Photodegradation stability study of PVDF- and PEI-based membranes for oily wastewater treatment process

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Abstract. In this work, an attempt was made to compare the effects of UV irradiation on the intrinsic and separation properties of membranes made of two different polymeric materials, i.e., polyvinylidene fluoride (PVDF) and polyetherimide (PEI). The changes on membrane structural morphologies and chemical characteristics upon UV-A exposure (up to 60 h) were studied by FESEM and FTIR, respectively. It was found that cracks and fractures were detected on the PVDF-based membrane surface when the membrane was exposed directly to UV light for up to 60 h. Furthermore, the mechanical strength and thermal stability of irradiated PVDF-based membrane was reported to decrease with increasing UV exposure time. The PEI membrane surface meanwhile remained almost intact throughout the entire UV irradiation process. Filtration experiments showed that the permeate flux of UV-irradiated PVDF membrane was significantly increased from approximately 11 to 16 L/m^2.h with increasing UV exposure time from zero to 60 h. Oil rejection meanwhile was decreased from 98 to 85%. For the PEI-based membrane, oil rejection of >97% was recorded and its overall structural integrity was marginally affected throughout the entire UV irradiation process. The findings of this work showed that the PEI-based membrane should be considered as the host for photocatalyts incorporation if the membrane was to be used for UV-assisted wastewater treatment process.

Keywords: ultrafiltration; polymer; UV irradiation; degradation; morphology

1. Introduction

Oily wastewater produced from manufacturing industries and domestic sewage has been commonly recognised as a serious threat to the natural environment in the world. A growing concern has been accumulated to find an effective way to reduce the amount of contaminants released to our nature water body system.

Although oily wastewater could be treated by several conventional techniques such as centrifugation (Hu *et al.* 2013, Diya'uddeen *et al.* 2011), electrocoagulation (Karhu *et al.* 2012), membrane filtration (Li *et al.* 2006, Zhu *et al.* 2014, Alzahrani and Mohammad 2014) and

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flotation process (Painmanakul *et al.* 2010, Ran *et al.* 2013), these techniques are associated with either high operating cost, larger foot print area or lack of capability in eliminating organic components.

Advanced oxidation process (AOP) has been considered as a promising solution due to its advantages of degrading recalcitrant, toxic and non-biodegradable compounds. Of the AOP methods available, submerged membrane photocatalytic reactor (SMPR) has drawn immense attention, mainly due to its capability of degrading organic pollutants and producing clean water simultaneously (Chong *et al.* 2010, Molinari *et al.* 2013, Mozia *et al.* 2013, Fernández *et al.* 2014, Ho *et al.* 2009, Kertèsz *et al.* 2014, Kim *et al.* 2010, Molinari *et al.* 2002, Ong *et al.* 2014, Sarasidis *et al.* 2014, Kushwaha *et al.* 2014a). Furthermore, SMPR offers great advantages such as low operating cost, ease of maintenance and high efficiency in removing organic substances (Chong *et al.* 2010). Nevertheless, one inherent problem for this configuration is the possible deterioration of the polymeric membrane material when membrane is directly exposed to UV light during treatment process. This problem is caused by the immobilized photocatalysts which absorb UV light energy, causing membrane ageing and further altering its surface morphology and separation performance.

Generally, it is known that the UV energy is the main factor damaging membrane surface structure as its high radiation energy tends to induce chain cleavage in the molecules, leading to not only structural deterioration but also chemical changes in polymeric membranes (Kushwaha *et al.* 2014a, Rupiasih *et al.* 2013). Jyothi *et al.* (2014) for instance reported that the surface of polysulfone/titanium dioxide (PSF/TiO_2) mixed matrix membrane was suffered from random cracks after subjecting to only 40 min UV exposure. Similar result was also reported by Rupiasih *et al.* (2013) in which cracks and fractures were detected on the surface of membrane made of PSF when the membrane was exposed to UV-C light (with intensity of 0.28 W/m^2) for only 45-60 min. It is explained that the surface damages are caused by the dissociation of bonds, i.e., C-S and C-O groups of polymeric materials upon UV exposure. The changes in membrane surface properties have also been found to significantly increase pure water flux of the control PSF membrane from 900 to >3,000 L/m^2h after 60 min UV exposure. Other than PSF, polymers such as polymethylmethacrylate (PMMA) (Torikai and Hasegawa, 1998), polyvinylpyrrolidone (PVP) (Horikoshi *et al.* 2001), poly(vinyl chloride) (PVC) (Gesenhues, 2000), polypropylene (PP) (Zhenfeng *et al.* 1996, Lonkar *et al.* 2012), chitosan (Kushwaha *et al.* 2015), polybenzimidazoles (PBIs) (Kushwaha *et al.* 2014b) and polycarbonate (PC) (Geretovszky *et al.* 2002) were also reported to suffer from severe degradation under UV light, owing to the breakage of the chemical bonds of the methine group (-CH-). Although most of the studies showed that there are significant changes on the membrane surface after UV irradiation, very limited research has concerned the sustainability of different polymer-based membrane separation performance with respect to the membrane microstructure, morphological changes and chemical composition under UV irradiation.

