
SYNTHESIS OF HYDROPHOBIC SUPERABSORBENT USING SODIUM ALGINATE AND SOY PROTEIN ISOLATE

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Abstract

The aerogel now become most famous thing from drug delivery carrier to superabsorbent. The superabsorbent made from the sodium alginate aerogel allow it to absorb water up to higher ratio per weight. But nowadays, there is an issue of oil become a threat in many processes such as wastewater. The high content of oil will hinder the process of treating the wastewater. The usage of oil superabsorbent has known to be expensive in cost and cannot be use more than once. By using sodium alginate and soy protein isolate, the sol-gel technique is applying to form superabsorbent to absorb oil. However, this can be done by soaking the hydrogel with Methyltrimethoxysilane (MTMS), Tetra Ethyl Orthosilane (TEOS) and ethanol with ratio of 1:1:2. The aerogel is left in room within 24 hours after surface modification. The aerogel combine with MTMS does affect the shrinkage at it lower shrink percentage by 5-7%, able to get hydrophobic aerogel with angle 112.5° and 117° with oil absorption above 40%. The hydrophobic superabsorbent can be made although it is not able to absorb much compare to superabsorbent.

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1.0 Introduction

Superabsorbent has been quite a unique innovation to simpler absorbent [1]. The usage of super absorbent is depending on their purpose. Some are used to remove heavy metal, dye or even separate water from saline water. Superabsorbent able to absorb as much from one time of its weight to 60 times of their weight making it able to absorb with small volume or weight per use. There are many kinds of superabsorbent either a powder, monolith or film. Among the superabsorbent, an aerogel gains many interest for the researchers who want to search for sustainability. The main issues involving the aerogel is that structural strength is the main weakness as the aerogel is fragile. Due to volume of air is 99% of its structure [2], it may break if heavy load of pressure and stress is applied to it. Furthermore, the density of the aerogel can increase which is can become disadvantages as some of the aerogel tend to be light weighted so that it can be easily carry around or bring it especially being as absorbent.[3]

The aerogel structure strength is not very good. As the aerogel compose of air of 99% in term of volume, they tend to break and shatter when apply pressure onto

it. Other issues about the aerogel is that while it is water loving hydrophilic allow the absorbent to absorb water, some engineer and scientist tend to know if sodium alginate aerogel can absorb oil instead of water. Since many absorbent of oil is very expensive to synthesis and it is one off use only, people start to research the more effective absorbent that can be use more than once. The sodium alginate aerogel would be a good absorbent if it can change the surface texture to allow absorbing oil [4]. On the other hand, the disaster involving oil is becoming quite a concern, Deepwater Horizon and Gulf Oil Spill become a worldwide attention due to catastrophic oil spill that take months to fully disperse the oil [5]. And oil spill from tanker become an issue with leak oil in open sea areas as well as both are immiscible each other that need to remove the mixture by solution using Liquid-Liquid Extraction process. [6]. While there are many oil superabsorbent, the cost and production complexity may affect the availability of the oil superabsorbent. Using soy protein isolate (SPI) to improve the strength for the aerogel as well reducing water absorption intake [7]. SPI is based on organic substance that are renewable and viable source of bio-based aerogel [8]. This can be done by

crosslinking the material with the chain branch inside the aerogel [9]. Crosslinking can be done by physically or internal gelation and chemically or external gelation [10].

The synthesis of aerogel is done by sol-gel. [11]. Since the production of aerogel may vary, but sol-gel is use for most type of aerogels including silica aerogel. [12]. Sol-gel technique derives from solution and gelation process which the material is disperse in solution while later on add material or process that will make it hydrogel [13], [14]. The moisture content need to be remove first before making an aerogel. To remove water content, solvent exchange can be done first before drying process. The drying process involve for final stage of aerogel production. Both organic and inorganic gel can be made from ambient drying [15]. Some of the material came from freeze drying [16]. Lastly, many hybrid aerogel is made by supercritical drying process. To make it hydrophobic, the most common method is using silane treatment[17] . Any precursor from silane group will be use to modify the surface of the aerogel. This will enhance the surface as well as the possibility to get hydrophobic.

