CHAPTER 4 RESULTS AND DISCUSSIONS

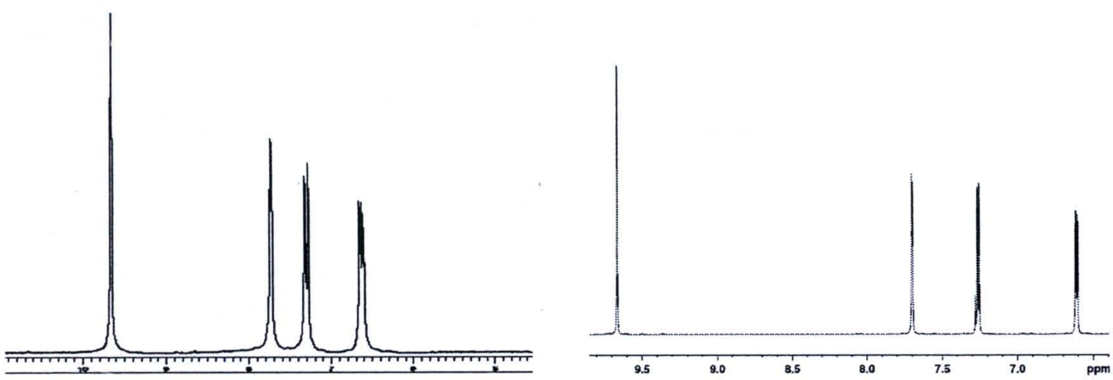
The results of the furfural-urea complex synthesis with different methods are presented in this chapter. Moreover, furfural in the laboratory is also characterized to determine the impurities before being used in this experiment. To verify the product, some techniques are required to characterize the product including NMR spectroscopy, TGA/DSC. In addition, the properties of furfural-urea complex imbedded within a biodegradable polymer are also characterized by using FT-IR and UV-vis spectrometer.

4.1 The synthesis of furfural-urea complex

The furfural-urea complex is synthesized in homogeneous phase with different methods to obtain the product with low impurities. There are two characterization techniques used to determine the product properties including NMR spectroscopy and TGA/DSC.

4.1.1 Characteristics of furfural and urea raw materials

In this research, proton NMR is considered as one of analysis techniques. The synthesized furfural-urea complex is examined by NMR spectrometer with 300 Mz frequency in dimethyl sulfoxide (DMSO) solvent. The NMR signals of DMSO are 2.5 ppm and 3.3 ppm [29]. Initially, pure furfural was characterized in order to determine the furfural impurities. The NMR result of furfural available in laboratory is in agreement with the furfural NMR spectrum from the experiment in published paper [30] due to the same frequency band and relative area under the peak. The result is shown in Figure 4.1.



Published paper Laboratory

Figure 4.1 Comparison of NMR spectra of furfural between laboratory and published paper [30]

After the furfural available in the laboratory was tested, the result shows that it can be used in the experiment without any purification process because there was no significant difference between both furfurals.

Purity and thermal stabilities of urea were characterized by TGA/DSC technique. To conduct this experiment, 30 mg of urea was placed on the alumina pan and then the sample was heated by the furnace with constant heating rate. The thermal stability of urea is shown in Figure 4.2. From the TGA curve, no mass loss is observed below 140°C. Therefore, urea is stable till 140°C.

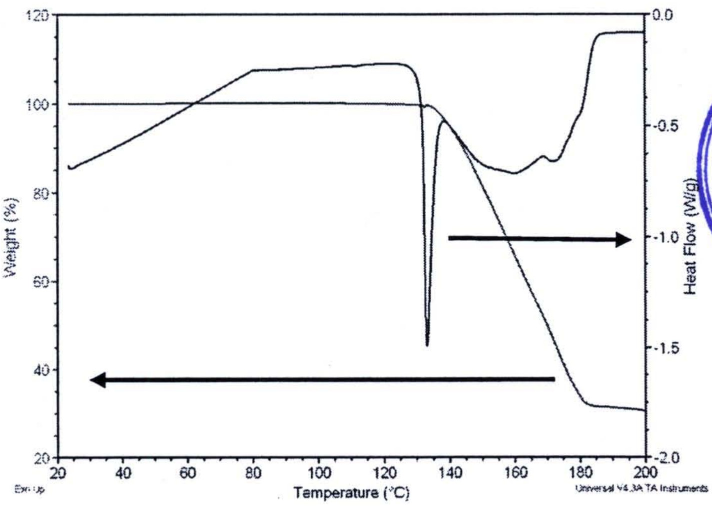


Figure 4.2 TGA/DSC curves of urea

4.1.2 Effect of Synthesis parameters on furfural-urea complex

The expected product of the combination of furfural and urea is difurfurilidentriurea or DFTU which undergoes under reversible reaction with incorporating acid as shown in Figure 3.2

To synthesize the furfural-urea complex, 2 to 1 ratio of urea to furfural is chosen. 1.2 g of urea was dissolved in 4 milliliters of water. After urea was completely dissolved, 0.83 milliliters of furfural was added into the solution. When the solution was mixed together, 0.024 milliliters of HCl was incorporated into the solution. The sample was then filtrated by vacuum filtration after a period of time. At this point, water was also added to wash the sample. Finally, the sample was dried to remove the remaining water. The expected NMR chemical shift or signal of product known as difurfurilidentriurea (DFTU) recorded in DMSO solvent is shown in the Figure 4.3.

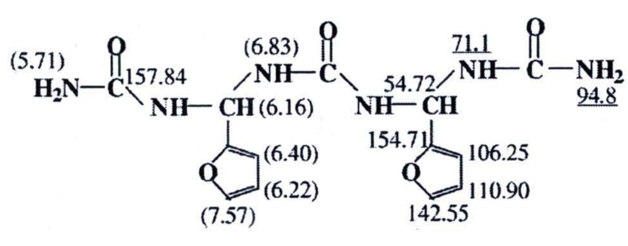


Figure 4.3 Proton and Carbon Chemical shift of the difurfurilidentriurea (DFTU).

- Drying Process

There are many factors affecting the product properties. The first considered factor is the drying process. Two different drying processes, oven and vacuum dryer, are compared in this section. The NMR results from the sample that was dried by conventional oven and that by the vacuum dryer are shown in Figure 4.4. The proton NMR signals are observed at 2.5 ppm and 3.3 ppm for DMSO solvent while the NMR signals of DFTU product are observed in the range between 5.7 ppm and 8 ppm. NMR signals at 5.71 ppm are corresponding to primary amine that is located at the edge of the DFTU molecule. Secondary amine shows the frequency band at 6.83 ppm. The frequency bands of furan ring appear at 6.22 ppm, 6.40 ppm, and 7.57 ppm.

