DEVELOPMENT OF POLYVINYLIDENE FLUORIDE (PVDF) – SILICA AEROGEL (SA) COMPOSITE AS EVAPORATION SUPPRESSION GEO-MEMBRANE FOR FRESH WATER RESERVOIR

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Abstract. Polyvinylidene fluoride (PVDF) membrane was synthesized using dimethylformamide (DMF) solvent then prepared by phase inversion casting. The properties of PVDF have been enhanced by adding 10 wt.% of aerogel. The aerogel undergoes surface modifying using 30 wt.% of trimethylsilyl chlorosilane (TMCS). Membrane microstructure had been characterized by Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The samples had been undergone hydrophobicity test to characterized the psychochemical properties and for mechanical properties had been characterized by tensile test. SEM results for silica aerogel shows its multi porous properties. While SEM results for PVDF membrane shows silica aerogel is well scattered in the membrane. Results also showed that contact angle of PVDF membrane has increased about 36 % and the hydrophobicity effect due to silylated has displayed by FTIR. FTIR result is highlight that crystalline conformation of the chain from 849 cm^{-1} wavelength. The tensile strength of membrane increased about 14.71 % from 1.45 MPa to 1.70 MPa for PVDF 10 wt.% and PVDF 10 wt.% with silica aerogel (with silylating TMCS 30 wt.%) respectively. It can be concluded that by adding optimum amount of silica aerogel will enhance PVDF membrane properties.

Keywords: Polyvinylidene fluoride; silica aerogel, hydrophobic membrane, tensile strength

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Introduction

In late 1970, history has recorded that the first floating cover was using chlorosulfonated polyethylene (CSPE), was known as Hypalon. Recent study shows that CSPE has bad potential effects on livings health who drink water which has CSPE cover due to chemical leaching by CSPE membrane in water covered [1]. It is due to the possibility of CCl4 evolution which has the route of chemical to enter the body through skin or breathing which can cause skin, nose, lung irritation, throat and eye. The ultimate targeted organ is liver and central nervous systems as well as kidneys. This is a big reason to make an improvement to substitute CSPE as a material for floating cover where among of them are poly vinyl chloride (PVC), linear low-density polyethylene (LLDPE), polypropylene (PP), high density poly ethylene (HDPE), butyl rubber, polyisobutylene, ethylene-propylene-diene monomers (IIR, PIB, EPDM), chlorinated polyethylene (CPE) and polypropylene (PP) [2].

Polyvinylidene fluoride (PVDF) nowadays become one of the main choices in membrane industries since the advantages of PVDF are anti-fungal, anti-bacterial, anti-fouling and anti-wetting properties [3,4]. As a good material for floating cover, PVDF publicizes its exceptional resistance to creep and fatigue, high thermal stability, chemical resistance, UV resistance, nuclear radiation resistance and weather resistance [5].

However, PVDF always work as a composite in order to enhance their properties subjected to their application. As refer to Summah [6], PVDF was coated with polydimethylsiloxane (PDMS) in order to increase permeability and selectivity of the membrane while Aryanti et al., [7] study on coating PVDF on polypropylene will increase the contact angle of the composite membrane, lowered the membrane porosity and swelled degree. Since PVDF is a conductor material, Wanga et al. [8] have used PVDF and lithium phosphorus sulfide chloride (LPSCl) in order to replace the ordinary electrolyte inside the commercial lithium-ion batteries to thin free-standing electrolyte to decrease their density.

Since PVDF often use as a membrane, the strength of membrane become the most important factor for membrane durability and anti-wetting properties also play an important factor as PVDF membrane will be used as floating cover for reservoir. In order to enhance these properties, aerogel powder will be added into PVDF mixture. This research will investigate on effect of 10 wt.% of aerogel in PVDF. The amorphous PVDF density is 1.78 g/cm^3 while water density is 1 g/cm^3, makes PVDF impossible to be float on water. PVDF needs filler to make it float and aerogel has been choosing as a suitable filler as it is a porous material.

