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# SURFACE MODIFICATION OF POLYANILINE ONTO PVDF MEMBRANE VIA RADIATION INDUCED GRAFTING

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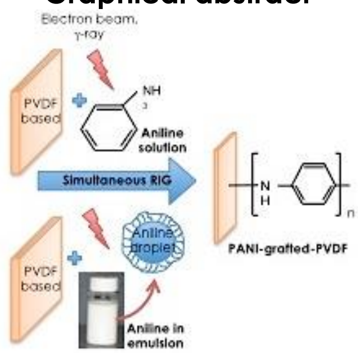
## Graphical abstract




## Abstract

A conductive polymer, polyaniline (PANI) has been grafted onto a poly (vinylidene fluoride) (PVDF) based polymer using simultaneous radiation induced grafting (RIG), which is a new approached in introducing the conductive properties into a preformed polymer for potential selective separation ability during filtration process. The possibility of coating PVDF membrane with PANI was investigated by looking at the effect of monomer concentration, radiation dose, and aniline in emulsion form on the degree of grafting (DOG). The DOG were obtained at 4.44 and 5.43 % for aniline concentration and its emulsion respectively, and increases with the increase in concentration. The PANI-grafted-PVDF membrane was also characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDX) and differential scanning calorimetry (DSC) techniques. The FTIR and SEM results show that PANI was successfully grafted onto PVDF membrane. EDX analysis also confirmed the grafting by the presence of $NH_2$ representing aniline in the PANI-grafted-PVDF membranes. The modification was found to have not change the overall properties of PVDF, still retaining its intrinsic properties.

*Keywords:* Conductive polymer, polyaniline, poly(vinylidene fluoride), simultaneous radiation induced grafting (RIG), selective separation

## Abstrak

Polimer konduktif polianilin (PANI) telah dicantum kepada poli (vinilidin fluorida) (PVDF) menggunakan radiasi cantuman serentak, kaedah baru dalam memperkenalkan polimer bersifat konduktif kepada polimer penyokong yang berpotensi untuk melakukan pemisahan terpilih semasa proses penapisan. Kebolehan untuk mencantumkan PVDF membran dengan PANI telah disiasat dengan melihat kesan kepekatan monomer, dos radiasi dan kepekatan anilin dalam bentuk emulsi kepada darjah percantuman (DOG). DOG yang diperolehi pada 4.44 dan 5.43 % adalah masing-masing untuk kepekatan anilin dan emulsi di mana ia meningkat dengan peningkatan kepekatan. Membran PANI-dicantumkan-PVDF juga dicirikan menggunakan spektroskopi Fourier penukaran inframerah (FTIR), mikroskop pengimbas elektron - spektroskopi tenaga serakan x-ray (SEM-EDX) dan teknik kalorimeter pengimbasan perbezaan (DSC). Keputusan FTIR and SEM menunjukkan bahawa PANI telah berjaya ditambah kepada membran PVDF. Analisis EDX juga mengesahkan cantuman dengan kehadiran $NH_2$ yang mewakili anilin dalam membran PANI-dicantumkan–PVDF. Pengubahsuaian tersebut telah didapati tidak mengubah keseluruhan sifat PVDF di mana PVDF masih mengekalkan ciri-ciri intrinsiknya.

*Kata kunci:* Polimer konduktif, polianilin, poli (vinilidin fluorida), radiasi serentak cantuman, pemisahan terpilih

## 1.0 INTRODUCTION

In separation processes, membrane is commonly utilized in wastewater treatment, bio-product separation and water purification due to its simplicity, cheap, easily fabricated membrane polymer and flexibility in polymer modification. However, the commercially available membranes are restricted for tunable selective separation during filtration process, which limits its application. In order to overcome this limitation, a conducting polymer (CP) is seen as a promising material to improve the complex molecular separation of a membrane for selective separation. The utilization of CP as membrane or for membrane modification enables a membrane to be electrochemically tune for separations [1, 2]. One of the potential CP is the PANI polymer. The membrane free volume, which controls the permeance diffusivity, can be tuned by doping/ dedoping process with acid dopants [3, 4].