In this study, an attempt is made to compare the properties of polyvinylidene fluoride (PVDF)-based membrane with another type of membrane made of higher UV resistance material, i.e., polyetherimide (PEI). PEI is known to have exceptional mechanical and thermal properties (Wang *et al.* 2016). Both membranes were incorporated with same amount of inorganic titanium dioxide (TiO_2) which as photocatalyts in order to expedite the ageing process under UV irradiation. The aim of this study is to provide more information on the effect of UV irradiation in longer term on the properties of two polymeric membranes with respect to structural morphologies and separation performance.

2. Experimental

2.1 Materials

PVDF (Kynar® 760) pellets were purchased from Arkema Inc, Philadelphia, USA. PEI (Ultem® 1000) pellets were purchased from Sabic, Singapore. N,N-dimethylacetamide (DMAc) (Merck, >99%) was used as solvent to dissolve polymer without further purification. PVP (Molecular weight: 40,000 g/mol) purchased from Sigma Aldrich and TiO_2 (Degussa P25, a mixture of 75% anatase and 25% rutile with BET surface area 50 m^2/g, average particle size ~21 nm and energy band gap 3.18 eV) from Evonik were used as the pore forming agent and photocatalyst, respectively.

2.2 Preparation of membrane and membrane module

18 wt% of PVDF was added into pre-weighed DMAC solvent after being dried for 24 h in oven at 50℃. The solution was then mechanically stirred at 600 rpm until all the polymeric pellets were completely dissolved. It was followed by the addition of 2 wt% of TiO_2 nanoparticles and 5 wt% of PVP into the mixture. The dope solution was then ultrasonicated to remove any air bubbles trapped in the solution prior to the spinning process. PEI-TiO_2 hollow fibers were prepared in the same way as PVDF-TiO_2.

Both PVDF- and PEI-based hollow fiber membranes were fabricated using dry-jet wet spinning method as described elsewhere (Molinari *et al.* 2002). The as-spun hollow fibers were immersed into water bath for two days to remove residual solvent. Prior to air drying, the fibers were post-treated by 10 wt% glycerol aqueous solution for 1 day to minimize fiber shrinkage and pore collapse. Lastly, the hollow fibers were dried at room temperature for 3 days before module fabrication.

A bundle of 60 hollow fibers with approximate length of 0.28 m was then potted into PVC tube using epoxy resin (E-30CL Locite® Corporation, USA). The membrane module was then left for hardening at room temperature before its protruding parts were cut and fixed into a PVC adaptor to complete the module preparation.

2.3 Membrane UV exposure chamber

Fig. 1 illustrates a membrane UV exposure chamber made of aluminium with size of 33 cm (W)×53 cm (L)×10 cm (H). Two 36 W UV-A lamps (Model: PL-L 36W/10/4P, Philips) were located at the top and bottom of the chamber. These hollow fiber membranes were placed in the middle of chamber with distance of around 4 cm to the top and bottom UV lamps. Total light intensity of approximately 170 mW/cm^2 (from two UV lamps) was recorded at the middle of chamber by a UVX radiometer (Model: UVP Inc., Upland, CA) with a UV-A sensor (Model: UVX-36, UVP Inc., Upland, CA). The membrane exposure period interval for UV irradiation was set at 0, 40 and 60 h. For each interval, several fibers were taken and used for further analysis.

