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Microstructure and cleanability of uncoated and fluoropolymer, zirconia and titania coated ceramic glazed surfaces

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Abstract

The aim of this investigation was to examine the effect of surface topography of different compositions and surface coatings of glazed ceramic tiles on their cleanability. The cleanability was estimated with color measurements. Contact angle measurements were used to describe the surface properties and profilometry and electron microscopy to describe the topography. The effect of additional coatings on the surface properties was compared by applying experimental zirconia and titania coatings as well as a commercial fluoropolymer coating on one of the experimental and all reference glazes. The results show that there were clear differences between the soiling tendencies of the glazes. Generally the topography measurements show that the rougher was ceramic glaze, the more soil adhered on its surface.

Keywords: Surfaces; Chemical properties; Cleanability; Coatings; Tiles

1. Introduction

Ceramic surfaces are used when an easy-to-clean surface is needed, for example, in hospital operating theatres and in industrial domestic clean rooms.[1] In addition, ceramic tiles are widely used throughout Europe for bathroom and kitchen floors in households, and other areas of high utility.[2] Glass-ceramic tiles are very important as surface materials because of their outstanding mechanical, thermal and chemical properties. The development of glass-ceramic glazes in the tile industry has recently received much attention because improved mechanical properties are demanded in the final products.[3]

Recently, glazed surfaces have been coated with special functional layers to achieve soil-repelling properties and to enhance the cleanability. Examples of special functional layers are fluoropolymer and titania coatings. However, mechanical properties and chemical durability of the new-soil repelling surface are quite poorly understood. Thus, basic knowledge of surface properties as parameters of soiling and cleanability is essential for developing better glazes and functional coatings to be applied on glazes.[4] The soil present in bathrooms consists of sebum fats, proteins and water derived lime and other deposits such as lime soap. In hospitals, protein is a typical component of soil. The 'natural' soil consists of a large variety of ingredients whose nature and properties vary according to their place of occurrence.[5] Commonly, experimental soil mixtures mimic natural soils that appear on surfaces in a specific environment. The soils that have been used in hard-surface cleaning tests are mixtures of fats and oils of different types as their main ingredient. According to literature, several standards of soils are available.[6,7]

Some investigations have been published concerning the cleanability of ceramic materials. Taylor and Holah[8] studied the bacterial cleanability of wall and floor surface materials. They found that grouted epoxy joints did not compromise the bacterial cleanabilities of tiled surfaces. The study focusing on cleanability of ceramic tile grout materials by Kemppainen et al.[9] was based on both a color measurement technique and visual

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evaluation of microscopic images. Hupa et al.[4] studied chemical resistance and cleanability of glazed surfaces. Their results showed that adhesion of soil on glazed surfaces and their cleanability depends on chemical composition, phase composition and roughness of the surface. Dondi et al.[10] studied the role of surface microstructure on the resistance to stains of porcelain stoneware tiles. Their results showed that the resistance to stains of polished porcelain stoneware tiles depended to a large extent on the surface microstructure. In a study by Tenorio Cavalcante et al.[11] the influence of microstructure on the performance of white porcelain stoneware was examined. In their study four polished white porcelain stoneware tiles were selected and thoroughly characterised by a wide spectrum of chemico-physical and microstructural analyses. Products exhibited excellent mechanical properties with a clear dependence of these properties on porosity and phase composition. Mullite and zircon tend to increase the mechanical performances, through a predominant mechanism of matrix reinforcement, while quartz plays an opposite role. Esposito et al.[12] studied stain resistance of porcelain stoneware tiles. The tested working surfaces and corresponding cross sections were observed using light microscopy and SEM in order to study the stain penetration mechanisms and their relationship to the microstructure. Colour measurements were made using reflectance spectrophotometry. The results help to clarify the relationship between stain resistance and microstructural features.

The aim of this investigation was to examine the effect of surface topography of different compositions and surface coatings of ceramic tiles on the cleanability. The cleanability was estimated by color measurements. Contact angle measurements were used to describe the surface properties and profilometry and electron microscopy to describe the topography.

