SILICA AEROGEL DERIVED FROM TMCS AND HMDZ SILYLATING AGENTS FOR RESORVOIR FLOATING COVER APPLICATION

Rozalina Amran[1], Muhamad Azizi Mat Yajid[1*], Nuha Awang[2], Abdillah Sani Mohd Najib[1]
[1]Department of Materials, Manufacturing & Industrial Engineering, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310, Skudai, Johor, Malaysia.
[2]Plant Engineering Technology (PETech), Universiti Kuala Lumpur Malaysia Institute of Industrial Technology (UniKL MITEC), Persiaran Sinaran Ilmu, Bandar Sri Alam, 81750, Johor, Malaysia.
* Corresponding author (azizi@utm.my)

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ABSTRACT

Aerogel is known as the lightest ever solid materials been produced. This research is focused on the optimization of the aerogel synthesize in order to be used as filler in aerogel polymer composite. The composite Poly(vinylidene) fluoride (PVDF) membrane was proposed in this study and the effectiveness of PVDF membrane after long exposure to UV light were investigated. The aerogel is synthesized by using two types of silylating agents namely trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDZ). The prepared aerogel was characterized using ATR-FTIR (Attenuate Total Reflectance Fourier Transforms Infra-Red), FE-SEM (Field Emission Scanning Electron Microscope), BET (Brunauer–Emmett–Teller) and contact angle analysis. The aerogel composite with PVDF matrix is then prepared through phase inversion casting method with PVDF 20 wt.% and aerogel mixture of 0.5, 1.0 and 1.5 g. Based on the current findings, aerogel which synthesize via TMCS silylating agent at 20wt. % is produced the highest hydrophobicity result at 88.05° compare with 23.33° for HMDZ silylating agent. For surface area analysis, it is found that aerogel with TMCS gives consistent results in comparison with HMDZ based aerogel. FTIR analysis is confirmed the synthesized aerogel is in hydrophobic form for both TMCS and HMDZ based samples. FESEM analysis shows that the produced silica is consists of highly porous nanostructures aerogel. Based on the preliminary results of aerogel – PVDF composite it is found that the aerogel is homogenously distributed within the PVDF composite. Results of the UV exposed aerogel samples at up to 150 hours found that, significant change in the strength about 40% reduction and hydrophobicity is reduced to up to 28%.

1 INTRODUCTION

Floating covers are widely used in arid climate and limited resources of surface water countries in North America, Europe, Australia, Israel, Saudi Arabia and others. There are many materials; chemicals and physical covers which can effectively and efficiently reduce the evaporation from open water bodies. Barnes et al., (2008) found that a chemical monolayer is potentially most effective in conditions where the rate of evaporation is high [1]. But monolayer efficiency reduces with wind speed and can be broken down by bacteria. Yao et al., (2010) study about continuous physical coverings (solid roofs, plastic covers, Evapmat, aquaspan, super-span, NetPro shade cloths, E-VapCap) may also reduce evaporation by 75 to 99% but lacks of mechanism in preserving the quality of the water [2].

Presently, polyvinylidene fluoride (PVDF) is a high-potential polymeric material that can be used to fabricate floating cover geomembranes [3,4]. However, the density of the material is higher than the density of water and does not meet the requirements for floating covers. To address the issue, silica aerogel will operate as a buoyancy support, allowing the PVDF to float while also acting as a thermal insulator. Silica aerogel is well known nanomaterial among researchers' due to its fabulous properties such as high thermal stability with low thermal conductivity (~0.02WmK^{-1}), high chemical stability, low density (~3 kgm^{-3}) and high surface area (~1,600m^{2}g^{-1}), as referred to Koebel et al., (2011) [5] and Abdul Halim et al., (2016) [6]. Ambient pressure drying become desirable method of drying among industries via solvent exchange and surface modification of silica aerogel. There are a lot of surface modification or silylating agents used such as trimethylchlorosilane (TMCS), hexamethyldisilazane (HMDS), ethyltriethoxysilane (ETES) and hexamethyldisilazane (HMDZ) which have been reported by Rao et al., (2003) [7]. This current study will highlight optimum synthetization process of silica aerogel and to measure the optimum amount of surface modification that can give good result. In the meantime, preliminary testing results on aerogel composite with Poly(vinylidene) fluoride (PVDF) as matrix was also been investigated.