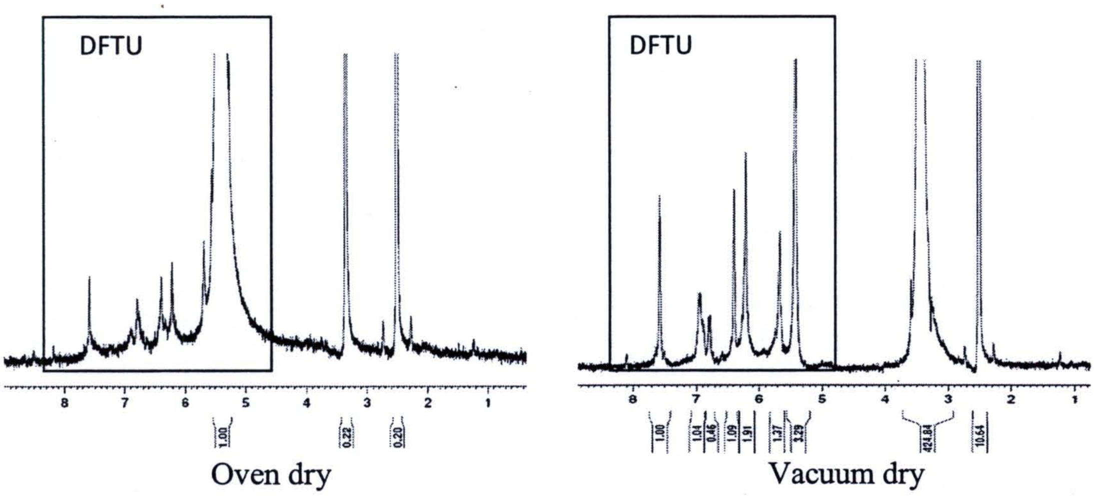


Figure 4.4 NMR spectra of samples dried in conventional oven and vacuum dryer

The result from Figure 4.4 implies that the sample which was dried through vacuum dryer having a higher portion of product compared to the sample dried by conventional oven, as can be seen by the higher ratio of product NMR peaks. Therefore, the vacuum dry is selected as a dryer method. However, the large ratio of peak occurred at 5.5 ppm frequency which is referred to the urea signal is observed. This means that there is a lot of urea in the product that needs to be eliminated.

-Reaction time

The reaction time after HCl was incorporated is then considered. Reaction time is counted after the white solid begins to precipitate. Samples at different reaction times which are at time zero, after 1 hr, after 1 day and after 4 days were taken for analysis. From the experiments, white solid was precipitated after adding HCl for half an hour. According to Figure 4.5, the results reveal that reaction time does not affect the molecular structure of the product under 1 day of reaction time. If the reaction time is too long, other byproduct with NMR signal at frequency above 8 ppm will be generated. Therefore, the 2 hours of reaction time is chosen. In addition, the time that white solid begins to precipitate is approximately 30 minutes. Therefore, the reaction will stop at

2.5 hour after HCl is incorporated. Furthermore, the furfural conversion of longer of mixing time after incorporating HCl acid is higher than that of shorter mixing time.

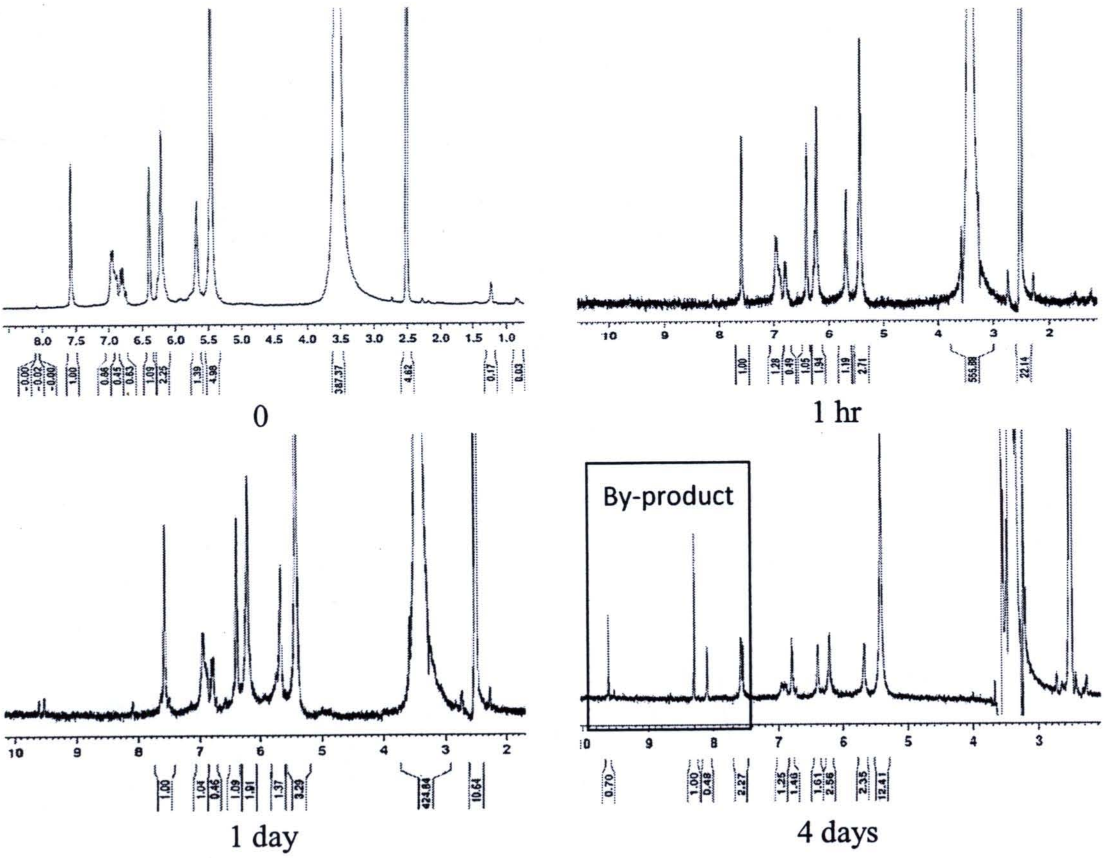


Figure 4.5 NMR spectra of samples with different reaction times after adding HCl

-Amount of washing water

To decrease the amount of urea in the product, additional water used to wash the sample during vacuum filtration is required as much as possible. In this study, 10 times of water was added to wash the sample. The results shown in Figure 4.6 can confirm that larger amount of water can reduce the amount of urea in product as can be seen by the decrease in relative area under the peak at 5.5 ppm from 3.3 to 0.34.

