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Effects of UV-radiation on the cleanability of titanium dioxide-coated glazed ceramic tiles

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Abstract

The effects of UV-radiation on the cleanability of three glazed tiles coated with ceramic sol–gel derived TiO_2 were evaluated. A quantitative radiochemical determination method was used to measure oil and organic particle soil residues on the surface. Surfaces were characterized with topography and contact angle measurements. The observed effects of UV-radiation were greatest on rough surfaces, implying that increasing roughness increases the surface area available for photo-induced phenomena in the TiO_2-surface. Organic particle soil was removed more efficiently after UV-radiation than without UV treatment, whereas UV-radiation did not affect the removal of oil soil. Contact angles decreased significantly after UV-radiation.

Keywords: Surfaces; Cleanability; TiO_2

1. Introduction

Surface coatings based on nanotechnology have been used to improve the properties of glazed ceramics. One of the main functions of the coating is to make the surface easy-to-clean or self-cleaning. One of the available coating materials is titanium dioxide, TiO_2, which is reported to improve the surface self-cleaning properties produced by UV-radiation.[1–3] TiO_2 is used very widely in different materials and applications. Commercial TiO_2-based photocatalytic products can be grouped into five main categories: exterior construction materials, interior furnishing materials, road construction materials, purification matrices and household goods.[4]

A unique aspect of TiO_2 is that it generates two separate photo-induced phenomena: a photocatalytic phenomenon and a superhydrophilic phenomenon. Sunlight and rainwater keep TiO_2-based self-cleaning exterior products clean based on these two phenomena. Thus adsorbed organic oil soil is decomposed by the photocatalytic property of TiO_2, while organic particle soil and dust can be cleaned by rainwater due to its superhydrophilic property.[4,5] The decomposition of organic compounds to carbon dioxide, CO_2, has been investigated in many studies. Minabe et al.[3] suggested that organic compounds, such as octadecane and glycerol trioleate, could be decomposed completely on the TiO_2 thin films on glass surface under weak UV illumination. In their study only the detectable gas-phase product CO_2 was evaluated. Stearic acid was not completely decomposed. Pore et al.[6] evaluated the degradation of a thin layer of stearic acid from thin films on glass under UV-light and visible light. In general the decrease of thickness of the stearic acid layer was greater on TiO_2 and $TiO_{2-x}N_x$ films after UV-radiation than after visible light radiation. Visible light was unable to activate samples to the superhydrophilic state. However, when UV light was applied some samples became superhydrophilic.[6] Photocatalysts are not very useful for decomposing large volumes of soil, but they are capable of preventing accumulation of soil layers.[4,7]

According to studies by Watanabe et al.[8], Nakajima et al.[9], Fujishima et al.[10] and Sakai et al.[11], when a surface of

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TiO_2 coated glass was radiated by UV-light the contact angles decreased with the illumination time. When water contact angles decreased close to 0° after irradiation of low-intensity UV, the films of TiO_2 on glass became highly hydrophilic surfaces. Contact angles by oily liquids have been reported to be decreased by UV-radiation.[1,9] The susceptibility of an exterior building surface to soiling is closely related to its contact angle with water.[5] A superhydrophilic material showing a water contact angle of 0° is far less likely to be soiled than any other material.[2,12] A small amount of water can be spread over its surface due to photo-induced superhydrophilicity, and soil can easily be swept away from the surface.

This paper is the second of a series of three papers in which the properties of additional coatings on glazed ceramics are examined and discussed. The focus of the first paper was on comparing the cleanabilities of the different coatings and glazed materials with radiochemical methods.[13] The focus of the third paper will be on the effect of chemical wear of the surface on its cleanability. In the present paper the influence of UV-radiation on cleanability of TiO_2-coated materials is presented. The effects of UV-radiation on cleanability of glazed surfaces were examined using two different model soils, organic particle soil and oil soil. The surfaces were characterized with roughness and contact angle measurements.