2.4 Ultrafiltration experiment

The separation performance was assessed by placing two U-shaped hollow fiber membrane modules at the bottom of a submerged tank containing approximately 14 L of oily wastewater. The
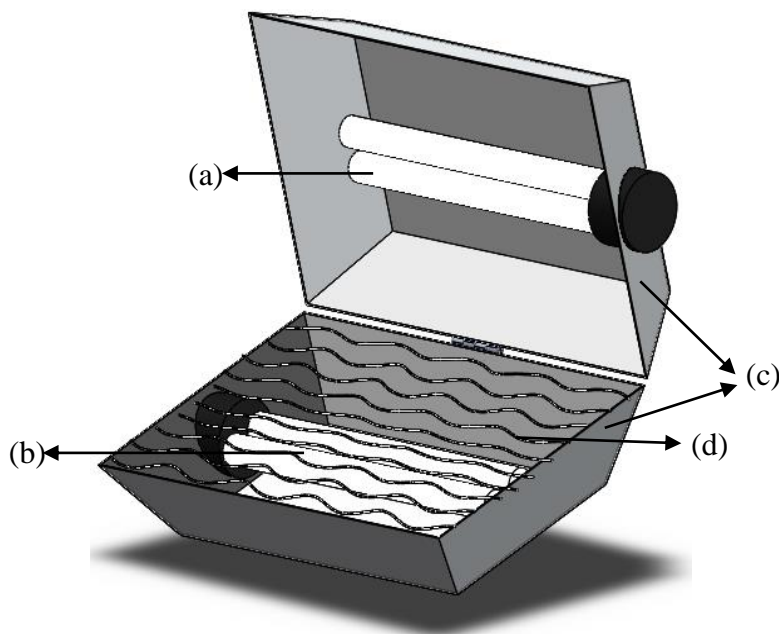
Fig. 1 Schematic diagram of the UV exposure chamber: (a) top UV-A lamp, (b) bottom UV-A lamp, (c) aluminium foil tray and (d) PVDF(or PEI)-TiO$_2$ hollow fibers

synthetic oily wastewater was prepared by mixing 1000 ppm (equivalent to mg/L) crude oil obtained from Terengganu Crude Oil Terminal (Location: RE110, Malaysia) and sodium dodecylbenzenesulfonate (SDS) at the ratio of 9:1 under an agitation speed of 50 Hz using a mechanical blender (Model: BL 310AW, Khind) for approximately 2 min at room temperature. To minimize the fouling effect, a constant air flow rate of 5 L/min generated by an air compressor (Model: 2HP single cylinder 24L tank, Orimas) was used to generate air bubbles within the submerged tank through air diffuser installed underneath the membrane modules. Water permeate was produced using a peristaltic pump (Model: 77200-60, Masterflex L/S, Cole Parmer) by creating a vacuum condition on the permeate side. Both the vacuum pressure and pump flow rate were kept constant at -15 inHg and 15 mL/min, respectively, throughout the experimental period. A 10 mL sample was taken from the permeate for sample analysis and the remaining permeate was recycled back to the tank. Three measurements were made for each sample and then the average value was reported. The membrane water flux (J) was determined according to Eq. (1).

$$J = \frac{Q}{At} \tag{1}$$

where J is the water flux (L/m^2.h), Q is the quantity of the permeate (L), A is the effective membrane area (m^2), and t is the time (h) to obtain the quantity of Q. The membrane oil rejection was then calculated using the following equation.

$$R = \left(1 - \frac{C_p}{C_F}\right) \times 100 \tag{2}$$

where R is the oil rejection (%), C_p and C_F are the concentration of oil in the permeate (ppm) and the feed (ppm), respectively. The oil concentration in the permeate and feed was determined using a UV-vis spectrophotometer (Model: DR5000, Hach) measured at a wavelength of 278 nm at which the maximum absorption occurs.

2.5 Membrane characterization

The membrane surface and cross-sections of the samples were examined using field-emission scanning electron microscope (FESEM) (Model: SU8020, Hitachi). The dry membrane samples were immersed in liquid nitrogen and fractured, followed by sputter-coating with platinum using a sputtering device. Fourier-transform infrared (FTIR) spectra of the membrane samples were performed using attenuated total reflectance Fourier transform infrared spectroscope (ATR-FTIR) (Model: Nicolet 5700, Thermo Electron Scientific Instruments Corporation). These spectra were recorded at resolution between 650 and 4000 cm^{-1}. Thermal gravimetric analysis (TGA) of the membrane samples were recorded by thermogravimetry analyzer (Model: TGA/SDTA85, Mettler Toledo). The membrane sample was cut into small pieces, weighed and placed into a pre-weighed aluminium crucible. The samples were heated from 30 to 800°C at a heating rate of 10°C/min, under nitrogen atmosphere, with a nitrogen flow rate of 20 mL/min. Fiber tensile test was performed at room temperature on a tensile tester (Model: LRX 2.5KN, LLYOD). The gauge length of membrane sample was fixed at 50 mm and the gauge running speed was set at 10 mm/min. The mechanical properties of the membrane were then evaluated with respect to tensile strength and elongation-at-break using NEXTGEN software.

