STUDIES ON VARIOUS FUNCTIONAL PROPERTIES OF TITANIA THIN FILM DEVELOPED ON GLAZED CERAMIC WALL TILES

ASHA ANIL^{*1}

ashata.36@gmail.com

BANGORIA DARSHANA R²

KSKV Kachh University, Gujarat

S. N. MISRA³

*CSIR-Central Glass & Ceramic Research Institute, Naroda Centre,^{1&3}
 Naroda Industrial Estate, Ahmedabad-382 330, Gujarat, India
 siccgcrinc@gmail.com*

A sol-gel based TiO₂ thin film was applied on glazed wall tiles for studying its various functional properties. Thin film was deposited by spin coating on the substrate and subjected to curing at different temperatures such as 600°C, 650, 700°C, 750°C and 800°C with 10 minutes soaking. The gel powder was characterized by FTIR, DTA/TG and XRD. Microstructure of thin film was analyzed by FESEM and EDX. Surface properties of the coatings such as gloss, colour difference, stain resistance, mineral hardness and wettability were extensively studied. The antibacterial activity of the surface of coated substrate against *E. coli* was also examined. The durability of the coated substrate in comparison to the uncoated was tested against alkali in accordance with ISO: 10545 (Part 13):1995 standard. FESEM images showed that thin films are dense and homogeneous. Coated substrates after firing results in lustre with high gloss, which increased from 330 to 420 GU as the curing temperature increases compared to that of uncoated one (72 GU). Coated substrate cured at 800°C shows higher mineral hardness (5 Mohs') compared to uncoated one (4 Mohs') and films cured at all temperatures showed stain resistance. The experimental results showed that the resistance towards alkali attack increase with increase in curing temperature and alkali resistance of sample cured at 800 °C was found to be superior compared to uncoated substrate. Contact angle of water on coated surface of substrates decreased with increase in temperature. Bacterial reduction percentages of the coated surface was 97% for sample cured at 700°C and it decreased from 97% to 87% as the curing temperature increased to 800 °C when treated with *E. coli* bacteria.

Keywords: TiO₂ coatings; glazed wall tiles; functional properties; chemical resistance.

1. Introduction

TiO₂ is a semiconductor and it is well known for its photocatalytic properties such as hydrophilicity, oxidizing power to decompose organic contaminants such as grease, dirt, bacteria etc. In recent years, this property of TiO₂ has been applied to important problems of environmental interests like detoxification of water, decomposing pollutants in air etc.

As studies showed that oxide based thin films coating can modify properties of various substrates, nano TiO_2 thin films were applied to get antifogging¹, antibacterial²⁻³, self-sterilizing⁴⁻⁵ self-cleaning effect⁶ etc. on various substrates such as glass, glazed ceramic surfaces etc. TiO_2 is also known for its optical applications due to its high refractive index. Nowadays, studies on fixing these nano TiO_2 thin film on glazed ceramic surfaces is also taking place⁷⁻¹⁵, as these tiles are also exposed to bacteria, pollutants, dust, dirt, oil etc. in hospitals, commercial and domestic places. Application of these thin film coatings could reduce infections and household work for cleaning by reducing time and cost of the cleaning agents and thereby improving surrounding hygiene. Literature shows that investigations on some specific properties of TiO_2 coated glazed ceramic wares such as gloss and wear resistance⁷, antibacterial⁸⁻¹¹, cleanability and chemical resistance¹²⁻¹⁶ of sol-gel based TiO_2 thin film were studied separately. However, to best of our knowledge, no one has done a systematic study on surface characteristics of the coated substrates in all aspects. Hence, the present work reports effect of curing temperature on surface characteristics of sol-gel based TiO_2 thin film deposited glazed ceramic wall tiles. These properties include gloss, colour difference, stain resistance, mineral hardness, wettability, antibacterial activity and alkali resistance in highly alkaline KOH solution.

