



EFFECT OF PROCESS PARAMETERS ON GELLING TIME OF SOL-GEL SILICA AND KENAF-SOL-GEL SILICA SYSTEMS

(Kesan Parameter Proses pada Masa Penggelen dalam Sistem Sol-Gel Silika dan Kenaf-Silika Sol-Gel)

Fahmi Asyadi Md Yusof^{1*}, Zulhafiz Tajudin², Ong Siew Kooi¹, Azanam Shah Hashim¹

¹Polymer Department

²Process Department

Malaysian Institute of Chemical & Bioengineering Technology,
Universiti Kuala Lumpur, 78000 Alor Gajah, Melaka, Malaysia

*Corresponding author: fahmiasyadi@unikl.edu.my

Received: 20 November 2019; Accepted: 6 July 2020; Published: 11 August 2020

Abstract

The gelation process of sol-gel silica and kenaf-sol-gel silica were rheologically investigated. The correlation between gelling time and process parameters (i.e., the catalyst ratios: 0.03, 0.05, 0.07, water ratios: 2, 4, 6 and temperatures: 30, 40, 50 °C) were elucidated. The gelling time was determined from crossing over of storage moduli (G') and loss moduli (G''). The effect of the process parameters on gelling time was analysed by using response surface methodology (RSM) based on a three-factorial design. Response surface methodology (RSM) based on 3-level factorial design. Analysis of variance (ANOVA) depicted that all examined parameters had a profound effect on the gelling time for both sol-gel silica and kenaf-sol-gel silica systems. In the sol-gel silica system, RSM predicted that the interaction between catalyst ratio and water ratio influenced the gelling time response. Interestingly, in the kenaf-sol-gel silica system, the interaction between catalyst ratio and temperature contributed to the gelling time response. In particular, gelling time for the kenaf-sol-gel silica system was faster as compared to the sol-gel silica system.

Keywords: kenaf, sol-gel silica, gelling time, response surface methodology

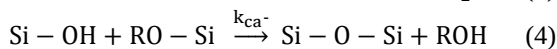
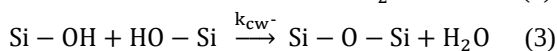
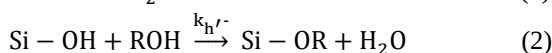
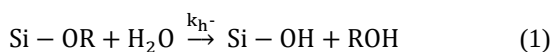
Abstrak

Proses gelasi silika sol-gel dan kenaf-silika sol-gel disiasat secara rheologi. Korelasi antara masa gelasi dan parameter proses (iaitu nisbah pemangkin: 0.03, 0.05, 0.07, nisbah air: 2, 4, 6 dan suhu: 30, 40, 50 °C) telah dijelaskan. Masa gelasi ditentukan daripada penyilangan moduli penyimpanan (G') dan moduli kehilangan (G''). Kesan parameter proses pada masa gelasi dianalisis menggunakan kaedah gerakbalas permukaan (RSM) berdasarkan rekabentuk tiga faktor. Analisis varians (ANOVA) menggambarkan bahawa semua parameter yang diperiksa mempunyai kesan yang mendalam terhadap masa gelasi untuk kedua-dua sistem silika sol-gel dan kenaf-silika sol-gel. Dalam sistem sol-gel silika, RSM meramalkan bahawa interaksi antara nisbah pemangkin dan nisbah air mempengaruhi tindak balas masa gelasi. Menariknya, dalam sistem kenaf-silika sol-gel, interaksi antara nisbah pemangkin dan suhu menyumbang kepada tindak balas masa gelasi. Khususnya, masa gelasi untuk sistem kenaf-silika sol-gel lebih cepat berbanding siste. silika sol-gel.