2. Experimental

2.1. Manufacturing process of the materials

In this study three experimental surfaces were used as bases for coatings with a laboratory-made glaze (coded 3A) and commercial matt (coded M) and glossy (coded K) floor tile glazes. The effects of additional sol–gel coatings on the surface properties of glazes were examined by applying experimental titania, prepared for this study, on the laboratory-made and all commercial glazes. Their codes, crystalline phases in the surface according to XRD (X-ray diffraction) analysis, coating, firing cycle and roughness according to profilometry are presented in Table 1. The manufacturing processes of the examined materials were presented earlier by Kuisma et al.[14]

2.2. UV-radiation of the materials

The ceramic materials were irradiated with UV-radiation twice: before soiling and during drying of the soil. The experimental procedures consisting of radiation, soiling, cleaning and measurements are presented in Figs. 1 and 2. Both radiation periods lasted for two hours. UV illumination was with a 15-W Sylvania Blacklight tube. The emitted wavelength of the UV-radiation was approximately 352 nm.

2.3. Water contact angle

Static water contact angles on ceramic tiles before and after UV-radiation were measured with a KSV CAM100 contact angle meter (Figs. 1 and 2). A water drop (ultra pure water Milli-Q) was placed on the surface and imaged for 20 sec by collecting one image per 2 s. Determination of contact angle was based on the Young–Laplace equation, yielding the contact angles on both sides of the droplet and their mean values. The result was the mean of drops on six replicate samples.

2.4. Topography

Topography was measured with white light using a COM (NanoFocus μSurf®) confocal optical microscope with cut-off wavelength 250 μm and with a lens giving 20 times magnification. The roughness value S_a provides the roughness as well as spatial and hybrid information for three-dimensional surfaces (DIN EN ISO 4287). The vertical resolution of the measurement was approximately 6 nm. The result was the mean of six replicate samples.

2.5. Soiling and cleaning of the materials

One of the two different model soils was labelled with the gamma-ray emitter ^{51}Cr and the other with the beta-ray emitter ^{14}C (Table 2). Soiling was carried out with the procedure described in detail in Pesonen-Leinonen et al.[15] The cleanabilities of different components of model soils were estimated by measuring the different radio-isotopes. The ^{51}Cr isotope labels particle components and the ^{14}C isotope labels oil components of model soil. An organic compound (chromium acetyl acetonate) represented natural organic soils. Triglyceride (triolein) was used as a model of natural oils and sebum. The model soils used represented organic soils found from typical use environments of ceramic materials.

The ceramic materials were subjected to one soiling and cleaning cycle (Figs. 1 and 2). The samples were UV-radiated first before soiling and second during the soil drying period. The fluid soil (50 μl) was applied to the middle of the sample with a pipette and 1-propanol was used as a carrier to assist dosage (Table 2). The soil was left to dry for 24 ± 1 h at room temperature. Cleaning was carried out with a Mini Cleanability Tester as described by Pesonen-Leinonen et al.[15] The estimated pressure applied to the sample was 25 kPa, velocity 30 rpm and the number of revolutions was three. The cleaning

Table 1
The crystal phase composition, coating, firing temperature and time and roughness of the glazed ceramic tiles (modified from Kuisma et al.[14])

Code	Crystalline phases in glazes	Firing	Peak firing temperature/firing cycle	Coating	Roughness, S_a (μ)
3A Ti	Diopside	Laboratory furnace	1260 °C/7.5 h	Ti titania (sol–gel)	0.38 ± 0.02
M Ti	Zircon	Industrial kiln	1215 °C/55 min	Ti titania (sol–gel)	0.38 ± 0.01
K Ti	Zircon	Industrial kiln	1215 °C/55 min	Ti titania (sol–gel)	0.09 ± 0.004

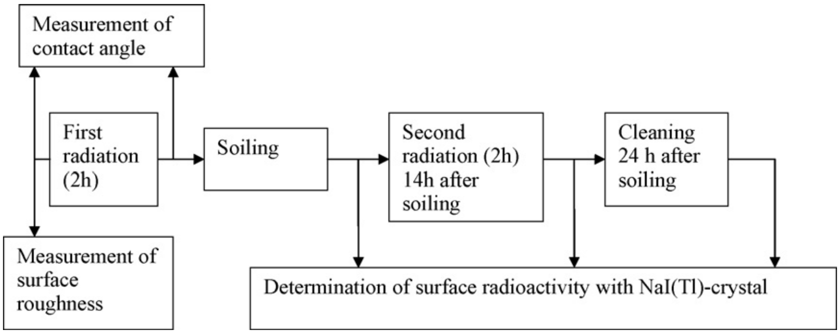

Fig. 1. Flow diagram of determination of surface properties and cleanability of ^{51}Cr-labelled model soil 1.

