

# EFFECT OF RICE STARCH CONTENT ON TUBULAR ALUMINA MEMBRANE SUPPORT FABRICATED BY AGAR GELCASTING

Suphitchaya Promsomboon<sup>1,3</sup>, Kowit Lertwittayanon<sup>1,3\*</sup>, and Supawan Vichaphund<sup>2</sup>

*Received: October 05, 2023; Revised: February 19, 2024; Accepted: March 14, 2024*

## Abstract

This study addresses the challenge of fabricating cost-effective tubular ceramic membranes through agar gelcasting. The addition of rice starch as the pore-forming agent in the ceramic membrane support layer, with varying contents from 0 to 6 wt%, was focused on improving the permeability of the tubular ceramic membrane. Scanning electron microscopy (SEM) revealed the co-existence of large pores from starch decomposition and small pores in the form of interparticle voids. When the rice starch was enhanced, the firing shrinkage and apparent porosity increased, and the bulk density decreased. Notably, the tubular ceramic membranes with 6 wt% of the rice starch addition exhibited a permeability of  $0.17 \text{ Lh}^{-1}\text{m}^{-2}\text{bar}^{-1}$  under a pressure of 2.5 bar.

**Keywords:** Alumina membrane; ceramic membrane; gel casting; starch

---

<sup>1</sup> Material Science Program, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, 90112, Thailand. E-mail: kowit.l@psu.ac.th; suphitchayaprom2543@gmail.com

<sup>2</sup> National Metal and Materials Technology Center (MTEC), Thailand Science Park, National Science and Technology Development Agency (NSTDA), Pathum Thani, 12120, Thailand. E-mail: supawank@mttc.or.th

<sup>3</sup> Center of Excellence in Membrane Science and Technology, Prince of Songkla University, Hat Yai, Songkhla, 90112, Thailand.

\* Corresponding author

DOI: <https://doi.org/10.55766/sujst-2024-02-e04948>

Suranaree J. Sci. Technol. 31(2):030189(1-6)

## Introduction

Porous ceramic membranes have become a focus of research. In advanced industrial applications, they offer several advantages over their polymer counterparts (Jarvis *et al.*, 2022; Schnittger *et al.*, 2023). Ceramic membranes stand out mainly due to their remarkable thermal, chemical and mechanical resistance, self-cleaning efficiency, long service life and environmentally friendly characteristics (El Magana *et al.*, 2022; Ma *et al.*, 2023; Jiachen *et al.*, 2024; Sawunyama *et al.*, 2024). However, a significant drawback that continues to impede their widespread adoption is their relatively high cost (Aryanti *et al.*, 2020; Hubadillah *et al.*, 2022).

To reduce costs, researchers have looked for cost-effective pore forming agents. Abundant and economical, starch stands out as a highly promising candidate. Several studies have examined the use of starch as a pore-forming agent in the production of ceramic membranes. Li *et al.* (2013) demonstrated the role of starch in linking ceramic powders to facilitate the formation of porosity within the membrane structure. Lorente-Ayza *et al.* (2015) explored using cheap, non-toxic starch derived from various sources as raw materials for creating porosity in ceramic membranes. Their investigation revealed the impact of starch particle size on the membranes' pore size distribution and permeability. It was found that potato starch content affected membrane properties by increasing porosity and water permeability. Lima *et al.* (2015) used corn starch as a pore-forming agent in membrane support layers to treat dairy wastewater. The developed membrane was found to have a porosity of 48% with sufficient mechanical strength and a high enough permeate flux of pure water to perform effectively as a filter for the dairy industry.

In our research, we aim to develop cost-effective ceramic membranes using gel-casting (Gao *et al.*, 2023; Ismail *et al.*, 2023), with alumina as the base material (Li *et al.*, 2013; Lima *et al.*, 2015; Yuan *et al.*, 2021). Our primary objective is to address the cost-related challenges that have hindered the broader application of ceramic membranes. We have chosen rice starch as our preferred pore-forming material due to its exceptional cost-effectiveness. This choice builds upon previous researchers' work who demonstrated starch's efficacy as a porosity enhancer (Li *et al.*, 2013; Lima *et al.*, 2015; Lorente-Ayza *et al.*, 2015a, 2015b;). Furthermore, our research emphasizes the meticulous control of membrane microstructure. In addition to studying the influence of starch content on microstructural characteristics, we also examined its impact on permeability and other

relevant properties. We aimed to design and produce low-cost ceramic membranes that reduce the cost currently associated with ceramic membranes and produce optimal performances. This research could advance the practicality and affordability of ceramic membranes, potentially paving the way for their broader adoption in various industrial applications.

