

CHAPTER 4

X-RAY DIFFRACTION AND SCANNING ELECTRON MICROSCOPY ANALYSIS

4.1 Introduction

Miya *et al.* (1984) have reported that homogeneous polymer can be prepared by blending chitosan and PVA. The blend between chitosan and PVA exhibits good mechanical strength [Mucha *et al.*, 1998; Mukhina *et al.*, 2001]. Bel'nikovich *et al.*, (2004) reported that there is no strong specific intermolecular interactions in chitosan-PVA blends that would lead to the formation of interpolymeric complexes. Experiments on sorption and solvent vapour show that chitosan and poly(vinyl alcohol) are compatible. Jiang *et al.*, (2008) have fabricated a direct methanol fuel cell (DMFC) using PVA-chitosan blend as a barrier membrane. Razak *et al.*, (2009) have reported the use of chitosan-PVA blend as a host for Li^+ ion conduction. Having known the compatibility between chitosan and PVA and its potential use as an ionic conductor, it is important in the opinion of the author to determine the appropriate amount of chitosan and PVA that would give a homogenous film.

4.2 X-Ray Diffraction (XRD) Analysis

4.2.1 X-Ray Diffractogram of PVA-Chitosan Blend Film

Following the compositions stated in Chapter Three, films of chitosan and PVA blends were prepared by the solution cast technique. The films were x-rayed and the results are depicted in Figure 4.1.

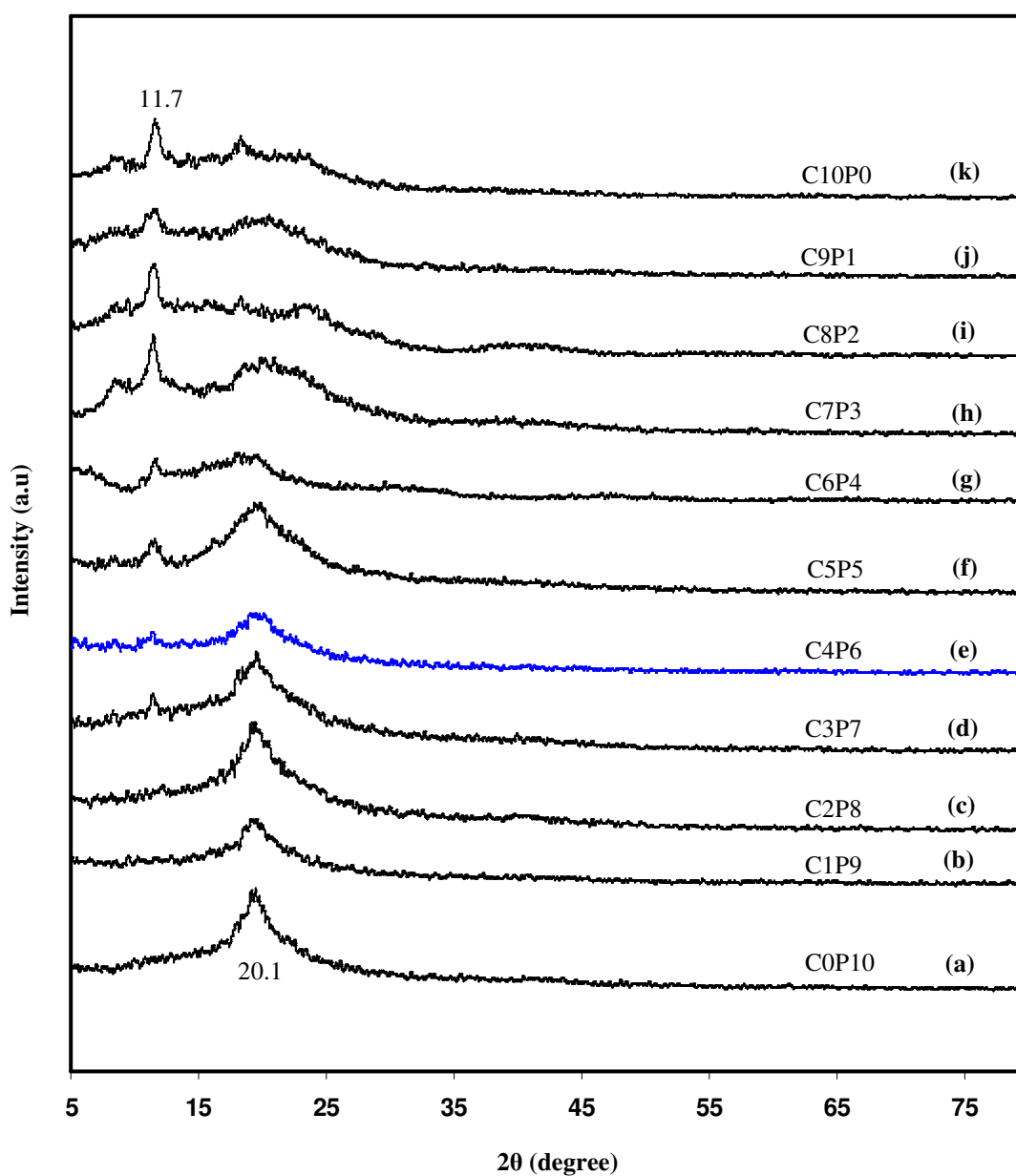


Figure 4.1: XRD pattern of PVA, chitosan and PVA-chitosan blends with the corresponding ratios.