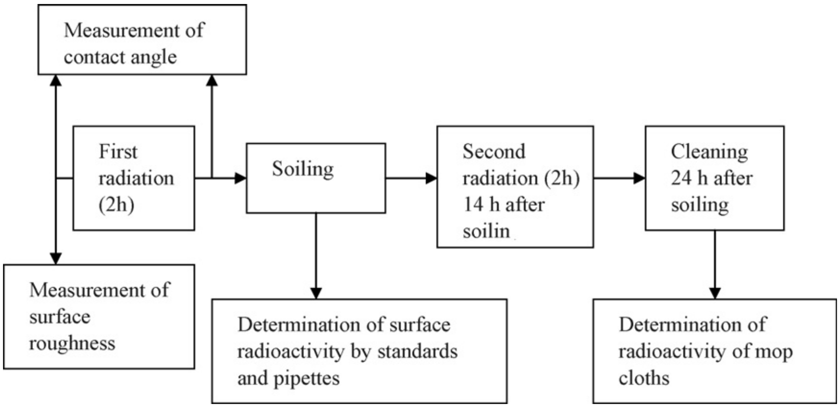

Fig. 2. Flow diagram of determination of surface properties and cleanability of ^{14}C-labelled model soil 2.

cloth was a microfibre cloth (Freudenberg Household Products, Finland).[15,16] The material of the microfibre cloth was polyester (100%) and the pile length was 8 mm. The cloth was moistened at 100% moisture regain with 5% detergent solution. The detergent was a weakly alkaline model detergent which contained triethanol amine soap of fatty acids (1.75% of weight), non-ionic surfactant (C13-oxoalcohol ethoxylate 9 wt.%) and tetrapotassium pyrophosphate (5 wt.%) (Farmos, Finland).[15,17]

2.6. Measurement of cleanability using the radiochemical method

Two different methods, a gammaspectrometric method and liquid scintillation counting, were used for evaluation of the cleanliness of the surfaces. The radioactivity of the surface was corresponded to the amount of the labelled component of soil on the sample.The cleaning result was presented as the proportion of the labelled component of soil after cleaning compared to that after soiling. Five replicate tests were performed for each test combination.

The cleanability of the model soil 1 (Table 2) was determined by a gammaspectrometric method using an NaI(Tl)-scintillation crystal. The counting system was composed of a 2″ × 2″ NaI(Tl)-crystal detector (Bicron Corporation, Ohio, USA), coupled to a multichannel analyser and standard electronics (Canberra Inc., Connecticut, USA). The number of counts was recorded from 2 to 5 min depending on the activity of the sample. The results were reported as counts per minute (cpm). In order to obtain reliable results, the cleaned samples needed longer measurement times for obtaining sufficient counts than the soiled samples. The soiled samples were placed on a plate

Table 2
Compositions and amounts of model soils used in the radiochemical study

Type of labelled component of the model soil	Components of the model soil				Amount of soil (μl) on a disc
	Radioisotope	Chromium compound ($m = 0.40$ g)	Fatty acid ($V = 0.60$ ml)	Solvent ($V = 10.0$ ml)	
(1) Organic particle	^{51}Cr	Chromium acetyl acetonate ($C_{15}H_{21}CrO_6$)	Triolein ($C_{57}H_{104}O_6$)	1-Propanol	50
(2) Oil component	^{14}C	Chromium (III)oxide (Cr_2O_3)	Triolein ($C_{57}H_{104}O_6$)	1-Propanol	50

In both soils, triolein refers to glyceryl trioleate.

constructed to ensure that the measuring geometry was the same for each measurement. To avoid contamination of the detector during counting, the plate was covered with clean plastic film. In order to monitor the reliability of the multichannel analyser, a reference sample of the radioactive soil was measured daily. The radioactivities of the soiled samples were measured before and after cleaning. The results were corrected for background activity and radioactive decay.

