EFFECT OF PROCESSING PARAMETERS OF HYDROPHOBIC FILM ON CERAMIC TILE

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Abstract

The work in this research fabricated hydrophobic SiO_2 nanoparticles modified with tetraethylorthosilicate (TEOS), poly-(dimethylsiloxane) (PDMS), and methyltriethoxysilane (MTES) using a sol-gel method. The effects of the precursors, coating techniques, and curing conditions were investigated. A water contact angle (WCA) measurement was done using a sessile drop method with an optical contact measuring apparatus. Morphologies of the hydrophobic films were depicted using scanning electron microscopy. All data were analyzed using Design Expert® software. The results showed that the morphology of the hydrophobic films had a nano-roughness as evidenced by the high contact angle. The largest predicted WCA of these is 150.306º, which will be obtained with a TEOS:SiO_2:PDMS:MTES ratio equal to 7.00:3.374:2.75:3.00 wt%, respectively. It is coated using a dipping technique and oven cured at 400°C.

Keywords: Hydrophobic, coating techniques, Design Expert® software

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Introduction

Ceramics generally have surfaces with strong, attractive, and colorful glazes. However, many ceramic glazes have hydrophilic properties that cause water stains which deteriorate the glaze color and can harbor bacteria. Many researchers have explored methods to fabricate hydrophobic films for coating on ceramic glazes to reduce their wetting properties, thus enhancing their self-cleaning properties (Lin *et al*., 2006; Wang *et al*., 2007; Wang *et al*., 2009; Hallmann *et al*., 2010; Nadargi *et al*., 2010; Hozumi *et al*., 2011; Lin *et al*., 2011; Wen *et al*., 2011). These films can be synthesised, coated, and cured using several techniques including lithographic patterning (Wang *et al*., 2009), electrochemical deposition (Wang *et al*., 2007), chemical vapour deposition (Wen *et al*., 2011), layer-by-layer assembly plus phase separation (Lin *et al*., 2006), high energy ball milling (Hallmann *et al*., 2010), and sol-gel methods (Nadargi *et al*., 2010). Nano silica particles are proven to have a rough surface film with a lotus-leaf-like structure (Wu *et al*., 2005; Prertkaew *et al*., 2012). Nanoroughness produced from silica particles can be modified with organic compounds. For instance, Liu *et al*. (2011) created a robust surface roughness from SiO_2 nanoparticles with a surface modification of polydimethylsiloxane (PDMS). Hwang *et al*. (2008) synthesized transparent hydrophobic SiO_2 nanoparticles with a matrix of 3-glycidoxy-propyltrimethoxy-silane (GPTS) and tetramethy-lorthosilicate (TMOS). Gurav *et al*. (2015) prepared self-cleaning superhydrophobic silica coatings that were modified from SiO_2 microparticles with methyltrichlorosilane (MTCS). Hsu *et al*. (2014) fabricated a hydrophobic and omnidirectional antireflective coating, that employed SiO_2 nanospheres using an n-octadecyl-triethoxysilane solution (C_{18}-TEOS).

In the current study, a hydrophobic film of SiO_2 nanoparticles modified with tetraethyl-lorthosilicate (TEOS), poly-(dimethylsiloxane) (PDMS), and methyl-triethoxysilane (MTES) was prepared using a sol-gel method. The purpose of this study was to find the optimum weight percentage of SiO_2 and MTES to synthesize TEOS:SiO_2:PDMS:MTES films. Additionally, this study compared films coated on ceramics by dipping and spraying methods. Finally, the most appropriate technique for film curing was investigated.

Materials and Methods

Chemicals

The chemicals used for synthesizing hydrophobic precursors were AEROSIL 90 and 200 hydrophobic fumed silica with an average primary particle size of 20 and 12 nm, respectively (Evonik Industries AG, Essen, Germany), 98% pure tetraethy-lorthosilicate (Acros Organics BVBA, Geel, Belgium), 98+% pure methyltri-ethoxysilane (Acros Organics BVBA), and poly-(dimethylsiloxane) (Acros Organics BVBA).

