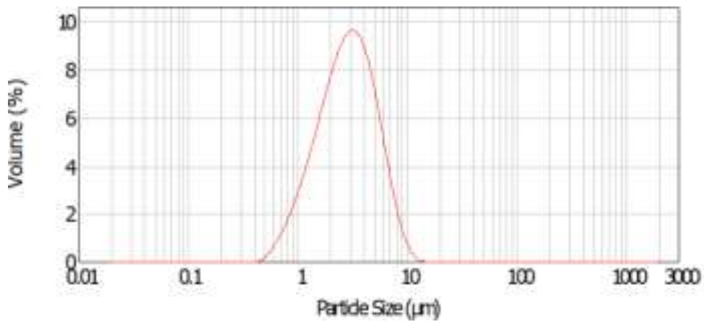

Fig-2: Particle size distribution of the industrially applicable opaque glaze

On the other hand, the data related to the burning or fuming away of the organic materials used for glaze modification was obtained by the thermogravimetric curves as shown in Figure 4. The weight loss of the organic materials revealed the burning temperatures. The burning temperatures of CMC and starch were 270-330°C with 40-60% mass loss. The waste paper cellulose fumed away at 300-370°C. PMMA, wax and PVB burned at 400-470°C with the mass loss of 80-90%.

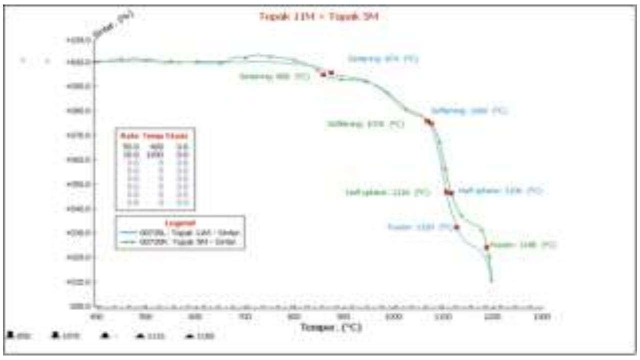

Fig-3: Thermal microscope image of the industrially applicable opaque glaze

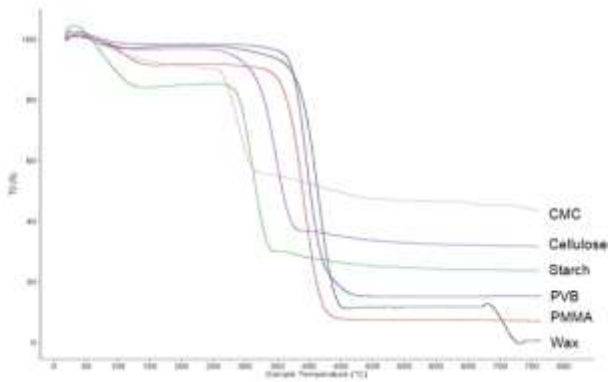

Fig-4: Thermogravimetric curves of the organic materials

The wall tiles glazed with the modified glazes were gloss fired at 980°C. The purpose was to change the surface texture and roughness by the combustion gas evolution. The particular surface topography thus created might be instrumental in entrapping of the air bubbles between the sessile water drops and the tile surface, which in turn might impart hydrophobic surface property due to Cassie-Baxter theory. The SEM pictures of the gloss fired tiles together with the corresponding sessile water contact angles are given in Figure 5, and the results are summarized in Table 1. The gloss fired glaze modified with the waste paper cellulose, flaked off the surface, therefore it was not included in the results.