2. Experimental

2.1. Materials

In this study 23 experimental surfaces were investigated. Their codes, crystalline phases in the surface according to XRD analysis, coating, firing cycle and roughness according to profilometry are presented in Table 1. Experimental glazes 2, 3, 7, 8, 10, 14 and 15 were ball-milled of commercial grade raw materials: kaolin, feldspar, dolomite, limestone, wollastonite, corundum and quartz.[13] The code A means that the tiles were fired in laboratory furnace and the code E means an industrial firing. Commercial matt (M) and glossy (K) floor tile glazes as well as a commercial sanitaryware glaze (S) were used as references. All these commercial glazes contain zircon as opacifying agent. The effect of additional coatings on the surface properties was compared by applying experimental zirconia and titania as well as a commercial fluoropolymer coating on one of the experimental and all reference glazes. The fluoropolymer 3 M^{TM} (ECC-4000) coating is typically applied from a very diluted solution containing about 0.1% by weight of product, resulting in a coating thickness of 20–100 nm. This coating contains according to the manufacturer 10% fluoropolymer, 60% alkoxysilane and 30% ethanol. After spraying with the fluoropolymer solution the samples were dried at room temperature. Thus, the fluoropolymer coated glazes were not heat-treated after coating. The experimental zirconia and titania coatings were applied using a

Table 1
The crystal phase composition,[10] coating, firing temperature and roughness R_a values

Firing	Code	Crystalline phases in glazes	Coating	Peak firing temperature/firing cycle	Roughness R_a (μm)
Laboratory furnace	2A	Quartz, albite, anorthite	None	1260 °C/450 min	2.44 ± 0.37
	12A	Albite, diopside			0.46 ± 0.06
Industrial kiln	7E	Quartz, wollastonite, corundum	None	1215 °C/55 min	0.63 ± 0.07
	8E	Quartz, diopside, corundum			0.22 ± 0.03
	10E	Quartz, wollastonite, corundum			0.27 ± 0.04
	14E	Quartz, wollastonite, corundum			0.22 ± 0.04
	15E	Quartz, diopside, corundum			0.16 ± 0.02
Laboratory furnace	3A	Diopside	none	1260 °C/450 min	0.73 ± 0.21
	3AF		F fluoropolymer		0.56 ± 0.07
	3AZR		ZR zirconia (sol–gel)		0.65 ± 0.06
	3AT		T titania (sol–gel)		0.69 ± 0.01
Industrial kiln	K	Zircon	None	1215 °C/55 min	0.22 ± 0.08
	KF		F fluoropolymer		0.25 ± 0.09
	KZR		ZR zirconia (sol–gel)		0.22 ± 0.05
	KT		T titania (sol–gel)		0.28 ± 0.11
Industrial kiln	M	Zircon	None	1215 °C/55 min	0.69 ± 0.11
	MF		F fluoropolymer		0.61 ± 0.08
	MZR		ZR zirconia (sol–gel)		0.61 ± 0.06
	MT		T titania (sol–gel)		0.63 ± 0.15
Industrial kiln	S	Zircon	None	1215 °C/18 h	0.11 ± 0.05
	SF		F fluoropolymer		0.16 ± 0.08
	SZR		ZR zirconia (sol–gel)		0.07 ± 0.02
	ST		T titania (sol–gel)		0.06 ± 0.04

sol–gel method. The coatings were applied by dip-coating and dried at room temperature for 2 h. The zirconia coated samples were first fired for 1 h, at 300 °C and after that temperature was raised up to 600 °C ($\Delta T = 5$ °C/min) and matured for 30 min. The titania coated glazes were fired for 55 min at 500 °C. For the experiments all the samples were cut into 3.0 cm × 3.0 cm pieces.

2.2. Soiling and cleaning of the ceramic tiles

Before soiling the surfaces were cleaned with a commercial weakly alkaline detergent (pH 8). The samples were soiled with a soil mixture, consisting of sebum (1.0 g), ethanol (50 ml) and soot (50 mg) as a color marker. The sebum, manufactured by Wfk Testgewebe GmbH (Germany), consisted of free fatty acids (18.0%), beef tallow (32.8%), fatty acid triglycerides (3.6%), lanoline (18.3%), cholesterol (3.7%), hydrocarbon mixture (12.0%) and cutina (11.6%). The soil mixture (200 μl) was spread with a pipette onto the tile surface. The soil was allowed to dry on the surfaces for 24 h, in the laboratory ($T = 23.5 \pm 2.5$ °C, RH = 31 ± 6%) before it was spread with two forward and backward movements using the Erichsen Washability and Scrubbing Resistance Tester (model 494, Erichsen Gmbh & CO KG) with a cotton cloth. This way the soil was spread on the surface evenly. The soil was left to dry for 24 h, at room temperature (23.5 ± 2.5 C°, 31 ± 6% RH), after which the surfaces were cleaned with the Mini Cleanability Tester[14] using a micro fibre cloth (100% polyester) (Freudenberg Household Products Oy Ab). The micro fibre cloth was moisturized to 100% moisture regain with water (pH 5.7) or aqueous solution of a weakly alkaline detergent solution (pH 5.7). The weakly alkaline detergent (Farmos Oy) consisted of soap (5%), non-ionic surfactant C13-oxoalchoholetoxylate (10%) and tetrapotassium pyrophosphate (5%).

