EFFECTS OF SOL-GEL PROCESSING FACTORS ON TRANSMITTANCE AND SURFACE FREE ENERGY OF TEOS-SIO_2-PDMS FILMS

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Abstract

Hydrophobic film coatings on ceramic surfaces have been widely studied for decades. Many hydrophobic films have been synthesized but only a few of them have high transmittance and low surface energy. This research investigated the sol-gel processing factors that affect the transmittance and surface free energy of hydrophobic films. In this study, films were made of TEOS (tetraethyl orthosilicate), nano-particle size silica and PDMS (poly-dimethylsiloxane). The amount of silica (0.5, 5, and 10 wt%), the size of the silica (12 and 20 nm), and the heat treatment temperature (300 and 400°C were varied as independent factors. Transmittance and surface free energy were observed to be dependent factors. Design-Expert® software was used to design and analyze the experiments. The results showed that the transmittance and surface free energy decreased significantly as the amount of silica was increased.The lowest transmittance value (62%) and surface free energy (3 mN/m) were observed when using a silica size of 20 nm at 10wt%with heat treatment at 300°C. The highest value of the transmittance (90%) was obtained when using a silica size of 12 or 20 nm at 0.5wt%and heat treatment at 300°C.

Keyword: Transmittance, surface free energy, statistical analysis

Introduction

Hydrophobic films are ones that tend to repel water. When water droplets impinge on these surfaces, the liquid droplets and film surface join with a contact angle that is greater than 90o. Surfaces coated with hydrophobic films tend not to become wet. There are many applications, especially for self-cleaning films. Sol-gel processes have been successfully used to fabricate hydrophobic films from poly-dimethylsiloxane (PDMS), tetraethyl orthosilicate (TEOS) and silica nano-particles. PDMS is typically used as the hydrophobic constituent because it can give optical transparency and low surface energy (Kamitani

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and Teranishi, 2003; Jones *et al*. 2004; Ma and Hill, 2006; Nimittrakoolchai and Sitthisuntorn, 2010). TEOS is added as a cross-linker agent to bind the particulate material. It also creates a crater-like roughness (Huang and Chou, 2003; Wu *et al*., 2005). In addition, silica nano-particles function to increase the solid content of the coating. This results in rough surfaces with a lotus leaf-like structure (Wu *et al*., 2005). Studies show that the hydrophobic property depends not only on the composition, but also is influenced by the processing parameters such as the heat treatment temperature (Shindou *et al*., 2004). In this study, the uses of hydrophobic films will be examined. Generally, hydrophobic films must have a low surface free energy. Surface free energy is correlated to the contact angle according to Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \qquad (1)$$

where θ is the measured contact angle and γ is the surface energy of the solid–vapor (sv), solid–liquid (sl), and liquid–vapor (lv) interface. The low surface free energy value of the sample is caused by the much different surface energy values of the solid and the liquid. This causes liquids to repel and a droplet formation indicated by high contact angles (Nakajima *et al*., 2001; Nadargi *et al*., 2010). In general, hydrophobic films have a high surface roughness in order to produce a phenomenon known as the lotus effect (Ma and Hill, 2006; Zheng *et al*., 2012). However, a high surface roughness can cause a problem for hydrophobic films because the higher surface roughness film tends to have less ability to transmit light (Nakajima *et al*., 2000). The result is that the appearance of materials covered by hydrophobic films will be changed (Hwang *et al*., 2008). This effect is considered to be negative.

The objective of this research was to examine the effect of the processing parameters and their interactions on the response properties of TEOS-SiO_2-PDMS films. This was done using statistical software to design the experiment and analyze the data. The silica amount (A), heat treatment temperature (B), and silica particle size (C) were varied as independent variables. Transmittance (y1) and surface free energy (y2) were measured and analyzed as response properties or dependent variables.