## Materials and Methods

### Raw Materials

$\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder (TM-5D, Taimei Co., Ltd., Japan) with an average particle size of 0.2  $\mu$ m was used to fabricate the support layer of the tubular ceramic membranes. MgO nanopowder (Alfa Aesar) was employed as a sintering aid to enhance the melting properties and sintering of materials.

The ammonium salt of polyacrylic acid (Dispex AA4040, BASF) was used as a dispersant (Udomsri *et al.*, 2022). Rice starch served as both a porosity generator and binder. Agar powder was used as the gelling agent in liquid suspensions, and acetone was used as a drying agent. During membrane preparation, reverse osmosis (RO) water was employed.

### Fabrication of Tubular Alumina Membrane Support

To create a well-balanced mixture, 80 wt% of alumina powder, 0.03 wt% of MgO, and Dispex dispersant were combined. This blend was then thoroughly mixed with RO water. The prepared alumina slurry was poured into high-density polyethylene (HDPE) bottle and ball-milled for 2 h to obtain a homogeneous distribution of particles within the slurry. After ball milling, the alumina slurry was weighed to maintain precision throughout the procedure. The slurry was then placed in an ultrasonic bath set to a temperature of 50°C. Separately, an agar solution was prepared by blending agar powder with RO water to an agar concentration of 2 wt%. The agar solution was then boiled and mixed with the alumina slurry at 50°C. Rice starch was introduced into the warm alumina slurry while the temperature was maintained at 50°C. Rice starch was incorporated at concentrations of 0, 2, 4, and 6 wt% of solid loading. The obtained mixture was poured into a glass tube. Once the ceramic membrane tube was formed, it was removed from the glass mold. The obtained membrane was cut and ground to the desired shape and dimensions. The various tube membranes were

then sintered at 1,300°C for 2 h and a heating rate of 10°C/min. The final products were characterized to assess their properties, integrity, and suitability for their intended application.

### Characterization of Tubular Alumina Membrane

The microstructure was employed to identify potential defects and evaluate the pore structure of the sintered tubular alumina membranes. The analysis used the Scanning Electron Microscope, specifically the JEOL JSM-5800 LV (SEM5800). Firing shrinkage, apparent porosity, and bulk density were measured following the ASTM C373-88 method, with RO water as the immersion medium. Roundness is linked to the maximum and minimum tube diameters ( $D_{\max}$  and  $D_{\min}$ ), measured from various positions around the sectional circumference, defined by Equation (1):

$$\text{OOR} = D_{\max} - D_{\min} \quad (1)$$

Where  $D_{\max}$  is the largest measured inside or outside diameter, and  $D_{\min}$  is the smallest measured inside or outside diameter (Bai and Bai, 2014).

### Water Permeability Experiment

In the filtration section, it is important to highlight that each experiment involved four distinct membrane samples. Water permeability was assessed through filtration at varying pressures under room temperature conditions. The applied transmembrane pressure ranged from 1 to 2.5 bar. The permeate flux ( $J$ ) in filtration parameters was computed using Equation (2):

$$J = \frac{V}{A \times t} \quad (2)$$

Where  $V$  (L) is the volume of permeate,  $A$  ( $\text{m}^2$ ) is the effective membrane area, and  $t$  (h) is the filtration time (Mobilian and Craft, 2022).

## Results and Discussion

### Microstructure of Ceramic Membrane

The prepared ceramic membranes were investigated using scanning electron microscopy (SEM). The SEM images of the membrane material with 0 wt.% rice starch, as shown in Figures 1(a) and 1(b), showed surfaces free from rice starch particles. This absence indicated that the membrane surface remained unaltered, preserving its original configuration. On the other hand, the SEM images of membranes with 6 wt.% of rice starch, as shown in Figures 1(c) and 1(d), revealed large pores caused by the addition of a pore-forming agent from the rice starch, which is a critical factor influencing membrane performance. The increased porosity was a result of the presence of the rice starch.

### Physical Properties

#### Firing Shrinkage Percentages

The ceramic alumina, adding rice starch at 0, 2, 4, and 6 wt%, exhibits varying shrinkage values: 0.79, 0.14, 0.54, and 0.68%, as shown in Figure 2.