Aerogel is well known for their small pore size, large specific area with superior optical transmission. It has incomparable properties such as low density (~0.03 g/cc), high surface area (600 – 1,000 m^2/g), low thermal conductivity (~0.01 W/m.K), high optical transmission (99 %) in the visible region, low dielectric constant (~1.0 – 2.0), high porosity (~99 %), low refractive index (~1.05) and low sound velocity (100 m/s) [9-12].

Since they have spectacular properties, silica aerogel become the most desired material in research and in industry. In several studies, silica aerogel was synthesis as composites for various applications. As example, thermal insulation using alumina-silica aerogel composite [13], magnetic properties of silica aerogel-iron oxide composite [14], used of silica/carbon composite in water treatment [15]. Silica aerogel also used as an absorbent, sensor, as material with Low-Dielectric constant, catalyst and in fact the usage is also in

space [16-21]. So, this study is going to take an advantage on this undeniable material to become part of composite PVDF membrane in order to enhance the properties which eventually become spectacular membrane for floating cover.

Materials and Methods

Materials

Sodium silicate (Na_2SiO_3) with purity of 100 % will be acted as a precursor was supplied by Merck KgaA, Germany. Acetic acid (CH_3COOH) with purity of 100 % act as an acid catalyst was purchased from RCI Labscan Limited, Thailand. Ethanol (C_2H_5OH) with purity of 95 % has purchased from QReC, New Zealand. The purpose of ethanol is to replace water molecules from hydrogen pores with alcohol molecules during solvent exchange process. Trimethylsilyl chlorosilane (TMCS) $(CH_3)_3$ SiCl with purity of 99 % is used as the silylating agent, the chemicals will be bought from Merck KgaA, Germany. N-hexane (C_6H_{14}) with purity of 98 % functions as solvent for TMCS has been purchased from QReC, New Zealand.

There are two materials that were involved in synthesis of PVDF sheet namely polyvinylidene fluoride (PDVF) (pellets) and dimethylformamide (DMF). PDVF (pellets) ($C_2F_2H_2$) was used as a main material in this stage. PVDF was purchased from Merck KgaA, Germany. DMF (C_3H_7NO) was used as solvent to dilute the PVDF pellets. The solvent was bought from Fisher Scientific Chemical, USA.

Synthesis and Characterization of Silica Aerogel

Synthesization of hydrophobic silica aerogel was referred to Shewale et al. [22]. According to the method, there are about five main steps in order to produce silica aerogel. Which are gelling, aging (hydrogel), solvent exchange (alcogel), silylating, and drying under ambient pressure. The first step involved preparation of hydrogel using sodium silicate as a precursor. 150 ml of distilled water pour into beaker with 50 ml of sodium silicate solution with ratio (Na_2O: SiO_2 mole ratio 1: 3.3). there are about 2.0 ml of 1.0 M Acetic acid (CH_3COOH) has been added into the solution with constant stirring to avoid instantaneous gelation of the sol. The solvents are left overnight to allowed gelated. Chemical reaction involved during this process as the following:

$$Na_2SiO_3 + H_2O + CH_3COOH \rightarrow Si(OH)_4 + 2CH_3COONa \quad (1)$$

$$Si(OH)_4 + Si(OH)_4 \rightarrow 2(OH)_3 2SiO + H_2O \quad (2)$$

The gel than rinsed with distilled water until pH is 7 and leave in bath overnight. It is now known as aqua gel. The optimum time for aging in distilled water is about 24 hours in order to strengthen the capillary structure to enhance the mechanical properties of silica aerogel as suggest by Iswar et al. [23] study.

Aqua gel then immersed in ethanol bath for five days with changing ethanol every day. After complete this process, aqua gel transforms to alcogel where water inside the pores

has been replaced by ethanol. Due to capillary effect, aqua gel tends to shrinkage as a consequences of Oswald ripening.

