

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Introduction

In this study, the different PVDF polymer solutions studied were basically comprised as binary solutions from polymer and solvent. From the mixture of PVDF and NMP solvent, the optimization of polymer concentrations were continuously studied with addition of different types of additives and surfactants. By using fourier-transform infra-red (FTIR) spectroscopy, the molecular orientation of functional group for the membranes were known while the membranes morphological structures can be seen by using scanning electron microscope (SEM). Thermogravimetric analysis (TGA) used to study the thermal stability and decomposition of the membranes in order to support performance results.

4.2 Polymer Concentration

A series of PVDF/NMP membranes with various polymer concentrations (13-19 wt%) for UF process in membrane application were fabricated via dry/wet phase inversion method. The PVDF membranes with polymer concentrations of 13, 15, 17 and 19 wt% in the membrane casting solutions were marked as PN-1, PN-2, PN-3 and PN-4

respectively. Polymer concentration has been identified as the most important parameter for tailoring of membrane properties during membrane making.

In addition, the solvent ratio also plays a significant role along with polymer concentration during membrane formation. The simultaneous adjustments of these two key parameters allow increase in the viscosity of the dope solution without significant loss in selectivity and productivity. All of the membranes were characterized in terms of PWP, protein separation, and pore properties (pore length and pore width). Besides, PWP and protein separation tests were used to study the performance and separation ability of the membranes.

4.2.1 Pure Water Permeation (PWP)

The membrane permeation test for pure water flux was first measured in order to determine the stability and porosity of the UF membranes. Before performing each fresh membrane for PWP tests, all the fabricated membranes were compacted. The membranes were subjected to compaction by pressurized distilled water for 30 min at pressure of 350 kPa which is the maximum operating pressure designed for the present experiments. The membranes were washed thoroughly before placing them in the membrane batch cell and tightened by a rubber O-ring for used in subsequent UF experiments.

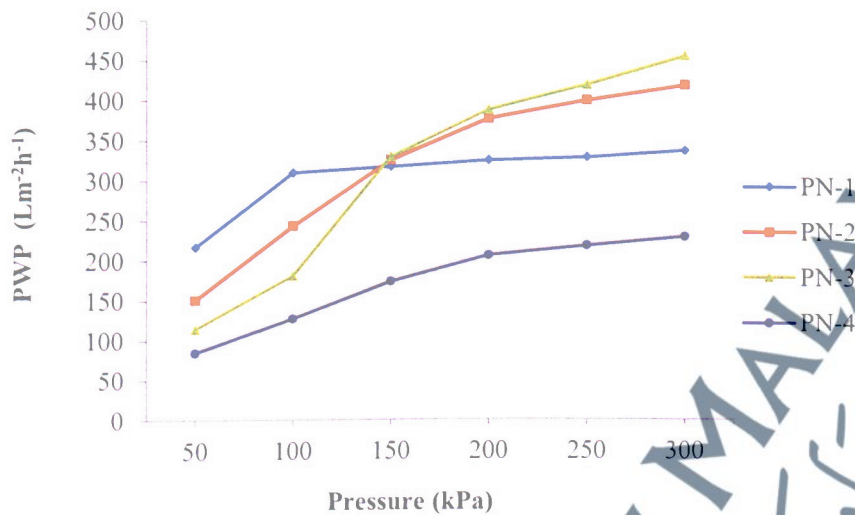
During the compaction test, all the membranes were observed having high PWP at the early stage of time and then the PWP were gradually decreased until the permeation rates reached the steady-state condition. When a polymeric membrane is

under pressure-driven process, its porous structure become denser and compress thus mechanical deformation occurs. The membrane mechanical deformation is an irreversible process and as a result the PWP will decline. At the initial time of the compaction process, the PWP is sharply decreased and the volume of PWP slowly turns down until it keeps constant where steady-state permeation rate was achieved. This initial reduction in PWP may be due to the fact that the membrane pores are being compacted leading to uniform pore size and steady-state PWP (Arthanareeswaran et al., 2004).

In addition, deformation of a polymeric structure is completed at a particular pressure during the steady-state PWP. For porous asymmetric membrane such as UF membranes, the compaction process was affected the sub-layer of the membranes. This irreversible mechanical deformation process increase whole resistance of the compacted porous UF membranes as well as the final PWP would not the same as initial PWP. Normally, the pressure used in this compaction experiment is the maximum operating pressure for an UF performance test which is aimed to make membranes with rigid pore structure and size. Hence, the membranes could further yield reproducible results in separation and performance evaluation.

After the compaction test, all the membranes were tested at various operating pressures, of about 50, 100, 150, 200, 250 and 300 kPa to study performance of the membranes. The performance test was measured under steady state flow to ensure that the membranes used were stable. The PWP of the UF membranes at different operating pressure are depicted in Figure 46.

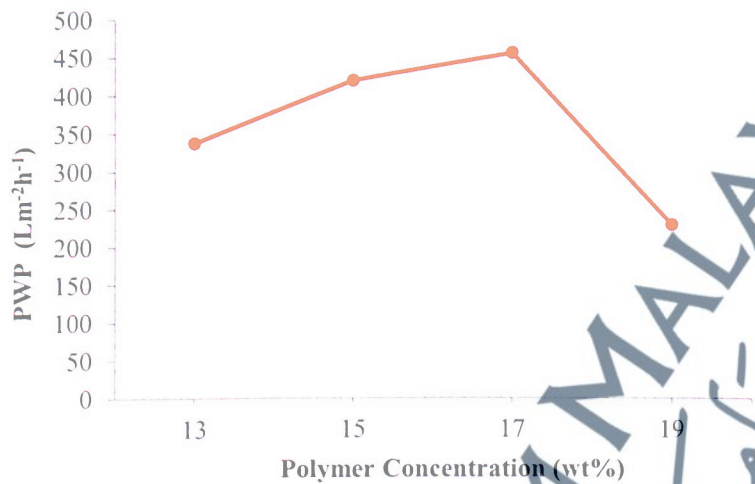
FIGURE 46: PWP of PVDF/NMP Membranes at Different Operating Pressure



Based on Figure 46, it can be seen that with increase in operating pressure during the experiment, PWP increases for all the membranes. This is due to the increase in effective driving force (transmembrane pressure) required for PWP. As the polymer concentration increased, the PWP of the membranes decreased in pressure range 50-100 kPa. However between 150-300 kPa, the PWP increased as polymer concentration increased up to 17 wt% then decreased at 19% wt polymer concentration. For example as illustrated in Figure 47, the PWP increased from 337.42 to 455.82 Lm²h⁻¹ when polymer concentration increases up to 17 wt%.

Figure 47 shows the influence of PVDF polymer concentration on PWP of compacted membranes at operating pressure of 300 kPa. From the figure, the best PWP of 455.82 Lm²h⁻¹ is demonstrated by PN-3 membrane which produced from 17 wt% of PVDF polymer. Therefore it has to be selected for further experiments as well as to produce higher selectivity. Hence, PN-3 membrane (17 wt% of PVDF) appears to be the best membrane for UF experiment.

FIGURE 47: Effect of Polymer Concentration on PWP of the Compacted PVDF Membranes at Operating Pressure of 300 kPa

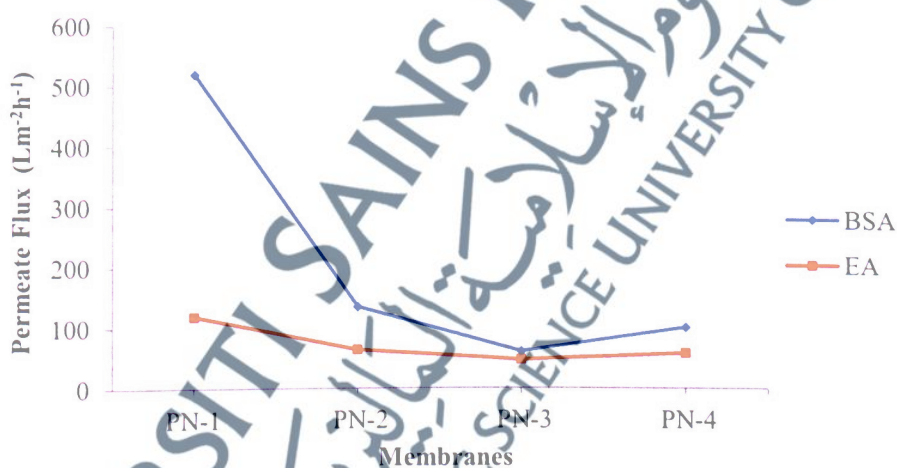


This observation is in agreement according to Marchese et al. (2003), the total PES polymer concentration was maintained at 17 wt% to have a balanced casting solution viscosity for the UF experiments including BSA filtration test. Separation of proteins by Cellulose acetate/ Aminated polyethersulfone (CA/APES) blend UF membranes were prepared by dissolving two polymers with different compositions and the final total polymer concentration is at 17.5 wt% (Kalaivizhi et al., 2011). Besides, Nagendran and Mohan (2008) who prepared UF membranes based on CA and Sulfonated poly(ether imide) (SPEI) with 17.5 wt% polymer concentration in the casting solution. The increasing of the polymer concentration beyond 17 wt% resulted into the unstable water permeation and PWP reduction. Therefore, the polymer concentration has a high influence on the membranes performance and based on the experimental data, the 17 wt% of polymer concentration are suitable for UF applications.

4.2.2 Protein Separation Performance

In protein separation studies, the modified and synthesized UF membranes were characterized with permeation experiment with proteins solution as feed. Bovine serum albumin (BSA; MW=69 kDa) and egg albumin (EA; MW=45 kDa) were used to investigate proteins solution flux and rejection of the proteins. The fluxes and rejections of the solute are considered to be the key factors for any membranes. Both permeate flux and rejection characteristics of the membranes strongly depend on the structure of the membrane as well as the properties of feed solution.

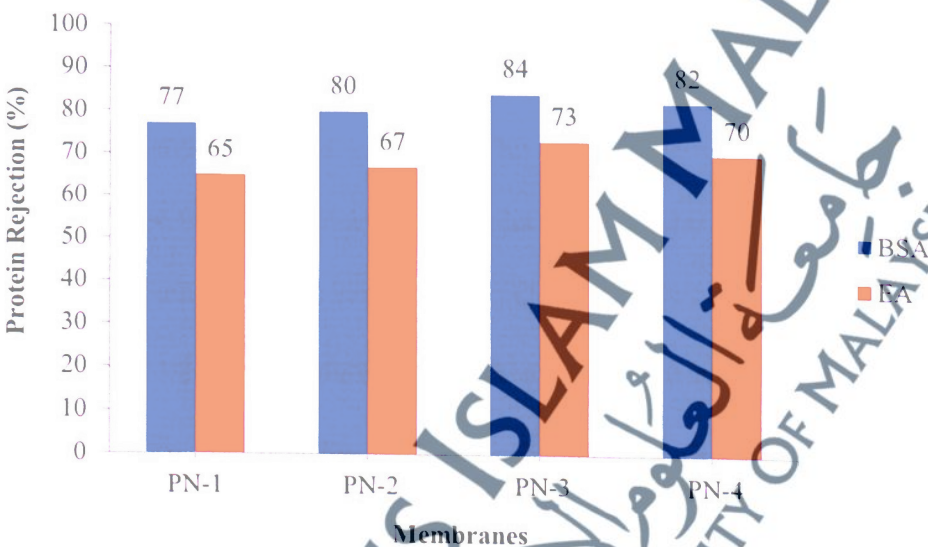
FIGURE 48: Proteins Permeation Flux of UF Membranes with Different Polymer Concentration



The permeate flux with different polymer concentration is shown in Figure 48. From this figure, it is understood that as the polymer concentration increased from 13 to 17 wt%, the BSA flux decreased from 519.63 to 59.96 Lm⁻²h⁻¹. The similar trends also exhibited by EA protein sample. However, PN-4 (19 wt%) shows an increment of BSA and EA permeate flux to 99.93 Lm⁻²h⁻¹ and 46.40 Lm⁻²h⁻¹ respectively. It can be

clearly seen that PN-3 membrane which contains 17 wt% of PVDF has the lowest permeate flux for each proteins sample.

FIGURE 49: Proteins Rejection of UF Membranes with Different Polymer Concentration



The protein rejection of BSA and EA with different polymer concentration in the blend casting solutions is illustrated in Figure 49. From the result obtained, as the polymer concentration increase up to 17 wt%, the percentage of rejection increase and slightly decrease when the polymer concentration is 19 wt%. Hence, with increases to 19 wt% of polymer in the casting solution was resulted in less productive asymmetric UF membranes for separation of proteins. PN-3 membrane which contains 17 wt% of PVDF in casting solution shows the highest percentage of proteins rejection which are 84% and 73% for BSA and EA respectively. Besides, PN-1 membrane shows the lowest rejection of proteins compared to PN-2, PN-3 and PN-4 membranes. Addition of 17 wt% hydrophilic polymer in the casting solutions produced low permeation of protein solutions and high rejection of proteins. This suggested that increasing

polymer concentration to 17 wt% resulting in more selective asymmetric UF membranes for protein separation. Membrane PN-3 (17 wt% of PVDF) appears to be the best membranes for further UF experiment.

While considering to molecular weight of proteins, it is observed that the permeate flux and solute rejection of protein solutions was increased with the increasing of proteins molecular weight. EA shows the lowest flux in the separation performance test compared to BSA protein. The order of permeate flux was found to be BSA > EA. These trends were due to the order of molecular weight of BSA and EA which are 69 kDa and 45 kDa, respectively. Generally, BSA is found to have the highest percentage rejection compared to EA as it is due to its highest molecular weight. In the other hand, based on Figure 46, and 49, it was found that PN-3 membrane shows the most promising results with high PWP and solute rejection as well as good membrane characteristics in terms of UF experiments in order to perform high productivity and selectivity of an UF membrane process.

4.2.3 Membrane Morphology

The morphological structure of membrane is one of the most important membrane characteristic. The top skin layer acts as a layer which controls the separation process and selectivity of the membranes. Besides, the sub-layer formation is controlled by variables of polymer dope solution such as composition, coagulant temperature and additives (Rahimpour et al., 2010). The support layer plays a role as a supporting structure and this supporting structure has porosity much greater than the top skin layer (Baker, 2004). Figure 50 shows the SEM micrographs of cross-sectional view of PVDF/NMP membrane with 17 wt% of PVDF.

FIGURE 50: Morphological Structures of 17 wt% PVDF/NMP



The cross-section structures of asymmetric PVDF/NMP UF membranes at different concentration of PVDF which are 13, 15, 17 and 19 wt% are shown in Figures 51(a), (b), (c) and (d), respectively. It was found that all the membranes exhibit typical morphological structure of asymmetric membrane which consists of a top layer and a porous sub-layer at the bottom of the membranes containing macrovoids, finger-like pores and microvoids.

It was revealed that membrane top skin layer is very thin while sub-layer has finger-like structures from the skin layer and macropores in the bottom to the support region. A thin finger-like structure from the top and gradually become tiny open channel of finger-like structure at the bottom layer. A dense spongy structure also formed beneath the skin layer and porous sub-layer of PVDF membrane. The casting solutions provided from hydrophobic polymers produced sponge-like structures due to delayed phase separation occurred during phase inversion process (Ghasem et al., 2012).

As increasing the polymer concentration, the larger (open) finger-like pores were formed in the membrane structure. This might be influenced by the exchange time between solvent and non-solvent in the coagulation bath. It may be seen from the Figure 51(a) to (d) that membranes formed are having short and finger-like structures from the top layer to middle of sub-layer of the membrane.

The non-solvent from coagulation bath diffuses into the polymer casting solution and inversely, the solvent from the polymer casting comes out into coagulation bath. This exchange of solvent and non-solvent proceeds at certain period of time until the casting solutions becomes thermodynamically unstable and demixing process starts to take place to form membrane that having asymmetric morphological structure. Thus, the demixing process produced porous membranes and resulted in dense membranes (Rahimpour et al., 2008).

FIGURE 51(a): Cross-Sectional Structure of PN-1 (13 wt% PVDF/NMP)

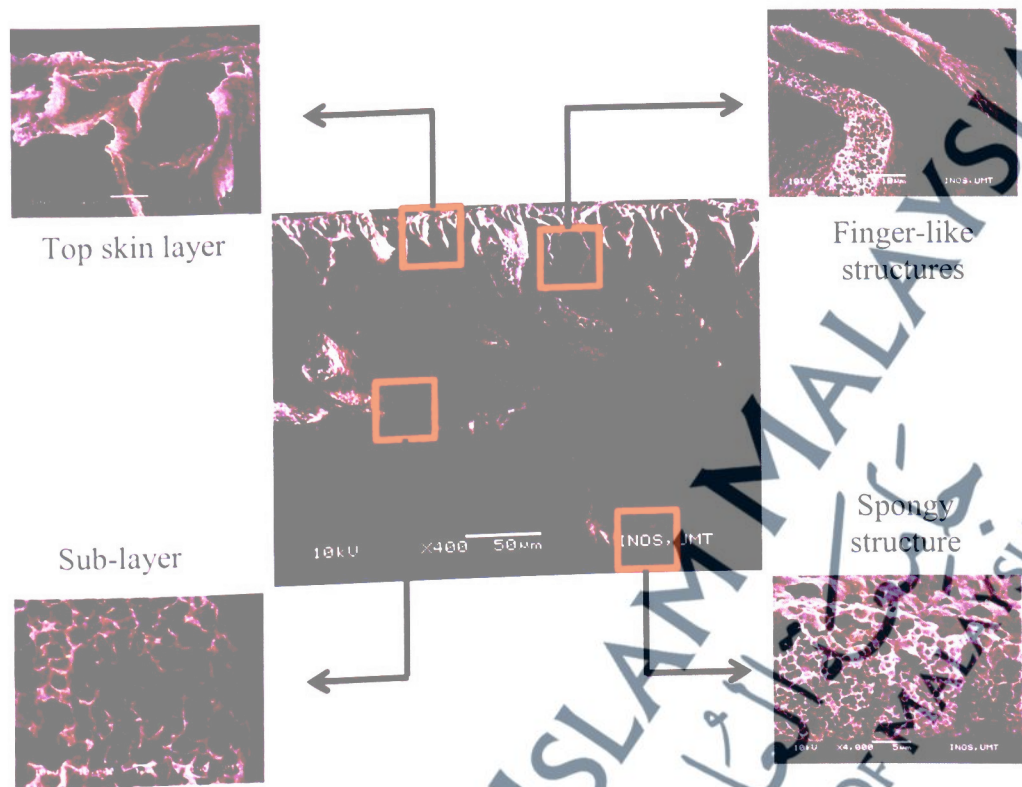
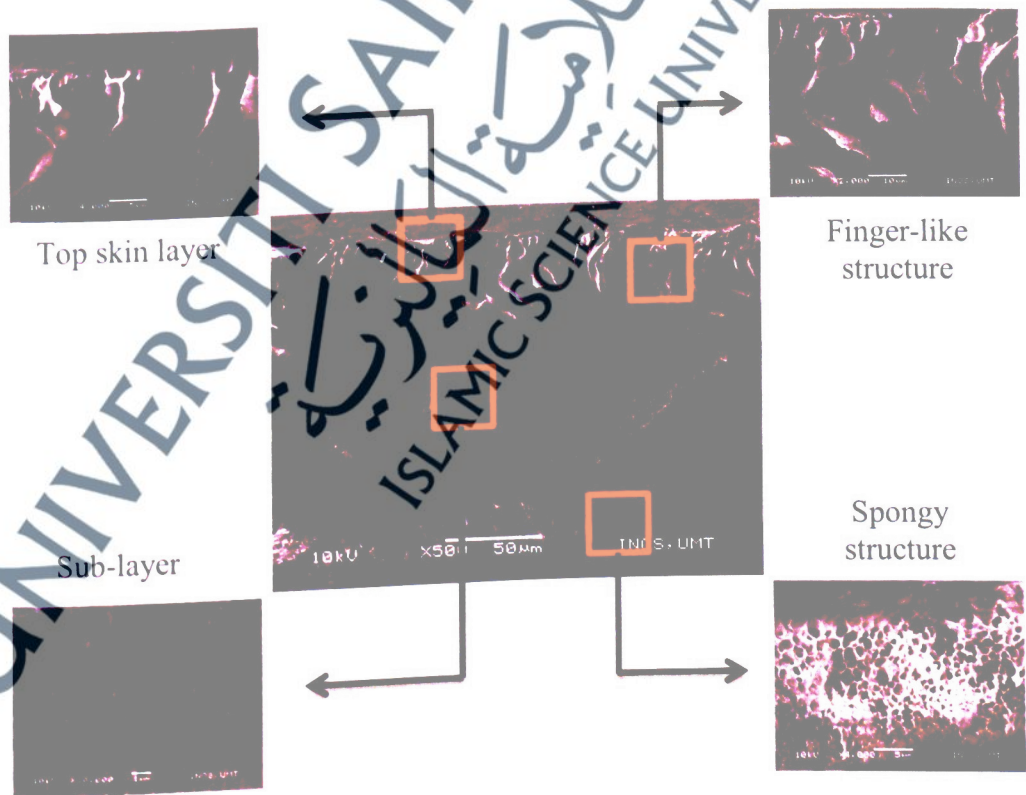


FIGURE 51(b): Cross-Sectional Structure of PN-2 (15 wt% PVDF/NMP)



In addition, the presence of hydrophobic polymer in the casting solution such as PVDF did not facilitate water as non-solvent to diffuse into the casting solution and consequently produced membrane with dense top layer and spongy sub-layer. Yoo (2004) reported in their study that the diffusional exchange rate between solvent (NMP) and non-solvent (water) slowed the precipitation rate of the sub-layer and hence formed a dense and thick skin layer supported by a closed cell-sub layer membrane.

It can be hypothesized that the increasing polymer concentration produced membrane which had thick skin layer, closed finger-like, small macrovoid and dense spongy structure that attributes to high resistance to permeation rate of the solute rejection. On the other hand, Figure 51(c) showed the cross-sectional of PN-3 membrane which contain 17 wt% of PVDF polymer.

However, the size of spongy structures for PN-4 becomes larger as shown in Figure 51(d). Membrane performance in term of PWP tends to drop drastically compared to previous membrane. Protein rejection performance was affected and decreased as well. Thus, the best membrane is PN-3 which containing 17 wt% PVDF polymer in the casting solution was chosen for further investigation. This is because the structure provides better resistance for PWP as well as protein rejection due to denser membrane sub-layer. The solute rejection for this membrane was much better because at this polymer composition started to achieve protein rejection rate up to 84% and 73% for BSA and EA, respectively.

FIGURE 51(c): Cross-Sectional Structure of PN-3 (17 wt% PVDF/NMP)

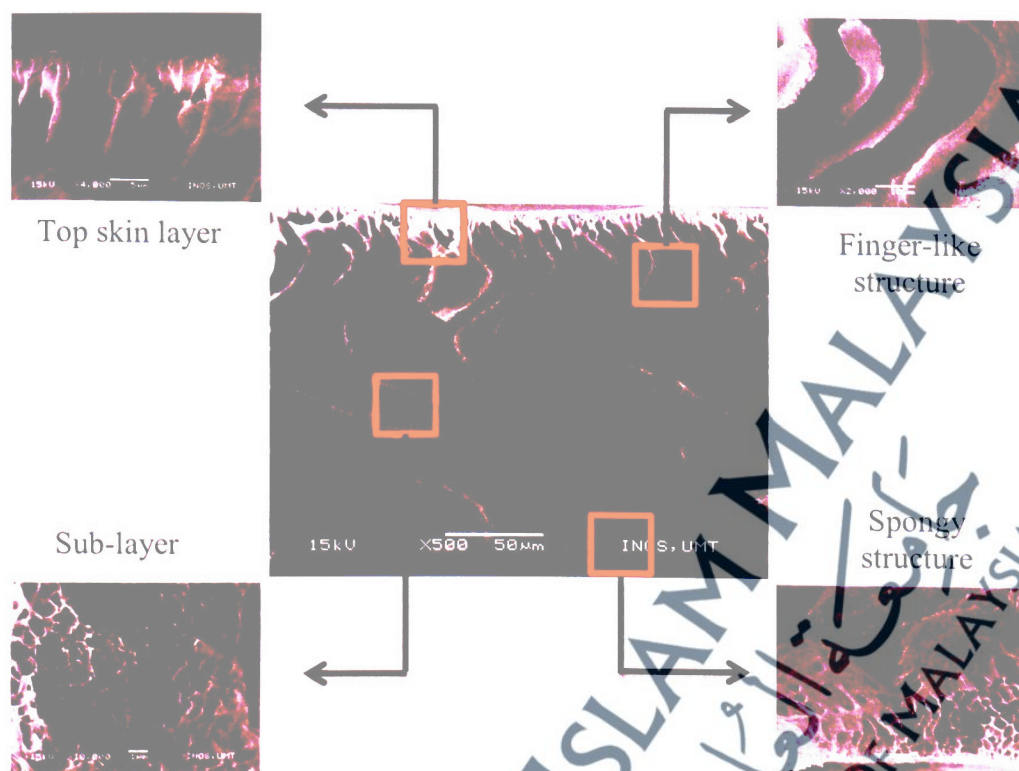
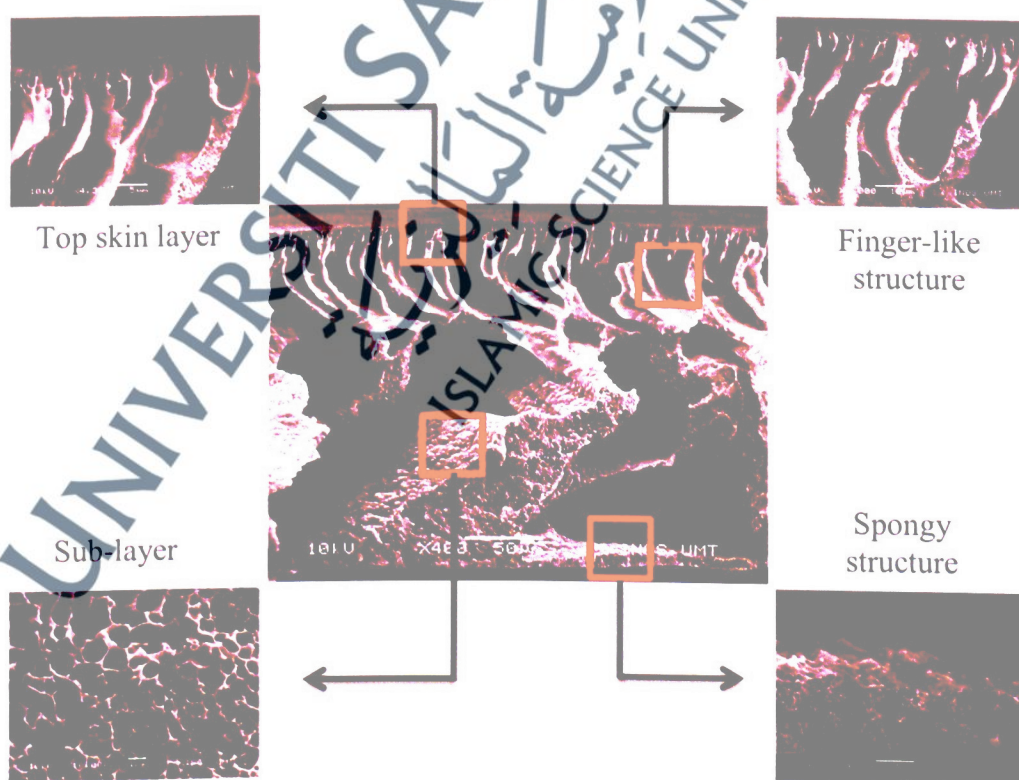


FIGURE 51(d): Cross-Sectional Structure of PN-4 (19 wt% PVDF/NMP)



As depicted in Table 12, increasing of polymer concentration in the casting solution would decrease the length-width of finger-like structures while increased the macrovoid length-width and size of pores in the membrane. It is observed the existence of macrovoid at the sub-layer to the bottom of the membrane. Further increment of PVDF composition from 13 to 19 wt% demonstrates significant changes in size of macrovoid in the membrane. The largest size of macrovoid and pore appeared in PN-4 membrane containing 19 wt% of PVDF polymer concentration. The existence of finger-like, macrovoid structures and pores in the membrane are significant characteristics of porous membrane. Furthermore, the UF membranes are categorized as porous membrane based on their porous structure and high PWP related to the membrane productivity.

TABLE 12: Dimensional membrane characteristics of PVDF membranes at different polymer concentration

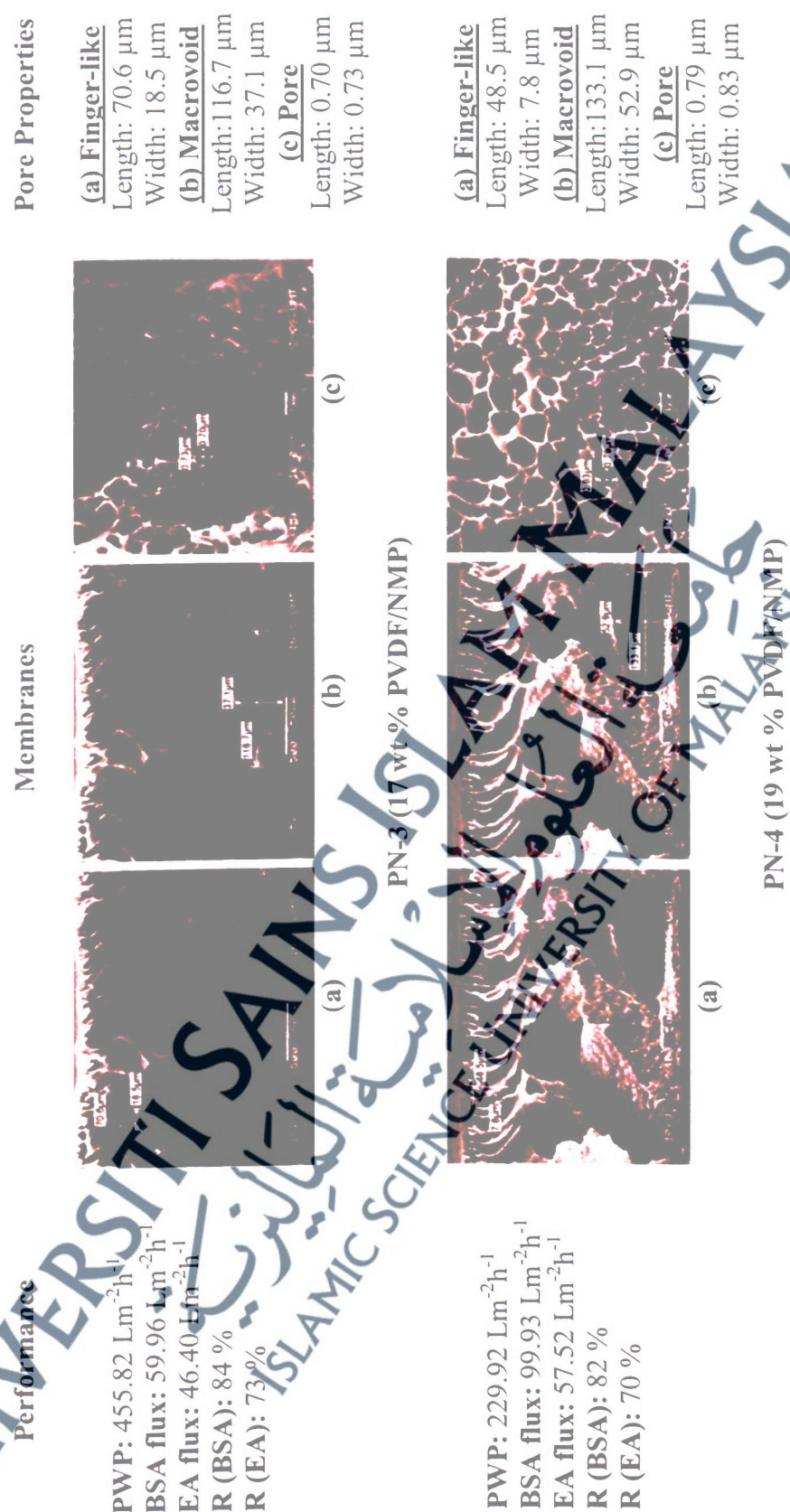
Membranes	Finger-like Length (μm)	Finger-like Width (μm)	Macrovoid Length (μm)	Macrovoid Width (μm)	Pore Length (μm)	Pore Width (μm)
PN-1	79.9	22.9	34.8	27.3	0.84	0.79
PN-2	72.5	20.3	111.6	35.6	0.85	0.78
PN-3	70.6	18.5	116.7	37.1	0.70	0.73
PN-4	48.5	7.8	133.1	52.9	0.79	0.83

FIGURE 52(a): Summary of Performance, Morphologies and Pore Properties of PVDF-UF Membrane at Different Polymer

Concentration at 13 wt% and 15 wt% PVDF



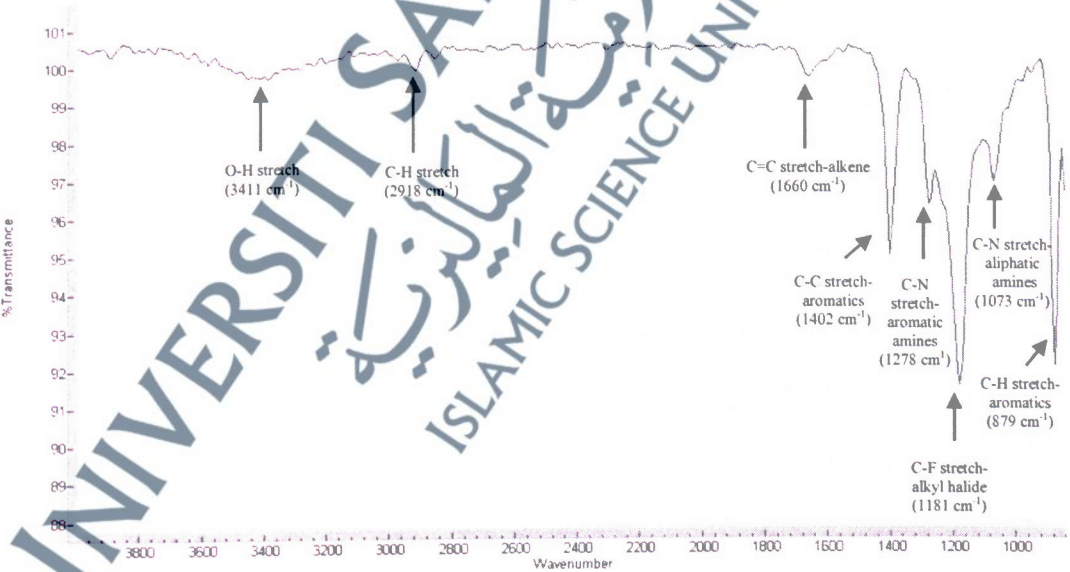
FIGURE 52(b): Summary of Performance, Morphologies and Pore Properties of PVDF-UF Membrane at Different Polymer Concentration at 17 wt% And 19 wt% PVDF



4.2.4 FTIR Studies

Molecular analyses of PVDF/NMP with different polymer concentration which are 13, 15, 17 and 19 wt% marked as PN-1, PN-2, PN-3 and PN-4, respectively were run through FTIR which allows for infrared (IR) analysis of surfaces. The IR spectrum can provide determination of vibrational frequencies and transition intensities of the molecules, including characteristic functional group frequencies. Knowledge of vibrational frequencies of functional groups allows for chemical identification of at least a class of compounds. FTIR will show the bands indicate the existing of functional groups in the membrane. Besides, the molecular orientations of molecules can also be observed based on the significant peaks formed. Figure 53(a) – (d) showed FTIR absorption bands of each membrane samples.