Table 1. Blends of TEOS:SiO_2:PDMS:MTES (wt%)

Blends	TEOS	:	SiO_2	:	PDMS	:	MTES
A	7.00		0.50		2.75		2.00
B	7.00		1.00		2.75		2.00
C	7.00		2.00		2.75		2.00
D	7.00		4.00		2.75		2.00
E	7.00		0.50		2.75		4.00
F	7.00		1.00		2.75		4.00
G	7.00		2.00		2.75		4.00
H	7.00		4.00		2.75		4.00
I	7.00		0.50		2.75		8.00
J	7.00		1.00		2.75		8.00
K	7.00		2.00		2.75		8.00
L	7.00		4.00		2.75		8.00

Coating Liquid Preparation

Twelve blends (A-L) of TEOS:SiO_2:PDMS:MTES precursors were prepared, as shown in Table 1.

Figure 1 depicts the experimental procedure as a flowchart. First, 7.00 wt% of TEOS was refluxed with a mixture of 6.00 wt% of HCl and 27.30 wt% of ethanol at 70°C for 3 h to form TEOS solutions. At the same time, equal amounts of 12 and 20 nm silica particles were mixed and dispersed by ultrasonication for 3 h in 50.55 wt% isopropanol to form nano silica mixtures. After that, 2.75 wt% of PDMS and 2.00-8.00 wt% of MTES were added. Next, the mixtures were refluxed again at 70°C for 12 h to form coating liquids. Then, they were coated on 102 cm^2 test tiles using either a dipping or spraying method. In order to assure that this work is industrially applicable, the test tiles were commercially available ceramic wall tiles. Each tile was treated with 15.00 mL of the coating liquid. After that, the tiles were cured by 1 of the following methods: 1) heating with an electric hair dryer, and 2) and 3) baking in an oven at either 300°C or 400°C for 15 min with a heating rate of 5°C/min.

Surface Coating Characterization and Analysis

The water contact angle (WCA) is a good indicator of the hydrophobic properties of a coated surface. A DataPhysics OCA 20 (DataPhysics Instruments GmbH, Filderstadt, Germany) equipped with a CCD camera was employed to measure the WCA in this work. The microscopic images of the hydrophobic films were obtained using a JEOL JSM-6010 LV (JEOL Ltd., Tokyo, Japan) with an Everhart-Thornley type of secondary electron detector scanning electron microscope (SEM).

Statistical Experimental Design and Analysis

Design Expert® software version 8 was employed to design the experiment and analyze the data. A general factorial design was selected for use in this study. The conditions used for investigation were as follows: 1) %SiO_2 in the coating liquid (0.5, 1.00, 2.00, and 4.00 wt%), 2) %MTES in the coating liquid (2.00, 4.00, and 8.00 wt%), 3) the coating method (dipping and spraying), and 4) the film curing techniques (hair dryer, 300°C in an oven, and 400°C in an oven). The WCA data were collected according to the experimental design and analysis using ANOVA to find which factors and their interactions that significantly (> 95% confidence) affected the WCA of the films. Furthermore, equations for predicting the WCA of the films were obtained from regression. Finally, contour and 3D graphs were made showing the WCA of the fabricated films as a function of the experimental conditions to find the optimum synthesis conditions, coating, and curing for the hydrophobic films.

