

SUPPLEMENTARY MATERIAL TO  
**Correlation between silane concentration and temperature  
operated toward conductivity of well-synthesized chitosan-fly  
ash composite membrane**

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INTERACTION BETWEEN MATRIX CHITOSAN AND FLY ASH FILLER

*Fourier transform infrared (FTIR)*

FTIR spectra of chitosan – fly ash composite membranes with different concentrations of silane is shown in Figure S-1. While various FTIR absorbances in the chitosan – fly ash composite membrane can be seen in Table S-1.

TABLE S-I. Various wavenumber of chitosan – fly ash composite membrane FTIR absorption with various silane concentration

| No. | Vibration type                         | Wavenumber, cm <sup>-1</sup> |                                    |
|-----|--|------------------------------|------------------------------------|
|     |  | 0 % (w/v) of silane          | 5, 10 and 15 % (w/v) of silane     |
| 1   | –OH (broad)                            | 3419.56                      | 3458.13; 3463.92                   |
| 2   | –NH <sub>2</sub>                       | 1631.67; 1529.45             | 1631.67; 1612.38; 1531.37; 1529.45 |
| 3   | –CH <sub>2</sub>                       | 2788.88                      | -                                  |
| 4   | C–O                                    | 1000.99                      | 1014.49; 1116.71; 1118.94          |
| 5   | –C–N                                   | 1305.72; 1382.87             | 1309.58; 1380.94                   |
| 6   | Si–O–Si                                | 621.04                       | 432.03                             |
| 7   | Al–O (Al <sub>2</sub> O <sub>3</sub> ) | 480.24                       | 472.53                             |
| 8   | Si–O                                   |                              | 457.1; 472.53                      |

Table S-I and Fig. S-1 illustrate typical band characteristics for chitosan, the typical bands are stretching –OH bond, bending –NH<sub>2</sub> bond, –CH<sub>2</sub> bond, and stretching CO bond appearing at wave numbers 3419.56 cm, 1631.67 cm, 1529.45 cm, 2788.88 cm, and 1000.99 cm<sup>-1</sup> respectively, (see Fig. S-1A). Typical fly ash bands also appear at wave numbers 621.04 and 480.24 cm<sup>-1</sup> respectively showing the presence of Si–O–Si symmetric stretching and vibrations of

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aluminum oxide (see Fig. S-1A). In the Fig. 4, it can be seen that the  $-OH$  absorption is getting wider. This shows an interaction between the chitosan matrix and fly ash (Fig. S-1A), and the chitosan matrix with silane coupling agent through the formed hydrogen bonds (see Fig. S-1B; S-1C and S-1D). Meanwhile, the interaction between fly ash and silane coupling agent can be seen by the altering wavenumber of the siloxane ( $Si-O-Si$ ) absorption from  $621.04$  to  $432.03\text{ cm}^{-1}$ . This condition is reinforced by the presence of strong enough bend of  $Si-O$  bond which appears in the wavenumbers  $457.1$  and  $472.53\text{ cm}^{-1}$  (see Fig. S-1B; S-1C and S-1D)<sup>1,2</sup>.