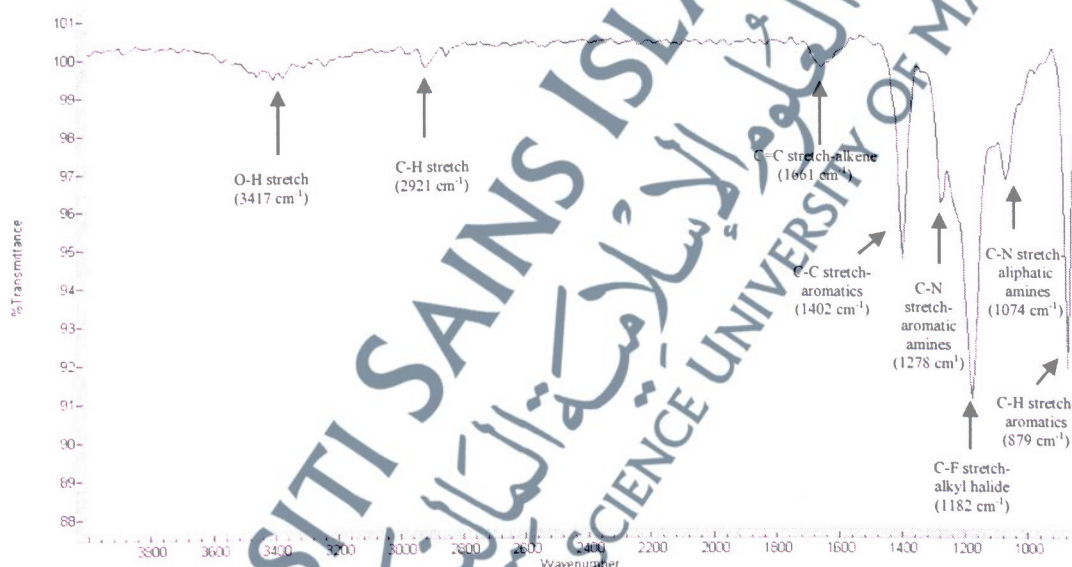
FIGURE 53(a): IR spectra of UF Membrane (PN-1) with 13 wt% PVDF



The FTIR spectrum of the PN-1 with 13 wt% PVDF polymer can be seen in Figure 53(a). The absorption peak at 3411 cm⁻¹ was due to –OH stretch, which is

broad and low peak. The aliphatic C-H and C=C stretches from PVDF also appeared at 2918 cm^{-1} and 1660 cm^{-1} , respectively and both peaks were showed at very weak point. Sharp and strong absorption has been detected at the wavelength 1181 cm^{-1} which can be assigned to the alkyl halide stretching vibrations of C-F bond in the PVDF chains. In addition, there are two sharp bands at 1402 cm^{-1} and 879 cm^{-1} which demonstrated C-C stretch aromatics and C-H stretch aromatics, respectively. Besides, peaks at 1278 cm^{-1} and 1073 cm^{-1} can be described to C-N stretch aromatics amines and C-N stretch aliphatic amines, respectively.

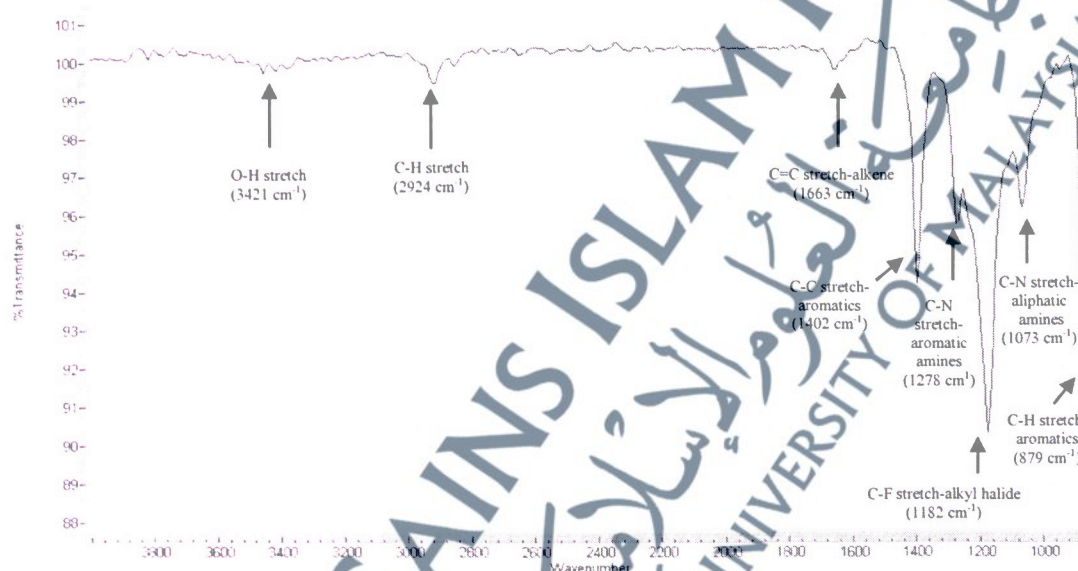
FIGURE 53(b): IR Spectra of UF Membrane (PN-2) with 15 wt% PVDF



The Figure 53(b) represents the FTIR spectra of the PN-2 membrane which containing 15 wt% of PVDF polymer in the casting solution. The characteristic peaks of PVDF were observed. Peak at around 2921 cm^{-1} and 1661 cm^{-1} were arising due to C-H and C=C stretching. Besides, there is C-C stretch (aromatics) vibrations at 1402 cm^{-1} . Also peaks (sharp and weak) at around 1278 cm^{-1} and 1074 cm^{-1} correspond to C-N aromatics amines and C-N aliphatic amines stretching vibrations, respectively.

As the PN-1 membrane used PVDF polymer, the characteristic of PVDF which is C-F stretching alkyl halides appears at 1182 cm^{-1} (sharp and strong peak). The C-C and C-H stretches aromatics in the PN-2 membranes have been identified at 1402 cm^{-1} and 879 cm^{-1} . The broad and weak peak of hydroxyl group stretching vibrations (-OH) showed at 3417 cm^{-1} in the IR spectrum.

FIGURE 53(c): IR Spectra of UF Membrane (PN-3) with 17 wt% PVDF

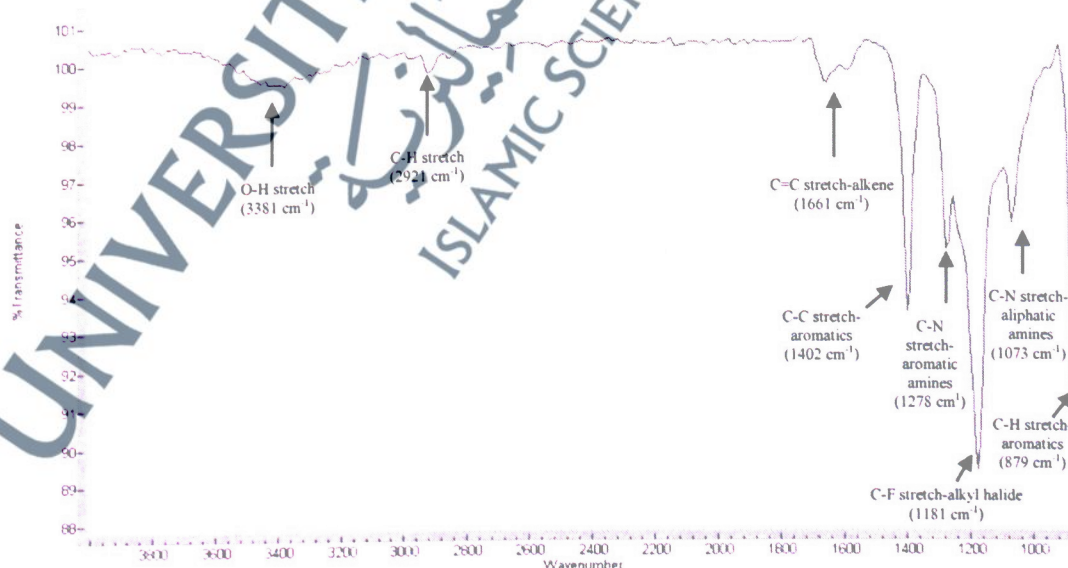


The FTIR spectrum of PN-3 membrane (containing 17 wt% of PVDF polymer) is shown in Figure 53(c). The results obtained were quite different to other membranes. The broad range of hydroxyl groups vibration (-OH) was observed at 3421 cm^{-1} as this terminal of hydroxyl group was increased 10 cm^{-1} from PN-2 membrane. As the PN-3 has the highest wavenumber of -OH peak, it indicates that the combination of 17 wt% PVDF polymer with the NMP solvent gives high molecular orientation of O-H. The characteristic peaks around 2924 cm^{-1} and 1663 cm^{-1} represent bending of C-H vibration and C=C stretching respectively. In addition, three sharp and strong peaks at 1402 cm^{-1} , 1182 cm^{-1} and 879 cm^{-1} were assigned to

the stretching vibration of C-C aromatics, C-F (alkyl halides) and C-H aromatics respectively. Another two weak bands at 1278 cm^{-1} and 1073 cm^{-1} were attributed to the stretching mode of the C-N aromatic amines and C-N aliphatic amines respectively shown in Figure 53(c).

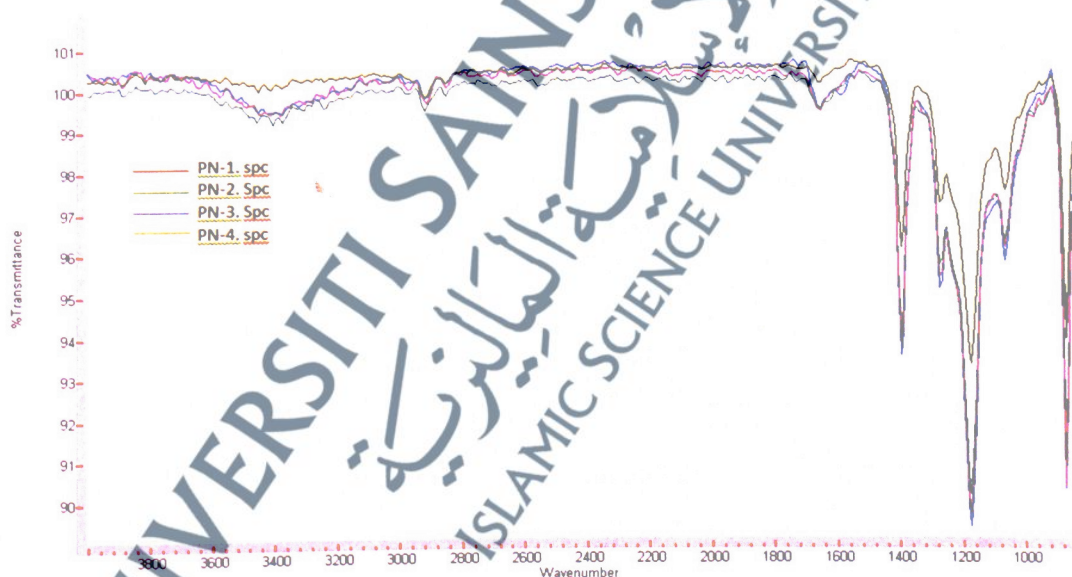
The Figure 53(d) below shows the molecular orientation of PN-4 membrane (19 wt% of PVDF polymer). In the FTIR spectrum of the PN-4 membrane, the band at 3381 cm^{-1} represented the broad stretching vibration of hydroxyl group (-OH). As expected, all the PVDF membranes showed typical spectra of PVDF for example C-H stretching at 2921 cm^{-1} and C=C bond stretch at 1661 cm^{-1} . The sharp and strong bands at 1402 cm^{-1} , 1181 cm^{-1} and 879 cm^{-1} indicated the presence of C-C aromatic stretching, C-F alkyl halide stretching and C-H aromatic stretching, respectively. In the spectrum of the blend membrane with NMP (solvent), two weak peaks around 1278 cm^{-1} and 1073 cm^{-1} were assigned to the C-N aromatic amines stretching and C-N aliphatic amines stretching, respectively.

FIGURE 53(d): IR Spectra of UF Membrane (PN-4) with 19 wt% PVDF



As can be seen in Figure 54, it showed the combination of four spectrums from different PVDF polymer concentrations to the casting solutions which are 13, 15, 17 and 19 wt%. As displayed in the spectrum, all of the membranes exhibit almost similar peaks, thus lead to a similar activity. For instance, there are three signals or peaks were observed which maintain in the same frequency among the four membranes (C-C aromatic stretch, 1402 cm^{-1} ; C-N aromatic amines stretch, 1278 cm^{-1} ; C-H aromatic stretch, 879 cm^{-1}). All the spectrums exhibit almost similar peaks because of the range of polymer concentration had been choose are in small gap (13-19 wt%). If the polymer concentrations have large gaps then, more distinct and significant difference between the spectrums can be seen clearly

FIGURE 54: Combination Spectrum of Four Membranes at Different PVDF Concentrations (wt%)



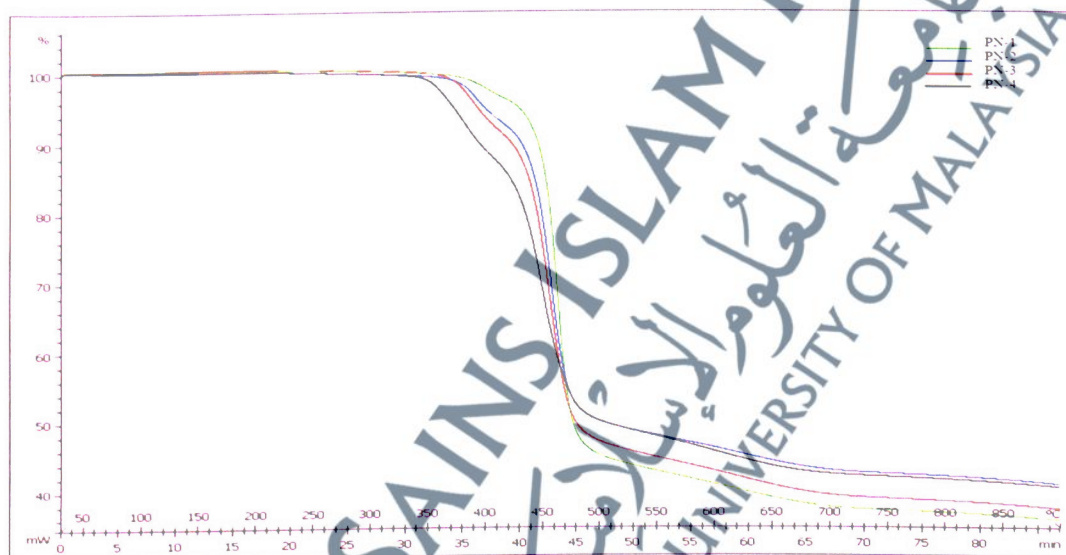
However, PN-3 membrane spectra shows distinct difference compared to other spectrum as it has highest peak. On the other hand, lowest peak goes to PN-1 membrane (13 wt% PVDF). The position of the spectra in the combined spectrum indicated that the molecular interaction, orientation and activity can be called as dichroism. Hence, it can be said that PN-1 membrane has low dichroism meanwhile PN-3 membrane has high dichroism. The high dichroism or high molecular orientation of PN-3 membrane has denser skin and porous membrane structure. It is compatible with the SEM result (Section 4.2.3) that PN-3 membrane had the most porous and dense structure compared to the other membranes. It shows that the molecule of materials (17 wt% PVDF/ NMP) is well oriented between each other during dope formulation and solvent exchange (coagulation bath).

A very strong molecular interaction occurs in the PN-3 membrane containing 17 wt% of PVDF. Infrared spectrum having many strong bands in the 'fingerprint' region of the spectrum below 1800 cm^{-1} and from the peak formed, we can observed the strongest values of transmittance depicted by molecular interactions from membrane having 17 wt% of PVDF content. Because of better alignment and interactions between molecular orientations, this PN-3 membrane exhibits a better performance compared to the other membranes and expected the optimum membrane performance in term of permeability and selectivity. Based on the result showed above, it is stated that the percentage of composition in the membrane fabricated is very important as well it gives changes in molecular orientations.

4.2.5 TGA Studies

The thermogravimetric (TG) curves of all the fabricated membranes at different concentration of polymer are shown in Figure 4.10. To compare the results of the decomposition characteristics in a more qualitative way, the decomposition curve of the membranes at various heating rates in air were combining in a curve in Figure 55.

FIGURE 55: TGA Curves of Various Concentration of PVDF Polymer



Generally, it is seen that the degradation of all the polymeric based membranes occurs in three steps. The first step, from the room temperature (30 °C) to ~360 °C, represents the volatilization of the volatile matter and/or the evaporation of residual absorbed water. The second step starts at ~360 °C and ends at ~700 °C, represents the main thermal degradation of the polymer chains. The third step starts at ~700 °C, symbolizes the carbonation of the degraded products to ash (Arthanareeswaran et al., 2004).

From the curve, the polymer is thermally stable up to 350 °C. The TG curve shows that the first decomposition temperature occurs at 360 °C with a gradual weight loss of 8, 9, 18 and 23 % for PN-1, PN-2, PN-3 and PN-4, respectively. The percentage of weight loss during the first stage of decomposition, for all the membranes increases with an increase of polymer concentration. This is due to the polymer itself which is very reactive and absorbs moisture easily when exposed to at room temperature.

These were followed by a rapid weight loss of 57, 52, 55 and 52 % up to ~500 °C for PN-1, PN-2, PN-3 and PN-4, respectively. After that, the complete decomposition of the membranes takes place between 700 and 900 °C. At 700 °C, the samples start to melt and the system is no longer stable. The total weight loss for all the membranes were decelerating between 700 and 900 °C which are 65, 60, 63, 59 % respectively for PN-1, PN-2, PN-3 and PN-4 membranes. It can be deduced that an increase in polymer concentration promotes and decrease in weight loss (Suriani et al., 2012).

4.3 Addition of Different Polymeric Additives

The PN-3 membrane contained 17 wt% of PVDF polymer concentration in the casting solution give the best result in the previous study was chosen for further investigation. In order to study the effect of addition of additives, Polyvinylpyrrolidone (PVP), Lithium Chloride (LiCl) and Polyethylene glycol 200 (PEG 200) were used as additives in the casting solution.

The PVDF/NMP membrane which no addition of additive was marked as PN-3 in this investigation which is same coded in the previous study. PN-3P, PN-3L and PN-3G membranes are the PVDF/NMP membranes which contained 3% of PVP, LiCl and PEG 200 respectively act as additives in the casting solution. The composition parameters of the membrane fabrication conditions with addition of different types of additives to the polymer casting solution are shown in Table 13.

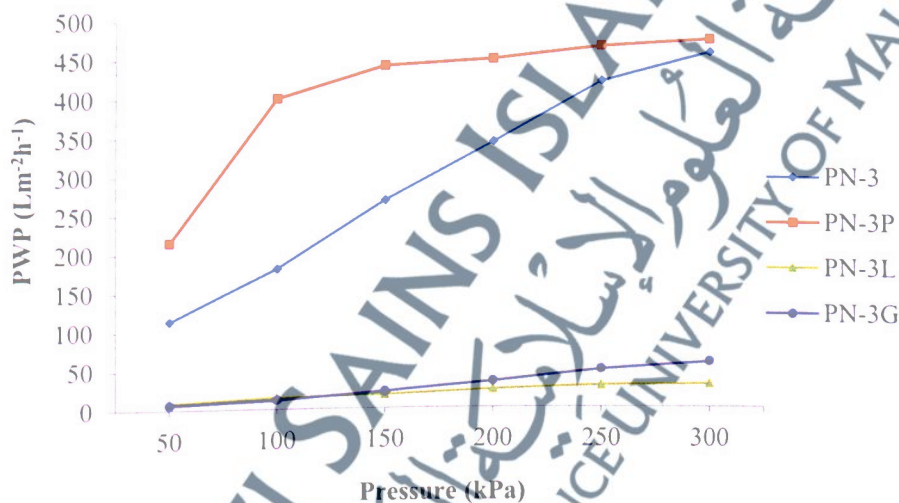
TABLE 13: The composition parameters of the PVDF/NMP membranes with different additives

Membranes	Total polymer (wt%)	Solvent (wt%)	Additives (wt%)		
			PVP	LiCl	PEG 200
PN-3	17	83	-	-	-
PN-3P	17	80	3	-	-
PN-3L	17	80	-	3	-
PN-3G	17	80	-	-	3

4.3.1 Pure Water Permeation (PWP)

Figure 56 illustrated the PWP of PVDF/NMP membranes with different types of additives at different operating pressures, i.e. 50, 100, 150, 200, 250 and 300 kPa. It is evident from the figure that an increase in the operating pressure increased the PWP of all membranes.

FIGURE 56: PWP of UF Membranes Contained Different Types of Additives at Different Operating Pressures



PN-3P membrane exhibited the highest PWP which is $472.39 \text{ Lm}^2\text{h}^{-1}$ at operating pressure of 300 kPa. It was observed an increase in PWP from 214.72 to $472.39 \text{ Lm}^2\text{h}^{-1}$ by increasing the operating pressure. It can be said that PN-3P membrane showed the highest PWP compared to other membranes because it was prepared in the presence of PVP, as a hydrophilic additive with non-solvent properties in the casting solution. It should be noted that PWP depends on membrane hydrophilicity. As well known, PVP is more hydrophilic compared to LiCl and PEG

200. Consequently, its presence in the casting solution increases the membrane hydrophilicity leading to encourage and facilitate water to permeate through the membrane surface area easily (Saljoughi and Mohammadi, 2009).

Besides, PN-3L membrane prepared in the presence of LiCl, act as low-molecular-weight inorganic salts additives. From the Figure 56, it was noticed that PN-3L shows the lowest PWP compared to other membranes. The increase of operating pressure from 50 to 300 kPa significantly increased the PWP of PN-3L from the range 8.96 to 29.16 $\text{Lm}^{-2}\text{h}^{-1}$. The lowest PWP data indicates that the presence of LiCl tended to enhance the affinity of the system to water and thus the water tolerance of the polymer solutions, which would decrease the solvent/non-solvent exchange rate due to stronger salt/polymer interaction. In contrast to polymer additives, small molecular inorganic additives can easily diffuse out during the membrane formation (Wang et al., 2000).

In addition, LiCl is an interesting inorganic additive for membrane fabrication because it interacts strongly with certain solvents and can form complexes with the carbonyl groups in such solvents N-methyl-2-pyrrolidone (NMP) via the ion-dipole interaction. The strong LiCl-solvent interaction may result in more favorable membrane morphology (Lee et al., 2002). Similar observation have also been reported that PWP of the membrane made from the dope with LiCl addition decreased, whereas the membrane made from the PVP contained dope solution presented an opposite trend of PWP increased (Shi et al., 2008).

The effect of polymeric additives, PEG 200 on PWP at various operating pressure which marked as PN-3G is shown in Figure 56. It is seen that within the range of 50-300 kPa, with increase in operating pressure, PWP increased from 6.17 to 57.74 $\text{Lm}^{-2}\text{h}^{-1}$. This is due to the increase in effective driving force (operating pressure) required for water permeation. However, the PWP of PN-3G at the maximum operating pressure is not high as PN-3P because small molecular weight PEG such as PEG 200 is not a pore forming agent but working as a pore reducing agent (Kim and Lee, 2004). From the above explanation, it was shown that PVP is the better additive for the preparation of membranes with higher PWP thus practical for further ultrafiltration application especially protein separation process.

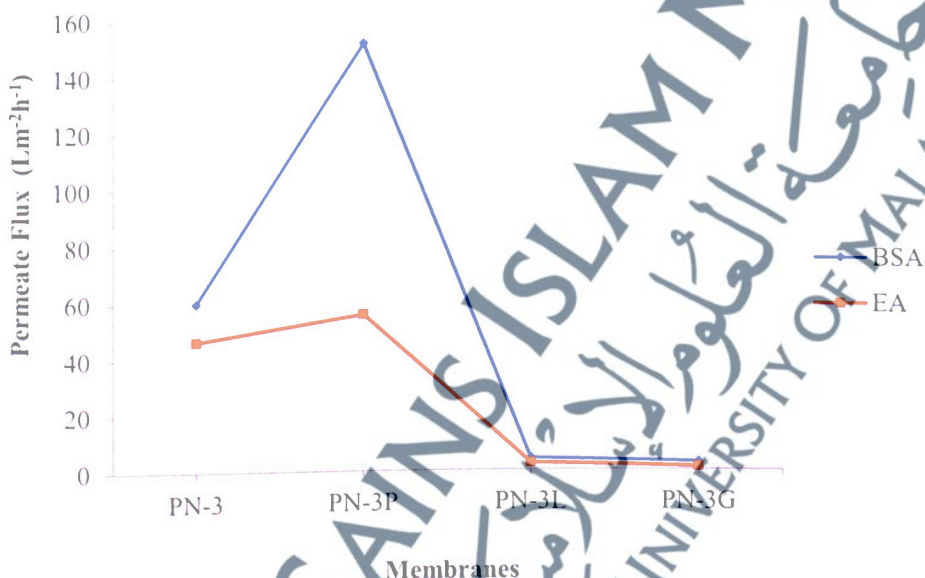
4.3.2 Protein Separation Performance

The selectivity of membrane is strongly determined by the skin layer, which also governs the membrane permeability. The formation of skin layer is affected by solvent evaporation and polymer precipitation, and so the permeability and selectivity of porous UF membranes can be tuned by controlling the evaporation and precipitation conditions. Therefore, the permeability and selectivity of porous UF membranes were characterized by protein separation performance.

The roles of different additives, PVP, LiCl and PEG 200 in the PVDF/NMP membranes on permeate flux and rejections of proteins were studied. In this performance studies, several of proteins such as bovine serum albumin (BSA) and egg albumin (EA) which have MW of 69 and 45 kDa respectively were used to examine the effect of additives towards the UF membranes. Figures 57 and 58 represent

permeate flux and rejection of different MW of protein solutions for PN-3, PN-3P, PN-3L and PN-3G membranes. Figure 57 clearly displays that the PN-3P membrane with containing PVP as polymeric additive behaved the highest permeate flux of protein solutions which is $151.72 \text{ Lm}^{-2}\text{h}^{-1}$. While the percentage of protein rejections were 85% and 78% for BSA and EA respectively as shown in Figure 58.

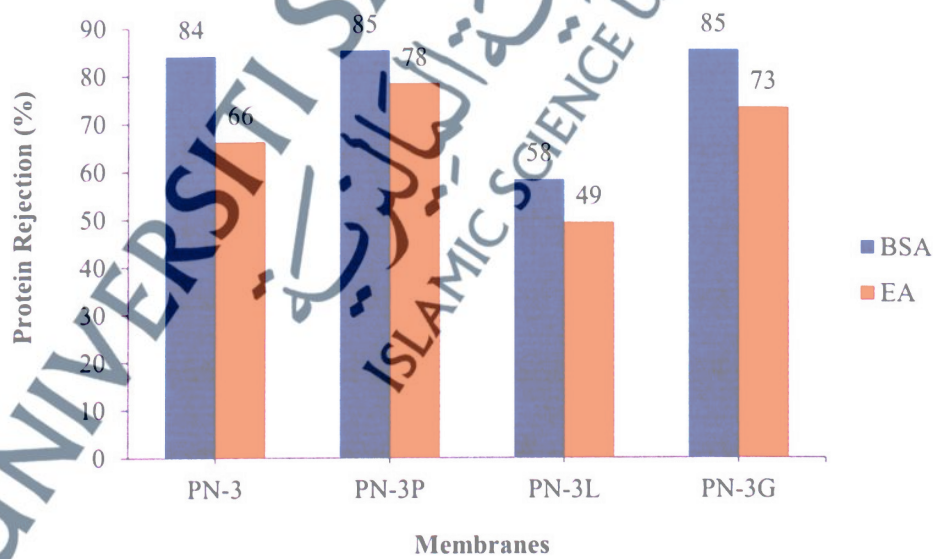
FIGURE 57: Proteins Permeation Flux of UF Membranes with Different Additives



The addition of PVP additive in the PVDF/NMP membrane casting solution significantly affected the performance results which enhanced the BSA permeation flux of PN-3P membrane up to $151.72 \text{ Lm}^{-2}\text{h}^{-1}$ and this permeation flux was higher than PN-3, PN-3L and PN-3G membranes. This results revealed that hydrophilicity properties and porous membrane morphological structure significantly contribute in improving the permeate flux of PN-3P membrane. Therefore, the highest value of permeate flux of proteins solution for PN-3P membrane was due to its highest hydrophilicity membrane properties.

In terms of solute permeation, since in an UF separation process, proteins rejection is based on the sieve mechanism thus the pore size on the membrane surface plays an important role in discriminating solutes passed through the membrane. The percentage of proteins rejection also increased for both of BSA and EA compared to PN-3 membrane (without additive). The results revealed that introduction of small amount of PVP increased the permeability coefficient and porosity of PN-3P membrane compared to PN-3 membrane. The highest proteins rejection for PN-3P (85% for BSA; 78% for EA) compared to other membranes was attributed to the existence of smaller size of macrovoids and pores on these membrane surfaces. The strong interpenetrating network relatively increased entanglements between polymer chains which in turns prevented PVP leached out and thus, as a result reflected the formation of small membrane pore size presence on the membrane skin layer (Xu et al., 2012).

FIGURE 58: Proteins Rejection of UF Membranes with Different Additives



In the other hand, from the Figure 57 we can see that the addition of LiCl as additives to the casting solution lower the permeation flux to $4.15 \text{ Lm}^{-2}\text{h}^{-1}$ and $2.38 \text{ Lm}^{-2}\text{h}^{-1}$ for BSA and EA, respectively. The proteins rejection of PN-3L membrane (58% for BSA; 49% for EA) were lower than the other membranes. The result obtained can be reasonable explained on the basis of a lower precipitation rate of the polymer with addition of LiCl from dopes during immersion precipitation step. This phenomenon is due to the less thermodynamic stability of the casting solution arising from the interactions taking place upon addition of LiCl, as well as to the high tendency of the additives mix with water in the coagulation bath. This suggested by Sun (2009) that the interactions between LiCl and polymer in the casting solution were very weak and therefore, the additive did not contribute significantly to the performance test which are permeation flux and proteins rejection.