2.3. Measurements

The topography of the ceramic glazes was measured with contact profilometer. SEM was used to image the surface structure. The cleanability of the ceramic glazes was measured with the colorimetric and contact angle methods before and after soiling and after cleaning. The contact angles were also measured before and after soiling and after cleaning.

2.3.1. Profilometry

Two- and three-dimensional roughness profiles were measured as three replicates using a contact profilometer (KLA Tencor P15). The vertical resolution of this profilometer is 1 nm and its horizontal resolution is 0.5 μm. Each 2D- scan was 10 mm in length. Scan speed was 100 μm/s and sampling rate 200 Hz. Vertical range was 327 μm and resolution was 1.9 nm. A Gaussian filter with short wavelength cut-off (off) and long wavelength cut-off (250 μm) was used to separate macro roughness (waviness) from micro roughness. 3D- scans were 500 μm in length. Scan speed was 10 μm/s and sampling rate 20 Hz. Vertical resolution range and resolution were the same as in 2D-scans. Roughness average (R_a), is based on the average centerline of a surface, and describes the average height or depth of the peaks above and below the centerline. The R_a value, usually stated in micrometer units, is the most commonly used descriptor of surface roughness.[15] In the profilometric measurements, roughness parameters were calculated in both two- and three-dimensional forms. Values of roughness, R_a, were measured as 3D-scans.

2.3.2. Microscopy (SEM)

Scanning electron microscopy (SEM) photomicrographs of test samples were taken with a (LEO 1530) electron microscope. The samples were sputter coated with carbon. Photomicrographs were taken with magnifications of 100, 500 and 1500, of which the 500 was used for the final observation of ceramic tiles. The number of replicate samples for each magnification was 5.

2.3.3. Colorimetry

The cleaning efficiency of the ceramic tiles was measured with a colorimeter Minolta Chroma Meter CR-210 (Minolta Co Ltd), equipped with Standard Illuminant D65. In this experiment the L^* (lightness) value was used for assessing the soiling and cleaning properties of the glazes. The color of the ceramic tiles was selected to be as light as possible to increase the contrast between the soil and glazes. A black, rectangular cardboard frame (12.0 cm × 12.0 cm) with a rectangular hole (2.4 cm × 2.4 cm) in the middle was used in the evaluation because the measuring range of the colorimeter was bigger than the ceramic tile. The colors of unsoiled, soiled and cleaned glazes were measured at one point. The number of replicate samples for each material was 5. The soiling and cleaning results were expressed with the absolute indices calculated from the means of the L^* values of a sample:

$$\text{Soiling } \Delta L^*_{\text{s}} = L^*_{\text{unsoiled}} - L^*_{\text{soiled}}$$

$$\text{Cleaning/cleanability } \Delta L^*_{\text{C}} = L^*_{\text{cleaned}} - L^*_{\text{soiled}}$$

$$\text{Soil residue } \Delta L^*_{\text{R}} = L^*_{\text{unsoiled}} - L^*_{\text{cleaned}}$$

2.3.4. Contact angle measurement

Contact angle measurements were performed using the sessile drop method with the optical contact angle meter, CAM 100. The contact angles on ceramic tiles were measured before and after soiling and after cleaning with ultra pure water (Milli-Q). Determination of contact angle was based on the Young–Laplace equation. The result was the mean of the drop on five replicate samples.

2.4. Statistical analysis

Variance analysis (Univariate model) of the SPSS12 statistical tool was used to examine differences between uncoated and coated glazes. Bivariate correlation analysis (Pearson's correlation coefficients, two-tailed test of significance) was used to examine the possible correlation between roughness, soil residue and contact angles, and between uncoated and coated glazes.

3. Results and discussion

3.1. Profilometry

Values of roughness (R_a) of the glazes, calculated from the three-dimensional form, varied between 0.06 and 2.44 μm (Table 1). Roughness values of the uncoated glaze 2A was the highest and ST the lowest. Examples of the two- and three-dimensional profilometric measurements are presented in Fig. 1 to illustrate the great differences between the surfaces of the ceramic tiles. Thus, the coatings can be used to enhance some specific surface property without affecting the desired surface roughness. There were no statistically significant differences between roughness of the uncoated and coated glazes ($p > 0.05$). In literature it is mentioned that hygienic surface criterion for roughness is set at a maximum R_a value of 0.8 μm.[16] Except the uncoated glazes 2A and 3A, all uncoated and coated glazes got a roughness value smaller than 0.8 μm.