2. Experimental Procedure

2.1. Sol preparation and sample preparation

The precursor used for titania sol preparation was technical grade titaniumtetraisopropoxide (TTIP) (M/s Sigma-Aldrich Chemie GmbH, Germany). For preparing 1.5 wt. % TiO_2 sol, acetyl acetone (M/s Merck Specialities Pvt. Ltd., Mumbai) was used as complexing agent, in order to control the hydrolysis rate and double distilled water was added as hydrolysing agent. The molar ratio of TTIP, acetyl acetone and water was kept as 1:2:4. The weight percentage of TiO_2 in the sol was fixed by adding required amount of Iso-propyl alcohol (M/s Astron Chemicals, Ahmedabad, Gujarat). The method of preparation of 1.5wt. % TiO_2 sol involved mixing required amount of TTIP and acetyl acetone on a magnetic stirrer at room temperature for around 30 minutes and finally adding necessary amount of water and isopropyl alcohol. This mixture was allowed to stir for 1 hour in order to ensure proper mixing of the chemicals and aged for 2 days.

Substrate taken for study was glazed ceramic wall tiles covered with white glossy glaze sourced from a tile company in Gujarat. The samples of glazed ceramic tiles were carefully cleaned by detergent to remove oily residues followed by washing with distilled water and a soft cotton cloth moistened with alcohol and then dried at 150°C and cooled to room temperature. Thin film coating was deposited by the spin-coating method (800 rpm for 30 sec) onto 80 x 80 mm plates cut out from tile sample by a laboratory made spinning machine. The amount of applied sol was 1.5ml / 4" X 4" tile size. The coated samples were fired in a Roller Hearth furnace (M/s. V.B. Ceramic Consultants, Chennai, India) at a heating rate of 20°C with a 10 minutes soaking time in peak firing

temperatures of 600°C, 650°C, 700°C, 750°C and 800°C temperatures and the sample thereafter mentioned as T-600, T-650, T-700, T-750 and T-800 respectively.

After firing, rectangular pieces of 80 mm in length and 40 mm in breadth were cut from the piece using a ceramic tile cutter using a diamond wheel. The uncoated tile pieces with the same dimension as mentioned above were also cut for comparative studies. These pieces were used for the subsequent characterization and assessment of alkali attack in immersion.

2.2. Characterization of gel powder

Gel powder sample was prepared by drying the sol at 150°C in an air bath, then ground in an agate mortar, and used for the following studies.

2.2.1. FTIR analysis

FTIR analysis was carried out for determining different types of bonding in the gel. KBr pellets were made using gel dried powder for FTIR measurement using Fourier transform Infrared spectroscopy (Spectrum 100, Perkin Elmer, USA) ranging from 400cm⁻¹ to 4000 cm⁻¹.

2.2.2. TG-DTA

TG-DTA of the dried gel was carried out by TG-DTA Analyzer, Model No. 6300 (Seiko Instruments Inc, Japan) at a heating rate of 20°C/minute from room temperature to 1000°C.

2.2.3. XRD

The XRD patterns obtained in a Philip's X-ray crystallographic unit (Model PW-1730) with a Goniometer PW-1710 in the 2θ range 10-90° using CuKα radiation (λ=1.5 Å) were used to investigate the phase analysis and transformation of the gel powder samples calcined at 450 °C, 600°C, 700°C, and 800°C.

2.3. Thin film characterization

2.3.1. FE-SEM and EDX

The thickness as well as the surface microstructure of the thin film applied over glazed layer of tiles cured at different temperatures was determined by 'Field Emission Scanning Electron Microscope coupled with link ISIS EDX detector (Model Supra 35VP, Carl Zeiss, Germany)'. The thickness of the film on the glaze was measured from a cross-sectional view of fractured sample. EDX mapping of thin film and glaze layer of (cross-sectional view) coated substrates cured at 700 °C, 750 °C (not shown) and 800 °C (shown) were carried out.

2.3.2. Colour difference (ΔE)

The colour difference was measured using Konica Minolta Spectrophotometer, Model CM-3600d and with measurement area of 8 mm under d/o SCI optical geometry as per ASTM C 609-90¹⁷. The values in terms of CIE ΔE have been measured and the average of 5 measurements has been furnished.