3. Results and discussion

Table 1 compares the FESEM image of cross-sectional structure of PVDF- and PEI-based membrane at two different magnifications (500× and 2000×) after exposing to UV-A light for up to 60 h. With respect to the virgin structure of the membranes, it is found that both membranes exhibited asymmetric morphology that consisted of top thin selective layer (outer surface) supported by porous structure. Although both membranes were made of same concentration of polymer and inorganic filler, their cross-sectional structures were totally different. This can be attributed to different solvent-non-solvent exchange rate during phase inversion process which was strongly dependent on the intrinsic characteristics of polymer itself. Large microvoids were found in the PVDF-based membrane compared to finger-like structure in the PEI-based membrane. The presence of small white particles throughout the structure of both membranes is due to the incorporation of TiO$_2$ into membrane matrix during dope solution preparation.

By subjecting the membranes to UV irradiation, it is found that the outer surface of PVDF-based membrane suffered significant change in comparison to the PEI-based membrane. Particularly for 60-h irradiation, the structure integrity of PVDF-based membrane was severely affected. The PEI-based membrane meanwhile suffered negligible change on the top layer. The results indicated that the PVDF material is not suitable to be used for UV irradiation process due to its relatively low resistance against UV light exposure.

Further surface analysis shown in Table 2 revealed that there were cracks and factures found on the outer surface of PVDF-based membrane. Selective layer (dense structure) of the membrane was obviously altered after 60-h UV light irradiation. The propagation of surface cracks at the

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early stage of UV exposure can be ascribed to the absorption of UV energy on membrane surface which generates a large amount of free radicals that causes membrane surface to deform (Kushwaha *et al.* 2013). Furthermore, the thermal-induced expansion and contraction between

Table 1 Comparison between the cross-sectional morphology of PVDF- and PEI-based hollow fiber membrane at different magnification after exposing to UV light for up to 60 h
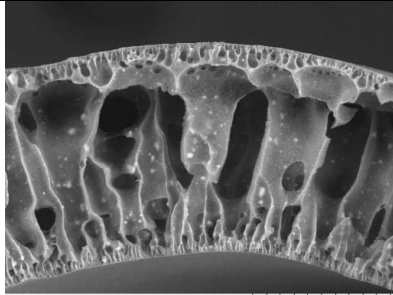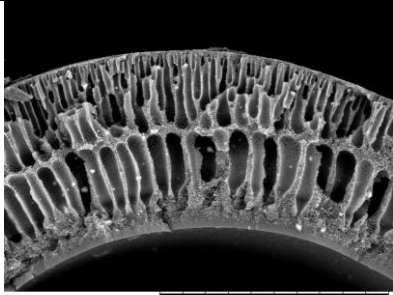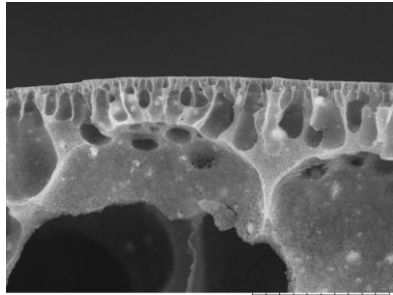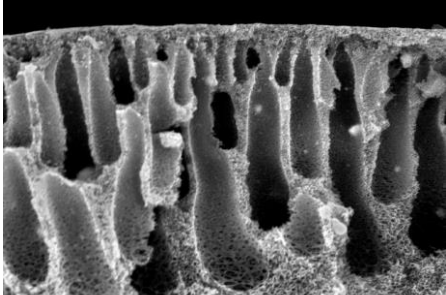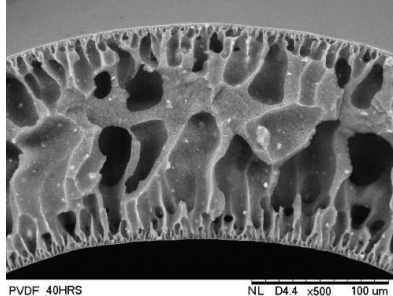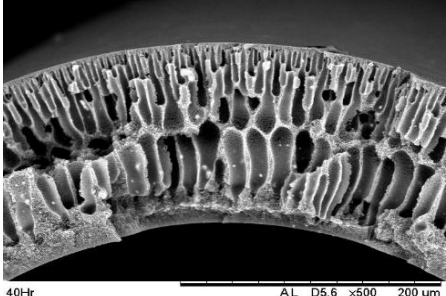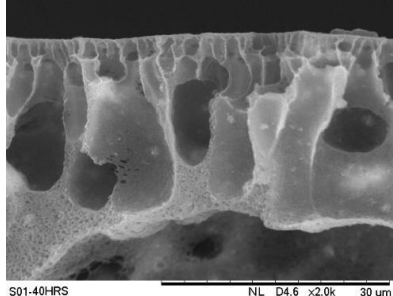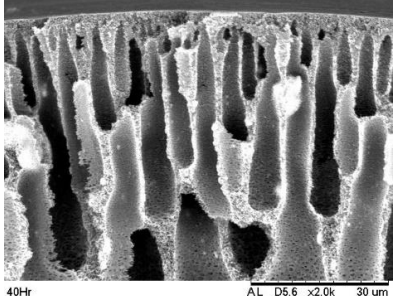
UV exposure time (h)	PVDF-TiO$_2$ membrane	PEI-TiO$_2$ membrane
0		
40		