Experimental Design

Statistical Experiment

The factorial design in Design-Expert® Version 8.0.1. software (Stat-Ease, Minneapolis, MN, USA) was used in this study. Three levels of silica (0.5, 5, and 10 wt%), 2 levels of silica particle size (12 and 20 nm), and 2 levels of heat treatment temperatures (300 and 400°C) were varied. Therefore, this experiment contains 3×2×2 or 12 treatment combinations. Two replicates were tested for each treatment combination. As seen in Table 1, 24 observations were made. Data were analyzed using analysis of variance (ANOVA). Models were generated by regression analysis. Graphs of transmittance and surface free energy as a function of silica content and heat treatment temperature were plotted.

Preparation of TEOS-SiO_2-PDMS Films

The films were prepared from 98% TEOS (Acros Organics), Silica nano-particles (Aerosil®200 (12 nm) and Aerosil®90 (20 nm)) and PDMS (Acros Organics). The sol-gel process was the method described by Jones *et al*. (2004). First, 5 g of TEOS, 2.5 g of ethanol, and 6 ml of 0.1M HCl were stirred and refluxed at 80ºC for 4-5 h to form a silica gel. Then 2.75 g of PDMS and 40 g of isopropanol were added to the above mixture. After that, 0.5, 5, or 10 wt% of either 12 or 20 nm silica particles was added to the gel. Resulting gels were ultrasonically mixed for 30 min, refluxed at 80ºC for 5-6 h, and aged for 15 h to become modified gels ready to coat onto glass microscope slides. Before coating, using the methodology of Nimittrakoolchai *et at*. (2010), the microscope glass slide substrates were washed with ethanol, acetone, and de-ionized water, respectively, and then dried at 60ºC. The modified gel was coated

Table 1. Effects of the silica amount, heat treatment temperatures, and silica particle size on the transmittance and surface free energy of all observation films

Std	Run	Factor 1	Factor 2	Factor 3	Response 1	Response 2
		A:silica amount (%)	B:heat treatment temperature (ºC)	C:silica particle size (nm)	Transmittance (%)	surface free energy (mN/m)
1	13	0.5	300	12	90	16
2	4	0.5	300	12	85	18
3	1	5	300	12	86	13
4	3	5	300	12	85	13
5	21	10	300	12	73	4
6	23	10	300	12	65	10
7	14	0.5	400	12	85	10
8	16	0.5	400	12	81	10
9	11	5	400	12	82	11
10	18	5	400	12	78	6
11	5	10	400	12	79	6
12	19	10	400	12	67	5
13	10	0.5	300	20	88	15
14	2	0.5	300	20	90	17
15	6	5	300	20	85	16
16	24	5	300	20	79	13
17	17	10	300	20	62	3
18	20	10	300	20	62	11
19	9	0.5	400	20	89	10
20	22	0.5	400	20	86	8
21	7	5	400	20	75	8
22	12	5	400	20	76	8
23	8	10	400	20	65	4
24	15	10	400	20	71	4

onto the cleaned glass slide substrates using a spin coating method at 1500 rpm for 10 s. Finally, the coated glass slide substrates were dried at room temperature and heat treated at 300 or 400ºC. A heating and cooling rate of 5ºC/min and a soaking time for 60 min was used.

Measurement

Transmittance was measured using a UV-VIS Spectrophotometer (Cary 1E). Data was averaged over the visible light range (400-700 nm wavelength).

Surface free energy was measured by determining the contact angle (Data Physics OCA20). The static contact angles of the water, ethlylene glycol, and diethylene glycol were measured to determine the surface free energy. The surface free energy calculation was done using the Owens-Wendt-Rabel and Kaelble (OWRK) analysis method (Data Physics Instruments GmbH, 2013).

Results and Discussion

Before coating with TEOS-SiO_2-PDMS, the glass slide substrates had a transmittance of 93%. After coating with these films, their transmittance decreased. Table 1 gives the transmittance values of the glass slides after they were coated with TEOS-SiO_2-PDMS films under various treatment conditions.

It is seen in Table 1 that the maximum transmittance of all observations is 90% while the minimum transmittance is 62%. Figures 1 and 2 display the transmittance of the coated glass slides as a function of the amount of silica (12 and 20 nm) and heat treatment temperature. The transmittance decreased with the increasing silica content (A). However it is unclear how the transmittance varied with the heat treatment temperature (B), silica particle size (C), and the interactions between these parameters.