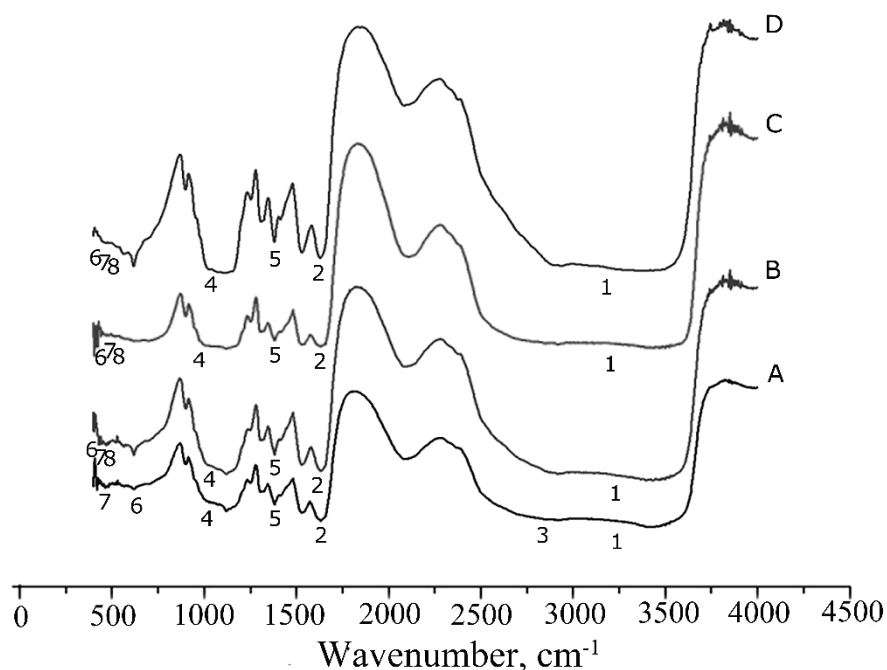


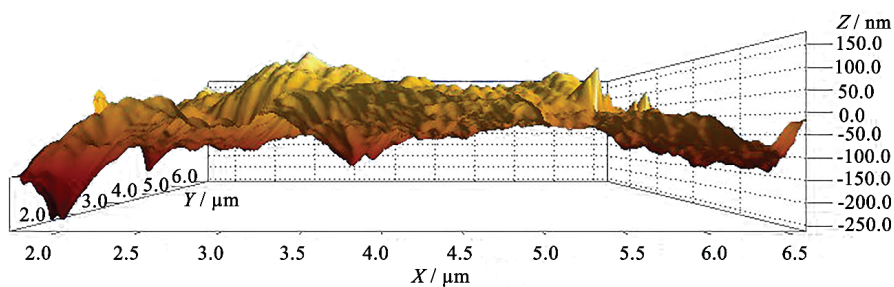
Fig. S-1. FTIR spectra composite membrane with various silane concentration variation; A - 0; B - 5; C - 10 and D - 15 %.

#### *Atomic force microscopy (AFM)*

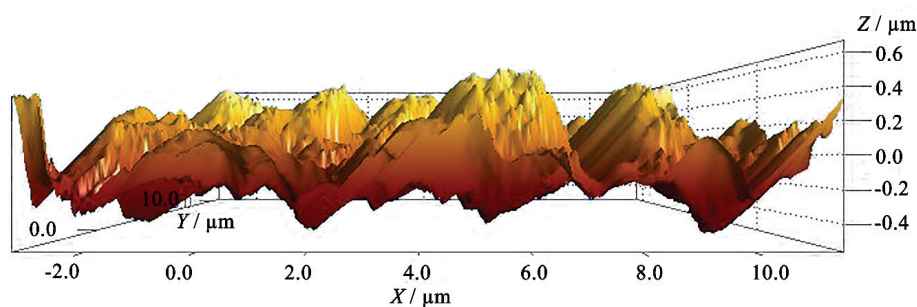
The results of analysing composite membrane chitosan–fly ash surface topography can be seen in Fig. S-2. It shows that the topography of membrane chitosan– fly ash contains hills and valleys which indicates that an interaction among chitosan, silane and fly ash occurs. The presence of silane in composite membranes causes hills and valleys become more numerous and evenly distributed. This indicates that there were strong interactions, not only between chitosan and silane but also between fly ash and silane. Nevertheless, if there is an excessive amount of silane (15 %), the hills and valleys on the surface of the

membrane is reduced notably because the interactions among chitosan, fly ash and silane become saturated.