PANI is one of the oldest known conducting polymers [5], nevertheless it is still extensively reviewed and draws high interest due to its high conductivity and good stability for wide variety of applications. Presently PANI has been widely used in the manufacturing of chemical sensors, battery electrodes, supercapacitors, fuel cells and anticorrosion coatings [6-9]. PANI is also highly favorable CP due to its simple preparation and doping procedure, low cost and good environmental stability [10]. PANI intrinsic transport properties of low dimensionality, light weight and biological compatibility has also made it a promising polymer to be utilized as robust membrane with controlled changes [11].

Presently, most studies in this field were devoted to the preparation of PANI membrane using immersion phase inversion. However, this process is restricted by the concentration of polymer as it easily forms gel above certain concentration [12, 13] depending on the type of polymer used. Looking into this problem, it is necessitate utilizing new synthesis and fabrication methods of PANI as CP for desired. One of the foreseen potential methods is by radiation induced grafting method, in which CP is grafted with other polymers having good mechanical and physical properties via radiation, thus introducing the conducting selective effect to a preformed polymer membrane.

Radiation induced grafting (RIG) is a method that uses high ionizing energy to form active sites (radicals) on a polymer matrix. The monomer, which is in contact with the radiated polymer, will initiate the graft copolymerization, propagated and finally terminated forming a side chain [14]. RIG is a convenient method to introduce new properties into preformed polymers without altering the properties to a significant extent. Moreover, this method also gives advantages in terms of ease in preparation, in tailoring the composition and in tuning for desired characteristic by only altering the monomer concentration and radiation parameters [15, 16]. The RIG method can be classified into two categories, which are the pre-irradiated and simultaneous irradiation. The former involves irradiating the polymer matrix prior contacting it with a monomer, while the later involves irradiating both polymer matrix and the monomer together at the same time. In this study, the motivation is to prepare a membrane with conductive/selective properties using PANI as the CP grafted onto PVDF membrane based polymer via simultaneous RIG due to the ease in preparation. As this is the first research reported so far on the simultaneous RIG of PANI onto PVDF membrane, the main objective was to determine the possibility of coating PANI on PVDF membrane using the above mentioned method. In this research, aniline monomer was used in diluted solvent and in emulsion form to investigate the degree of grafting (DOG) of PANI. The properties of the grafted membrane were also characterized using Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDX), and differential scanning calorimetry (DSC) techniques.

**Table 1** Parameters of radiation induced grafting of PANI onto PVDF at fixed diluent of 1 M HCl, PVDF support, dose rate of 33 Qy/min and $N_2$ atmosphere*

| Conditions | Experiment A | Experiment B | Experiment C |
|---|---|---|---|
| Aniline Con. (M) | 1.5, 1.3, 1.0, 0.8, 0.6 | 1.3 | 0.5, 0.4, 0.3, 0.2 |
| Radiation Dose (kGy) | 30 | 30, 20, 15, 10, 5 | 30 |
| Surfactant | - | - | 0.03 M Tween-80 in Xylene |

[a]All reactions were carried out at fixed diluent of 1 M HCL, PVDF support, dose rate of 33 Gy/min and in $N_2$ atmosphere.

## 2.0 EXPERIMENTAL

### 2.1 Materials

Polyvinylidene fluoride (PVDF) having a 0.2 µm nominal pore size purchased from Millipore was used in this study. Aniline monomer (ReagentPlus®, 99 %), xylene, ethanol and hydrochloric acid (HCl) 37.5 % assay were purchased from Sigma-Aldrich and used without purification. Deionized water (18 MΩ) and purified nitrogen (99.99 %) were also used in this study.

### 2.2 Radiation of Base Polymer Films

Commercial PDVF films were washed with 50 % ethanol and dried in vacuum oven at 70 $^0$C for 1 hour. The initial weights of the films were recorded.

Meanwhile the grafting of aniline onto PVDF films was carried out by first dissolving nonionic surfactant sorbiton monoleate (Tween 80) in an organic solvent (xylene), while aniline was dissolved in an aqueous solution of 1 M HCl [17]. The two solutions were then mixed together generating a milky solution. Tween 80 was used as it could stabilized the emulsion system long enough before the irradiation took place. The PVDF membrane was then brought into contact with the aniline solutions and the solution was bubbled with purified nitrogen gas to remove air for 10 minutes. The simultaneous irradiation grafting of monomer aniline onto PVDF membrane was carried out under γ-rays from $^{60}$Co source. Radiation dose were varied from 5 to 30 kGy. After irradiation, the PANI-g-PVDF thin films were dried in vacuum oven at 50 $^0$C.