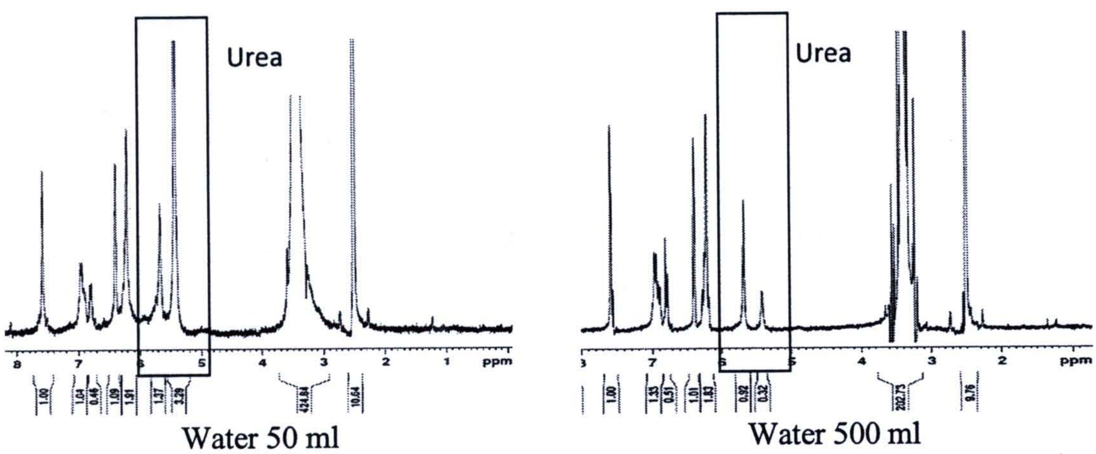


Figure 4.6 NMR spectra of samples with different amounts of water addition

-The presence of HCl acid

Acid catalyst is one factor that affects the product properties. In this study, HCl is used as acid catalyst. Synthesis procedure without any HCl acid incorporation is compared to the one with 0.024 ml of 6 molar of acid. Sample without acid incorporation was taken for analysis after 1 day of reaction time while the sample with HCl incorporation was analyzed after 2 hours after adding HCl acid. The results shown in Figure 4.7 reveal that there is not significant distinct between both samples. The presence of HCl acid can accelerate the synthesis procedure.

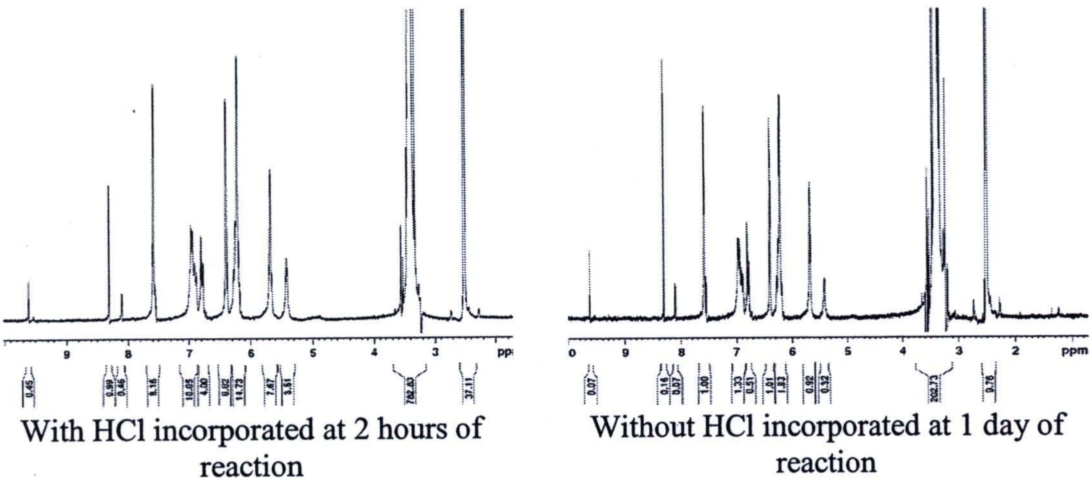


Figure 4.7 NMR spectra of samples with and without HCl acid

-Amount of HCl acid addition

If the HCl acid is used as catalyst, there is a question that how much of catalyst that needs to be incorporated into the sample. Therefore, the effect of acid concentration is studied by varying acid concentration to 0.072and 0.12 ml of 6 M of HCl acid, while the normal concentration is 0.024 ml of 6M. The NMR signals in Figure 4.8 show that the greater concentration of HCL acid incorporated, the higher the impurities as indicated by the signals above 8 ppm. Therefore, the suitable HCl acid concentration is 0.024 ml of 6 M. In addition, the greater amount of HCl acid leads to higher furfural conversion as well.

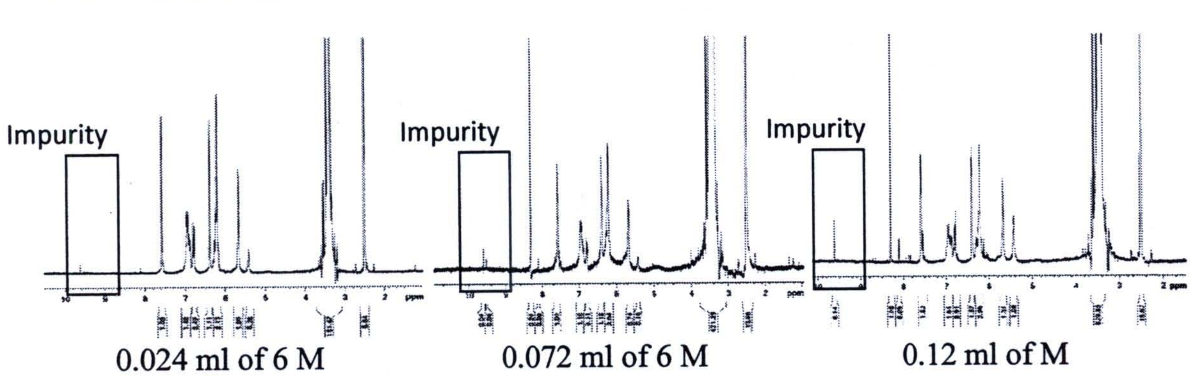


Figure 4.8 NMR spectra of samples with different HCl acid concentrations

-Furfural-urea mixing time

According to the synthesis procedure, HCl acid will be incorporated after urea and furfural are mixed together. Typically, almost 2 hours are taken for both of them to become homogeneous. At this point, mixing time of urea and furfural was reduced to avoid the impurities from the side reaction. Figure 4.9 shows the NMR spectra at different mixing times after urea and furfural are mixed. The results show that only 15 minutes of mixing time is enough. Longer mixing time leads to the increase in side reaction which other byproducts will be generated. Moreover, the conversion of furfural is increased by increasing the mixing time of furfural and urea.