3.2. Microscopy (SEM)

Qualitative SEM photomicrographs of different types of glazes are presented in Fig. 1. With the help of magnifications of 100 and 1500, examples of surface images from the replicate measurements of the magnification of 500 were selected to present types of different surfaces. The examples shown clearly indicate the complicated nature of the glazes. The uncoated glazes (12A, 7E, 8E, 10E, 14E and 15E) were similar and rather smooth. The glaze of the material 2A had an uneven surface (Fig. 1). None of the other materials was similar with 2A. The uncoated glaze M was uneven and had some bumps on its surface. The uncoated and coated glazes were rather similar within some groups: e.g. there were no remarkable differences between the surfaces of the uncoated glaze 3A and the coated versions of that material (3A F, 3A ZR and 3A T). Similarly, there were no big differences between the uncoated and coated surfaces of the materials S, K and M. As seen in Fig. 1, the surface of the glaze M was rather uneven but with no deep hollows, but the coated versions were more like the surface 3A. Liu et al.[17] mentioned that ceramic films of up to 0.5 μm are deposited in a single layer and thicker films are achieved by depositing multiple coats. The sol–gel process has become a popular method for fabricating ceramic thin films. The main advantage of the sol–gel process is the ability to form inorganic structures at relatively low temperature and to produce thin homogeneous inorganic

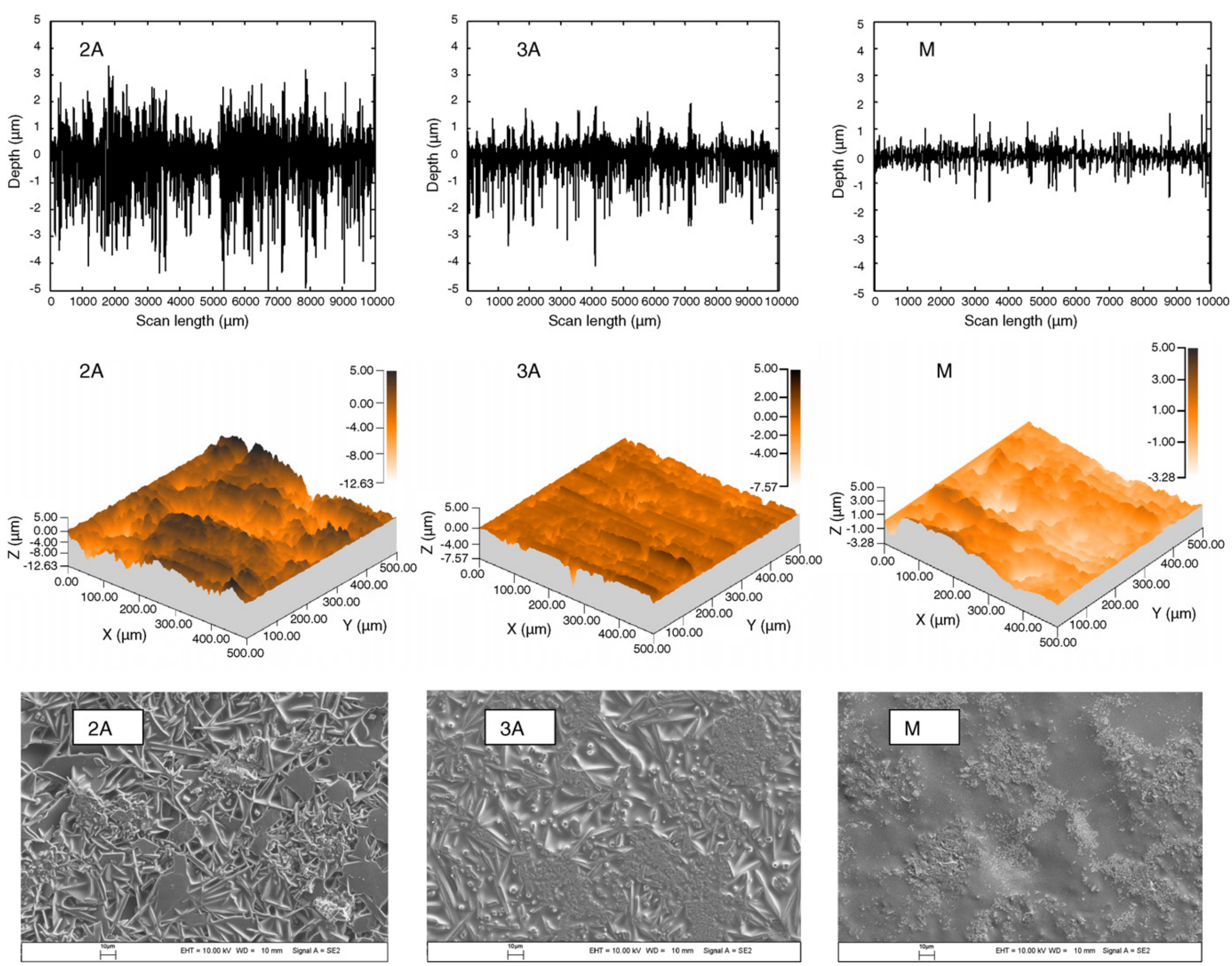

Fig. 1. Two- and three -dimensional profilometric measurements and SEM micrographs of glazes (2A, 3A and M). The details of the glazes are given in Table 1.