Alcogel then immersed in silylating agent solvent overnight. There are 30 wt.% of trimethylsilyl chlorosilane (TMCS) and 70 wt.% of n-Hexane mixture to do surface modification of silica aerogel. Alcogel then rinse with n-hexane repeatedly to remove excessive unreacted chemical. Expected chemical reaction for this mixture as the following:

$$C_2H_5OH + (CH_3)_3SiCl \rightarrow (CH_3)_3SiOCH_2CH_3 + HCl \quad (3)$$

$$2(CH_3)_3SiCl[TMCS] + H_2O \rightarrow 2(CH_3)_3Si_2O + 2HCl \quad (4)$$

$$2(CH_3)_3SiOCH_2CH_3 + H_2O \rightarrow 2(CH_3)_3 2SiO + 2C_2H_5OH \quad (5)$$

$$(CH_3)_3SiCl + SiOH \rightarrow 2SiO(CH_3)_3 + HCl \quad (6)$$

Aerogel then undergo drying process, which is Ambient Pressure Drying (APD) in oven with controlled temperature 120 ℃. Perfect drying is important to ensure the solvents is completely evaporate which lead to have porous structure of aerogel.

Synthesization of Polyvinylidene Fluoride

PVDF membrane was prepared using phase inversion via immersion-precipitation according to Tao et al. [24]. This is a common method in membrane preparation approach where the polymer solvent will be casted on a proper support and submerged in a coagulation bat bath. PVDF pellets has been dissolved in dimethylformamide (DMF) solvent with ratio of 10 wt.%: 90 wt.% respectively at 80 ℃ and constantly stirred for 24 hours to ensure it is completely dissolved and form an homogenuous PVDF casting solution. The solution is set to cooled at room temperature for 24 hours to remove the air bubbles and then were poured uniformly on a glass plate and being spread using glass rod. Solvent on the glass left for 60 second to allow the solvent to evaporate before immersed in a coagulation bath at room temperature. Membrane then were immersed into distilled water for 48 hours to remove the traces of solvent and were air-dried at room temperature for 24 hours before characterized.

Fabrication of Polyvinylidene fluoride Membrane with Silica Aerogel

Silica aerogel (1 g) has been mixed well with PVDF solution (99 g) in glass bottle on the hot plate for 30 minutes at 60 ℃ to scatter the aerogel. After complete scattering of silica aerogel, the mixture has been placed in sonicator for 1 hour to ensure the aerogel is well scattered in PVDF solution.

Phase inversion casting has been employed in this study to fabricate the PVDF membrane. Pour the PVDF solution onto 8-inch-wide of first-grade casting glass and leveling using the glass rod that had been taped with masking tape. The masking tape has been rolled at the end of the rod three times in order to get uniform thickness of the membrane. The thickness produced is about 1 mm. Left the glass in the air for 60 s then, immersed it in coagulation bath at room temperature. Immersed the PVDF membrane into distilled water for 48 hours to remove the traces of solvent. Lastly, air-dried the membrane in room temperature for 24 hours before characterized.

Characterizations

Psychochemical properties of silica aerogel involved hydrophobicity, density and porosity. Hydrophobicity of aerogels are proved by contact angle test using travelling microscope at least count of of 0.001 cm. PVDF membrane's samples was cut into rectangular shape with size of 5 mm width and 70 mm length. There are 0.50 µL/s deionized water was placed on the samples and repeated 10 times at different locations to have accurate measurements. The samples are considered hydrophobic if the contact angle is greater than 90°, super-hydrophobicity if angle is excess 150°. Samples are said to be hydrophilic if the angle is approaching 0° or less than 90°.

Brunauer–Emmett–Teller (BET) was used to analyze silica aerogel specific surface area. The testing was carried out in nitrogen gas at various partial pressure at 77 K with Belsorp-mini, BEL Co., Japan. Samples were preheated for three hours at 200 ℃ in nitrogen flow to remove all volatile materials. There are three parameters to measure porosity which are specific surface area, specific pore volume or porosity, pore size and its distribution.

$$\text{Specific Surface Area, } m^2/g = \frac{\text{Total surface area, } m^2}{\text{Mass of the solid, g}} \quad (7)$$

$$\text{Porosity, \%} = \frac{\text{Volume of pores}}{\text{Volume of solid (including pores)}} \quad (8)$$

$$\text{Specific Pore Volume, } cm^3/g = \frac{\text{Total pore volume, } cm^3}{\text{Mass of the solid, g}} \quad (9)$$

Total pore volume was calculated at $P / P_0 = 0.024,$ for diameter less than 1.2918 nm

Scanning electron microscopy equipped with energy dispersive x-ray used SEM/EDX model Hitachi SUS8020 to examine morphology compositional information of aerogel and PVDF membrane. Samples were coated using sputter-coated with platinum using Automated Platinum Sputter Coater, Quorum, Q150R S.

