Evaluation of Effective Parameters on Wet Ability of the Silica Nano Coating by the Use of Fractional Factorial Design

Ali Arastehnodeh[1], Solmaz Broomandi[2]

***Abstract*—** The overall goal of this study was to synthesis hydrophobic and thermally stable nano silica coating on hard porcelain substrate in order to prevent water and pollutant accumulation on the surface. In addition, the effect of possible parameters on wettability of the nano coating was investigated using the fractional factorial method. A simple sol-gel method and a polymeric solution was added to sol as co-precursor or surface modifying reagent in order to increase non-wet ability properties of the final product. In the next step, the ceramic pieces have been spin coated with different spin speeds according to fractional factorial table. The parameters that were studied here consist of catalyst concentration, the concentration of polymeric solution added to the sol, the molar proportion of water to silane and the spin speed. Results shows the increase in all parameters except catalyst concentration leads to a rise in water contact angle, which indicates the wet ability.

***Keywords*—** ceramic glaze- hydrophobic coatings- silica-PMMA- factorial design

I. Introduction

DEMANDS for self-cleaning coatings on every kind of substrates have faced a raise in the last few years. Titania, Zirconia, and Fluoro polymers were the most popular coatings for this need. Using these kinds of coatings have become common in ceramic industry but not on hard porcelain surfaces.

There are different methods in order to achieve an easy to clean surface.

1) Increasing water contact angle with the surface: In this method by applying coatings with low surface free energy, the contact angle of water with the surface is raised and as a result, contaminants cannot adhere to the surface.
2) Nano-semiconductor films: TiO2 nano coatings not only can catalytically degrade the organic materials adhered to the surface, but also it can form a water film that is able to clean out the degraded products automatically [1].
3) Antibacterial and self-cleaning technique: in this method, antibacterial metals that are able to decompose bacteria such as copper are added into the glaze or coatings [2].

The method used for each surface depends on its application. For instance, because Titania coatings are activated at the emission of sunlight they are suitable for outdoor surfaces. Also, it is recommended to avoid using Fluoropolymer coatings in food contact applications due to their harmful effects on human's body. In contrast for hard porcelain surfaces silica coatings are preferable because of their low annealing temperature, health safety properties, and ease of operation.

One of the most popular methods of synthesizing nano coatings is the sol-gel process that can be controlled by several factors. In this method gels are prepared under a range of conditions in which the rate of hydrolysis reaction varies from fast to slow with respect to the rate of condensation. When hydrolysis is fast, larger and more highly condensed polymers are formed during gelation. Conversely, for slow hydrolysis, smaller and less condensed polymers are formed. These gels dried to low density coarse textured and high density fine textured gels respectively. High temperatures (>800°C) are required to condence the coarse gels by viscous sintering. Lower temperatures are sufficient to condence fine gels by a process which was postulated to consist of polymer relaxation followed by condensation and pore collapse [4]. Pope and Mackenzie investigated the effect of catalyst on the chemistry of the process [1] and Milea and Bogatu focused on the precursor's types, PH, catalyst and temperature [3]. But the effect of process parameters on water contact angle is the area that was not studied yet.There are also different methods of applying the coating on the surface including: spin coating, dip coating, spray coating etc. The film properties depend on the method of applying film on the surface and parameters that are important in each method. One of the most important factors affecting film properties in spin coating is the spin speed due to its effects on coating thickness and uniformity.

The goal of this study is to construct an easy-to-clean silica surface by the aim of sol-gel technique and benefiting of spin coating method in order to achieve a uniform coating on the surface and identifying the effective parameters on water contact angle(CA) by the use of design of experiment (DOE) method.

II. Material and Methods

The chemicals used for the preparation of nano coating were Methyltrimethoxysilane(MTMS, 246174 Sigma–Aldrich Chemie,Germany), Methanol, Ammonium Fluoride,

[1]Ali. Arastehnodeh is with the Department of Chemical engineering, Quchan branch, Islamic Azad University, Quchan, Iran (corresponding author's phone: 00989153164051 ; e-mail: aliarastehnodeh@iauq.ac.ir).

[2]Solmaz. Boroomandi is with the Department of Chemical engineering, Quchan branch, Islamic Azad University, Quchan, Iran

Polymethyl-methacrylate (PMMA, 182230 Sigma–Aldrich Chemie,Germany), double distilled water and Toluene. All chemicals were used as received without further purification. The main sol was prepared by keeping the molar ratio of MTMS: Methanol constant at 1:5.63 and different amounts of water according to table I. the mixture was magnetically stirred to get homogenous solution and catalyst, which was the solution of NH4F in double distilled water, was added drop wise to the sol to increase the rate of gelation process. Then sols were coated on the circle ceramic pieces by means of a spin coating device with different spin speeds. Furthermore, in the half of the experiments the solution of PMMA in Toluene was added to the main sol in order to improve the hydrophobicity properties. Details of each experiment are demonstrated in tableI. All the pieces were annealed at 120c for 3 hours.