The purpose of this research is to see the characteristic of aerogel made from the sodium alginate as well as making hydrophobic superabsorbent by treating it with methyltrimethoxysilane. Since there is not many research about this, this experiment will identify if the hydrophobic modified sodium alginate aerogel that incorporated with soy protein isolate can use in oil absorption. This will make development of aerogel become an interest to many scientists. [18]

2.0 Methodology

2.1 Material

Sodium Alginate from brown sea algae from Sigma, Glutano- δ -Lactone (GDL) from Sigma, Calcium Carbonate (CaCO_3) from SIgma, Soy Protein Isolate (SPI) ,Deionised Water, Methyltrimethoxysilane (MTMS) from Merck, Tetra Ethyl Orthosilane (TEOS) from Sigma, Ethanol from Sigma.

2.2 Methods

The production of aerogel can be produced by including GDL into the solution which sodium alginate and sodium carbonate (CaCO_3). This can be done by adding alginate sodium salt was dissolved in water to obtain the weightage of 1.5 and 3% w/w stirred until it completely dissolved [19]. Then, the soy protein isolate of 1.5% w/w was added. Calcium Carbonate (CaCO_3) is added by

1.5% wt into the solution. The Glutano- δ -Lactone (GDL) was then added to the solution with continuous stirring up to 0.4% wt. The hydrogels were then transferred into molds and stored in refrigerator (4°C) until they were completely gelled. Prior to the ambient drying, the hydrogels undergone surface treatment which discussed in 3.1 B before a successive solvent exchange (30, 50, 70, 90% v/v in 24 hours for each concentration, and finished by twice washing with pure ethanol) to remove water and its impurities. The alginate hydrogels are then called as Alco gel. The solvent exchange procedures were completed. For the surface modification, the alginate hydrogel will be soaked with Methyltrimethoxysilane (MTMS), Tetra Ethyl Orthosilicate (TEOS) and ethanol with volume ratio of 1:1:2. Which is 25mL: 25mL: 50mL [20]. The alginate will be soaked for 24 hours. Then, the aerogel will be undergoing ambient drying which the sample will be drying in room for 24 hours.

The performance of the aerogel is tested using oil from pure used engine oil and left for 24 hours. The efficiency was calculated as shown in Eq. (1):

$$\% \text{ oil absorbed} = \frac{\text{Final Weight, } G_f - \text{Initial Weight, } G_i}{\text{Initial Weight, } G_i} \times 100\%$$

where: G_i is the initial weight, G_f is the final weight where the efficiency is calculated in percentage.

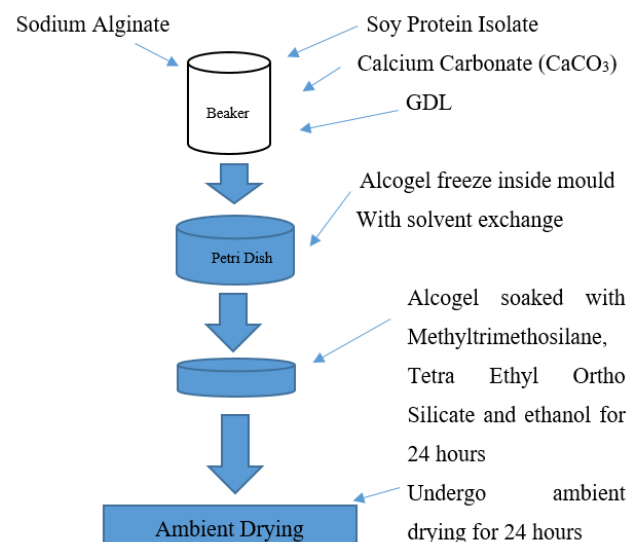


Figure 1: Preparation of Aerogel

2.3 Equipment

2.3.1 VCA 3000 Contact Angle Equipment is an equipment that use to test the hydrophobicity of the substance. Each sample will be test with a drop of water with syringe size of $2\mu\text{L}$.

