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Original Article

Statistical analysis parameters effect on contact angle of TEOS-SiO_2-PDMS films prepared by sol-gel process

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Abstract

This work investigated the effects of levels of silica content, silica nano-particle size and heat treatment temperature on the contact angle of TEOS-SiO_2-PDMS films. Design-Expert® software was used to design the experiments and analyze experimental results. The results indicate that both silica amount and heat treatment have significant effects on the contact angle of TEOS-SiO_2-PMDS films, while silica particle size and interactions between factors have no important effect.

Keywords: hydrophobic, contact angle, statistical analysis, PDMS, TEOS

1. Introduction

Hydrophobic films are currently a topic of great interest. Many types of materials and various methods have been developed to synthesize hydrophobic films (Minglin and Randal, 2006). 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 and Teranishi, 2003; Ashley and Norman, 2004; Minglin and Randal, 2006; On-uma and Sitthisuntorn, 2010). TEOS is added as cross-linker agent to bind the particulate material. It also creates 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 composition, but is also influenced by the processing parameters, such as a heat treatment temperature (Shindou *et al*., 2004).

As discussed by Montgomery (2005), experimental design and statistical methods are useful in many applications. The general factorial design is efficient for an experiment involving the study of the effect of two or more variables. Analysis of variance (ANOVA) is a statistical method that makes simultaneous comparisons between two or more means. ANOVA in factorial design determines not only the effect of independent variable (x_i) on dependent variables or response (y_i) but also interprets the interaction between independent variables. Moreover, regression analysis in factorial design data enables us to generate the model to predict the dependent variables and plot the response surface or cube plot between a predicted response in the dependent variable plane over the range of experimental conditions (Rocak *et al*., 2002; Douglas, 2005).

The objective of this research was to examine the effect of processing parameters and their interactions on response property of TEOS-SiO_2-PDMS films by 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

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while contact angle (y_1) was measured and analyzed as a response property or dependent variable.

2. Experiment

2.1 Statistical experiment

Factorial design in the Design-Expert® Version 8.0.1 software (Stat-Ease, Minneapolis, MN USA) was used in this study. Three levels of silica amount (0.5, 5, and 10 wt-%), two levels of silica particle size (12 and 20 nm), and two levels of heat treatment temperatures (300 and 400ºC) were varied. Therefore, this experiment contains 3×2×2 or 12 treatment combinations. Two replicates were tested on each treatment combination. As a result, 24 observations were made. This is shown in Table 1. Data were analyzed by ANOVA. Models were generated by regression analysis and graphs of contact angle as a function of silica amount and heat treatment temperature were plotted.

2.2 Preparation of TEOS-SiO_2-PDMS films

The films were prepared from 98% TEOS (Acros Organics), silica nano-particles (Aerosil®200 (12nm) and Aerosil®90 (20nm)) and PDMS (Acros Organics). The sol-gel process followed the method of Ashley and Norman (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 hrs to form a silica gel. Then 2.75 g of PDMS and 40 g of iso-propanol were added to the above mixture. After that, 0.5, 5 or 10 wt–% of either 12- or 20- nm silica particle was added into the gel. Resulting gels were ultrasonically mixed for 30 min, refluxed at 80ºC for 5-6 hrs and aged for 15 hrs to become modified gel ready to coat on microscope slides. Before coating, as described by On-uma and Sitthisuntorn (2010) the microscope glass slide substrates were washed with cleaning agents (ethanol, acetone and de-ionized water, respectively) and then dried at 60ºC. The modified gel was coated on the cleaned glass slide substrates by spin coating at 1,500 rpm for 10 s. Finally, the coated glass slide substrates were dried at room temperature and heat treated at 300 or 400ºC with a heating and cooling rate of 5ºC /min and soaking time of 60 min.

2.3 Contact angle measurement

Static contact angle measurements were performed by using the sessile drop method with optical contact measuring apparatus. Data was taken using a DataPhysics OCA20 instrument (Particle & Surface Sciences Pty Ltd). The resulting static contact angle was the mean of three 5-µL water

Table 1. Effects of the silica amount, heat treatment temperatures, and silica particle size on the contact angle of all observation films.

Observation	Silica amount (wt–%)	Heat treatment temperature (°C)	Silica particle size (nm)	Contact angle (degree)
1	0.5	300	12	106
2	0.5	300	12	106
3	5	300	12	111
4	5	300	12	109
5	10	300	12	132
6	10	300	12	118
7	0.5	400	12	114
8	0.5	400	12	108
9	5	400	12	117
10	5	400	12	123
11	10	400	12	143
12	10	400	12	135
13	0.5	300	20	108
14	0.5	300	20	106
15	5	300	20	110
16	5	300	20	113
17	10	300	20	143
18	10	300	20	117
19	0.5	400	20	111
20	0.5	400	20	115
21	5	400	20	121
22	5	400	20	126
23	10	400	20	152
24	10	400	20	143

droplets measurements.