The percentage of grafting were calculated by Equation (1):

$$Degree\ of\ grafting\ (DOG\ \%) = \frac{W_g - W_0}{W_0}\ x\ 100 \qquad (1)$$

where $W_g$ and $W_0$ denote, respectively, are the weight of grafted PVDF and original PVDF.

To study the grafting behavior, aniline concentration (M) and irradiation dose (kGy) have been varied and the effects on the DOG were investigated. Details of parameters of grafting and irradiation conditions of PVDF are given in Table 1.

### 2.3 Characterization

#### *2.3.1 Fourier Transform Infrared Measurement (FTIR)*

Fourier Transform Infrared (FTIR) measurements were carried out using Perkin Elmer Spectrum BX spectrometer to determine the chemical composition of the obtained grafted membrane in comparison to the original PVDF membrane. The measurements were made in the transmittance mode in a wave number range from 4000-450 cm$^{-1}$ with resolution of 4 cm$^{-1}$.

#### *2.3.2 Scanning Transmission Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDX)*

The surface morphologies and chemical components of the membranes were studied using SEM-EDX. The specimen was prepared by initially mounted the dried samples on stubs. They were then sputter-coated with gold using sputter coater (QUORUM Q150RS, UK). Micrographs of samples were taken using SEM-EDX instrument (Carl Zess EVO MA10, UK and Apollo XSDD).

#### *2.3.3 Differential Scanning Calorimetry (DSC)*

Structural properties such as degree of crystallinity and the thermal properties including melting ($T_m$) and crystallization temperature (Tc) were determined using differential scanning calorimetry (DSC) analysis (DSC 822e METTLER TOLEDO). Samples were cut into small pieces of between 5 – 10 mg, placed in aluminum pans and sealed using lid with sealing press (METTLER TOLEDO). The samples were heated over a temperature range of 15 – 350 $^0$C at heating rate of 10 $^0$C/min. The results were taken from the second heating cycle to avoid thermal history interruption of samples. Grafted membrane were analyzed and compared to the original PVDF membrane.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Effects of Simultaneous Irradiation Grafting Parameters on the DOG

The simultaneous irradiation grafting between aniline monomer onto PVDF membrane as based-polymer were investigated at three different conditions: a) effect of variation in aniline monomer concentration on the DOG, b) the effect of different irradiation dose on the DOG and c) the effect of variation in aniline emulsion concentration on the DOG. The study of aniline in emulsion form was carried out to utilize the opportunity of minimizing the consumption of monomer during the grafting process, which consequently introducing an alternative route to a more economical process. Emulsion was also used as it provides a large interfacial area of droplets, which is believed could enhanced the grafting of aniline monomer onto PVDF membrane [17].

#### *3.1.1 Effect of Variation in Aniline Monomer Concentration on DOG*

The effect of variation of aniline monomer concentration on the DOG of aniline onto PVDF membrane irradiated at 30 kGy irradiation dose was investigated and the data obtained is plotted in Figure 1. Figure 1 shows that the DOG increases with the increase in the aniline concentration up to 1.5 M, the highest aniline concentration used. The increase in the concentration of monomer increases the amount of monomer molecules present in the solution, thus more monomer can react with the free radicals resulted in the increase in the DOG above 1 M aniline concentration. The highest DOG was obtained at 4.44 % DOG for 1.5 aniline concentration, the same phenomenon observed in simultaneous grafting of PANI onto chitosan [18] and other polymers [19, 20]. Maximum aniline concentration of 1.5 M was selected due to the limited solubility of aniline in 1 M HCl, above which two layers of solutions were observed. As the concentration of aniline increases, the amount of acid used is insufficient/not acidic enough to protonate all aniline and draw it into aqueous phase. Therefore this resulted in some unprotonated aniline, which explain the limited solubility.