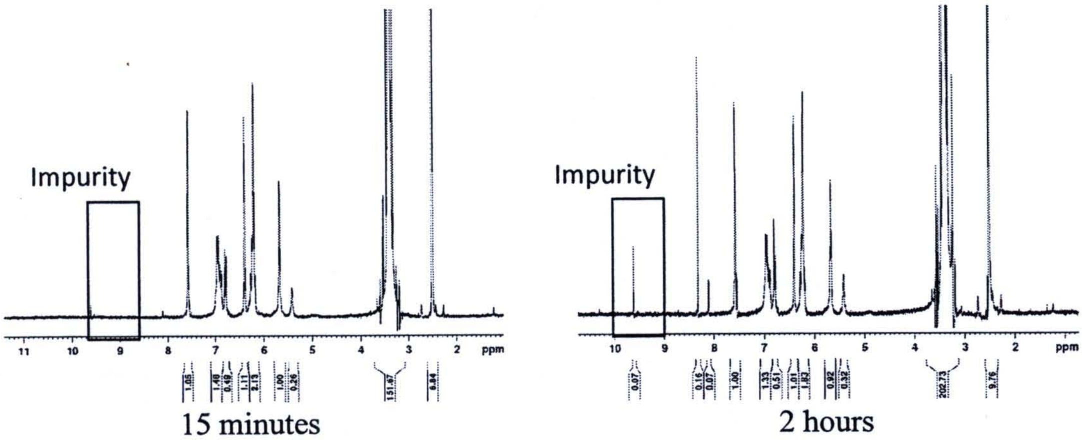


Figure 4.9 NMR spectra of samples with different mixing times of urea and furfural

According to the factors mentioned above, furfural conversion achieved by the synthesis method with low impurities is around 30-40 %.

4.1.3 Characteristics of Furfural-urea complex

After performing all the above experiments, the suitable synthesis procedure of furfural-urea complex is achieved by considering the effect of each parameter. The synthesis begins with dissolving 1.2 g of urea in 4 ml of water. After 5 minutes or until urea is completely dissolved, 0.83 milliliters of furfural is added into the solution. The solution is stirred for 15 minutes before adding 0.024 milliliters of 6M HCl. After HCl is incorporated into the sample, the reaction starts and stays for 2 hours with continuous stirring. The sample is then filtrated by vacuum filtration and washed with 500 milliliters of water. Finally, the sample is dried in a vacuum dryer for 2 days to remove the remaining water. This procedure will result in the sample corresponding to Figure 4.9 with 15 minutes of mixing time of urea and furfural.

Since the relative area under the peak can be used to identify the portion of proton in each location, the molecular structure of the sample displayed in Figure 4.9 agrees well with the DFTU molecular structure. Urea peak at 5.5 ppm has small proportion of relative area under the peak compared to other peaks. Primary amine which could be represented by the peak at 6.8 ppm has the highest proportion of relative area since there are 4 hydrogen atoms located in the molecule of primary amine, while there are only 2 other hydrogen atoms in each location. However, high proportion of relative area occurs at 6.1 ppm which represents C-H bond. This means that the edge of the structure may contain other C-H bonds resulted from a longer chain product. The continuous reactions lead to undesired products. Three to 2 ratio of urea to furan rings are considered as the desired product, DFTU. However, the synthesized product can have more or less urea and furan rings than DFTU product. The number of urea and furan rings results in the different proton chemical shift. This can be concluded that the peak upper than 8 ppm represents the chemical shift of urea and furan ring at different location.

The complex of urea and furfural was also characterized by using TGA/DSC to determine the thermal stability of the synthesized product. The experiment was conducted from room temperature until 200°C with 1°C/min of heating rate in nitrogen atmosphere. The initial weight of furfural-urea complex is 2.185 mg. Thermal analysis of the complex is shown in Figure. 4.10. Initial weight loss of about 5% in the region of 50–100°C is due to the evaporation of crystallized water in the sample. This means that the vacuum dryer cannot totally eliminate water in that period of time. Two well defined endothermic peaks are seen in the DSC curve at 25 and 200°C. The first one corresponds to a 5% weight loss, and the second DSC peak is associated with about 55% of weight loss. Similar thermal behavior was reported by Martinez [4] for the furfural and urea condensation compound difurfuralidinetriurea as well, where the two corresponding DSC peaks were found at 35°C and 210°C accompanying 10 and 40% weight losses, respectively.

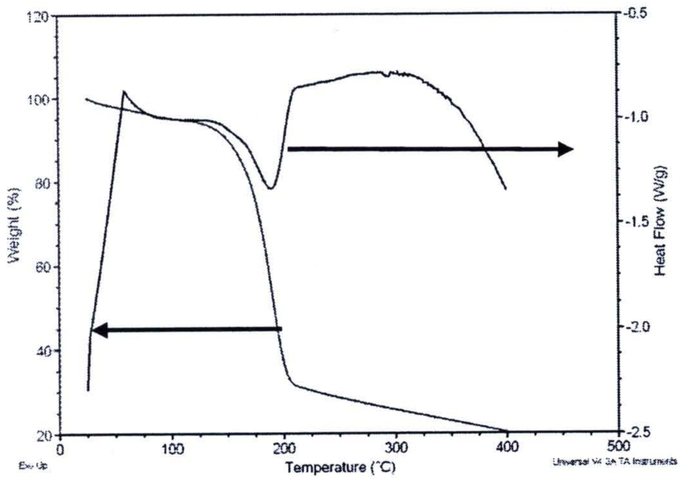


Figure 4.10 TGA/DSC curves of furfural-urea complex

Furfural and urea complex was also characterized by using ATR technique. ATR is used instead of FT-IR because the furfural-urea complex is a fine powder which is difficult to do the transmission. According to Figure 4.11, the ATR spectrum of furfural-urea complex shows the frequency at 3630 cm^{-1} which corresponds to O-H bond. This hydrogen bond is due to the bonding between the remaining water in the complex. The frequency bands at 3210 and 2950 cm^{-1}are assigned to the N-H and C-H absorption, respectively, whereas the corresponding absorptions for urea are observed at 1650 and 1540 cm^{-1}. The furan ring is absorbed at the frequency of 1020 cm^{-1}. Furthermore, the frequency bands at 2326 cm^{-1} show the negative peak of absorption [26].