Kata kunci: kenaf, silika sol-gel, masa penggelen, kaedah gerakbalas permukaan

Introduction

Major efforts were made on kenaf fibers instead of synthetic fibers. The main advantages of kenaf fiber are abundance, biodegradable, cost-effective, and low density as compared to synthetic fibers. Despite its benefits, kenaf fibers suffer from several major drawbacks, such as low strength, low moisture resistance, low durability, and low compatibility with polymer matrix [1-3]. To address these issues, organic-inorganic hybrid technology was widely studied as it can design the product with specific surface properties and multiple functionalities in a single material. Sol-gel silica method is one of the most promising techniques for producing organic-inorganic mixtures. It is a low-temperature solution process to produce inorganic materials and thus the decomposition of organic components can be minimised.



The sol-gel silica synthesis involves two major reactions (equations 1-4) namely hydrolysis of alkoxy silane groups to form silanol and condensation between silanol groups of products and/or between these groups to form siloxane networks. The most commonly used precursor for sol-gel silica synthesis is tetraethyl orthosilicate (TEOS), with a solvent for homogenisation of water-alkoxy silane mixture. Typically, a basic or acidic catalyst is added to increase the rate of hydrolysis reaction [4-6]. In this case, hybridisation is achieved whereby the kenaf fibers were added during the *in-situ* synthesis of sol-gel silica.

The investigation of sol-gel silica processes has great significance, in particular, the gel point, to illustrate the development of the system structure responsible for the potential use of the material. In relation to the gel point, gelling time is a critical parameter in assessing their suitability because gelation cannot be too fast, to encourage its use (penetration into voids or surface coatings) on kenaf fibers or too slow, to avoid

evaporation of volatile molecules [7]. One of the best ways to test gelling time is to perform dynamic viscoelastic experiments. The small-amplitude friction motion technique can measure the viscoelastic reaction of the gel as a function of shear rate.

This study provides an important opportunity to advance the understanding of kenaf-sol-gel silica nanocomposites vis-a-vis organic-inorganic hybrids. The influence of sol-gel process parameters (i.e. catalyst ratio, water ratio, and temperature) in two systems, namely sol-gel silica and kenaf-sol-gel silica system was successfully determined. The RSM based on three-factorial design was used to derive gelling time behaviour for both systems. The effects and relations of the synthesised parameters during the gelation time of both systems were investigated.

Materials and Methods

Materials

Kenaf (KF, 300-400µm, 500g) was obtained from the National Kenaf and Tobacco Board (LKTN, Malaysia). Tetraethyl orthosilicate (TEOS, 98%) was purchased from Acros Organics. Ethanol (99.5%) was supplied by Fisher Scientific and n-butylamine (99.5%) was obtained from Merck. All reagents were used as received.

Synthesis of kenaf-sol-gel silica

Kenaf fibers (2 g) were added to 1M TEOS (22.83 mL) and ethanol (80 mL) in a water bath at different temperatures (30, 40, 50 °C). The amount of catalyst (n-butylamine) and water was added based on the molar ratio with TEOS. All reactions were performed in a 250 mL reactor with a mixing speed of 300 rpm. After 2 minutes, the sample was measured with a rheometer to analyse the gelling time.

Design of experiment

Gelling time was determined as the optimisation response (results) performed by using the three-factorial design in the RSM method (Design-Expert® ver.10, Stat-Ease, Inc.). Gelling time was calculated from crossing over the storage module (G') and loss module (G'') by using a rheometer (MC 302, Anton Paar). The

independent variables were the catalyst ratio (0.03, 0.05, and 0.07), temperature (30, 40, 50 °C) and water ratios (2, 4, and 6). The range values set for the independent variables (Table 1) were created as low (-1), middle (0), and high (+1). The three-factorial design generated 32

different conditions of sol-gel silica and kenaf-sol-gel silica systems as shown in Table 2. Analysis of variance (ANOVA) was used to calculate the statistical relation of independent variables.