The physiochemical properties of membrane were analyzed using Fourier-transform infrared spectroscopy (FTIR) with wave number range from 400 to 4000 cm^{-1} in order to confirm the chemical structure of the membrane. Tensile test was employed in order to check the strength of membrane. Five samples was cut into rectangular shape with 4 mm width, 100 mm length accrording to ASTM D882, specifically for membrane thickness < 100 µm and undergo test using Instron 5982 which was setting up with 10 N load cell, 25 mm gauge length and 50 mm/min cross head speed.

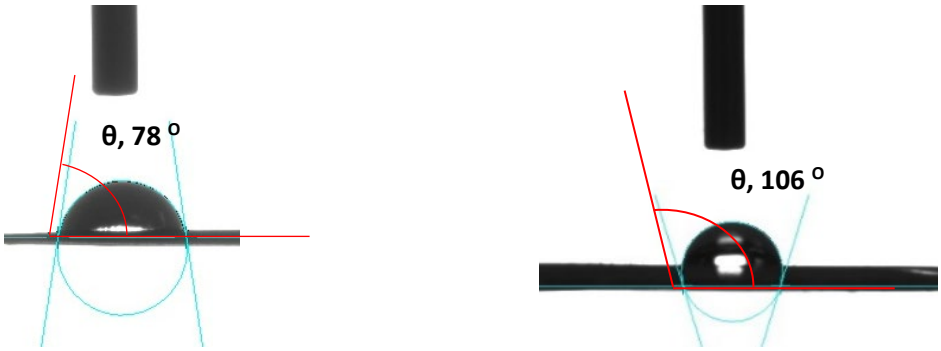
Results and Discussion

Hydrophobicity of silica aerogel has been improved by adding 30 wt.% of TMCS which gives the improved contact angle as much as 135° by referring to Figure 1. As compared to silica aerogel without surface modification, the apparent contact angle, Θ, is 34°. The increasing of contact angle of silica aerogel shows that the increasing of hydrophobicity of modified silica aerogel. This increment due to replacement of polar -OH groups on the surface by non-polar -CH_3 groups due to silylation.

While contact angle for PVDF membrane is 78° before adding silica aerogel as per Figure 2. Contact angle of membrane become, Θ, 106° after adding silylated silica aerogel with 30 wt.% TMCS. Silica aerogel need to be well dispersed to ensure it gives optimum mechanical properties.

(a) (b)

Figure 1: Contact angle of (a) silica aerogel before and (b) after surface modified with TMCS 30 wt.%.

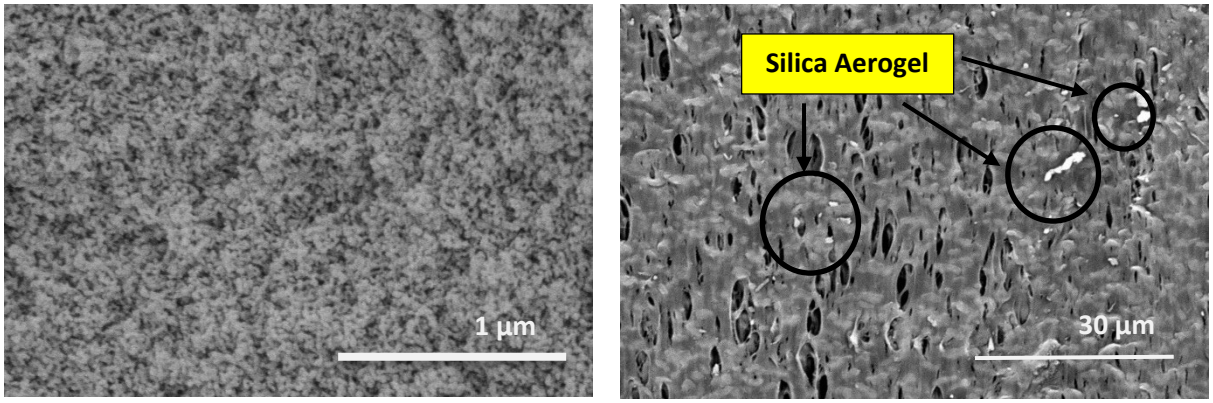


(a) (b)

Figure 2: Contact angle of (a) PVDF membrane before and (b) after adding modified silica aerogel.