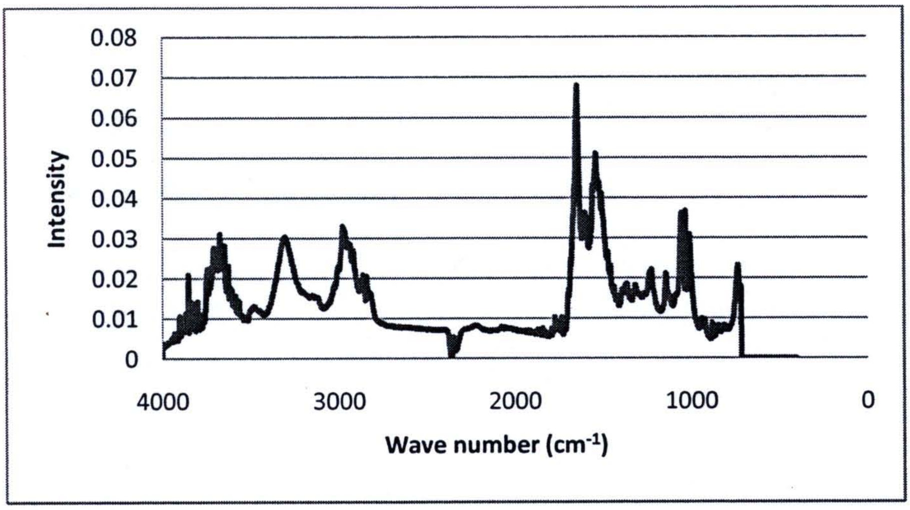


Figure 4.11 ATR spectra of furfural-urea complex

4.2 The characterization of furfural-urea complex imbedded with PBSA characterization

Furfural-urea synthesized complex is then combined with a biodegradable polymer, poly(butylenes succinate-co-butylene adipate) or PBSA. Several techniques including TGA/DSC, FT-IR and ATR are used to characterize the mixture of PBSA polymer and furfural-urea complex which is an additive.

4.2.1 Characteristics of PBSA polymer

Thermal stabilities of the PBSA biodegradable polymer characterized by TGA/DSC is shown in the Figure 4.12. The characterization is conducted from room temperature to 200°C and the heating rate is 1°C/min in nitrogen atmosphere with 32.82 mg of initial polymer weight. In the region of 20–100°C, 0.8% initial weight loss is attributed to water evaporation and also evaporation of some additive in the polymer such as plasticizer. The polymer begins to fall apart after 100°C. Two endothermic peaks are observed from the DSC curve at 30 and 100°C. The first endothermic peak corresponds to a 0.8% weight loss, and the second DSC peak is associated with about further 0.2% of weight loss.

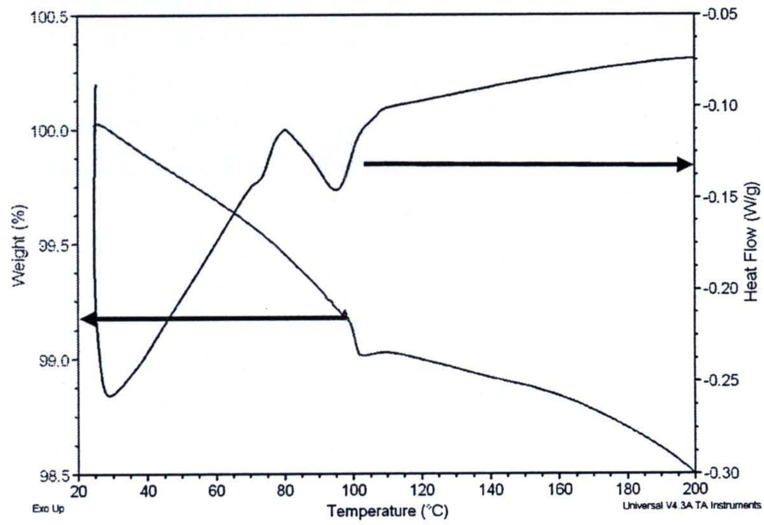


Figure 4.12 TGA/DSC curve of PBSA polymer

According to the TGA/DSC plot, both PBSA polymer and furfural-urea complex (Figure 4.10) are stable only below 100˚C and 140˚C, respectively. This is the key to determine the further conditions in this study to avoid the degradation of these two materials.

PBSA polymer film was then characterized by FT-IR. In Figure 4.13, FT-IR spectrum of the pure PBSA polymer shows a broad band at 2943 cm^{-1}, and is assigned to the C-H absorption. Carbonyl group and C-N bond absorptions of the new resin are found at 1705 and 1350 cm^{-1}, respectively. The frequency bands correspond to C-O are observed at 1243 and 1135 cm^{-1}. Typical furan ring absorption at 1051 cm^{-1} is also observed in the spectrum. Moreover, the C=H absorption is assigned at the frequency of 953cm^{-1}.

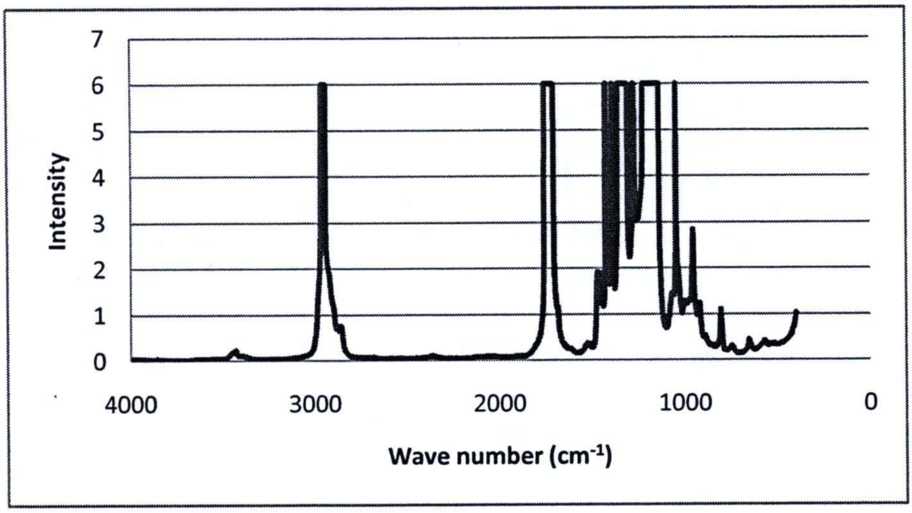


Figure 4.13 FT-IR spectra of PBSA polymer

To produce the extruded film with different thicknesses, the ejecting velocity is focused. The lower velocity results in the thicker extruded film.