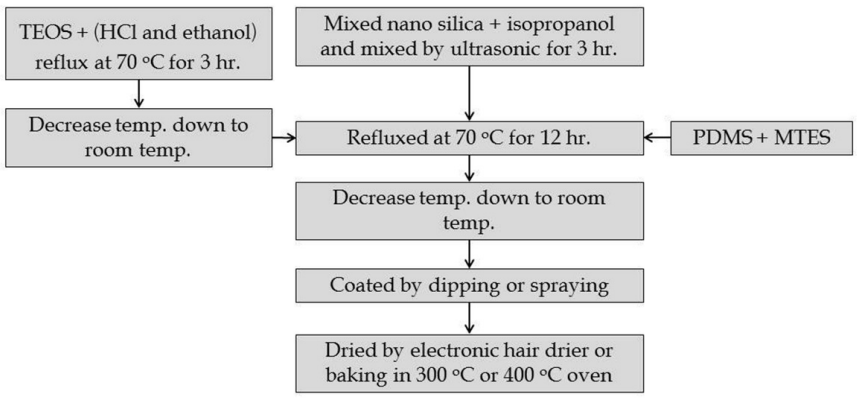

Figure 1. Flowchart of the experimental procedure

Results and Discussion

WCA Results

In Table 2, the WCA data of H-blends were prepared using different coating and curing conditions. Five replicates for each combination of coating and curing technique were made, as indicated by (1) to (5). The WCA data of other blends were collected and tabulated but are not shown here.

The data of all the blends were analyzed using ANOVA. The results showed that $\%SiO_2$, %MTES, and the coating technique significantly affected the WCA. Although the curing technique did not have a significant effect by itself, it interacted with other factors and this did affect the WCA. The WCA predictions were obtained from the regression analysis. Equation 1 and Figure 2(a) show the predicted WCA of the films coated by dipping and cured with the hair drier, while Equation 2 and Figure 2(b) present the predicted WCA of the spray coated and hair drier cured films. It can be seen that silica addition improved the WCA. However, MTES addition can either increase or decrease the WCA. This is because %MTES interacted with $\%SiO_2$. Although a maximal WCA was obtained from the spray coated films, the difference was small. Generally, both coating methods yield roughly the same WCA.

Table 2. The measured WCA of H-blends

Blend	WCA	Blend	WCA
Hdh (1)	136.10	Hsh (1)	141.95
Hdh(2)	139.90	Hsh (2)	144.15
Hdh (3)	141.85	Hsh (3)	134.70
Hdh (4)	140.65	Hsh (4)	144.45
Hdh (5)	136.95	Hsh (5)	139.70
Hd300 (1)	146.60	Hs300 (1)	144.40
Hd300 (2)	147.75	Hs300 (2)	146.10
Hd300 (3)	147.65	Hs300 (3)	143.80
Hd300 (4)	149.20	Hs300 (4)	137.25
Hd300 (5)	146.65	Hs300 (5)	146.00
Hd400 (1)	143.60	Hs400 (1)	142.35
Hd400 (2)	147.20	Hs400 (2)	143.30
Hd400 (3)	149.50	Hs400 (3)	144.35
Hd400 (4)	144.05	Hs400 (4)	142.30
Hd400 (5)	143.30	Hs400 (5)	147.25

H=H blend, d=dip coated, s=spray coated, h=hair drier, 300=300°C oven, 400=400°C oven, and numbers inside parentheses are replicated numbers.

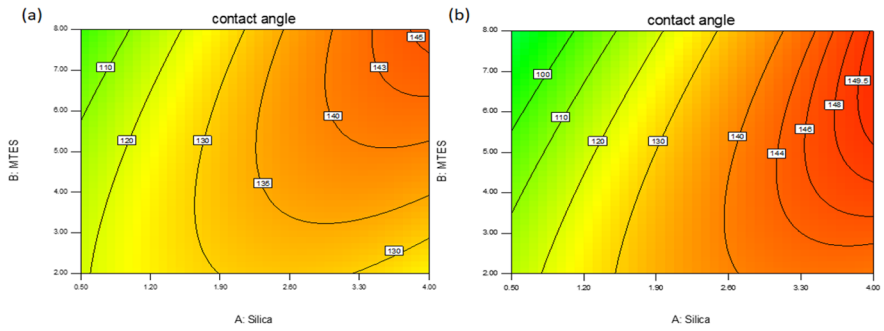

Figure 2. The predicted WCA as a function of $\%SiO_2$ and %MTES of the (a) dip coated and hair drier cured films and (b) spray coated and hair driercured films

$$WCA = 114.01 + 11.22\cdot SiO_2(\%) - 0.14\cdot MTES(\%) + 1.91\cdot SiO_2(\%)\cdot MTES(\%) - 2.94\cdot SiO_2{}^2(\%)^2 - 0.41\cdot MTES^2(\%)^2 \quad (1)$$

$$WCA = 111.43 + 16.90\cdot SiO_2(\%) - 2.15\cdot MTES(\%) + 1.91\cdot SiO_2(\%) MTES(\%) - 2.94\cdot SiO_2{}^2(\%)^2 - 0.41\cdot MTES^2(\%)^2 \quad (2)$$