### *3.1.2 Effect of Variation in Irradiation Dose on DOG*

The DOG of 1.3 M aniline concentration in 1 M HCl grafted onto PVDF membrane at various irradiation doses ranging from 5 to 30 kGy is presented in Figure 2. From the figure it can be seen that the DOG slightly decreases from 3.59 to 3.12 % as the radiation dose increases from 5 to 30 kGy. The slight reduction is may be due to the fact that above a certain radiation dose, rapid transformation of monomer into homopolymer may occur resulting in the reduction of polymer chain mobility, thus reduces the grafting rate [20]. This effect, which is known as Trommsdorff effect, was also found in the grafting of other monomer such as MMA and vinyl acetate onto cellulose [21].

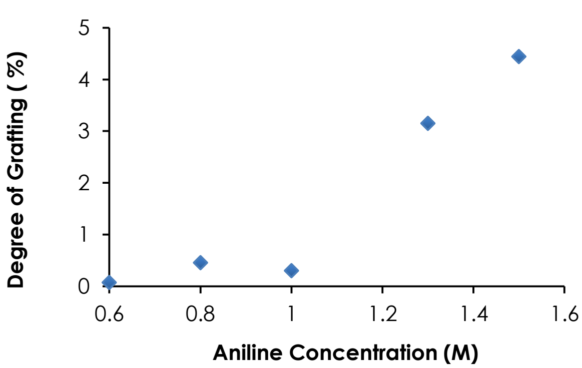



**Figure 1** Degree of grafting (DOG %) against various aniline monomer concentrations (M) in 1 M HCl as solvent at 30 kGy irradiation dose under nitrogen atmosphere

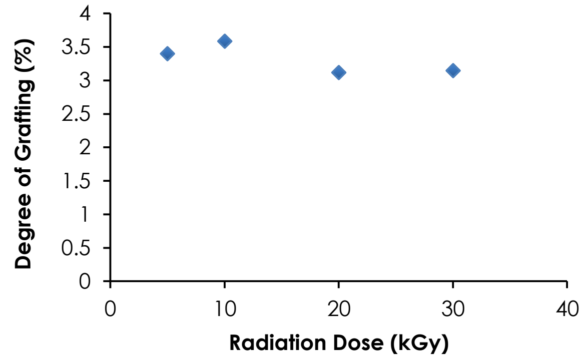



**Figure 2** Degree of grafting (DOG %) against various irradiation doses (kGy) at aniline concentration of 1.3 M in 1 M HCl as solvent under nitrogen atmosphere

### *3.1.3 Effect of Variation in Emulsion Monomer Concentration*

The effect of variation of aniline concentration in emulsion on the DOG of PANI-grafted- PVDF membrane irradiated at 30 kGy irradiation dose was investigated and the data obtained is plotted in Figure 3. It shows that the DOG increases with the increase in the aniline concentration up to 0.4 M beyond which it declines. It is believed that the increase in the DOG is caused by the increase in monomer molecules, which reacts with the number at grafting sites. However once the concentration exceeds 0.4 M, the excess monomer starts to homopolymerize, causing the grafting medium to be more viscous limiting the mobility of the unreacted monomer and its diffusion towards grafting sites.

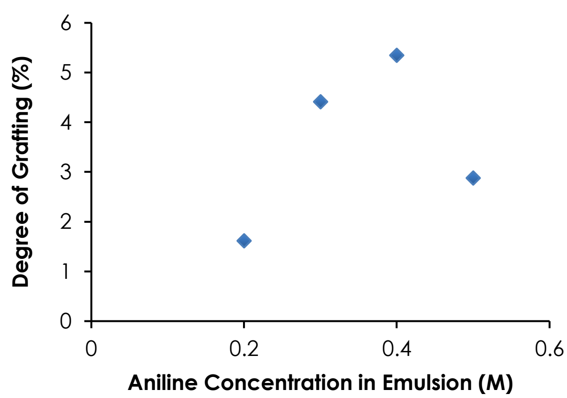



**Figure 3** Degree of grafting (DOG %) against various aniline concentrations in emulsion at 30 kGy irradiation dose under nitrogen atmosphere.