Meanwhile, the effect of addition PEG 200 to the casting solution towards permeation flux and solute rejection were presented in Figures 57 and 58, respectively. As shown in the figure, the permeation flux of PN-3G as in the range $2.74 \text{ Lm}^{-2}\text{h}^{-1}$ and $1.03 \text{ Lm}^{-2}\text{h}^{-1}$ for BSA and EA, respectively. The range of permeate flux of PN-3G was lower compared to PN-3, PN-3P and PN-3L membranes. Based on the proteins rejection profile, PN-3G membrane keeps the percentage of BSA rejection to 85% as same as PN-3P membrane. It was found that PN-3G membrane had the higher protein rejection and the lowest permeate flux among the proteins studied. This observation in contrast to PN-3P membrane which described as higher protein rejection and highest permeate flux.

This is due to the properties of PEG 200 itself as lower MW of PEG can reduce the pore formed. However, addition of PEG 200 to the casting polymer solution could not acts as a pore forming agent but capable of working as pore reducing agent in other words, it can increased the percentage of protein rejection whereas the permeate flux is the lowest (Kim and Lee, 2004).

Based on the individual MW of protein performance as illustrated in Figures 57 and 58, respectively, BSA shows the highest protein rejection compared to EA in the protein separation performance test. The order of percentage rejection is BSA > EA, which relatively corresponds to their MW of 69 kDa and 45 kDa, respectively. It was hypothesized that with addition of pore forming agent as polymeric additive, PVP results to higher permeation flux and percentage of solute rejection.

Besides, by addition of pore reducing agent as polymeric additive, PEG 200 with low MW to the dope polymer solution results to lower permeation flux and high proteins rejection. Therefore, it is proven that the existence of PVP and PEG 200 in PVDF/NMP membrane was effective to produce membrane with high productivity and separation performance. Hence, PN-3P and PN-3G membranes were selected the best performance membranes to be employed for the next UF separation process studies.

4.3.3 Membrane Morphology

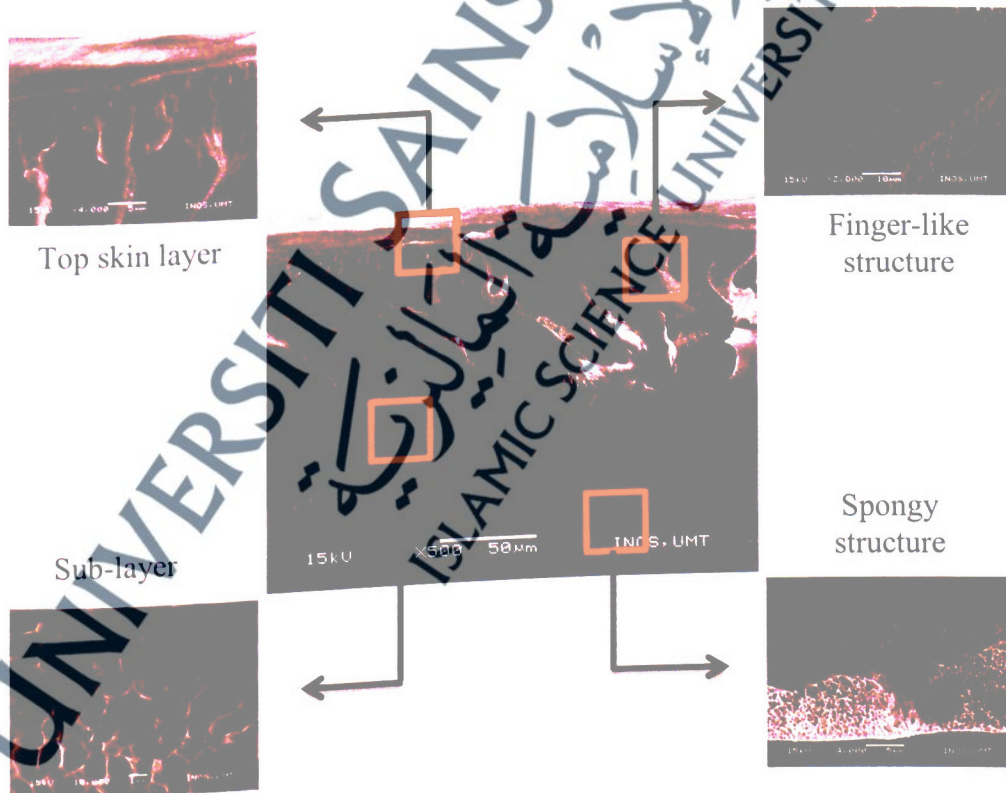
In this study, different types of additives, PVP, LiCl and PEG 200 were introduced to polymer casting solution in order to produce the membranes with better morphological structures compared to the original membrane which without addition of additive, consequently improved their productivity and separation performance.

Figures 59(a), (b) and (c) depict the cross-section of SEM micrographs of PVDF/NMP membranes with addition of different additives, PVP, LiCl and PEG 200 respectively. The PVDF/NMP membrane without additives content marked as PN-3 was used as standard membrane in this study and shown in Figure 51 (c). As discussed in previous part (refer to section 4.2.3), PN-3 membrane comprised of finger-like structures from the top layer to middle of sub-structure of the membrane.

The SEM image of PN-3P membrane as presented in Figure 59(a) exhibit loose and thick skin layer, large acicular pores and also fully developed macrovoids. This membrane shows the typical asymmetrical structure of UF membrane including a dense top layer (skin layer, acicular pores) and porous sub-layer (finger-like, macrovoids). These dense top layer including dense skin layer, spongy structures and macrovoids pores towards the bottom of the membrane might be ascribed to the large amount of water permeation during filtration process (Section 4.3.2). The addition of hydrophilic additives in the membrane casting solutions enhanced instantaneous phase separation in an immersion precipitation process and led to produce macrovoids sub-structure which in turns improved water permeation of PN-3P membrane (Yeow et al., 2003).

The character of the cross-section structure PN-3P membrane as shown in Figure 59(a) could be attributed to water solubility of PVP and the properties of the casting solution. Furthermore, the addition of PVP led to thermodynamic instability on the casting solution, which accelerated the instantaneous demixing in the coagulation bath. On the other hand, PVP is a water-soluble additive which could easily encourage and form PVP-rich phase, which acted as the weak spots during the precipitation process. These caused the formation of loose top-layer and full developed macrovoids (Zhou et al., 2011). Ismail and Hassan (2007) claimed that when PVP is entrapped by membrane materials, PVP should increase the membranes hydrophilicity and also resulted in the alteration of UF membranes performance in terms of water permeation and solute rejection.

FIGURE 59(a): Cross-Sectional Structure of PN-3P (PVDF/NMP/PVP)



The morphology of the PN-3L membrane containing LiCl as the additive is presented in Figure 59(b). When pure water was used as the internal coagulant, the presence of LiCl favored the formation of thinner top skin layer. The finger-like structures and macrovoids can be observed in the membrane structure. In addition, LiCl has good affinity with water. Its addition increased the polymer solution's instability in reaction with water, which facilitated a rapid phase demixing and thus resulted in macrovoids formation. However, the addition of LiCl to the casting solution possessed strong interaction with the polymer and solvent. Therefore, the strong interactions among the components of the solution tend to delay the precipitation, which partially offset the thermodynamic impact of LiCl addition. As a result, the size of macrovoids was reduced (Shi et al., 2008).

FIGURE 59(b): Cross-Sectional Structure of PN-3L (PVDF/NMP/LiCl)

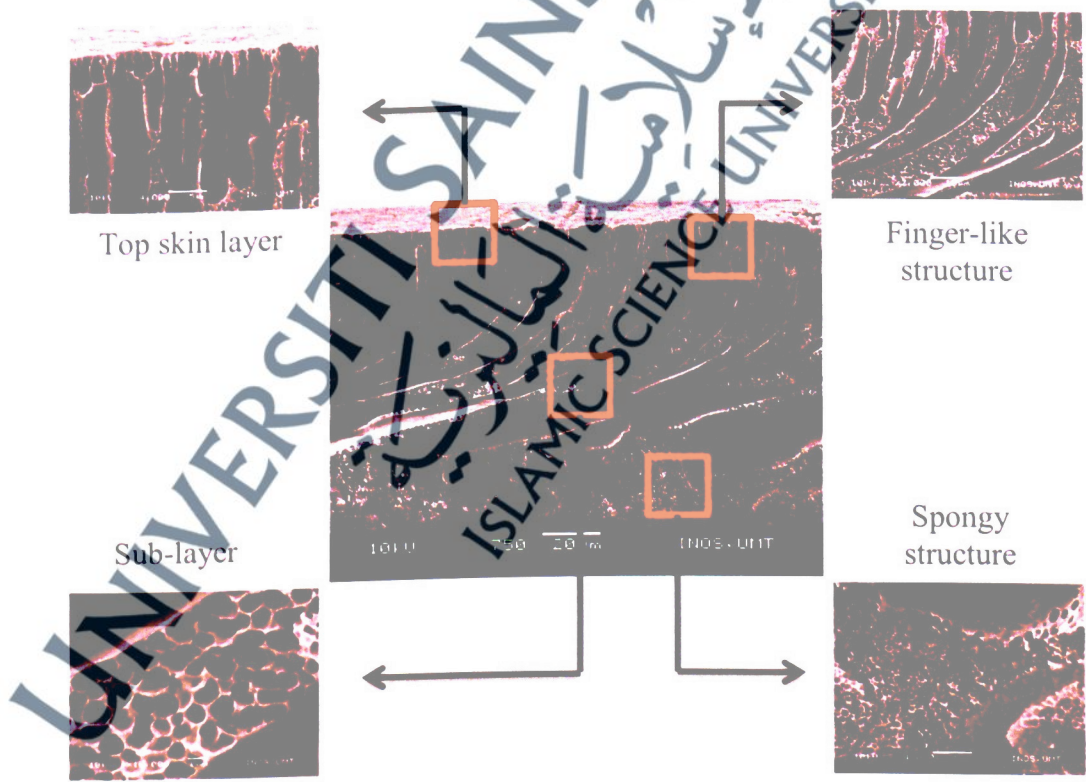
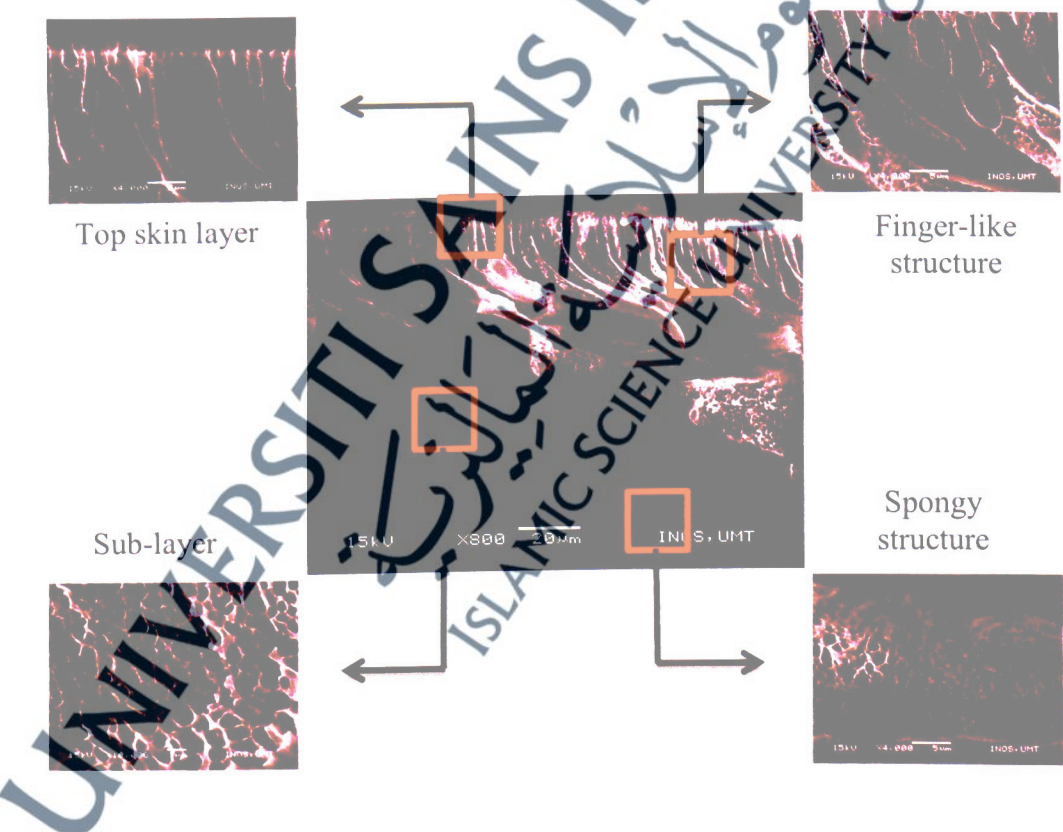


Figure 59(c) shows the morphology of the PN-3G membrane. It may be seen that membranes containing PEG 200 are having asymmetric structure consisting of a dense top surface layer (skin layer), a porous sub-layer (support layer), and a small portion of sponge-like bottom surface layer. The skin layer acts as a separation layer and the support layer provides the mechanical strength. As shown in the zooming figure, the sub-layer seems to have finger-like cavities beneath the top surface layer and large voids (macrovoids) near the bottom surface layer. The formation of finger-like cavities in the sub-layer of the prepared membranes resulted from instantaneous demixing which is due to high mutual affinity of solvent, NMP for water (Ma et al., 2011).

FIGURE 59(c): Cross-Sectional Structure of PN-3G (PVDF/NMP/PEG 200)



As the polymer solution containing PEG 200 as an additive (PN-3G), it was formed a thin film between the solution and the air interface as soon as they are exposed to the air. The formed thin film can prevent the coagulants from entering the casting solution. In other words, solvents located between polymer chains can be rapidly diffused out means that the skin layer of the asymmetric membrane can be dense. In addition, by adding PEG 200 in the casting solution, the fine sponge-type structures appeared as it is easier to flow out into coagulation bath. According to general theory of pore formation, the rapid outflow rate offers macrovoids, porous interconnecting channels of the sponge-type (Kim and Lee, 2004).

Ma et al. (2011) reported that the existence of PEG additives in the membrane casting solutions has two effects. (1) The dissolution of PEG consumes some of the solvent and leads to higher viscosity of membrane casting solutions. The membrane dope becomes thermodynamically less stable, which results in rapid instantaneous demixing when the membrane dope is immersed into the coagulation bath. (2) PEG is hydrophilic in nature. The hydrophilicity of PEG in membrane dope affects the exchange rate of solvent and non-solvent during phase inversion process and influences the precipitation kinetics and the formation of resulting membrane morphology consequently.

It is observed the existence of macrovoid at the sub-layer to the bottom of the all membranes. The addition of different additives had demonstrated significant changes in size of finger-like structures, macrovoid and pores in the membrane. As depicted in Table 14, the addition of PVP in the casting solution would decrease the length-width of pores and macrovoids structures while the length-width of finger-like

structures in the membrane quite same as the PN-3 membrane. Although the largest size of macrovoid appeared in PN-3G membrane containing PEG 200 as additive in the polymer dope solution, but the length-width of finger-like structures had the lowest compare to the others membrane. Besides, PN-3G membrane get the higher protein rejection as same as PN-3P membrane which is 85% because of the lowest width of finger-like structures in the membrane (4.1 μm). The existence of finger-like, macrovoid structures and pores in the membrane are significant characteristics of porous membrane. Furthermore, the UF membranes are categorized as porous membrane based on their porous structure and high PWP related to the membrane productivity.

TABLE 14: UF membranes structural details with different additives

Membranes	Finger-like Length (μm)	Finger-like Width (μm)	Macrovoid Length (μm)	Macrovoid Width (μm)	Pore Length (μm)	Pore Width (μm)
PN-3	70.6	18.5	116.7	32.1	0.70	0.73
PN-3P	79.5	18.0	32.3	26.3	1.95	1.49
PN-3L	55.3	9.2	73.5	13.7	2.31	1.27
PN-3G	40.9	4.1	130.1	26.6	1.11	1.18

FIGURE 60(a): Summary of Performance, Morphologies and Pore Properties of PVDF-UF Membrane with Additive (PVP)



4.3.4 FTIR Studies

Three membranes will be discussed in this FTIR studies as well the additives were added to each of the membrane casting solution. The PN-3P, PN-3L and PN-3G membranes with addition of PVP, LiCl and PEG 200, respectively. The spectra from pure PVDF membrane prepared with 17 wt% with 83 wt% NMP in the casting solution is shown in Figure 53(c). As discussed earlier regarding PN-3 membrane (refer to section 4.2.4), the spectrum of original PVDF membrane without addition of additive revealed a very weak band at 3400-3600 cm^{-1} that is associated with the O-H stretching of water molecules.

FIGURE 61(a): IR Spectra of UF Membrane (PN-3P) with Addition of PVP

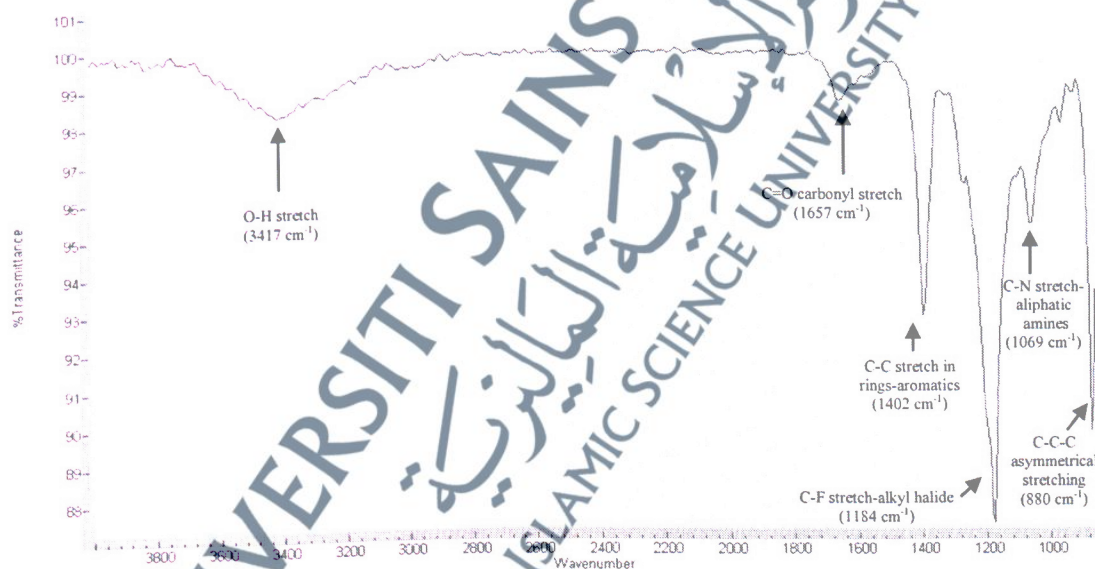
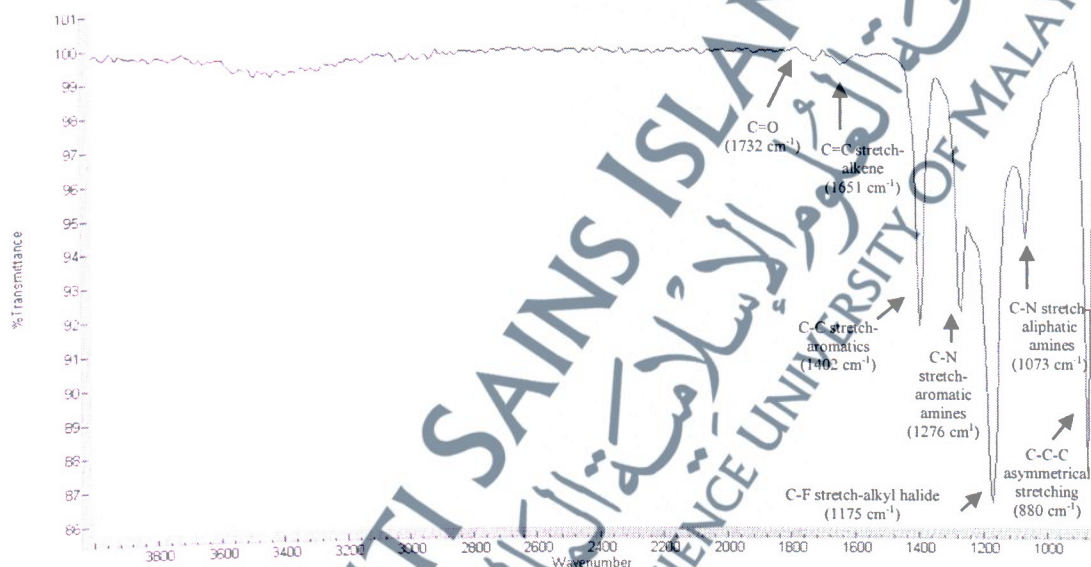


Figure 61(a) above shows the spectrum of PN-3P membrane where the membrane structural changes when PVP was used as an additive in the casting solution. As the presence of PVP in the membrane dope solution thus its high tendency to water may cause a broad band in the area of O-H stretching (Rahimpour

and Madaeni, 2010). The absorption peak in the infrared spectrum of O-H stretches at 3417 cm^{-1} , was more prominent in PVP-containing PVDF membrane while the rest of the spectrum remained similar. In addition, a new band is assigned to the carbonyl group (C=O stretches) of PVP at 1657 cm^{-1} . This indicates that PVP trapped in the polymer network and form an integral part of the polymeric structure, providing the polymer surface with a more hydrophilic nature than the surface of pure PVDF membrane (Vatsha et al., 2014).

FIGURE 61(b): IR Spectra of UF Membrane (PN-3L) with Addition of LiCl

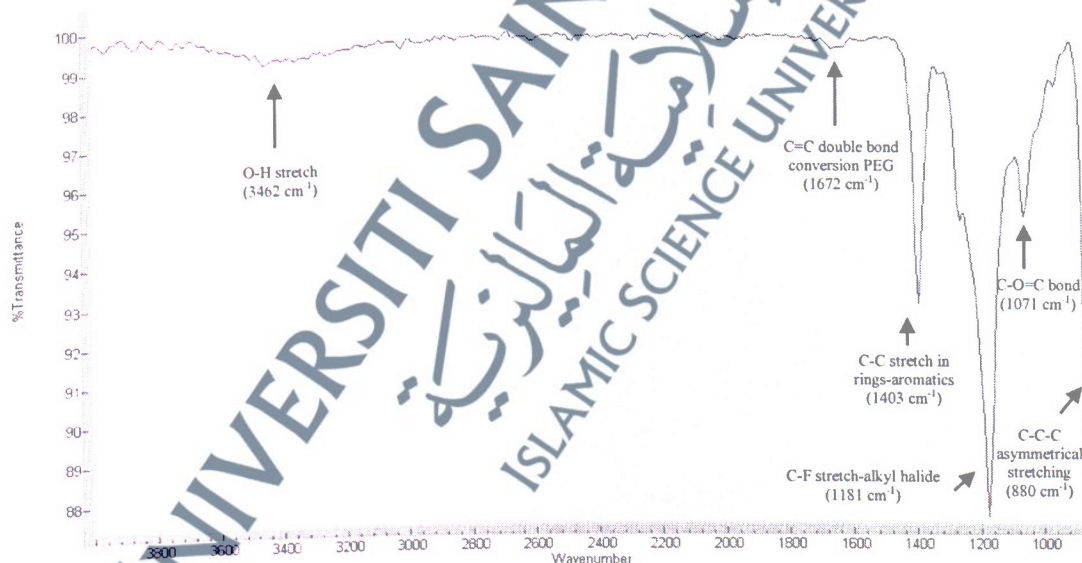


On the other hand, Figure 61(b) shows the infrared spectrum of the PN-3L membrane and its surface changes as LiCl was added. The band at 1732 cm^{-1} is attributed to C=O asymmetric stretching vibrations. Moreover, the sharp and strong absorption bands at 1175 cm^{-1} and 880 cm^{-1} correspond to the C-F stretching alkyl halide and C-C-C stretching vibration, respectively. The characteristics of two absorption bands at 1276 cm^{-1} and 1073 cm^{-1} were attributed to C-N stretch aromatic

amines and C-N stretch aliphatic amines, respectively. Besides, another strong peak around 1402 cm^{-1} was assigned to the aromatic stretching vibration of the C-C group.

Figure 61(c) shows the infrared spectrum of macromolecular PEG 200 additives used for membrane casting solution (PN-3G membrane). In the FTIR spectrum of the PN-3G membrane, the low peak at 3462 cm^{-1} representing stretching of O-H, hence evidencing the presence of glycols. Besides, the band at 1672 cm^{-1} corresponds to the stretching modes of the C=C double bond conversion of PEG. Another peak at 1071 cm^{-1} which is due to additional intensity of C-O=C bond stretch (from PEG 200) was observed and this confirms the presence of the additives in the membrane polymer matrix (Susanto and Ulbricht, 2009).

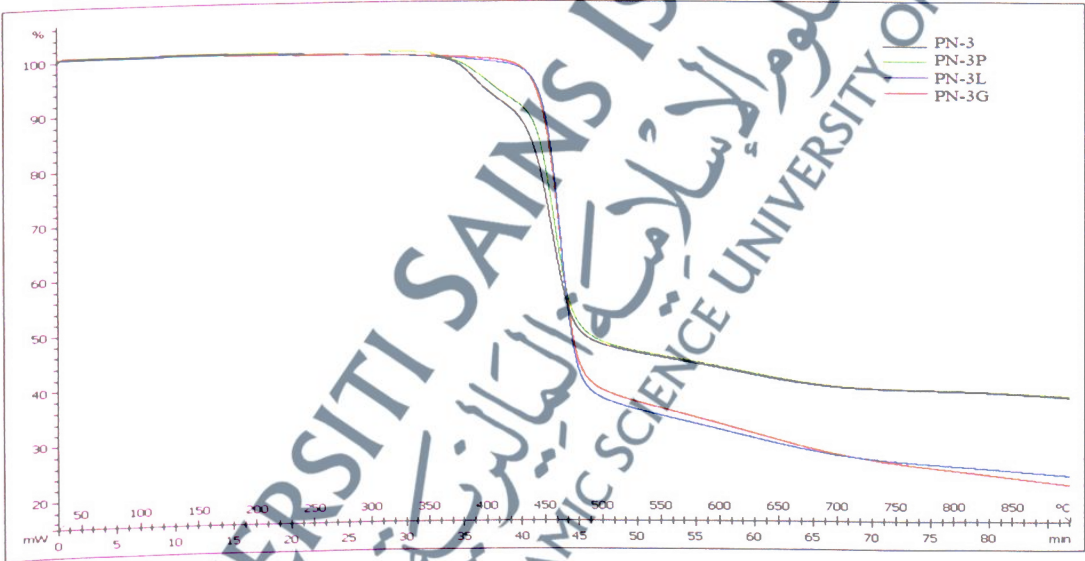
FIGURE 61(c): IR Spectra of UF Membrane (PN-3G) with Addition of PEG 200



4.3.5 TGA Studies

Figure 62 shows the TGA results generated on PVDF ultrafiltration membranes. The membrane without addition of additive was marked as PN-3 membrane while with additives PVP, LiCl and PEG 200 added to the casting solution, the membranes were marked as PN-3P, PN-3L and PN-3G, respectively. The plot shows the percent mass as a function of sample temperature for the prepared membranes under a nitrogen purge. It was observed that the thermal stability of PN-3P, PN-3L and PN-3G membranes were slightly modified by the presence of additives.

FIGURE 62: TGA Curves of PVDF Membrane with Addition of Different Additives



The TG results show that the PN-3 and PN-3P membranes undergo thermal degradation beginning at ~400 °C and with a total mass loss of 63 and 60 %, respectively. The thermal stability of PVDF polymer membrane is improved by adding of PVP additive. As it can be seen, the PN-3 and PN-3P membranes exhibited two degradation stages located at ~400 °C and ~450 °C. The weight losses for the first

and second stages were 5 % and 14 % for PN-3 membrane meanwhile 6 % and 18 % for PN-3P membrane. In this sense, it has been reported that the first weight loss during thermal degradation is due to the degradation of the hard segment as a consequence of the relatively low thermal stability whereas the second weight loss has been associated to soft segment decomposition (Cervantes et al., 2009).

By adding PVP into the polymer casting solution, degradation starts at lower temperature at 306.3 °C. This is because PVP played a role as a pore former, contributed to pores enlargement and increase in membrane porosity, hence made the structure easier to degrade (Hatijah et al., 2011). The TGA plots of PN-3L membrane did not have a similar changing tendency compared to plain membrane (PN-3 membrane), which substantially improved the thermal stability of the membrane. It is seen also that the decomposition temperature of PN-3L membrane (490 °C) was higher than that of the PN-3 membrane. Besides, the total weight loss of PN-3L membrane is 75.2 % which is due to the decomposition of both the compound and also due to the organic compound evaporation (Nirmala and Prakash, 2012).

From the TG curve, it was seen that the addition of PEG 200 additive resulted in increased thermal stability. In particular, the PN-3G membrane which is consisting PEG 200 additive showed improvement in thermal degradation where starting at a higher temperature (353 °C) compared to the plain membrane. According to Ali et al. (2011), the enhanced thermal stability was a result of the stronger interaction between the polymer and PEG 200 in the membrane by forming hydrogen bonds.

During the first decomposition stage of the PN-3G membrane, initially 6 % weight loss took place in the temperature range from 30 to ~410 °C. The second stage of thermal decomposition of PN-3G membrane started above 410 °C and terminated at ~490 °C, therefore in this stage highest weight loss of about 62 % was observed. This loss of weight may probably due to main thermal decomposition of additive chains. The final stage started from ~500 to 850 °C, represented the degraded membrane to ash. The TGA plots of membrane revealed that the degradation temperature of additive-membranes were much higher than that of plain PVDF/NMP membrane (PN-3). This showed that incorporation of additives into the PVDF membrane significantly improved thermal properties of the membranes (Zafar et al., 2012).

4.4 Addition of Different Surfactant (Single Surfactant) towards PVP additive

In the previous studies, it was shown that the addition of different additives significantly affected the properties and structures of the PVDF membranes. The changed in membrane properties and its morphological structures contributed to the variation in their separation performance. The PVDF/NMP/PVP and PVDF/NMP/PEG 200 membranes which contained 3 wt% for both PVP (as a pore former additive) and PEG 200 (as a pore reducer additive) in the membrane casting solution showed the best results in the separation performance of proteins. Hence, both of membranes have favorable characteristics to be used in the next UF studies with addition different types of surfactants. However, the addition of surfactants towards PEG 200 additive was discussed in Section 4.5.

In order to optimize the membrane separation performance, the PVDF/NMP/PVP membrane was added different types of surfactants which are Sodium dodecyl sulfate (SDS), Triton X-100, and Tween 80 to the casting solution to induce molecular orientation which in turn altered the separation performance of these membranes. The Table 15 shows the composition parameters of the membrane fabrication conditions with addition of different types of surfactants to the polymer casting solution.