The hydrophobicity properties were measured by the water droplet contact angle. All the CAs Were measured by keeping 5µL water droplet on coated glaze at room temperature. The surface properties were studied by the Fourier transform infrared (FTIR), the surface morphology by scanning electron microscopy (SEM) and Transmission electron microscopic (TEM). Thermal gravimetric analysis was used to investigate the coating stability during temperature rise.

TABLE I
INFLUENCE OF EXPERIMENT CONDITIONS ON CA EFFECTIVE PARAMETERS ON CA

Run	polymer %	spin speed (rpm)	water/silane	Catalyst concentration(molar)	CA
1	0	290	0	1	65±1
2	0	290	0.028	0.5	77±2
3	1	290	0	1	56±1
4	0	290	0.028	0.5	108±1
5	1	490	0.028	0.5	92±2
6	1	490	0.028	1	84±0.2
7	1	490	0	0.5	80±1
8	1	490	0	1	65±1

III. RESULTS AND DISCUSSION

Figure1 depicts the CA of each experiment. By comparing figure 1 and table I it can be clearly seen that the highest water contact angle is related to the coatings with catalyst concentration of 0.5 molar and the proportion of water to silane equal to 0.028 with and without polymer in the sol.

According to table I the increase in all parameters except catalyst concentration leads to a rise in CA. The results can be explained in two ways one of which is the effects of parameters on the physical properties of the coating, which are a function of gelation time and the other is the effects of parameters on chemical properties of the coating. It was resulted from the experiments that by increase in gelation time the CA will increase too. By addition of catalyst the viscosity of the sol starts to increase and the Newtonian fluid turns to tixotropic fluid till gelation occurs and the liquid phase turns into solid phase [4]. Therefore, in equal time past from the addition of catalyst sols with lower gelation time are more viscous. Additionally, the more viscous the sol becomes while coating, the less uniform the film would be. CA of water on the coated surface will go down by the decrease in coating uniformity.

A. Catalyst Concentration :

As it is shown in figure 2 the increase in catalyst concentration leads to decrease in gelation time. This means that in equal periods of time past after mixing sol and catalyst, sols with higher amount of catalyst concentration experience higher percentage of completion of hydrolysis and at the same time polymerization reaction. Consequently the viscosity of the sols with higher amount of catalyst concentration is greater while coating and thus the uniformity of the film decreases. Figures 3 and 4 show the influence of Fluoride catalyst on the mechanism of the hydrolysis and polymerization reactions.

In figure 3, the increment in the rate of hydrolysis reaction due to the increase in catalyst concentration is exhibited. In this step, an unstable compound is formed during the interaction between fluorine anions and MTMS molecules named pentcovalent activated intermediate. A partially fluorinated silicon alkoxide is then formed by the rapid decomposition of this complex in the presence of H3O+, the byproducts of this reaction are water and alcohol. The presence of water in the reaction environment leads to form another pentacovalent complex that decomposes into a partially hydrated silicon alkoxide and regenerated fluorine and hydronium. This reaction will continue till almost all of the ethoxide bonds are replaced by OH group. The polymerization reaction starts before the hydrolysis completed.

Additionally, catalyst concentration affects the rate of polymerization reaction according to the mechanism presented in figure4. According to this mechanism it is occurred due to the fluorine anions have relatively smaller radius than hydroxyl groups that performs the same function of temporarily increasing the coordination of silicon.[5]

B. Water to Silane Molar Ratio:

As it was mentioned before, the effect of the water to silane molar ratio on the wettability of the coating can be explained by its impact on gelation time. Based on the figure 5 by increasing water to silane molar ratio from 0 to 0.028 the gelation time goes to higher than 200 seconds from its initial value at 180 seconds. This is due to the dilution of the system, which means that in the same amount of silane by the addition of water sol gets more dilute, therefore the distance between ions increases and as a result the reaction rate decreases. Consequently the coated film becomes less uniform and the water CA with the surface will decrease.

C. Spin Speed:

Spin speed affects the film thickness according to equation1 [48].

h = Aη0.45ω-0.62 (1)

h= film thickness in Angstrom

η= viscosity in cP

ω= spin speed in rpm

This equation shows that more spin speed will lead to a thinner film formation on the surface. On the other hand, the film will be formed more uniformly on the surface and this will lead to the increment of the CA.