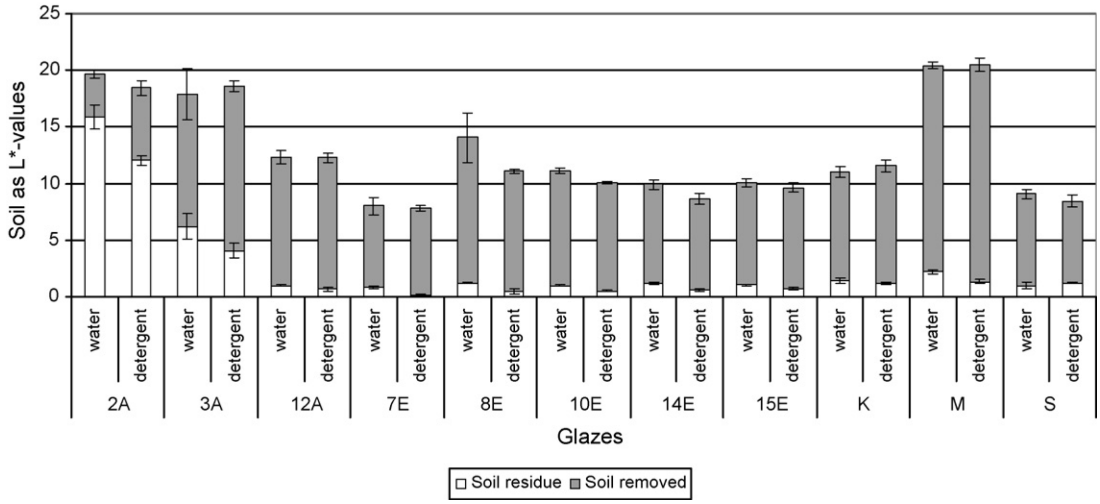

Fig. 2. Cleanability of uncoated glazes. The amounts of the soil on the glazes after soiling (the whole bar $\Delta L^*_{\mathrm{Total}}$). The soiling and cleaning results (presented as soil removed and soil residues) are means of the five replicates. Bars in columns are standard errors of means (±S.E.). The details of glazes are given in Table 1.

films on large scale. The main limitation for titania and zirconia sol–gel processing has been the film thicknesses. It is difficult to make crack-free films thicker than 10 μm[18] and fluoropolymer coatings thickness is generally 20–100 nm (product information 3 M). Consistent with that, the effect of the coatings had no marked effect on the profilometric results.

3.3. Colorimetry

As it can be seen in Figs. 2 and 3, the mean ΔL^*_s values of the soiled glazes were between 5.1 and 20.5 units, indicating very clear differences between the soiling tendencies of the materials. The uncoated glazes 2A, 3A and M were the most soiled with ΔL^*_s values greater than 15. The effect of the fluoropolymer, zircon and titania coatings on the soiling tendency were varying. All coatings clearly decreased the soiling of the materials 3A and M but had a negligible effect on the soiling tendency of the materials S and K, as shown in Fig. 3. The colorimetric measurement used to measure the soiling tendency detects only the colour of the surface layer. As the experimental unsoiled surfaces are relatively similar in colour but show clear differences after soiling, the colour measurement can be used to compare their soiling tendency. The highest colour values were observed for the roughest surfaces. Thus, the soiling tendencies are assumed to depend on soil accumulated in surface irregularities mostly due to surface roughness but also to surface defects such as pinholes or cracks.

The soiling value is important also because it provides an indication of the need for cleaning of the surfaces.[19] According to Anton[20] fluoropolymer has some very desirable properties when