From the XRD patterns in Figure 4.1, crystalline peaks at $2\theta = 11.7^\circ$ and 19° are attributed to chitosan, Figure 4.1 (k) and at 20.1° attributed to PVA, Figure 4.1 (a). The chitosan peak at $2\theta = 11.7^\circ$ is comparable with that observed in the diffractogram reported by Morni and Arof, (1999). The peaks at $2\theta = 11.7^\circ$ can still be observed in the diffractogram of the PVA-chitosan blend sample with high PVA content. i.e up to 70 wt. %, but the peak at $2\theta = 19^\circ$ has disappeared. At chitosan-PVA weight ratio = 1 peaks at $2\theta = 11.7^\circ$ and 20.1° are observed. The shift in position of the peaks is probably attributed to the interaction between chitosan and PVA [Jia *et al.*, 2007]. Jia *et al.*, (2007) also reported that higher content of chitosan in the PVA/chitosan blend is not favourable for high crystallinity. In their work, the ratio of PVA/chitosan blends was varied from 100/0 to 75/25 weight ratios.

The PVA-chitosan blend electrolyte with higher ratio of PVA has a crystalline peak at $2\theta = 20.1^\circ$. This is the PVA peak from the diffractograms of the different blends. It may be inferred that the most amorphous sample is the blend of 40 wt. % chitosan and 60 wt. % PVA. The peak at $2\theta = 11.7^\circ$ is small and broad. So is the peak at $2\theta = 20.1^\circ$. From the work of Zhang *et al.*, (2007), it has been deduced that the electrospun chitosan/PVA membranes with weight ratio of 40 wt. % chitosan and 60 wt. % PVA is the least crystalline..

4.3 SEM Micrographs of PVA-Chitosan Blend Film

SEM micrographs of the surface and cross section of pure PVA-chitosan blended film with the composition of 40 wt. % chitosan and 60 wt. % PVA (C4P6) are shown in Figure 4.2 and 4.3.

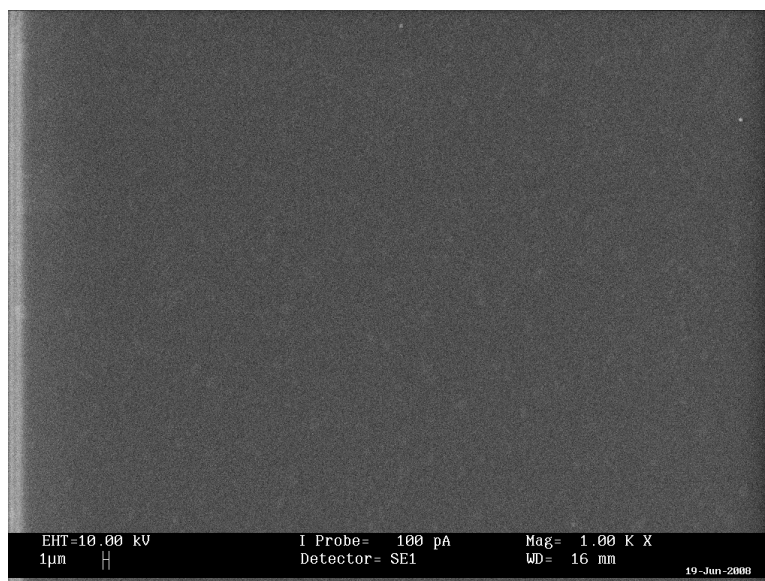


Figure 4.2: SEM surface morphology of pure C4P6 film.

The miscibility of the polymers can be implied from the smooth and homogeneous surface of the film. Lin *et al.*, (2008) reported that in the chitosan modified polyvinylacetal sponge, chitosan is embedded in the pores of the material. This results in a smooth and homogeneous surface of the blend. The micrograph of the cross-section in Figure 4.3 is proof of the miscibility of chitosan and PVA.