Table 1 Continued

60

surface and interior of the irradiated membrane under continuous UV irradiation are also likely to cause the formation of cracks and fractures on the PVDF-based membrane. For the membrane made of PEI material, it can be seen that the membrane surface pore sizes were slightly increased and the overall surface integrity of this membrane was marginally affected by UV irradiation.
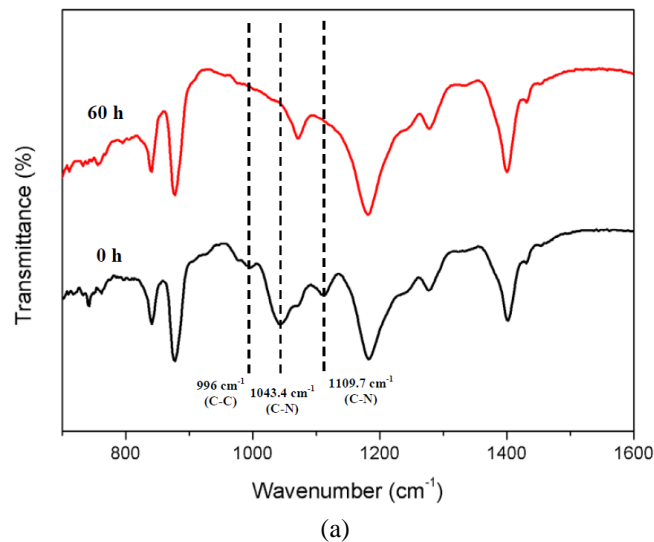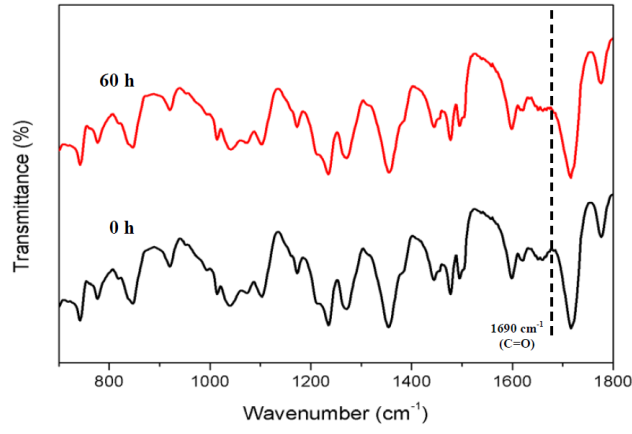

(a)

Fig. 2 FTIR spectra of polymeric membrane at zero (pristine) and 60 h UV irradiation, (a) PVDF-TiO_2 composite and (b) PEI-TiO_2 composite membranes