2 MATERIALS AND METHOD

Silica aerogel was prepared using sodium silicate (Merck KgaA, Germany) as a precursor. For gelation, about 2.0 ml, 1.0 M acetic acid (CH_3COOH) had been added slowly to the solution. Gelation of the sol droplets into hydrogel occurred upon contact with the aqueous sodium silicate. The solvent was left overnight to allow for complete gelation process.

The microstructure of PVDF membrane has been analyzed using Scanning Electron Microscopy (SEM), Hitachi S-3400N, at 15kV. Hydrophobicity of the synthesized silica aerogel can be measured using contact angle test. Brunauer–Emmett–Teller (BET) has been used for measurement of the specific surface area of materials with N_2 gas adsorbed at various partial pressure at 77 K with Belsorp-mini, BEL Co., Japan. To identify the surface chemical structure of silica aerogel Fourier-transform infrared spectroscopy (FTIR) has been used in the wavelength range of 400 to 4000 cm^{-1}.

The aerogel – PVDF composite was prepared at 20wt.% PVDF with DMF as solvent. The aerogel is set at optimum condition of aerogel properties. The composite membrane samples were freeze-fracture in liquid nitrogen for microstructural cross section analysis. The samples were also undergone tensile test in order to study their strength using Instron 5982. Figure 1 shows the setup of UV testing with 36-W UV-A lamps (Model: PL-L 36W/10/4P, Philips) located on top of the membrane with distance of around 4 cm. The membranes exposure intervals for UV irradiation were set at 0, 24, 48, 72, 100, 120 and 150 hours.

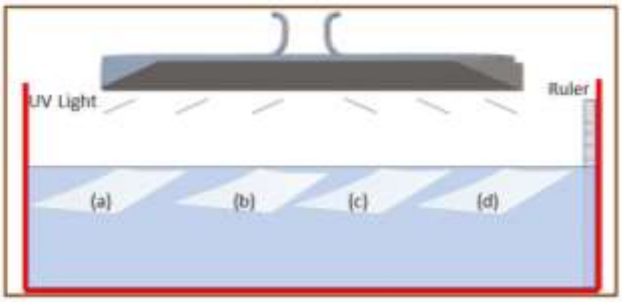


Figure 1. UV Test of PVDF membrane under UV light. (a) 24 hours exposure (b) 48 hours exposure (c) 72 hours exposure (d) 100/120/150 hours exposure.

3 RESULTS AND DISCUSSION

Figures 2 shows microstructural evaluation of the synthesized silica aerogel at various amount of silylating agent. It can be confirmed that different silylating agent conditions give different morphological structures which influenced the microstructure of prepared silica aerogel.