2.3.3. Gloss

Gloss is an optical property, refers to the ability of a surface to reflect light in specular direction and depends on many parameters such as refractive index of the material, the angle of incidence of light, surface topography etc. Specular reflection is the perfect mirror like reflection of light from a surface in which light from a single incoming direction is reflected into a single outgoing direction. Reflection is a fundamental optical phenomenon, which occurs when light propagates across a boundary between two media that have different refractive indices¹⁸.

The gloss of the test specimens were measured by NovaglossTM Statistical Glossmeter (Rhopoint Instrumentation Ltd., U.K) with an angle of 20°, calibrated using a reference polished black glass with a gloss of 88.8 GU at an angle of 20°. This was as per standard ASTM test method (D523-89)¹⁹, which relates the light reflected from the test specimens to that reflected from the black glass. All gloss readings are given in Gloss Units (GU).

2.3.4. Wettability

The wettability of the films was evaluated by examining the contact angle of water on TiO₂ coated surface. The static contact angle of water on coated specimens was measured by contact angle analyzer (Model, phoenix 300, Korea).

2.3.5. Mineral Hardness

The surface hardness test of coated tiles was measured in terms of Mohs' hardness scale. The test is performed by drawing minerals of defined hardness over the surface of the tile (different minerals having hardness ranging from 1 to 10 in the moh's scale) by hand and subjectively assigning a Mohs' number to the glazed tile. The mineral of highest Moh's hardness that produces not more than one scratch is reported.

2.3.6. Stain resistance

The stain resistance of coated tile was carried out by exposing the coated surface to 1% Methylene blue solution for 24 h and washed with water to remove the same. If there is no stain mark after washing, then it can be reported as stain resistant.

2.3.7. Alkali resistance test

The alkali resistance of the coated substrates were performed in accordance with ISO: 10545 (Part 13): 1995²⁰. The test includes immersion of the test specimens in 10wt. % KOH for 4 days at 25°C and is often classified by visual assessment. However, in the present study, alkali resistance was evaluated quantitatively by gloss measurement before and after immersing the samples in alkali solution. The tile specimens were removed, washed and dried at an interval of 24h for gloss measurements. Five pieces of each coated piece fired at each temperature were used for the study. To remove any error in gloss values, frequent calibration checks were made throughout the experiments and the measurement area was marked and positioned in the same way after each intervals of time.

2.3.8. Antibacterial activity test

Escherichia coli were used for the antibacterial activity test of the samples and the test was carried out as per JIS Z 2801:2000²¹. A bacterial suspension of *E. coli* was prepared by cultivating the bacteria for one night, washing and then diluting the solution so that the initial bacterial count was around $8 \text{ to } 10 \times 10^5$ colony forming units (CFU)/mL. The surface of the substrate was sterilized by alcohol and dried, then dripped with 0.4 ml of the bacterial suspension. The tile was covered with non-alkaline glass to improve contact of the bacterial suspension with the surface and to prevent suspension from drying. The sample was irradiated for 30 min under UV light. The suspension was collected on a petri dish, to cultivate the bacteria, for ~24 h at $35 \pm 1^\circ \text{C}$, so that bacterial colonies would form. The number of living bacteria was counted. Bacterial reduction rate was obtained by comparing the number of living bacteria on the examined tile sample with that of a conventional tile sample. The glazed surface of conventional tile without TiO_2 coating was tested as a control sample.

3. Results and Discussions

3.1. Characterization of gel powder

3.1.1. FTIR

As shown as in Fig.1., the dried gel presented a large band centered at 3430 cm^{-1} corresponding to lattice water absorbed (anti symmetric and symmetric OH stretching)²². The two very small bands present at 2923 cm^{-1} and 2852 cm^{-1} in the spectrum of dried gel are due to CH_2 anti symmetric stretching and symmetric stretching of C-H bond respectively. The strong bands at 1585 and 1531 cm^{-1} are due to AcAc groups bonded to titanium²²⁻²³. In the spectra of our gel, IR bands due to titanium isopropoxide at 620 cm^{-1} assigned to Ti-O -Pr and CO stretching metal alkoxide at 1029 cm^{-1} are also observed. The characteristic band of Ti-O-Ti ($436 - 495 \text{ cm}^{-1}$) is also observed.

Fig.1. FTIR spectrum of the dried gel.