(b)

Fig. 2 Continued

Table 2 Comparison between outer surface of PVDF- and PEI-based hollow fiber membrane after exposing to UV light for up to 60 h
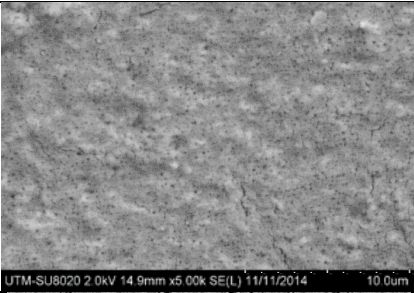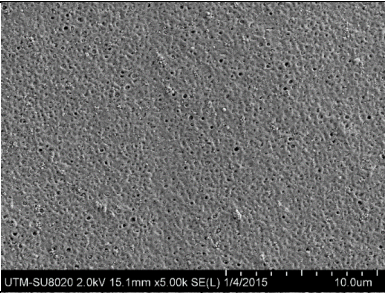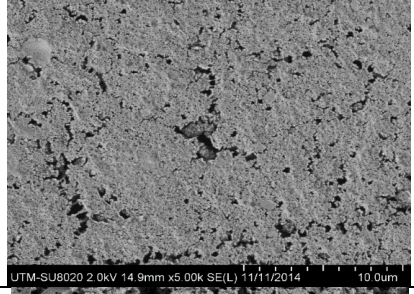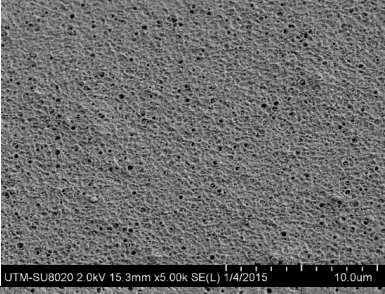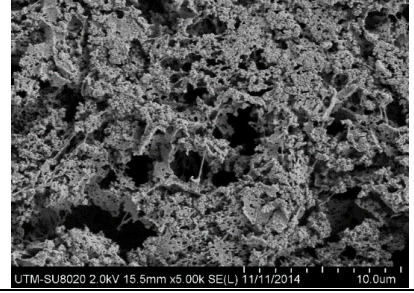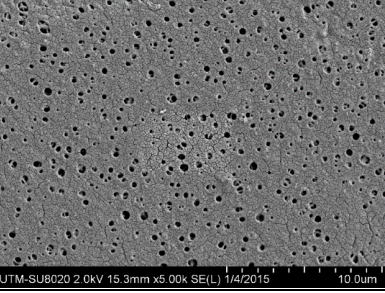
UV exposure time (h)	PVDF-TiO$_2$ membrane	PEI-TiO$_2$ membrane
0		
40		
60		

Fig. 2 compares the FTIR spectra of the pristine polymeric membrane with its spectra after 60-h UV irradiation change. Comparing between the PVDF- and PEI-based membranes, it can be clearly seen that PVDF-based membrane suffered significant changes in its spectra. Two major peaks (at 996 and 1109.7 cm^{-1}) found in the original PVDF-based membranes were disappeared in the UV-irradiated membrane while one peak at 1043.4 cm^{-1} was shifted to ~1072 cm^{-1} which is α-phase of PVDF polymer after UV exposure (Peng *et al.* 2014). The peak at 996 cm^{-1} is assigned to stretching vibration of C-C bonds in the PVDF-TiO$_2$ membrane while peaks at 1043.4 cm^{-1} and 1109.7 cm^{-1} are due to the stretching vibration of C-N bonds (Socrates, 2002), owing to the existence of PVP as pore former in the membrane. Upon UV illumination, C-N and C-C bonds on the membrane were dissociated, leading to photodegradation of polymer and further change in structural morphology as evidenced in Table 1 and 2. In the case of PEI-based membrane, only one marginal change in the peak intensity was observed throughout the spectra. The broadening of the peak (up to 1690 cm^{-1}) centred at ~1720 cm^{-1} took place because of extensive photo-oxidation process due to UV irradiation of PEI. The minor change in the FTIR spectra of PEI-based membrane suggested its superior resistance against UV irradiation, even in the case where photocatalyst was embedded to expedite the ageing process.