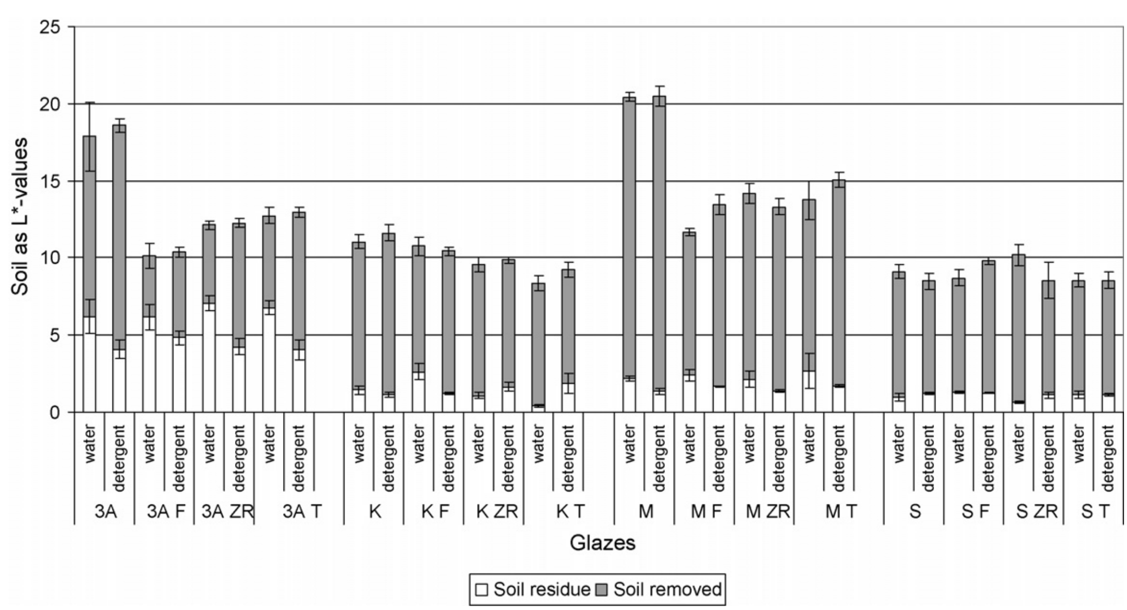

Fig. 3. Cleanability of glazes. The amounts of the soil on the glazes after soiling (the whole bar $\Delta L^*_{\mathrm{Total}}$). The soiling and cleaning results (presented as soil removed and soil residues) are means of the five replicates. Bars in columns are standard errors of means (±S.E.). The details of glazes are given in Table 1. The glazes are uncoated (codes 3A, K, M and S) and coated (F: fluoropolymer, ZR: zirconia (sol–gel) and T: titania (sol–gel)).

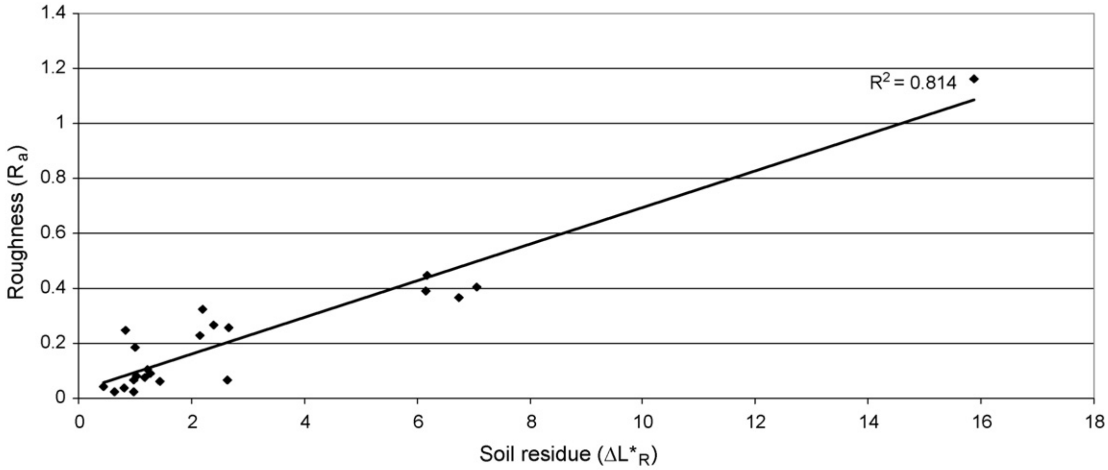

Fig. 4. Comparison of roughness (R_a) and colorimetric results (soil residue ΔL^*_R) when glazes were cleaned with water.

it is used as a coating. It is resistant to most chemicals and thermally quite stable. Fluoropolymer has a low surface tension and because of this its surface is repellent to contaminants and is easy to clean. The cleanability of surface is directly related to the work of adhesion of the contaminant on the surface. The less strongly a material adheres to the surface, the easier it is to be removed. However, in our study we did not perceive the fluoropolymer coating as superior to other uncoated and coated ceramic glazes. Titania and zirconia have been extensively studied as catalyst or catalyst support for heterogeneous catalytic reactions.[21–23] Transparent films and coatings of titanium dioxide anatase have been studied for a number of years now. Technological interest has focused around their potential in self-cleaning applications due to their photocatalytic and hydrophilic properties.[24,25] In our study we did not utilise the photocatalytic properties of coatings. Thus, the cleanability results were rather similar between uncoated and coated ceramic glazes, likely due to their equal roughness values.