The decrease in shrinkage from 0.79 to 0.14 with increasing rice starch indicates the influence on overall shrinkage dynamics during the sintering process. At the lower loadings (0-2 wt% rice starch), the decreased shrinkage (0.14%) at 2 wt% indicates a small quantity of rice starch added, serving as a binder is well-distributed with the alumina ceramic particles. In the preparation process, the rice starch dissolves and then encapsulates,

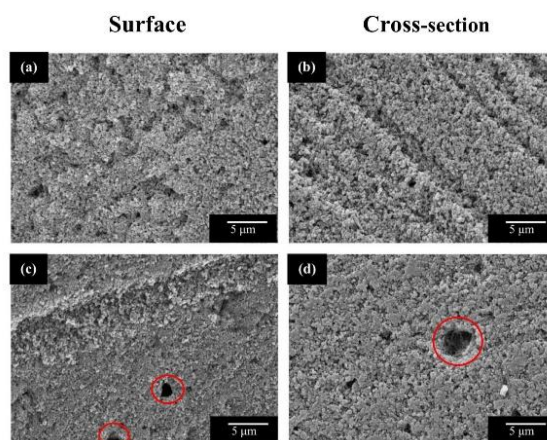


Figure 1. SEM images show the proposed membrane material with rice starch content of 0 wt% at (a) the membrane surface and (b) the cross section and with rice starch content of 6 wt% at (c) the surface and (d) the cross section

wrapping around the alumina ceramic particles. This effect of the preparation process results in the combined shrinkage between the alumina particles and the rice starch, ultimately reducing the overall shrinkage.

Conversely, when the rice starch content exceeds 2 wt%, the enhanced solubility of the rice starch causes it to encase the alumina ceramic particles, forming a thick layer. During the sintering process, this thick layer leads to the loose arrangement of the sintered ceramic particles and, consequently, increased shrinkage. The shrinkage from adding rice starch content ranging from 0 to 6 wt% was a very small value, less than 1%. This suggests that adding rice starch during this period has little effect on shrinkage.

### Porosity and Bulk Density

As the porosity of the membrane increased, bulk density declined, as shown in Figure 3. This result is rooted in the fundamental principle that porosity and bulk density share an inverse relationship (Mobilian and Craft, 2022). At elevated amounts of rice starch, the tubular alumina membrane undergoes pronounced shrinkage

initially due to densification during the sintering process. However, as the rice starch content further increases, it serves as a pore-forming agent. The still granular rice starch decomposes throughout firing, creating voids or pores within the membrane structure. The porosity of the sintered membrane diminishes the overall mass per unit volume, consequently resulting in reduced density.

For rice starch amounts at 0-4 wt%, the percentage of porosity increased slightly and reached 4%, while the percentage of porosity at 4-6 wt% rapidly increased to 19%. This suggests that its effect may imply a decrease in the strength of the tubular membrane support, leading to increased shrinkage percentages, as shown in Figure 2. However, the subsequent presence of rice starch-induced pores impedes the extent of contraction, resulting in a ceramic structure characterized by lower density and increased porosity.

### Roundness

The roundness of the various tubular ceramic membranes followed a consistent trend, increasing as the rice starch content increased (Figure 4).

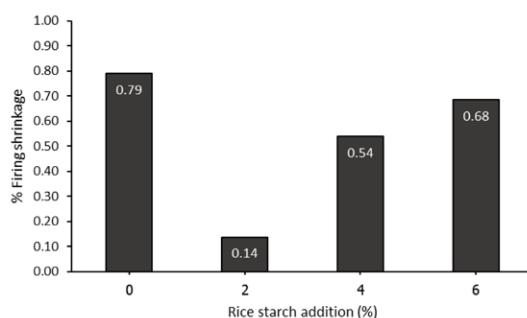


Figure 2. Firing shrinkage percentage of tubular ceramic membrane with contents of rice starch at 0, 2, 4 and 6 wt%

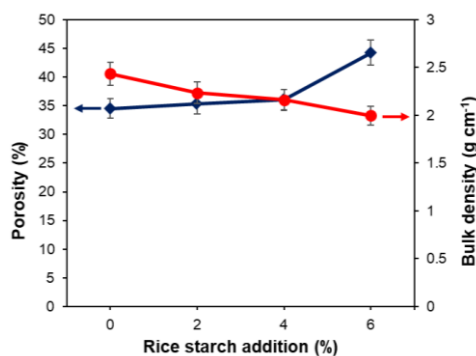


Figure 3. Porosity and bulk density of tubular ceramic membranes with rice starch contents at 0, 2, 4 and 6 wt%

