CHAPTER 4

DETERMINATION AND CHARACTERIZATION OF POLYMER BLEND HOST

4.1 Introduction

The amorphousness of a polymer host is a crucial factor for ionic conduction since ions are preferably mobile in the amorphous region (Agrawal, Sahu, Mahipal, & Ashrafi, 2013; Gadjourova, Andreev, Tunstall, & Bruce, 2001; Johan & Ting, 2011). For a polymer blend, the crystallinity and amorphousness of the blend are affected by the ratio of the polymer components (Kadir et al., 2010; Kadir, Teo, Majid, & Arof, 2009; Shibayama, Uenoyama, Oura, Nomura, & Iwamoto, 1995). This is because the presence of an amorphous component affects the crystallization process of the other polymer component (Pereira, Paulino, Rubira, & Muniz, 2010). Report by Sasaki, Bala, Yoshida, and Ito (1995) shows that the increasing PMMA concentration causes the rate of PVdF crystallization to decrease. Kadir et al. (2009) reported that the crystallinity of PEO decreases as chitosan content increases to 60 wt.% in the chitosan-PEO blend. Ramly et al. (2011) reported that starch-PEO blend with a ratio of 7:3 exhibits the least amount of crystallinity and was chosen in the preparation of polymer electrolyte.

Studies on the structure of starch-chitosan blend revealed that starch and chitosan are miscible to each other (Bourtoom & Chinnan, 2008). Liu, Adhikari, Guo, and Adhikari (2013) reported that the addition of chitosan to starch decreases the crystallinity of the starch film. Report by Xu et al. (2005) showed that the crystalline
peaks of chitosan were suppressed when the starch ratio in the blend film was increased. Based on information obtained from the literature, it is important to determine the appropriate amount of starch and chitosan to serve as the polymer host.

### 4.2 XRD Analysis

The XRD results are shown in Figure 4.1.

![Figure 4.1: XRD patterns of various starch-chitosan blend films.](image-url)
From the X-ray diffractogram of S10C0 film, three strong diffraction peaks appear at $2\theta = 17.1^\circ$, $19.1^\circ$ and $23^\circ$, corresponding to crystalline region of starch (Zhai et al., 2004). These crystalline peaks are observed to superimpose on a broad amorphous background. This result demonstrates that the film shows two phase morphology i.e. crystalline and amorphous states, proving that starch is a semi-crystalline material (El-Kader & Ragab, 2013; Liew, Ramesh, Ramesh, & Arof, 2012). In the X-ray diffractogram of S0C10 film, two crystalline peaks appear at $2\theta = 16.3^\circ$ and $23^\circ$. In the work reported by Aziz et al. (2012), the crystalline peaks of chitosan are observed at $2\theta = 16.5^\circ$ and $22.5^\circ$, which are comparable with the present result. The XRD patterns of S10C0 and S0C10 films were used as references to see any changes in pattern or peaks position in the diffractogram of starch-chitosan blend films. In the diffractogram of S8C2 film, the crystalline peaks seem to be suppressed by a broad amorphous peak centered at $2\theta = 20.3^\circ$. This result demonstrates the good miscibility and interaction between starch and chitosan. The interaction may occur through hydrogen bonding between hydroxyl groups of starch and hydroxyl and/or amine groups of chitosan. X-ray diffractogram of S6C4 film consists of a diffraction peak centered at $2\theta = 20.6^\circ$, but with a narrower XRD hump than S8C2 film, indicating that the amorphous phase of S6C4 is lesser than S8C2 film. According to a report by Salleh et al. (2009), chitosan structure is not influenced by the addition of starch when the chitosan content is higher than starch content in the blend. The similar phenomenon can be observed in the present work as XRD pattern of S4C6 film is almost similar to XRD pattern of S0C10 film. New crystalline peaks are observed in the X-ray diffractogram of S2C8 film at $2\theta = 9.4^\circ$, $11.8^\circ$ and $25.5^\circ$. This phenomenon indicates that the crystallinity of S2C8 film is higher than S0C10 film.
To confirm the amorphousness of the blend films, the degree of crystallinity ($\chi_c$) of each film is investigated by using two approaches. Firstly, Nara-Komiya method (Nara & Komiya, 1983) has been used. Nara-Komiya method is a technique to analyze the X-ray diffractograms by separating the crystalline and amorphous portions using a line. In this work, the investigation of the degree of crystallinity using Nara-Komiya method is focused in the region of $5^\circ \leq 2\theta \leq 50^\circ$ where crystalline and amorphous phases of starch, chitosan and starch-chitosan blends can be observed (Liew et al., 2012; Salleh et al., 2009). A baseline curve was drawn beginning from $2\theta = 5^\circ$ to $2\theta = 50^\circ$ by

