The Functionalization Study of PVDF/TiO2 Hollow Fibre Membranes Under Vacuum Calcination Exposure

The Functionalization Study of PVDF/TiO_2 Hollow Fibre Membranes Under Vacuum Calcination Exposure

E A Pradhana[1,4], M Elma[1,3,4], M H D Othman[2], N Huda[1,4], M D Ul-haq[1,4], Erdina L.A. Rampun[1,4], A Rahma[1,4]

[1]Chemical Engineering Department, Engineering Faculty, Lambung Mangkurat University, Jl. A. Yani KM 36, Banjarbaru, South Kalimantan 70714, Indonesia

[2]Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

[3]Wetland-Based Materials Research Center, Lambung Mangkurat University, 70714 Banjarbaru, South Kalimantan, Indonesia

[4]Material and Membrane Research Group (M^2ReG), Lambung Mangkurat University, Jl. A. Yani KM 36, 70714 Banjarbaru, South Kalimantan, Indonesia

Email : melma@ulm.ac.id

Abstract. In this study, polyvinylidene fluoride (PVDF) hollow fibre membrane was modified by adding TiO_2. TiO_2 presence affects the membrane structure becomes more less hydrophobic which makes the membrane less fouling. Membranes were made via dry-wet spinning method and calcined under vacuum condition by furnace (100, 300, and 500 °C). Besides, PVDF-TiO_2 uncalcined membrane were also prepared as comparison to investigated the effect of calcination on hollow fibre membrane's functional groups. Fourier Transform Infrared (FT-IR) spectra indicated that all PVDF-TiO_2 membranes have bands of OH in the TiO_2 at ~1600 cm^{-1}. Peaks of α-phase PVDF crystals appeared at ~876, ~876, and ~872 cm^{-1} for uncalcined, 100 and 300 °C, while for 500 °C the PVDF peak only shows at 874 cm^{-1}. The peaks at ~1200 cm^{-1} represent CF_2 groups. Peaks at ~1400 cm^{-1} assigned to CH_2 groups, but it does not observed for 500 °C. Deconvolution by Fityk software that shows calcination using vacuum condition gives the compounds gradually decomposes. At high temperature calcination lead the CH_2 peak extremely lost.

1. Introduction

Nowadays, a method for removing salt of water through a selective barrier called membrane is known as desalination technology. To save more energy consumption, desalination via pervaporation is preferred to reverse osmosis (RO) because it only requires 1 bar pressure [1-3]. Pervaporation has been applied for water desalination, alcohol dehydration, and volatile removal [2, 4-10]. Pervaporation separates the mixture by partial vaporization. Polyvinylidene fluoride (PVDF) suits for desalination because of their high salt rejection [11]. Moreover, the hydrophobicity of membrane caused on fouling.

In the last decade, polymeric membranes immobilized with TiO_2 have gained much attention due to specific benefits. Firstly, chemical modification cannot be happened because there is no covalent bond formation between polymeric and catalyst. Secondly, different chemicals show different affinities for polymeric membranes [12]. TiO_2 was also chosen because it is inexpensive, non- toxic, and

commercially available. TiO_2 addition within the PVDF material combination creates a new material that will increase the advantages such as reduce the membrane hydrophobicity and formed a less fouling material [13]. Because TiO_2 has an anti-fouling properties [14]. Fouling has been known as a major problem in membrane technology field that resulting in flux reduction. Among all polymeric membranes, polyvinylidene fluoride (PVDF) is often used because it provides good chemical resistance, chemical stability, temperature stability and mechanical strength [4, 15-18]. There are various transitions of PVDF polymorph such as as α, β, γ, and δ and density alters[19]. One of common material used in hollow fibre membrane is made from PVDF [20].