BET result for silica aerogel that has been prepared gives BET surface area is 130 m^2/g while adsorption pore volume is 0.037 cm^3/g and adsorption pore size is 1.14 nm. This silica aerogel is said to be micropores due to IUPAC classification, where it has three terms to classified porous material which are micropores with pore size less than 2 nm in diameter, mesopores with diameter within 2 and 50 nm and which are more than 50 nm of pore diameter are classified as macropores.

SEM images of the silica aerogel and PVDF membrane was shown in Figure 1. Figure 3(a) under 50K magnification is microstructure of silica aerogel with silylating agent, TMCS 30 wt.% under ambient pressure drying while Figure 3(b) under 1.5K magnification is microstructure of composite PVDF membrane with highlighted silica aerogel.



(a) (b)

Figure 3: The microstructure of (a) silica aerogel with TMCS 30 wt.% of silylating agent and (b) PVDF membrane with modified silica aerogel.

FTIR spectrum of pure and composite PVDF membrane as shown in Figure 4 and the spectrum peak assignation for PVDF membrane as per Table 1. As refer to Alberto Naranjo et al., [25] peaks occurred are the common peaks for pure PVDF and it is showing that, there are no new peak shifting for composite membrane due to no chemical reaction between PVDF and silica aerogel.

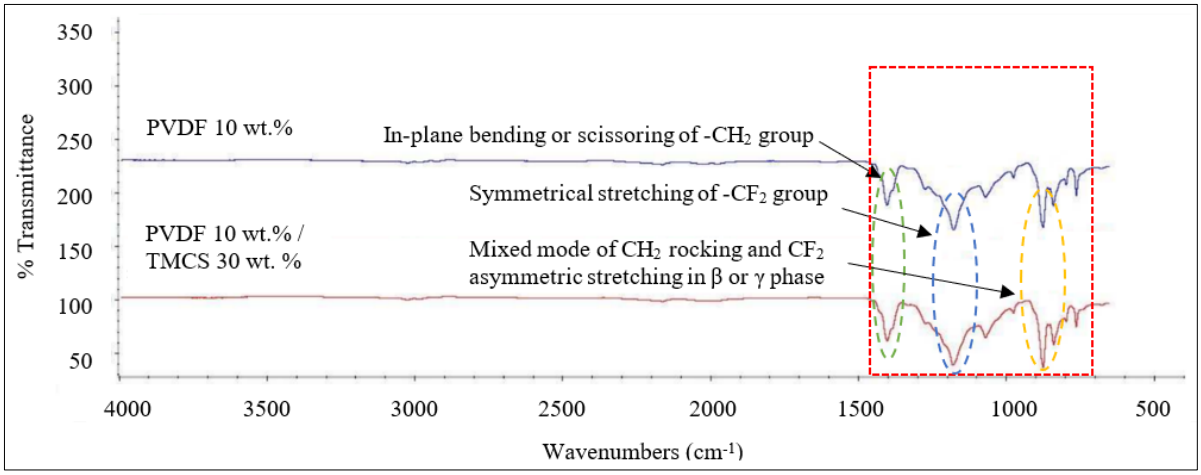


Figure 4: FTIR spectrum of pure and composite PVDF membrane with SA/TMCS 30 wt. %.

The impact of well dispersed silica aerogel is by improvement of mechanical strength of membrane. It can be proved by enhancement of tensile strength properties. As refer to Figure 5, tensile test results show the tensile strength of pure PVDF 10 wt.% and composite PVDF 10 wt.% membrane are 1.45 MPa and 1.70 MPa respectively. These show that by adding silica aerogel with surface modification by TMCS 30 wt.%, increased strength of membrane by 14.71 %. Which means that performance of membrane has improved and the life of membrane can be increased.