The DOG of PVDF when aniline emulsion was used is found to be higher (5.34 %) than that of aniline solution (4.44 %). The comparison was made based on the highest DOG obtained when grafting was carried out with and without surfactant, which are 5.34 and 4.44% respectively. This indicates that higher DOG could be achieved in the presence of surfactant. In addition to that, it was observed that, when surfactant was utilized, the maximum DOG can be obtained at lower aniline concentration of 0.4 M compared to 1.5 M that was needed to achieve maximum DOG in condition without surfactant. This accounts around 73% reduction in monomer usage. Emulsion polymerization provides a more environmentally friendly route and economical as HCl is used as the dispersion medium instead of organic solvents and only small amount of monomer is required. It also allows good dissipation of heat during reaction and contributes to a higher molecular weight and polymerization rate compared to the normally achieved values in solution, which explain the higher DOG obtain when using emulsion [22].

### 3.2 FTIR Analysis of PANI Grafted PVDF

FTIR analysis is presented to chemical characterize the membrane prepared at different monomer concentration. Figure 4 presents the comparison of FTIR spectra of PVDF membrane, pure aniline and PANI-grafted PVDF membrane. From Figure 4, the spectra of PVDF membrane shows small absorption band at 2990 and 3020 $cm^{-1}$ corresponding to the symmetric and asymmetric stretching vibration of $CH_2$ respectively. The absorption peaks in the FTIR spectra of PVDF at 1402 and 1178 $cm^{-1}$ corresponds to CH stretching mode and $–CF_2$ stretching [23].

In the FTIR spectra of aniline, the analysis indicates the presence of aromatic ring stretching and C-C stretched vibration at around 1600 $cm^{-1}$ (quinonoid) and 1500 $cm^{-1}$ (benzenoid). It is also evident from the spectra the presence of aromatic CN bonding around 1276 $cm^{-1}$, CH stretching and in plane deformation around 3036 and 1175 $cm^{-1}$ respectively. NH stretching is also observed at around 3213 $cm^{-1}$ [24].

For PANI-grafted PVDF membrane at different aniline concentrations, the successful grafting of aniline onto PVDF is confirmed by the presence of additional bands at the based polymer characteristic spectra indicating grafted PANI. The FTIR spectrum shows a small shifted peak at around 1454 and 1526 $cm^{-1}$ for all PANI-grafted-PVDF membrane corresponding to an aromatic ring stretching; benzenoid and quinonoid in the PANI chains [18, 25]. The disappearance of sharp peaks between 2900-3496 $cm^{-1}$ in aniline spectra after radiation indicated by the small arrow show the successful polymerization of aniline into PANI [26]. The size of peaks for 1.5 M aniline concentration was also found to be slightly larger than of DOG of 0.6 M aniline concentration, which in agreement by the higher DOG of 4.44 and 0.07 % respectively.

Similar spectrum was also observed for 0.4 M aniline emulsions used in the grafting of PVDF membrane, whereby no additional peaks representing the surfactant was observed, indicating unaffected PANI/PVDF functional groups and no impurities left that could affect the properties of the PANI-grafted-PVDF membrane.

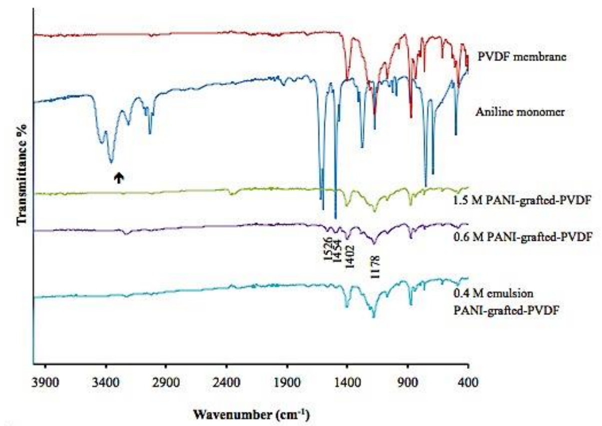



**Figure 4** FTIR spectra of pure aniline, PVDF membrane and PANI-grafted-PVDF membrane using pure and emulsion aniline at different concentrations of 1.5 M and 0.6 M and 0.4 M aniline concentration, respectively irradiated at 30 kGy

### 3.3 SEM-EDX Analysis of PANI Grafted PVDF

The surface topography of pure PVDF, which is used as reference and PANI-grafted-PVDF were analyzed using SEM-EDX analysis are presented in Figure 5 and 6. SEM images of pure PVDF membrane show that the pure PVDF is composed of sponge-like structure having micro-size pores indicating high porosity membrane.