As it is seen in Fig. 2, the soil residue ΔL^*_R was clearly highest on the glaze 2A ($\Delta L^*_R = 15.8$) and relatively high also on the uncoated and coated versions of the material 3A cleaned with water ($\Delta L^*_R = 6.2$–7.1). The soil residues of all the other materials were rather similar with the ΔL^*_R values between 0.4 and 2.6, but the variance analysis showed statistically significant differences between glazes K and M or M and S ($p < 0.05$). Despite the remarkable soiling of the uncoated matt glaze M, it was relatively well cleaned: the mean ΔL^*_R value was 2.2 and 1.3 units after cleaning with water and alkaline detergent, respectively. As is seen in Fig. 3, the effect of the coatings on the soil residue values was negligible. Slightly better cleaning results were obtained for the uncoated and coated glaze 3A ($p < 0.05$), M ($p < 0.01$) by using the alkaline detergent than water (Fig. 3). For the other materials, no significant difference between water and detergent was observed ($p > 0.05$). The rougher the glaze was, the more soil adhered on its surface. Including all the examined surfaces, the ΔL^*_R values of the glazes for surfaces cleaned with water correlate significantly ($r = 0.814$, $p < 0.01$) with the roughness (R_a) parameter, compare Fig. 4. The figure shows that the behavior of glaze 2A differs from the other materials, but excluding this result did not decrease the correlation between surface roughness and soil residue markedly ($r = 0.725$, $p < 0.01$). Fig. 1 shows that the microstructure of the uncoated glazes 2A and 3A were different from those of the other glazes. The cleanability of the glazes 2A and 3A was also poorer than the cleanability of the other glazes. Hupa et al.[4] stated that soiling and cleaning degree of traditional glaze surfaces consisting of different crystalline phases embedded in a glassy phase depends rather on surface micro- and macro-roughness than on chemical composition of the phases in the surface. Profilometry provided a part of the necessary information about functionality of ceramic glazes.

3.4. Contact angle

The contact angles of water on glazes are presented in Figs. 5 and 6. The water contact angles of unsoiled and coated glazes were below 90° with a wide variation range. The contact angles of the fluoropolymer coatings were the highest ranging between 70° and 90°. After soiling the water contact angles were about 75° on all materials. The contact angle measurements after cleaning showed that oily soil remained on the surfaces of the materials (Figs. 5 and 6). When soil and solid surface have different hydrophobic-hydrophilic characteristics, contact angle measurements are employed as pass/fail test in precision cleaning.[26] According to the manufacturer, the fluoropolymer (EEC-4000) coating provides a hydrophobic surface that allows simple rinsing away of soils and sludge from the surface with no residual surface staining, which is in accordance with our results. Contact angle measurements are employed in precision cleaning to detect soil on surfaces. The contact angles are known to be sensitive to surface roughness and surface chemical heterogeneity.[27] However, in the present study roughness parameters had no significant correlation with contact angle of water ($p > 0.05$). The differences in the contact angle, 20–40 °, were not found to correlate with the phase composition of the surface. The surface phase composition also seems to have a negligible effect on the contact angle. Thus, within the roughness range tested the contact angle seems to correspond to typical values of glazes surfaces and this not within the range typical that resulting the

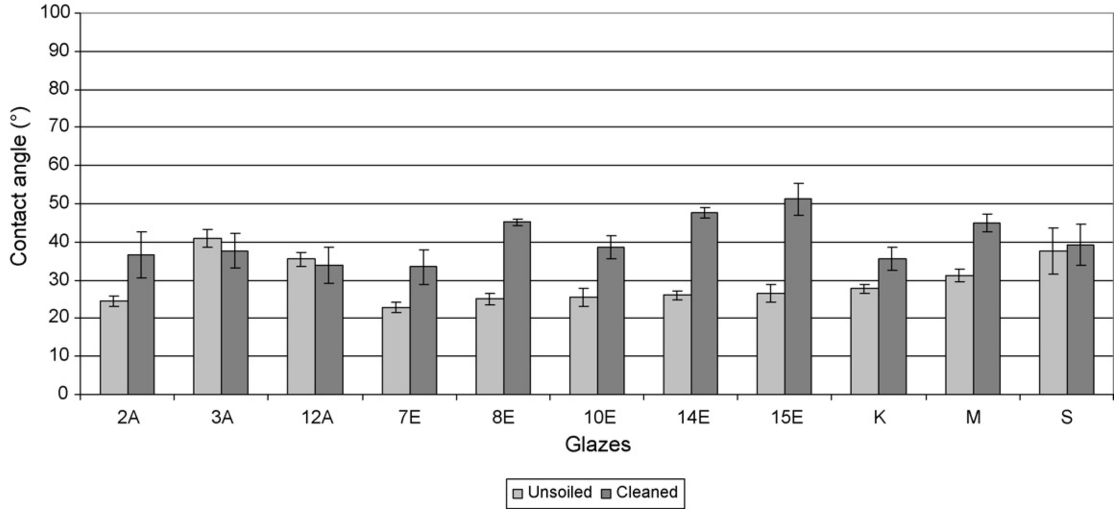

Fig. 5. Contact angles of unsoiled and cleaned uncoated glazes as means of five replicates. Bars in columns are standard errors of means (±S.E.). The details of glazes are given in Table 1.

