

MORPHOLOGY AND HYDROPHOBICITY OF AGAR, BEESWAX, AND AGAR-BEESWAX EMULSION COATED ON POROUS ALUMINA SUPPORT

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Abstract

Membrane degassing technology is based on the principle of hydrophobicity. Up-to-date, the membrane degasifier is industrially produced by extrusion and then stretched to form a hollow fiber shape with long narrow pores along membrane length. Typical degasifiers are engineered with polypropylene (PP) due to its high toughness and flexibility. However, finding environmentally safe materials at a low cost for replacement for PP would be worth investigating. In this work, agar, beeswax, and their emulsion were coated on a tubular alumina membrane for use as a selective layer of the membrane degasifier. The agar solution with different concentrations between 1 and 4 wt% was coated on the alumina membrane support to create a pore network. Beeswax was coated on agar film to enhance the hydrophobicity. SEM images showed that the increase in the concentrations of agar led to a decreased pore size of the selective layer. Moreover, the contact angle increased up to 100° when the concentration of agar solution increased to 4 wt%. The increase in contact angle to 120° was obtained when the beeswax was coated, appropriate for hydrophobic applications.

Keywords: Agar; beeswax; contact angle; hydrophobicity; membrane degasifier

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Introduction

In the process of producing clean water for power plants generating electricity by steam turbine method, membrane degasifiers are used for CO₂ degassing out of water. The presence of carbon dioxide (CO₂) in the water, forming as carbonic acid (H₂CO₃) and thereby dissolving in the water, provokes adverse effects such as corrosion and erosion of the metallic turbines, ultimately disturbing the overall process of the electricity generated. The membrane degasifier stands out as a promising method due to numerous advantages, such as high CO₂ selectivity, reduced energy consumption, lower chemical usage, continuous operation, and adaptability (Svoboda *et al.*, 2003; Svoboda, 2009; Lee *et al.*, 2015; Lee and Park, 2016; Abdulhameed *et al.*, 2017; Goh *et al.*, 2019; Zhao *et al.*, 2022).

Typically, the membrane degasifier is fabricated into a hollow microporous fiber made of polymeric materials, for example, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), and polypropylene (PP) due to their excellent toughness and flexibility. However, these polymer-based membranes were susceptible to heat and chemical corrosion, necessitating frequent replacement, thereby leading to long-term costs (Lee *et al.*, 2015; Lee and Park, 2016; Goh *et al.*, 2019; Zhao *et al.*, 2022). In addition to the susceptibilities, the inherent porous single layer from their preparation resulted in a common leakage issue when the operation pressure increased. Consequently, finding alternative materials for membrane construction is a significant challenge. Among various options, composite membranes were particularly intriguing due to several advantages in various separation processes compared to single-material membranes. It harnessed the strengths of different materials by combining the high strength of inorganic materials support, such as ceramic membrane (alumina, titanium, zirconium oxides, silicon carbide) (Macedonio *et al.*, 2017), with the cost-effective and environmentally safe biopolymers, resulting in a positive trade-off between performance and costs (Buonomenna, 2016; Ioioiu *et al.*, 2017). Additionally, it was highly likely to reuse the ceramic support in the case of degradation of the biopolymers. Therefore, the cost of membrane preparation markedly decreased, which was attractive for industrial uses.

Agar, a kind of biopolymer extracted from red seaweeds, is an economical material known for its unique gelation process. It leads to the formation of robust three-dimensional structures when cooled after dissolving in hot water (Yarnpakdee *et al.*,

2015; Wang *et al.*, 2018). The specific gel structure created is closely related to the concentration of agar solution. Thus, it is intriguing to consider agar as the selective layer for modifying the surface properties of ceramic membrane support. However, both the ceramic support and the agar selective layer is hydrophilic. To optimize the degasification process, it is crucial to ensure that only gases can permeate the membrane while effectively preventing the passage of water. Therefore, exploring environmentally friendly hydrophobic materials is a critical step toward sustainability. Beeswax, a natural wax distinguished by its non-polar carbon-hydrogen bonds in its hydrocarbon chains, offers significant water-repelling capability (Abdikheibari *et al.*, 2015; Naderizadeh *et al.*, 2019; Malik *et al.*, 2020; Dong *et al.*, 2021; Zhang *et al.*, 2022). This capability makes beeswax particularly appealing for enhancing the resistance to water permeation of agar coated on ceramic surfaces. Agar and beeswax are cheap, natural substances and readily available materials. Thus, when the top layer is damaged and delaminated, it is possible to apply a re-coat while retaining the old support layer, resulting in a highly cost-effective solution. However, there has been no prior research on the combined utilization of these materials. Therefore, in this study, we aim to investigate the potential of natural wax in combination with agar to form a hydrophobic coating on alumina membrane tubes. Our focus was on conducting preliminary experiments to prepare and characterize alumina-kaolin membranes coated with agar as an intermediate layer, followed by using beeswax and agar-beeswax emulsion as the top layer using the dip-coating method. The Al₂O₃ support layer with a tubular shape was prepared using the same formula employed consistently throughout the experiment. Various concentrations of agar solution, ranging from 1 to 4 wt%, were utilized to modulate the porous structure and pore size. We investigated the influence of agar solution concentrations, beeswax solution, and agar-beeswax emulsion on the morphology and hydrophobicity using SEM, FE-SEM, and contact angle measurements, respectively.