Figure 5a shows the surface microstructure of the wall tile gloss fired with the unmodified industrial glaze. The surface was smooth as compared to the gloss fired modified glazes. The surface roughness was the lowest with Ra=2.6 µm in accord with the average particle size (Figure 1). Figure 5b-f show the microstructure of the gloss fired tiles with the organic matter modified glaze. The gasification of the organic matter left behind pores in the glaze and perhaps provided zones inside the glaze with lower softening temperatures. Therefore, during the fuming off the organics the surface acquired a particular topography. The surface roughness changed from 20-560 μm with the organic matter addition. The surface roughness increased in the order of CMC, corn starch, PMMA, wax, PVB modification. The burning temperatures of these organic materials also increased in the same order. This pointed out that the later the fuming of the organics, due to the quantity of the liquid phase formed and the viscosity of the glaze at the gloss firing temperature, the smoothing out of the pores left behind was less effective. The lowered softening temperatures at the pore bordering zones might be instrumental in the more prominent crest to trough distances as evidenced by the increasing roughness.

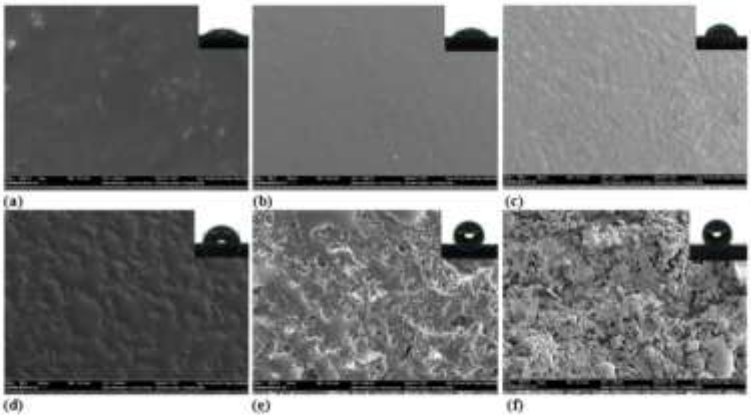

Fig-5: SEM and related sessile water drop contact angle images of wall tiles glazed with (a) unmodified, (b) CMC modified, (c) corn starch modified, (d) PMMA modified, (e) wax modified, and (f) PVB modified glazes gloss fired at 980°C maximum temperature

Table-1: Surface roughness and sessile water drop contact angles of the gloss fired wall tiles

Glaze modifying material	Surface roughness (Ra)	Contact angle (γ_{sl})
Unmodified	2.6 μm	35°
Carboxymethyl cellulose (CMC)	20 μm	50°
Corn starch	80 μm	68°
Polymethyl methacrylate (PMMA)	160 μm	83°
Wax	500 μm	125°
Polyvinyl butyrate	560 μm	128°

There existed a correlation between the surface roughness and the sessile drop contact angle as Figure 6 indicated. The fuming of the organic matter during gloss firing evidently formed specific surface topographies which effectively increased the surface contact angles. For the PVB and wax modifications of the glaze the sessile water drop contact angles on the ceramic tile surface changed to the hydrophobic range as targeted. Most probably the fuming process described above also provided the particular surface topography which was effective in entrapping the air bubbles between the surface and the sessile drop. The chemically hydrophilic glazed ceramic tile surfaces became hydrophobic in accord with Cassie-Baxter theory, which was possible if γwater-air > γglazed surface-air.

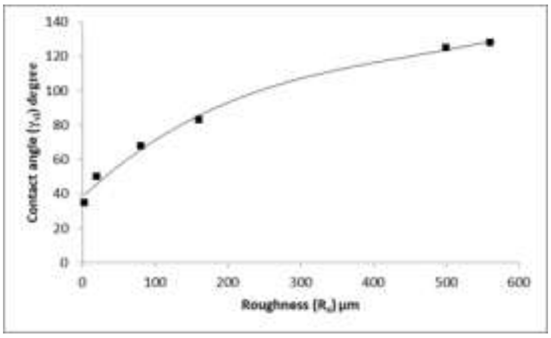

Fig-6: The correlation between sessile water drop contact angle and surface roughness

CONCLUSIONS

Organic materials were incorporated in an industrial wall tile glaze successfully modifying the surface texture, and more importantly the surface topography of the gloss fired wall tiles. The changed surface topography changed the sessile water drop contact angle, with the trend that an increasing surface roughness provided an increasing contact angle. Polyvinyl butyrate and wax modifications provided hydrophobic contact angles.