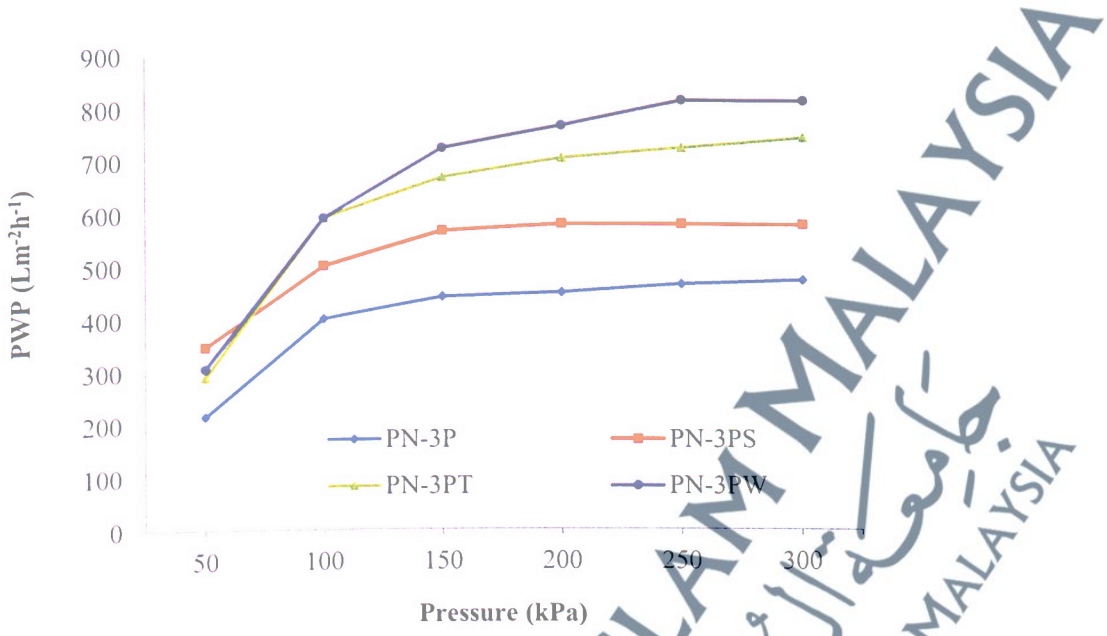
TABLE 15: The PVDF/NMP/PVP membrane formulations

Membranes	Total polymer (wt%)	Solvent (wt%)	Additives (wt%)	Surfactants (wt%)		
			PVP	SDS	Triton X-100	Tween 80
PN-3P	17	80	3	-	-	-
PN-3PS	17	78	3	2	-	-
PN-3PT	17	78	3	-	2	-
PN-3PW	17	78	3	-	-	2

4.4.1 Pure Water Permeation (PWP)

The PWP of the membranes fabricated with addition of different types of surfactants are shown in Figure 63. The PWP measurements of all fabricated membranes were measured at six different pressures from 50 to 300 kPa. As displayed in Figure 63, the PWP of all the membranes increased with the increasing operating pressure. Based on the graph, it was showed that all the PN-3PS, PN-3PT and PN-3PW membranes containing surfactants SDS, Triton X-100 and Tween 80, respectively give the high values of PWP compared to membrane without additional any of surfactant (PN-3P).

FIGURE 63: PWP of PVDF/NMP/PVP Membranes with Different Types of Surfactants



The addition of SDS surfactant in the casting solution (PN-3PS membrane) altered the membrane performance. As clearly seen in Figure 63, the obtained results demonstrated that PWP of PN-3PS membrane increase from 346.42 to 577.37 Lm⁻²h⁻¹ as increase the operating pressure from 50 to 300 kPa. The PN-3PS (SDS treated membrane) produced higher water permeation compared to PN-3P membranes at similar pressure. However, while comparing to other surfactants, the PWP of PN-3PS is the lowest at the maximum operating pressure which is 577.37 Lm⁻²h⁻¹. The PWP is closely influenced by the membrane morphology and properties. In fact, the alteration in PWP is expected on the basis of the changes in the membrane morphology after addition of SDS. The membrane morphology of PN-3PS membrane was discussed in section 4.4.3.

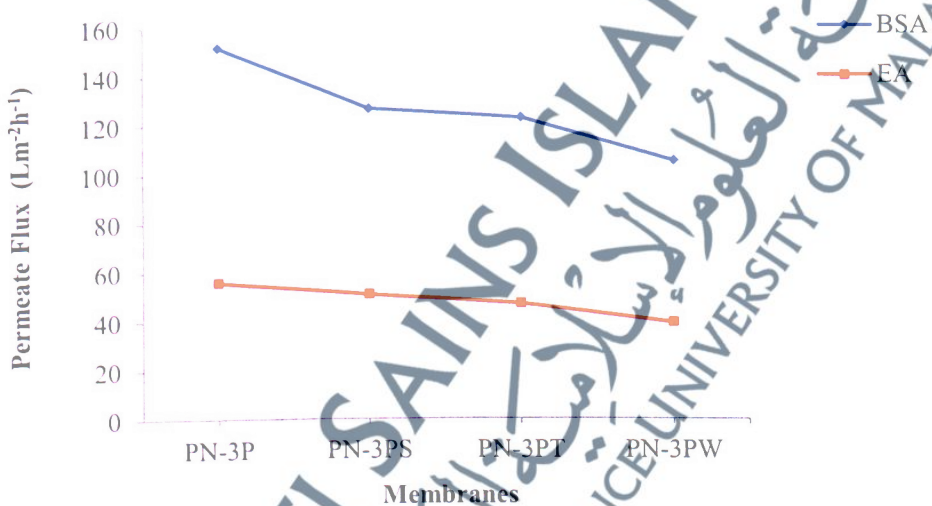
On the other hand, the effect of Triton X-100 surfactant on the PWP is seen in Figure 63 as the membrane was marked as PN-3PT. An increase of operating pressure from 50 to 300 kPa significantly PWP of PN-3PT membrane increase from 288.68 to 742.33 $\text{Lm}^{-2}\text{h}^{-1}$. This is due to the increase in effective driving force (operating pressure) required for water permeation. The addition of Triton X-100 as surfactant in the casting solution slightly increases the value ($\text{Lm}^{-2}\text{h}^{-1}$) up to 30% of water permeation. This is because the presence of Triton X-100 as secondary additive in the casting solution causes the formation of large finger-like pores in the sub layer of the membranes (refer to section 4.4.3).

In addition, the effect of Tween 80 surfactant on PWP at various operating pressure which marked as PN-3PW is shown in Figure 63. It is seen that within the range of 50-300 kPa, with increase in operating pressure, PWP increased from 305.66 to 811.92 $\text{Lm}^{-2}\text{h}^{-1}$. As observed in Figure 63, addition of Tween 80 to the casting solution results in an increase in PWP of the prepared membranes. For instance, when the membrane is prepared without addition of Tween 80 in the casting solution, PWP of the membrane is 472.39 $\text{Lm}^{-2}\text{h}^{-1}$. The PWP increases by addition of 2 wt% of Tween 80 to the casting solution and reaches to a maximum value of 811.92 $\text{Lm}^{-2}\text{h}^{-1}$. Therefore, the addition of Tween 80 as surfactant additive in the casting solution can be responsible for high performance which is higher water permeation of the membranes as it would increase the porosity of the membrane support layer. Hence, this result led to higher pure water permeation (Amirilargani et al., 2009).

4.4.2 Protein Separation Performance

In UF membrane process, the membrane separation performance was measured in terms of its productivity and rejection towards solute rejection. The permeate flux and proteins rejection for PN-3P, PN-3PS, PN-3PT and PN-3PW membranes are illustrated in Figure 64 and Figure 65, respectively.

FIGURE 64: Proteins Permeation Flux of UF Membranes with Different Types of Surfactants towards PVP Additive

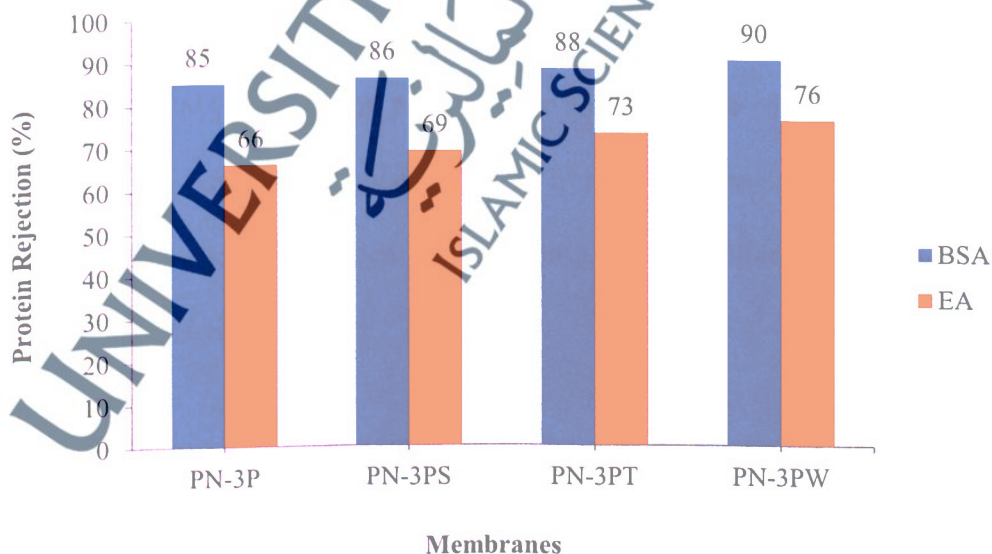


It has been reported that surfactants has a significant effect on the membrane properties and morphology (Mansourpanah et al., 2011). Figure 64 shows the effect of surfactants SDS, Triton X-100 and Tween 80 in the membrane casting solution on the permeate flux using BSA and EA solution through the UF process. It is observed from the graph that with addition of surfactants to the casting solution, the BSA permeate flux decrease from 151.72 Lm⁻²h⁻¹ to 126.74 Lm⁻²h⁻¹, 122.99 Lm⁻²h⁻¹, and 105.51 Lm⁻²h⁻¹ when SDS, Triton-X and Tween 80 added, respectively. This decreasing trend of permeate flux is similar to the EA protein.

According to both figures, the addition of surfactants in the casting solution significantly affected the permeate flux and rejection of each protein solution. It is observed from the bar chart that the addition of surfactants to the casting solution significantly increased both BSA and EA protein rejections (Figure 65). The permeate flux and rejection characteristics of the membrane strongly depend on the structure of the membrane as well as the properties of the feed solution.

Based on the proteins separation profile as seen in Figure 65, the addition of surfactants to the polymer casting solution increased the rejection of proteins towards the PVDF-PVP membranes. With addition of SDS, Triton X-100 and Tween 80 in the polymer casting solution, the BSA protein rejection increased from 85% (PN-3P) to 86%, 88% and 90%, respectively.

FIGURE 65: Proteins Rejection of UF Membranes with Different Types of Surfactants towards PVP Additive



While comparing these three surfactants (SDS, Triton X-100 and Tween 80) on the permeation performance towards the PVDF-PVP membranes, membrane prepared with SDS surfactant give the highest permeate flux which is $126.74 \text{ Lm}^{-2}\text{h}^{-1}$ and $50.70 \text{ Lm}^{-2}\text{h}^{-1}$ for BSA and EA, respectively, and the lowest proteins rejection (86% BSA and 69% EA). This results shows that the addition of SDS enhances the protein permeation flux. It can be attributed to the non-uniform distribution, severe aggregation and precipitation of dope solution containing PVP additives in aqueous phase using SDS as surfactant even after ultrasonic, which could be observed during the experiment (Wu et al., 2013). In addition, Saedi et al. (2012) also reported that the addition of surfactant SDS in the polymer casting solution contributed to decrease in the proteins selectivity as well the membrane surface defect.

The permeation flux of proteins at 100 kPa for the PN-3PT membrane from addition of Triton X-100 surfactant is presented in Figure 64. As it can be seen, the presence of Triton X-100 decreased the BSA permeation flux from $151.72 \text{ Lm}^{-2}\text{h}^{-1}$ to $122.99 \text{ Lm}^{-2}\text{h}^{-1}$, decreased the EA permeation flux from $55.72 \text{ Lm}^{-2}\text{h}^{-1}$ to $46.92 \text{ Lm}^{-2}\text{h}^{-1}$ and increased membrane selectivity; the selectivity of BSA and EA proteins rejection increasing from 85% to 88% and from 66% to 73%, respectively. This result showed that PN-3PT membrane has a modest increase in selectivity as the membrane structure including selective layer and membrane substrate are modified by the addition of a surfactant to the casting solution.

Saedi et al. (2012) was suggested that the increase in selectivity could be caused by the reduction of the number of skin defects or antiplasticization of the polymer. This is due to the fact that skin formation is caused by surface tension forces,

and addition of Triton X-100 changes the surface tension of the casting solution. It is possible that the closing of defects during skin formation occurred as a result of the presence surfactant which is Triton X-100.

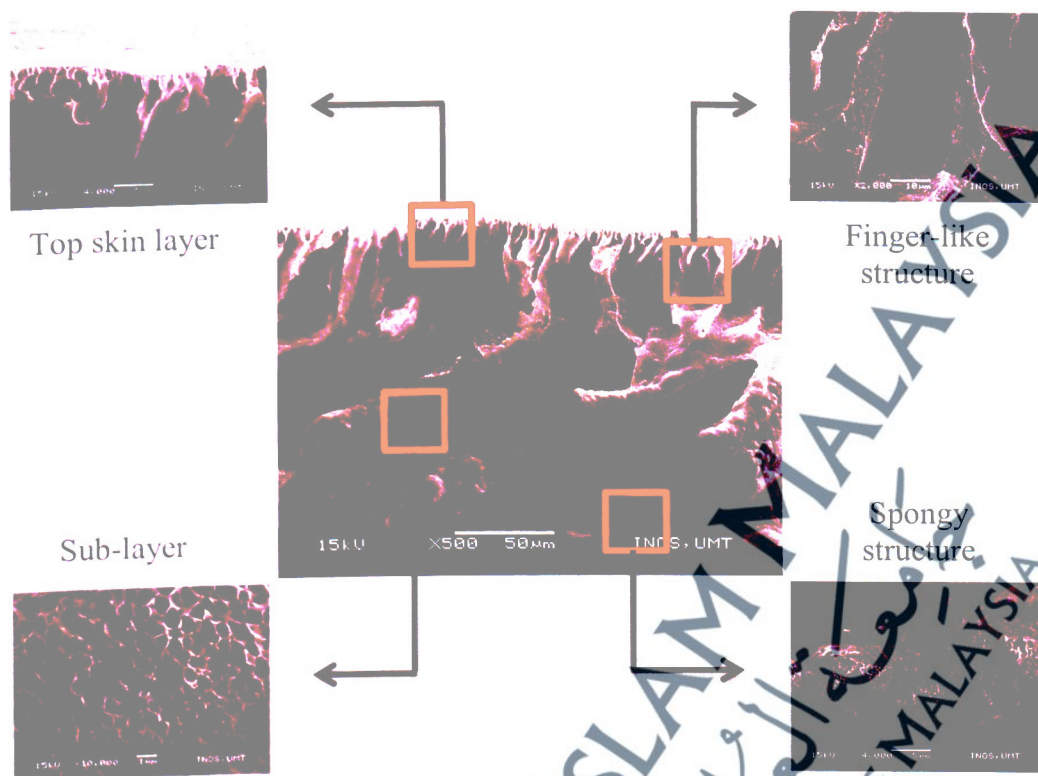
Besides, the effect of Tween 80 surfactant in the PVDF-PVP dope casting solution on the protein permeation flux and solute rejection are illustrated in Figures 64 and 65, respectively. As observed in Figure 64, addition of Tween 80 to the casting solution results in the lowest protein permeation flux which is $105.51 \text{ Lm}^{-2}\text{h}^{-1}$ and $39.29 \text{ Lm}^{-2}\text{h}^{-1}$ for BSA and EA, respectively. For example, when the membrane is prepared without addition of Tween 80 (PN-3P), the BSA and EA permeate flux are $151.72 \text{ Lm}^{-2}\text{h}^{-1}$ and $55.72 \text{ Lm}^{-2}\text{h}^{-1}$, respectively. As is expected, the proteins permeation fluxes of PN-3PW membrane decreased but percentage rejection of protein increased from 85% to 90% and from 66% to 76% for BSA and EA, respectively.

While comparing to the other surfactants towards PVDF-PVP membranes, it is shown that the membrane fabricated with addition of Tween 80 surfactant to the polymer casting solution give the best performance due to high rejection of proteins at favorable permeation flux of protein solution. In addition, by using Tween 80 as a pore former surfactant, a porous structure of PVDF membranes that allow UF operation was formed and exhibit an uncommon type of morphology being composed of a thin nano-porous top layer, followed by a short region of columnar voids and then a thick bi-continuous porous support (refer to section 4.4.3).

4.4.3 Membrane Morphology

Figure 66 shows SEM micrographs of the cross-section of PVDF/PVP membranes prepared with addition of different surfactant types to the polymer casting solution. Figures 69(a), (b) and (c) depict the cross-section of SEM micrographs of PVDF/NMP/PVP membranes with addition of different surfactants SDS, Triton X-100 and Tween 80 respectively. The PVDF/NMP/PVP membrane without addition of surfactant (PVP content) marked as PN-3P was used as standard membrane in this study and shown in Figure 59(a) and was discussed in section 4.3.3. All the membranes studied were demonstrated that so-called asymmetric morphology which was characterized by a dense top-layer, thick or thin skin layer and porous spongy sub-layer.

The SEM zooming images of the cross-sections of membranes (PN-3PS) prepared with addition of SDS in the casting solution is shown in Figure 66(a). The SEM images indicate that addition of small amount of SDS in the casting solution results in considerably thinner top-layer and more porous sub-layer membranes, and SDS also can incite macrovoids formation. As discussed before, the PWP of PN-3PS was increased from $477.39 \text{ Lm}^2\text{h}^{-1}$ to $577.37 \text{ Lm}^2\text{h}^{-1}$ when SDS added in the polymer casting solution. It was evidence that the existence of finger-like pores and high porosity of sub-layer of PN-3PS membrane prepared can be responsible for high performance PWP of membranes.

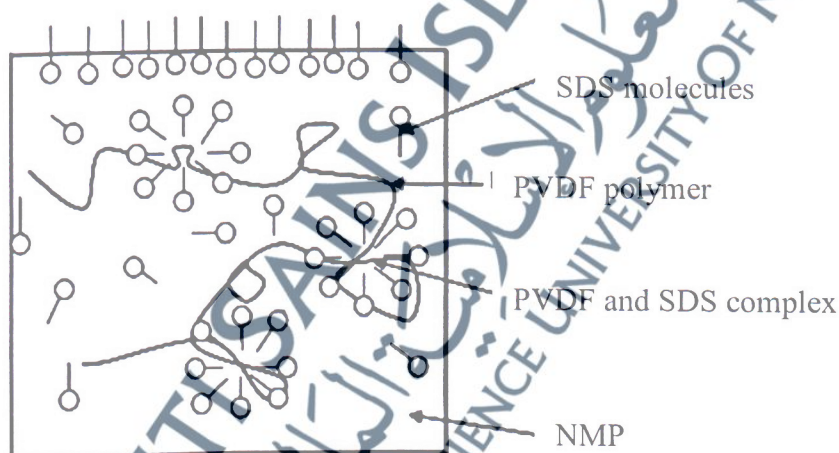
FIGURE 66 (a): Cross-Sectional Structure of PN-3PS (PVDF/NMP/PVP/SDS)

Moreover, according to Rahimpour et al. (2007), the addition of SDS surfactant in the casting solution may have two effects on the membrane formation processes as shown schematically in Figure 67; (i) a decline of the solvent evaporation rate and (ii) a diminish of interaction between polymer chain due to formation of polymer-surfactant complex. SDS has an amphiphilic structure (i.e comprising of hydrophilic head and hydrophobic tail), while the solvent (NMP) is hydrophilic property. As a result, a layer of SDS molecules is formed on the surface of the casting film. This layer decreases the rate of solvent evaporation leading to slower growth of the highly concentrated polymer in the casting film.

On the other hand, NMP is hydrophilic and PVDF is hydrophobic. The SDS molecules and PVDF are likely to form a micelle-like complex in the solution. The

formation of polymer-surfactant complex reduces the interaction between the polymer chains. Both aforementioned phenomena result in a delay in the coagulation of polymer in the presence of SDS (i.e instantaneous demixing). Consequently, the growth of skin layer is diminished and formation of finger-like pores in the support is improved. Besides, the SDS molecules corrupt the pores and become large then, leave defects in the membrane structure. This indicates PN-3PS membranes exhibit in higher PWP and low protein rejection (86% BSA; 69% EA) as exhibited in Section 4.4.2.

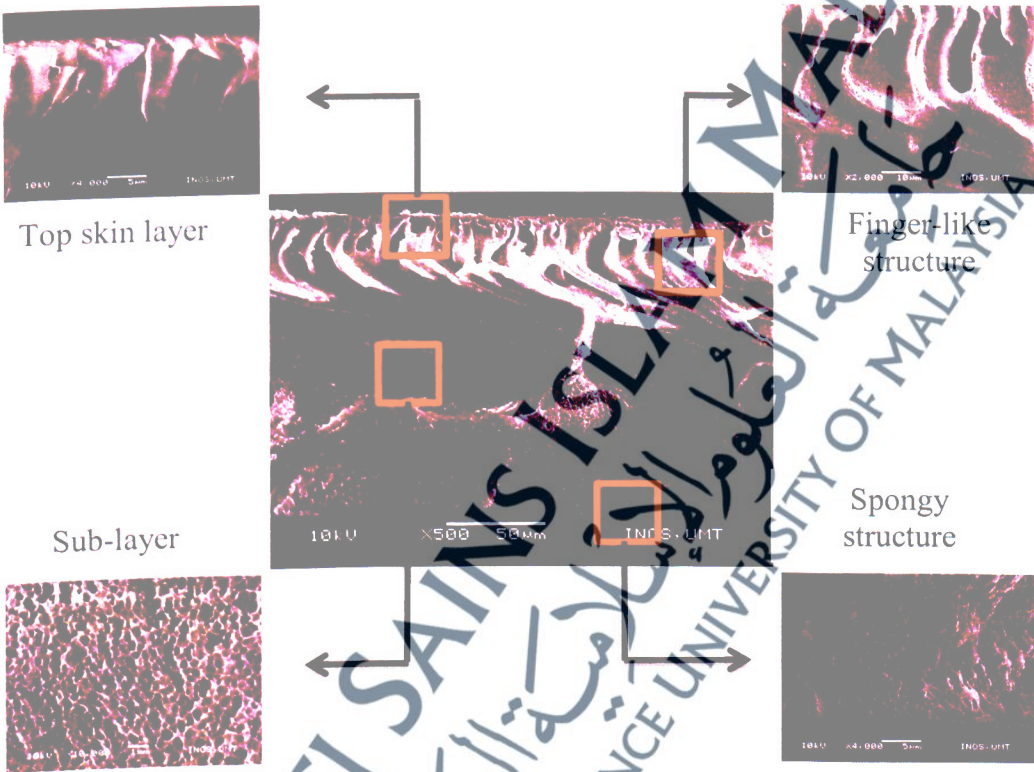
FIGURE 67: The Effect of SDS on the Formation of PVDF Membranes by Phase Inversion



The effect of surfactant Triton X-100 on the membrane morphology is seen in Figure 66(b). As shown in the figure, the SEM images of PN-3PT membrane with addition of Triton X-100 in the polymer casting solution exhibit the typical asymmetric structure and fully developed finger-like pores in the sub-layer which are larger than pores exists in the PN-3P membrane prepared without Triton X-100. Asymmetric structure of PN-3PT membrane consists of a dense top-layer, a porous

sub-layer that is occupied by closed cell within polymer matrix and finger-like pores. Besides, there is significant difference between cross-sectional morphology of PN-3P and PN-3PT membranes.

FIGURE 66(b): Cross-Sectional Structure of PN-3PT (PVDF/NMP/PVP/TRITON X-100)

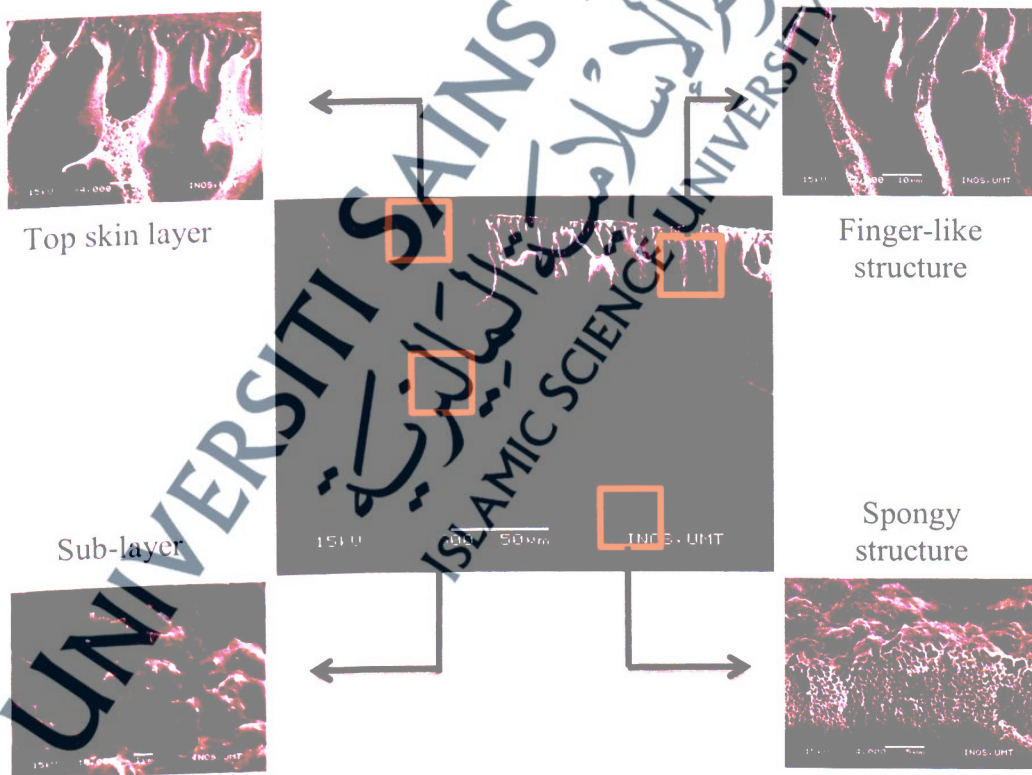


The presence of Triton X-100 as surfactant additive in the polymer casting solution causes the formation of large finger-like pores in the sub layer of membranes. These cross-sectional morphologies of the PN-3PT membrane justify the high PWP and proteins permeate flux in the presence of Triton X-100 due to the porous structure of the membranes. Saedi et al. (2012) reported that in the presence of surfactant Triton X-100 in the PVDF membrane casting solution, the electrostatic repulsion in the polymer-surfactant is less than surfactant SDS, and therefore the polymer chain can

accommodate in a more packed structure. Consequently, the protein rejection of PN-3PT membrane (88% BSA; 73% EA) was higher than PN-3PS membrane (86% BSA; 69% EA).

In Figure 66 (c), the cross-sectional SEM zooming images of the membranes prepared by immersing casting dopes containing Tween 80 as surfactant additive is demonstrated and marked as PN-3PW membrane. The SEM images indicate that large pores are formed in the sub-layer of the PN-3PW membrane prepared with addition of 2 wt% of Tween 80 to the casting solution. The addition of Tween 80 as surfactant to the casting solution can incite the macrovoids formation.

FIGURE 66(c): Cross-Sectional Structure of PN-3PW (PVDF/NMP/PVP/TWEEN 80)



As observed in the SEM images, seen in Figure 66(c), there are big macrovoids in the sub-layer of PN-3PW membrane. Obviously, Tween 80 can enhance the formation of macrovoids. Therefore, it was evidence that the existence of big macrovoids in the sub-layer of PN-3PW membrane prepared can be responsible for highest performance PWP of membranes and proteins rejection which is up to 90% and 76% for BSA and EA respectively.

This phenomenon can be explained by miscibility between added surfactant and the coagulant. The property of low solubility of Tween 80 as hydrophilic surfactant additive in the NMP solvent was introduced as factor for changing the membrane morphology and performance. The miscibility between surfactant and coagulant plays an important role in the formation process of various pores. The macrovoids and finger-like pores in the sub-layer can be induced or suppressed by addition of appropriate surfactants, depending on their miscibility with coagulants. The addition of surfactants that have high miscibility with coagulants may be able to extend the formation of finger-like pores and macrovoids. On the other hand, the addition of surfactants with low miscibility with coagulants suppresses the macrovoids formation (Amirilargani et al., 2009).

Generally, the addition of small amount of surfactant has strong effect on morphology of PVDF membrane. As depicted in Table 16, the addition of SDS to the casting solution would decrease the length of finger-like and pores of the membranes. It is observed the existence of macrovoids at the sub-layer of the membrane. The PVDF membrane prepared without addition of surfactant which is marked as PN-3P membrane exhibit relatively large pores in the middle surface area and the formation

of pores in the middle surface area of the membrane were approximately reduced as surfactants were introduced to the casting solution.

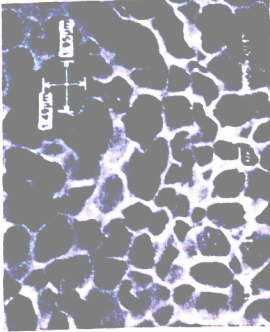
For example, PN-3P membrane have 1.95 μm and 1.49 μm as pore length and pore width, respectively therefore, both of these values were reduced to 0.43 μm and 0.46 μm respectively when Triton X-100 is added to the membrane casting solution. Rahimpour et al. (2007) has similar results which demonstrated that the pore size of membrane prepared without surfactant is larger than the membrane pores prepared by surfactant. The largest macrovoids formed in the sub-layer of the membrane was appeared in the PN-3PW membrane containing Tween 80 as surfactant additives in the polymer casting solution, which showed the longest length of macrovoid (154 μm).

TABLE 16: UF membranes structural details with different surfactants towards PVP additive

Membranes	Finger-like Length (μm)	Finger-like Width (μm)	Macrovoid Length (μm)	Macrovoid Width (μm)	Pore Length (μm)	Pore Width (μm)
PN-3P	79.5	18.0	32.3	26.3	1.95	1.49
PN-3PS	47.8	22.5	146.5	61.1	0.70	0.76
PN-3PT	42.7	15.3	102.2	42.3	0.64	0.64
PN-3PW	87.0	28.1	154.2	47.9	1.13	0.94

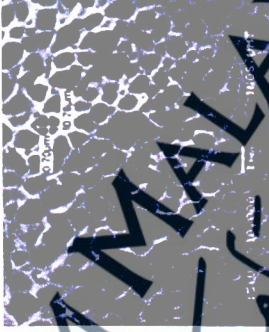
FIGURE 68(a): Summary of Performance, Morphologies and Pore Properties of PVDF-UF Membrane with Surfactant (SDS) towards

PVP Additive

Performance	Membranes	Pore Properties
PWP: 472.39 Lm ⁻² h ⁻¹ BSA flux: 151.72Lm ⁻² h ⁻¹ EA flux: 55.72 Lm ⁻² h ⁻¹ R (BSA): 85 % R (EA): 78 %	 (a)  (b)  (c)	<u>(a) Finger-like</u> Length: 79.5 μm Width: 18.0 μm <u>(b) Macrovoid</u> Length: 32.3 μm Width: 26.3 μm <u>(c) Pore</u> Length: 1.95 μm Width: 1.49 μm

PN-3P (PVDF/NMP/PVP)

PWP: 577.37 Lm⁻²h⁻¹
BSA flux: 126.74Lm⁻²h⁻¹
EA flux: 50.70 Lm⁻²h⁻¹
R (BSA): 86 %
R (EA): 69 %

Performance	Membranes	Pore Properties
PWP: 577.37 Lm ⁻² h ⁻¹ BSA flux: 126.74Lm ⁻² h ⁻¹ EA flux: 50.70 Lm ⁻² h ⁻¹ R (BSA): 86 % R (EA): 69 %	 (a)  (b)  (c)	<u>(a) Finger-like</u> Length: 47.8 μm Width: 22.5 μm <u>(b) Macrovoid</u> Length: 146.5 μm Width: 61.1 μm <u>(c) Pore</u> Length: 0.70 μm Width: 0.76 μm

PN-3PS (PVDF/NMP/PVP/SDS)

FIGURE 68 (b): Summary of Performance, Morphologies and Pore Properties of PVDF-UF Membrane with Different Surfactants

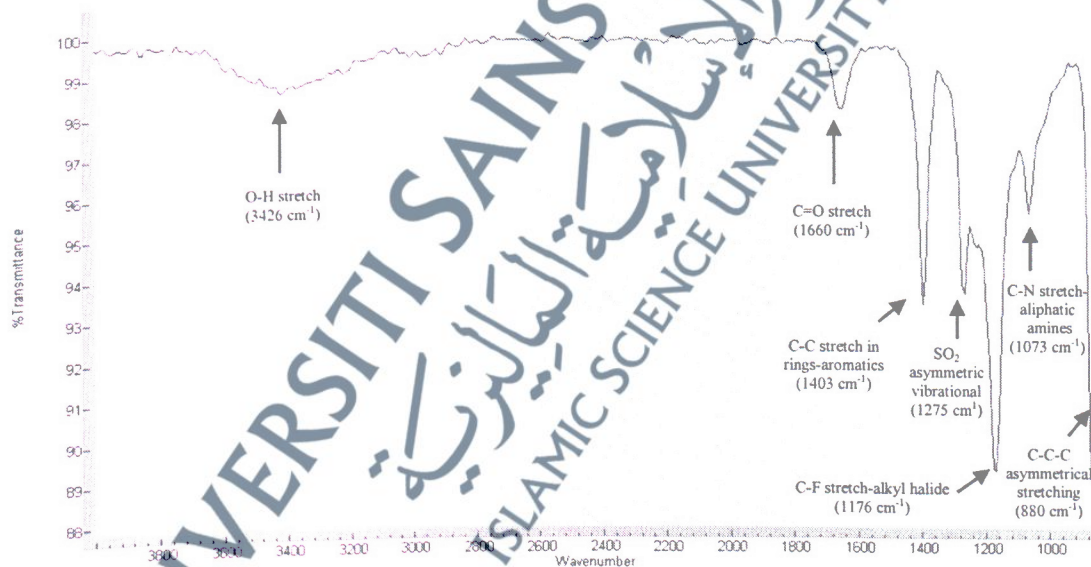
(Triton X-100 and Tween 80) towards PVP Additive



4.4.4 FTIR Studies

The FTIR spectrum of PN-3P membrane is shown in Figure 61(a). As discussed earlier, the spectrum of PN-3P membrane as presence of PVP and without addition of surfactant shows three characteristics sharp and strong bands around 1402 cm^{-1} , 1184 cm^{-1} and 880 cm^{-1} that are, respectively attributed to C-C aromatic stretch in rings, C-F stretch alkyl halide and C-C-C asymmetrical stretching vibrations (refer to section 4.3.4). The functional groups of PN-3PS membrane with addition of SDS surfactant towards PVP additive is shown in Figure 69(a).