Fig. 3 further compares the performance of membranes after UV-irradiation with respect to water flux and oil rejection. For the PVDF-based membrane, the water flux was reported to increase from 10.9 to 16.0 L/m^2.h while oil rejection decreased from 97 to 85% with increasing UV irradiation from zero to 60 h. The change in the performance was in good agreement with the change in membrane structural morphology. Upon 60 h UV exposure, the top selective layer of PVDF-based membrane was negatively affected which led to increase in surface porosity and pore size. Because of this, the membrane exhibited lower resistance against oil molecules which as a consequence affected the oil removal rate. The PEI-based membrane on the other hand maintained its excellent oil rejection (at least 97%) regardless of UV irradiation period. Its water flux was slightly improved from 1.36 to 4.81 L/m^2.h upon UV irradiation. This is likely due to the enlargement of surface pore size as observed from the FESEM image. Overall, it can be said that UV irradiation can further enhance its physical properties in terms of surface pore size (based on FESEM image) but did not alter the surface chemistry of PEI-based membrane (based on FTIR result).

Table 3 presents the mechanical and thermal properties of the studied PVDF-TiO$_2$ membrane exposed to different UV irradiation time. With increasing UV exposure time, the PVDF-TiO$_2$ membrane demonstrated a reduction in the tensile strength and elongation-at-break. The deterioration in membrane mechanical properties can be well-correlated to the formation of cracks on the membrane surface as well as reduced wall thickness as evidenced in Tables 1 and 2, respectively. Although the mechanism involved is not fully understood, it is believed that the surface defects and reduction in membrane wall thickness would act as weak points of the entire membrane integrity and further results in high tendency of membrane structure collapse (Andrew 2008). Cui *et al.* (2013) also found that increasing UV exposure time for a bio-renewable polymer from 250 h to 2,000 h could lead to deleterious effect on polymer mechanical strength following the formation of surface cracks on the studied polymer during photodegradation. Apart from the weakening mechanical properties, the membrane thermal property with respect to decomposition temperature (T$_d$) was reported to decrease from 406 to 390°C after only 120-h UV irradiation. The lower thermal stability of irradiated membrane can be ascribed to the change in structural morphologies of PVDF-TiO$_2$ composite membrane as a result of free radical-induced degradation. Similar pattern was observed by Kushwaha *et al.* (2014) in which a significant decrease of T_d was

(a)

(b)
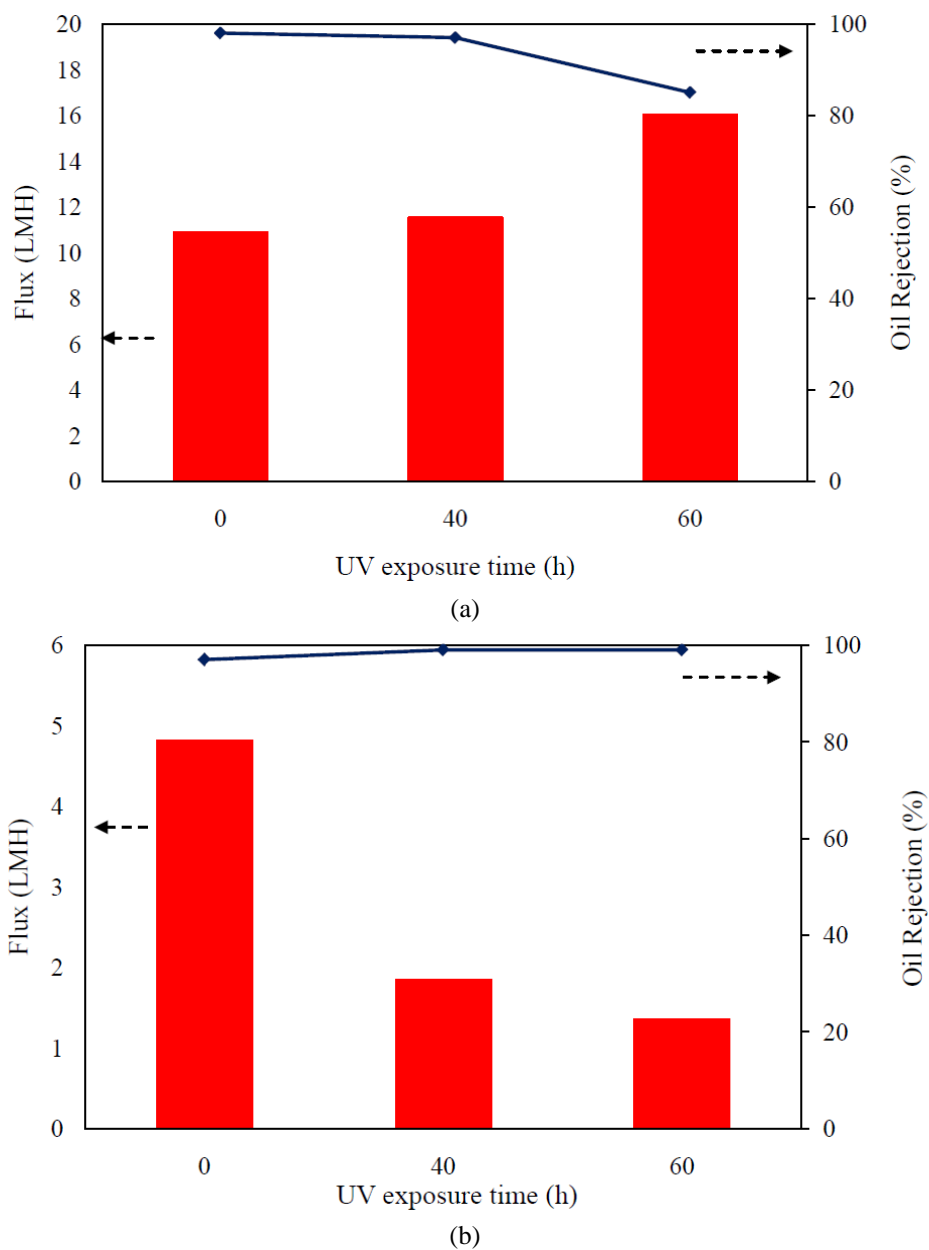
Fig. 3 Comparison of water flux and oil rejection of (a) PVDF-based and (b) PEI-based hollow fiber composite membrane at different UV exposure period