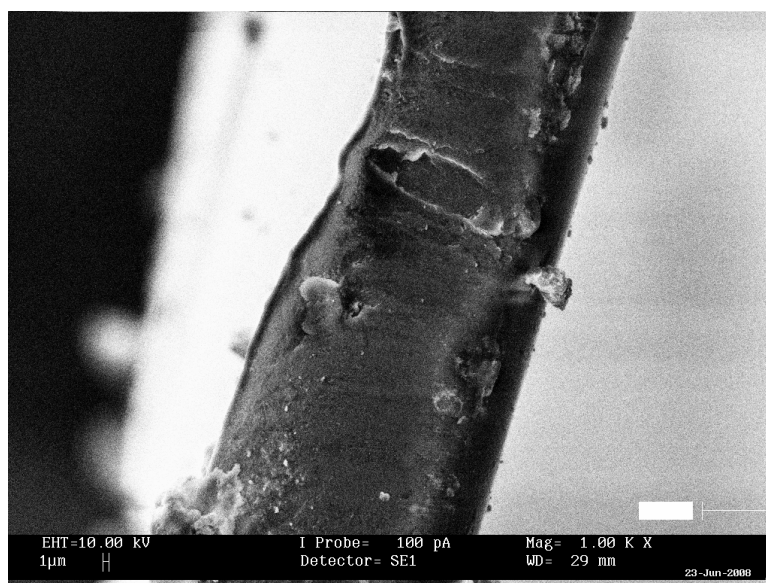


Figure 4.3: SEM cross section morphology of pure C4P6 film.

Figure 4.4 depicts the surface of a film with a higher weight ratio of chitosan (C7P3).

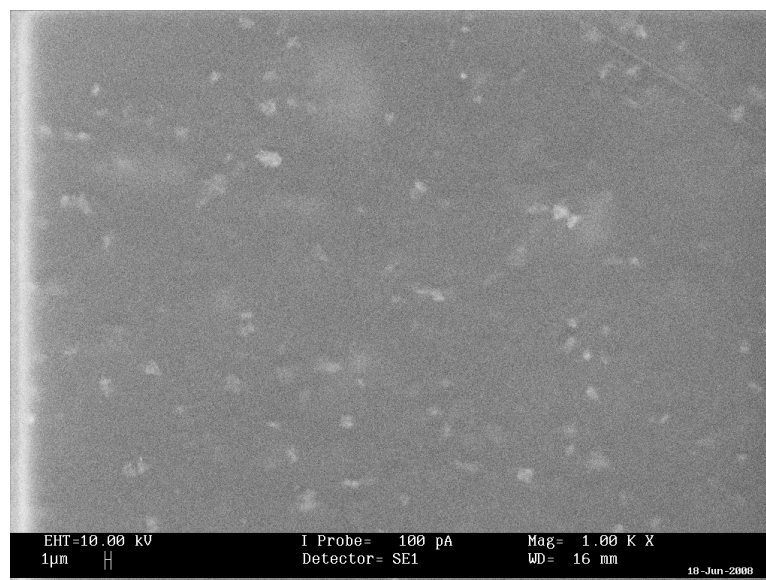


Figure 4.4: SEM surface morphology of pure C7P3 film.

It can be observed that the surface consist of white spots on a dark and smooth background. The pores of PVA are not obvious due to its smaller weight ratio compared to chitosan. It is inferred that the white spots are excess chitosan that maybe have protruded the surface. The diffractogram of this surface is depicted in Figure 4.1 (h) where chitosan peaks at $2\theta = 11.5^\circ$ and 8.9° are observed and a broad halo that centres around the PVA peak at $2\theta = 20.1^\circ$

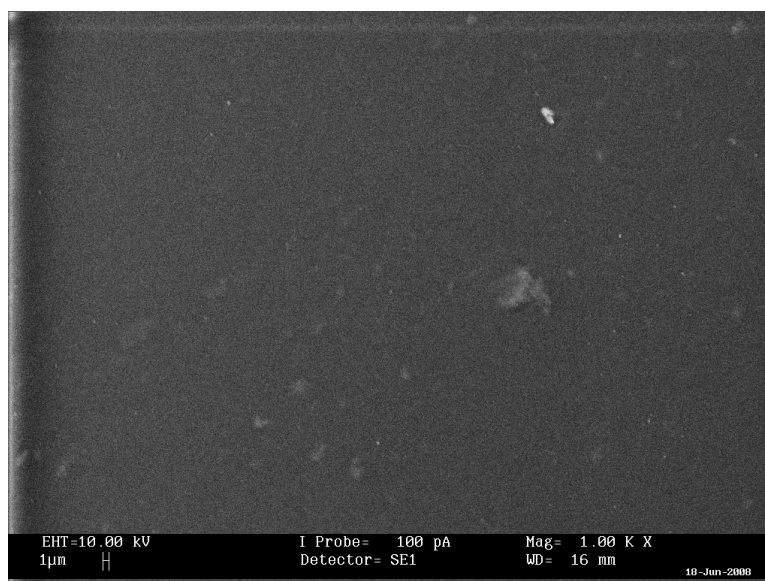


Figure 4.5: SEM surface morphology of pure C8P2 film.