**Figure 4.2:** XRD pattern of S0C10 film.

**Figure 4.3:** XRD pattern of S4C6 film.
joining together the minimum intensities corresponding to the crystalline peaks. The area above the baseline curve is corresponded to crystalline region while area below the baseline curve is corresponded to amorphous region (Nara & Komiya, 1983; Noor et al., 2013). Figures 4.2 to 4.5 show the analysis of selected starch-chitosan blend films using Nara-Komiya method. The degree of crystallinity was then calculated by using the following equation:

\[
\chi_c = \frac{A_T - A_a}{A_T} \times 100\% 
\]  

(4.1)

Figure 4.4: XRD pattern of S8C2 film.

Figure 4.5: XRD pattern of S10C0 film.
Here, \( A_a \) and \( A_T \) are the areas of amorphous and total humps, respectively. The areas of amorphous and total humps have been calculated using the OriginPro 9.0 software. The degree of crystallinity values estimated by Nara-Komiya method are tabulated in Table 4.1. The degree of crystallinity of S8C2 film is the lowest, confirming this blend as the most amorphous.

**Table 4.1:** Degree of crystallinity of starch-chitosan blend films using Nara-Komiya method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \chi_c ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10C0</td>
<td>38.93</td>
</tr>
<tr>
<td>S9C1</td>
<td>35.07</td>
</tr>
<tr>
<td>S8C2</td>
<td>26.31</td>
</tr>
<tr>
<td>S7C3</td>
<td>29.81</td>
</tr>
<tr>
<td>S6C4</td>
<td>28.67</td>
</tr>
<tr>
<td>S5C5</td>
<td>29.30</td>
</tr>
<tr>
<td>S4C6</td>
<td>30.00</td>
</tr>
<tr>
<td>S3C7</td>
<td>32.94</td>
</tr>
<tr>
<td>S2C8</td>
<td>36.82</td>
</tr>
<tr>
<td>S1C9</td>
<td>29.44</td>
</tr>
<tr>
<td>S0C10</td>
<td>33.72</td>
</tr>
</tbody>
</table>

In an XRD pattern, overlapping of peaks can occur e.g. crystalline peaks superimposed on the amorphous humps. In order to separate the overlapping patterns, the XRD diffractograms were deconvoluted using the OriginPro 9.0 software. One of the advantages of this method is that the diffraction peaks can be separated from the continuous scattering background. Baseline correction was done prior to fitting multi-peaks using Gaussian distribution. The sharp, narrow and small peaks indicate crystalline peaks while broad peaks indicate amorphous regions. The area under the
deconvoluted peaks was used to calculate the degree of crystallinity using Equation (4.1).

Figure 4.6 shows the result of deconvolution on XRD pattern of S0C10 film. Instead of two, there are three crystalline peaks appear in the diffractogram at $2\theta = 15.5^\circ$, $18.1^\circ$ and $21.9^\circ$. It is revealed that there are two broad amorphous peaks centered at $2\theta = 17.7^\circ$ and $38.1^\circ$. The present results are comparable with the reports from literature (Aziz, 2012; Buraidah, 2012; Fadzallah, Majid, Careem, & Arof, 2014; Hassan, Woo, Aziz, Kufian, & Majid, 2013).