FIGURE 69(a): IR Spectra of UF Membrane (PN-3PS) with Addition of SDS towards PVP Additive

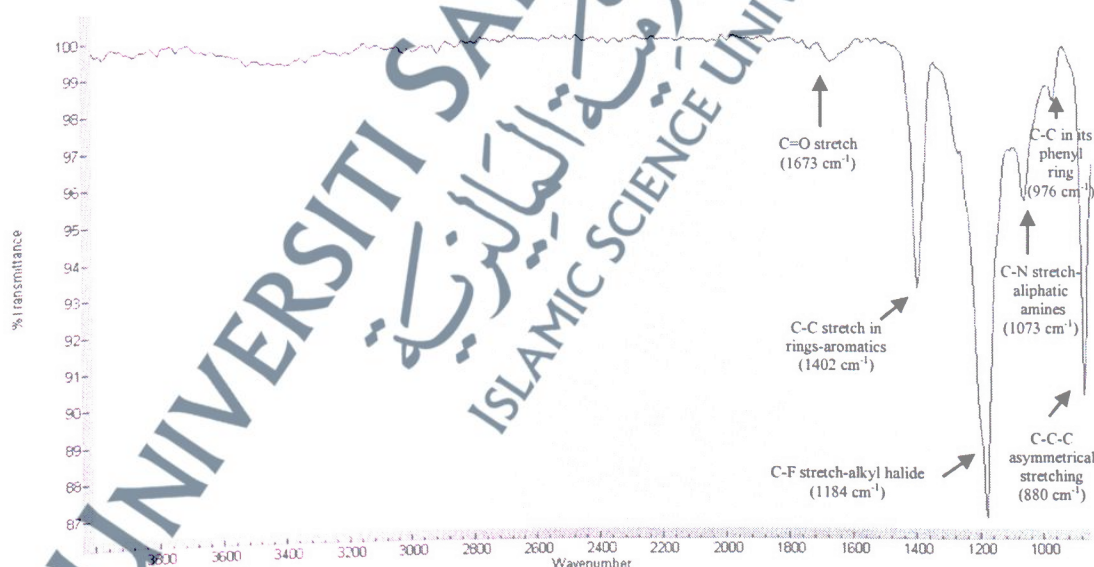


The characteristics bands of PN-3PS membrane are quite similar to the PN-3P membrane in Figure 61(a) in section 4.3.4, including to a broad peak related to the O-H stretching vibration (3426 cm^{-1}), stretching vibration C=O band (1660 cm^{-1}), C-C aromatics stretch in rings (1403 cm^{-1}), C-F stretch of alkyl halide (1176 cm^{-1}), C-N

stretch of aliphatic amine (1073 cm^{-1}) and C-C-C asymmetric stretching (880 cm^{-1}) are observed. However, the FTIR spectrum of the PN-3PS membrane after addition of SDS reveals one extra peak at 1275 cm^{-1} comparing to PN-3P spectrum. The observed peak is due to the presence of SDS, which attributed to the S=O stretching vibration resulting from vibration of sulfone group (SO_2 asymmetric vibrational) (Ghaemi et al., 2012).

Figure 69(b) shows the FTIR spectroscopy of PN-3PT membrane and its mixture with the Triton X-100 surfactant in the polymer casting solution. The absorption intensity was altered and the IR spectrum was small shifted in the presence of Triton X-100 surfactant.

FIGURE 69(b): IR Spectra of UF Membrane (PN-3PT) with Addition of Triton X-100 towards PVP Additive



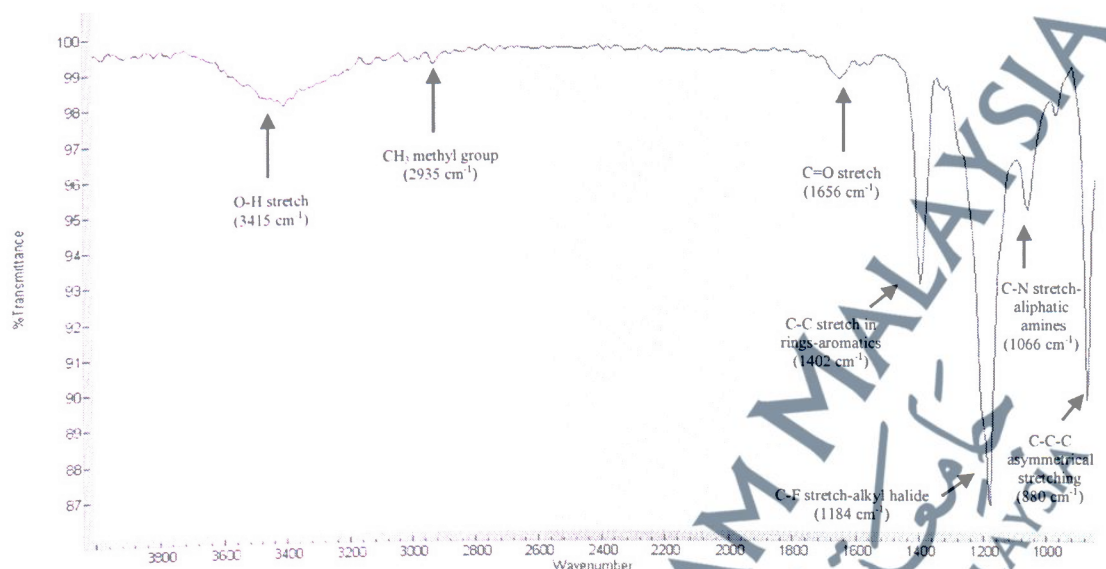
This observation demonstrated that there are intermolecular interactions between PVDF and the surfactant. In the presence of Triton x-100, there is no

frequency of O-H group. The absence of O-H wave number caused by decreased in bond order between oxygen from PVP and Triton x-100 resulting in a reduction in the vibration energy and subsequently a reduction in the wave number. The overall reduction of absorption intensity in the presence of the Triton X-100 surfactants can be explained by the fact that the surfactants increased the membrane porosity and subsequently caused a reduction in absorption (Saedi et al., 2012). Another peak was observed in the presence of Triton X-100 at around 976 cm^{-1} indicating of C=C stretching vibration in its phenyl ring. The bands characteristics of C=O stretching vibration at 1673 cm^{-1} , sharp and strong bands at 1402 cm^{-1} (C-C aromatic stretch in ring), 1184 cm^{-1} (C-F stretch of alkyl halide) and 880 cm^{-1} (C-C-C asymmetrical stretching of PVDF) were detected in the PN-3PT spectrum.

FTIR spectrum given in Figure 69(c) represents PN-3PW membrane with addition of Tween 80 as surfactant towards PVP additive mixed together in the polymer casting solution. From the spectrum showed above, a strong absorption band at 3415 cm^{-1} , due to the stretching of the terminal hydroxyl group from H_2O . This indicates that there is strong intermolecular hydrogen binding among the Tween 80 molecules since Tween 80 introduces three additional O-H groups per molecule.

The peak at 2935 cm^{-1} corresponds to CH_3 (methyl group) stretching vibration in Tween 80. The C=O stretching vibrations of Tween 80 appears at 1656 cm^{-1} . In addition, very small peak was observed at 1066 cm^{-1} related to C-N aliphatic amines stretching vibration. There are three strong and sharp peaks showed at 1402 cm^{-1} , 1184 cm^{-1} and 880 cm^{-1} which due to C-C aromatic stretch in rings, C-F stretch of alkyl halide and C-C-C asymmetrical stretch of PVDF, respectively.

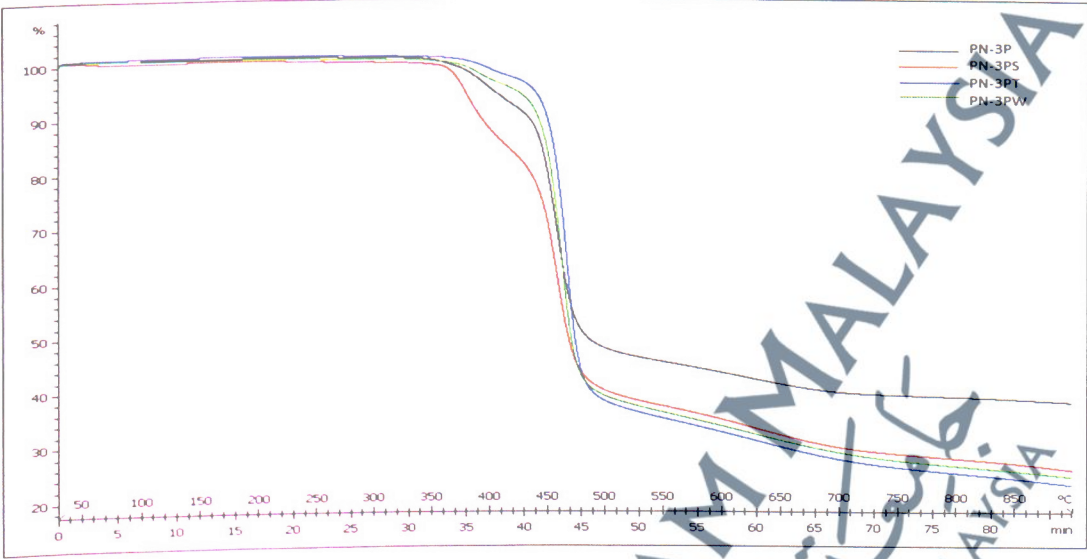
FIGURE 69(c): IR Spectra of UF Membrane (PN-3PW) with Addition of Tween 80 towards PVP Additive



4.4.5 TGA Studies

The thermal analyses of the prepared membranes are shown in Figure 70 for PVP-membrane samples at different addition of surfactants which are SDS, Triton X-100 and Tween 80. Most of the TGA curves present similar behavior with one main weight loss step in the temperature range of 30 °C to ~ 500 °C which including the dehydration of physically adsorbed water from 30 °C to ~ 200 °C and decomposition of surfactants from 200 °C to ~ 500 °C. However, it can be easily interpreted from the curves that the remaining weight did not level off even near to 900 °C. Therefore, there is possibility of gradual decomposition of surfactants and shifting to higher temperature (Ramimoghadam et al., 2012).

FIGURE 70: TGA Curves of PVDF-PVP Membranes with Addition of Different Surfactants



From the curves, the decomposition temperature of PN-3P, PN-3PT and PN-3PW membranes is about 400-450 °C, which is very close to each membrane. On the other hand, the result of PN-3PS membrane is also seen that the decomposition temperature (~350 °C) was lower than other membranes. For example, the PN-3PS membrane undergoes the first small weight loss of 12 % is described as removal of bonded water and the second weight loss of 24 % was observed between 430-450 °C, due to the surfactants removal. Samaele et al. (2010) reported that the SDS-modified Zn) particles via the precipitation method also start the decomposition between temperature of 500-600 °C. The higher temperature for surfactant degradation can be attributed to relatively high heating rate and the quality of the material (Samaele et al., 2010).

In addition, the highest total weight loss (77 %) was assigned for PN-3PT membrane which is consisting of Triton X-100 as surfactants in the polymer casting solution. As shown in Figure 70, from the weight loss was due to the burning and decomposition of the molecules. As measured the temperature up to ~ 500 °C, the Triton X-100 weight loss was estimated as ~ 61 % and ~ 16 % for the temperature above 500 °C. It was verified that the thermal degradation of PN-3PT membrane is thermally stable up to temperature above 900 °C where after a small initial lost weight due to the water/solvent removal. Thus, its weight is constant by increasing the temperature up to 1000 °C (Merino, 2012).

The typical thermal degradation profiles for PN-3PW membrane is shown in the TG curves (Figure 70). The PN-3PW curve has two main regions of weight loss. The main second stage of thermal decomposition of PN-3PW membrane started from 350 to 500 °C with highest weight loss of about 60 % was observed. Then, from 500 to 900 °C, the weight loss is about 74 % was determined. Each turning point marked the combustion of a new component in the polymer. The 400-450 °C and 480-530 °C combustion zones were attributed to the Tween 80 components in the polymer solution (Ma et al., 2011).

4.5 Addition of Different Surfactant (Single Surfactant) towards PEG 200 additive

In the previous Section 4.4, the effect of addition different surfactants towards 3 wt% of PVP additive in total composition in the membrane casting solution was investigated. The changed in membrane composition, properties and its morphological structures contributed to the variation in their separation performance. The addition of different types of surfactants was produced results of different membrane structures and characteristics. Therefore, the effect of addition different surfactants towards 3 wt% of PEG 200 additive in total polymer composition in the membrane casting solution was investigated in this section.

In this study, the PVDF/NMP/PEG 200 membranes which contained 80 wt% of NMP and 3 wt % PEG 200 additive in the membrane dope solutions were prepared with addition of different surfactant types in order to optimize membrane separation performance towards protein separation. The flat sheet PVDF/NMP/PEG 200 membranes were introduced to surfactants of Sodium dodecyl sulfate (SDS), Triton X-100, and Tween 80 to the casting solution and marked as PN-3GS, PN-3GT and PN-3GW respectively.

The standard flat sheet PVDF/NMP/PEG 200 membrane which is no addition of surfactant is marked as PN-3G membrane. The composition parameters of the membrane fabrication conditions with addition of different types of surfactants to the polymer casting solution are shown in Table 17. All the membranes were characterized in terms of pure water permeation (PWP), proteins permeate flux and

rejection of solutes. Both of these parameters (PWP and proteins separation tests) were used to study the performance and separation ability of the membranes.

TABLE 17: The PVDF/NMP/PEG 200 membranes formulations

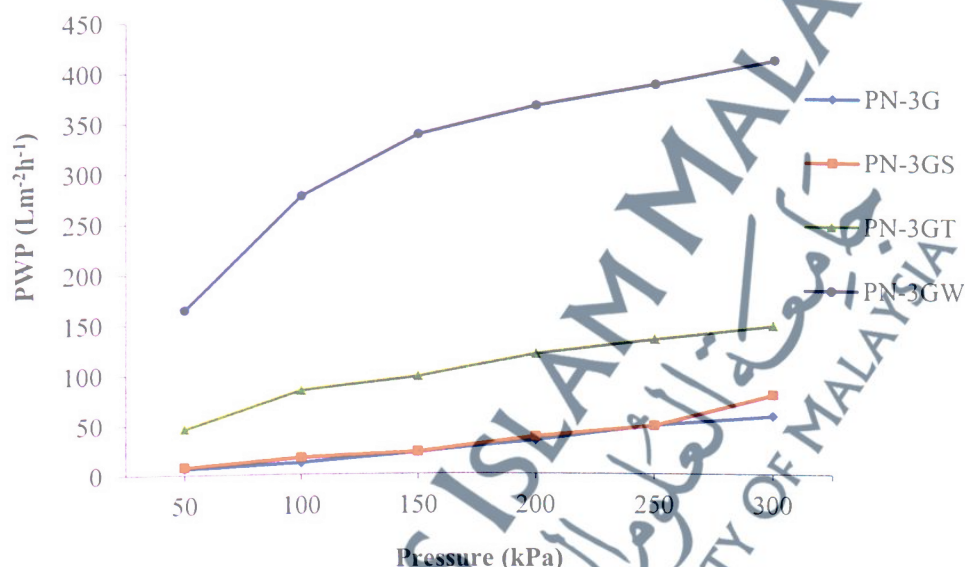
Membranes	Total polymer (wt%)	Solvent (wt%)	Additives (wt%)	Surfactants (wt%)		
			PEG 200	SDS	Triton X-100	Tween 80
PN-3G	17	80	3	-	-	-
PN-3GS	17	78	3	2	-	-
PN-3GT	17	78	3	-	2	-
PN-3GW	17	78	3	-	-	2

4.5.1 Pure Water Permeation (PWP)

Figure 71 represents the influence of addition of different types of surfactants on the PWP of the compacted membranes measured at various operating pressure in the range of 50 to 300 kPa. As presented in Figure 71, the results indicated that all the membranes showed the trend of line PWP was increased significantly with the rising operating pressure applied during the experiments. This is due to the increase in effective driving force (transmembrane pressure) required for PWP. As discussed earlier, the addition of surfactants to the casting solution was effectively improved the membrane performance in terms of PWP. It was showed that all the PN-3GS, PN-3GT and PN-3GW membranes containing surfactants SDS, Triton X-100 and Tween 80 respectively give the high values of PWP compared to membrane without additional any of surfactant (PN-3G). Similar results have been reported in the relevant literatures that addition of surfactants to the polymer casting solutions may increase

PWP of the membranes (Rahimpour et al., 2007; Amirilargani et al., 2009; Mansourpanah et al., 2011).

FIGURE 71: PWP of PVDF/NMP/PEG 200 Membrane with Addition of Different Types of Surfactants



The PWP of PN-3GS membrane which containing surfactant SDS in the casting solution at different operating pressures are shown in Figure 71. The PWP of PN-3GS membrane increased from 7.42 to 78.97 $\text{Lm}^{-2}\text{h}^{-1}$ by increasing the operating pressure from 50 to 300 kPa. The results indicated that the PN-3GS membrane with addition of SDS had higher PWP than PN-3G membrane which increased from 57.74 to 78.97 $\text{Lm}^{-2}\text{h}^{-1}$ at maximum operating pressure, 300 kPa. However, while comparing to other surfactants, the PWP of PN-3GS is the lowest value at the maximum operating pressure compared to PN-3GT and PN-3GW membranes. The PWP of asymmetric UF membranes is usually affected by the pore size of the skin layer and the porosity of sub-layer. Therefore, the decreasing pore size and porosity can

subsequently decrease the PWP. The membrane morphology of PN-3GS membrane was discussed in section 4.5.3.

Besides, the effect of surfactant Triton X-100 on PWP at various operating pressure which marked as PN-3GT is shown in Figure 71. It was observed that within the range of 50-300 kPa, with increase in operating pressure, PWP increased from 45.58 to 147.62 $\text{Lm}^{-2}\text{h}^{-1}$. For example, when the membrane is prepared without addition of Triton X-100 in the casting solution, PWP of the PN-3G membrane at 300 kPa is 57.74 $\text{Lm}^{-2}\text{h}^{-1}$. The PWP increases by addition of 2 wt% of Triton X-100 to the casting solution and reaches to a maximum value of 147.62 $\text{Lm}^{-2}\text{h}^{-1}$. The changes imposed on membrane structure and properties after surfactant Triton X-100 is the major reasons for PWP changes. At first, it should be noted that PWP is highly depends on membrane porosity and particularly the thickness of top layer. The above results of PWP are in agreement with observed in SEM images discussed at section 4.5.3. As the surfactant Triton X-100 was added to the casting solution results increased in top layer thickness and consequently increased the water permeation (Omidvar et al., 2014).

As can be seen in Figure 71, the PWP of PN-3GW membrane increase from 164.44 to 412.41 $\text{Lm}^{-2}\text{h}^{-1}$ with increasing applied operating pressures, since the driving force for permeation of water is enhanced by an increase in the operating pressure. In addition, the PN-3GW membrane exhibits the highest PWP compared to other membranes. As discussed earlier, the addition of Tween 80 as secondary surfactant additive to the polymer casting solution results in an increase in PWP of the prepared membranes and reaches to a maximum value of 412.41 $\text{Lm}^{-2}\text{h}^{-1}$. The above finding is

consistent with the study by Amirilargani et al. (2009) which examined that addition of Tween 80 to the casting solution increases porosity of the membrane support layer and thus, produced the higher PWP.

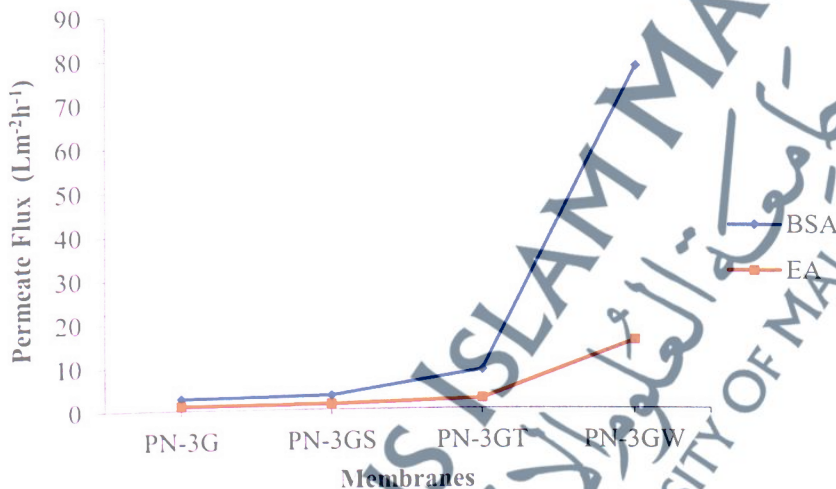
4.5.2 Protein Separation Performance

The variation of permeate flux and proteins rejection are illustrated in Figure 72 and Figure 73 respectively for PN-3G, PN-3GS, PN-3GT and PN-3GW membranes when the feed proteins solution are maintained at pH 7.2. From both figures, it is understood that the permeate flux and solutes rejection of a membrane is strongly depend on the structure of the membrane as well as the properties of the feed solution. On the other hand, the permeate flux and rejection of proteins by UF membranes can be explained under the concept of pore narrower or wider, thus as a result of both hydrophobic and electrostatic interactions between the membrane surface and the proteins molecule.

According to Figure 72, the trend of proteins permeate flux towards PEG 200-additive membrane is contrast to the proteins permeate flux of PVP-additive membrane (Section 4.4.2; Figure 64). The addition of different surfactants to the polymer casting solution significantly affected the permeate flux and rejection of each protein solution. It was evident that the addition of surfactants to the membranes with PEG 200 as additive resulted in the increase of permeates flux but the percentage rejection of each protein was decreased. The high rejection of proteins and comparatively low permeate flux with addition of surfactants towards PEG 200 membranes also be understood from the morphology of their cross-section (as discussed in Section 4.5.3). The thin asymmetric layer probably explains for the

improvement in the proteins rejection rate while the thick sponge-like sub-layer offers resistance resulting in low permeates flux and high rejection of solutes (Chakrabarty et al., 2009).

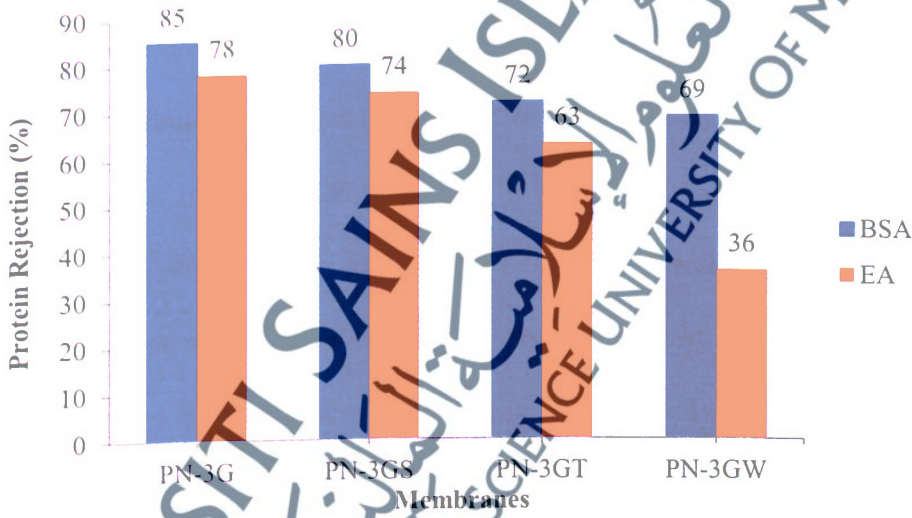
FIGURE 72: Proteins Permeation Flux of UF Membranes Containing Different Types of Surfactants towards PEG 200 Additive



The effect of surfactants on the permeate flux is shown in Figure 72. It can be seen that permeates flux increase as surfactants were added to the polymer casting solution. When there is no addition of surfactant to the polymer casting solution (PN-3G membrane), the BSA and EA permeate flux are $2.74 \text{ Lm}^2\text{h}^{-1}$ and $1.03 \text{ Lm}^2\text{h}^{-1}$ respectively. When there is addition of SDS, Triton X-100 and Tween 80 as secondary surfactant additives into the dope solution, the BSA permeate flux increased up to $3.19 \text{ Lm}^2\text{h}^{-1}$, $8.84 \text{ Lm}^2\text{h}^{-1}$, and $78.14 \text{ Lm}^2\text{h}^{-1}$ respectively. This result showed that the membrane presence of surfactants have higher permeate fluxes than PN-3G membrane which is no surfactant inside the dope solution. In addition, this is supported by Mansourpanah et al. (2011) which revealed that the surfactants have a significant effect on the membrane performance, properties and morphology.

The proteins rejection capabilities were determined to investigated the performance of membranes. In Figure 73, the BSA rejection value for PN-3G, PN-3GS, PN-3GT and PN-3GW membranes were calculated as 85%, 80%, 72% and 69%, respectively. The role of surfactants in the casting solution on rejection of proteins can also be noted from the figure. It is seen that for PN-3G (without addition surfactant), the percentage rejection of both proteins were found to be highest which is 85% for BSA and 78% for EA.

FIGURE 73: Proteins Rejection of UF Membranes Containing Different Types of Surfactants towards PEG 200 Additive



When there is addition of surfactants which are SDS, Triton X-100 and Tween 80 as secondary surfactant towards PEG 200 the BSA rejection decreased to 80%, 72% and 69%, respectively. This may be because the addition of surfactants towards PEG 200 additives is not too performed in the performance of proteins rejection because PEG 200 (lower MW) is easier to transport with the solvent in the phase separation process and results in the homogeneous skin layer and higher rejection (Ma et al., 2011).

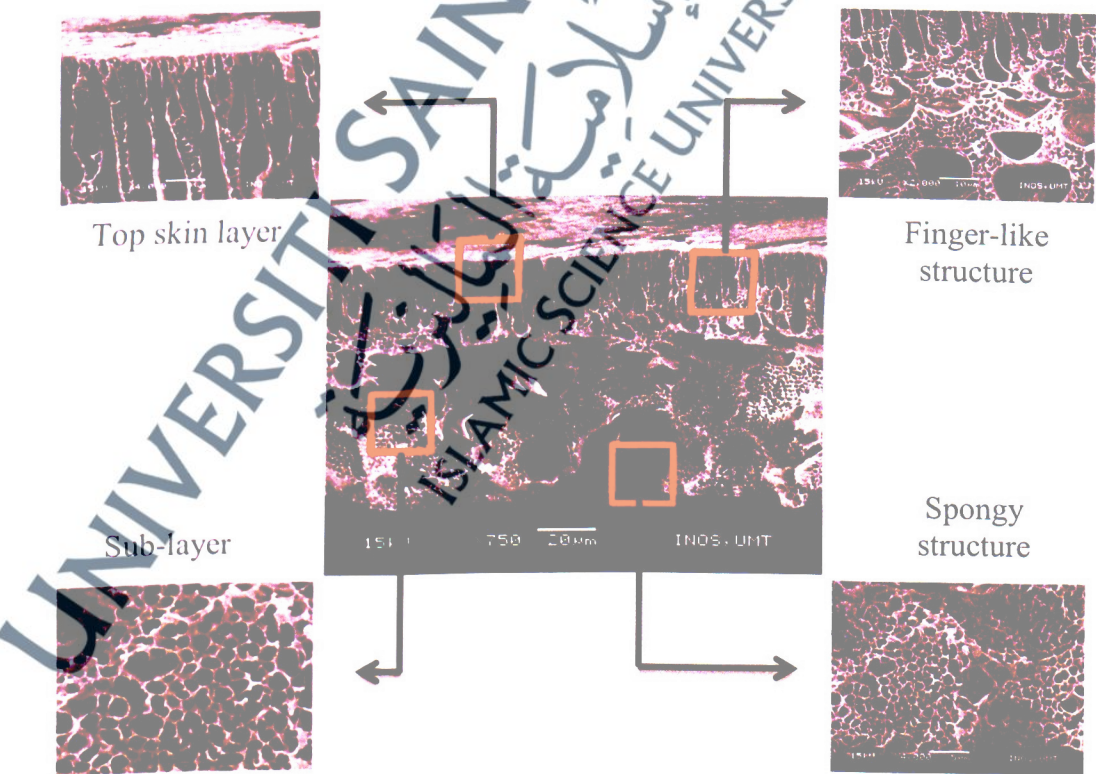
4.5.3 Membrane Morphology

In order to obtain high performance membranes for specific applications, it is essential to manipulate the morphological structures of the membranes. Figure 74(a), (b) and (c) depicts the cross-section of SEM micrographs of PVDF/NMP/PEG 200 membranes with addition of different surfactants SDS, Triton X-100 and Tween 80, respectively. The PVDF/NMP/PEG 200 membrane without addition of surfactant (just addition of additive; PEG 200 content) marked as PN-3G was used as standard membrane in this surfactant study and shown in Figure 59(c) and discussed in section 4.3.3.

As in this study, by using PEG 200 with lower MW as a material with non-solvent properties thus it increases thermodynamically instability of the cast film and consequently causes instantaneous demixing in the coagulation bath. This facilitates formation of macrovoids in the sub-layer of the membranes structure. Moreover, precipitation process which starts after immersion of the cast film in the coagulation bath and is occurred due to the weak miscibility between polymers (PVDF) and non-solvent (water), is also stopped quickly. Hence, this results in an increased the membrane thickness. These findings emerged and responsible for the better performance of proteins rejection as the PN-3G membrane had highest BSA and EA proteins rejections which are 85% and 78%, respectively.

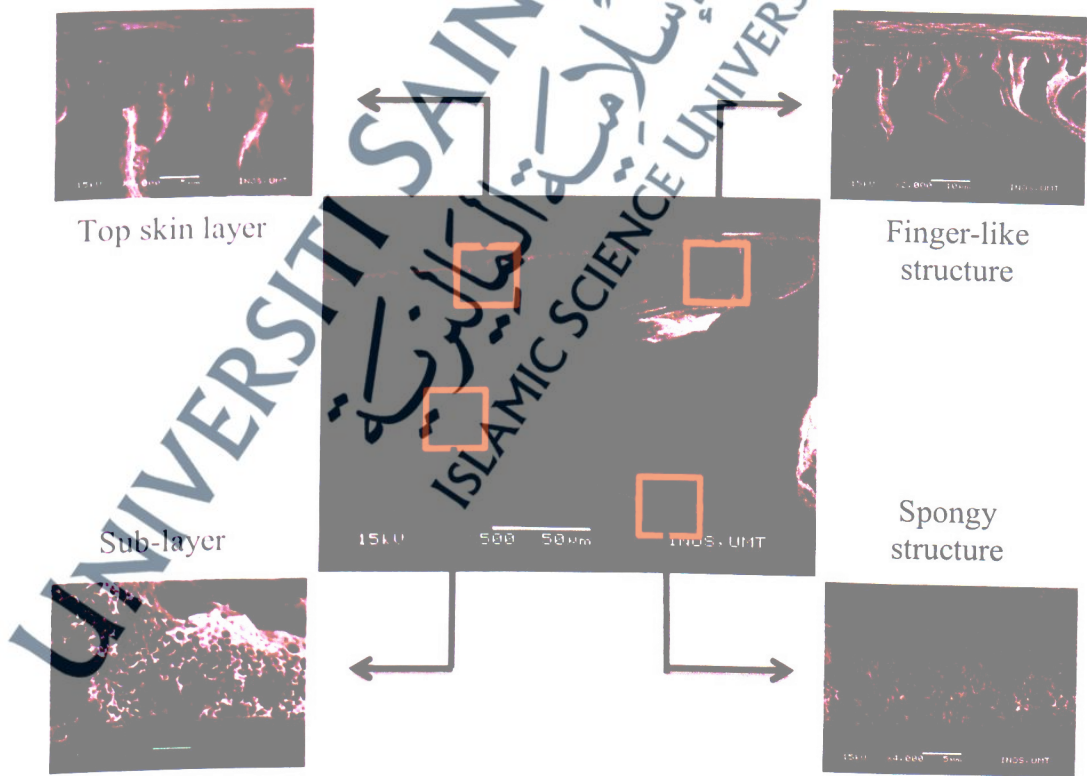
Figure 74(a) shows the SEM photograph of the membrane in the presence of surfactant SDS (PN-3GS). It can be seen that the cross-section of morphological structure of PN-3GS membrane had an open finger-like structure and macrovoids. Besides, SDS is a hydrophilic surfactant can affect membrane morphology and porosity of sub-layer in three manners. Firstly, enhancement in macrovoids formation and increasing the membrane porosity by increasing solvent-non-solvent mixing affinity and increasing demixing rate via distribution of SDS molecules as free molecules in NMP and formation of free micelles. Secondly, the enhancement in membrane structure (porosity and macrovoids formation) via development of polymer-surfactant complexes. Thirdly, it was decreased sub-layer porosity by decreasing demixing rate via increasing casting solution viscosity (Saedi et al., 2012).