Figure 4.5 shows the SEM surface micrograph of C8P2. This sample is also chitosan-rich. It can be observed from the XRD pattern in Figure 4.1 for that the diffractogram of C8P2 exhibits a sharp peak at $2\theta = 11.6^\circ$. The SEM micrographs of both samples were captured in order to support the inference that the sample is less homogenous compared to the C4P6 sample. From the SEM micrographs it maybe deduced that chitosan-rich samples are not homogeneous compared to C4P6.

Figure 4.6 and 4.7 represents the SEM surface micrographs of the same PVA-rich sample (C1P9).

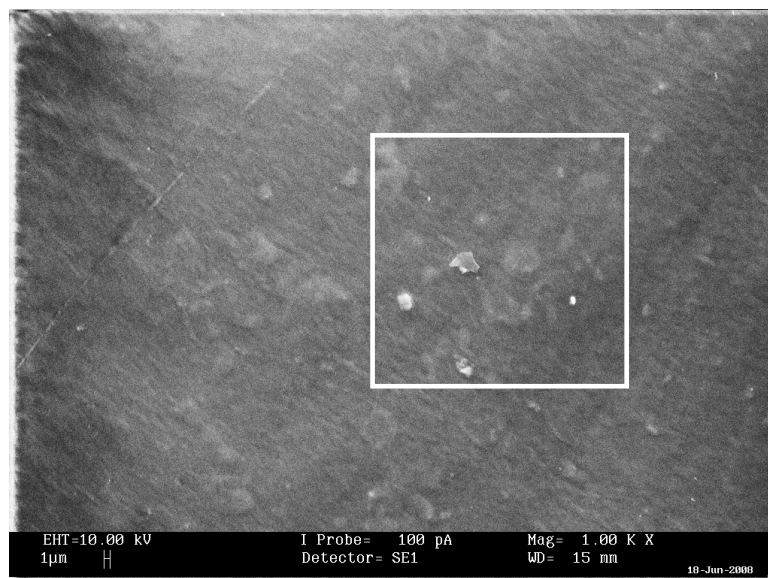


Figure 4.6: SEM surface morphology of pure C1P9 film.

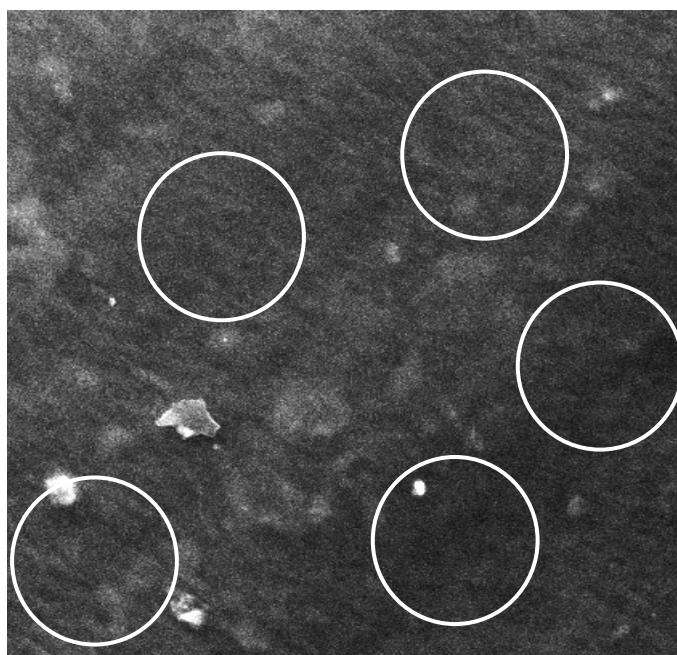


Figure 4.7: Enlarged portion of C1P9 showing the pores (white circles) that can be observed on the surface of a PVA-rich sample.

It can be seen in Figure 4.1 (b) that the diffractogram for sample C1P9 exhibits a halo that peaks at $2\theta = 20.1^\circ$. The SEM micrographs of these samples are captured in order to support the inference that the samples rich in PVA are less homogenous compared to C4P6 sample. The SEM micrograph of enlarged portion (in white loops) for the sample C1P9 is shown in Figure 4.7. From the enlarged portion SEM micrograph in Figure 4.7 the pores of the PVA component can now be observed.

4.4 Summary

From X-ray diffraction and SEM analysis of the polymer blend, it has been confirmed that the 2:3 ratio of chitosan-PVA membrane (C4P6) gives the most amorphous and homogeneous film. This film will be used as the polymer host in the salted system.