Materials and Methods

Materials

Al₂O₃ powder (α -Al₂O₃) with an average particle size of 0.167 μ m (TMDAR, Taimei Co., Ltd., Japan) was used for preparing the tubular

Al₂O₃ membrane support. Ranong kaolin (local supplier, Thailand) was mixed with Al₂O₃ powder to create a more porous structure. Ammonium salt of polyacrylic acid (Dispex AA 4040, BASF) was used as a dispersant. MgO nanopowder (Alfa Aesar) was used as a sintering aid. Acetone (99%) was used for liquid-assisted drying. Agar (local supplier, Thailand) was used as a gelling agent. Beeswax (Chemipan Corporation Co., Ltd., Thailand) was used to improve the hydrophobicity. Glycerol monostearate (GMS, Chemipan Corporation Co., Ltd., Thailand) and polyethylene glycol 400 (PEG 400) were used as emulsifiers.

Preparation of Al₂O₃ Membrane Support

For the alumina membrane support, which has been consistently utilized in this work based on experiments conducted in our laboratory, it exhibits optimal properties as required by this study (Udomsri *et al.*, 2022). The Al₂O₃ support was fabricated using the agar gel casting method. The preparation process involved mixing 8 wt% kaolin particles with the Al₂O₃ powder to prepare an Al₂O₃ slurry with 75 wt% solid loading. Dispex AA 4040 was added at 1 wt% of solid loading following a deflocculating curve test, and MgO was included at 0.03 wt% of solid loading. The kaolin particles were ball-milled for 45 min to ensure proper dispersion before being mixed with the Al₂O₃ powder. All raw materials were ball-milled in high-density polyethylene bottles for 2 h. The Al₂O₃-kaolin mixture was then homogenized at 700 rpm for 30 min.

The agar powder was dissolved in deionized water by boiling to prepare agar solutions at concentrations of 1-4 wt%. The warm agar solution was mixed with the warm Al₂O₃ slurry at 0.5 wt% of solid loading and stirred to obtain a homogeneous gel casting mixture. The mixture was poured into glass tube molds carefully to avoid trapping air bubbles. After gelation, the gel cast tube was removed from the molds and soaked in acetone. Finally, the gelled tube was removed from the acetone container and dried before sintering at 1,350°C for 1 h.

Dip Coating on Tubular Porous Al₂O₃ Support

After sintering to obtain the tubular porous Al₂O₃ support, dip coating was applied to an intermediate layer to anchor the top layer. The intermediate layer was prepared from agar solution at different concentrations at 1, 2, 3, and 4 wt% before being individually coated on the Al₂O₃ support. The surface of coated Al₂O₃ support was observed by SEM and then selected for further coating the top layer functioning as the degasifying layer. The top layer must be hydrophobic to allow

only CO₂ gas to pass through but prevent water from permeation. The emulsion of agar/beeswax as well as the pristine beeswax, were prepared as a solution for the dip coat on the intermediate layer. To prepare the emulsion of agar/beeswax, the agar powder was dissolved by boiling in de-ionized water until a clear yellow solution was obtained. Subsequently, glycerol was added into the agar solution at 30 wt%. The emulsifiers, i.e. GMS and PEG400, were mixed at a ratio of 7 to 1. Finally, the water-in-oil (w/o) emulsion of beeswax, emulsifiers, and agar solution was prepared at a proportion of 40, 50, and 10 wt%, respectively. All the warm prepared solutions were mixed at 180°C for 30 min. To eliminate entrapped air bubbles, the emulsion was treated in a 15-min ultrasonic bath and subsequently homogenized at 12,000 rpm for 10 min. In the top-layer dip coating process, the agar-modified support surface was immersed in the emulsion and pristine beeswax at 50°C for 3 sec, followed by air-drying at room temperature.

Characterization

The surface morphology and microstructure of coated Al₂O₃ support tubes in the first and second dip-coatings were observed with SEM (JEOL: JSM-5,800 LV/Bruker XFlash EDS) at 10,000x magnification. The samples of coated support were placed on a brass substrate and then sputtered by gold under an Ar atmosphere for 3 min. The top coating layer was observed for the surface microstructure using Field Emission Scanning Electron Microscope (FEI/Apreo FE-SEM) at 1,000x, 5,000x, and 10,000x magnification. The ceramic membrane surface was evaluated by a water drop contact angle meter (OCA 15 EC, SCA 20 software). To minimize the experimental error, the water contact angle was averaged by the three measurements.

Results and Discussion

Microstructure of Agar-Coated Ceramic Support for Intermediate Layer

Surface morphology of tubular alumina-kaolin support coated by agar prepared from the different concentrations of agar solution ranging from 1 to 4 wt% was observed using SEM at 10,000x magnification, as shown in Figure 1. The SEM results revealed a notable distinction in the surface morphology, demonstrating the effective solution concentration. At low concentrations of 1 to 2 wt%, the coated layer appeared as a thin film with evident cracks, likely stemming from the insufficient amount of agar and excess water. Consequently, during the drying stage, water evaporation led to

separation between the clusters of agar double helixes, eventually resulting in ruptures. The positively critical transition occurred at the solution concentration of 3 wt%, where no crack was observed, although the surface remained rough. However, when considering coating the support layer with 4 wt% agar solution concentration a smooth film surface without crack was yielded. The absence of cracks at these higher concentrations of 3 and 4 wt% implies the formation of a more cohesive and stable agar layer, effectively mitigating potential surface defects or discontinuities. Furthermore, the augmentation of agar molecules or the concentrations were found to correspond with an increased density of the brush-pile structure of micelles, thereby influencing the gel strength (Kendrick, 1950; Bertasa *et al.*, 2020). Consequently, to achieve a crack-free coating, the 3 and 4 wt% agar solution concentrations were chosen for further

blending with beeswax to form a top-layer emulsion and provide hydrophobicity.