Table 1. Levels of the variables by using three-factorial design

Variables	Code	Unit	Level		
			-1	0	1
Catalyst Ratio	A		0.03	0.05	0.07
Temperature	B	°C	30	40	50
Water Ratio	C		2	4	6

Results and Discussion

RSM modelling of gelling time with respect to silica sol-gel processing parameters

The results of each experimental run are tabulated in Table 2. The gelling time for the sol-gel silica system is in the range of between 185 and 2089 s. The determination of the appropriate polynomial equation to represent the relationship between the input parameters

and output response (gelling time) was performed by carrying out sequential model sum of squares (SMSS) and Lack of Fit tests. Both analyses suggested that the relation between input parameters and resultant gelling time can be modelled by using a 2FI equation. The equation in terms of coded factors used to predict the response for given levels of each factor is indicated below:

$$\text{Gelling Time} = 988.75 - 525.5A + 290.22B - 140.28C - 111.75AB + 33.99AC + 94.67BC \quad (5)$$

Table 2. Design of experiments and results by using three-level factorial for sol-gel silica system

Run	Catalyst Ratio	Water Ratio	Temperature (°C)	Gelling Time (s)
1	0.05	2	30	958
2	0.07	4	30	468
3	0.03	4	50	1198
4	0.07	2	50	185
5	0.05	6	30	1403
6	0.07	6	50	619
7	0.05	4	30	978
8	0.03	6	50	2089
9	0.03	4	40	1459
10	0.07	4	50	349
11	0.05	4	40	959
12	0.03	2	50	680
13	0.03	6	30	1930
14	0.07	2	40	319

Table 2 (cont'd). Design of experiments and results by using three-level factorial for sol-gel silica system

Run	Catalyst Ratio	Water Ratio	Temperature (°C)	Gelling Time (s)
15	0.05	6	50	1239
16	0.05	2	40	902
17	0.05	6	40	1438
18	0.07	4	40	496
19	0.07	6	40	542
20	0.07	2	30	450
21	0.05	4	40	962
22	0.05	2	50	539
23	0.05	4	40	990
24	0.05	4	50	750
25	0.05	4	40	501
26	0.03	2	40	1409
27	0.05	4	40	961
28	0.05	4	40	957
29	0.03	4	30	1680
30	0.07	6	30	894
31	0.03	2	30	1412
32	0.03	6	40	1924

The ANOVA analysis for the 2FI model of the sol-gel silica system is shown in Table 3. The model F-value of 45.44 implied that the model was significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of “Prob > F” of less than 0.001 indicated that the model terms were significant. In this study, factors such as catalyst ratio, water ratio, temperature, and interaction between catalyst ratio and water ratio were considered as significant model terms. The “Lack of Fit F-value” of 0.65 implied the Lack of Fit was not significant relative to the pure error. There was a 77.59% chance that a “Lack of Fit F-value” this large could occur due to noise.

The behaviour of the gelling time in response to variations in catalyst ratio, water ratio, and temperature in the sol-gel silica system is shown in Figure 1. The main effects plot indicated that the catalyst ratio was the most influential factor, followed by water ratio and temperature. It was expected that by increasing the

catalyst concentration the gelling time will increase. As the concentration of catalyst (n-butylamine) increased, the rate of hydrolysis and condensation increased in all studied scales. This occurred when the intermediates reached the supersaturation region. The intermediate speed also increased, most likely to shorten the nucleation time. Therefore, the total number of nuclei formed will be less, and the gelation time will be faster [8, 9].

Further analysis of the main effects revealed that the gelling time was highest when the water ratio was kept at high level. The increase in gelling time with the increased water ratio was because as more water was added, the amount of solvent was constant, and the silicate concentration was reduced [10]. This dilution effect will change the rate of hydrolysis and condensation which eventually led to higher gelling time. It is interesting to note that temperature had the least influence on the gelling time whereby it can be kept

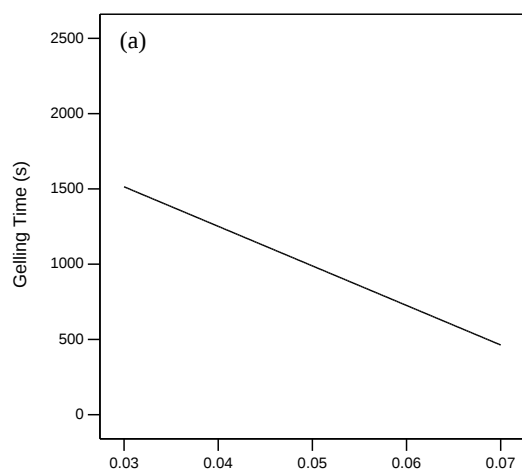
within 30-50°C. As this factor did not appear to be the most important, it can be safely kept at a low-level setting (30 °C).