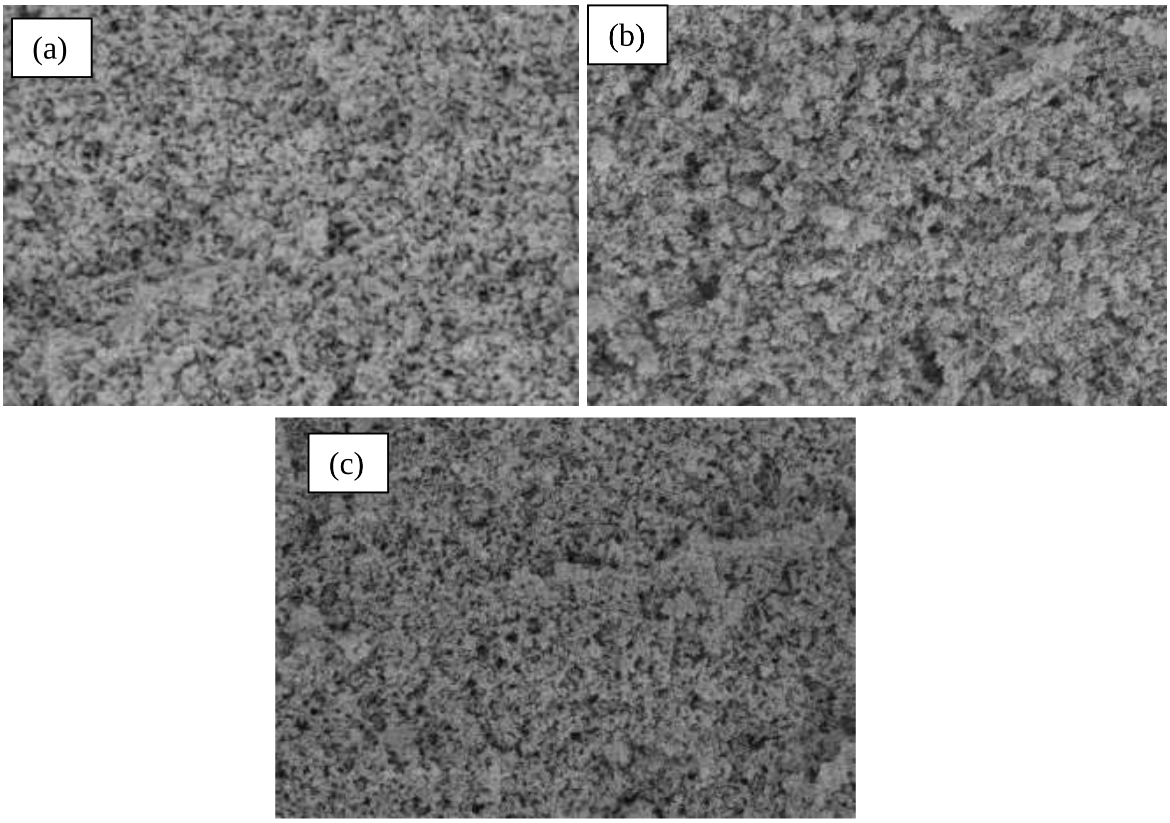


Figure 2. SEM images of aerogels with (a) 20 wt.%, (b) 25 wt.%, of TMCS and (c) 25 wt% of HMDZ silylating agent

As shown in Figure 3, silica aerogel with 20 wt.% TMCS give remarkable hydrophobicity (88.05^{o}) than HMDZ silylating agent. This is due to the optimum amount of surface modification, where it is as a result from the replacement of -OH groups with Si-CH3 groups during silylation process. TMCS modifier gives better result due to its branching structure that can produce more effective hydrophobic effects rather than HMDZ's liner chain. Therefore, it needs less amount of percentage of silylating agent were resulted in less usage of chemical and more environmentally friendly which make it safest formula.

Figure 4 is a graph of BET surface area and Table 1 is the data analysis of BET. The results are revealed that by increasing percentage of silylating agent will increased the surface area and HMDZ showing a good result in giving high surface area than TMCS. The maximum value of BET surface area (171.89) is corresponded to sample HMDZ 30 wt.% but, as refer to objective, the safest amount of surface modification will be TMCS 20 wt.%. TMCS 20 wt.% become the optimum formulation as safest surface modification due to its pore volume (0.037 cm^3/g) with BET surface area (124.87 m^2/g) and highest hydrophobicity (88.05^{o}).

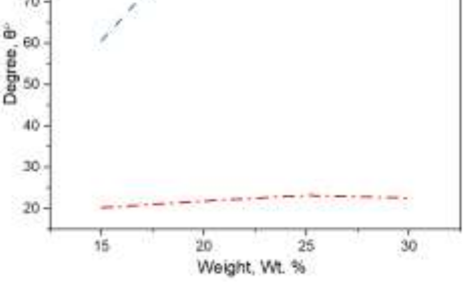


Figure 3. Graph of contact angle of silica aerogel with HMDZ and TMCS modifier.

BET result is important to identify the capability of optimum formula to act as a floating filler and thermal insulator due to the BET surface area and pore volume of hydrophobic silica aerogel. High BET surface area shows high porosity of the prepared silica aerogel. While high pore volume entrapped heat more than lower volume makes them suitable as a thermal insulator. In this study, as refer to Figure 4, the highest BET surface aera of TMCS and HMDZ is 129.99 m^2/g and 171.89 m^2/g correspondingly. The lowest BET surface area of TMCS and HMDZ is 119.40 m^2/g and 80.57 m^2/g. Meanwhile, in the Table 1, indicated the highest pore size of TMCS and HMDZ is 1.156 nm and 1.135 nm respectively. The pore volume showing stagnant reading after 20 wt.% of TMCS and this is mean that even increasing in volume of silylating agent, the pore volume is same. The lowest pore volume of TMCS and HMDZ is 0.034 cm^3/g and 0.023 cm^3/g accordingly.