![Figure 4.6: Deconvoluted XRD pattern of S0C10 film.](image)

![Figure 4.7: Deconvoluted XRD pattern of S10C0 film.](image)
The result of deconvolution on XRD pattern of S10C0 film is represented in Figure 4.7. It can be observed that the diffractogram consists of four crystalline peaks at $2\theta = 15.8^\circ$, $20.1^\circ$, $22.5^\circ$ and $24.0^\circ$ and two broad amorphous peaks centered at $2\theta = 18.6^\circ$ and $36.4^\circ$.

Figures 4.8 to 4.11 show the results of deconvolution of selected starch-chitosan blend films. It is observed that the crystalline peaks in the XRD pattern of S8C2 film are less sharp and less intense compared to the other blends.

![Deconvoluted XRD pattern of S1C9 film.](image)

**Figure 4.8:** Deconvoluted XRD pattern of S1C9 film.

![Deconvoluted XRD pattern of S3C7 film.](image)

**Figure 4.9:** Deconvoluted XRD pattern of S3C7 film.
From Figures 4.6 and 4.7, the deconvoluted XRD patterns for S0C10 and S10C0 films reveal the existence of two broad amorphous peaks. These amorphous peaks are observed in the diffractograms of starch-chitosan blend films regardless of starch:chitosan ratio as shown in Figures 4.8 to 4.11. By knowing the area under the deconvoluted peaks, the degree of crystallinity of the films have been calculated and showed in Table 4.2. It is observed that by using the deconvolution method, S8C2 film is still the most amorphous blend with the least degree of crystallinity that strengthen the fact that this sample is the most suitable to be chosen as polymer host.
Table 4.2: Degree of crystallinity of starch-chitosan blend films using deconvolution method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10C0</td>
<td>20.53</td>
</tr>
<tr>
<td>S9C1</td>
<td>18.66</td>
</tr>
<tr>
<td>S8C2</td>
<td>12.05</td>
</tr>
<tr>
<td>S7C3</td>
<td>16.04</td>
</tr>
<tr>
<td>S6C4</td>
<td>13.13</td>
</tr>
<tr>
<td>S5C5</td>
<td>13.66</td>
</tr>
<tr>
<td>S4C6</td>
<td>15.35</td>
</tr>
<tr>
<td>S3C7</td>
<td>15.42</td>
</tr>
<tr>
<td>S2C8</td>
<td>18.68</td>
</tr>
<tr>
<td>S1C9</td>
<td>17.12</td>
</tr>
<tr>
<td>S0C10</td>
<td>18.09</td>
</tr>
</tbody>
</table>

4.3 Miscibility Studies

4.3.1 SEM Analysis

Figure 4.12: Surface micrograph of S10C0 film.
SEM analysis is one of the techniques to study the miscibility between the components in a polymer blend. The miscibility can be implied from the smooth and homogenous surface of the blend film (Kadir, 2010). The surface micrograph of S10C0 film is shown in Figure 4.12. It is observed that the micrograph of S10C0 film exhibits characteristic patterns on the surface. These patterns represent the withered ghost granules of starch (Salleh et al., 2009). These ghosts were formed during the gelatinization process where the external layers of starch granules form granule envelopes which degrade into ghost remnants (Atkin, Abeysekera, & Robards, 1998).

In Figure 4.13, the micrograph of S0C10 film shows a smooth and homogenous surface. The same observation on pure chitosan film has been reported in the literature (Chen et al., 2009).

![Surface micrograph of S0C10 film](image)

**Figure 4.13:** Surface micrograph of S0C10 film.

Figure 4.14 depicts the SEM micrograph of S9C1 film. The surface is observed to have a rough structure. This observation indicates partial immiscibility of the
polymers, as reported in other polymer blend systems (Rotta, Minatti, & Barreto, 2011; Yin, Luo, Chen, & Khutoryanskiy, 2006).

Figure 4.14: Surface micrograph of S9C1 film.

Figure 4.15: Surface micrograph of S8C2 film.