The interaction effect of catalyst ratio and water ratio on gelling time is shown in Figure 2. The non-parallel lines indicated that there was a strong interaction between the process variables catalyst ratio and water ratio. As it can be observed from the plot, the effect of catalyst ratio on

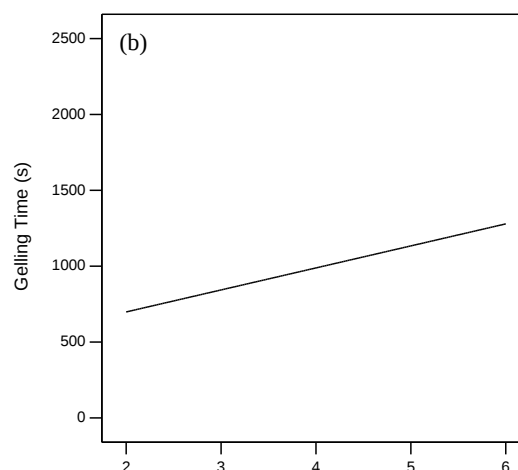
gelling time was different at low and high water ratios levels. The minimum variability of gelling time was observed at the low water ratio level. On the other hand, the gelling time was higher at the low catalyst ratio (0.03) level and the high water ratio (6) level.

Table 3. Analysis of variance for sol-gel silica system

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	7.11E+06	6	1.19E+06	45.44	< 0.0001	significant
A-Catalyst Ratio	4.97E+06	1	4.97E+06	190.57	< 0.0001	significant
B-Water Ratio	1.52E+06	1	1.52E+06	58.12	< 0.0001	significant
C-Temperature	3.54E+05	1	3.54E+05	13.58	0.0011	significant
AB	1.50E+05	1	1.50E+05	5.75	0.0243	significant
AC	13068	1	13068	0.50	0.4856	not significant
BC	1.08E+05	1	1.08E+05	4.12	0.0531	not significant
Residual	6.52E+05	25	26083.81			
Lack of Fit	4.71E+05	20	23565.79	0.65	0.7759	not significant
Pure Error	1.81E+05	5	36155.87			
Cor Total	7.76E+06	31				



A: Catalyst Ratio



B: Water Ratio

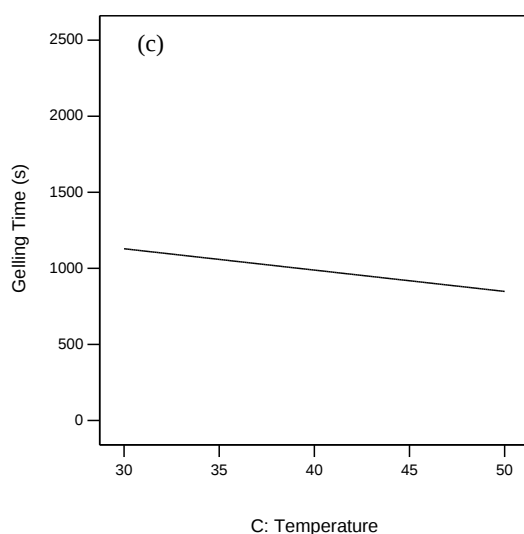


Figure 1. Behaviour of gelling time in response to variation of (a) catalyst ratio, (b) water ratio, and (c) temperature in sol-gel silica system