3.1.2. TG-DTA

TG-DTA of air dried gel sample in Fig.2. demonstrates that thermal decomposition continued till 575°C. During heating, there was continuous weight loss of 42% up to 650°C indicating decomposition of volatiles present in the gel material. DTA curve revealed that endothermic reaction at a temperature of 125°C is mostly owing to evaporation of physical water and volatile organic components and at a higher temperature (i.e. from 200°C onwards) decomposition of carbonaceous material from the organic metallic complex takes place leading to exothermic reaction in presence of air. Major broad exothermic peaks at 309.09°C is due to decomposition of carbonaceous material and exothermic peak at 454.40°C is due to crystallization of titania as supported by the observations from the X-ray diffraction pattern of gel (Fig. 3) which gave well-defined anatase peaks. The minor peaks at 476.21°C could be attributed to anatase to rutile phase transformation.

Fig. 2. TG-DTA of air dried gel.

3.1.3. XRD

XRD patterns obtained from the calcined powders of the gel having same composition as that of the thin film are shown in Fig.3. The patterns labeled T-450, T-600, T-700 and T-800 represent the TiO_2 gel powder after calcinations at 450, 600°C, 700°C and 800°C respectively. It can be seen that strong peak at $2\theta = 25.3^\circ$ which corresponds to the (101) crystal plane for T-450, confirms crystallization of anatase. At 600°C, it was observed that rutile phase [strong peak at $2\theta = 27.4^\circ$ which corresponds to the (110) crystal plane] predominate over anatase phase. As the temperature increases from 600°C to 700°C, intensity of anatase phase reduced and rutile phase increased. However, at 800 °C, titania was completely transformed to rutile phase.

Fig.3. X-ray diffraction pattern of gel calcined at different temperatures

3.2. Thin film characterization

The deposited film was observed as crack free and homogeneous after curing at test temperatures.

3.2.1. FESEM study

Titania thin film cured at 600°C was found to be completely wiped out after rubbing with hand or tissue paper and those cured at 650°C was found to be too soft as it shows a lot of scratches after rubbing with hand on the film. Hence, sample cured at 700°C, 750°C and 800°C was only taken for FESEM study.

Cross-sectional image of the thin film coated glazed ceramic tile cured at 750°C and 800 °C are depicted in Fig.4a and 4b. Thickness of the applied coating of T750 and T800 is found to be about ~63 nm and ~50 nm respectively. In Fig. 4a and 4b, interface boundary between applied coating and glaze (zircon crystals embedded in glassy matrix) can be distinguished on the basis of their micro structural difference.

Fig.4. FESEM images of cross-section of TiO_2 thin film coated substrate cured at (a) 750 °C and (b) 800 °C.

Fig.5. FESEM images of surface microstructures of TiO_2 multi-oxide thin film coated substrate cured at (a) 700 °C, (b) 750 °C and (c) 800 °C.

Surface microstructures of thin film coating on T-700, T-750 and T-800 (coated tile fired at 700 °C, 750 °C and 800 °C) are shown in Figs. 5a, 5b and 5c. In the case of T-700 and T-750, nano-crystalline particles of titania are visible. However, some precipitation of titania was also observed on T750. However, in the case of T800, nano particles are not clearly distinguished and it seems particles became immersed in glassy matrix of glaze which could be attributed to either softening of the glaze or film at 800 °C. The softening of film could be due to the presence of alkali ions diffused from glaze to the film as evident from EDX (Fig. 7).

Fig.6. EDX of glaze layer of coated substrate cured at 800 °C (marked position of glaze layer as shown in cross-sectional image (inset) is mapped for EDX).

Energy Dispersive X-ray analysis of both the glaze and TiO₂ thin film layer of coated substrate cured at 800°C are shown in Fig.6 and Fig.7 respectively. Fig.6 shows the presence of glaze elements such as Na, Mg, Al, Si, K, Ca, Zn, P and O in the glaze layer of substrate. Presence of Ti besides other elements in glaze has been established from Fig.7, which ensures presence of titania thin film on the glaze layer. It is also established that the metal ions are diffused into the thin film layer due to which a low concentration of element in the glaze layer is also detected in the EDX of thin film (Fig.7). It is to be noted that film of T700 and T750 also showed all the components corresponds to glaze along with peaks of Ti (not shown).