More specifically, membrane preparation technique depends on the material used, desired structure and morphology. Several membrane configurations included hollow fibre, tubular and flat sheet are found in the membrane modules. In application, hollow fibre membrane has a better flux performance compare to flat sheet [21], because of their huge of square meters of membrane per cubic meter [22]. Hollow fibre also has high mass transfer and thermal transfer efficiency that makes it less affected by temperature [23-25]. In other hand, flat sheet membranes require membrane support as well as tubular membrane because the packing density [26].

Several works have investigated PVDF-TiO_2 in various configuration and fabrication method. Previous study has developed PVDF-TIO_2 flat sheets membrane [27]. Méricq, Mendret, Brosillon and Faur [28] reported PVDF-TiO_2 preparation by non-solvent induced phase separation (NPIS) wet process. It resulting in finger-like macrovoid structure and hydrophilic properties. Other studies made a PVDF-TiO_2 hollow fibre ultrafiltration membrane using a wet-spinning method. It reported a strong interaction between inorganic network and polymeric that led to TiO_2 dispersed uniformly. A few amounts of TiO_2 addition even increases mean pore size compare to PVDF without TiO_2. It also found TiO_2 limit the PVDF decomposition during calcination and enhances stiffness of polymer chains and limited their thermal action [29].

This aim of this work is to brings a new insight to prepare PVDF-TiO_2 with various of vacuum calcination temperature for pervaporation via dry-wet spinning and investigated the functional groups. The simplicity, fast method, and able to produce asymmetric cross section structures become the beneficial of dry-wet spinning [30]. In addition, vacuum sintering offers a clean atmosphere and evaporate impurities in membrane material [31]. Deconvolution was carried out using fityk software to know the material's surface area during vibration and stretching [32, 33].

2. Experimental

The fabrication of PVDF-TiO_2 hollow fiber membranes followed the process on previous research [34]. It consist of three stages (1) dope solution preparation to remove moisture with drying 21 wt% PVDF and 3 wt% commercial TiO2 at 50ºC for 24 h, (2) mixing PVDF (PVDF, kynar 760 powder series), commercial TiO_2 with DMAC (DMAc, QReC) as a solvent (3) spinning membrane through dry-wet spinning technique. The obtained PVDF/TiO_2 hollow fibre membranes were calcined at varied temperature using furnace vacuum for an hour. Membranes were characterized using Fourier Transform Infra Red (FTIR). Fityk was used to deconvoluted overlapping peaks in PVDF-TiO_2 material. Schematic set up spinning hollow fibre membrane can be seen in **Figure 1**, as follow.