Field Emission Scanning Electron Microscopy (FE-SEM) of the Coating Layer

The overall surface morphology of alumina coated with 3-4 wt% agar as the intermediate layer, followed by beeswax, and agar-beeswax emulsion shown in Table 1.

Agar Coating For an Intermediate Layer

Field Emission Scanning Electron Microscopy (FE-SEM) at 5000 $\times$ magnification revealed the structural surface morphology of the tubular alumina-kaolin support, showing uniformly distributed pores (Figure 2). When the support was coated with agar solution as an intermediate layer, further examination at 50,000 $\times$ magnification using FE-SEM showed intricate and fine cracks on

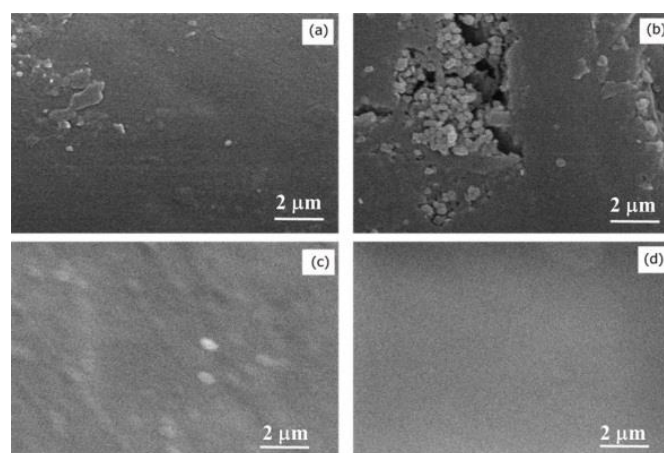


Figure 1. Shows SEM images of the surface (10,000 $\times$ magnification) prepared at different concentration agar coating on ceramic membrane tube. (a) agar 1 wt%, (b) agar 2 wt%, (c) agar 3 wt%, and (d) agar 4 wt%

Table 1. Shows the overall preparation and characterization of the composite samples

Sample	Preparation Procedures	Morphology by FESEM	Hydrophobicity (contact angle $^{\circ}$)
1	Alumina-kaolin support	Uniform porous structure	7.6
2	Alumina support coated by 3wt% agar solution	Quite smooth surface, rough cracks	43.1
3	Alumina support coated by 4wt% agar solution	Smoothest surface, finer cracks	105.7
4	Alumina support coated by 3wt% concentrated agar solution and then followed by 3wt% agar-beeswax emulsion	Macro-emulsion system, uneven dispersion of agar droplets	73.4
5	Alumina support coated by 4wt% concentrated agar solution and then followed by 4wt% agar-beeswax emulsion	Two main regions: evenly distributed clusters of droplets, smooth surface	86.1
6	Alumina support coated by 3wt% concentrated agar solution and then followed by pure beeswax,	Random accumulation of beeswax, some areas had tiny voids.	87
7	Alumina support coated by 4wt% concentrated agar solution and then followed by pure beeswax.	Roughness surface, more uniform spread of beeswax, and larger agglomerates of beeswax particles.	123.4

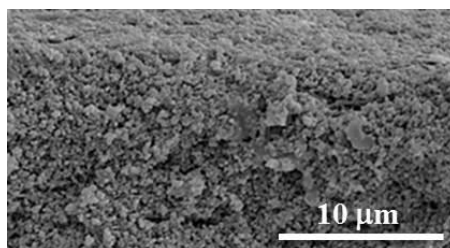


Figure 2. Shows FE-SEM images of the surface of alumina-kaolin tabular support at 5,000X magnification

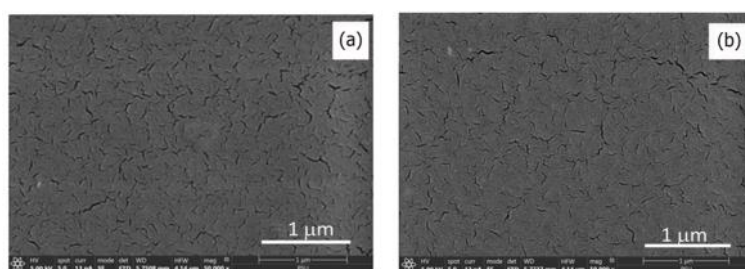


Figure 3. Shows FE-SEM images of the surface coated on alumina-kaolin tabular support at 50,000X magnification for the concentrations of agar solution at (a) 3 and (b) 4 wt%