Table 1: Common PVDF membrane spectrum peak assignment [25]

Functional group	ω Transmittance(cm^{-1})
Existence of hydroxyl group (-OH)	1402
Symmetrical stretching of -CF_2 group	1173
Asymmetric extension -C-O-C-	1070
Inorganic filler	877
In-plane bending or rocking vibration in α-phase	763
Stretching in β-phase or γ-phase	840
Head-to-head and tail-to-tail configurations	677

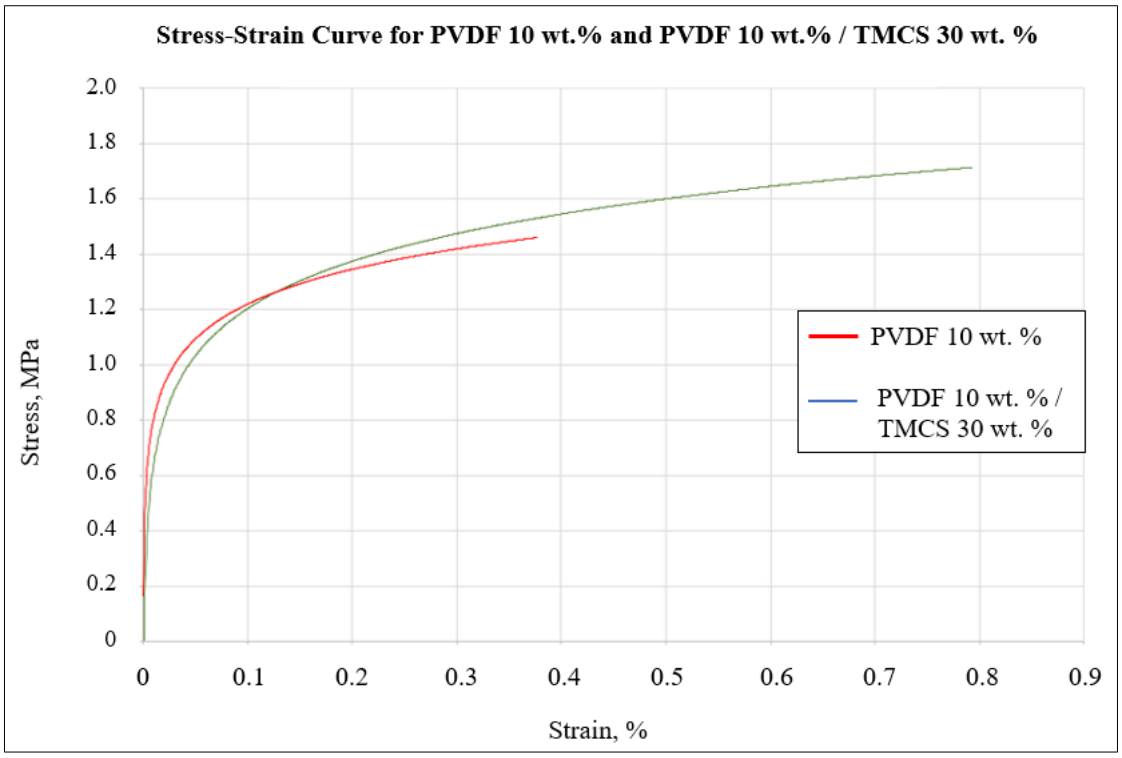


Figure 5: Stress–Strain curve for PVDF 10 wt. % and PVDF 10 wt. %/TMCS 30 wt. %.

Conclusions

By taking the advantages on worth properties of SA, it is a good opportunity to add SA in producing geomembrane. It can be concluded that by adding 10 wt.% of TMCS 30 wt.% silica aerogel will increase the properties of PVDF membrane with tensile strength of membrane has increased by 14.71 % and contact angle is increased by 36 %. It is important to ensure the well scattering of silica aerogel to produced uniform properties of membrane.

Membrane that has been prepared is an anti-fouling membrane with enhancement in hydrophobicity and strength which can act as a good potential as a geomembrane.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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