D. Polymer Percentage:

Another important parameter is the amount of polymer added to the sol. Figure 6 shows the Fourier transform infrared (FTIR) spectra prepared from coating with and without PMMA. According to this figure, by addition of polymer in the sol, the functional hydrophobic groups of Si-CH3 in the final film will increase. In details, the peaks appeared in the range of 450-4000

cm-1 indicating the presence of methyl groups in the sample. The characteristic absorption peaks were observed at 946 cm-1 demonstrates Si-O-Si bond. The board absorption presented at 2958 and 1732 cm-1 are due to stretching and bending modes of C-H bond and peaks at 946 and 1100 cm-1 indicate Si-C bonds. The absorption peak at 3435cm−1 are corresponding to the polar OH bonds, the residual Si–OH groups are the main source of hydrophobic character of the coating.

In the spectrum of the sample without PMMA, the intensity of the absorption peaks of Si-C and C-H bonds are less than peaks observed in the sample with 1% of PMMA. It confirms the less number of Si-CH3 groups in coating without polymer.

As it was mentioned before, the highest water CA with the surface are obtained with water to silane molar ratio equal to 0.028 and catalyst concentration equal to 0.5 molar with and without polymeric solution. Figures 7 and 8 show the scanning electron microscopy (SEM) images of these two films. The figures demonstrate that a uniform structure of silica particles is formed and the aggregation between spheres is not apparent. Also by comparing the two figures it will reveal that with increasing PMMA, the uniformity of the film will increase while the size of particles will reduce.

In figure 9 the Transmission electron microscopy (TEM) of the coating with water/silane = 0.028, catalyst concentration=0.5 molar with 1 percent of polymer is demonstrated. According to this figure a nanostructure of particles with the size of less than 5 nano meters has been formed which can be the main cause of the hydrophobicity property.

One of the most important properties of coatings are their stability during increasing in temperature. Figure 10 depicts the TGA and DTG results of the coating with water to silane molar ratio equal to 0.028 and catalyst concentration equal to 0.5 molar with 1 percent polymeric solution. This figure shows a decrease of 5.42 percent in weight till 100□c, which is related to the evaporation of water molecules has been kept in gel structure. The second step at about 400°C is a result of radical transfer to unsaturated chain ends and is about 4.756 weight percent. It can be clearly seen from the figure that in 1000□c just about 10 percent of the film loss and this means that the coating is highly thermally stable.

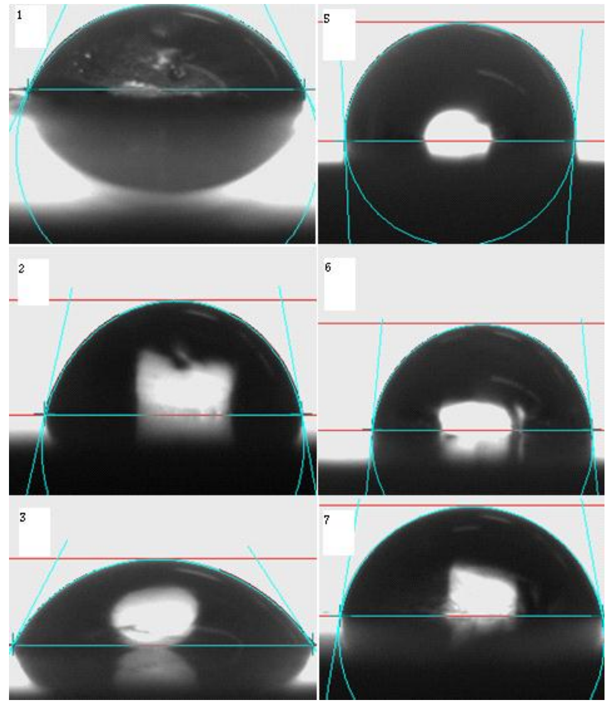

Fig. 1 Tthe water CA with the surface coatings. The numbers on the graphs related to the run number