'The ATR spectrum of different thicknesses of the extruded film is investigated for the PBSA polymer film. Thicker thickness leads to higher frequency band as shown in Figure 4.14. However, the thickness affects only the intensity, while the wave number of peak is not significantly different. This means that any part of polymer film will provide the same frequency band but difference in intensity depending on the thickness.

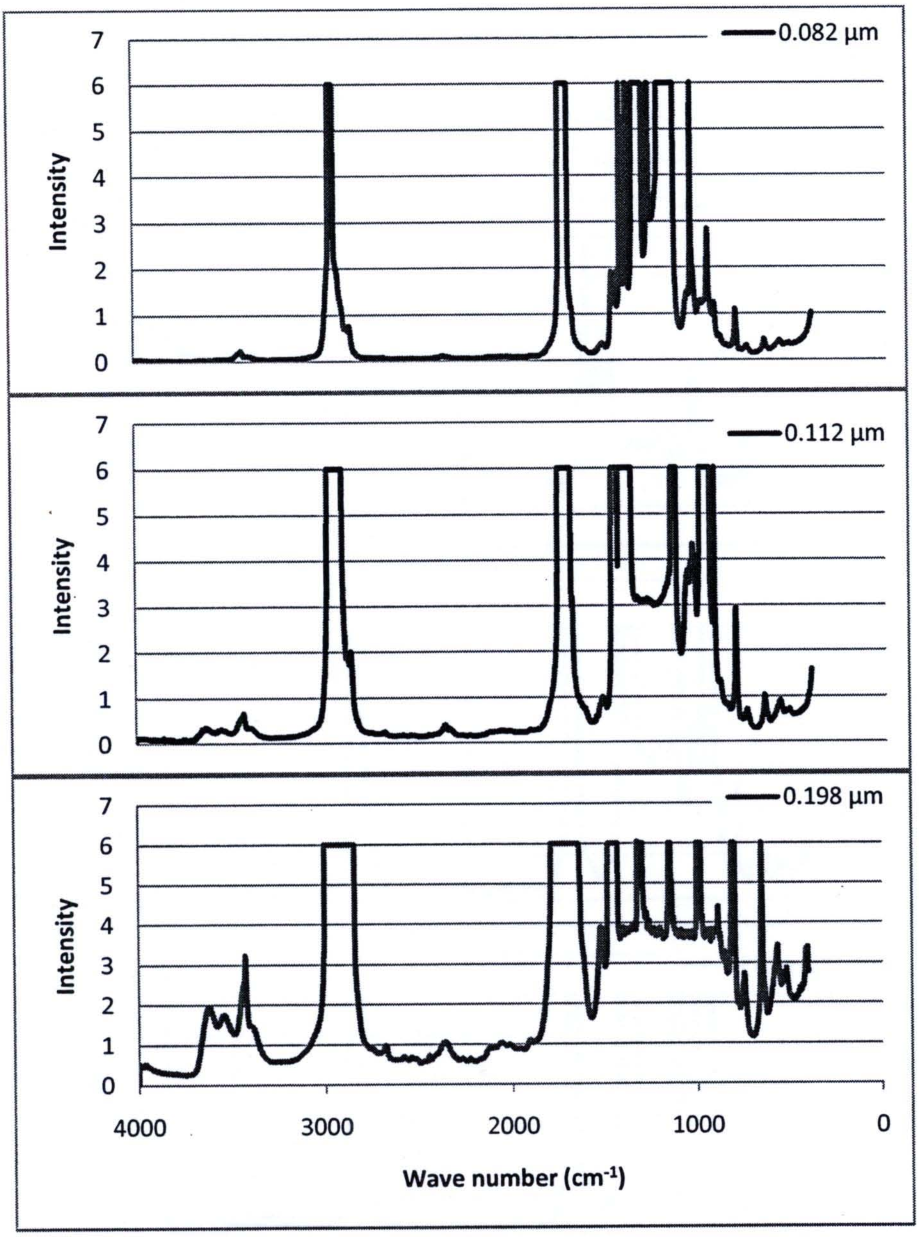


Figure 4.14 FT-IR spectra of PBSA film with different thicknesses

4.2.2 Synthesis of furfural-urea complex imbedded with PBSA polymer

The film production was carried out by extrusion process. The pellets of PBSA biodegradable polymer was incorporated with furfural-urea complex before being extruded via twin screw extruder. The furfural-urea complex is represented as an additive. Five percent of furfural-urea complex was mixed with the PBSA pellets. The extruder was operated at 120°C with 50 screw rotational speeds. After a period of time, the mixture of polymer and furfural-urea complex was removed through a film die. The average thickness of a product film was 0.12 µm.

The FT-IR spectra of furfural-urea complex imbedded with PBSA polymer in comparison with those of pure PBSA polymer and furfural-urea complex are shown in Figure 4.15. The results reveal that most frequency bands from furfural-urea complex are overlap with the PBSA polymer film absorption signals. In addition, there are some signals that can be seen in furfural-urea complex but is not observed in PBSA with an additive. This is probably caused by too low concentration of furfural-urea complex so that the higher concentration will be used in the next section.