Based on research by Nah et al., (2018) [8], the BET surface area for TMCS 20 wt.% is about 118 m^2/g and the synthesized silica aerogel's trend showed in the Table 1 is 129.99 cm^3/g. It can be concluded that the best formulation is TMCS 20 wt.% and it is the predicted formula will act as a floating filler and thermal insulator.

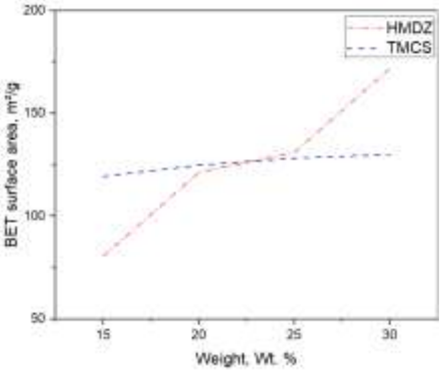
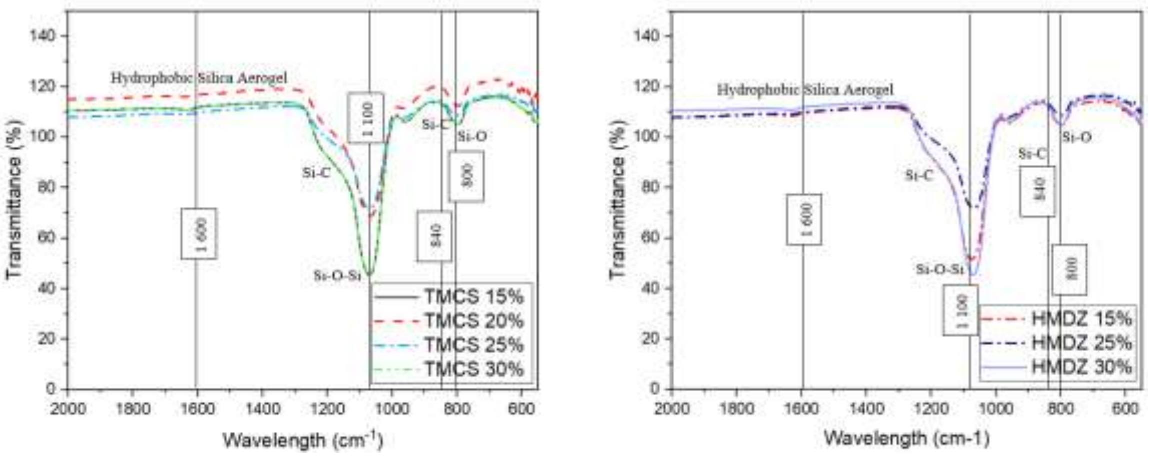


Figure 4. Graph of BET surface area for silica aerogel with HMDZ and TMCS modifier

Table 1. Density and porosity data of different formulations silica aerogel.

Silica Aerogel	Weight percentage, wt. %	BET surface area, m^2/g	Pore Volume, cm^3/g	Pore Size, nm	Tapped Density, g/cm^3
HMDZ	15	80.57	0.023	1.125	0.250
	20	121.33	0.033	1.135	0.275
	25	131.13	0.036	1.111	0.350
	30	171.89	0.046	1.082	0.245
TMCS	15	119.40	0.034	1.151	0.327
	20	124.87	0.037	1.156	0.388
	25	128.28	0.037	1.154	0.412
	30	129.99	0.037	1.144	0.427

In order to ensure the synthesized silica aerogel, have complete reaction, the samples were tested using Attenuate Total Reflectance Fourier Transforms Infra-Red (ATR-FTIR). Figure 5 show examples of the FT-IR spectra of aerogels synthesized with TMCS and HMDZ as modifier. The strong absorption peaks near 1100 and 1220 cm-1 and the weak peak around 800 cm-1 were assigned to the asymmetry and symmetry bending modes of Si–O–Si, respectively. The strong peak near 460 cm-1 was assigned to the Si–O–Si bending stretching mode. These peaks are characteristic peaks showing a typical silica aerogel network structure. The peaks at 1260, 1150 and 850 cm-1 indicate the presence of Si–C, while the peak at 2900 cm-1 is due to C–H stretching. These peaks show that the aerogels are modified into a hydrophobic form. Fidalgo and Ilharco (2005) also mention that it is due to asymmetric stretching vibration of the Si-O bond that makes the skeletal SiO_2 network and is expected for the silica materials [9].