The ANOVA in the Design-Expert® software was employed to analyze the data in Table 1 And the results are shown in Table 2. It is obvious that the silica amount (A) and interaction between the silica amount and silica particle size (AC) have significant effects (at more than 95% confidence) on transmittance because their p-values are less than 0.05. Conversely, the heat treatment temperature (B), silica particle size (C), and their interaction (BC) show no significant

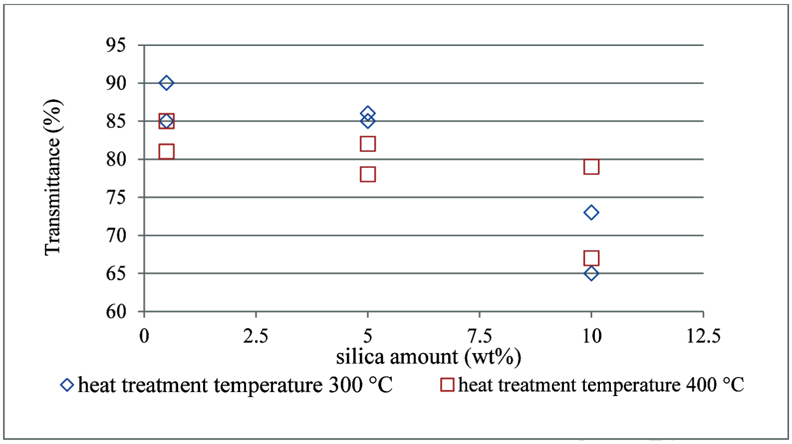

Figure 1. Transmittance of TEOS-SiO_2-PDMS films prepared with a silica particle size of 12 nm at 0.5, 5, and 10 wt% and heat treatment temperature of 300 and 400ºC

effects on transmittance because their p-values are larger than 0.10.Additionally, the interaction between variables (AB) affects the transparency of the film with less than 95% confidence because its p-value is between 0.05-0.10. Regression analysis in the Design-Expert® software was employed to fit a model to find the relationship between transmittance and the independent variables, silica level, and heat treatment temperature. The fitted equation was found to be:

$$\text{Transmittance (\%)} = 104.08 - 3.14 \times \text{silica amount} - 0.06 \times \text{heat treatment temperature} + 0.31 \times \text{silica particle size} + 8.67 \times 10^{-3} \times \text{silica amount} \times \text{heat treatment temperature} - 0.12 \times \text{silica amount} \times \text{silica particle size}$$

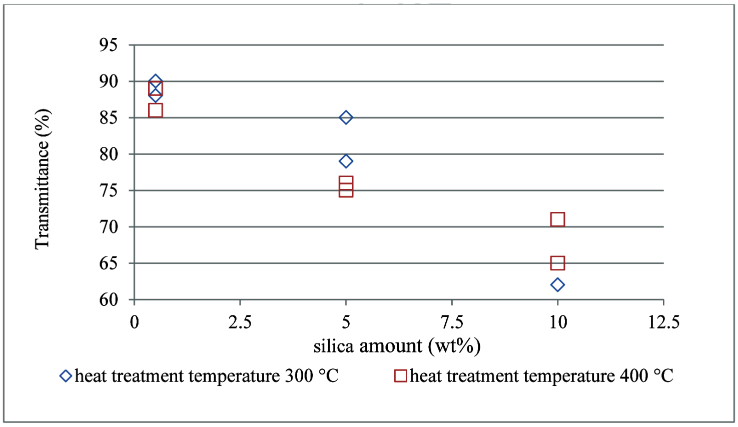

Figure 2. Transmittance of TEOS-SiO_2-PDMS films prepared with a silica particle size of 20 nm at 0.5, 5, and 10 wt% and heat treatment temperature of 300 and 400°C

Table 2. ANOVA of the transmittance for the Response Surface Reduced Quadratic Model. (Partial sum of squares - Type III)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1616.04	6	269.34	15.47	< 0.0001	significant
A-silica amount	1422.76	1	1422.76	81.72	< 0.0001	
B-heat treatment temperature	9.54	1	9.54	0.55	0.4693	
C-silica particle size	34.87	1	34.87	2.00	0.1750	
AB	67.93	1	67.93	3.90	0.0647	
AC	79.36	1	79.36	4.56	0.0476	
BC	2.67	1	2.67	0.15	0.7004	
Residual	295.96	17	17.41			
Lack of Fit	119.96	5	23.99	1.64	0.2244	not significant
Pure Error	176.00	12	14.67			
Cor Total	1912.00	23				