FIGURE 74(a): Cross-Sectional Sstructure of PN-3GS (PVDF/NMP/PEG 200/SDS)



The cross-sectional SEM zooming images of the membranes prepared by immersing casting dopes containing Triton X-100 as surfactant additive is demonstrated and marked as PN-3GT membrane is displayed in Figure 74(b). This image showed that PN-3GT membrane had a finger-like structure having good interconnection. The treated PN-3GT membrane with 2 wt% of Triton X-100 towards PEG 200 additive presented more porosity compared to other membranes. The PN-3GT membrane showed opening gaps between finger-like structures. The gaps indicated a lamellar structure when the membrane turning to the side. Besides, the PN-3GT membrane showed individual randomly distributed pores in the micrometer scale (Table 18) (Tevi et al., 2014).

FIGURE 74(b): Cross-Sectional Structure of PN-3GT (PVDF/NMP/PEG 200/TRITON X-100)



The SEM micrographs of PVDF membrane filled with 2 wt% surfactants (Tween 80) towards 3 wt% additive (PEG 200) contents is shown in Figure 74(c) (PN-3GW membrane). The figure shows PN-3GW membrane exhibit a typical asymmetric structure and fully developed pores. The pores formation is due to fast rate of precipitation resulting in a dense membrane with impact on PWP and permeation flux. Asymmetric structure of the PN-3GTW membrane comprises a dense thin top-layer and a porous sub-layer which is filled up by the closed cells within polymer and finger-like macrovoids.

FIGURE 74(c): Cross-Sectional Structure of PN-3GW (PVDF/NMP/PEG 200/TWEEN 80)



As there is Tween 80 presented in the dope polymer solution, it will favors macrovoid formation. This is due to the factor of phase demixing rate which is useful

for judging whether or not finger-like macrovoids. Generally as discussed ealier, instantaneous demixing favors macrovoids formation whereas delayed demixing disfavors it (Chang et al., 2014).

As represented in Table 18, the addition of surfactants towards PEG 200 additive in one dope of casting solution were decreased the length of macrovoid and increased the size of pore in the sub-layer of the membrane. The largest size of macrovoid appeared at PN-3G membrane which no contain any of surfactant. For example, with addition of SDS, the length of macrovoid reduced from 130.1 μm to 28.9 μm . Other than that, it is observed PN-3GT membrane has the bigger finger-like structure (length, 90.0 μm ; width, 26.8 μm) which promote to higher PWP at the maximum operating pressure (300 kPa). The presence of finger-like, macrovoid structures and pores in the membrane are major features of UF porous membrane which can produced higher PWP related to the membrane productivity.

TABLE 18: UF membranes structural details with different surfactants towards PEG 200 additive

Membranes	Finger-like Length (μm)	Finger-like Width (μm)	Macrovoid Length (μm)	Macrovoid Width (μm)	Pore Length (μm)	Pore Width (μm)
PN-3G	40.9	4.1	130.1	26.6	1.11	1.18
PN-3GS	30.3	6.4	28.9	13.2	1.19	1.25
PN-3GT	90.0	26.8	99.8	73.0	1.25	1.29
PN-3GW	25.3	4.5	115.3	68.2	1.35	1.44

FIGURE 75(a): Summary of Performance, Morphologies and Pore Properties of PVDF-UF Membrane with Surfactant (SDS) towards PEG 200 Additive

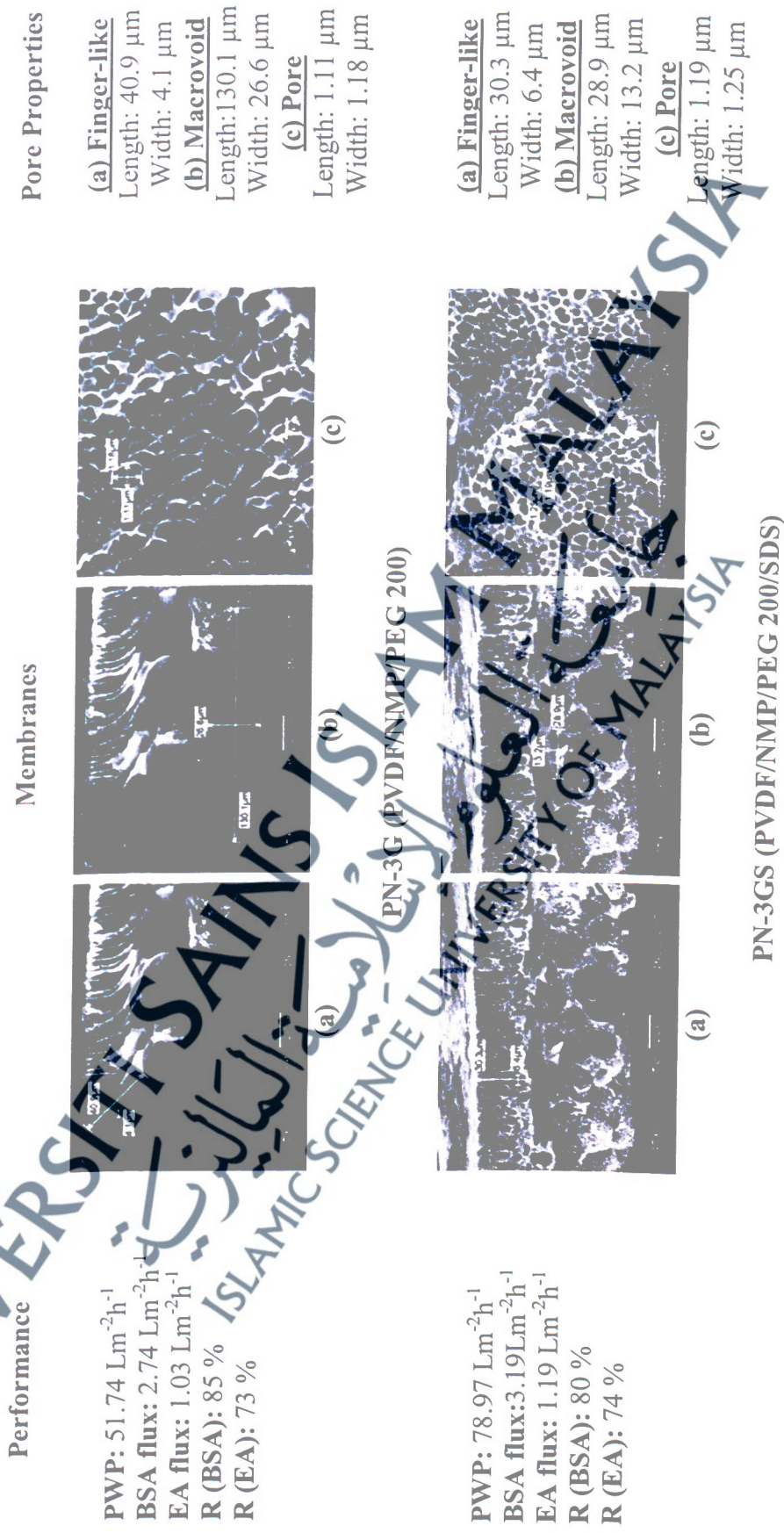
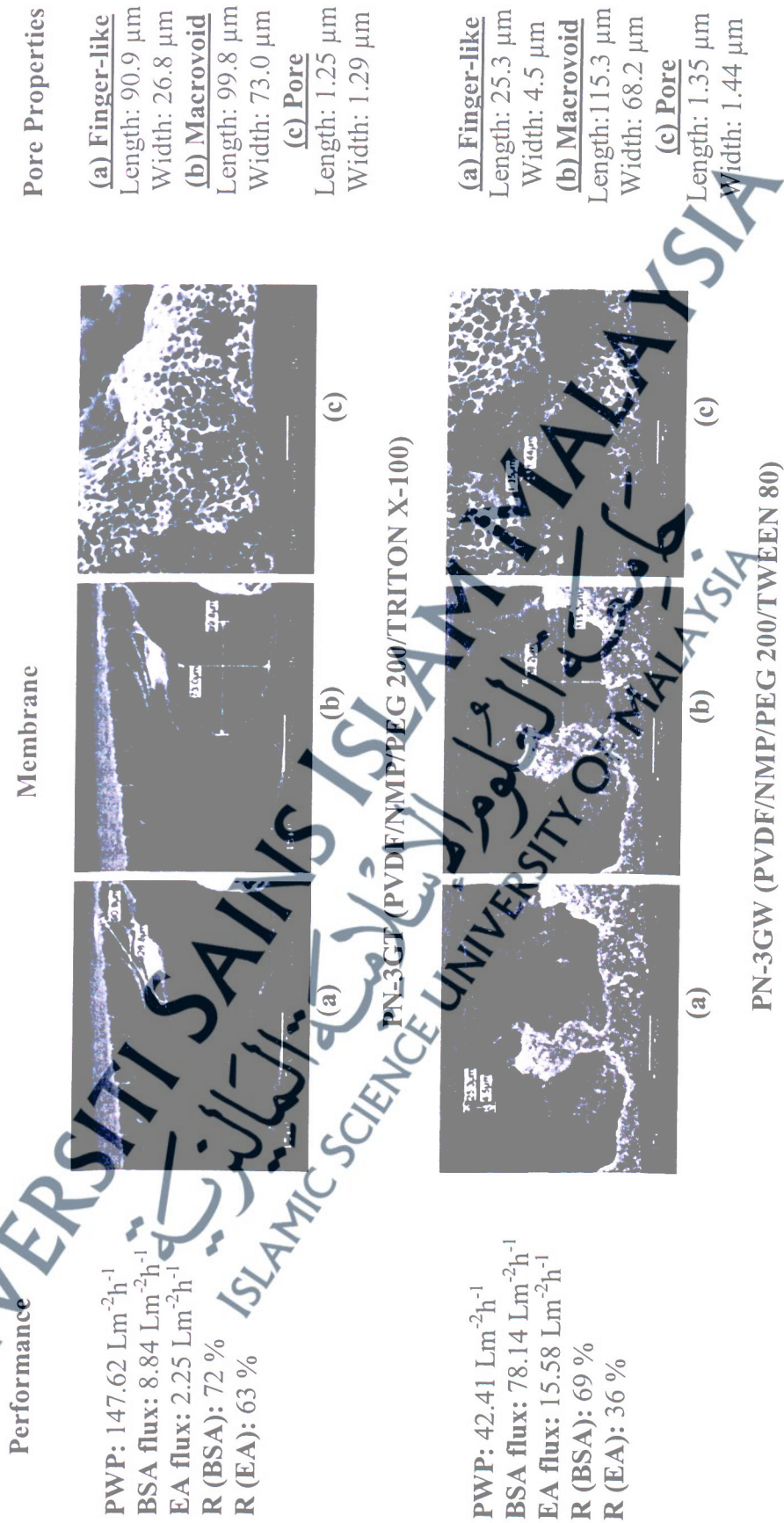


FIGURE 75(b): Summary of Performance, Morphologies and Pore Properties of PVDF-UF Membrane with Different Surfactants (Triton X-100 and Tween 80) towards PEG 200 Additive



4.5.4 FTIR Studies

Three membranes will be discussed in this FTIR studies as well the surfactants were added to each of the membrane casting solution towards PEG 200 as additive. The PN-3GS, PN-3GT and PN-3GW membranes with addition of SDS, Triton X-100 and Tween 80, respectively were studied. The obtained FTIR spectra of the plain PVDF with addition of PEG 200 additive was already presented in Figure 61 (c). As discussed earlier (Section 4.3.4), in the FTIR spectrum of the PN-3G membrane addition with PEG 200 and without surfactant, two peaks confirmed the presence of PEG 200 around 1672 cm^{-1} and 1071 cm^{-1} were assigned to the C=C (double bond conversion of PEG 200) and C-O=C bonds between PEG 200 macromolecules, respectively.

The FTIR spectra of PN-3GS membrane is shown in Figure 76(a). In this case of PN-3GS membrane with addition PEG 200 and SDS as additive and surfactant respectively, the absorption band due to stretching of the double bond conversion PEG 200 at around 1672 cm^{-1} , while the peak at 1073 cm^{-1} correspond to the C-O=C bonds from PEG 200 molecules. Hydrogen bonds were observed in all cases however, in this spectrum O-H group appears at the low peak around 3438 cm^{-1} .

The most notable interaction described in the PN-3GS membrane in the presence of SDS is due to the difference in the stretching frequencies of the chemical groups. The stretching frequency of S=O resulting from vibration of sulfone group (SO_2) is observed at 1274 cm^{-1} when small amount of SDS is added to the polymer casting solution. Further, the C-F stretching of alkyl halide is noticeable at 1174 cm^{-1}

and C-C-C asymmetric vibrational stretching of pure PVDF is marked at 880 cm^{-1} . This shows that polymer PVDF also contributes in the molecular interaction of the components solution.

FIGURE 76(a): IR Spectra of UF Membrane (PN-3GS) with Addition of SDS towards PEG 200 Additive

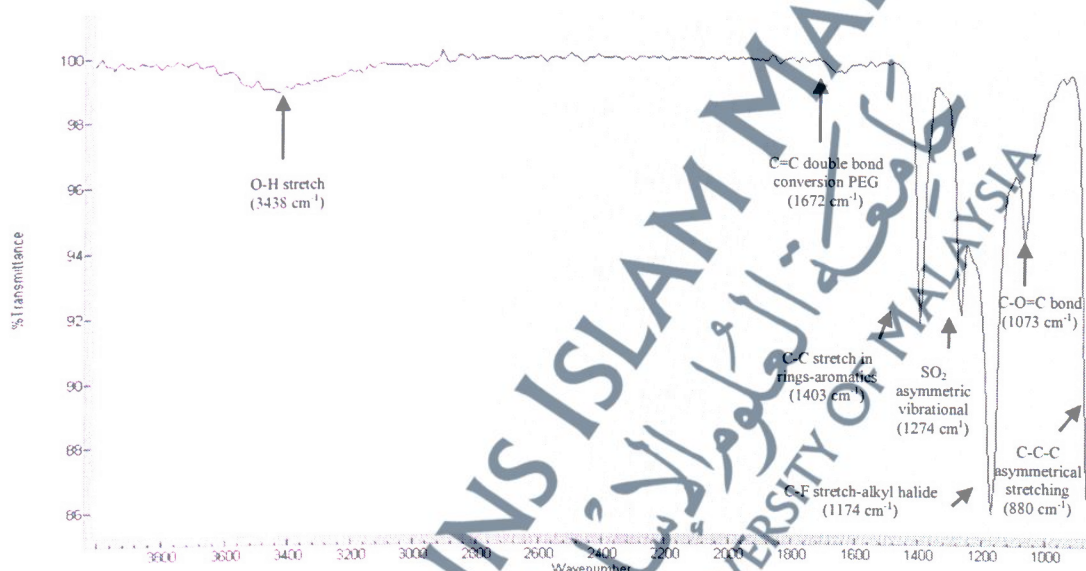
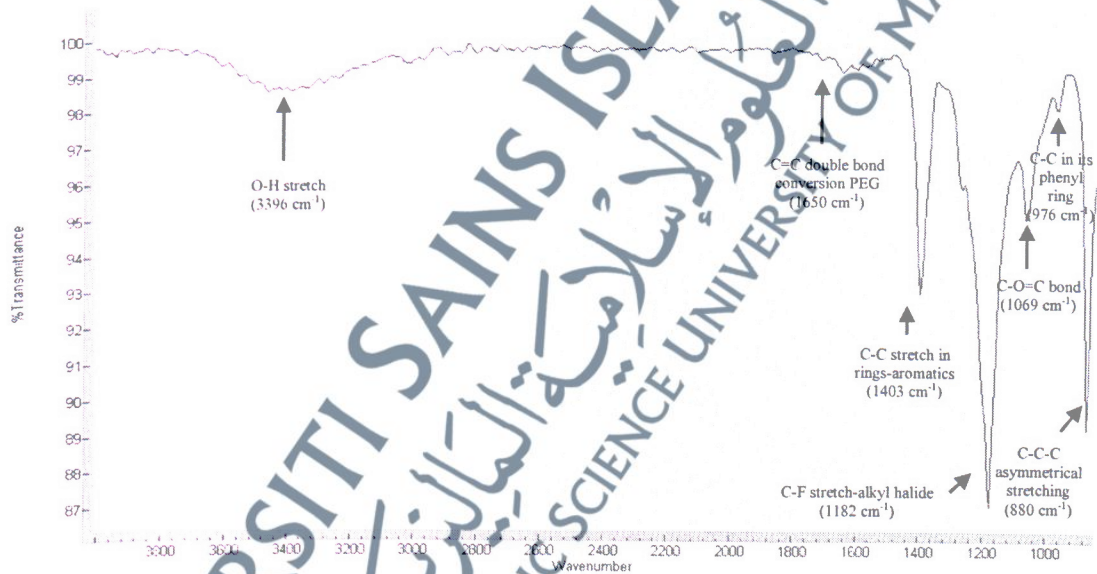


Figure 76(b) shows the molecular orientation of PN-3GT membrane with addition of and Triton X-100 as surfactant. Presence of Triton X-100 in the polymer casting solution makes O-H stretching shifted from 3462 cm^{-1} to 33.96 cm^{-1} from narrow to broad band. The infrared spectrum of Triton X-100 show additional band ascribed to the phenyl ring of the hydrophobic part of Triton X-100 which can be used to differentiate from the other bands. One noticeable change in the spectrum is the intensity of a weak band around 976 cm^{-1} corresponding to the alkenes C=C stretching in its phenyl ring of Triton X-100 molecule.

Another characteristics feature of the above infrared spectrum of PN-3GT membrane containing Triton X-100 is quite similar to the PN-3G membrane which is does not have significant changes. The absorption peak in the infrared spectrum of C-C double aromatic stretch in ring is noted at 1650 cm^{-1} . The characteristics of pure PVDF is remain unchanged, still at the same frequencies (C-F stretch of alkyl halide at 1182 cm^{-1} and C-C-C asymmetric vibrational at 880 cm^{-1}). Besides, the C-O=C bonds from PEG molecules is attributed to 1609 cm^{-1} .

FIGURE 76(b): IR Spectra of UF Membrane (PN-3GT) with Addition of Triton X-100 towards PEG 200 Additive

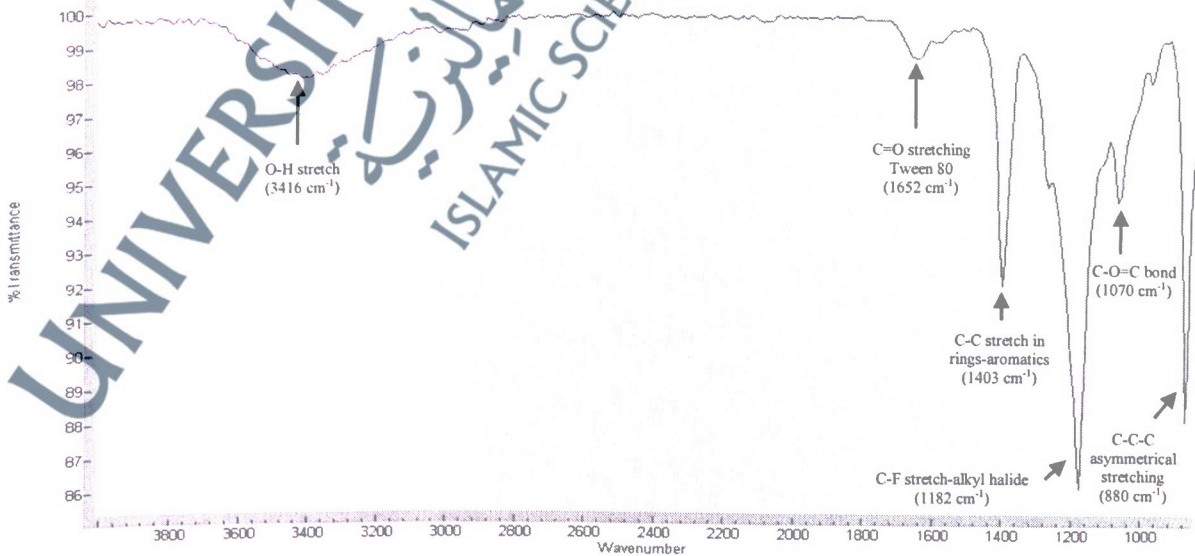


The infrared spectrum of the PN-3GW membrane was recorded in Figure 76(c). As displayed in the spectrum, it was contributing to strong absorption band in 3416 cm^{-1} due to the hydroxyl groups from H_2O . It was producing a broad band O-H stretching in the presence of Tween 80 surfactant since Tween 80 introduce three additional O-H groups per molecule. Besides, an increase in intensity of the hydroxyl

stretching absorption in FTIR spectra verified the phenomena of the pure *NMP* and water absorbing in the dry-wet phase inversion (Lv et al., 2014).

However, the adsorbed bands show weak absorbance at 1652 cm^{-1} and 1070 cm^{-1} were due to the stretching vibration of C=O and C-O=C bonds, respectively interaction from Tween 80. The presence of these two peaks from the infrared spectrum of PN-3GW prepared in the presence of Tween 80 confirmed the presence of active groups on the surface of the membrane. The others three sharp and strong bands does not have significant changes compared to the PN-3G membrane (without adding surfactant). The band around 1403 cm^{-1} and 880 cm^{-1} were corresponds to C-C aromatic stretch in rings and C-C-C asymmetric vibrational, respectively. The pure PVDF polymer shows a characteristics band at 1182 cm^{-1} (C-F stretching of alkyl halide).

FIGURE 76(c): IR Spectra of UF Membrane (PN-3GW) with Addition of Tween 80 towards PEG 200 Additive



4.5.5 TGA Studies

The thermogravimetric analysis (TGA) records the decrease in the weight of the sample as a function of the temperature. TGA curves provide addition evidences about the interaction of polymer (PVDF), additive (PEG 200) and surfactants (SDS, Triton X-100 and Tween 80) in one dope preparation separately, thus indicates the dehydration and decomposition of the sample. In this method, the membrane samples are heated up to 900 °C under N₂ and recorded the changes in mass due to the loss of materials from the synthesized membranes. Generally, the materials with strong bond to the particles can be desorbed at higher temperature. (Bastami et al., 2012).

FIGURE 77: TGA Curves of PVDF-PEG 200 Membranes with Addition of Different Surfactants

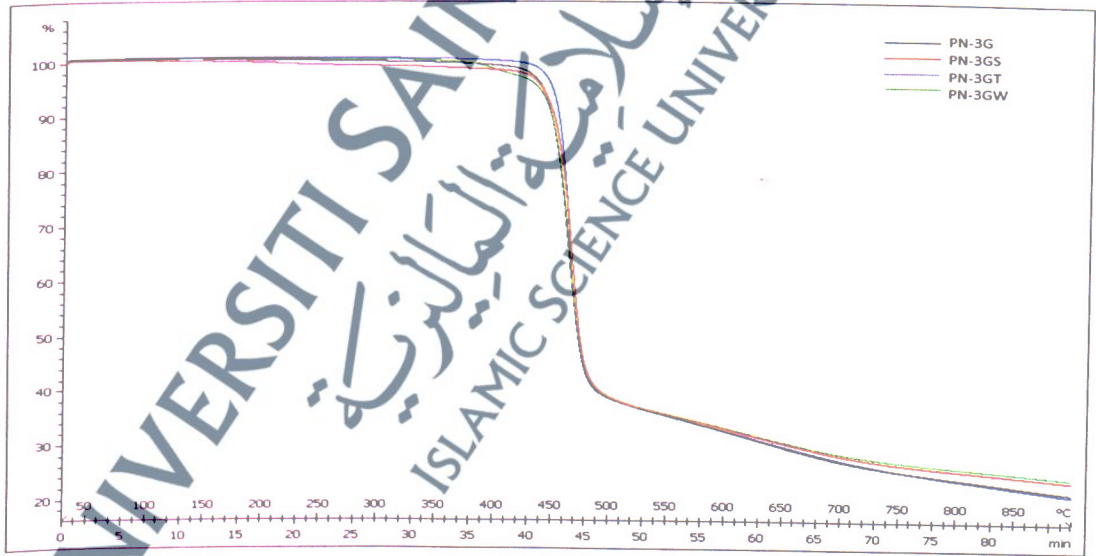


Figure 77 shows the TGA analysis of membranes with different preparation conditions. For all membrane samples, the total loss of mass increased with increasing the reaction time and temperature during the synthesis process. The trend of

decomposition of the prepared membranes does not showed significant changes. The decomposition temperatures of all membranes are in the vicinity of 500 °C and above.

All the PN-3G, PN-3GS, PN-3GT and PN-3GW membranes were observed in three weight losses. In all cases, the initial weight loss is attributed to the loss of surface-adsorbed water. The first loss about 5, 6 and 4 % for PN-3GS, PN-3GT and PN-3GW membranes, respectively were related to the free water or water loss from the surface of polymeric membranes. This loss was occurred between the room temperature and ~400 °C. The second loss of 66, 66 and 64 % for PN-3GS, PN-3GT and PN-3GW membranes, respectively were observed in the range of 400-500 °C. The second weight loss is due to the loss of ions bound by weak electrostatic interaction from polymer chains.

Then, the third loss of 75, 76 and 76 % for PN-3GS, PN-3GT and PN-3GW membranes, respectively were appeared between 550-850 °C. The third phase of decomposition is may be due to the degradation of polymer main chain (Eren et al., 2015). As the PN-3GS membrane contains SDS as surfactant shows the lowest total mass loss in the TG analysis. Generally, the free sulphonate groups are thermally active and possibly weaken the thermal degradation of the polymeric membrane. However, the higher thermal stability of sulphonate group results when it forms a complex with counter-ions in the membrane. Several studies show that conducting polymers doped with SDS surfactant having long alkyl chains showed enhanced thermal stability (Hazarika and Kumar, 2013).

4.6 Combination of Surfactant (Dual-Surfactant) towards PVP additive

The aim of this part was to study the performance of combination surfactants towards PVP-additive UF membrane at different operating conditions for two groups of surfactants (anionic; non-ionic) which are Sodium dodecyl sulfate (SDS), Triton X-100, and Tween 80. The membranes were combined the SDS (anionic)/Tween 80 (non-ionic) and Triton X-100 (non-ionic)/Tween 80 (non-ionic) surfactants in the polymer casting solutions were marked as PN-3PSW and PN-3PTW respectively.

The combination of different type surfactants was produced results of different membrane structures and characteristics. The percentage concentration of PVP additive and surfactants in the casting solution was maintained at 3 wt% and 2 wt% respectively. However, the addition of surfactants are divided into two groups which is 1 wt % per group of surfactant itself. The Table 19 shows the composition parameters of the membrane fabrication conditions with addition and combination of different groups of surfactants towards PVP-additive in the polymer casting solution.

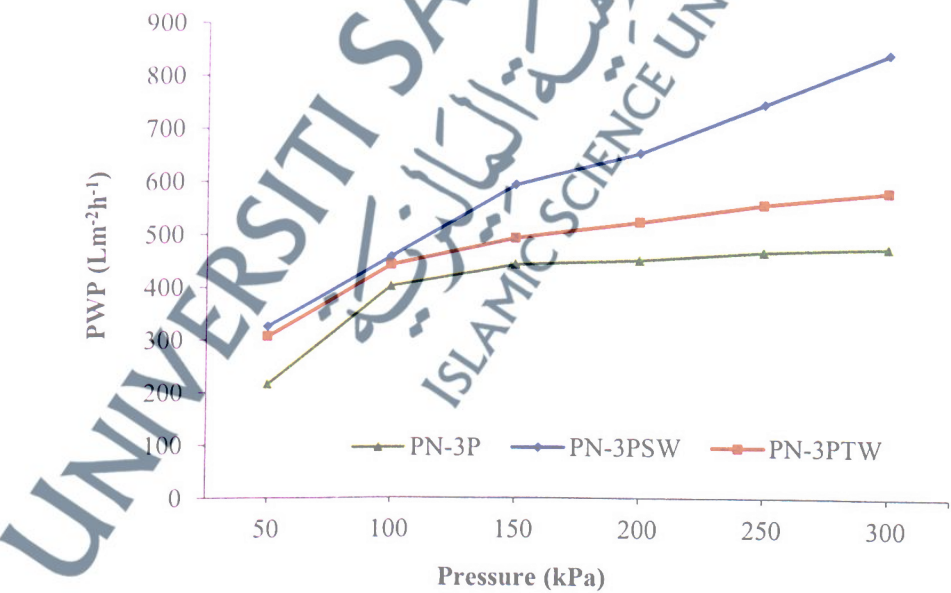
TABLE 19: The PVDF/NMP/PVP membranes formulations

Membranes	Total polymer (wt%)	Solvent (wt%)	Additives (wt%)	Surfactants (wt%)		
			PVP	SDS (anionic)	Triton X-100 (non-ionic)	Tween 80 (non-ionic)
PN-3P	17	80	3	-	-	-
PN-3PSW	17	78	3	1	-	1
PN-3PTW	17	78	3	-	1	1

4.6.1 Pure Water Permeation (PWP)

Ultrafiltration (UF) experiments were performed to explore the performance of PVDF/NMP/PVP additives membrane with addition of anionic/non-ionic and non-ionic/non-ionic surfactants. Figure 78 shows the pressure-dependent fluxes of pure water for the membranes prepared. All the modified membranes gradually increased of PWP with increase the pressure up to 300 kPa. The figure also presents the effect of combinations surfactants in the casting solution with PVP as additive on PWP for the prepared membranes. It appears from the Figure 78 that the combination of two groups of surfactant in one dope solution increased the PWP compared to polymer solution without surfactant (PN-3P).

FIGURE 78: PWP of Fabricated UFS Membranes with Different Groups of Surfactants towards PVP Additive



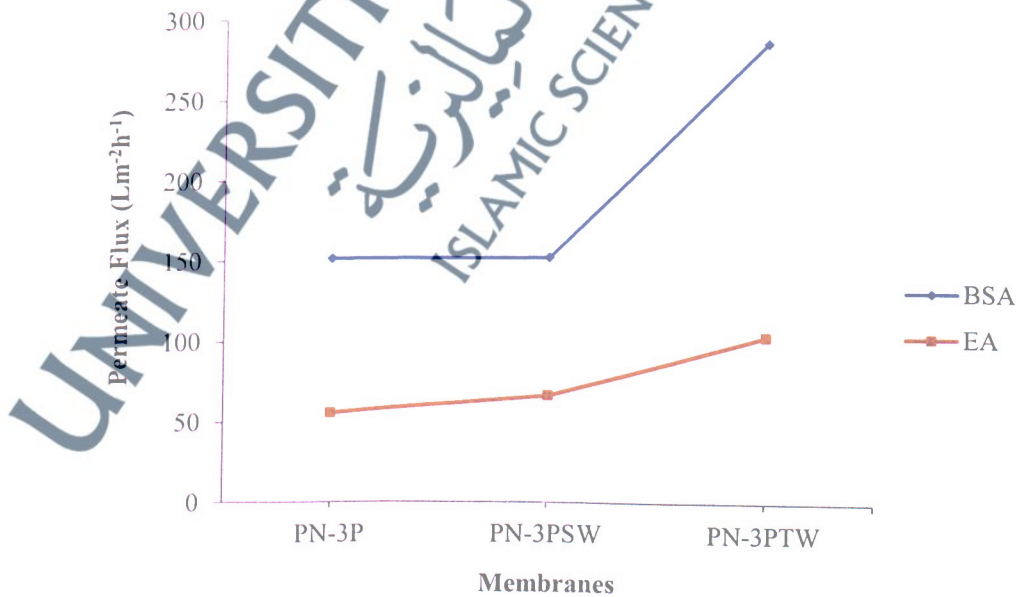
As plotted in Figure 78 clearly show the combination of anionic/non-ionic surfactants, PN-3PSW membrane exhibited a higher PWP compared to PN-3PTW and PN-3P membranes. As increasing the operating pressure from 50 to 300 kPa, the PWP of PN-3PSW membrane increase from $324.77 \text{ Lm}^{-2}\text{h}^{-1}$ to $838.11 \text{ Lm}^{-2}\text{h}^{-1}$. From the result obtained, PWP of the PN-3PSW membrane attained a maximum value of $838.11 \text{ Lm}^{-2}\text{h}^{-1}$ at 300 kPa. Therefore, the water flux variation can be explained as the incorporation and electrostatic attraction of combination anionic with non-ionic surfactants enhanced the hydrophilicity of the membranes which improved the water permeation to a certain extent. In the other hand, the value of PWP for the membrane which combine both of non-ionic surfactants in one dope solution (PN-3PTW) was found increased from $305.66 \text{ Lm}^{-2}\text{h}^{-1}$ to $577.37 \text{ Lm}^{-2}\text{h}^{-1}$, which is higher than PN-3P membrane (without surfactant) which increased from $214.72 \text{ Lm}^{-2}\text{h}^{-1}$ to $472.39 \text{ Lm}^{-2}\text{h}^{-1}$. This correlates with the combination of non-ionic/non-ionic surfactants have high hydrophilicity compared to membranes without surfactant.