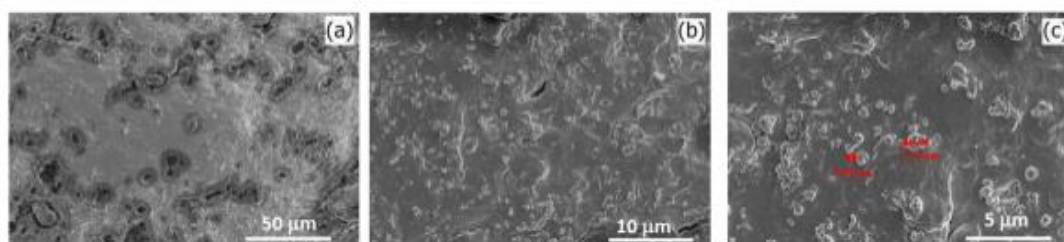


Figure 4. Shows FE-SEM images of the surface initially coated with an agar solution of 3 wt% concentration and subsequently layered with an emulsion composed of agar of 3 wt% and beeswax at (a) 1,000x, (b) 5,000x, and (c) 10,000x magnification

the surface, resembling patterns seen in soil undergoing desiccation-induced cracking. These cracks were particularly evident on the surface coated with the 3 wt% agar solution (Figure 3(a)). In the layer coated with the 4 wt% agar solution (Figure 3(b)), the surface appeared notably smoother, with smaller cracks than the 3 wt% agar solution. From the mechanism of gelling formation from the random coil while still in the solution until the temperature decreases to form a double helix, which combines with hydrogen bonds resulting in a strong 3D lattice structure. Higher concentrations of agar enhance the strength, leading to the assembly of more double helices in the molecular chains and causing the polymer network to shrink into smaller cavities (Kendrick, 1950).

Agar-Beeswax Emulsion Top-Layer

To emulsify agar, recognized as a hydrophilic polysaccharide (Kendrick, 1950), and beeswax, a naturally hydrophobic wax (Martins *et al.*, 2016), emulsifiers were added containing both hydrophilic and hydrophobic groups, such as GMS, and PEG400. These bonding agents facilitated a more even dispersion of smaller agar particles throughout the film matrix (Zhang *et al.*, 2022). Figure 4 shows the surface morphology of 3 wt% agar-beeswax emulsion top layer coated on the intermediate layer of 3 wt% agar solution. FE-SEM analysis revealed uneven dispersion of the agar solution droplet with varying sizes and shapes ranging from 0.69 to 1.55 μm in diameter within the continuous beeswax matrix. It was found that the emulsion was at

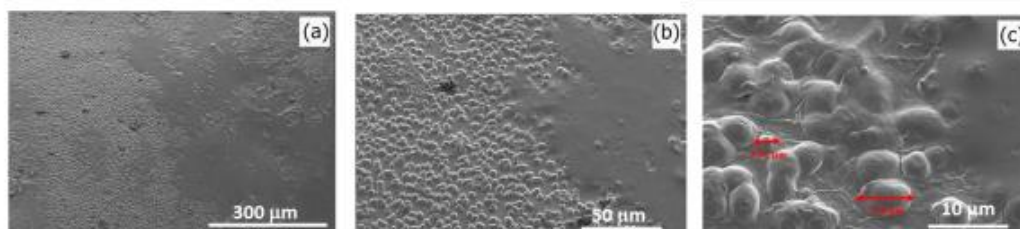


Figure 5. Shows FE-SEM images of the surface initially coated with an agar solution of 4 wt% concentration and subsequently layered with an emulsion composed of agar of 4 wt% and beeswax at (a) 1,000x, (b) 5,000x, and (c) 10,000x magnification

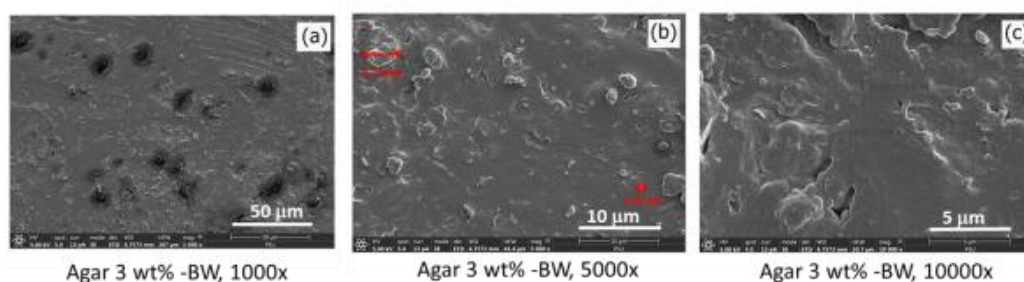


Figure 6. Shows FE-SEM images of the ceramic tube surface were initially coated with 3 wt% agar solution and subsequently layered with beeswax at (a) 1,000x, (b) 5,000x, and (c) 10,000x magnification

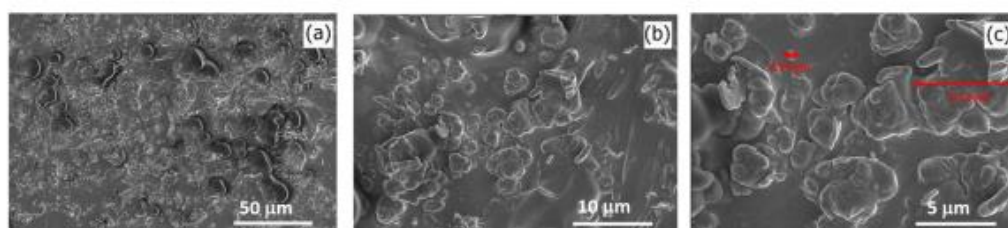


Figure 7. Shows FE-SEM images of the ceramic tube surface were initially coated with an agar solution 4 wt% and subsequently layered with beeswax at (a) 1,000x, (b) 5,000x, and (c) 10,000x magnification

the macro emulsion level because there was not enough mechanical energy to create a smaller droplet size (Akbari and Nour, 2018).