The cleanability of model soil labelled with the beta-ray emitter ^{14}C (Table 2) was measured using liquid scintillation counting. When preparing samples for measurement after cleaning, the ceramic materials were too hard to be cut into small enough pieces without loosening activity. Therefore the activities of the mop cloths were measured in this case and the activities of the ceramic materials were calculated using these results. The mop cloths were oxidized in an oxidizer (Maricont 781, Junitek, Finland), radiolabeled carbon dioxide was trapped in a trapping agent and the radioactivity was measured using liquid scintillation counting. The counting system consisted of a scintillation counter (Wallac 1411 Liquid Scintillation Counter, Wallac, Finland) and a measuring program (1414 WinSpectral^{TM}). The measurement time was 10 min. The results were reported as disintegrations per minute (dpm). The radioactivities of ceramic materials after soiling were determined using five dosages of soil. Calculation of the results included the attenuation equalizer and subtraction of the background. Correction for radioactive decay was not needed because of the long half-life of carbon.

In order to observe possible decomposition of the organic components of soil to CO_2, the following checking measurements were carried out. Measurement of CO_2 evaporated from inactive oil soil decomposed as a result of UV-radiation on the soiled surfaces was determined with an FTIR multi gas analyzer (Gasmet^{TM} model Dx-4000 portable Fourier Transform Infrared Spectrometry multi gas analyzer). The decomposition of radioactive oil soil was trapped in a trapping agent and the radioactivity of the trapping agent was measured using liquid scintillation counting. However, in these measurements decomposition of oil components to CO_2 was not observed and thus the effect of evaporation was omitted from calculation of the soil residues.

2.7. Statistical methods

The cleaning result was presented as the proportion of the soil residue after cleaning compared to the amount of soil on the surface after soiling. Statistical analyses were performed using SPSS version 12.0 (SPSS Inc., Chicago IL, USA), based on the mean values of the results. The cleanability results for the two soils (Table 2) were analysed separately. Analysis of variance was used to examine differences between the materials and treatments. Bivariate correlation analysis (Pearson's correlation coefficients, two-tailed test of significance) was used to examine possible correlations between roughness values, contact angles and soil residues. The significance used was 0.05 in analysis of variance and 0.01 in analysis of correlation.

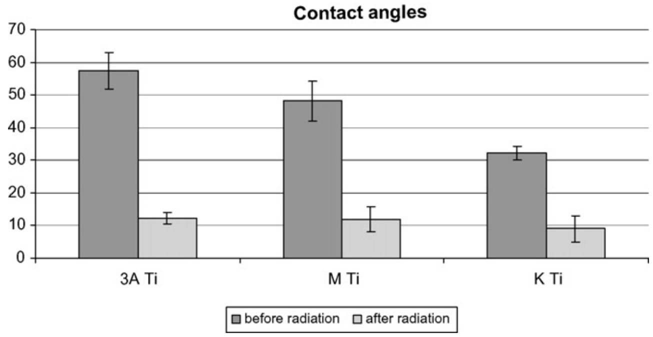

Fig. 3. Contact angle values before and after two hours of UV-radiation. Columns are means of six replicates, bars in columns are standard deviations of means of the replicates (±S.D.).

3. Results

3.1. Topography and water contact angle

The roughness values S_a are presented in Table 1. The glaze K Ti had lower roughness values than glazes 3A Ti and M Ti. The water contact angles varied between 32° and 58° before UV-radiation. The contact angle of K Ti surface was the lowest and the contact angle of 3A Ti surface the highest. The contact angle of ceramic materials is commonly reported to range between 30° and 50°. The ceramic tiles were irradiated with UV-radiation for 2 h, after which the contact angles of all evaluated samples were decreased. After irradiation the contact angles were approximately 10°. The contact angles before and after UV-radiation are presented in Fig. 3. Significant correlations were observed between examined roughness parameters and contact angle values after UV-radiation (Pearson's correlation coefficient $r = 0.997$).