2.3.2 Thermogravimetric Analysis also use determine the heating value of the sample. The analysis is carry out in the 20 to 600 °C using heating rate of 10 °C/min in Nitrogen gas environment.

3.0 Results and discussion

3.1 Effect of Ambient Drying on Shrinkage

Sodium alginate drying using ambient drying does have huge effect on shrinking. Without surface modified MTMS, TEOS and Ethanol, the shrinking of the aerogel is around 80% while the surface modified aerogel only shrink 73 to 75%. The reason for this shrinking occur is that temperature is varying during drying because of the temperature of the night is lower than daytime. The ambient drying should be 50-60%. Aside that, inconsistency of the room temperature may affect the shrinking of the aerogel.

Table 1: Comparison between ambient drying and weight loss in percentage

Sample	Drying technique	% weight loss
1.5% SA+SPI	ambient	80.1408
3.0% SA+SPI	ambient	80.0090
1.5% SA+SPI+MTMS	ambient	73.8026
3.0% SA+SPA+MTMS	ambient	75.8525

The mechanical strength improves after SPI is added. It feels the aerogel sturdier and rigid. While adding MTMS, the surface feels a little bit coarse and the smelly due to TEOS which act as activator for surface modifying agent. Mechanical test was not applicable due to hardness of the aerogel.

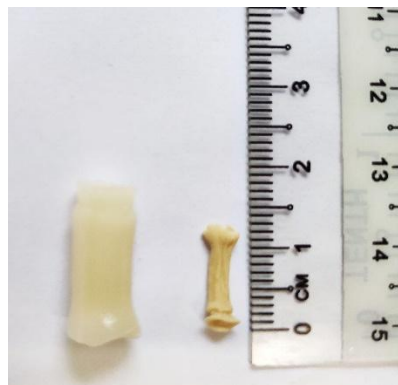


Figure 2: Size of aerogel before and after ambient drying

3.2 TGA Analysis

The analysis below shows that the graph trend for TGA. For the range of 30 °C to 200 °C, the removal of water content has been removed. At 200 °C, there is significant drop to 260 °C where the degradation of SPI occurred at higher temperature which is 260 °C to 265 °C. Although the addition of MTMS into the aerogel, the plot seem rather identical for all four line. However, the gradient for 1.5%SA+SPI are less steep than 3.0% SA+SPI.

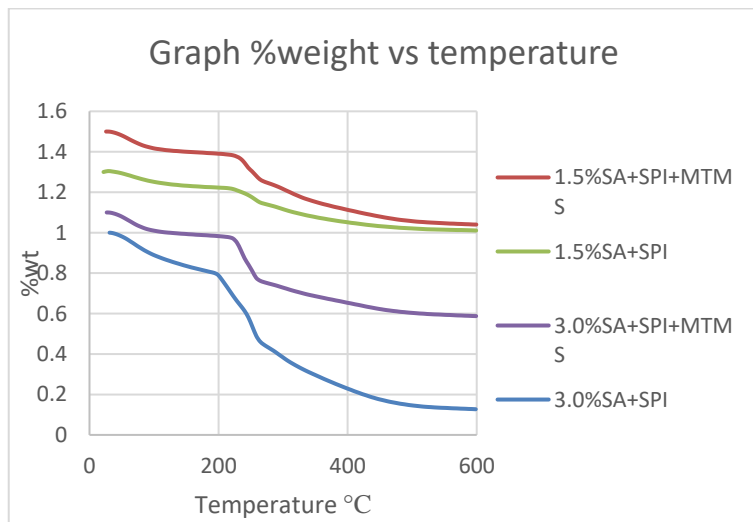


Figure 3: graph of weight percentage loss versus temperature

3.3 Contact Angle Analysis

The analysis of the for the contact angle compare both sample between before adding MTMS and after adding MTMS. The analysis shows that from hydrophilic SA-SPI of 1.5% increase from 43.1° to 112.5° and for 3.0% SA-SPI increase from 34° to 117°.