This equation was used to predict transmittance as a function of the silica amount, heat treatment temperature, and silica particle size over the experimental range. The three dimensional (3D) response surface and contour plots showing the relationship between the predicted transmittance, silica amount, and heat treatment temperature were made. They are shown in Figures 3 and 4. It can be seen that transmittance significantly decreases as the silica content increases. However, little difference is seen with the heat treatment temperature.

ANOVA is based on several assumptions. In order to verify these assumptions, normal probability plots and residuals versus predicted

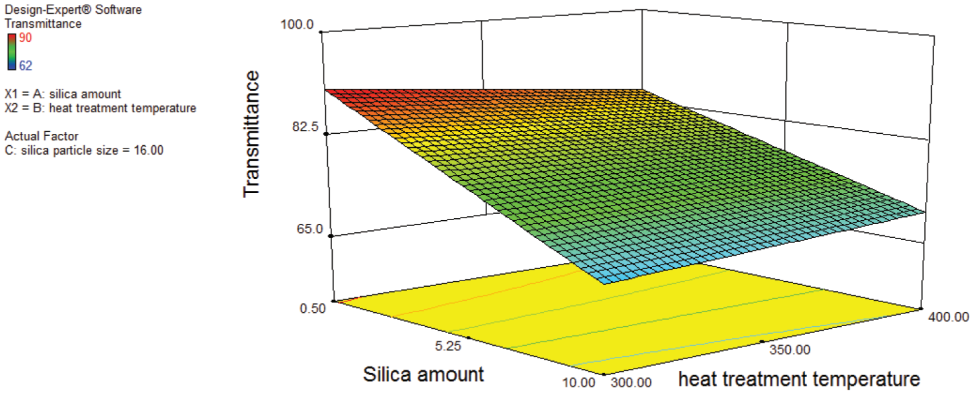

Figure 3. A 3D surface plot of the predicted transmittance as a function of the silica content and heat treatment temperature

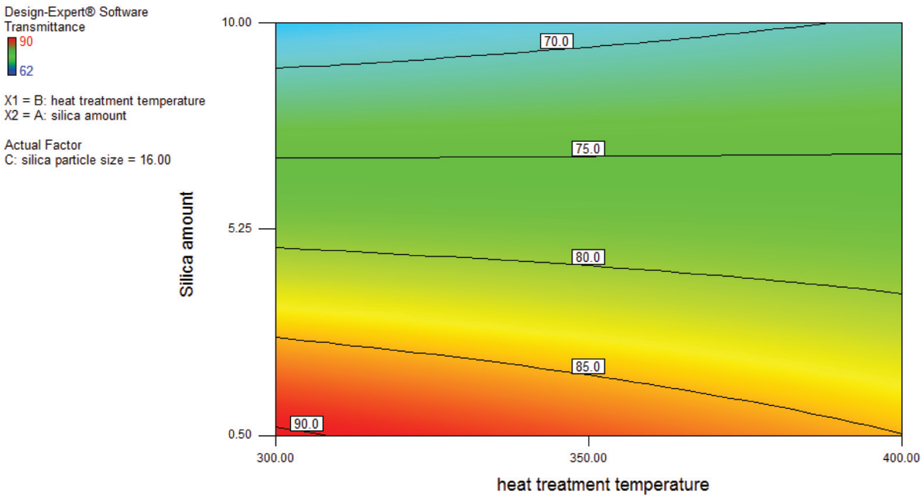

Figure 4. The contour plot of the predicted transmittance as a function of the silica amount and heat treatment temperature

transmittance graphs were made and are shown in Figures 5 and 6, respectively. The normal probability plot is the plot for checking the ANOVA assumption that the residual has a mean value equal to zero and is normally distributed.The residuals vesus predicted transmittance plot is to verify the ANOVA assumption of constant variance within the data. It can be seen that the normal probability plot does not deviate from a straight line. The residuals vesus predicted transmittance is structureless. Therefore both ANOVA assumptions were satisfied.