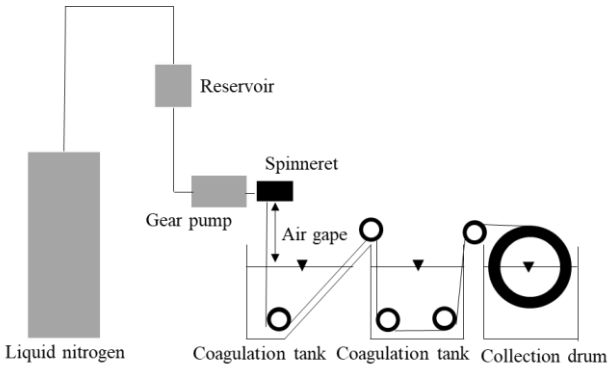

Figure 1. Schematic set up spinning hollow fibre membrane

3. Results and discussion

The FTIR analysis was carried out to know the crystal structure of PVDF/TiO_2 hollow fibre. As can be seen in Figure 2. Strong bands at ~1600 cm^{-1} and below 800 cm^{-1} attributed to OH area in the spectrum of immobilized TiO_2. Bands at 876, 876, and 872 cm^{-1} could be indicated as α-phase PVDF [35] for uncalcined, 100 and 300 ◦C, respectively. Small difference of α-phase PVDF band become very weak was observed at 874 cm^{-1} for 500 ◦C. This indicates that α-phase PVDF transformation to β-phase PVDF has occurred along with increasing temperature during vacuum calcination. This transition results similar to earlier study in literature [36]. PVDF crystalline has different phases such as α, β, and γ depending on processing methods [37]. Specifically, there are strong peak of CF_2 groups at ~1200 cm^{-1} for uncalcined, 100 and 300 with a weak peak of CH_2 at 500 ◦C. While, CH_2 groups found at ~1400 cm^{-1}. However, the CH_2 peak does not appeared in 500 ◦C. $(CH_2\text{-}CF_2)n$ itself is the chemical structure in the PVDF molecules. Solvent impurities almost completely disappeared at higher calcination. This condition promotes TiO_2 crystallization at 500 ◦C [38].The result obtained in this study is same with Dzinun, Othman, Ismail, Puteh, Rahman and Jaafar [39] which fabricated dual layer of hollow fibre membrane. There are many overlapping peaks in PVDF. This peak can be deconvoluted using fityk software.

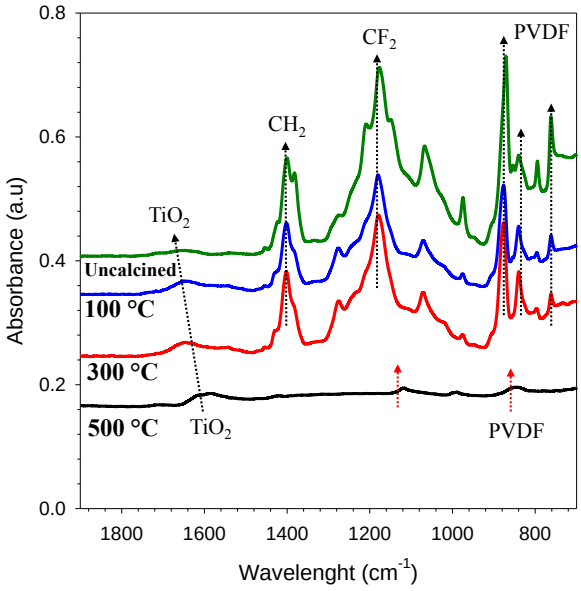

Figure 2. Spectra FTIR of PVDF/TiO_2 hollow fibre membranes in the region between 1800 and 700 cm^{-1} for uncalcined; calcined at 100, 300 and 500 °C

To confirm the network structure is affected by calcination temperature, a quantitative analysis was conducted by deconvolution of the FTIR patterns using Fityk software. **Figure 3** illustrated Gaussian bands of IR spectra of PVDF/TiO_2 hollow fibre membranes which uncalcined and calcined varied temperature. Deconvolution method was applied to deconvolute the FTIR spectra by fitting the peaks until the deconvolution spectra approach the experimental data [4, 40]. The peak envelope in the range 1600 and 700 cm^{-1} is assumed to consist of peaks components arising from the CH_2, CF_2, PVDF, and TiO_2 group. It is found that there are large reductions on the areas under the 1500 to 700 cm^{-1} wavelength after calcination process over 300 °C. The results in Figure 3 prove that the stretching β-crystal transformed into α-crystal by the calcination.