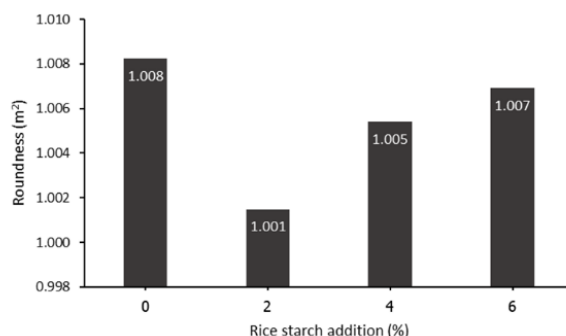


Figure 4. Roundness of tubular ceramic membranes with rice starch contents of 0, 2, 4 and 6 wt%

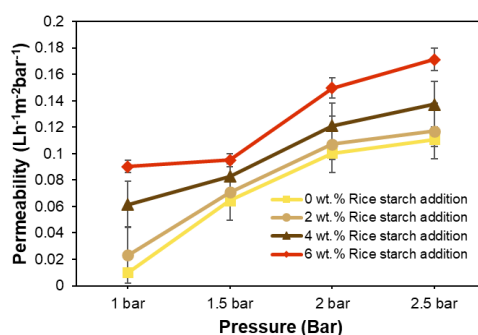


Figure 5. Permeability of tubular ceramic membranes with rice starch contents of 0, 2, 4 and 6 wt%

All compositions exhibited a uniform roundness value of approximately 1, underscoring a consistent morphology.

### The Permeability of the Prepared Membranes

As the rice starch content increased, the permeability of the tubular ceramic membrane also increased, as shown in Figure 5. The heightened porosity leads to increased permeability. The rise in permeability due to the addition of rice starch up to 6 wt% can be attributed to the pore-forming effect of rice starch, creating the most porous structure that finally enhances fluid flow through the membrane. This result aligns with the findings on the porosity and density of the tubular ceramic membrane in Figure 3.

### Conclusions

The rice starch significantly influences membrane properties and serves as the pore-forming agent in the support layer of alumina ceramic membranes through the gel casting method. SEM examination revealed that the porosity increases with higher rice

starch contents. Additionally, there is increased firing shrinkage and decreased density. The increased porosity, leading to the expansion within the membrane structure, potentially enhanced the substance flow through the membrane. The highest permeability observed of the sample containing the rice starch of 6 wt% reached  $0.17 \text{ Lh}^{-1}\text{m}^{-2}\text{bar}^{-1}$ , under the pressure of 2.5 bar.

### Acknowledgement

This research work was financially supported by the Thailand Graduate Institute of Science and Technology (TGIST) (grantee code: SCA-CO-2565-17190-TH)

### References

- Aryanti, P.T.P., Subroto, E., Mangindaan, D., Widiasta, I.N., and Wenten, I.G. (2020). Semi-industrial high-temperature ceramic membrane clarification during starch hydrolysis. *Journal of Food Engineering*, 274:109844.
- Bai, Q. and Bai, Y. (2014). 4 - Limit-state based strength design. *Subsea Pipeline Design, Analysis, and Installation*, p. 67–87. <https://doi.org/10.1016/B978-0-12-386888-6.00004-3>