Moreover, the combination both non-ionic surfactants in a polymer dope solution, PN-3PTW membrane give lower PWP compared to PN-3PSW membrane which containing different grouping anionic and non-ionic surfactants. For example, at maximum operating pressure of 300 kPa, the value of PN-3PTW membrane is 577.37 which lower than PN-3PSW membrane by valuing PWP of $838.11 \text{ Lm}^{-2}\text{h}^{-1}$. Thus, it can be said that the differences in term on percentage is nearly 30%. According to Xiarchos and Doulla (2006), when the non-ionic surfactants combine towards hydrophobic polymer membrane and pore forming additive, the hydrophobic forces were getting weaker thus significantly affect the membrane performance.

4.6.2 Protein Separation Performance

The permeability and selectivity of porous ultrafiltration (UF) membranes were characterized by protein separation performance. Figures 79 and 80 represent permeate flux and rejection of different MW of protein solutions for PN-3P, PN-3PSW and PN-3PTW membranes. As presented in Figure 82, the highest BSA permeate flux was 285.51 Lm⁻²h⁻¹ are obtained for the PN-3PTW membrane containing combination of non-ionic surfactants. The highest permeate flux is due to the formation of macrovoids in the sub-layer membrane which is faster rated leaching out during immersion process. Besides, for the combination non-ionic/non-ionic surfactants, interaction between hydrophobic chain and the non-polar sites of the membranes were observed which leading to hydrophilization of the membrane surface and pores (Fernandez et al., 2005).

FIGURE 79: Proteins Permeation Flux of UFS Membranes Containing Combination of Anionic and Non-Ionic Surfactants towards PVP Additive



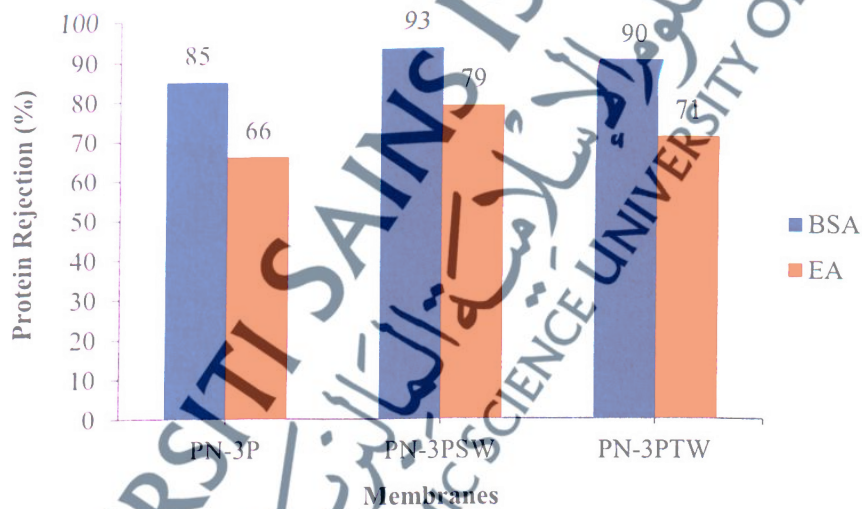
As clearly seen from the Figure 79, it is showed that the BSA permeate fluxes were higher than EA permeate fluxes. This is considering to molecular weight of proteins permeation fluxes EA shows the lowest flux in the separation performance test compared to BSA protein. The order of permeate flux was found to be BSA > EA. These trends were due to the order of molecular weight of BSA and EA which are 69 kDa and 45 kDa, respectively. In the other hand, the lowest BSA permeate flux was $151.72 \text{ Lm}^{-2}\text{h}^{-1}$ for the PN-3P membrane (without surfactant). The lowest value of permeate flux is may be due to immiscible phase behavior of blend composition without surfactant, which predominates due to lower molecular attractive forces between its blend components. During the filtration process, certain protein molecules can be deposited on the membrane surface, which caused an abrupt drop in flux. Additionally, protein molecules can be swept from the surface due to stirring, which resulted in equilibrium between depositions and sweeping (Sun, 2009).

Apart from the permeate flux, the solute rejection of the membrane also depend on the properties of the feed solution. Filtration experiments with the BSA and EA proteins solution were carried out to study the permeation performance behaviors of the prepared membranes. The effect of anionic/nonionic and non-ionic/non-ionic surfactants towards PVP additive in the composition on the protein rejection is shown in Figure 80.

As the protein rejection of BSA and EA are illustrated in Figure 80 for all the modified membranes when the feed solution is maintained at pH 7.2, since a change in pH may increase the adsorptive fouling of the membranes. In addition, if the pH of the proteins solution changes, intermolecular forces between protein molecules and

membranes will predominate and affect the efficiency of membranes (Arthanareeswaran et al., 2004). Based on the proteins rejection results, the combinations of ionic and non-ionic surfactants in one dope polymer solution were enhanced the solute BSA and EA rejection. The PN-3P membrane containing just PVP additive and no any combination surfactant recorded the lowest proteins rejection (85% BSA; 66% EA) among the PN-3PSW and PN-3PTW membranes. The presence of PVP in the casting solution has contributed to the enlargement of microvoids in the membrane structure (Nurul et al., 2013).

FIGURE 80: Proteins Rejection of UFS Membranes Containing Combination of Anionic and Non-Ionic Surfactants towards PVP Additive



From the result obtained, the PN-3PSW membrane exhibited higher rejection up to 93% and 79% for BSA and EA respectively, compared with other membranes. The BSA rejection is maximum with combination of ionic/non-ionic surfactants in the composition is due to the pore size of skin layer becomes smaller as there is strong interaction between two different groups of surfactant. Higher rejection of BSA

protein may be due to larger solute size of BSA compared with EA. In the other hand, the PN-3PTW membrane which combines non-ionic/non-ionic surfactants showed the BSA rejection 90%, lower than PN-3PSW membrane which combines ionic/non-ionic surfactants, may be because of homogeneity between the surfactants in the polymer solution. This will resulted in the formation of pores in membranes as discussed in SEM analysis

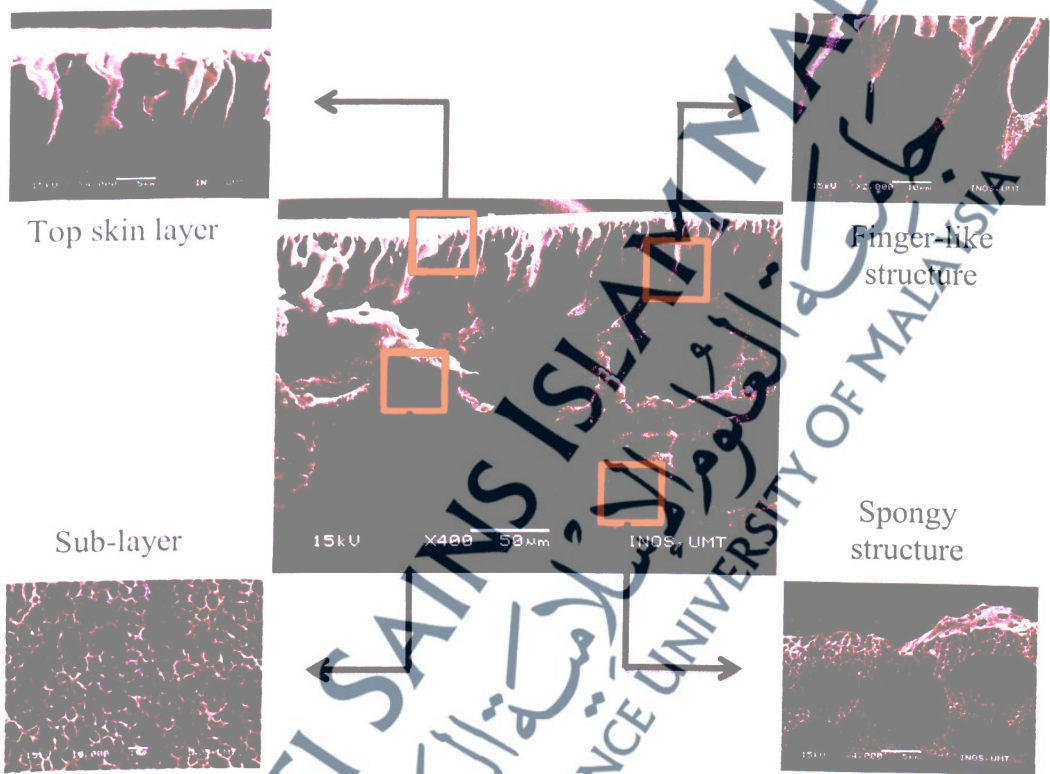
4.6.3 Membrane Morphology

The zooming and cross sectional morphologies of PVDF membrane prepared using on PVP as additives, combination (anionic/non-ionic) and (non-ionic/non-ionic) surfactants towards PVP additives in a dope polymer solution were shown in Figure 59(a) (refer to section 4.3.3), 81(a) and 81(b) respectively. All images showed the membranes were having asymmetric structure consisting of a dense top layer, a porous sub layer and a portion of sponge-like structure at the bottom layer of the membrane. The skin layer acts as a separation layer and the support layer provides the mechanical strength. The sub layer seems to have finger-like cavities beneath the top surface layer as well as macrovoids structure.

The SEM images of PN-3PSW and PN-3PTW membranes in Figures 81(a) and 81(b) respectively showed the existence of macrovoids in the presence of combination anionic/non-ionic and non-ionic/non-ionic surfactants in the PVDF/NMP/PVP blend membrane. Both of these membranes had asymmetric structure consisting of a fine porous selective barrier and a much thicker porous sub-layer. A dense spongy structure also formed beneath the skin layer and porous sub-

layer of PVDF membrane. The casting solutions provided from hydrophobic polymers produced sponge-like structures due to delayed phase separation occurred during phase inversion process (Ghasem et al., 2012).

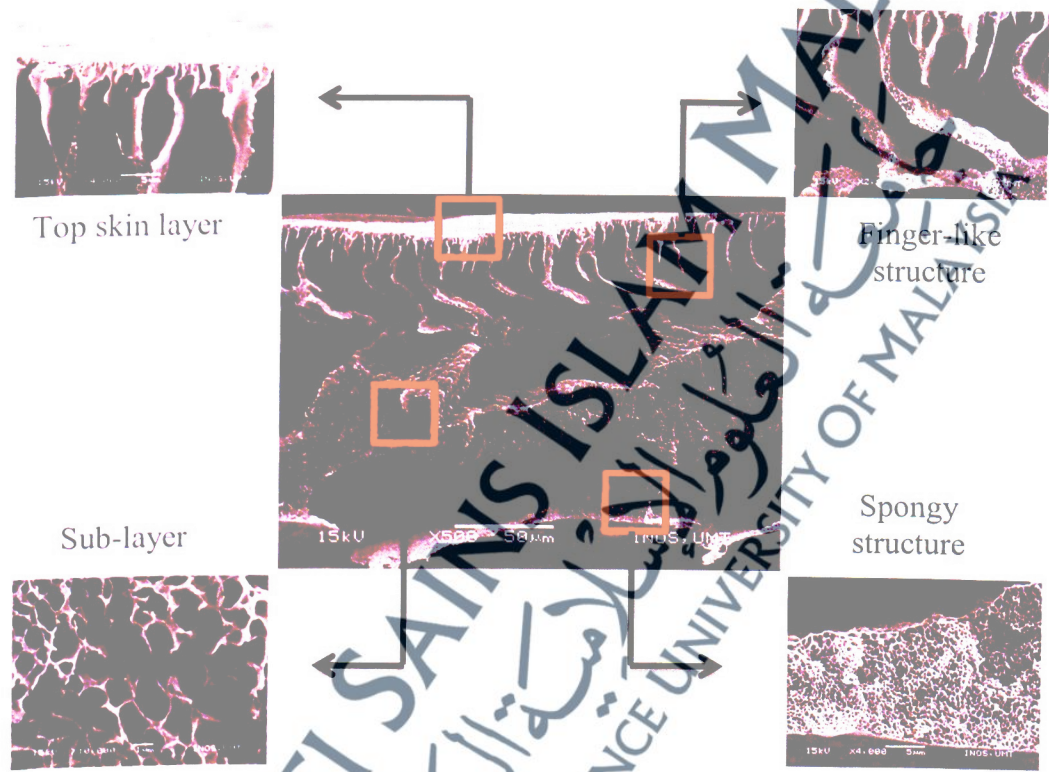
FIGURE 81(a): Cross-Sectional Structure of PN-3PSW (PVDF/NMP/PVP/SDS/TWEEN 80)



A dense top layer and a porous sub-layer that is occupied by closed cell within polymer matrix and finger-like pore as well as interactions of anionic/non-ionic and non-ionic/non-ionic surfactants were shown clearly in Figures 81(a) and 81(b), respectively. Obviously, large pores are formed in the sub-layer of the membranes and therefore, it can be explained by miscibility between the added ionic, non-ionic surfactants and the coagulant. The miscibility between surfactant and coagulant plays an important role in the formation process of various sizes of pores. The macrovoids

and finger-like pores in the sub-layer can be induced or suppressed by addition of appropriate surfactants, depending on their miscibility with coagulants (Amirilargani et al., 2009).

FIGURE 81(b): Cross-Sectional Structure of PN-3PTW (PVDF/NMP/PVP/TRITON X-100/TWEEN 80)



The addition of surfactants that have high miscibility with coagulants may be able to extend the formation of finger-like pores and macrovoids. It was found out that the combination of small amounts ionic surfactant (i.e SDS) and non-ionic surfactants (i.e Tween 80 and Triton X) to the casting solution increases formation of macrovoids and finger-like pores in the sub-layer of the membranes. With this little addition of surfactants to the casting solutions, the thickness of the prepared membranes significantly increases and hence, probably enhanced the PWP and proteins rejection.

For example, for PN-3PSW membrane (Figure 81(a)) as the addition of ionic/non-ionic surfactants to the polymer casting solution, there is strong interaction between two different groups of surfactants thus the structure of the PN-3PSW membrane become more rigid, compact and regular composition. Therefore, the membrane itself can producing highest PWP, lowest proteins permeate flux and give better performance compared to PN-3PTW membrane (combination non-ionic/non-ionic surfactants) to obtain highest proteins rejection which are 93% and 79% for BSA and EA respectively.

The morphological structures observed that the existence of macrovoids at the sub layer to the bottom of the all membranes. It is confirmed that the combination of different groups of surfactants had demonstrated significant changes in size of finger-like structures, macrovoid and pores in the membranes. Table 20 demonstrated that the measurements of the membranes properties with different combination surfactants towards PVP additive in the UF membranes. It is observed that the combination of ionic/non-ionic surfactants in a dope polymer solution (PN-3PSW membrane) would increase the macrovoids length-width while decrease the pores length-width.

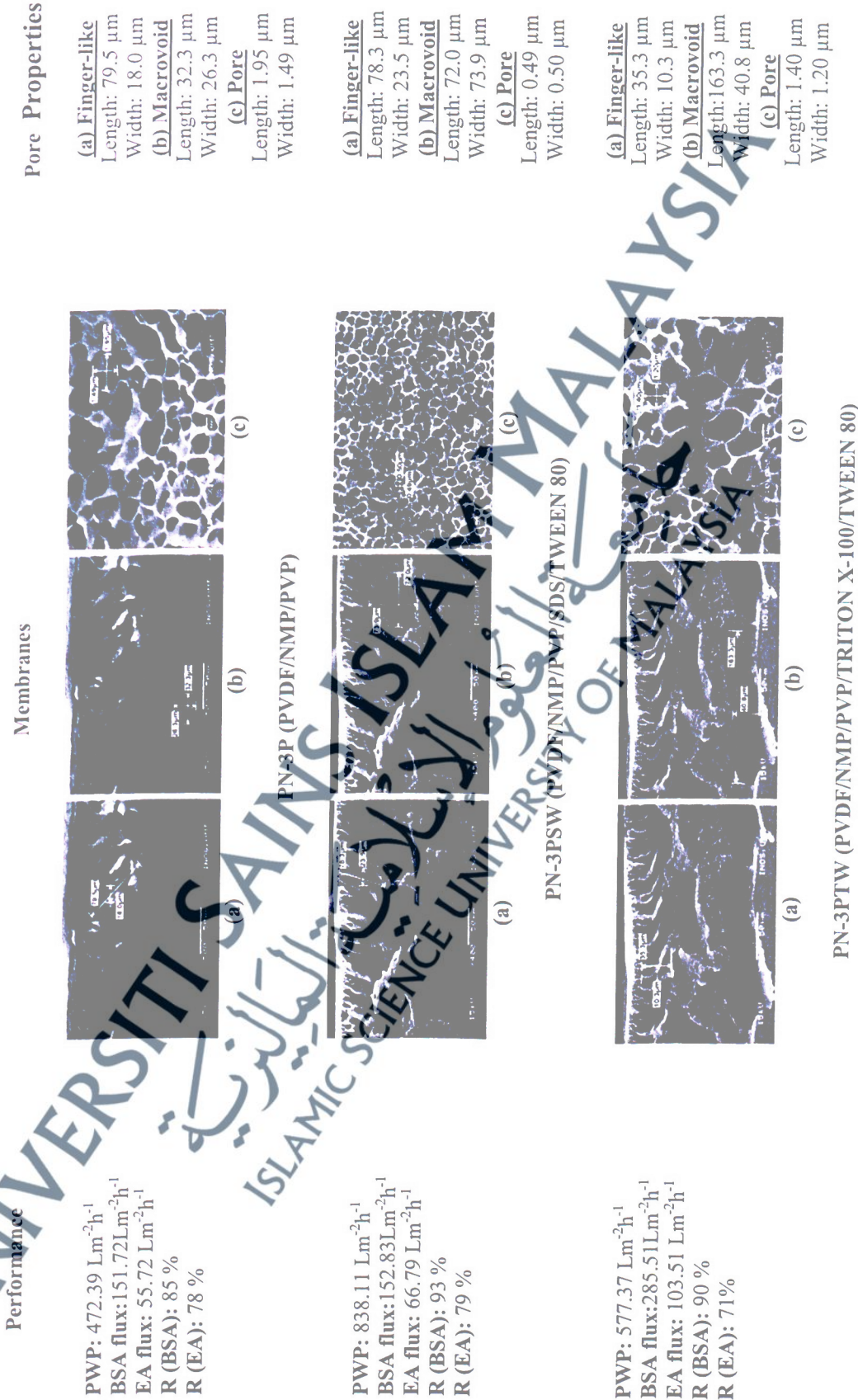
TABLE 20: UFS membranes structural details with different combination surfactants towards PVP additive

Membranes	Finger-like Length (μm)	Finger-like Width (μm)	Macrovoid Length (μm)	Macrovoid Width (μm)	Pore Length (μm)	Pore Width (μm)
PN-3P	79.5	18.0	32.3	26.3	1.95	1.49
PN-3PSW	78.3	23.5	72.0	73.9	0.49	0.50
PN-3PTW	35.3	10.3	163.3	40.8	1.40	1.20

Because of the small pore properties, the membrane can give highest proteins rejection as discussed on previous section. As well from the data, the combination of non-ionic/non-ionic surfactants (PN-3PTW membrane), the finger-like structure become shorter and irregular sponge macrovoids become larger in sizes at the bottom layer. This largest macrovoids (163.3 μm length; 40.8 μm width) structure formed give better proteins permeation flux. The existence of finger-like, macrovoid structures and pores in the membrane are significant characteristics of porous membrane. Moreover, the UF membranes are categorized as porous membrane based on their porous structure and high PWP related to the membrane productivity

FIGURE 82: Summary of Performance, Morphologies and Pore Properties of PVDF-UF Membrane with Different Combination of

Surfactants and PV/P Additive



PN-3P (PVDF/NMP/PVP)
PN-3PSW (PVDF/NMP/PVP/SDS/TWEEN 80)
PN-3PTW (PVDF/NMP/PVP/TRITON X-100/TWEEN 80)

4.6.4 FTIR Studies

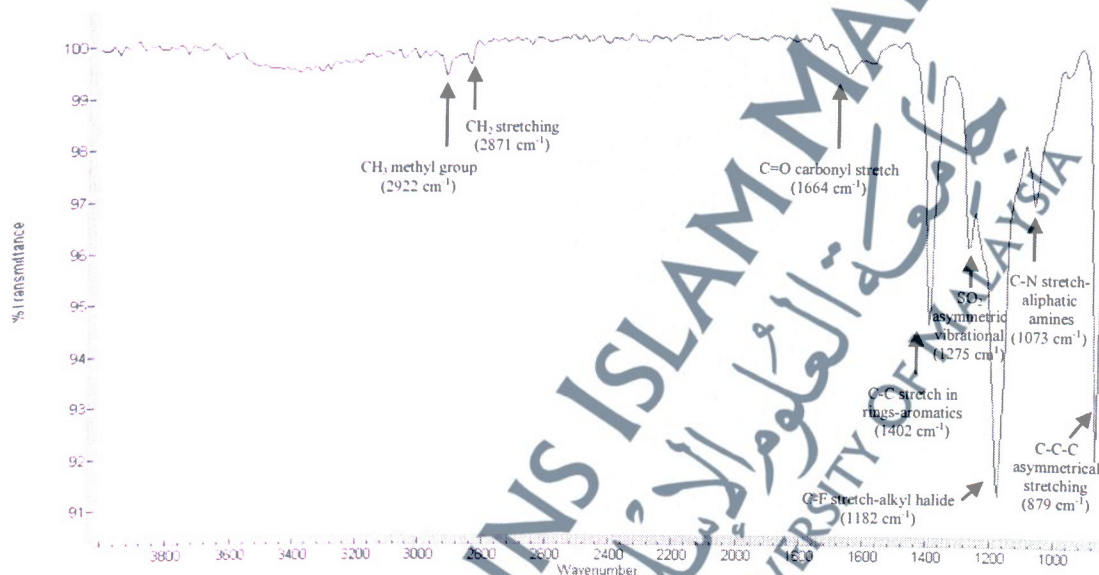
The vibration modes of chemical bonds are characterized by the absorption bands of infrared spectroscopy. The chemical structures of PN-3PSW (SDS/Tween 80) and PN-3PTW (Triton X-100/Tween 80) membranes with different combination of surfactants in PVP as additive are characterized with the help of Fourier transform infrared (FTIR) spectroscopy. The effect of PVP on the PVDF-UF membrane (PN-3P membrane) was clearly discussed in Figure 61(a) in section 4.3.4.

The influence of the combination of two surfactants (anionic/non-ionic) on the molecular orientation has been observed in Figure 83(a). The peak of PN-3PSW membrane did not showed significant differences compared to PN-3P membrane as well C=O stretching was shifted from 1657 to 1664 cm^{-1} . The characteristic of carbonyl group (C=O), which could generate from PVP has been found to increase membrane hydrophilicity (Puspitasari et al., 2010). However, the C-C aromatic stretch in rings (characteristic of pure PVDF) is maintained at frequency 1402 cm^{-1} because the PN-3PSW membrane is also used the same PVDF polymer.

As there is Tween 80 surfactant in the PN-3PSW membrane solution, the characteristic of CH_3 methyl group appeared at 2922 cm^{-1} . Besides, another significant peak different from PN-3P membrane is marked at 1275 cm^{-1} which correspond to S=O stretching frequency from vibration of sulfone group (SO_2). This peak is confirming that the PN-3PSW membrane presenting of surfactant SDS in the solution. As the anionic/nonionic surfactants are combining, the ionic head of the SDS surfactant are hydrated and are associated with their counter ions. The effect of ionic

surfactants would depend on the degree of dissociation of the surfactant aggregates and competition between Na^+ for available sites at the surface of the surfactant aggregates (Das et al., 2013).

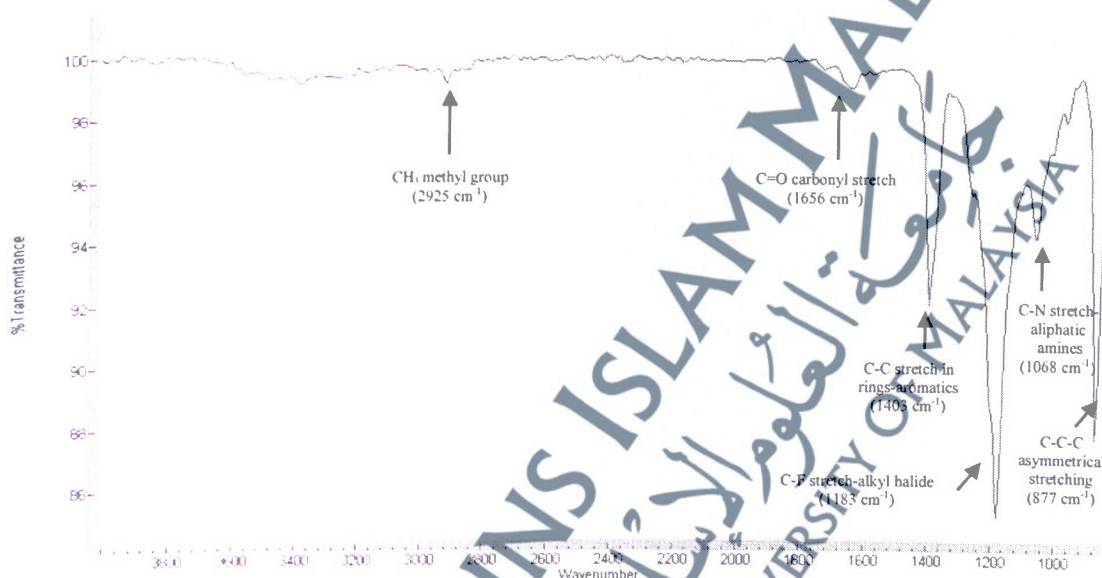
FIGURE 83(a): IR Spectra of UF Membrane (PN-3PSW) with Combination of SDS/Tween 80 towards PVP Additive



FTIR spectrum of PN-3PTW membrane (combination of non-ionic/non-ionic surfactants) is illustrated in Figure 83(b). From the spectrum, several results can be obtained. There was a group of weak adsorption peaks at 2925 cm^{-1} , 1656 cm^{-1} and 1068 cm^{-1} , which was due to stretching band of the CH_3 methyl group, $\text{C}=\text{O}$ carbonyl stretch and $\text{C}-\text{N}$ aliphatic amines, respectively. Since all the membranes used the same PVDF polymer, thus the FTIR results shows almost the same bands of functional groups PVDF that appeared. Sharp and strong absorptions have been detected at the wavelength 877 cm^{-1} which can be assigned to the alkyl halides stretching vibrations of $\text{C}-\text{F}$ bond in the PVDF chains. However, the combination of nonionic/nonionic surfactants towards PVP additive does not give any peak of $\text{O}-\text{H}$ stretching in the

spectrum. Generally, the water molecules are mainly located as “interstitial” water bounded to the surfactant polar head group and thus, position of O-H band reveals the interactions (Mehta et al., 2007).

FIGURE 83(b): IR Spectra of UF Membrane (PN-3PTW) with Combination of Triton X-100/Tween 80 towards PVP Additive

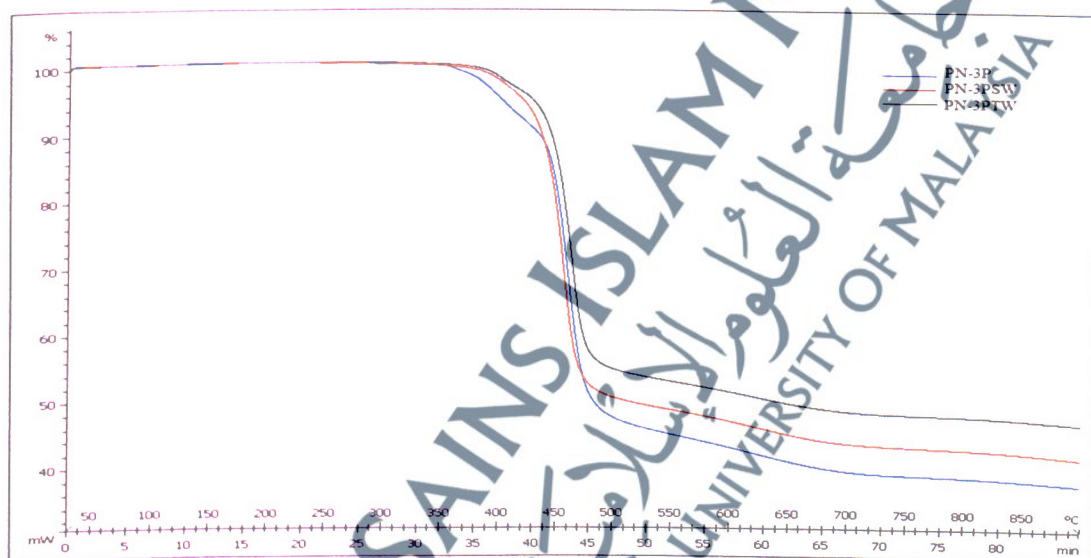


4.6.5 TGA Studies

Thermal degradation of PVDF/PVP with addition of anionic/non-ionic (PN-3PSW membrane) and non-ionic/non-ionic (PN-3PTW membrane) surfactants was shown in Figure 84. All of the prepared membranes occurred in three steps between 80 to 900 °C. Since the PVDF is a highly thermo stable polymer it exhibited three weight loss steps. The first step indicated the loss of bound water and traces of solvent up to a temperature of ~ 400 °C, which the mass loss of 16 and 10 % for PN-3PSW and PN-3PTW membranes, respectively. The next step loss in weight was observed beyond this temperature suggested that beyond 400°C up to 450 °C. The second gradual

degradation was assigned to the loss of surfactants groups. The mass loss of PN-3PSW and PN-3PTW membranes at this second stage decomposition were 51 and 47 %, respectively. The third thermal degradation starting at ~ 460 °C was allocated to the degradation of the polymer main chain with percentage total mass loss of about 58 and 53 % for PN-3PSW and PN-3PTW membranes, respectively.

FIGURE 84: TGA Curves of PVDF-PVP Membranes with Combination of Anionic and Non-Ionic Surfactants



In comparison between PN-3PSW and PN-3PTW membranes as can be seen from the curves, the PN-3PSW membrane containing ionic/non-ionic surfactants having higher percentage of mass loss (16%) during the first stage of decomposition compared to PN-3PTW membrane which containing non-ionic/nonionic surfactants (10%). This is due to combination of ionic/non-ionic surfactants hold on to water most tenaciously compared to PN-3PTW membrane containing the non-ionic/non-ionic surfactants. Hence, it can lose water more easily as produced higher mass loss in the first stage decomposition (Prasad et al., 2005).

4.7 Combination of Surfactant (Dual-Surfactant) towards PEG 200 additive

In this section, flat sheet PVDF membranes were prepared using different addition of anionic and non-ionic surfactants towards PEG 200 (as a pore reducer additive) in one dope polymer solution and makes NMP as solvent. The ionic surfactant used in the study is Sodium dodecyl sulfate (SDS) while the non-ionic surfactants used were Triton X-100, and Tween 80.

In addition, a basic approach to membrane-surfactant interaction is also presented. The membranes were combined the SDS (anionic)/Tween 80 (non-ionic) and Triton X-100 (non-ionic)/Tween 80 (non-ionic) surfactants towards PEG 200 additive in the polymer casting solutions were marked as PN-3GSW and PN-3GTW membranes respectively. The membrane without combination surfactant is marked as PN-3G membrane. The polymer and additive concentration was kept constant at 17 wt% and 3 wt% respectively. Table 21 shows the composition parameters of all the membranes prepared with combination of different groups of surfactants towards PEG 200- pore reducer additive in the polymer casting solution.