A



B



C

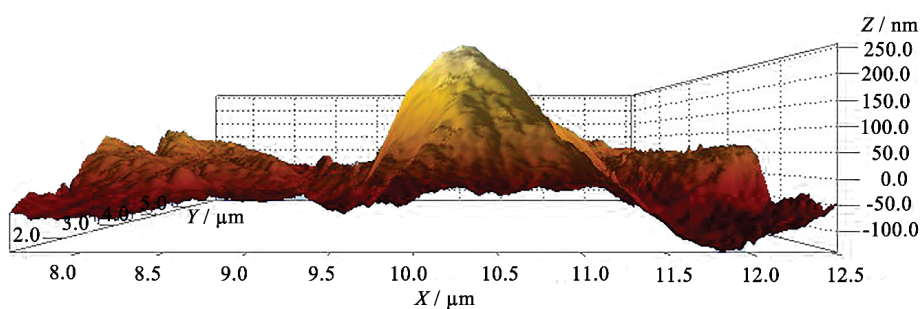


Fig. S-2. Topography analysis of composite membrane chitosan - fly ash with various silane concentrations (A) 0 % (B) 5 % (C) 15 % using AFM.

A similar study was carried out by Enescu and co-workers, who synthesized chitosan- $\gamma$ -glycidoxypropyltrimethoxysilane (GPTMS) composite membrane. The results of their AFM analysis showed that pure chitosan membranes have flat membrane surface. Whereas, composite membrane of chitosan-GPTMS has rough surface topography with the appearance of hills and valleys on the surface.

Those hills and valleys emerge because of the presence of GPTMS which interacts with chitosan as a membrane matrix.<sup>3</sup>

Interface interaction among chitosan, silane and fly ash is shown in Fig. S-3. It can be seen that the compatibility between the surface of chitosan and fly ash is a key issue in determining the final membrane property and performance. While, the transitional phase is expected to occur between organic and inorganic phases to improve the interface morphology in the composite membrane. In this study, the function of organosilane of silane agent is to modify the surface of fly ash and create the desired transitional phase. Aryloxy group (RO-, R-CH<sub>3</sub> or CH<sub>3</sub>CH<sub>2</sub>) on silane can be hydrolyzed to the silanol groups (Si-OH) and to polymerized condensation as well to form oxane bond between silane with one another on the fly ash surface. After the modification, organosilane group (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si≡) interacts with SiO<sub>2</sub> on the surface of fly ash to form a polysiloxane network. When the modified fly ash is blended with chitosan, hydroxyl group (-OH) will interact with the amine group (NH<sub>2</sub>) on chitosan to form hydrogen bonds. As a result, the transitional phase with good flexibility can be produced, because the hydrogen bonds can create interface between chitosan and fly ash which has compatible properties.<sup>1,4</sup>

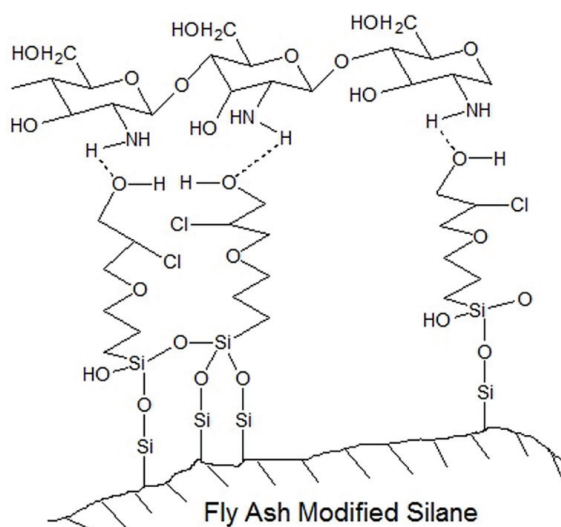


Fig. S-3. Interface interaction in composite membranes chitosan–fly ash modified silane.

TGA test was performed to find out the thermal stability of chitosan-fly ash composite membrane. The result of TGA analysis of composite membrane is shown in Fig. S-4.