- El Magana, Y., Elhadiri, N., Benchanaa, M., Chikri, R., Idouhli, R., and Tabit, K. (2022). Low-cast and high-performance ceramic membrane from sugar industry waste: Characterization and optimization using experimental design. *Materials Today: Proceedings*, 53(2):310-317. <https://doi.org/10.1016/j.matpr.2022.02.208>
- Gao, J., Cao, H., Hu, X., Mao, H., Chen, X., Qiu, M., Verweij, H., and Fanm Y. (2023). Piezoelectric porous  $\alpha$ -quartz membrane by aqueous gel-casting with enhanced antifouling and mechanical properties. *Journal of the European Ceramic Society*, 43(1):109-120. <https://doi.org/10.1016/j.jeurceramsoc.2022.09.038>
- Hubadillah, S.K., Jamalludin, M.R., Othman, M.H.D., and Iwamoto, Y. (2022). Recent progress on low-cost ceramic membrane for water and wastewater treatment. *Ceramic International*, 48(17):24157–24191. <https://doi.org/10.1016/j.ceramint.2022.05.255>
- Ismail, H., Zakri, M.N.Z., Ahmad, A., and Mohamad, H. (2023). Effect of sintering temperature on the phase, microstructural, physical, mechanical, and in vitro biomineralisation properties of porous wollastonite ceramics fabricated using the gel casting method. *Ceramics International*, 49(9):14166-14176. <https://doi.org/10.1016/j.ceramint.2023.01.003>
- Jarvis, P., Carra, I., Jafari, M., and Judd, S.J. (2022). Ceramic vs polymeric membrane implementation for potable water treatment. *Water Research*, 215:118269. <https://doi.org/10.1016/j.watres.2022.118269>
- Jiachen, M., Tao, L., Wei, L., Zhengbin, Z., and Yong, Y. (2024). Cleaning efficiency and mechanism of ozone micro-nano-bubbles on ceramic membrane fouling. *Separation and Purification Technology*, 331:125698. <https://doi.org/10.1016/j.seppur.2023.125698>
- Li, S., Wang, C.-A., and Zhou, J. (2013). Effect of starch addition on microstructure and properties of highly porous alumina ceramic. *Ceramics International*, 39(8):8833–8839. <https://doi.org/10.1016/j.ceramint.2013.04.072>
- Lima, L.K.S., Santana, L.N.L., Lira, H.L., Rodríguez, M.A., Souza, M.Y.M., Júnior, M.G.S., and Lira, B.S. (2024). Development of asymmetric ceramic membranes for dairy wastewater treatment - A comparison between co-sintering and conventional firing process. *Journal of Water Process Engineering*, 57:104611. <https://doi.org/10.1016/j.jwpe.2023.104611>
- Lorente-Ayza, M.M., Orts, M.J., Perez-Herranz, V., and Mestre, S. (2015). Role of starch characteristics in the properties of low-cost ceramic membranes. *Journal of the European Ceramic Society*, 35:2333-2341. <https://doi.org/10.1016/j.jeurceramsoc.2015.02.026>
- Lorente-Ayza, M-M., Sanchez, E., and Mestre, S. (2015). Influence of starch content on the properties of low-cost microfiltration ceramic membranes. *Ceramics International*, 41(10):13064-13073. <https://doi.org/10.1016/j.ceramint.2015.07.092>
- Ma, J., Chen, W., Qian, J., Shui, A., Du, B., and He, C. (2023). Co-pressing and co-sintering preparation of cost-effective and high-performance asymmetric ceramic membrane for oily wastewater treatment. *Separation and Purification Technology*, 323:124373. <https://doi.org/10.1016/j.seppur.2023.124373>
- Mobilian, C. and Craft, C.B. (2022). Wetland Soils: Physical and Chemical Properties and Biogeochemical Processes. In: *Encyclopedia of Inland Waters*. 2<sup>nd</sup> ed. Mehner, T. and Tockner, K. (eds.). Elsevier, p. 157-168. <https://doi.org/10.1016/B978-0-12-819166-8.00049-9>
- Sawunyama, L., Ajiboye, T.O., Oyewo, O., and Onwudiwe, D.C. (2024). Ceramic-polymer composite membranes: Synthesis methods and environmental applications. *Ceramic International*, 50(3):5067-5079. <https://doi.org/10.1016/j.ceramint.2023.11.337>
- Schnittger, J., McCutcheon, J.R., Hoyer, T., Weyd, M., Voigt, I., and Lerch, A. (2023). Modified ceramic membranes for the treatment of highly saline mixtures utilized in vacuum membrane distillation. *Desalination*, 567:116943. <https://doi.org/10.1016/j.desal.2023.116943>
- Udomsri, N., Promsawat, M., Sirijarakul, S., and Lertwittayanon, K. (2022). Effect of clay addition to  $\text{Al}_2\text{O}_3$ -agar mixture on pore size and distribution of tubular  $\text{Al}_2\text{O}_3$  membrane support fabricated by agar gelcasting. *Materials Today: Proceedings*, 65(4):2426-2431. <https://doi.org/10.1016/j.matpr.2022.06.043>
- Yuan, L., Liu, Z., Tian, C., Yan, Z., Yu, J., Hou, X., and Zhu, Q. (2021). Structure and properties of  $\text{Al}_2\text{O}_3$ -bonded porous fibrous YSZ ceramic fabricated by aqueous gel-casting. *Ceramics International*, 47(18):25408–25415. <https://doi.org/10.1016/j.ceramint.2021.05.263>