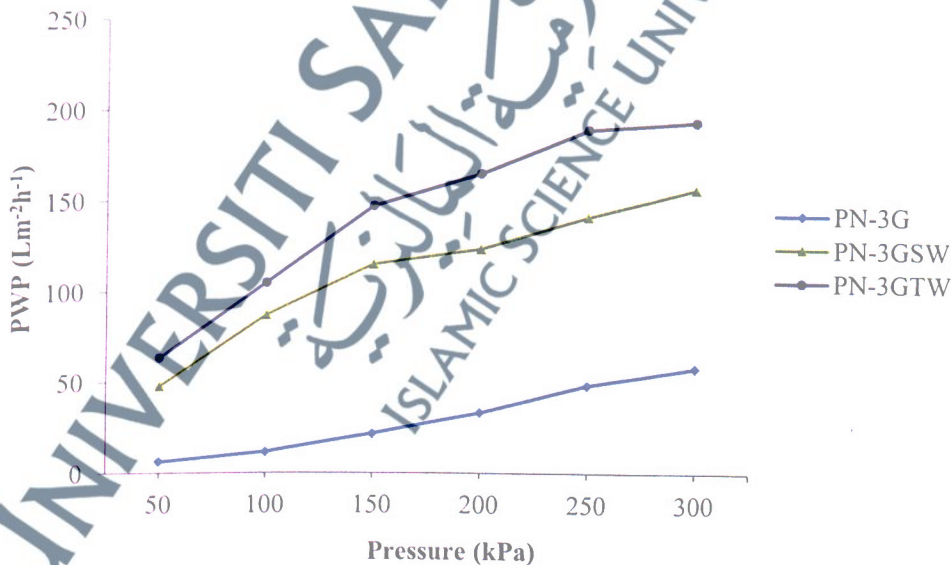
TABLE 21: The PVDF/NMP/PEG 200 membranes formulations

Membranes	Total polymer (wt%)	Solvent (wt%)	Additives (wt%)	Surfactants (wt%)		
			PEG 200	SDS (anionic)	Triton X-100 (non-ionic)	Tween 80 (non-ionic)
PN-3P	17	80	3	-	-	-
PN-3PSW	17	78	3	1	-	1
PN-3PTW	17	78	3	-	1	1

4.7.1 Pure Water Permeation (PWP)

The effect of ionic/non-ionic and non-ionic/non-ionic surfactants towards PEG 200 additive on the PWP performance is illustrated in Figure 85. From the figure, all the membranes have increasing PWP with increase the operating pressure from 50 to 300 kPa. As expected as well as according to Fernandez et al. (2005), the PWP for all the membrane increases linearly with operating pressure. All the PWP experiments follow the same trend because it is due to the increase in effective driving force required for PWP. Based on the experimental results, the combination of different groups of surfactants can enhanced the PWP as well showed that PN-3GTW and PN-3GSW membranes give higher PWP compared to PN-3G membrane.

FIGURE 85: PWP of Fabricated UFS membranes with Different Groups of Surfactants towards PEG 200 Additive



The PWP of PVDF/NMP/PEG 200 which is marked as PN-3G membrane was increased from $6.17 \text{ Lm}^{-2}\text{h}^{-1}$ to $57.74 \text{ Lm}^{-2}\text{h}^{-1}$. On the other hand, the PWP of PN-3G membrane was the lowest PWP ($57.74 \text{ Lm}^{-2}\text{h}^{-1}$) at the maximum operating pressure which is 300 kPa. The addition of PEG 200 only to the casting solution decreased the water permeation because without adding surfactant which can enhance the PWP. In the casting solution, PEG 200 was used as pore reducing agent to improve the solute permeation properties of membrane. Therefore, this additive somehow can lead to better solute permeation in the membrane performance (Kim and Lee, 2004).

As presented in Figure 85, it was observed that membrane PN-3GTW, which was prepared with combination non-ionic/non-ionic surfactants in a dope polymer solution, exhibit a very highest PWP of $192.46 \text{ Lm}^{-2}\text{h}^{-1}$ when the operating pressure at 300 kPa was used. When addition of both 1 wt% Triton X-100 and Tween 80 as non-ionic surfactants to the dope formulation, the PWP of PN-3GTW membrane increased gradually from $63.52 \text{ Lm}^{-2}\text{h}^{-1}$ to $192.46 \text{ Lm}^{-2}\text{h}^{-1}$. The significant improvement of PWP might be attributed to the enhanced surface porosity while the combination of both non-ionic surfactants towards PEG 200, indicates the formation of large surface pores when Triton X-100 and Tween 80 were added as non-ionic surfactants to the polymer dopes. According to Holmberg et al. (2002), the growing interest in polymeric non-ionic surfactants has attractive properties as the PN-3GTW membranes have a strong driving force, with this tendency to collect the productivity (water permeation).

In addition, while comparing PN-3GSW and PN-3GTW membranes, it was showed that PN-3GSW (combination of anionic/non-ionic surfactant) give a lower PWP compared to PN-3GTW (combination of non-ionic/non-ionic surfactant). As

increasing the operating pressure from 50 to 300 kPa, the PWP of PN-3GSW membrane increase from $47.76 \text{ Lm}^{-2}\text{h}^{-1}$ to $155.58 \text{ Lm}^{-2}\text{h}^{-1}$. Generally, a mixture of two oppositely charged anionic and non-ionic surfactants shows a strongly interaction behavior, as demonstrated by a strong tendency to phase separation. However, this behavior was vice-versa when the PEG 200 was added as a pore reducer additive (Lindman, 2002).

4.7.2 Protein Separation Performance

The effects of combination anionic/non-ionic and non-ionic/non-ionic surfactants on proteins permeate flux and rejections are shown in Figures 86 and 87 respectively. It can be seen from Figure 86 that the addition of both ionic/non-ionic (PN-3GSW membrane) and non-ionic/non-ionic (PN-3GTW membrane) surfactants were enhanced the permeate flux of BSA and EA proteins. From the graph, it shows PN-3G membrane has the lowest BSA and EA permeate flux which are $2.74 \text{ Lm}^{-2}\text{h}^{-1}$ and $1.03 \text{ Lm}^{-2}\text{h}^{-1}$ respectively compared to the other membranes. This is because the PEG 200 additive used in the casting solution is a pore reducer agent will effect on diminished the pore size and thus directly reduce the membrane porosity (Nurul et al., 2013).

Furthermore, based on Figure 86, PN-3GTW membrane, which containing combination of non-ionic/non-ionic surfactants show the highest BSA and EA permeate flux which value are $120.84 \text{ Lm}^{-2}\text{h}^{-1}$ and $23.01 \text{ Lm}^{-2}\text{h}^{-1}$ respectively. As discussed in the previous section (Section 4.6.2), according to Fernandez et al. (2005), the combination of non-ionic/non-ionic surfactants in a dope polymer solution, a different behavior was observed. The interaction between hydrophobic chain and the

non-polar sites of the membranes were observed which leading to hydrophilization of the membrane surface and pores. Thus because it can produce highest permeate flux compared to the other membranes.

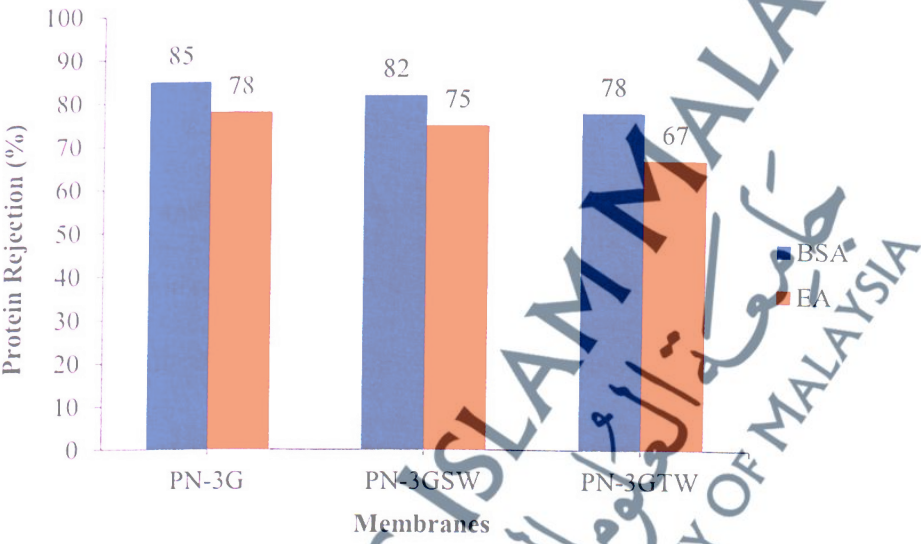
FIGURE 86: Proteins Permeation Flux of UFS Membranes Containing Combination of Anionic and Non-Ionic Surfactants towards PEG 200 Additive



Besides that, studies on the rejection of proteins such as BSA and EA through the prepared membranes are important in the UF performance test. The rejection of proteins through the developed membranes is shown in Figure 87. It is seen that the combination of ionic/non-ionic (PN-3GSW membrane) and non-ionic/non-ionic (PN-3GTW membrane) surfactants decreased the proteins rejection. Based on the experimental result in Figure 87, PN-3G (without surfactant) shows the highest BSA and EA rejection which are 85% and 78% respectively. This is because addition of PEG 200 to the polymer casting solution affects the membrane pores and thus decrease the pore size of the PN-3G membrane. Hence the solutes of high molecular weight cannot pass through the smaller pore size of the membrane during UF protein

experiments. Therefore, PN-3G membrane exhibited lowest permeate flux and highest proteins rejection.

FIGURE 37: Proteins Rejection of UFS Membranes Containing Combination of Anionic and Non-Ionic Surfactants towards PEG 200 Additive



The Figure 87 shows BSA and EA separation performance of PVDF/NMP/PEG 200 with combination of anionic/non-ionic and non-ionic/non-ionic surfactants. As shown in the figure, the BSA and EA proteins rejection for PN-3GSW membrane were 82% and 75% respectively which are higher than PN-3GTW membrane. The results illustrated that the combination of anionic/non-ionic surfactants in a dope polymer solution may directly interact with hydrophobic regions in the surface of the membrane. However, PN-3GTW membrane showed the lower proteins rejections (BSA=78% and EA=67%) than PN-3GSW membrane.

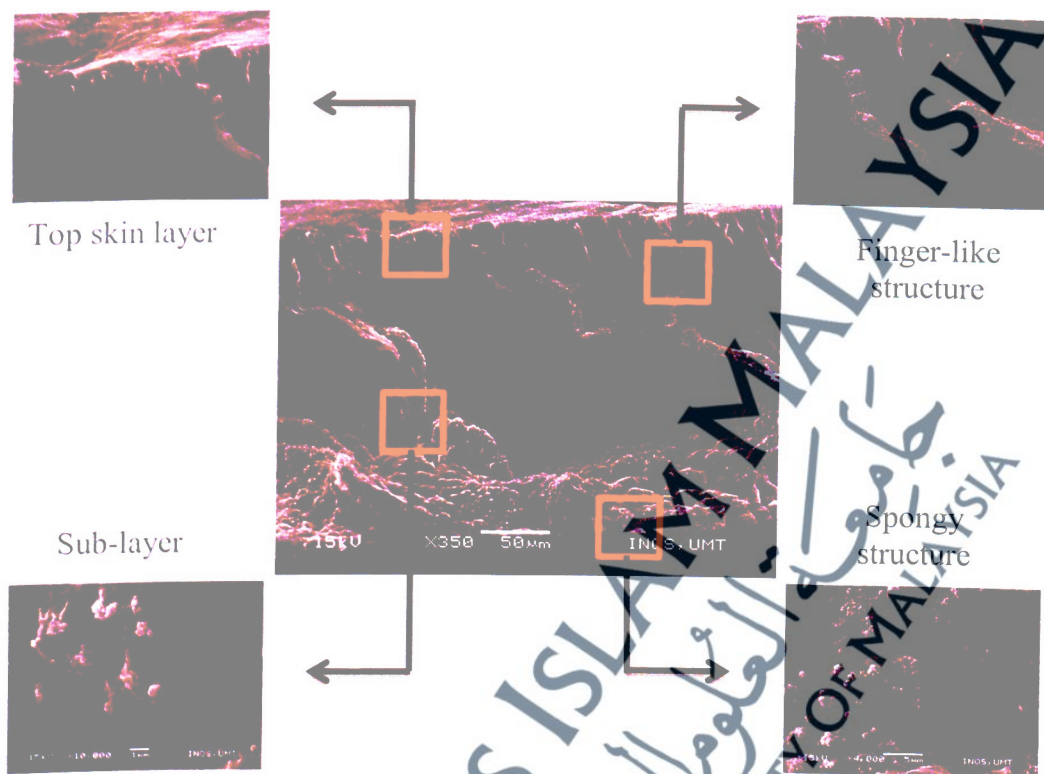
This is relates to the combination of both non-ionic surfactants which is commonly used throughout the proteins filtration to inhibit proteins aggregation due

to agitation or shaking. Hence, the protein molecules difficult to compete for hydrophobic surfaces such as air–water interfaces, thereby preventing proteins from unfolding at these hydrophobic polymeric membrane interfaces. Because of these properties of proteins with combination of both non-ionic surfactants decreased the proteins rejection meanwhile highest permeate fluxes (Kamerzell et al., 2011).

4.7.3 Membrane Morphology

The zooming and cross-sectional morphology of PVDF membrane prepared using PEG 200 as additive and no combination of surfactant to the polymer casting solution (PN-3G membrane) is shown and already discussed in Figure 59(c) (refer to section 4.3.3). Figure 88(a) presented the cross-section SEM images of membranes with addition of anionic/non-ionic surfactants to the polymer casting solution. This image showed that the PN-3GSW membrane had finger-like and macrovoids structure having good interconnection. The fact that surfactants whether anionic or non-ionic were able to speed-up phase demixing and lead to macrovoids structure has been reported by many authors (Rahimpour et al., 2012(a); Loh et al., 2012 and Chang et al., 2014). Besides, with addition of merely 1 wt% of surfactant, macrovoids would already be observed to occupy most of the membrane cross section. Similar result can be found for preparation of polyethersulfone membranes from dopes containing different types of surfactants such as SDS, Triton X-100 and CTAB (Rahimpour et al., 2012(a)).

FIGURE 88(a): Cross-Sectional Structure of PN-3GSW (PVDF/NMP/PEG 200/SDS/TWEEN 80)



In Figure 88(b), the cross-sectional SEM images of the membrane prepared by immersion casting dope containing different combination of non-ionic surfactants; Triton X-100 and Tween 80 is demonstrated (PN-3GTW membrane). Because of non-ionic surfactants presence in the dope solution, Tween 80 and water are highly solvable mutually, thus would exchange instantly upon their contact at immersion. Such rapid mass transfer events certainly promote fast phase demixing which is confirmed by the decreased precipitation times for immersion. According to Chang et al. (2014), after adding 1 wt % of Tween 80 in the dope, the pores start to appear on the top surface of the membrane. As shown in the Figure 88(b), the pores observed are actually penetrated through the skin layer and connect with the pores in the cross section. For the use of surfactants, Triton X-100 and Tween 80 as non-ionic

surfactants would be expected to show no electrostatic interaction and instead may interact with polymer solely by hydrophobic bonding (Khalid et al., 2011). As depicted in Table 22, the highest finger-like length and width are 86.0 and 19.0 μm respectively, which related to highest PWP and proteins permeate flux.

FIGURE 88(b): Cross-Sectional Structure of PN-3GTW (PVDF/NMP/PEG 200/TRITON X-100/TWEEN 80)

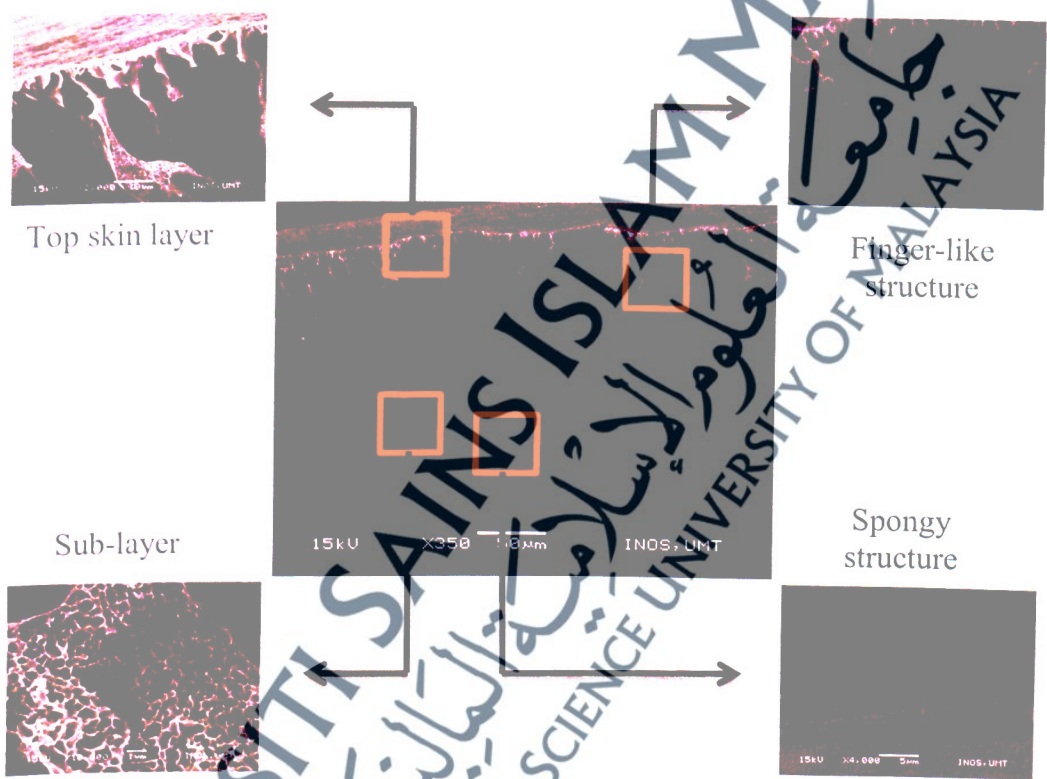
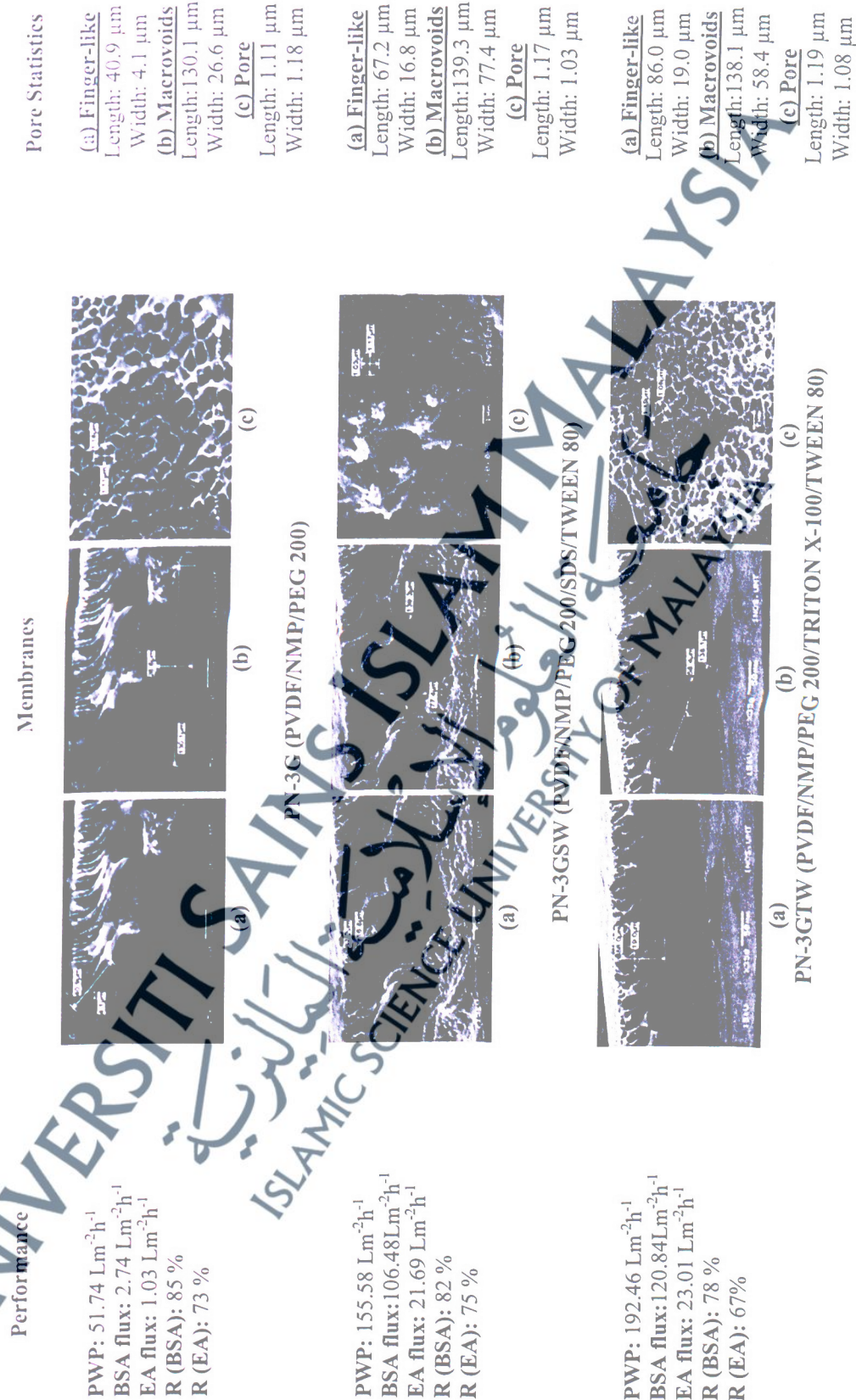


TABLE 22: UFS membrane structural details with different combination surfactants towards PEG 200 additive

Membranes	Finger-like Length (µm)	Finger-like Width (µm)	Macrovoid Length (µm)	Macrovoid Width (µm)	Pore Length (µm)	Pore Width (µm)
PN-3G	40.9	4.1	130.1	26.6	1.11	1.18
PN-3GSW	67.2	16.8	139.3	77.4	1.17	1.03
PN-3GTW	86.0	19.0	138.1	58.4	1.19	1.08

FIGURE 89: Summary of Performance, Morphologies and Pore Statistic of PVDF-UF Membrane with Different Combination of

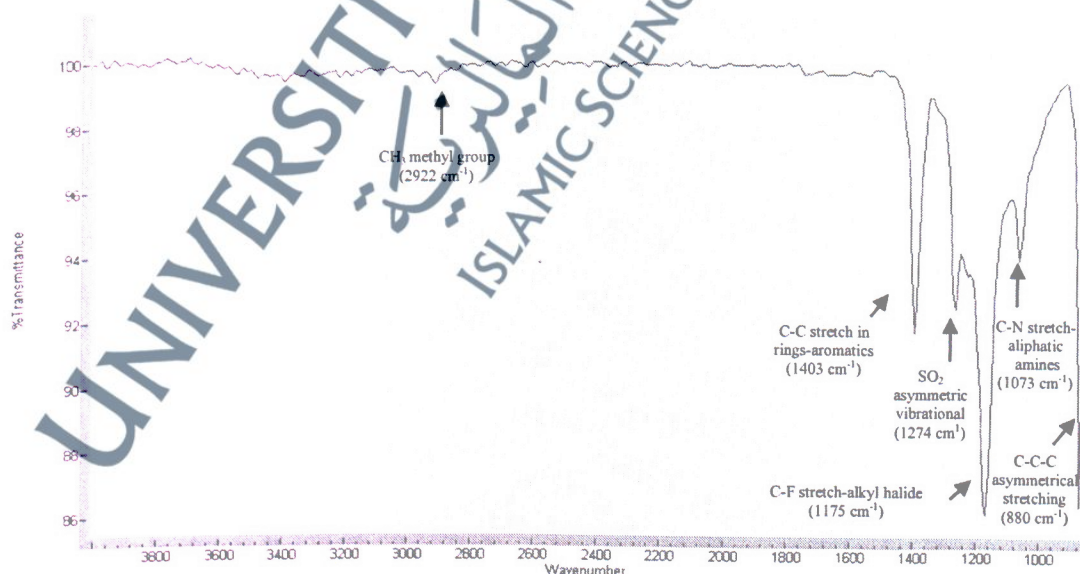
Surfactants and PEG 200 Additive



4.7.4 FTIR Studies

The FTIR spectrum of PN-3G membrane with addition of PEG 200 in the polymer casting solution is shown in Figure 61(c). This membrane was discussed earlier in Section 4.3.4. The main absorption band appears at 1672 cm^{-1} corresponds to the stretching modes of the C=C double bond conversion of PEG (Oh et al., 2014). The functional groups of PN-3GSW membrane with combination of anionic/non-ionic surfactants towards PEG 200 additive is shown in Figure 90(a). The characteristics bands were observed, including strong and sharp peaks related to C-C aromatics stretch in rings (1403 cm^{-1}), C-F stretch of alkyl halide (1175 cm^{-1}) and C-C-C asymmetric stretching (880 cm^{-1}). As the PN-3GSW membrane presence of SDS surfactant, the stretching frequency of S=O resulting from vibration of sulfone group (SO_2) is observed at 1274 cm^{-1} .

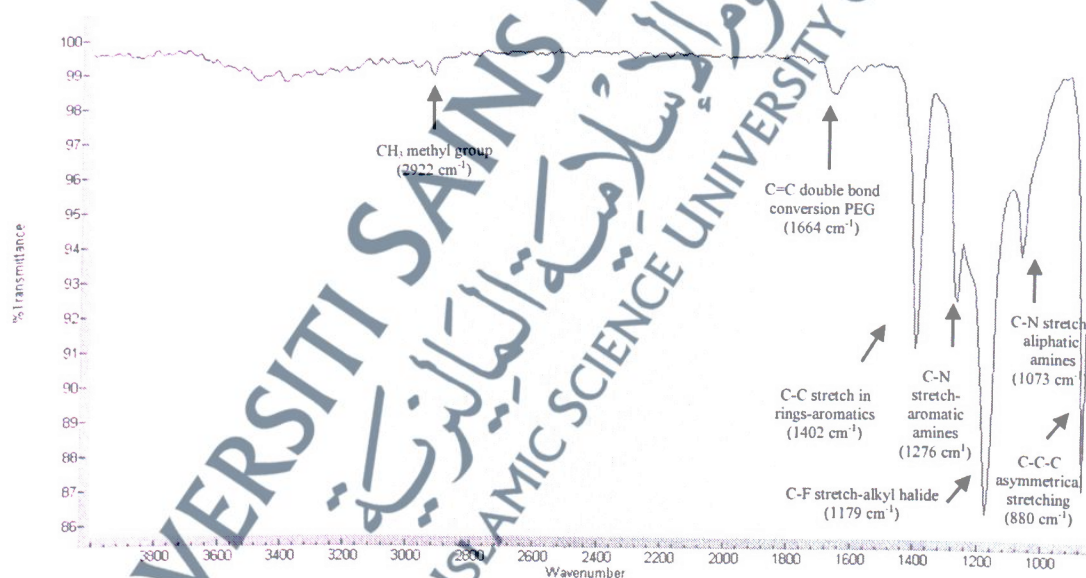
FIGURE 90(a): IR Spectra of UF Membrane (PN-3GSW) with Combination of SDS/Tween 80 towards PEG 200 Additive



Based on the result, generally modified and unmodified membranes have similar infrared absorption bands at the 1403 cm^{-1} and 880 cm^{-1} . The similarity of the infrared spectra over this range confirmed that the membranes had the same basic structure of PVDF after modification (Wei et al., 2012).

The Figure 90(b) shows the infrared spectrum of UF membrane with combination of non-ionic/non-ionic surfactant towards PEG 200 additive. The combination of these surfactants does not showed significant changes in the spectrum and just quite similar to the other membranes.

FIGURE 90(b): IR Spectra of UF Membrane (PN-3GTW) with Combination of Triton X-100/Tween 80 towards PEG 200 Additive



The FTIR spectrum shows CH_3 (methyl group) stretching vibration at 2922 cm^{-1} . Besides, two weak bands at 1276 cm^{-1} and 1073 cm^{-1} . They could be assigned to the C-N aromatic amines and C-N aliphatic amines stretch vibration, respectively. The bending vibrations at 1179 cm^{-1} (C-F stretch) and 880 cm^{-1} (C-C-C stretch) supported

the interaction of PVDF polymer molecules in the PN-3GTW membrane. Similarly the spectral peak observed at 880 cm^{-1} is assigned to CH_2 wagging vibration and CF_2 bending vibration of the vinylidene groups. These characteristics absorption peaks corresponded to those of PVDF membrane.

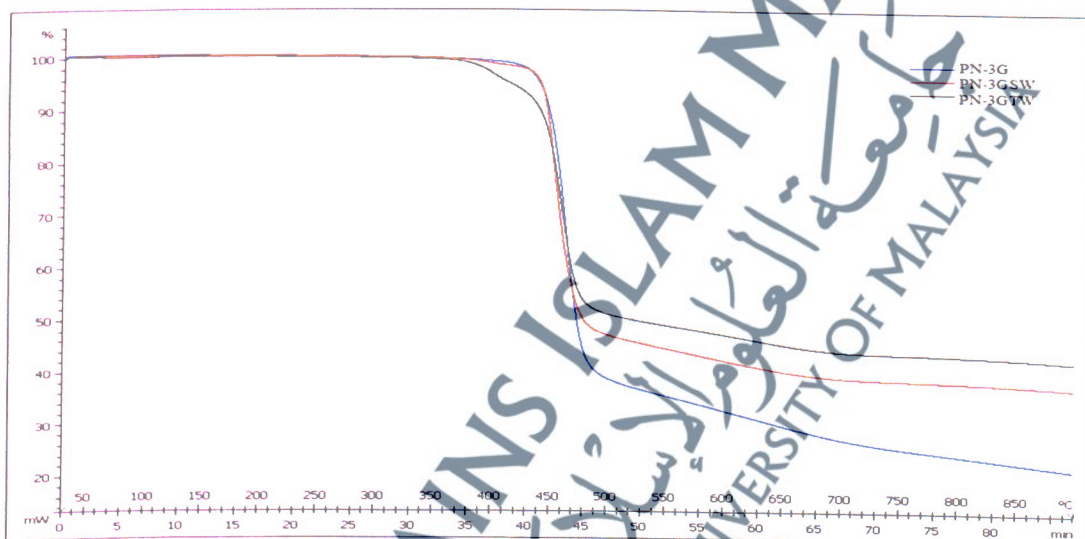
4.7.5 TGA Studies

The thermal stability of the PVDF-PEG 200 membrane samples prepared in the presence of anionic/non-ionic and non-ionic/non-ionic surfactants was studied by TGA as shown in Figure 91. It is obvious that they have similar trends weight loss of TG curves. As test temperature rises, the weight loss curves are divided into three sections. Firstly, the weight loss under $350\text{ }^\circ\text{C}$ and secondly, the weight loss transition begins $\sim 400\text{ }^\circ\text{C}$ to $\sim 480\text{ }^\circ\text{C}$. Then, it is possible that a continuous mass decrease on account molecular chain after $500\text{ }^\circ\text{C}$. Finally, it is substantially completed at above $750\text{ }^\circ\text{C}$.

Figure 91 represents the curves of weight loss versus temperature showing the behavior of PN-3G, PN-3GSW and PN-3GTW membranes. The first significant weight loss occurs already at temperature between 30 and $350\text{ }^\circ\text{C}$. Then, the main mass loss, which corresponds to polymer degradation starts at about $\sim 400\text{ }^\circ\text{C}$. Although the curves look like the same shape, PN-3GTW membrane (consisting of non-ionic/non-ionic surfactants) seems to be slightly more stable if compared to PN-3GSW membrane (consisting of anionic/non-ionic surfactants). The PN-3GTW membrane starts to decompose at lower temperature compared to other membranes. The reason is because the lower decomposition temperature of the non-ionic

surfactants. Also the mass loss of PN-3GTW membrane prepared in the presence of non-ionic surfactants amount about 3 % in the temperature region below 350 °C, indicating almost no change in the affinity of the membrane towards humidity (Omastova et al., 2003).

FIGURE 91: TGA Curves of PVDF-PEG 200 Membranes with Combination of Anionic and Non-Ionic Surfactants



As seen in the curves presented, the PN-3GSW membrane starts decompose at high temperature than PN-3G membrane. For this case of PN-3GSW membrane, the high temperature was due to decomposition of sulphate head group (negatively charged) of anionic SDS. Decomposition of sulphate head group at higher temperature suggested the stronger interaction of sulphate group with the blending polymer (Patel et al., 2014). More particularly, membrane PN-3G show highest total mass loss in thermal degradation which is value 76 % compared to other membranes. In other words, membranes PN-3GSW and PN-3GTW have lower total mass losses which are 63 % and 58 %, respectively. Higher percentage of total weight loss for PN-3G membrane may be attributed to the decomposition of without surfactant.