The predicted WCA of the dip coated films cured in an oven at 300°C are shown in Figure 3(a) and Equation 3. Those of the spray coated films are shown in Figure 3(b) and Equation 4. It is clear that dip coating resulted in a larger WCA than spray coating. The maximum predicted WCA of the dip coated hydrophobic films oven cured at 300°C is located at the center of the oval in Figure 3(a) and is ≅148º. The + and – signs on % SiO_2 and %MTES in the equations indicate that increasing %SiO_2 can increase the WCA while increasing %MTES can lower the WCA.

$$WCA = 136.31+11.39\cdot SiO_2(\%) - 3.11\cdot MTES(\%) + 1.91\ SiO_2(\%) MTES(\%) - 2.94\ SiO_2{}^2(\%)^2 - 0.41\cdot MTES^2(\%)^2 \quad (3)$$

$$WCA = 118.26 + 17.07\cdot SiO_2(\%) - 5.12\cdot MTES(\%) + 1.91\cdot SiO_2(\%) MTES(\%) - 2.94\cdot SiO_2{}^2(\%)^2 - 0.41\cdot MTES^2(\%)^2 \quad (4)$$

Figures 4(a) and 4(b) illustrate the predicted WCA of the dip and spray coated

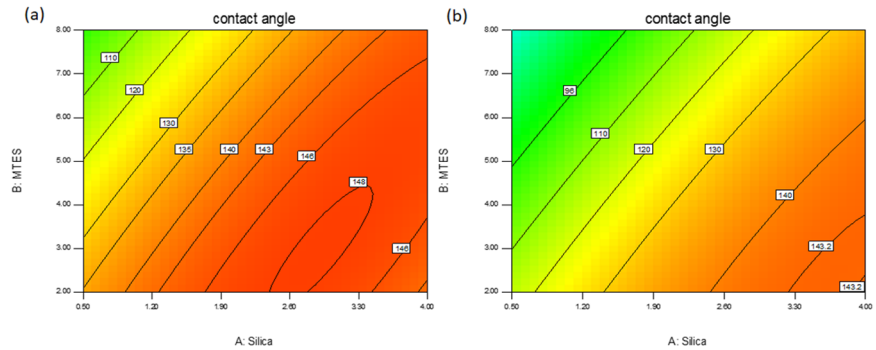

Figure 3. The predicted WCA as a function of %SiO_2 and %MTES of the (a) dip coated and 300°C oven cured films and (b) spray coated and 300°C oven cured films

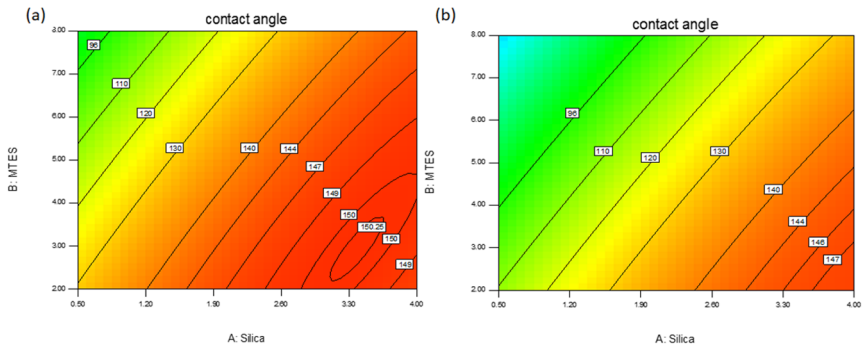

Figure 4. The predicted WCA as a function of %SiO_2 and %MTES of the (a) dip coated and 400°C oven cured films and (b) spray coated and 400°C oven cured films

films, respectively, oven cured at 400°C. Additionally, Equations 5 and 6 predict the WCA of these films. It is clear that curing at 400°C has almost the same effect as at 300°C. However, the 400°C cured films had larger predicted WCA values. Furthermore, the maximum WCA predicted by regression analysis for the 400°C cured film was ≅150.306º. This max WCA would be obtained from a dip coated film made with 3.398 wt% SiO_2 and 3.0 wt% MTES cured at 400°C.