Nevertheless, the surface morphology of 4 wt% agar-beeswax emulsion top layer coated on the intermediate layer of 3 wt% agar solution in Figure 5 shows the two main regions consisting of the region characterized by the clusters of the evenly distributed agar droplets more than 3 wt% agar ranging from 3.31 to 7.24 μm in diameter within the beeswax matrix and the region exhibiting the smooth surface of the beeswax, suggesting partial encapsulation of beeswax droplets within the agar matrix. Notably, when examining agar clusters at 5,000x magnification (Figure 5(c)), no voids were evident between the interfaces. Higher agar concentrations lead to decreased water

content, resulting in a more viscous emulsion that enhances stability. The region with agar droplets appears more evenly distributed than in 3% agar. Additionally, many factors such as surfactants, temperature, stirring speed, and emulsification duration can cause separation into two sides. Emulsion systems are thermodynamically unstable due to contact between molecules of different phases, which can break over time (Akbari and Nour, 2018).

Pure Beeswax Top-Layer

The surface of the top layer from the coating pure beeswax on the agar layer was observed by FE-SEM, as shown in Figures 6 and 7. Furthermore, Table 1. presents the comprehensive results of the surface characteristics. In the context of a 3 wt%

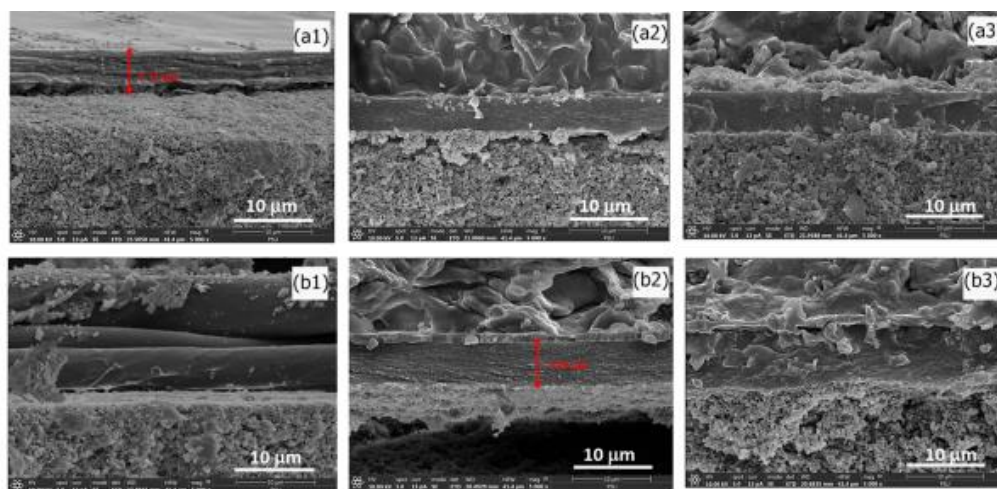


Figure 8. Shows FE-SEM images of a cross section of the composite tube samples with 5,000x magnification for
 (a1) alumina support coated by 3 wt% concentrated agar solution,
 (a2) alumina support coated by 3 wt% concentrated agar solution and then followed by 3 wt% agar-beeswax emulsion,
 (a3) alumina support coated by 3 wt% concentrated agar solution and then followed by pure beeswax,
 (b1) alumina support coated by 4 wt% concentrated agar solution,
 (b2) alumina support coated by 4 wt% concentrated agar solution and then followed by 4 wt% agar-beeswax emulsion, and
 (b3) alumina support coated by 4 wt% concentrated agar solution and then followed by pure beeswax

agar concentration referred to in Figure 6, the beeswax was randomly accumulated, displaying diverse sizes. The diameter of the beeswax clusters exhibited a range from 1.39 to 4.70 μm . The investigation of the beeswax surface revealed a blend of smooth textures and the existence of smaller particles, with certain areas featuring small voids, which may be the cause of the low hydrophobicity of the surface. In contrast, when applying pure beeswax at the 4 wt% agar concentration, as shown in Figure 7, certain areas of the coating beeswax displayed a rough surface, appeared more evenly spread, and a majority of beeswax clusters formed larger agglomerates compared to those observed at the 3 wt% agar concentration. The distribution size of the beeswax particles ranged from 0.94 to 6.52 micrometers. Beeswax was characterized by notable attributes of elevated hardness and strong cohesiveness (Fei and Wang, 2017). It possessed gelling capacity, particularly at minimal crystalline mass fractions. Furthermore, the linear arrangement of beeswax crystals, formed by their molecular constituents, mimics the structural network found in fat crystals (Rocha *et al.*, 2013; Martins *et al.*, 2016; Gupta and Anjali, 2023).