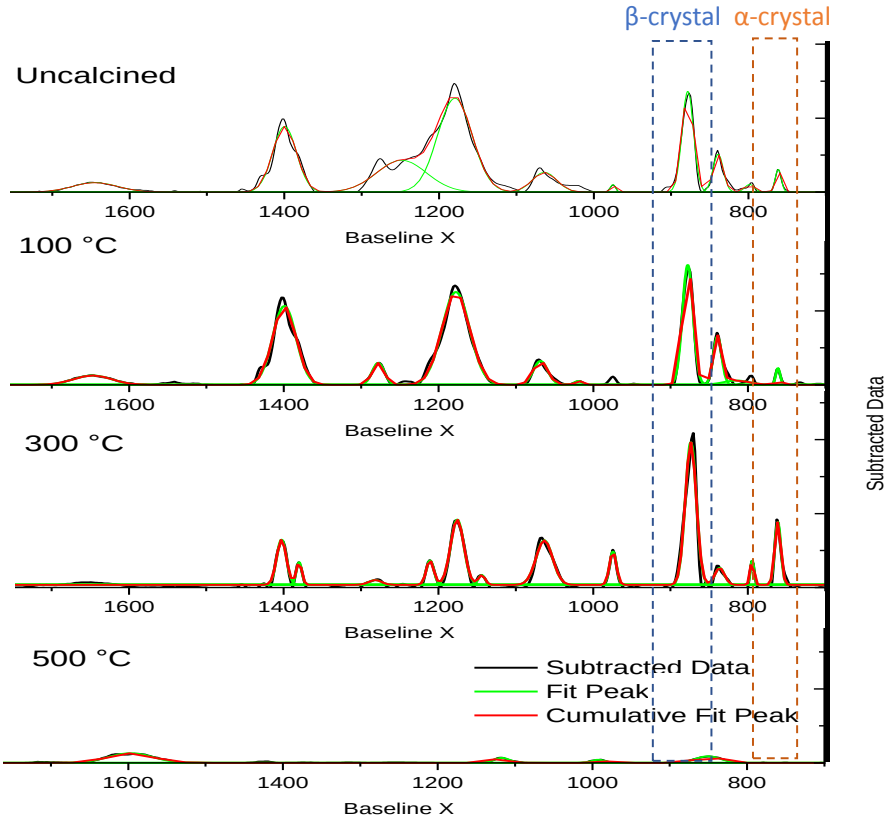

Figure 3. Deconvolution of the FTIR spectra of PVDF/TiO_2 hollow fibre membranes in the region between 1800 and 700 cm^{-1} for uncalcined; calcined at 100, 300 and 500 °C

The peak area value of PVDF/TiO_2 hollow fibre membrane which uncalcined and calcined to high temperature was presented on **Figure 4**. The uncalcined of PVDF/TiO_2 hollow fibre membrane shows five main peaks which consist strong TiO_2, CH_2, CF_2 and PVDF groups. When the samples calcined at 100-500 °C, the PVDF and both of C group gradually decomposed. The CH_2 and CF_2 groups extremely disappear at calcined temperature of 500 °C and left over the TiO_2 (1.69 unit area) and weak PVDF groups (0.51 unit area) based on **Figure 4**. It is only exhibited the TiO_2 group and small PVDF peaks. The α PVDF was transformed into β-crystal as increasing calcined temperature at 300 °C. β-crystal is the most desired crystal structure in PVDF as TTTT configuration which produce the highest dipole moment [41].

Uncalcined hollow fibre membranes showed sharp and narrow curve at absorption band of 1400 cm^{-1}. The absorption band at 1400 cm^{-1} is referred to the in plane bending vibration of CH_2 bond, which belongs to the PVDF chain (Figure 3). Reduced in absorbance for absorption band 1400 cm^{-1} signified low bending vibration it is due to at 500 °C that CH_2 groups are already oxidized [4, 42]. As observed for calcined hollow fibre membranes at 300 °C was presented the low PVDF group of 1.38 which indicating the existence of β-crystal [41]. It concluded that PVDF/TiO_2 hollow fibre membrane with calcination temperature of 300 ◦C was the optimized membrane in this work due to the β-crystal of PVDF was increased.