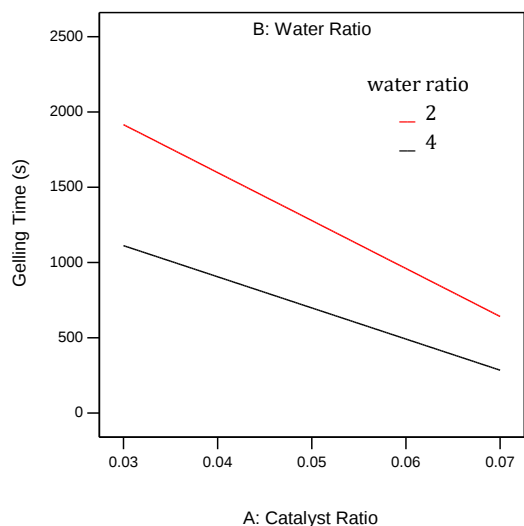


Figure 2. Behaviour of gelling time in response to interaction between catalyst ratio and water ratio in sol-gel silica system

RSM modelling of gelling time with respect to kenaf-sol-gel silica processing parameters

The results of each experimental run are tabulated in Table 4. The gelling time for the kenaf-sol-gel silica system is in the range of 157 and 1173s. Similar to the sol-gel silica system, the determination of appropriate polynomial equation to represent the relation between the input parameters and the output response (gelling

time) was performed by carrying out the sequential model sum of squares (SMSS) and the Lack of Fit tests. The relation between input parameters and resultant gelling time was modelled by using a 2FI equation. The equation in terms of coded factors used to make predictions about the response for the given levels of each factor is indicated below:

$$\text{Gelling Time} = 462.16 - 209.94A + 126.94B - 73.11C - 39.00AB + 48.83AC - 51.42BC \quad (6)$$

Table 4. Design of experiments and results by using three-level factorial for kenaf-sol-gel silica

Run	Catalyst Ratio	Water Ratio	Temperature (°C)	Gelling Time (s)
1	0.05	4	40	431
2	0.05	4	40	433
3	0.05	6	30	679
4	0.05	4	40	502
5	0.05	4	30	439
6	0.05	4	40	438
7	0.07	6	30	404
8	0.05	2	40	289
9	0.07	2	40	198
10	0.03	6	30	1173
11	0.05	2	30	350
12	0.03	6	40	700
13	0.07	6	40	352
14	0.03	2	40	509
15	0.07	4	40	239
16	0.07	2	30	219
17	0.07	4	50	223
18	0.03	4	50	600
19	0.03	4	40	609
20	0.03	2	50	509
21	0.03	4	30	819
22	0.05	4	50	369
23	0.05	2	50	274
24	0.05	6	40	588
25	0.07	6	50	275
26	0.05	6	50	549
27	0.03	2	30	558
28	0.05	4	40	429
29	0.03	6	50	628
30	0.07	2	50	157
31	0.07	4	30	259
32	0.05	4	40	588

The ANOVA analysis for the 2FI model of the kenaf-sol-gel silica system is shown in Table 5. The model F-value of 46.84 implied that the model was significant. There was only a 0.01% chance that an F-value this large

could occur due to noise. Values of “Prob>F” of less than 0.001 indicated that model terms were significant. In this study, parameters A, B, C, AC, and BC were considered as significant model terms. The “Lack of Fit

F-value” of 1.11 implied that the Lack of Fit was not significant relative to the pure error. There was a 49.92% chance that a “Lack of Fit F-value” this large could occur due to noise. In this study, catalyst ratio, water ratio, temperature, the interaction between catalyst ratio-temperature and interaction between water ratio-temperature were as considered significant model terms.

It can be seen from Figure 3 that the catalyst ratio has a significant impact on gelling time, while the water ratio has a lower impact on whatever gelling time. It is interesting to note that temperature had the lowest sensitivity to variability in gelling time as compared to other variables. The behaviour of the main effects on gelling time in the kenaf-sol-gel silica system was similar to the sol-gel silica system. However, there was a clear trend of decreasing gelling time in the kenaf-sol-gel silica system as compared to the sol-gel silica system for all variables, whereby reduction was almost half. This result may be explained by the fact that the addition of kenaf fibers had changed the hydrolysis rate of sol-gel silica process. It was postulated that the hydrolysis reaction followed a second-order mechanism and could be described as a bimolecular nucleophilic substitution (S_N2 -type), forming the silanol groups. The hydrolysis proceeds by nucleophilic attack of a hydroxide ion (OH^-) at the silicon atom, with an alkoxy

group (RO^-) as the leaving group [11]. Therefore, the gelling time for sol-gel silica hydrolysis was faster with additional hydroxyl groups derived from the kenaf fibers. It is noteworthy that changes in gelling times affected the size and distribution of silica formed at the end of the reaction.