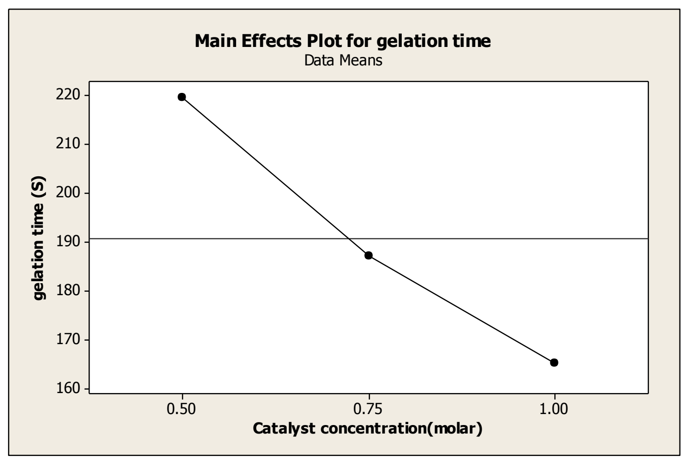

Fig. 2 The relation between gelation time and catalyst concentration

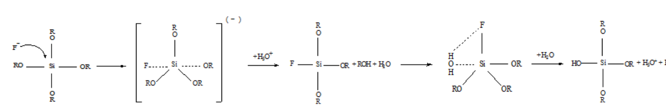

Fig. 3 Mechanism of fluorine catalyzed hydrolysis

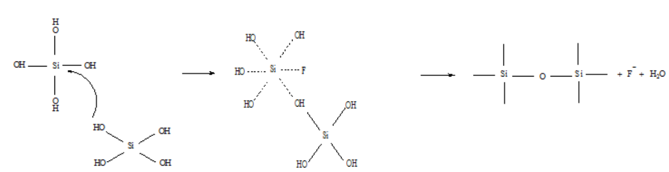

Fig. 4 Mechanism of fluorine catalyzed polymerization

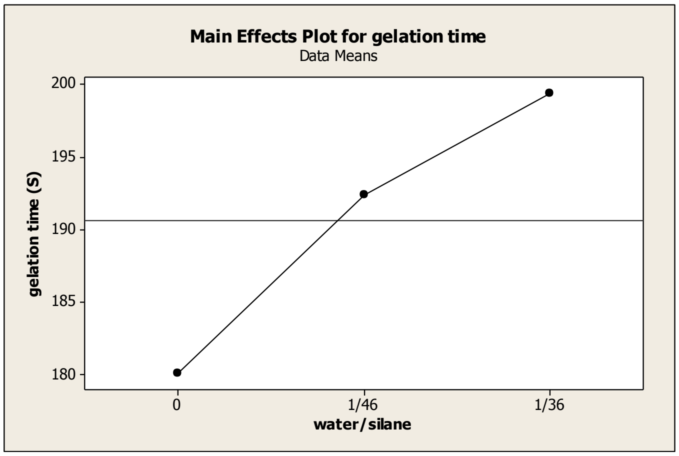

Fig. 5 The relation between gelation time and the molar ration of water to silan

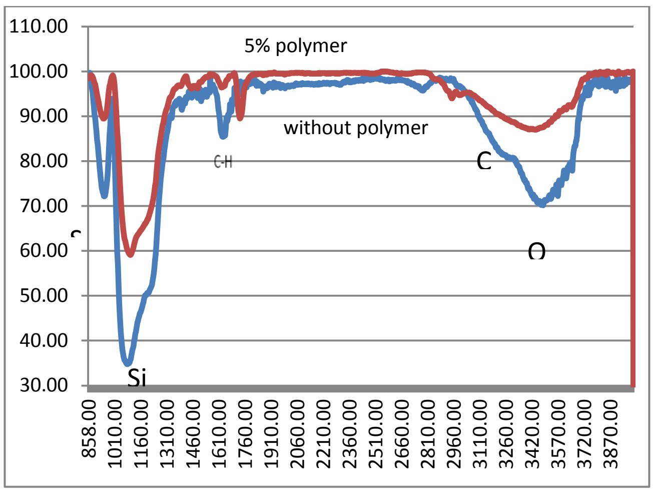

Fig. 6 The FTIR spectras of silica coating with and without polymer

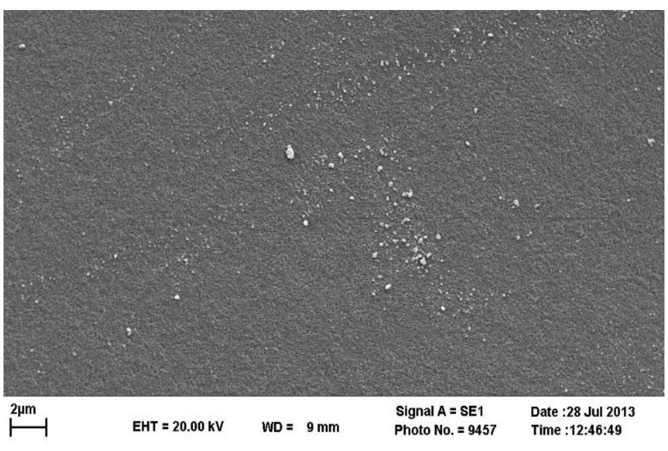

Fig 7 Scanning electron microscopy (SEM) spectra's of the silica coating with water/silane = 0.028, catalyst concentration=0.5 molar without polymer