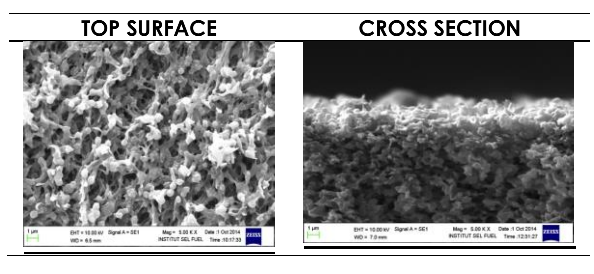



**Figure 5** SEM images of top surface and cross section of pure PVDF membrane

When PANI is grafted via radiation onto the PVDF membrane, a new layer of non-uniform morphological rod-like structure deposited on top of the PVDF membrane surface is observed as seen in Figure 6 A-F, a typical structure of PANI synthesized in aqueous solution [17]. This indicates that the grafting of aniline onto PVDF membrane was successful. Figure A-B represents PANI-grafted-PVDF using 1.5

and 0.6 M aniline concentration, irradiated at 30 kGy radiation dose. The later shows the highest DOG of 4.44 %. Figure B also shows that more deposition of non-uniform morphological rod-like structure of aniline can be seen formed when higher concentration of aniline was used. Similar results were observed for the PANI-grafted-PVDF using 0.4 and 0.2 M aniline emulsion concentration radiated at 30 kGy. These samples represented the highest DOG of aniline emulsion of 5.34 % for 0.4 M and the lowest DOG of 1.62 % for 0.2 M aniline emulsion concentration. The SEM topography of PANI-grafted-PVDF was also analyzed at different radiation dose of 30 and 5 kGy using 1.3 M aniline concentration as presented in Figure E-F, each having a DOG of 3.15 and 3.40 % respectively. As their DOG do not differ much, the density of the non-uniform morphological rod-like structure observed was quite similar