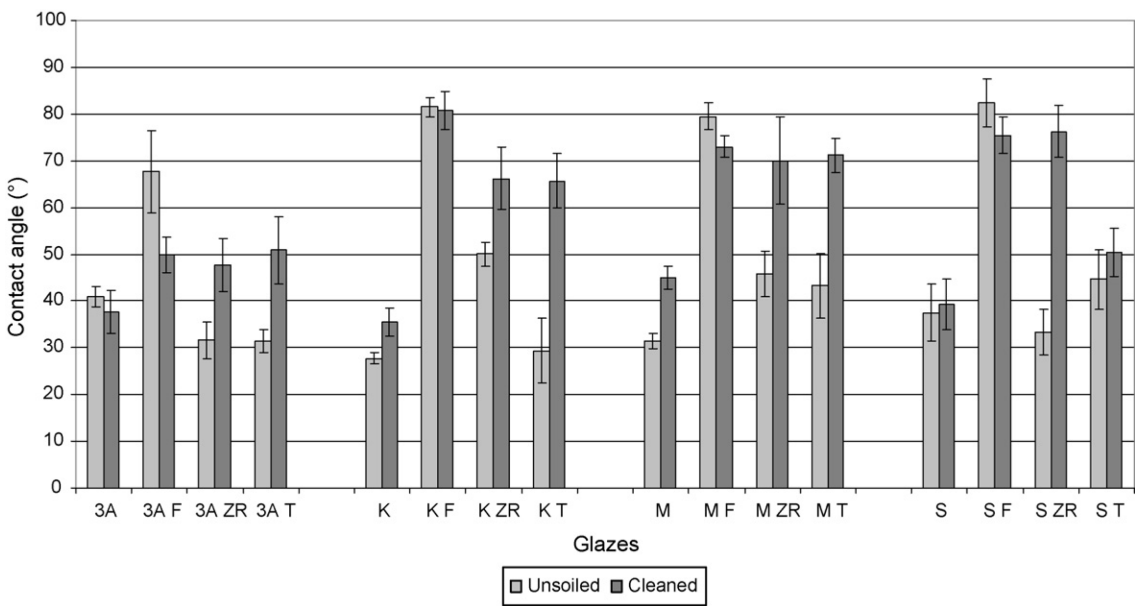

Fig. 6. Contact angles of unsoiled and cleaned glazes as means of five replicates. Bars in columns are standard errors of means (±S.E.). The details of glazes are given in Table 1. The glazes are uncoated (codes 3A, K, M and S) and coated (F: fluoropolymer, ZR: zirconia (sol–gel) and T: titania (sol–gel)).

surface self-cleaning properties. Fluoropolymer coating clearly increases the contact angle and is thus likely to give an easy-to-clean or self-cleaning effect especially for oblique surfaces. The contact angle for the titania coating is likely to be lowered when exposed to ultraviolet light, and thus to give active self-cleaning properties for the surface. However, this effect was not tested in this work.

4. Conclusions

In the present study the effect of surface topography on the cleanability of different compositions and surface coatings of glazed tiles was examined. The basic composition of the glaze affected the roughness values but the effect of the coatings on the roughness was negligible. Thus, the coatings are feasible alternatives for applications where increased surface qualifications are required without changes in surface topography. There were clear differences between the soiling tendencies of surfaces were observed. The rougher the glaze was, the more soil adhered on its surface. There was no conformity concerning the effect of the coatings on cleanability as given by the soiling and cleaning method used: the cleanability results were rather similar between the uncoated and coated ceramic glazes, likely due to their equal roughness values. The roughness parameter, R_a appeared to be useful for comparing cleaning properties of different glazes, and thus topography had a clear role in soiling and cleaning. However, the contact angle measurements suggest that fluoropolymer coating would give a lower soil attachment and thus a better cleanability especially on sloping surfaces. Titania coating is likely to give increased cleanability in environments where its special characteristics can be fully used. The zirconia coating tested however, is not likely to enhance the cleanability of the glazes.

The cleanability of the uncoated surfaces was observed to depend on their surface roughness and thus on the surface phase composition. However, no marked differences in cleanability of surfaces with different phase composition but same average roughness were observed. Selective corrosion of some of the phases in the surface might affect the surface roughness, and thus interfere with its soiling tendency and cleanability.

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