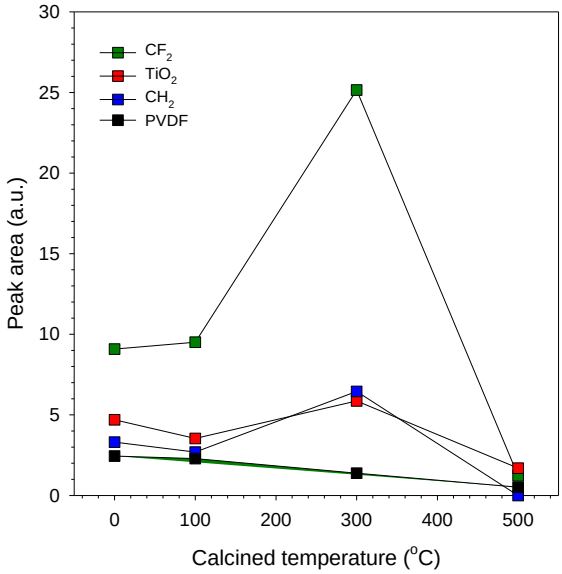

Figure 4. represents peak area of PVDF-TiO_2

Conclusion

This work shows that calcination temperature has a considerable influence on structure properties of hollow fibre membranes derived from PVDF/TiO_2. The FTIR spectra of all PVDF/TiO_2 membranes indicated bands of OH in the TiO_2 at ~1600 cm^{-1}. Peaks of α-phase PVDF crystals appeared at ~876, ~876, and=~872 cm^{-1} for uncalcined, 100 and 300 °C, while for 500 °C the PVDF peak only shows at 874 cm^{-1}. The peaks at ~1200 cm^{-1} represent CF_2 groups. Peaks at ~1400 cm^{-1} assigned to CH_2 groups, but it does not observed for 500 °C. Deconvolution by Fityk software that shows calcination using vacuum condition gives the compounds gradually decomposes. At high temperature calcination lead the CH_2 peak extremely lost due to oxidized reaction. The highest β-crystal PVDF properties is necessary obtained by calcined at temperature 300 °C. It is considered that in Gaussian peak component are related to the different calcined temperature which allow us to design the polymer structure of PVDF/TiO_2 based on its peak intensities.

Acknowledgment

Authors thanks to Materials and Membranes Research Group (M2ReG) Lambung Mangkurat University for the research facilities. Nurul Huda Thanks to AMTEC, UTM for the membrane hollow fibre fabrication. Muthia thanks to Applied Research Universities Grant 2019-2020 & 2021-2023, Basic Research Universities Grant 2021-2022, Thesis Magister Grant 2020, World Class Research Grant 2021-2022 the Directorate of Research and Community Service, the Ministry of Research and

Technology/the National Agency for Research and Innovation Republic of Indonesia and Lambung Mangkurat University Research Grant 2020.