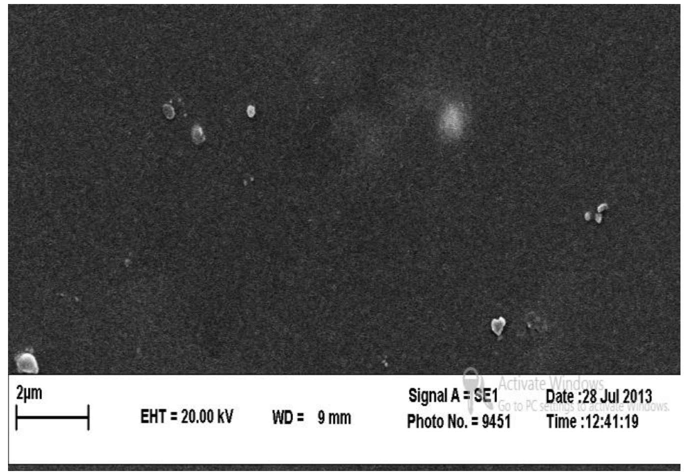

Fig. 7 Scanning electron microscopy (SEM) spectra's of the silica coating with water/silane = 0.028, catalyst concentration=0.5 molar with 1 percent of polymer

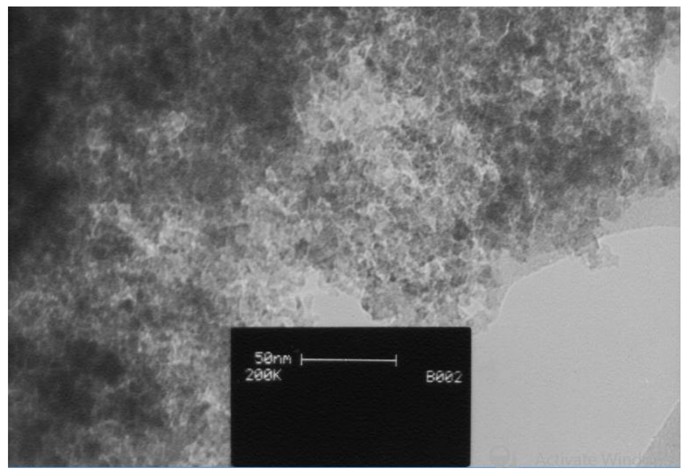

Fig. 8 The Transmission electron microscopic (TEM) of the coating with water/silane = 0.028, catalyst concentration=0.5 molar with 1 percent of polymer

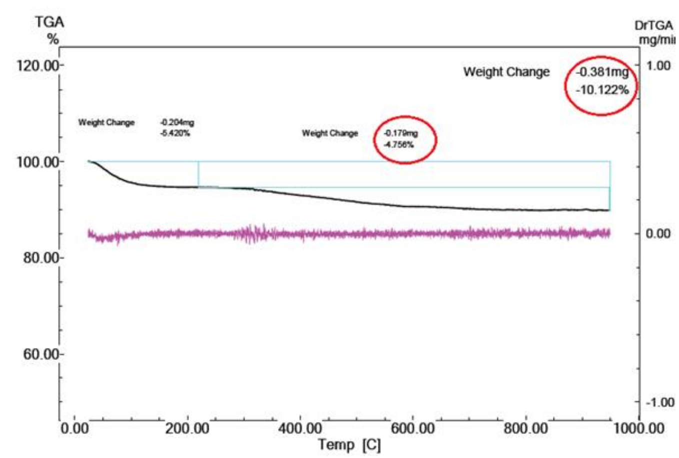

Fig. 9 Depicts the thermal gravimetric result of the coating with water to silane molar ratio equal 0.028 and catalyst concentration equal 0.5 molar with 1 percent polymeric solution

IV. Conclusion

Eight hydrophobic coatings of silica nano particles were synthesized by a one-step sol-gel process with MTMS, methanol and water in the presence and absence of PMMA and corresponding parameters on CA were investigated by FFD method in Minitab.

The more statistically effective parameters on CA are catalyst concentration, polymer concantration, the proportion of water to silane and spin speed that all of them have direct relationship with CA except the first one due to its Sevier effect on film uniformity.

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