The surface free energy of all observations was 3-18 mN/m as shown in Figures 7 and 8. It can be seen that the surface free energy

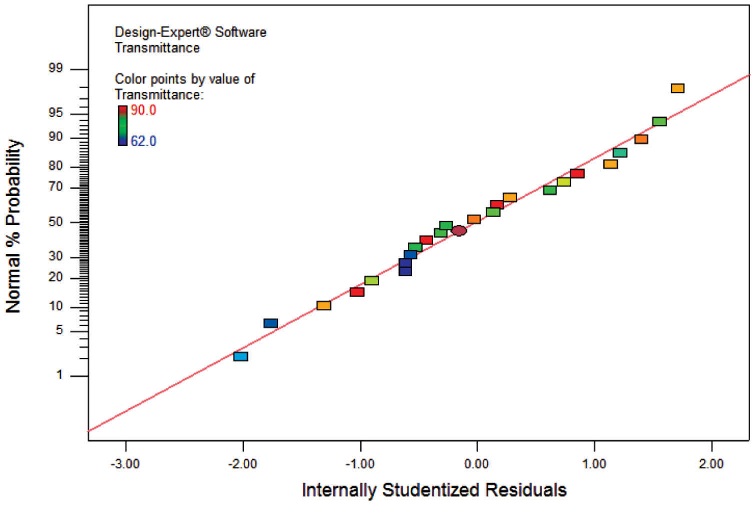

Figure 5. Normal probability plot of transmittance of TEOS-SiO_2-PDMS films

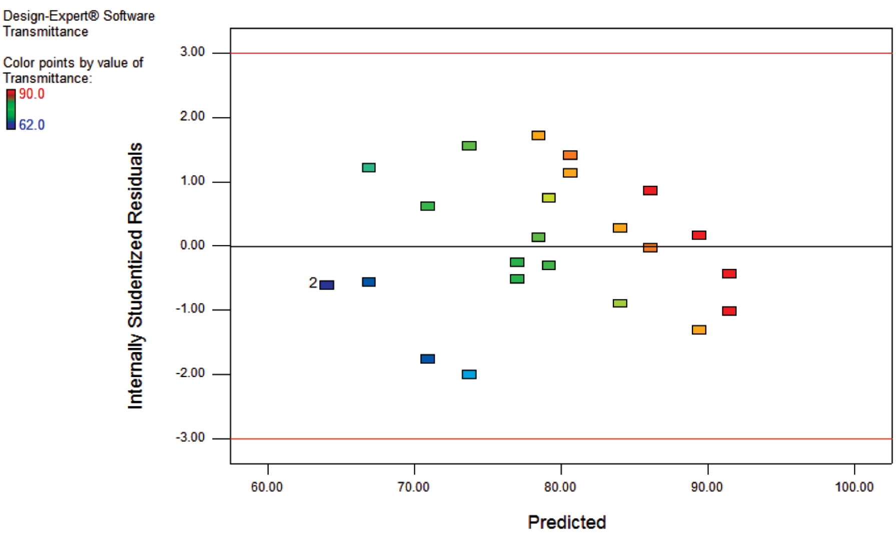

Figure 6. Plot of studentized residuals versus predicted transmittance

significantly decreases with the increasing heat treatment temperature and silica content. However, it is not clear how it changes with the silica particle size. Thus ANOVA in the Design-Expert® software was employed to analyze the surface free energy data of Table 1. As shown in Table 3, the results indicate that the silica amount (A), heat treatment temperature (B), and interaction between the silica amount and heat treatment temperature (AB) have important effects on the surface free energy. Concurrently, the silica particle size (C) and its interaction with either AC or BC have no significant effect on the surface