Cross-Section Thickness of Intermediate and Top Layers

The cross-section images of the tabular support coated with the agar solution and subsequently treated with the beeswax or the agar-beeswax emulsion are displayed in Figure 8(a1-b3). For the 3 wt% agar concentration, as shown in Figure 8(a1), an average thickness of approximately 5 μm was achieved. The surface exhibited voids at the junctions of the agar and alumina support layer, which might be attributed to the forces exerted during the sample preparation for FE-SEM analysis. At the higher agar concentration of 4 wt%, as shown in Figure 8(b1), the increased molecular density of agar resulted in a thicker layer (Kendrick, 1950), measuring 6-7 μm under the same coating condition. Within the emulsion layer between agar and beeswax, observed at the 3 wt% agar concentration referred to Figure 8(a2) and 4 wt% agar concentrations referred to Figure 8(b2), three distinct and well-defined layers were evident: the alumina support, the agar intermediate layer, and the emulsion top layer. In the case of 3 wt% agar concentration, the interface between the agar and beeswax exhibited good adhesion, while a slight separation between the agar and alumina support

layers were observed, likely due to the forces applied during sample analysis via FE-SEM. Conversely, for the 4 wt% agar concentration, the interfaces between the layers appeared smooth and well-bonded. The top emulsion layer revealed interstitial spaces between particles of the agar-beeswax emulsion, similar to the situation when pure beeswax was applied to 3 wt% agar layer (Figure 8(a3)), showing minor interstices between the beeswax layers. However, when the beeswax was applied to the 4 wt% agar concentration (Figure 8(b3)), the beeswax particles were densely packed due to the base provided by the higher concentration of agar molecules, which is associated with higher gel strength (Bertasa *et al.*, 2020).

Contact Angle

The hydrophobicity of tubular alumina support coated with three distinct solutions agar (3–4 wt%), an agar-beeswax emulsion, and pure beeswax, alumina membrane support was evaluated through the contact angle measurement as shown overall in Table 1 and in Figure 9(a1)–9(c). Applying the 3 wt% agar solution to coat the alumina support tubular (Figure 9(a1)) resulted in a notable rise in the contact angle with the support layer (Figure 9(c)), increasing from 7.6° to 43°. However, the observed values still fall within the category of low contact angles. This outcome aligns with the recognized hydrophilic properties of agar (Wang

et al., 2018). The observed inadequacy of 3 wt% agar concentration may stem from its high water content and insufficient agar molecules. Conversely, elevating agar concentration to 4 wt% (Figure 9(b1)) induced a substantial change in surface behavior, with the contact angle significantly increasing to around 106°. The disparity in behavior between 3 and 4 wt% agar concentrations implies that a higher concentration of anhydrous units contributes to hydrogel with enhanced mechanical properties (Bertasa *et al.*, 2020). This transformation from hydrophilic to hydrophobic behavior was attributed to the higher agar concentration, fostering the formation of a more cohesive and hydrophobic surface layer. The use of an agar-beeswax emulsion as a coating on the composite membrane surface moderately enhanced hydrophobicity. Contact angle measurements (Figure 9(a2) and 9(b2)) revealed an increase in surface hydrophobicity to approximately 73° and 87°, respectively, in Table 1. However, this increase was noticeably less significant compared to the shift achieved with the 4 wt% agar coating. The results suggested that achieving practical compatibility by blending an emulsion of agar and beeswax, despite the use of the emulsifier, might not be optimal. Emulsifiers typically possessed both hydrophilic and lipophilic groups, which might limit their ability to effectively resist water droplets (Naderizadeh *et al.*, 2019; Zhang *et al.*, 2022). Coating the

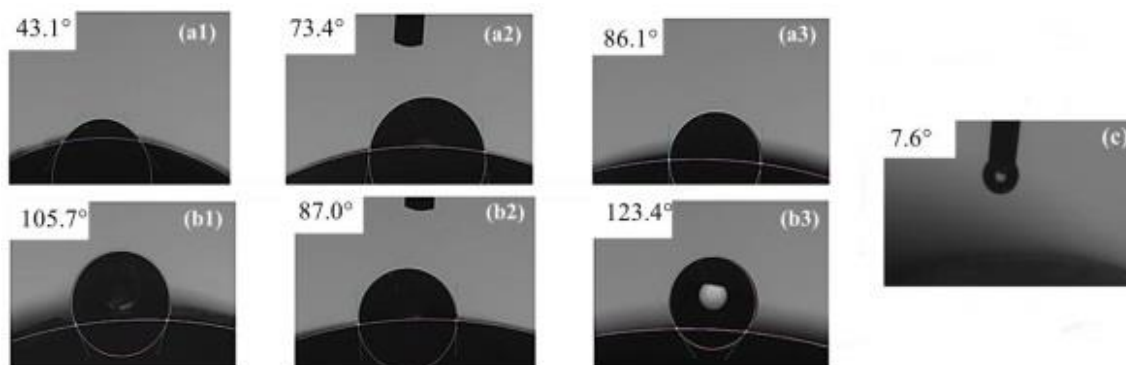


Figure 9. The water contact angle of the composite tube samples for
 (a1) alumina support coated by 3 wt% concentrated agar solution,
 (a2) alumina support coated by 3 wt% concentrated agar solution and then followed by 3 wt% agar-beeswax emulsion,
 (a3) alumina support coated by 3 wt% concentrated agar solution and then followed by pure beeswax,
 (b1) alumina support coated by 4 wt% concentrated agar solution,
 (b2) alumina support coated by 4 wt% concentrated agar solution and then followed by 4 wt% agar-beeswax emulsion,
 (b3) alumina support coated by 4 wt% concentrated agar solution and then followed by pure beeswax, and
 (c) the alumina membrane support