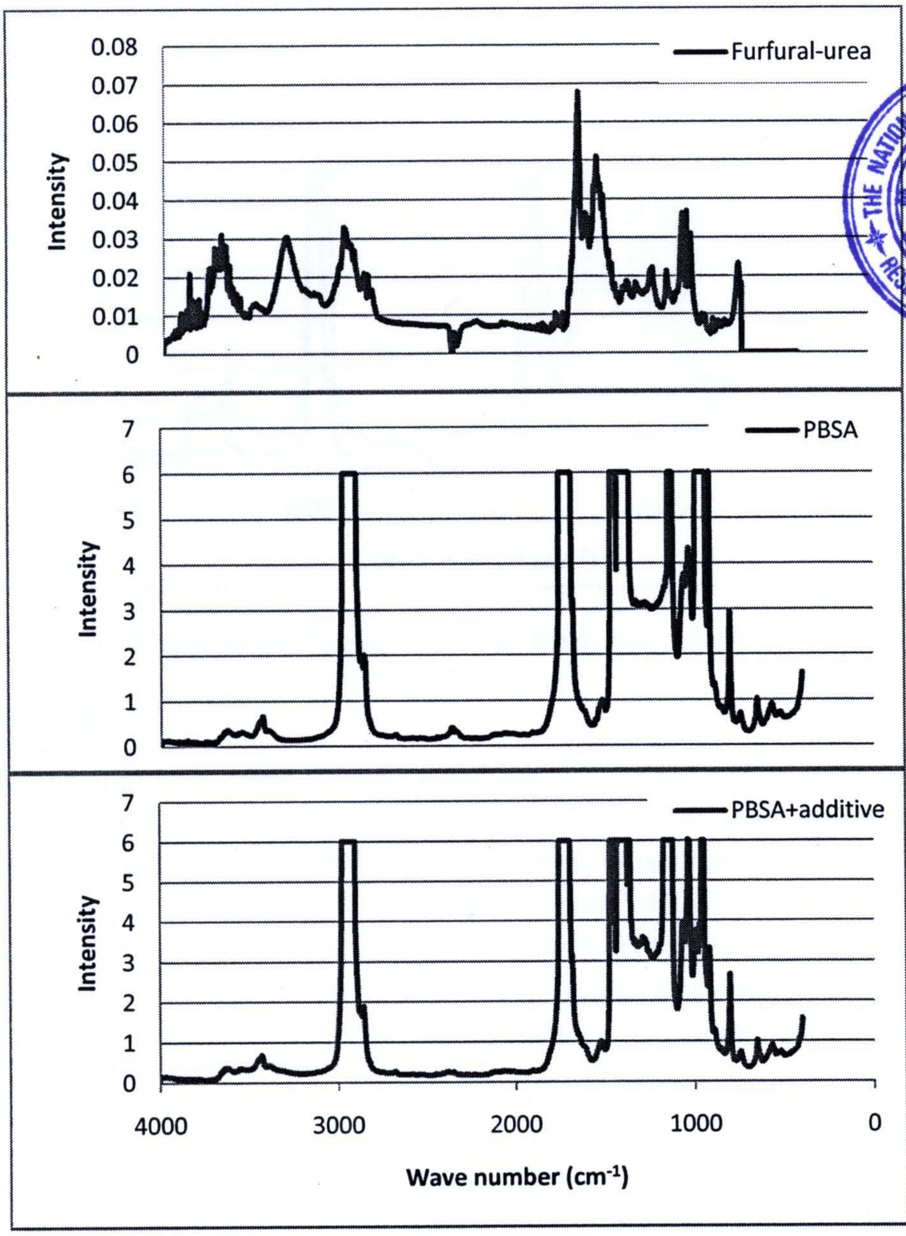


Figure 4.15 FT-IR and ATR spectra of furfural-urea complex, PBSA and PBSA+additive

-Concentration of furfural-urea complex in PBSA polymer

To study the effect of furfural-urea complex concentration, 10% of furfural-urea complex mixed with PBSA polymer pellet was selected to compare with the 5% concentration. The thicknesses of 10% and 5% of furfural-urea complex are 0.131 and 0.124 μm, respectively. The compared result is shown in Figure 4.16. FT-IR frequency bands obtained from 10% and 5% concentration are very similar. The intensity of the 10% furfural-urea complex is slightly greater than that of the 5% furfural-urea complex due to the higher concentration and the thicker thickness. However, the peaks that can be seen in the furfural-urea complex are still dismissed although higher concentration are used. It can be concluded that concentration of furfural-urea complex does not significantly affect the amount of furfural-urea complex occurred on polymer film as can be confirmed by the similar FT-IR frequency bands.

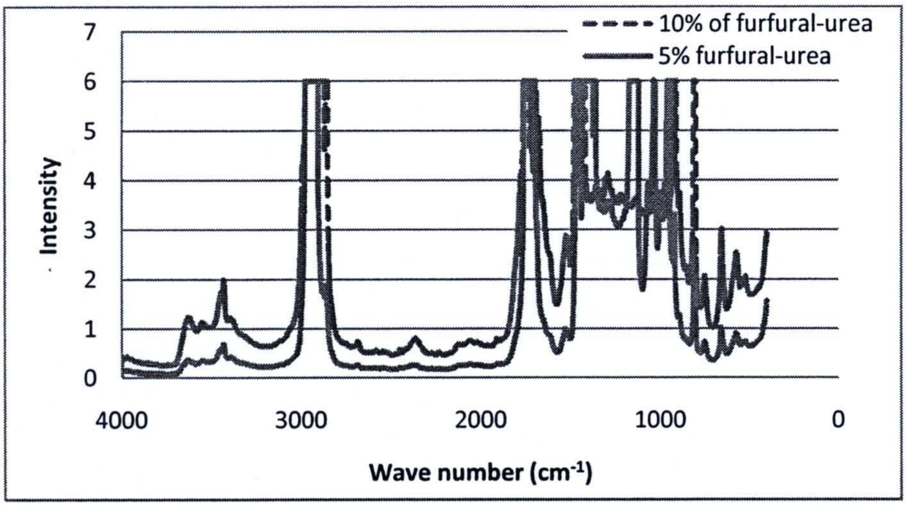


Figure 4.16 FT-IR spectra of 5% and 10% of furfural-urea complex in PBSA polymer

-Solvent Casting

To produce a film with more uniform distribution, solvent casting is selected as the compared method. The highest solubility solvent is required in the solvent casting. Choices of solvents are chloroform, tetrahydrofuran, ethanol and water. All solvents were tested for their solubility of both furfural-urea additive and PBSA polymer. Initially, 5 g of PBSA polymer and 0.05 g of furfural-urea complex were incorporated into 5 ml of each solvent to test the solubility. The results were collected after 1 hour, 2 hours, 1 day and 2 days. The solubility of the complex and polymer in each solvent is shown in Tables 4.1 and 4.2.