(a) (b)

Figure 5. FTIR spectra of the silica aerogel modified using (a) TMCS and (b) HMDZ.

Figure 6 shows the cross sectional view of silica aerogel-PVDF composite with silica aerogel weight of 1.0 and 1.5g. From EDX mapping as shown in Figure 6 (c, d) dispersion of aerogel within on the composite membrane is obviously increased with the amount of added aerogel. Based on this cross sectional figure, the composite membrane showing two different regions which are finger-like and sponge-like layer. This is due to de-mixing time between solvent in the polymer film and non-solvent from coagulation bath. Finger-like layer formed due to prompt de-mixing by solvent and non-solvent. In contrast with sponge-like layer which formed due to delay de-mixing of solvent and non-solvent. A well scattering of silica aerogel PVDF composite membrane plays an important factor of membrane properties by means of good thermal stability and strength.

Figure 7 shows, by adding silica aerogel it will drastically increase the strength of the composite membrane. Initially, pristine PVDF membrane strength is about 0.85MPa and after adding silica aerogel in the membrane, it's given the maximum strength with silica aerogel (TMCS 20 wt.%) about 12.5 MPa for loading 0.5g. However, if further increased of aerogel, it will severely reduce the overall strength of the materials to up to ~40% reduction for 1.5g addition. Therefore, based on strength, the optimum amount needed for this formulation is 0.5g of aerogel added to the PVDF.

Figure 8 shows graphs of tensile test of membrane with addition of 0.5g silica aerogel at up to 150 hours UV exposure. After 150 hours UV exposure, the deterioration percentage is about 40%. Therefore, the optimum formulation with aerogel is needed to prolong the stability of the composite.