alumina support with beeswax, especially when applied to a high-concentration agar layer (4 wt%, Figure 9(b3), results in a high contact angle, signifying enhanced surface hydrophobicity. Beeswax contains hydrophobic compounds, such as long-chain fatty acids and esters, which repel water, resulting in a high contact angle when in contact with water droplets. The rough surface of the beeswax-coated layer effectively resisted water due to its high moisture transport resistance (Aris *et al.*, 2019), coupled with the reduced contact area between the water droplet and the surface (Wang *et al.*, 2021). Therefore, beeswax coating significantly enhanced surface hydrophobicity, particularly when applied to the 4 wt% agar layer, exhibiting a higher structural density (Kendrick, 1950).

Conclusions

The biopolymer-alumina composite membrane was fabricated using the gel casting method and dip-coating technique to achieve hydrophobic modification by applying coatings of the agar, the beeswax, and the agar-beeswax emulsion. Agar was employed to alter surface properties to anchor the support and the top layer, while the beeswax and the emulsion of beeswax and agar were used to create the water-repellent surface. SEM analysis revealed that at the lower agar concentrations (1-2 wt%), minor surface cracks were observed, while higher agar concentrations (3-4 wt%) resulted in a smooth surface with tiny cracks. Contact angle measurements indicated that the beeswax significantly enhanced the hydrophobicity of the surface, particularly when applied in conjunction with the higher agar concentration. The alumina support coated with the 4 wt% agar and the beeswax exhibited excellent surface hydrophobicity. Even though the FESEM results do not clearly show pores, this does not necessarily mean that the surface's top layer is entirely non-porous. There may be small pores present, particularly when using high magnification. Consequently, this work is an interesting trend as an environmentally friendly alternative for modification has promising potential for application in degasifier systems.

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References

- Abdikheibari, S., Parvizi, R., Moayed, M., Zebarjad, S., and Sajjadi, S. (2015). Beeswax-Colophony Blend: A Novel Green Organic Coating for Protection of Steel Drinking Water Storage Tanks. *Metals*, 5(3):1645-1664. <https://doi.org/10.3390/met5031645>
- Abdulhameed, M.A., Othman, Mohd, H.D., Ismail, A.F., Matsuura, T., Harun, Z., Rahman, M.A., Puteh, M.H., Jaafar, J., Rezaei, M., and Hubadillah, S.K. (2017). Carbon dioxide capture using a superhydrophobic ceramic hollow fibre membrane for gas-liquid contacting process. *Journal of Cleaner Production*, 140(Part 3):1731-1738. <https://doi.org/10.1016/j.jclepro.2016.07.015>
- Akbari, S. and Nour, A.H. (2018). Emulsion types, stability mechanisms and rheology: A review. *International Journal of Innovative Research and Scientific Studies*, 1(1):11-17. <https://doi.org/10.53894/ijirss.v1i1.4>
- Aris, Z.F.M., Bavishi, V., Sharma, R., and Nagarajan, R. (2019). Barrier properties and abrasion resistance of biopolymer-based coatings on biodegradable poly(lactic acid) films. *Polymer Engineering and Science*, 59(9):1874-1881. <https://doi.org/10.1002/pen.25187>
- Bertasa, M., Doderio, A., Alloisio, M., Vicini, S., Riedo, C., and Sansonetti, A. (2020). Agar gel strength: A correlation study between chemical composition and rheological properties. *European Polymer Journal*, 123:109442. <https://doi.org/10.1016/j.eurpolymj.2019.109442>
- Buonomenna, M.G. (2016). 14 - Smart composite membranes for advanced wastewater treatments. In: *Smart Composite Coatings and Membranes*. Montemor, M.F. (ed). Woodhead Publishing, p. 371-419: <https://doi.org/10.1016/B978-1-78242-283-9.00014-2>
- Dong, Z., Fan, W., Xu, J., Drioli, E., Chen, X., and Qiu, M. (2021). One-step engineering of low-cost kaolin/fly ash ceramic membranes for efficient separation of oil-water emulsions. *Journal of Membrane Science*, 621:118954. <https://doi.org/10.1016/j.memsci.2020.118954>
- Fei, T. and Wang, T. (2017). A review of recent development of sustainable waxes derived from vegetable oils. *Current Opinion in Food Science*, 16:7-14. <https://doi.org/10.1016/j.cofs.2017.06.006>
- Goh, P.S., Naim, R., Rahbari-Sisakht, M., and Ismail, A.F. (2019). Modification of membrane hydrophobicity in membrane contactors for environmental remediation. *Separation and Purification Technology*, 227:115721. <https://doi.org/10.1016/j.seppur.2019.115721>
- Gupta, G. and Anjali, K. (2023). Environmentally Friendly Beeswax: Properties, Composition, Adulteration, and its Therapeutic Benefits. *IOP Conference Series: Earth and Environmental Science*, 1110:012041. <https://doi.org/10.1088/1755-1315/1110/1/012041>
- Iojoiu, C., Danyliv, O., and Alloin, F. (2017). 16 - Ionic Liquids and Polymers for Battery and Fuel Cells. In: *Modern Synthesis Processes and Reactivity of Fluorinated Compounds*. Groult, H., Leroux, F.R., and Tressaud, A. (eds.). Elsevier, p. 465-497: <https://doi.org/10.1016/B978-0-12-803740-9.00016-0>
- Kendrick, Z.V. (1950). The physical properties of agar type hydrocolloid impression material. *The Journal of the American Dental Association*, 40(5):575-584. <https://doi.org/10.14219/jada.archive.1950.0086>
- Lee, H.J. and Park, J.H. (2016). Effect of hydrophobic modification on carbon dioxide absorption using porous alumina (Al₂O₃) hollow fiber membrane contactor. *Journal of Membrane Science*, 518:79-87. <https://doi.org/10.1016/j.memsci.2016.06.038>