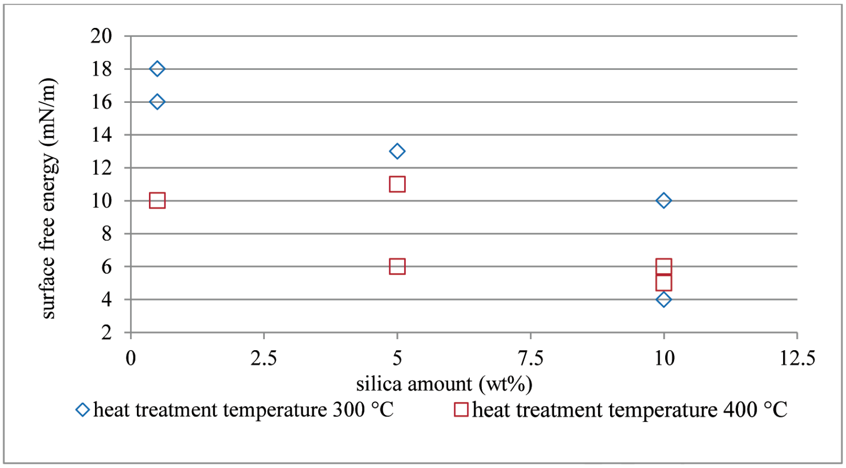

Figure 7. Surface free energy of TEOS-SiO$_2$- PDMS films prepared with silica particle size of 12 nm at 0.5, 5, and 10 wt% and heat treatment temperature at 300 and 400ºC, respectively

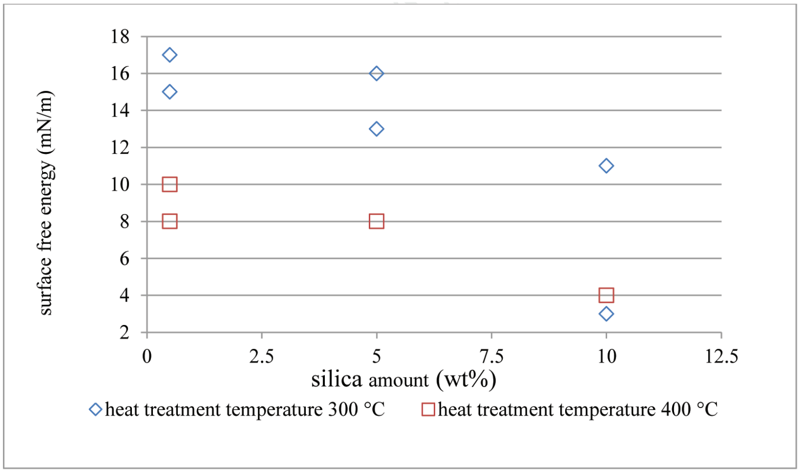

Figure 8. Surface free energy of TEOS-SiO$_2$- PDMS films prepared with silica particle size of 20 nm at 0.5, 5, and 10 wt% and heat treatment temperature at 300 and 400ºC, respectively

free energy. Regression analysis in the Design-Expert® software was employed to fit a model predicting the relationship between the transmittance and the independent variables, silica level, and treatment temperature. The fitted equation was found to be:

Surface free energy (mN/m)

$$= 40.16 - 2.51 \times \text{silica amount} - 0.08 \times \text{heat treatment temperature} + 5.03 \times 10^{-3} \times \text{silica amount} \times \text{heat treatment temperature}$$

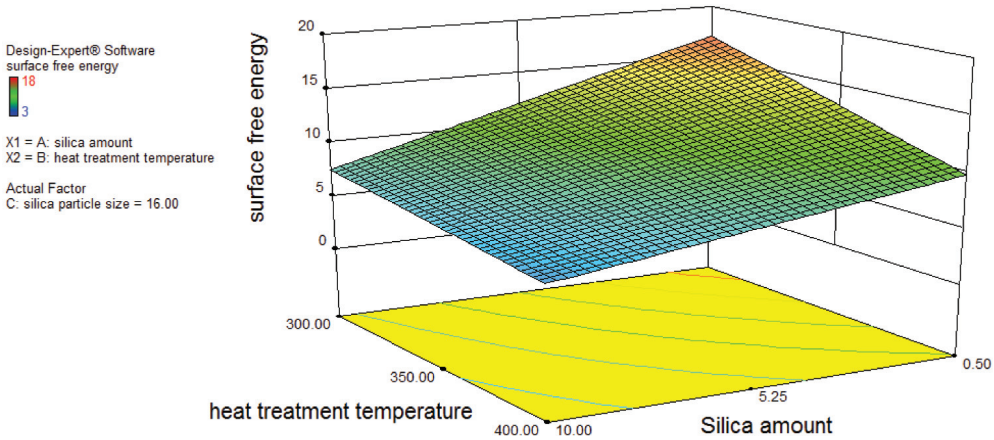

Figure 9. Surface free energy as a function of the silica level and heat treatment temperature