Fig.7. EDX of thin film portion of coated substrate cured at 800 °C (marked position of thin film layer as shown in cross-sectional image (inset) is mapped for EDX).

Table 1. Colour difference between coated and uncoated substrates cured at different temperatures.

Sample reference	T600	T650	T700	T750	T800
ΔE	0.35±0.2	0.72±0.2	0.68±0.2	0.73±0.2	0.93±0.2

3.2.2. Colour difference (ΔE)

Thin film coated samples showed mirror like reflectivity after curing at all the temperatures. It is evident from the above table that coating has changed the colour of the

coated tiles by a factor which ranges between 0.15-0.93. However, it is marginal as the value is less than 1. CIE 1976 limiting value for colour difference between two samples of same colour is described as usually non-visible difference if ΔE scale is found as $0 < \Delta E < 1$ ²⁴.

3.2.3. Gloss

It is evident from Fig.8. that the thin film coated substrates are having high gloss compared to uncoated one at all the curing temperatures and it increases with increase in curing temperature; especially from 750°C (390±20 GU) and showed maximum gloss for coated substrate cured at 800°C (420±20). The increase in gloss of the coated substrate is due to the high refractive index (2.4-2.6) of the coating compared to that of the glaze (1.54-1.56)⁷ as it is also reported elsewhere^{7, 18} that reflectivity of glass (gloss) surfaces can be increased simply by covering its surface with a single layer of metal oxide having a higher refractive index than that of glass and glaze is also a form of glass. The increase in gloss with increase in curing temperature could be attributed to phase transition from anatase to rutile with rise in temperature as evident from XRD results (Fig.3.). As per the literature²⁵, rutile phase has high refractive index (2.6) compared to anatase phase (2.4) of TiO₂. The increase in refractive index of the coating with increase in curing temperature could also be attributed to the increase in density of the film.

Fig.8. Effect of curing temperature on gloss of uncoated and coated substrates.

3.2.4. Wettability of coated surface

Table 2. shows contact angles of water on TiO₂ film deposited substrates cured at different temperatures and uncoated. It was found that contact angle of water on T600 is higher than uncoated having a contact angle of 45 ± 10 . However, as the curing temperature increases from 600 °C to 800 °C, it was found that contact angle slightly decreases, especially for samples cured at 750°C and 800°C²⁶, which could be attributed to fine roughness generated on the surface of thin film at high temperature. This may be due to inter reaction between thin film and the glaze. It is known that wettability of a

Table 2. Contact angle of water on the substrates under study.

Sample reference	Curing temperature °C	Contact Angle of water (°)
Uncoated	N/A	45±10
T600	600	66±8
T650	650	60±5
T700	700	60±5
T750	750	55±3
T800	800	50±3

Table 3. Mineral hardness of coated and uncoated substrates.

Sample reference	Curing temperature °C	Mineral hardness moh's scale
Uncoated	N/A	4
T600	600	2
T650	650	2
T700	700	3
T750	750	4
T800	800	5

solid surface with liquids is not only governed by its chemical properties but also by its geometry²⁷.

3.2.5. Mineral hardness

It is evident from Table-3 that with the increase in curing temperature, Mohs' mineral hardness of coated substrates increased as compared to the uncoated one. The uncoated substrate was having a hardness of 4 in Mohs' scale and coated tiles T600, T650 and T700 showed a hardness value, which is lower than that of uncoated substrate. The decrease in hardness of coated substrate cured at 600°C, 650°C and 700°C could be attributed to lack of proper adhesion of thin film on the substrate at these temperatures.

However, coated substrates cured at 750°C and 800°C showed a mineral hardness of 4 and 5 in Mohs' scale. The increase in hardness of the same could be attributed to densification and proper adhesion of the film on glazed surface due to softening of glaze at these temperatures. The relative hardness of glazed tile is an important issue that should be addressed when selecting a tile. Mineral that provides Moh's values of 3 (Min) is suitable for most residential wall applications as per the ISO standard²⁰. It is evident from the table that test samples marked T700, T750 and T800 showed hardness values which meet the requirement of the standards.