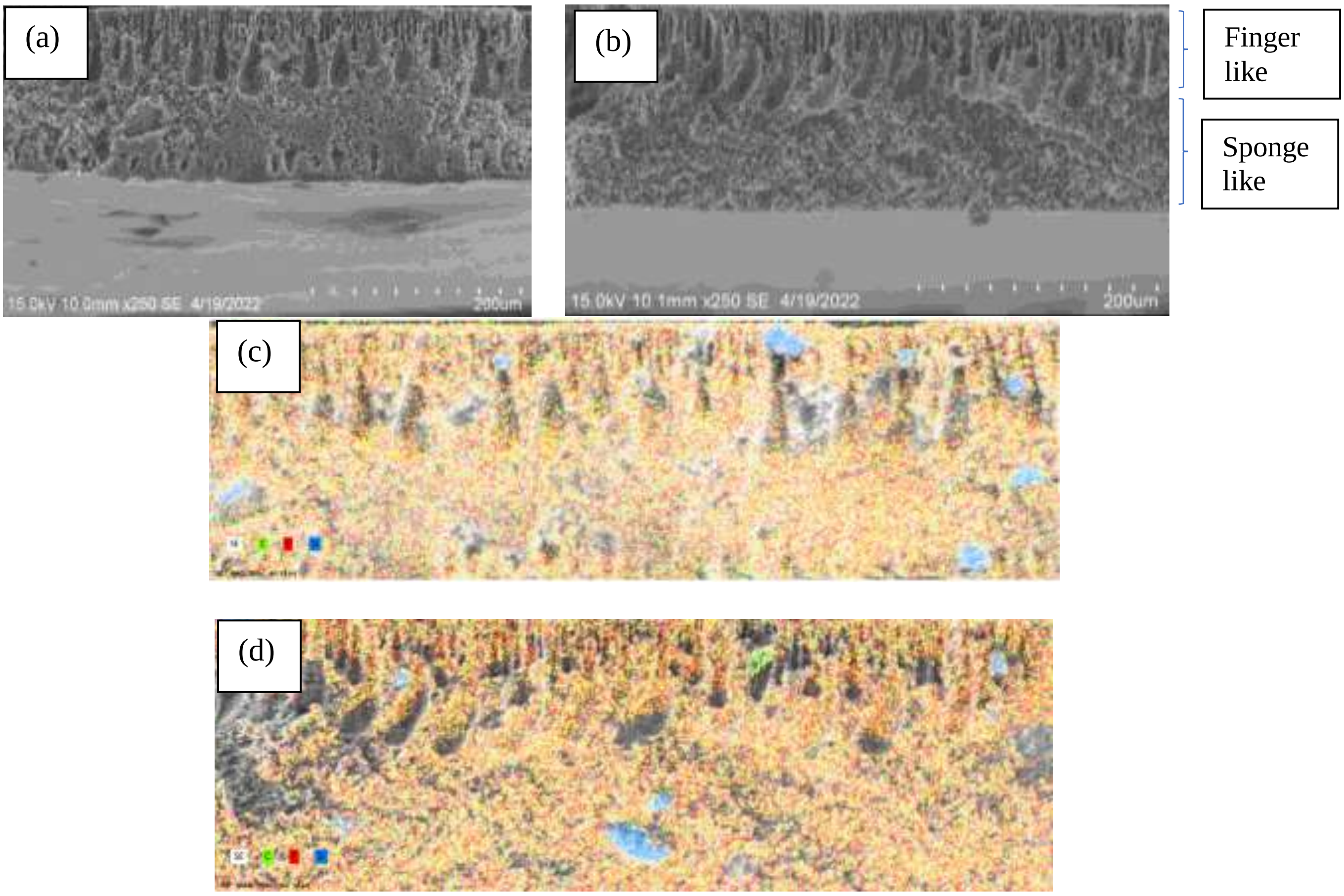


Figure 6. Silica aerogel PVDF composite with (a,c) 1.0 g and (b,d) 1.5 g of silica aerogel with formulation of 20wt. % PVDF. Image (b) and (d) are refer to EDX mapping

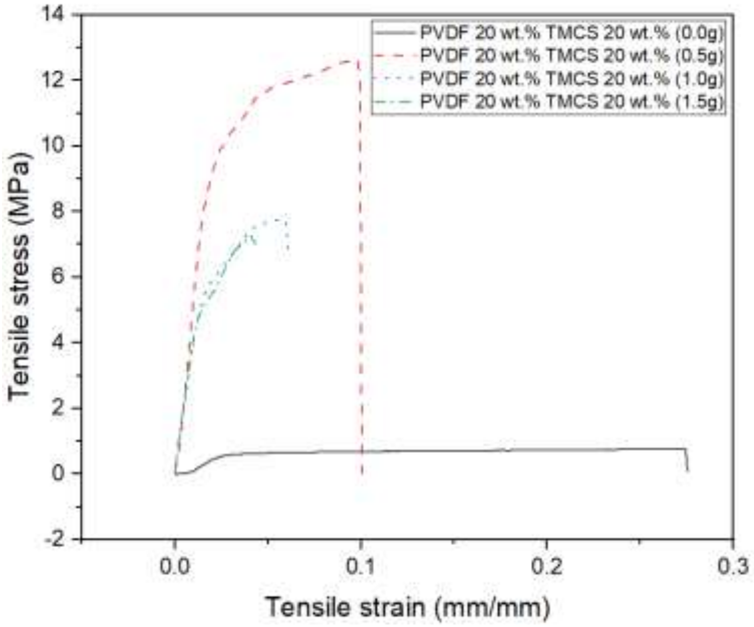


Figure 7. Stress Strain Curve of PVDF Composite membrane with SA-TMCS 20 wt.%.