Table 3. ANOVA of the surface free energy for the Response Surface Reduced Quadratic Model. (Partial sum of squares - Type III)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	377.01	6	62.83	12.15	< 0.0001	significant
A-silica amount	206.01	1	206.01	39.82	< 0.0001	
B-heat treatment temperature	142.51	1	142.51	27.55	< 0.0001	
C-silica particle size	1.03	1	1.03	0.20	0.6607	
AB	22.83	1	22.83	4.41	0.0509	
AC	0.04	1	0.04	0.01	0.9304	
BC	2.04	1	2.04	0.39	0.5382	
Residual	87.95	17	5.17			
Lack of Fit	14.45	5	2.89	0.47	0.7904	not significant
Pure Error	73.50	12	6.13			
Cor Total	464.96	23				

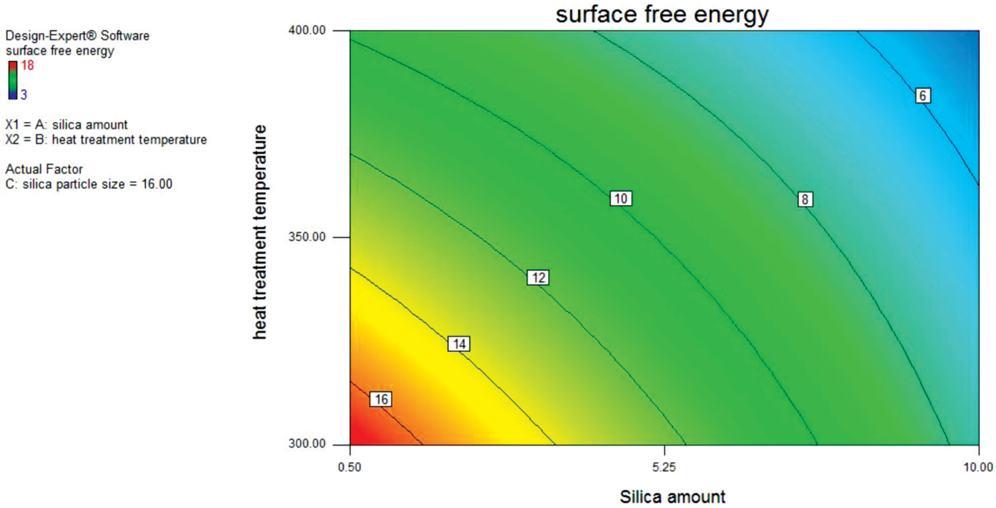

Figure 10. Contour plot of the predicted surface free energy as a function of silica amount and heat treatment temperature