3.2. Cleanability

In the case of organic particle soil (model soil 1), UV-radiation improved the cleanability of all samples (Fig. 4). The difference between the untreated and UV-treated surfaces was statistically significant ($p = 0.029$). The soil was removed most efficiently from the 3A Ti-surface, which is a matt-glazed rough surface. The soil residue of the smooth K Ti-surface was the

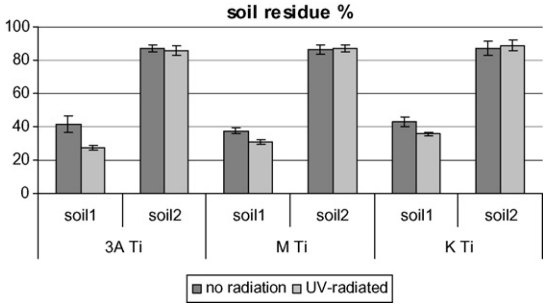

Fig. 4. Effects UV-radiation on cleanability of TiO_2-coated ceramic materials. Columns are means of five replicates, bars in columns are standard errors of means of the replicates (±S.E.).

highest. However, no correlations were observed between roughness values, contact angles and soil residues.

In the case of oil soil (model soil 2) no effect of UV-radiation was observed (Fig. 4): the soil residues after irradiation of all samples were almost the same as before UV-radiation. This was confirmed by the statistical analysis ($p = 0.518$). Despite small differences between glazes (Fig. 4), the glaze material did not statistically significantly affect cleanability from either of the soils ($p = 0.740$ for soil 1 and $p = 0.391$ for soil 2).

4. Discussion

According to this study the effect of UV-radiation on cleanability of surfaces depended on the type of model soil. It was found that organic particle soil was removed more efficiently after UV-radiation than without radiation, but no such effect was found in the case of oil soil.

In earlier studies TiO_2 surfaces have been reported to become highly hydrophilic after low-intensity UV-irradiation.[8–11] Similarly, according to the present study the UV-radiation affected the contact angles of the examined ceramic tiles. The contact angles of the evaluated samples decreased to around 10° or less after 2 h of UV-radiation.

In earlier studies it was observed that after UV-radiation TiO_2-coatings can decompose organic compounds.[3,6] Surface roughness and porosity influence the amount of film surface available for organic decomposition and therefore have an important role in the overall photocatalytic phenomena.[18] The photocatalytic reaction rate increases with increasing roughness of the TiO_2 thin film on a glass substrate. An increase in roughness increases the surface area available for photocatalytic decomposition of organic soil.[18] According to this study the organic particle soil was removed most efficiently from the surface coded 3A Ti, which is a rough surface. The effect of UV-radiation on the amount of soil on the surface was also greatest on 3A Ti surfaces.

Fujishima et al.[2] suggested that TiO_2 surfaces generate two separate photo-induced phenomena: a photocatalytic phenomenon decomposing organic compounds and superhydrophilic surface properties. These phenomena may occur on the same TiO_2 surface at the same time. However, the composition and the processing of the ceramic material can make the surface more photocatalytic and less superhydrophilic, or vice versa. In our study it was observed that after two hours of UV-radiation the superhydrophilic character of the examined surfaces was stronger than the photocatalytic character. The decomposition of organic compounds, representing the photocatalytic phenomenon, may need a longer UV-radiation time than the two hours used in this study.

The radiochemical method provides quantitative information on the amount of soil on the surface and is thus ideal for cleanability studies. It also takes into account the soil entrapped in surface flaws such as cracks or cavities. The radiochemical method was earlier used for examining the cleanability of flooring materials[19,20] and for determination of soil accumulation on plastic surfaces.[15] According to this study the radiochemical methods are also suitable for determination of cleanability of ceramic materials.

5. Conclusions

The cleanability of the TiO_2-coated glazed materials was examined without UV-radiation in our earlier study. In the present study radiochemical determination methods were adapted to glazed materials and samples were irradiated with UV-light. The observed effects of UV-radiation were greatest on rough surfaces, which implies that increasing roughness provides a greater surface area for photo-induced phenomena on TiO_2-surfaces.

It was observed that UV-radiation decreased contact angles of the examined surfaces. UV-radiation affected the cleanability of organic particle soil but had no effect on the cleanability of oil soil. Decomposition of organic particles to CO_2 was not observed. This indicates that the hydrophilic phenomenon was stronger in the evaluated samples after two hours of UV-radiation than the decomposition of organic compounds.

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