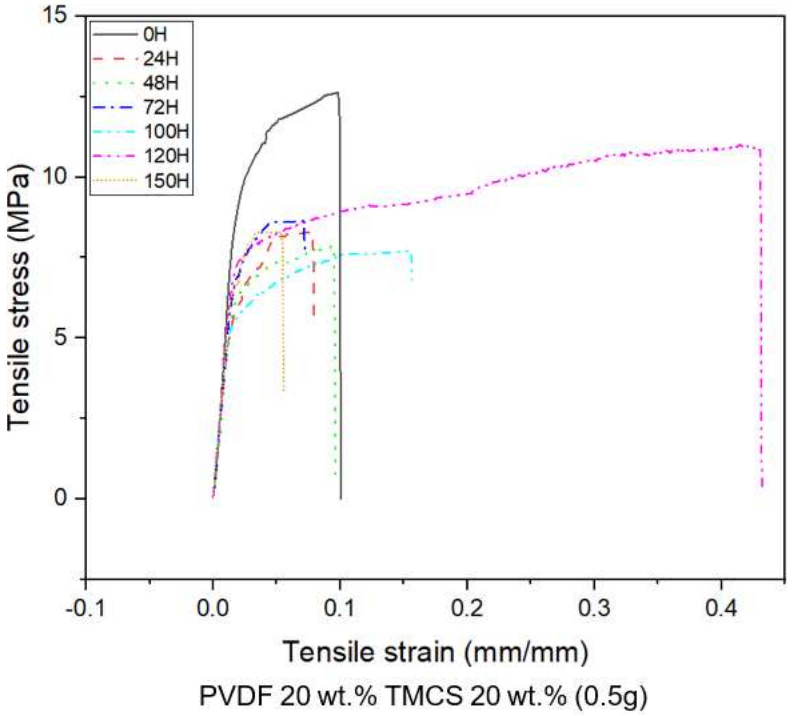


Figure 8. Stress Strain Curve of PVDF Composite membrane with SA-TMCS 20 wt.% (0.5g aerogel) with various UV exposure times

The affected membranes were then analysed by the hydrophobic behaviour after 100 and 150 hours of exposure to UV radiation as shown in Figure 9. Obviously after long exposure, 150 hours, the membranes loss its hydrophobic properties as stated previously with similar trend by Leong et. al. (2014) [10], due to the contact angle reading lies in the range of ca. 70^o.

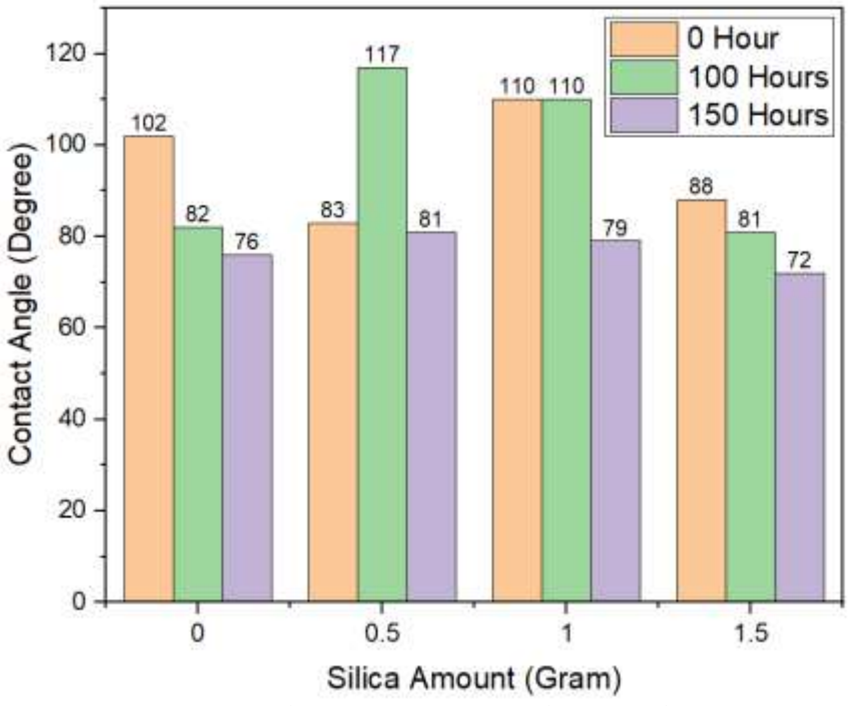


Figure 9. Contact angle of PVDF membrane before and after UV exposure.

4 CONCLUSIONS

The major findings in this work are as follow:

i. Silica aerogels that surface modify using 20 wt. % of TMCS gives highest hydrophobicity as much as ca. 88.05° compared to 25 wt. % of HMDZ modifier only gives ca. 23.33^{O}.
ii. As refer to BET result, it is showing that 30 wt. % of TMCS gives constant increment in surface area with highest surface are is 130 m²/g compared to 30 wt. % of HMDZ which gives significant increment with the highest surface area is 171 m²/g.
iii. As result from FTIR spectra, it is showing that the surface modification of prepared silica aerogel is confirmed and the hydrophobicity nature of aerogels is also confirmed with the absence of peak at 1600 cm-1.
iv. It is observed that phase inversion casting of aerogel – polymer (Poly(vinylidene) fluoride (PVDF can produced composite with homogeneous distribution of aerogel filler within the PVDF composite.
v. The optimum amount of silica aerogel is 0.5g to be added in PVDF composite which can give maximum strength at ~12.5 MPa.
vi. Results of the UV exposed aerogel composite samples at up to 150 hours found that, 40% reduction in the strength and up to 28% reduction in its hydrophobicity.

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