Figure 4.15 depicts the SEM micrograph of S8C2 film. It is observed that the surface is homogeneous without phase separation, suggesting that 80 wt.% starch and
20 wt.% chitosan are miscible to each other. The same type of micrograph can be seen for other blend films as shown in Figures 4.16-4.19. The present observation is quite similar to a report by Jayaprakash, Kumar, Sreenivasa, Mohan, and Shashidar (2013) for potato starch-chitosan blend.

**Figure 4.16:** Surface micrograph of S5C5 film.

**Figure 4.17:** Surface micrograph of S4C6 film.
4.3.2 DSC Analysis

Thermal characterization of polymer blends is a well established method for determining the miscibility of polymer blends. Thus, to further confirm the miscibility
between starch and chitosan in S8C2 film, DSC measurements on S10C0, S0C10 and S8C2 films were carried out. In DSC technique, if the blend shows two transitions, it means that there is phase separation and the polymer components are immiscible to each other (Chiou et al., 2014; Kok, Demirelli, & Aydogdu, 2008). If the polymer components are miscible to each other, only one transition will be observed (Chiou et al., 2014).

Figures 4.20 to 4.22 show the DSC curves of S10C0, S0C10 and S8C2 films, respectively. The $T_g$ value for S10C0 and S0C10 films are found to be 67.21 °C and 97.41 °C, respectively. These results are close to the values reported by Liu, Yu, Liu, Chen, and Li (2009) and Cheung, Wan, and Yu (as cited in Correia, Caridade, & Mano, 2014). Only one $T_g$ value is observed for S8C2 film, which is found to fall in between the $T_g$ values of S10C0 and S0C10 films, at 82.33 °C. The DSC results confirm the miscibility between starch and chitosan in S8C2 film.

**Figure 4.20:** DSC thermogram of S10C0 film.
Figure 4.21: DSC thermogram of S0C10 film.

Figure 4.22: DSC thermogram of S8C2 film.
4.4 TGA Analysis

To study the effect of polymer blending on thermal stability, TGA measurements of S10C0, S0C10 and S8C2 films were carried out. Figure 4.23 shows the TGA thermograms of S10C0, S0C10 and S8C2 films.

![TGA thermograms of S10C0, S0C10 and S8C2 films.](image)

**Figure 4.23:** TGA thermograms of S10C0, S0C10 and S8C2 films.

From Figure 4.23, both S10C0 and S0C10 films exhibit first weight loss in between room temperature to 160 °C due to loss of water. In this region, S0C10 film exhibits ~ 10% weight loss, while S10C0 film exhibits ~ 12% weight loss. Major decomposition of S0C10 film occurs at 270 °C with a weight loss of ~ 30%. The second weight loss of ~ 58% for S10C0 film starts at 280 °C. Ramesh, Shanti, and Morris (2012) reported that pure corn starch undergoes one-step weight loss process with the
decomposition temperature of 280 °C, which is similar as the present result. The glucose monomers that initially built up the corn starch tend to detach from the long polymer chain and subsequent heating beyond the decomposition temperature results in carbonization and ash formation (Ramesh et al., 2012). Since pure starch has high moisture sensitivity, blending starch with other polymers is one of the methods to overcome the problem (Lu et al., 2009). From the thermogram of S8C2 film, a weight loss of ~ 6% from room temperature to 160 °C is observed. This result shows that the water content of starch is decreased by blending starch with chitosan. The decomposition temperature does not change on blending starch with chitosan, as S8C2 film decomposes at 270 °C.

4.5 Summary

The suitable ratio of starch-chitosan blend to serve as polymer host has been examined using XRD analysis where the blend of 80 wt.% starch and 20 wt.% chitosan is the most amorphous blend. SEM analysis confirmed that starch and chitosan is miscible to one another by forming homogenous films. Further confirmation of starch-chitosan miscibility has been made to the blend of 80 wt.% starch and 20 wt.% chitosan by DSC. Blending 80 wt.% starch with 20 wt.% chitosan has decreased the water content of the film as shown in TGA thermograms. Thus, the blend of 80 wt.% starch and 20 wt.% chitosan has been chosen as the polymer host for further characterization.