experienced for poly (2,2'-ethylene-5,5'-bibenzimidazole) (PBIE) membrane irradiated for >250 h UV light. They attributed the deterioration in thermal stability of irradiated membrane to the change in molecular structure and molecular weight of PBIE as oxidized by strong radicals produced from UV irradiation. The PEI-based membrane on the other hand maintained its excellent mechanical strength and thermal stability due to marginal change throughout the entire

Table 3 Effect of UV irradiation on mechanical strength and thermal stability of PVDF-TiO$_2$ membrane as a function of UV exposure time

UV exposure time (h)	Tensile strength (MPa)	Elongation-at-break (%)	T_d (°C)
0	0.57	326%	406
40	0.50	160%	421
60	0.42	128%	406

Table 4 Effect of UV irradiation on mechanical strength and thermal stability of PEI-TiO$_2$ membrane as a function of UV exposure time

UV exposure time (h)	Tensile strength (MPa)	Elongation-at-break (%)	T_d (°C)
0	1.45	456%	525
40	1.43	425%	520
60	1.42	420%	516

UV irradiation process (as shown in Table 4) regardless of UV irradiation period. Overall, it can be said that PEI-based membrane has higher thermal stability and mechanical strength than PVDF-based membrane throughout the entire UV irradiation process.

4. Conclusions

The intrinsic and separation properties of membranes made of two different polymeric materials, i.e., polyvinylidene fluoride (PVDF) and polyetherimide (PEI) irradiated for 60 h have been studied in this work. It was found that cracks and fractures were detected on the PVDF-based membrane surface when the membrane was exposed directly to UV light for up to 60 h. Those changes in membrane physical appearance and chemical composition had resulted in deleterious effect to PVDF-based membrane mechanical strength and thermal stability. The PEI membrane surface meanwhile remained almost intact throughout the entire UV irradiation process. Filtration experiments showed that the permeate flux of UV-irradiated PVDF membrane was significantly increased from 11 to 16 L/m^2.h with increasing UV exposure time from zero to 60 h. Oil rejection meanwhile was decreased from 98 to 85%. For the PEI-based membrane, promising oil rejection (>97%) was recorded throughout the entire UV irradiation process. The findings showed that PEI-based membrane could achieve higher UV resistance than PVDF-based membrane owing to the marginal changes in membrane microstructure, surface chemistry and separation performance under UV irradiation.

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