$$\begin{aligned} WCA = {} & 132.20+14.25\cdot SiO_2(\%) \\ & -4.05\cdot MTES(\%) + 1.91\, SiO_2(\%) \\ & MTES(\%) -2.94\cdot SiO_2^2(\%)^2 \\ & -0.41\cdot MTES^2(\%)^2 \end{aligned} \quad (5)$$

$$\begin{aligned} WCA = {} & 113.38 + 19.93\cdot SiO_2(\%) \\ & -6.06\cdot MTES(\%) + 1.91\cdot SiO_2(\%) \\ & MTES(\%) - 2.94\cdot SiO_2^2(\%)^2 \\ & -0.41\cdot MTES^2(\%)^2 \end{aligned} \quad (6)$$

Figures 5(a) and 5(b) show SEM micrographs of the dip and spray coated films, respectively. These films were made with 4 wt% of SiO_2 and 4 wt% of MTES and oven cured at 400°C. The TEOS:SiO_2:PDMS:MTES films fabricated in this work had very fine surface morphology, and thus the lotus effect was established. The insets of Figures 5(a) and 5(b) show hydrophobic water droplets on the films producing actual WCA values of 149.50º and 147.25º, respectively. The WCA of the dip coated film was larger than that of the spray coated film, although the dip coated film had a finer morphology. This result is not consistent

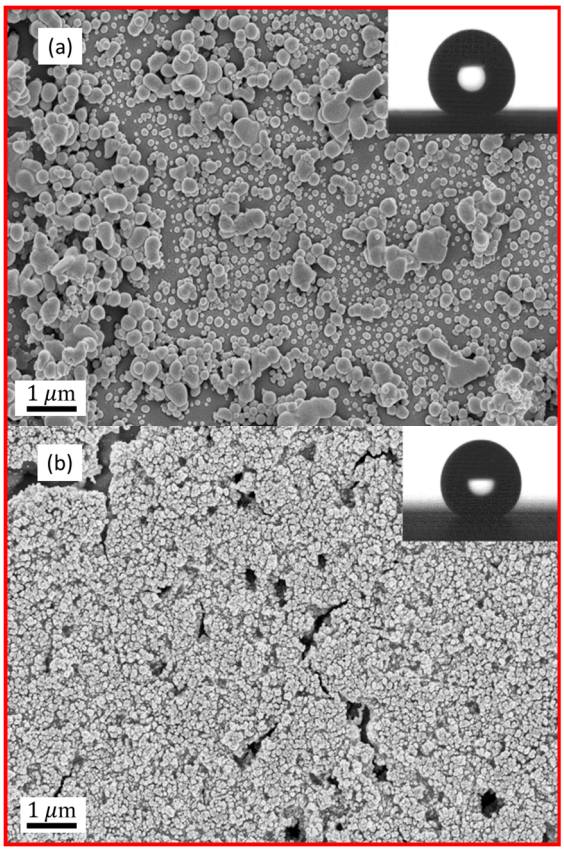

Figure 5. SEM micrographs with hydrophobic water droplets on 4 wt.% of SiO_2 and 4 wt.% of MTES films which were coated by (a) dipping and (b) spraying and oven cured at 400°C

with the almost universal observation of researchers that a film with a finer morphology tends to exhibit a higher degree of hydrophobicity. One possible reason for this is that these films are more likely to crack.

Conclusions

The TEOS:SiO_2:PDMS:MTES films fabricated in this work had a fine microscopic morphology which contributed to their hydrophobic properties. Equations were developed for predicting the WCA of the films containing various levels of SiO_2 and MTES applied on ceramic tiles using 2 different techniques and cured by 3 methods. It was predicted that the film which had the maximal WCA would be the one containing 3.398 wt% SiO_2 and 3.00 wt% MTES, dip coated and oven cured at 400°C.

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