References

[1] Rampun E L A, Elma M, Syauqiah I, Putra M D, Rahma A and Pratiwi A E J J K S d A 2019 Interlayer-free Silica Pectin Membrane for Wetland Saline Water via Pervaporation **22** 99-104
[2] Gao A 2016 Desalination of high-salinity water by membranes. University of Waterloo)
[3] Elma M and Riskawati N 2018 Silica membranes for wetland saline water desalination: performance and long term stability *E&ES* **175** 012006
[4] Elma M, Rampun E L A, Rahma A, Assyaifi Z L, Sumardi A, Lestari A E, Saputro G S, Bilad M R and Darmawan A 2020 Carbon templated strategies of mesoporous silica applied for water desalination: A review *Journal of Water Process Engineering* **38** 101520
[5] Elma M, Pratiwi A E, Rahma A, Rampun E L A and Handayani N 2020 The Performance of Membranes Interlayer-Free Silica-Pectin Templated for Seawater Desalination via Pervaporation Operated at High Temperature of Feed Solution *Materials Science Forum* **981** 349-55
[6] Elma M, Hairullah and Assyaifi Z L 2018 Desalination Process via Pervaporation of Wetland Saline Water *IOP Conference Series: Earth and Environmental Science* **175** 012009
[7] Elma M, Fitriani, Rakhman A and Hidayati R 2018 Silica P123 Membranes for Desalination of Wetland Saline Water in South Kalimantan *IOP Conference Series: Earth and Environmental Science* **175** 012007
[8] Elma M and Saputro G S 2020 Performance of Cobalt-Silica Membranes through Pervaporation Process with Different Feed Solution Concentrations *Materials Science Forum* **981** 342-8
[9] Uragami T, Fukuyama E and Miyata T J J o M S 2016 Selective removal of dilute benzene from water by poly (methyl methacrylate)-graft-poly (dimethylsiloxane) membranes containing hydrophobic ionic liquid by pervaporation **510** 131-40
[10] Yang H, Elma M, Wang D K, Motuzas J and Diniz da Costa J C 2017 Interlayer-free hybrid carbon-silica membranes for processing brackish to brine salt solutions by pervaporation *Journal of Membrane Science* **523** 197-204
[11] Fan H and Peng Y 2012 Application of PVDF membranes in desalination and comparison of the VMD and DCMD processes *Chemical Engineering Science* **79** 94-102
[12] D'Arienzo M, Crippa M, Essawy A A, Scotti R, Wahba L, Morazzoni F, Gentile P, Bellobono I R and Polizzi S 2010 Membrane-Assisted Charge Separation and Photocatalytic Activity in Embedded TiO2: A Kinetic and Mechanistic Study *The Journal of Physical Chemistry C* **114** 15755-62
[13] Sun J, Qian X, Wang Z, Zeng F, Bai H and Li N 2020 Tailoring the microstructure of poly (vinyl alcohol)-intercalated graphene oxide membranes for enhanced desalination performance of high-salinity water by pervaporation *Journal of Membrane Science* 117838
[14] Parvizian F, Ansari F and Bandehali S 2020 Oleic acid-functionalized TiO2 nanoparticles for fabrication of PES-based nanofiltration membranes *Chemical Engineering Research and Design*
[15] Shi H, Liu F and Xue L 2013 Fabrication and characterization of antibacterial PVDF hollow fibre membrane by doping Ag-loaded zeolites *Journal of Membrane Science* **437** 205-15
[16] Deshmukh S P and Li K 1998 Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fibre membranes *Journal of Membrane Science* **150** 75-85
[17] Rahma A, Elma M, Rampun E L A, Pratiwi A E, Rakhman A and Fitriani 2020 Rapid thermal processing and long term stability of interlayer-free Silica-P123 membranes for wetland saline water desalination *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* **71** 1-9