2.4 Surface topography

Surface topography was imaged by non-contact mode by atomic force microscopy (AFM, XE-70 Park System). Surface roughness was measured by AFM and calculated surface roughness average (R_a) values from AFM image analysis.

3. Results and Discussion

Table 1 illustrates the response property (contact angle) as a function of independent variables (silica amount, heat treatment temperature, and silica particle size). It shows that the contact angles of all observations are more than 90° and the maximum contact angle is 152°. All films fabricated in this experiment have hydrophobic properties because all films have contact angle more than 90°. Figure 1a-c display the water droplet shapes in observation numbers 19, 17, and 23 of which their contact angles are 111°, 143°, and 152°, respectively. ANOVA in Design-Expert® software was employed to analyze the data in Table 1. Results are shown in Table 2. It is clear that the silica amount (A) and heat treatment temperature (B) have significant effects on contact angle because their p-values are less than 0.05. On the other hand silica particle size (C) and interaction between variables (AB, AC, and BC) have no significant effects on contact angle because their p-values are larger than 0.10. Regression analysis in the Design-Expert® software was employed to fit a model to find the relation between contact angle and the independent variables, silica level, and treatment temperature. The fitted equation was found to be:

$$\text{Contact angle} = 68.36 + (2.77 \times \text{silica amount}) + (0.11 \times \text{heat treatment temperature}) \quad (1)$$

The fitted equation was used to calculate the predicted contact angle as a function of silica amount in the range of 12-20 nm and heat treatment temperature in the range of 300-400ºC. After that the response surface plot, which shows the relationship between the contact angle and silica amount and heat treatment temperature was plotted as shown in Figure 2. It can be seen that the contact angle increases with an increase of the heat treatment temperature. This is not consistent with earlier studies (Shindou *et al.*, 2003; On-uma and Sitthisuntorn, 2010;). These studies found that PDMS-based hybrids tend to thermally degrade when heated above 300ºC. However, in our study, the film can withstand up to 400ºC with an increasing value of contact angle. It is seen in Figure 2 that contact angle increases with the increase of silica amount. The results of adding nano-particle silica show the concurrent increase in the film roughness and consequently create a lotus leaf effect. This is confirmed by AFM images. Figure 3a-c display 2D and 3D AFM topographical images for films of observation numbers 8, 10, and 12. It is

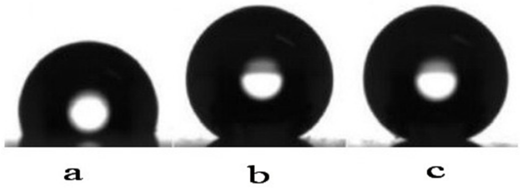

Figure 1. Water droplet shapes on observation number 19 (a), 17 (b) and 23(c).

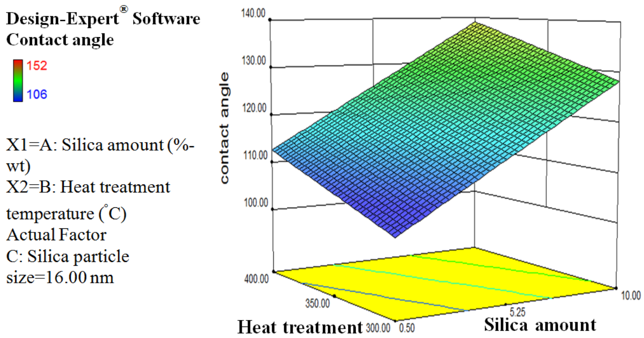

Figure 2. Contact angles as a function of the silica level and heat treatment temperature.

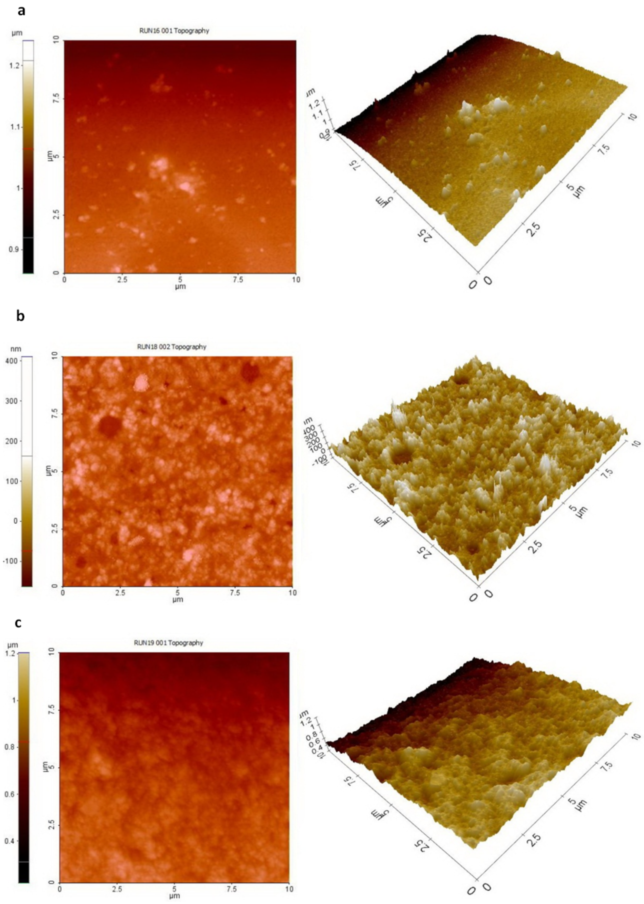

Figure 3. 2D and 3D AFM topographical images of TEOS-SiO_2-PDMS films on observation numbers 8(a), 10(b) and 12 (c) which contain SiO_2 0.5, 5, and 10 wt–%, respectively.