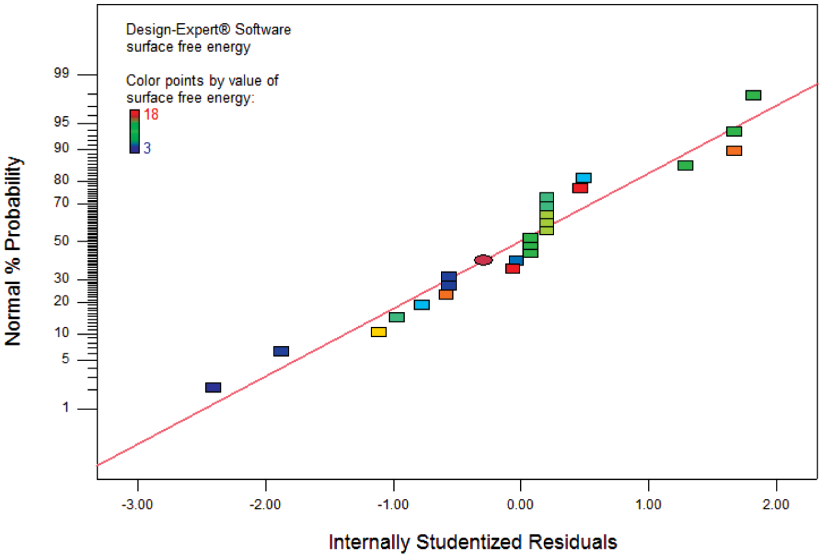

Figure 11. Normal probability plot of surface free energy of TEOS-SiO$_2$-PDMS films

The fitted equation was used to predict the surface free energy as a function of the silica amount, heat treatment temperature, and silica particle size over the range of experimental values. Next, the 3D response surface and contour plots were done. They show the relationship between the predicted surface free energy and the independent variables, silica amount, and heat treatment temperature. The plots are presented in Figures 9 and 10. It can be seen that the surface free energy significantly decreases with the increasing silica content. In order to verify the assumptions of the ANOVA, the normal probability plot and residuals versus the predicted surface free energy graphs were made and given as Figures 11 and 12, respectively. It can be seen that the normal probability plot does not deviate from a straight line and the residuals versus predicted surface free energy is structureless. Therefore both ANOVA assumptions are verified and the ANOVA results are reliable.

Conclusions

In this study, we examined the effects of the silica content (0.5, 5, and 10 wt%), heat treatment temperature (300 and 400ºC), and silica particle size (12 and 20 nm) on the transmittance and surface free energy of TEOS-SiO_2-PDMS film using statistical

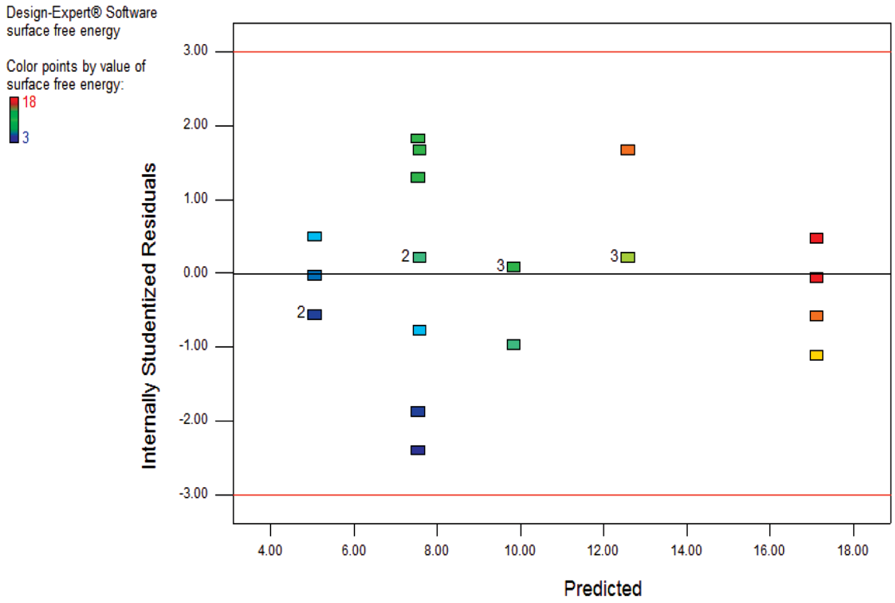

Figure 12. Plot of studentized residuals versus predicted surface free energy

analysis. It was found that the silica content and interaction between the silica content and silica particle size had significant effects on the transmittance of the films (95% confidence level). The interaction between the silica content and heat treatment temperature had no significant effect on film transmittance (95% confidence level). This work also confirmed that the silica content, heat treatment temperature, and interaction between the silica amount and heat treatment temperature had significant effects on the surface free energy of the films (95% confidence level). Finally, it was found that the film synthesized using 0.5 wt% of 12 or 20 nm particle size silica heat treated at 300ºC had the highest transmittance. The lowest surface free energy (3mN/m) film can be obtained when using 10 wt% of 20 nm silica and heat treating the film at 300ºC.

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