The non-parallel lines in the graph of Figure 4 (a) indicated that there was an interaction effect, in which the significant p-value (Table 5) for the catalyst ratio and temperature term confirmed. Figure 4 (a) shows that the highest gelling time for the catalyst ratio was 0.03 and temperature was 50 °C. In contrast, the gelling time was low when the parameter settings for the catalyst and temperature ratios were 0.07 and 30 °C, respectively. Figure 4(b) shows the interaction between water ratio and temperature in the kenaf-sol-gel silica system. The interaction lines showed that the ratio of water at different temperatures was non-parallel. This indicated that there was a strong interaction between these two factors. The graph also shows that the highest gelling time was achieved when the water ratio was kept at 6 and the temperature at 50 °C.

Table 5. Analysis of variance table for kenaf-sol-gel silica

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1.26E+06	6	209709.13	46.84	2.1E-12	significant
A-Catalyst Ratio	7.93E+05	1	793380.06	177.20	7.5E-13	significant
B-Water Ratio	2.90E+05	1	290068.06	64.79	2.1E-08	significant
C-Temperature	9.62E+04	1	96214.222	21.50	9.6E-05	significant
AB	1.83E+04	1	18252	4.08	0.05433	not significant
AC	2.86E+04	1	28616.333	6.40	0.01816	significant
BC	3.17E+04	1	31724.083	7.09	0.01339	significant
Residual	1.12E+05	25	4477.4188			
Lack of Fit	9.14E+04	20	4569.6318	1.11	0.49924	not significant
Pure Error	2.05E+04	5	4108.5667			
Cor Total	1.37E+06	31				