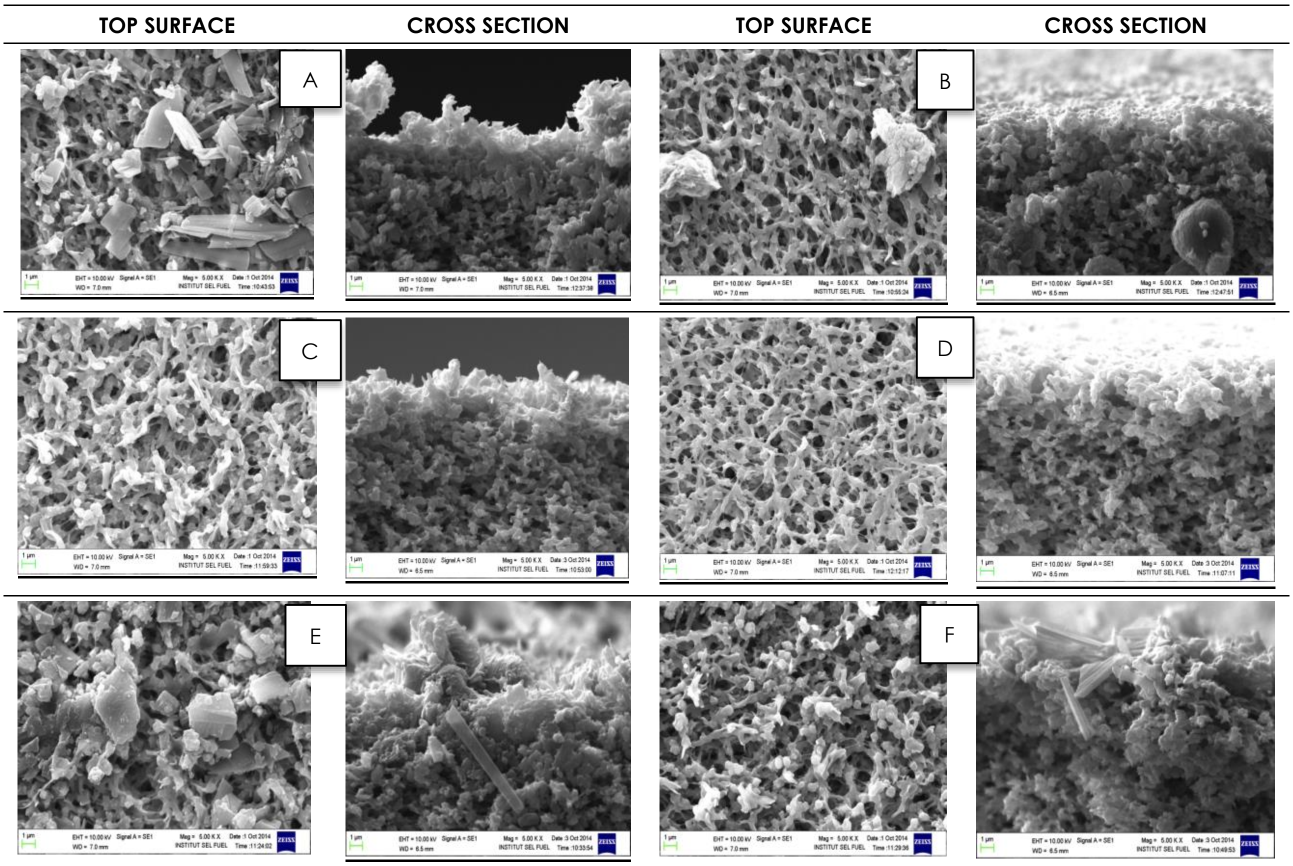



**Figure 6** SEM images of top surface and cross section of PANI- grafted-PVDF membrane using A) 1.5 M and B) 0.6 M aniline concentration, C) 0.4 M and D) 0.2 M aniline emulsion concentration at 30 kGy irradiation dose and 1.3 M aniline concentration at E) 30 kGy and F) 5 kGy

**Table 2** Elements composition from the top surfaces of pure PVDF, PANI-grafted-PVDF grafted with 1.5 M and 0.6 M aniline concentration and 0.4 M and 0.2 M aniline emulsion concentration at 30 kGy irradiation dose and 1.3 M aniline grafted PVDF membrane irradiated at 30 and 5 kGy

| Aniline Con. | C (wt. %) | C (at. %) | N (wt %) | N (at. %) | F (wt. %) | F (at. %) |
|---|---|---|---|---|---|---|
| **Pure PVDF** | 38.68 | 49.94 | - | - | 61.32 | 50.06 |
| **1.5 M** | 38.79 | 49.54 | 3.59 | 3.93 | 57.62 | 46.53 |
| **0.6 M** | 38.70 | 49.51 | 3.14 | 3.45 | 58.15 | 47.04 |
| **0.4 M (Emulsion)** | 36.66 | 47.16 | 4.58 | 5.05 | 58.76 | 47.79 |
| **0.2 M (Emulsion)** | 39.63 | 50.54 | 3.21 | 3.51 | 57.15 | 46.02 |

| Irradiation Dose | C (wt. %) | C (at. %) | N (wt. %) | N (at. %) | F (wt. %) | F (at. %) |
|---|---|---|---|---|---|---|
| **30 kGy** | 56.19 | 66.46 | 2.92 | 2.97 | 40.89 | 30.58 |
| **5 kGy** | 37.07 | 47.73 | 3.54 | 3.91 | 59.40 | 48.36 |

The SEM results are also supported by the EDX analysis, where new peak indicating N element representing aniline appeared in all EDX spectrum of PANI-grafted-PVDF membrane as presented in Table 4. The wt% of N was found to be higher in PVDF grafted with higher concentration of aniline. 1.5 M aniline concentration contain 3.59 wt% of N compared to when 0.6 M was used which is 3.14 wt%. Similar results were also obtained for the PVDF grafted with aniline emulsion using 0.4 and 0.2 M concentration, which contained 4.58 and 3.21 wt% of N respectively. These results are in agreement with the SEM images, which is the higher the concentration of aniline the more deposition of non-uniform morphological rod-like structure on top of the PVDF membrane, therefore the higher the DOG. EDX analyses also shows that PVDF membrane grafted at 5 kGy has higher N wt% of 3.54 compared to membrane irradiated at 30 kGy of 2.92, which is in accordance with the DOG of 3.40 and 3.15 % at respective 5 and 30 kGy. At higher irradiation dose, homopolymerization may have occurred reducing the amount of successful aniline grafted onto the PVDF.