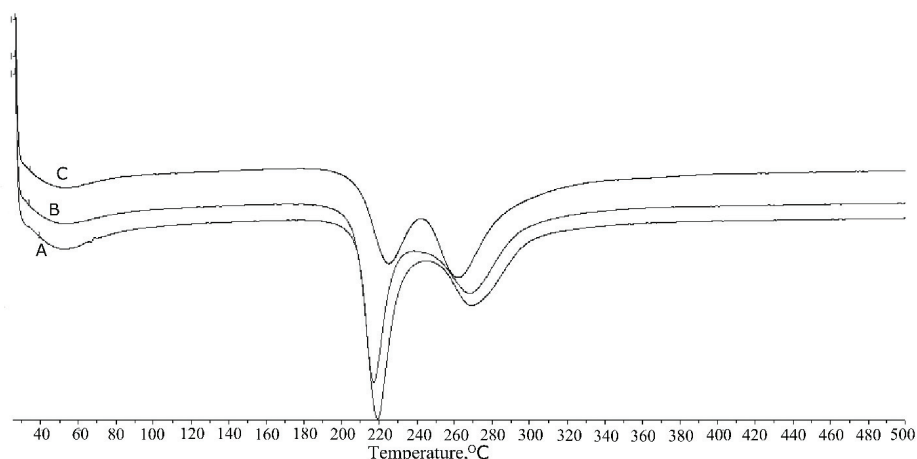


Fig. S-4. Thermogram of mass data of composite membrane chitosan – fly ash modified with silane A - 0, B – 5 and C - 15 %.

Based on Fig. S-4, it can be seen that the composite membrane of chitosan–fly ash has two decomposition patterns. The first decomposition occurs at 220°C, which is generated by the release of hydrogen bonds between the amine groups on chitosan and epoxy group on the silane for composite membranes with 5 and 15 % silane. While in composite membranes with 0% silane, first decomposition is generated by the release of hydrogen bonds between the amine groups on chitosan and silica groups on fly ash. From the figure, it also can be seen that the silane concentration in the composite membrane also affects the sharpness of the thermogram spectra. This is because the presence of silane in the composite membrane can make strong hydrogen bond between the silane and the chitosan matrix. The aforementioned fact reinforced by Zawadzki *et al.*<sup>5</sup> who conducted a research on thermal analysis of chitosan in various conditions. The result of the study showed that chitosan decomposition started to take place at temperatures above 180 °C due to the broken hydrogen bonds.<sup>5</sup>

The second decomposition related to chitosan chain breakdown polymer due to the dehydration at high temperatures occurs at a temperature of about 270 °C. In addition, temperature of 270 °C, is also related to the elimination of the polysiloxane network formed between silane and fly ash. Thermogram spectra which is constant at temperatures above 270 °C indicates that the composite membrane has completely decomposed. The literature confirmed the second decomposition. It revealed that at a temperature of 274 °C, the decomposition is associated with polymer chain breakdown from chitosan due to the dehydration at high temperatures.<sup>5</sup> Another research was conducted by Lin and co-workers<sup>1</sup> on thermal analysis of hybrid membrane between sulfonated poly (ketone ether arylene ether) hybrid membranes bearing a carboxyl group (SPAEEK-C) utilizing

silane coupling agent (3-glycidyloxypropyltrimethoxy silane). The results of the study showed that in a temperature range of 250 – 350 °C, the decomposition is associated with the destruction of the siloxane groups in the silane.<sup>1</sup>

## REFERENCES

1. H. Lin, C. Zhao, W. Ma, K. Shao, H. Li, Y. Zhang, H. Na, *J. Power Sources* **195** (2010) 762 (<https://dx.doi.org/10.1016/j.jpowsour.2009.08.020>)
2. Y. Wen, Z. Tang, Y. Chen, Y. Gu, *Chem. Eng. J.* **175** (2011) 110 (<https://dx.doi.org/10.1016/j.cej.2011.09.066>)
3. D. Enescu, V. Hamciuc, R. Ardeleanu, M. Cristea, A. Ioanid, V. Harabagiu, B. C. Simionescu, *Carbohydr. Polym.* **76** (2009) 268 (<https://dx.doi.org/10.1016/j.carbpol.2008.10.026>)
4. H. Wu, B. Zheng, X. Zheng, J. Wang, W. Yuan, Z. Jiang, *J. Power Sources* **173** (2007) 842 (<https://dx.doi.org/10.1016/j.jpowsour.2007.08.020>)
5. J. Zawadzki, H. Kaczmarek, *Carbohydr. Polym.* **80** (2010) 394 (<https://dx.doi.org/10.1016/j.carbpol.2009.11.037>).