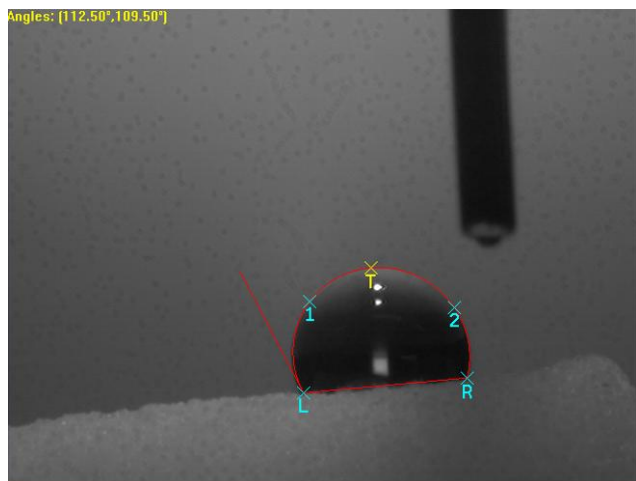


Figure 4: Contact Angle analysis for 1.5%SA-SPI-MTMS

3.4 Oil Absorption

For the absorption of oil, there is not much it can absorb. For the oil absorption of 1.5% SA-SPI-MTMS, it only able to absorb up to 47.37% while the 3.0% SA-SPI-MTMS, it able to absorb to 42.8%. This is because MTMS able to absorb the oil due to silane group in the MTMS. Higher content of SA will decrease the performance of oil absorbing.

4 Conclusions

The aerogel produce able to have good tensile strength due to adding SPI while adding MTMS improve the shrinking content while able to hydrophobic superabsorbent although it is more to absorbent rather than superabsorbent as it cannot absorb oil much more and did not swell after the absorption occur.

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References

- [1] Spagnol, C., Rodrigues, F. H. A., Pereira, A. G. B., Fajardo, A. R., Rubira, A. F., & Muniz, E. C. (2012). Superabsorbent hydrogel composite made of cellulose nanofibrils and chitosan-graft-poly(acrylic acid). *Carbohydrate Polymers*, 87(3), 2038–2045. <https://doi.org/10.1016/j.carbpol.2011.10.017>
- [2] Crystall, B. (2014). Future stuff: Aerogels. *New Scientist*, 224(2990), 39. [https://doi.org/10.1016/S0262-4079\(14\)61958-8](https://doi.org/10.1016/S0262-4079(14)61958-8)
- [3] Rigacci, A., Budtova, T., & Smirnova, I. (2017). Aerogels: a fascinating class of materials with a wide potential of application fields. *Journal of Sol-Gel Science and Technology*, 84(3), 375–376. <https://doi.org/10.1007/s10971-017-4538-1>
- [4] Cortez, J. S. A., Kharisov, B. I., Quezada, T. E. S., & García, T. C. H. (2017). Micro- and nanoporous materials capable of absorbing solvents and oils reversibly: the state of the art. *Petroleum Science*, 14(1), 84–104. <https://doi.org/10.1007/s12182-016-0143-0>
- [5] Greening, H., Swann, R., St. Pé, K., Testroet-Bergeron, S., Allen, R., Alderson, M., ... Bernhardt, S. P. (2018). Local implementation of a national program: The National Estuary Program response following the Deepwater Horizon oil spill in the Gulf of Mexico. *Marine Policy*, 87(July 2017), 60–64. <https://doi.org/10.1016/j.marpol.2017.10.011>
- [6] Zhang, J., & Hu, B. (2013). Liquid-Liquid Extraction (LLE). *Separation and Purification Technologies in Biorefineries*, 61–78. <https://doi.org/10.1002/9781118493441.ch3>
- [7] Arboleda, J. C., Hughes, M., Lucia, L. A., Laine, J., Ekman, K., & Rojas, O. J. (2013). Soy protein-nanocellulose composite aerogels. *Cellulose*, 20(5), 2417–2426. <https://doi.org/10.1007/s10570-013-9993-4>
- [8] Cuadri, A. A., Romero, A., Bengoechea, C., & Guerrero, A. (2017). Natural superabsorbent plastic materials based on a functionalized soy protein. *Polymer Testing*, 58, 126–134. <https://doi.org/10.1016/j.polymertesting.2016.12.024>
- [9] Aghabararpour, M., Mohsenpour, M., Motahari, S., & Abolghasemi, A. (2018). Mechanical properties of isocyanate crosslinked resorcinol formaldehyde aerogels. *Journal of Non-Crystalline Solids*, 481(November), 548–555. <https://doi.org/10.1016/j.jnoncrysol.2017.11.048>
- [10] Wu, X., Wu, Y., Zou, W., Wang, X., Du, A., Zhang, Z., & Shen, J. (2019). Synthesis of Highly Cross-linked Uniform Polyurea Aerogels. *The Journal of Supercritical Fluids*. <https://doi.org/10.1016/j.supflu.2019.04.010>
- [11] Mallepally, R. R., Bernard, I., Marin, M. A., Ward, K. R., & McHugh, M. A. (2013). Superabsorbent alginate aerogels. *Journal of Supercritical Fluids*, 79, 202–208. <https://doi.org/10.1016/j.supflu.2012.11.024>
- [12] Mazraeh-shahi, Z. T., Shoushtari, A. M., & Bahramian, A. R. (2015). A New Approach for Synthesizing the Hybrid Silica Aerogels. *Procedia Materials Science*, 11, 571–575. <https://doi.org/10.1016/j.mspro.2015.11.072>
- [13] Gurav, J. L., Jung, I.-K., Park, H.-H., Kang, E. S., & Nadargi, D. Y. (2010). Silica Aerogel: Synthesis and Applications. *Journal of Nanomaterials*, 2010, 1–11. <https://doi.org/10.1155/2010/409310>