- Lee, H.J., Magnone, E., and Park, J.H. (2015). Preparation, characterization and laboratory-scale application of modified hydrophobic aluminum oxide hollow fiber membrane for CO₂ capture using H₂O as low-cost absorbent. *Journal of Membrane Science*, 494:143-153. <https://doi.org/10.1016/j.memsci.2015.07.042>
- Macedonio, F., Ali, A., and Drioli, E. (2017). 3.10 Membrane Distillation and Osmotic Distillation. In: *Comprehensive Membrane Science and Engineering*. 2nd ed. Drioli, E., Giorno, L., and Fontananova, E., (eds.). Oxford: Elsevier, p. 282-296. <https://doi.org/10.1016/B978-0-12-409547-2.12221-8>
- Malik, N., Bulasara, V.K., and Basu, S. (2020). Preparation of novel porous ceramic microfiltration membranes from fly ash, kaolin and dolomite mixtures. *Ceramics International*, 46(5):6889-6898. <https://doi.org/10.1016/j.ceramint.2019.11.184>
- Martins, A.J., Cerqueira, M.A., Fasolin, L.H., Cunha, R.L., and Vicente, A.A. (2016). Beeswax organogels: Influence of gelator concentration and oil type in the gelation process. *Food Research International*, 84:170-179. <https://doi.org/10.1016/j.foodres.2016.03.035>
- Naderizadeh, S., Heredia-Guerrero, J.A., Caputo, G., Grasselli, S., Malchiodi, A., Athanassiou, A., and Bayer, I.S. (2019). Superhydrophobic Coatings from Beeswax-in-Water Emulsions with Latent Heat Storage Capability. *Advanced Materials Interfaces*, 6(5):1801782. <https://doi.org/10.1002/admi.201801782>
- Rocha, Julio Cesar Barbosa, J.D. Lopse, and M.C.N Mascarenhas. (2013). Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil. *Food Research International*, 50(1):318-323. <https://doi.org/10.1016/j.foodres.2012.10.043>
- Svoboda, R. (2009). The effect of carbon dioxide and organics in a steam turbine. *Power Plant Chemistry*, 1:20-27.
- Svoboda, R., Denk, J., and Maggi, C. (2003). Influence of Carbon Dioxide on Corrosion in Steam Turbines. *PowerPlant Chemistry*, 5(10):581-586.
- Udomsri, N., Promsawat, M., Sirijarakul, S., and Lertwittayanon, K. (2022). Effect of clay addition to Al₂O₃-agar mixture on pore size and distribution of tubular Al₂O₃ membrane support fabricated by agar gelcasting. *Materials Today: Proceedings*, 65:2426-2431. <https://doi.org/10.1016/j.matpr.2022.06.043>
- Wang, X., Guo, C., Hao, W., Ullah, N., Chen, L., Li, Z., and Feng, X. (2018). Development and characterization of agar-based edible films reinforced with nano-bacterial cellulose. *International Journal of Biological Macromolecules*, 118(Part A):722-730. <https://doi.org/10.1016/j.ijbiomac.2018.06.089>
- Wang, Y., Chen, X., Liang, Y., and Yu, C. (2021). Fabrication of super-hydrophobic filter paper via mixed wax phase separation for efficient oil/water separation. *BioResources* 16(3):5794-5805. <https://doi.org/10.15376/biores.16.3.5794-5805>
- Yarnpakdee, S., Benjakul, S., and Kingwascharapong, P. (2015). Physico-chemical and gel properties of agar from *Gracilaria tenuistipitata* from the lake of Songkhla, Thailand. *Food Hydrocolloids*, 51:217-226. <https://doi.org/10.1016/j.foodhyd.2015.05.004>
- Zhang, R., Zhai, X., Wang, W., and Huo, H. (2022). Preparation and evaluation of agar/maltodextrin-beeswax emulsion films with various hydrophilic-lipophilic balance emulsifiers. *Food Chemistry*, 384:132541. <https://doi.org/10.1016/j.foodchem.2022.132541>
- Zhao, C., Hussain, W., Alkaaby, H.H.C., AL-Khafaji, R.M., Alghazali, T., Izzat, S.E., Shams, M.A., Abood, E.S., Yu, A.E., and Ehab, M. (2022). Polymeric nanocomposite membranes for gas separation: Performance, applications, restrictions and future perspectives. *Case Studies in Thermal Engineering*, 38:102323. <https://doi.org/10.1016/j.csite.2022.102323>