clear that the average surface roughness of the film is increased from 8.00 to 38.53 and 166.00 nm as silica amount is increased from 0.5 to 5 and 10 wt–%, respectively. It is consistent with the results of other studies such as Jeong *et al*. (2000), Nakajiam *et al*. (2000), Nakajima *et al*. (2001), Janssen *et al*. (2006), Su *et al*. (2006) and Hwang *et al*. (2008).

ANOVA is based on two important assumptions. The first assumption is the residuals are normally and independently distribute. The second assumption is that residuals are unrelated to other variables. To check if the first assumption is valid, the log normal probability of residuals is plotted as shown in Figure 4. It can be seen that all points in the plot are close to have linear relationship, therefore it can be concluded that the first assumption is not violated. A simple way to check the second assumption is to plot the residual versus predicted values as shown in Figure 5. It is clear from Figure 5 as the predicted values increase from 100° to 130° the residual range raises; however when the predicted value increase from 130° to 140° the residual range decrease, thus there is no obvious pattern in the residual versus predicted values. As a result the second assumption is met. In addition, it is clear from Figure 5 that all Studentized residuals are less than 3, therefore there is no outlier data in our experiment. Since, the important assumptions had been checked and it was found that there was very little deviation from the assumption we therefore were confident in the ANOVA analysis as shown in Table 2.

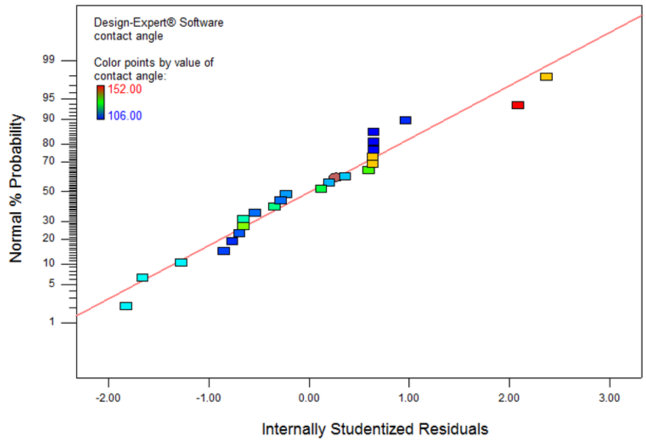

Figure 4. Normal probability plot of contact angle values.

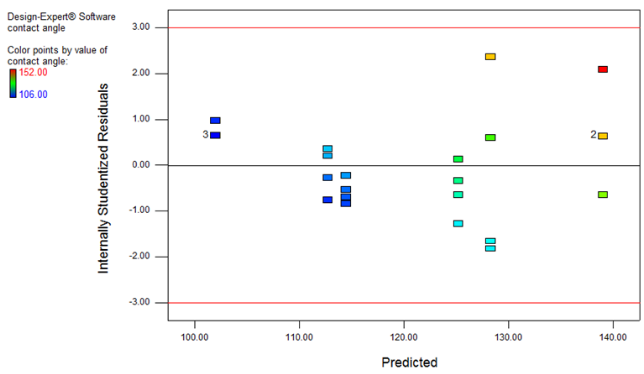

Figure 5. Plot of residuals versus predicted contact angles.

4. Conclusion

In this study, the effects of silica level, heat treatment temperature and silica particle size on contact angle of TEOS-SiO_2-PDMS films were investigated and statistical analyses performed. ANOVA analysis found that silica amount and heat treatment temperature had significant effects on contact angle of the films whereas the silica particle size and interactions between silica amount, heat treatment temperature and silica particle size had no significant effects on contact angle of the films. Finally, it was found that the film synthesized from the precursor consisting of 10 wt–% of 20- nm particles size silica and heat treated at 400 °C had the highest contact angles.

Table 2. ANOVA of the contact angle 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	3682.44	6	613.74	14.24	< 0.0001
A-silica level	2772.14	1	2772.14	64.33	< 0.0001
B-heat treatment temperature	704.67	1	704.67	16.35	0.0008
C-silica particle size	79.02	1	79.02	1.83	0.1934
AB	104.70	1	104.70	2.43	0.1375
AC	28.14	1	28.14	0.65	0.4302
BC	7.04	1	7.04	0.16	0.6911
Residual	732.52	17	43.09		
Lack of Fit	159.02	5	31.80	0.67	0.6568
Pure Error	573.50	12	47.79		
Cor Total	4414.96	23			

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