3.2.6. Stain resistance

Studies showed that coated and uncoated substrate did not show any stain marks after washing out the methylene blue which was applied on the tile. This could be due to the presence of high dense film on the surface of coated substrate.

Fig.9. Alkali resistance of uncoated and coated substrate cured at 600°C, 700°C and 800°C as a function of immersing time in KOH soln. for 96 h.

3.2.7. Alkali resistance

Fig.9. gives a comparison of alkali resistance of uncoated and TiO_2 coated substrates cured at different temperatures against 10wt. % KOH solution. T 600 and T650 were not taken for chemical resistance studies due to weak adhesion of the film. It is evident from Fig.9. that gloss of uncoated substrate reduced from 83 GU to 51 GU after 96 hrs of immersion. It is also observed that T700 and T750 lost gloss after immersion in solution for 24 hrs and 72 hrs respectively and coating was found to be completely removed. It is also evident from Fig.9. that as the curing temperature increases, the alkali resistance of thin film increased and alkali resistance of T 800 was found to be superior compared to uncoated substrate.

3.2.8. Antibacterial activity

Fig.10. shows the effect of the curing temperature on the antibacterial activity of TiO_2 thin film coated glazed ceramic wall tiles. The antibacterial activity was tested by contact

Fig.10. Effect of the curing temperature on the antibacterial activity TiO_2 Thin film coated glazed ceramic wall tiles.

between *E. coli* and the sample surface under UV light for 30 min. As shown in Fig.10, antibacterial activity measured in terms of bacterial reduction percentages decreased from 97% to 87% when the curing temperature increased from 700°C to 800 °C. The low antibacterial effect of sample cured at 800 °C could be attributed to the following reasons as reported earlier [10].

1. Photocatalytic property depends on the ratio of anatase to rutile. XRD results show that ratio of anatase to rutile phase decreased as the curing temperature increased.
2. The glaze might be softened and diffusion of glaze elements on to the thin film surface might be taken place at 800 °C as evident from EDX photographs.

4. Conclusions

Sol-gel based TiO_2 thin film was applied on glazed wall tiles using spin coating. The deposited film was observed as crack free and homogeneous after curing at test temperatures. The film thickness was found to be ~ 63 nm and 50 nm after curing at 750°C and 800°C. Calcination of gel powder at 450°C results in crystalline titania with anatase phase and as the temperature increases from 600°C to 700°C, anatase phase reduced and rutile phase increased and at 800°C, only rutile phase was detected. Microstructure analysis of the thin film coated substrates showed nanocrystalline thin film at 700 °C and 750°C and at 800°C, nano crystalline particles were found to be immersed in glassy matrix. Coated tiles showed high gloss in the range of 380-420 GU as compared to uncoated one (72 GU) with the rise in curing temperature from 600° C to 800° C. The contact angle of water was $66 \pm 8^\circ$ for T600 compared to uncoated $45 \pm 10^\circ$ and it shows a descending trend as the temperature increases and T800 shows contact angle of $50 \pm 3^\circ$. TiO_2 oxide thin film deposition on the glazed surface and subsequent curing at 800°C resulted a hardness of 5 Moh's which is higher as compared to the uncoated substrate (4 Moh's). Alkali resistance studies showed that coated substrates marked T800 showed superior resistance compared to uncoated. TiO_2 thin film coated substrates cured at all the temperatures showed bacterial reduction percentage greater than 85%. However, as the curing temperature increased, it was found to be reduced from 97% to 87%. Above studies substantiate the potential effect of the Titania thin film coating reported herein for improvement not only the quality and aesthetic appeal but also the functional properties of the glazed ceramic wall tile.

Acknowledgments

The authors are thankful to the Director, CSIR-CGCRI, Kolkata for his permission to publish the paper. The authors acknowledge with thanks the help extended by all the members of Naroda Centre during different stages of this work. Thanks are also due to the members of X-ray & SEM sections of CGCRI, Kolkata for helping in characterization of the samples. Authors also greatly acknowledge help of ATIRA, Ahmedabad, Gujarat for antibacterial testing and Industries Commissionerate, Govt. of Gujarat for sponsoring GAP 1207 project under which this study was carried out.

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