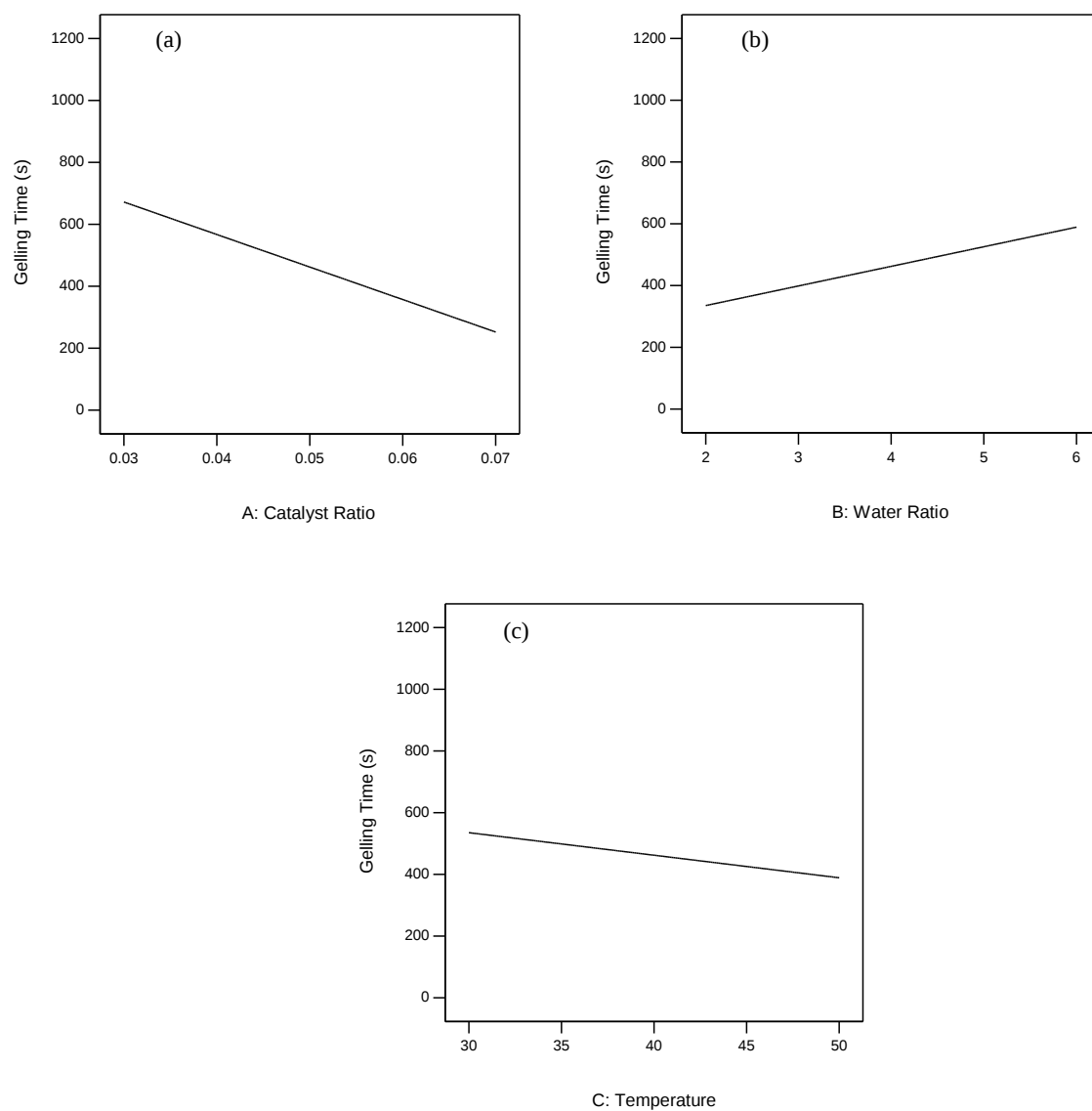


Figure 3. Behaviour of gelling time in response to variation of (a) catalyst ratio, (b) water ratio, and (c) temperature in kenaf-sol-gel silica system

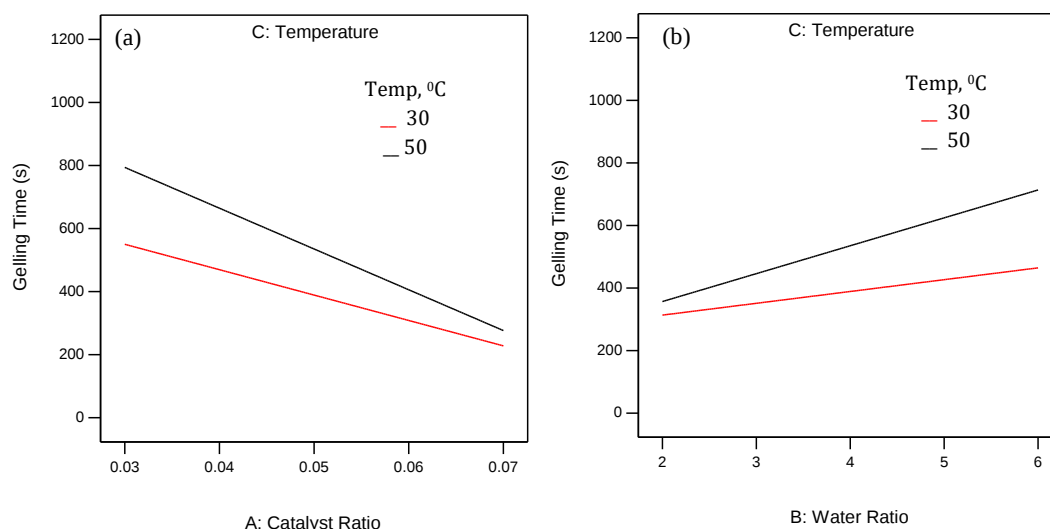


Figure 4. Behaviour of gelling time in response to the interaction between (a) catalyst ratio and temperature and (b) water ratio and temperature in kenaf-sol-gel silica system