REFERENCES

1. Anderson, D. M., Chief Lexicographer (2010). Dorland's Illustrated Medical Dictionary, 32nd ed., Elsevier Saunders, Philadelphia, PA, pp. 11–17.
2. Higgs, B., White, W. (1994). Solid Antimicrobial, U.S. Pat. 5359104.
3. Isquith, A. J., Abbott, E. A., Walters, P. A. (1972). Surface-bonded antimicrobial activity of an organosilicon quaternary ammonium chloride. Applied Microbiology, 24(6), 859–863.
4. Acikbas, G. (2007). Micromorphology Formation on Ceramic Surfaces. Master'sThesis, Anadolu University, Eskisehir, Turkey.
5. Good, R. J. (1993). Contact angle, wetting and adhesion: a critical review, in: K.L. Mittal(Ed.), Contact Angle, Wettability and Adhesion. Festschrift in Honor of Professor Robert J. Good, Utrecht, pp. 3–36.
6. Wenzel, R. N. (1936). Resistance of solid surfaces to wetting by water. Ind. Eng. Chem., 28(8) 988–994.
7. Cassie, A. B. D., Baxter, S. (1944). Wettability of porous surfaces. Trans. Faraday Soc., 40, 546–551.
8. Ozcan, S., Acikbas G., Calis Acikbas N. (2017). Induced superhydrophobic and antimicrobial character of zinc metal modified ceramic wall tile surfaces. Applied Surface Science, http://dx.doi.org/10.1016/j.apsusc.2017.08.014
9. Ashokkumar, S., Adler-Nissen, J., Moller, P. (2012). Factors affecting the wettability of different surface materials with vegetable oil at high temperatures and its relation to cleanability. Applied Surface Science, 263, 86–94.
10. Chen, X., Suo, Y. G. X., Huang, J., Liu, Y., Li, H. (2015). Construction of mechanically durable superhydrophobic surfaces by thermal spray deposition and further surface modification. Applied Surface Science, 356, 639–644.
11. Yilbas, B. S., Khaled, M., Abu-Dheir, N., Aqeeli, N., Furquan, S. Z. (2013). Laser texturing of alumina surface for improved hydrophobicity. Applied Surface Science 286, 161–170.
12. Jia, Y., Yue, R., Liu, G., Yang, J., Ni, Y., Wu, X., Chen, Y. (2013). Facile fabrication of nano-structured silica hybrid film with superhydrophobicity by one-step VAFS approach. Applied Surface Science, 265, 405–411.
13. Acikbas, G., Kara, F., Suvaci, E. (2008). Modification of Surface Morphology of Glaze by Fugitive Additives. In: Kavas T, editor. Ceramic Congress. Proceeding of VII. Ceramic Congress with International Participation; Afyon, Turkey: Afyon Kocatepe University; 2007. p. 280-287.
14. Ozcan, S., Calis Acikbas, N. (2014). Formation of Superhydrophobic Character on Ceramic Surfaces. ISITES2014, 2nd International symposium on innovative technologies in engineering and science proceeding book, pp. 606-613.
15. Ozcan, S., Calis Acikbas, N., Acikbas, G. (2015). Development of Antimicrobial Effect on Ceramic Surfaces. IX Ceramic Congress with International Participation; 2015 Nov. 26-28; Afyon, Turkey.
16. Ozcan, S., Calis Acikbas, N., Acikbas, G. (2017). Formation of antibacterial effect on ceramic tile surfaces. Anadolu Univ. J. Sci. Technol. A − Appl. Sci. Eng., 18(1), 122–130.
17. Calis Acikbas, N., Acikbas, G., Ozcan, S. (2017). İnorganik yüzey modifikasyonu ile süperhidrofobik yüzeylerin eldesi için bir yöntem. Turkish Patent, Turkish Patent and Trademark Office, TR 2015 03257 B.