[18] Elma M, Mujiyanti D R, Ismail N M, Bilad M R, Rahma A, Rahman S K, Fitriani, Rakhman A and Rampun E L A 2020 Development of hybrid and templated silica-p123 membranes for brackish water desalination *Polymers* **12** 1-13
[19] Ebnesajjad S 2017 *Applied Plastics Engineering Handbook (Second Edition),* ed M Kutz: William Andrew Publishing) pp 55-71
[20] Camacho L M, Dumée L, Zhang J, Li J-d, Duke M, Gomez J and Gray S 2013 Advances in Membrane Distillation for Water Desalination and Purification Applications **5** 94-196
[21] Krzeminski P, Gil J A, Nieuwenhuijzen A F and van der Graaf J 2012 Flat sheet or hollow fibre — comparison of full-scale membrane bio-reactor configurations *Desalination and Water Treatment* **42** 100-6
[22] Berk Z 2009 *Food Process Engineering and Technology,* ed Z Berk (San Diego: Academic Press) pp 233-57
[23] Thomas N, Mavukkandy M O, Loutatidou S and Arafat H A 2017 Membrane distillation research & implementation: Lessons from the past five decades *Separation and Purification Technology* **189** 108-27
[24] Elma M, Ayu R, Rampun E L, Annahdliyah S, Suparsih D R, Sari N L and Pratomo D A 2019 Fabrication of interlayer-free silica-based membranes–effect of low calcination temperature using an organo-catalyst *Membrane Technology* **2019** 6-10
[25] Wang D K, Elma M, Motuzas J, Hou W-C, Schmeda-Lopez D R, Zhang T and Zhang X 2016 Physicochemical and photocatalytic properties of carbonaceous char and titania composite hollow fibers for wastewater treatment *Carbon* **109** 182-91
[26] Zare S and Kargari A 2018 *Emerging Technologies for Sustainable Desalination Handbook,* ed V G Gude: Butterworth-Heinemann) pp 107-56
[27] Oh S J, Kim N and Lee Y T 2009 Preparation and characterization of PVDF/TiO2 organic–inorganic composite membranes for fouling resistance improvement *Journal of Membrane Science* **345** 13-20
[28] Méricq J P, Mendret J, Brosillon S and Faur C 2015 High performance PVDF-TiO2 membranes for water treatment *Chemical Engineering Science* **123** 283-91
[29] Yu L Y, Shen H M and Xu Z L J J o A P S 2009 PVDF–TiO2 composite hollow fiber ultrafiltration membranes prepared by TiO2 sol–gel method and blending method **113** 1763-72
[30] Othman M H D, Hubadillah S K, Adam M R, Ismail A F, Rahman M A and Jaafar J 2017 *Current Trends and Future Developments on (Bio-) Membranes*: Elsevier) pp 157-80
[31] Heaney D F 2010 *Sintering of Advanced Materials,* ed Z Z Fang: Woodhead Publishing) pp 189-221
[32] Maimunawaro, Karina Rahman S, Lulu Atika Rampun E, Rahma A and Elma M 2020 Deconvolution of carbon silica templated thin film using ES40 and P123 via rapid thermal processing method *Materials Today: Proceedings*
[33] Ayu Lestari R, Elma M, Rampun E L A, Sumardi A, Paramitha A, Eka Lestari A, Rabiah S, Assyaifi Z L and Satriaji G J E S W C 2020 Functionalization of Si-C Using TEOS (Tetra Ethyl Ortho Silica) as Precursor and Organic Catalyst **148** 07008
[34] Kamaludin R, Puad A S M, Othman M H D, Kadir S H S A and Harun Z 2019 Incorporation of N-doped TiO2 into dual layer hollow fiber (DLHF) membrane for visible light-driven photocatalytic removal of reactive black 5 *Polymer Testing* **78** 105939
[35] Hashim N, Liu Y and Li K 2011 Stability of PVDF hollow fibre membranes in sodium hydroxide aqueous solution *Chemical Engineering Science - CHEM ENG SCI* **66** 1565-75
[36] Luongo J J J o P S P A P P 1972 Far-infrared spectra of piezoelectric polyvinylidene fluoride **10** 1119-23
[37] Ruan L, Yao X, Chang Y, Zhou L, Qin G and Zhang X J P 2018 Properties and Applications of the β Phase Poly (vinylidene fluoride) **10** 228

[38] Yu J-G, Yu H-G, Cheng B, Zhao X-J, Yu J C and Ho W-K 2003 The Effect of Calcination Temperature on the Surface Microstructure and Photocatalytic Activity of TiO2 Thin Films Prepared by Liquid Phase Deposition *The Journal of Physical Chemistry B* **107** 13871-9
[39] Dzinun H, Othman M H D, Ismail A, Puteh M H, Rahman M A and Jaafar J 2016 Photocatalytic degradation of nonylphenol using co-extruded dual-layer hollow fibre membranes incorporated with a different ratio of TiO2/PVDF *Reactive and Functional Polymers* **99** 80-7
[40] Rahma A, Elma M, Rampun E L A, Pratiwi A E, Rakhman A and Fitriani 2020 Rapid Thermal Processing and Long Term Stability of Interlayer-free Silica-P123 Membranes for Wetland Saline Water Desalination *Advanced Research in Fluid Mechanics and Thermal Sciences* **71** 1-9
[41] Rozana M D, Arshad A N, Wahid M H M, Habibah Z, Sarip M N and Rusop M 2018 Effect of annealing temperatures on the morphology and structural properties of PVDF/MgO nanocomposites thin films *AIP Conference Proceedings* **1963** 020035
[42] Saputra R E, Astuti Y and Darmawan A 2018 Hydrophobicity of silica thin films: The deconvolution and interpretation by Fourier-transform infrared spectroscopy *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **199** 12-20