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- [14] Hernandez-Ortiz, J. C., & Vivaldo-lima, E. (2013). 9.1 Introduction. *Handbook of Polymer Synthesis, Characterization, and Processing*, 187–204. <https://doi.org/10.1016/B978-0-444-63249-4.00010-5>
- [15] Baldino, L., Zuppolini, S., Cardea, S., Diodato, L., Borriello, A., Reverchon, E., & Nicolais, L. (2020). Production of biodegradable superabsorbent aerogels using a supercritical CO₂ assisted drying. *Journal of Supercritical Fluids*, 156, 104681. <https://doi.org/10.1016/j.supflu.2019.104681>
- [16] Wang, Y., Su, Y., Wang, W., Fang, Y., Riffat, S. B., & Jiang, F. (2019). The advances of polysaccharide-based aerogels: Preparation and potential application. *Carbohydrate Polymers*, 226(April), 115242. <https://doi.org/10.1016/j.carbpol.2019.115242>
- [17] Júlio, M. de F., & Ilharco, L. M. (2020). Hydrophobic granular silica-based aerogels obtained from ambient pressure monoliths. *Materialia*, 9(November 2019). <https://doi.org/10.1016/j.mtla.2019.100527>
- [18] Smirnova, I., & Gurikov, P. (2018). Aerogel production: Current status, research directions, and future opportunities. *Journal of Supercritical Fluids*, 134(October 2017), 228–233. <https://doi.org/10.1016/j.supflu.2017.12.037>
- [19] Mustapa, A.N., E. Al. (2018). *Alginate Aerogels Dried By Supercritical Co 2 As Herbal*. 22(3), 522–531.
- [20] Meng, C., Zhang, H., Zhang, S., Guo, J., & Zou, X. (2018). The preparation of hydrophobic alginate-based fibrous aerogel and its oil absorption property. *Journal of Sol-Gel Science and Technology*, 87(3), 704–712. <https://doi.org/10.1007/s10971-018-4748-1>