### 3.4 Differential Scanning Calorimeter (DSC)

Figure 7 shows the DSC results of the grafted membrane at different aniline concentration in aqueous and emulsion form. From the DSC analyses, it can be seen that overall only one endothermic peak was detected at approximately 162 $^0$C, which correspond to the crystallization melting temperature. The results indicate that the presence of aniline thus not alter the crystallization melting temperature of PVDF. Such results may be due to the very small amount of aniline used to affect the crystallization melting temperature. However, it is expected that if sufficient PANI is grafted onto PVDF membrane, the overall crystallization temperature of the grafted membrane could be increased due to PANI high crystallization temperature of 250 $^o$C compared to PVDF of 162 $^o$C as presented in Figure 7. The high crystallization temperature will results in increasing membrane thermal stability [27]. The increase in the membrane thermal stability is believed could enhance the filtration ability especially in performing filtration in long run.

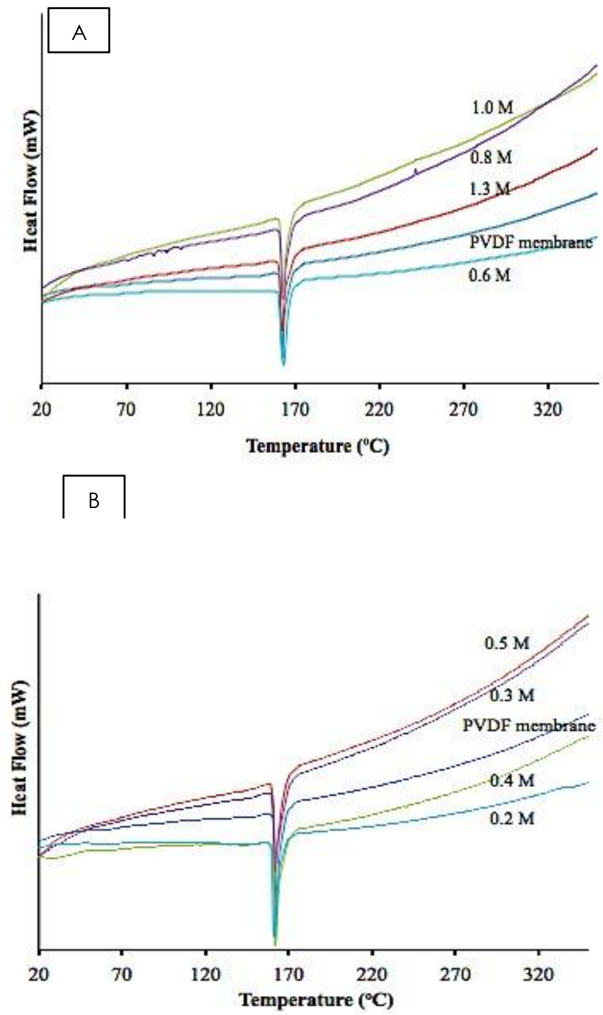



**Figure 7** DSC analyses of pure PVDF membrane and aniline grafted PVDF membrane at A) different aniline concentration of 1.3, 1.0, 0.8 and 0.6 M and B) different aniline emulsion concentration of 0.5, 0.4, 0.3 and 0.2 M irradiated at 30 kGy radiated dose

## 4.0 CONCLUSION

PANI-grafted-PVDF membrane was successfully prepared using simultaneous irradiation grafting using HCl as solvent, proven by the FTIR, SEM and EDX analyses. The DOG of aniline is found to be dependent on the aniline concentration and the irradiation dose. The higher the concentration of aniline the higher the DOG, but the DOG reduces with the increase in irradiation dose. The highest DOG for aniline concentration was found to be 4.44 % while for aniline in emulsion was found to be 5.34 %

for 1.5 M and 0.4 M aniline concentration respectively. This shows an increase of 20 % DOG when PVDF membrane was grafted in the presence of surfactant. It was also found that the DOG increases by 20 % when PVDF membrane was grafted in aniline emulsions form compared to when only aniline solution is used. The DOG was found to be 5.34 % at 0.4 M aniline emulsion. Therefore, this indicates that simultaneous irradiation grafting could be a new promising approach in coating PVDF membrane with PANI for potential appplication in filtration process as selective separation

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