Conclusion

The gelling time of sol-gel silica and kenaf-sol-gel silica systems was successfully measured as a function of catalyst ratio, water ratio and temperature, and their interaction by using RSM-based on three-factorial design. Among these factors, the catalyst ratio was the most significant factor which influenced the gelling time as compared to the water ratio and temperature in both sol-gel silica and kenaf-sol-gel silica systems. The findings from the ANOVA also revealed that by increasing the catalyst ratio and temperature and lowering the water ratio, individually, the gelling time decreased in both systems. In the sol-gel silica system, there was a strong interaction between the catalyst ratio and water ratio. Interestingly, in the kenaf-sol-gel silica system, the interactions which influenced the gelling time were between catalyst ratio and temperature as well as the water ratio and temperature. It is concluded that RSM can be a successful technique to identify the significant factors and their interactions that influence the gelling time of sol-gel silica and kenaf-sol-gel silica systems. This method can provide a framework for further research on other cellulosic fibers.

Acknowledgement

The authors gratefully acknowledge the financial support for this work through the *Skim Geran*

Penyelidikan & Inovasi Mara (SGPIM) for the project number 1/33/19/18(1).

References

- Guerrero-Martínez, A., Pérez-Juste, J. and Liz-Marzán, L. M. (2010). Recent progress on silica coating of nanoparticles and related nanomaterials. *Advanced Materials*, 22(11): 1182-1195.
- Wang, J., Shah, Z. H., Zhang, S. and Lu, R. (2014). Silica-based nanocomposites via reverse microemulsions: Classifications, preparations, and applications. *Nanoscale*, 6(9): 4418-4437.
- Kim, T. G., An, G. S., Han, J. S., Hur, J. U., Park, B. G. and Choi, S. C. (2017). Synthesis of size controlled spherical silica nanoparticles via sol-gel process within hydrophilic solvent. *Journal of the Korean Ceramic Society*, 54(1): 49-54.
- Bogush, G. H., Tracy, M. A. and Zukoski IV, C. F. (1988). Preparation of monodisperse silica particles: Control of size and mass fraction. *Journal of Non-Crystalline Solids*, 104(1): 95-106.
- Rao, K. S., El-Hami, K., Kodaki, T., Matsushige, K. and Makino, K. (2005). A novel method for synthesis of silica nanoparticles. *Journal of Colloid and Interface Science*, 289(1): 125-131.

6. Rahman, I. A. and Padavettan, V. (2012). Synthesis of silica nanoparticles by sol-gel: Size-dependent properties, surface modification, and applications in silica-polymer nanocomposites. A review. *Journal of Nanomaterials*, 2012: 1155-1170.
7. Mika, J., Györfvay, E. and Rosenholm, J. B. (1998). Viscoelastic characterization of three different sol-gel derived silica gels. *Colloids and Surfaces*, 141: 205-216.
8. Greasley, S. L., Page, S. J., Sirovica, S., Chen, S., Martin, R. A., Riveiro, A. and Jones, J. R. (2016). Controlling particle size in the Stöber process and incorporation of calcium. *Journal of Colloid and Interface Science*, 469: 213-223.
9. Zulkifli, M., Hossain, M. S., Khalil, N. A., Yahaya, A. N. A., Yusof, F. A. M. and Hashim, A. S. (2018). Preparation and characterization of sol-gel silica modified kenaf bast microfiber/polypropylene composites. *BioResources*, 13(1): 1977-1992.
10. Shekarriz, M., Khadivi, R., Taghipoor, S. and Eslamian, M. (2014). Systematic synthesis of high surface area silica nanoparticles in the sol-gel condition by using the central composite design (CCD) method. *The Canadian Journal of Chemical Engineering*, 92(5): 828-834.
11. Arantes, T. M., Pinto, A. H., Leite, E. R., Longo, E. and Camargo, E. R. (2012). Synthesis and optimization of colloidal silica nanoparticles and their functionalization with methacrylic acid. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 415: 209-217.