Table 4.1 Solubility of furfural-urea complex in different solvents

	1 hour	2 hours	1 day	2 days
Chloroform	None	Partial	Partial	Partial
Tetrahydrofuran	None	None	Partial	Partial
Ethanol	None	None	None	Partial
Water	None	None	None	Partial

Table 4.2 Solubility of PBSA polymer in different solvents

	1 hour	2 hours	1 day	2 days
Chloroform	Partial	Completely	Completely	Completely
Tetrahydrofuran	None	Partial	Partial	Partial
Ethanol	None	None	None	None
Water	None	None	,None	None

From Tables 4.1 and 4.2, chloroform was selected as a solvent for polymer solvent casting as it has the greatest solubility. The mixture of 0.25 g of furfural-urea complex and 5 g of PBSA polymer was incorporated into 5 ml of chloroform solution before continuously stirring for 2 hours. Mechanical agitator was used to stir to break the large particles into smaller ones. Next, the solution was poured into a flat plate and dried for 15 minutes with blower. The polymer imbedded with furfural-urea additive film produced by solvent casting was then characterized by FT-IR. The results of polymer solvent casting film are shown in Figure 4.17 by comparing with the extruded polymer film with 5% of furfural-urea complex.

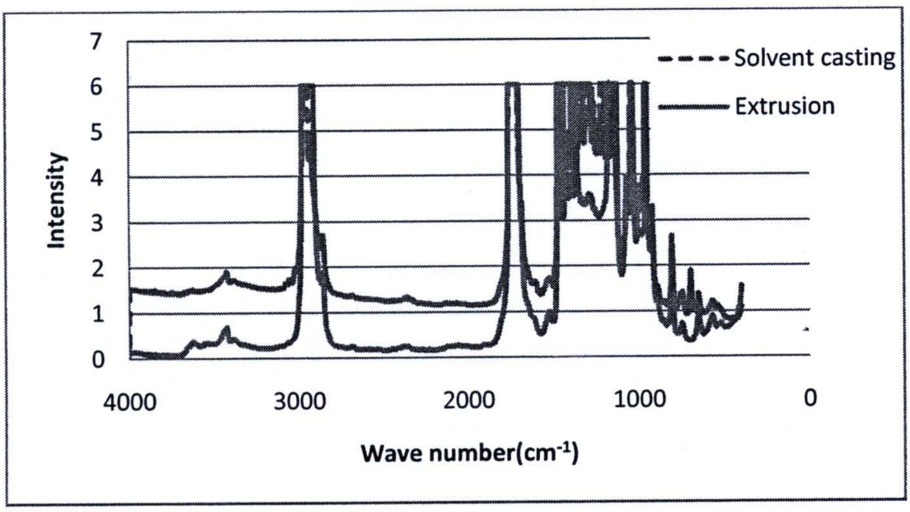
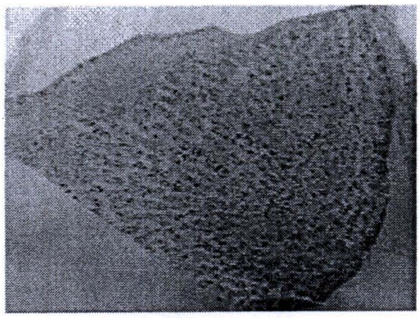
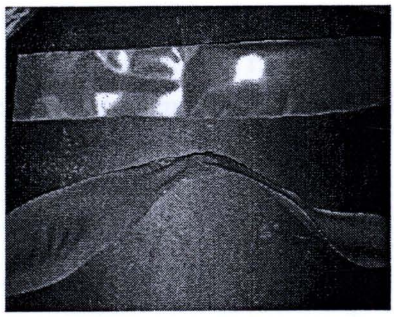


Figure 4.17 FT-IR spectra of extruded and solvent casting film

The FT-IR results obtained from Figure 4.17 show that either extrusion or solvent casting can produce the polymer film with similar FT-IR spectra. The polymer film produced by solvent casting provides greater intensity than extruded film due to the higher concentration of the particles on the polymer film. However, the solvent casting method can produce a film which is more uniform than extruded film as can be seen in Figure 4.18.



Solvent casting film



Extruded film with 5% additive

Figure 4.18 Solvent casting film and extruded film

According to the FT-IR spectrum, either extruded film or solvent casting film can be used in the further study. To study the release rate of this material in water, extruded film was chosen as a sample. The release rate of the furfural-urea complex imbedded into polymer film in water was obtained from the UV-Vis spectrometer. Before measuring the amount of furfural or urea released, the standard curves of those compounds have to be constructed. The calibration curves were constructed for both furfural and urea. To construct the calibration curve, the absorbance ranges of both furfural and urea were determined. The experiment was conducted by dissolving the 36.4 mg of furfural and 33.6 mg of urea in 100 ml of water. The intensity of furfural and urea absorbance versus wavelength of in visible region are shown in Figure 4.19. The visible range is between 400 to 800 nm.

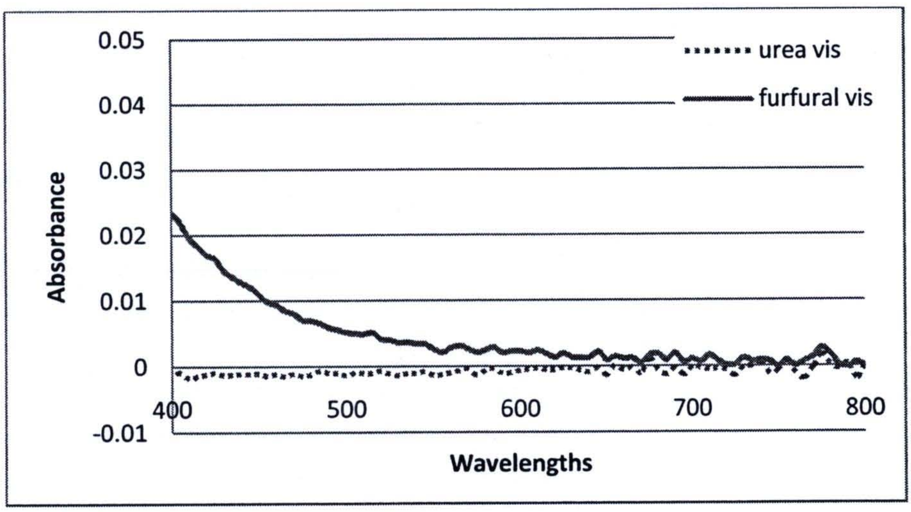


Figure 4.19 Absorption of furfural and urea dissolved in water in visible region

The results obtained in Figure 4.19 describe that only small amount of furfural is absorbed in visible region but none of urea absorbs the light in visible range. Therefore, the samples were tested in the UV region which is between 200 and 400 nm of wavelengths. The results are shown in Figure 4.20.

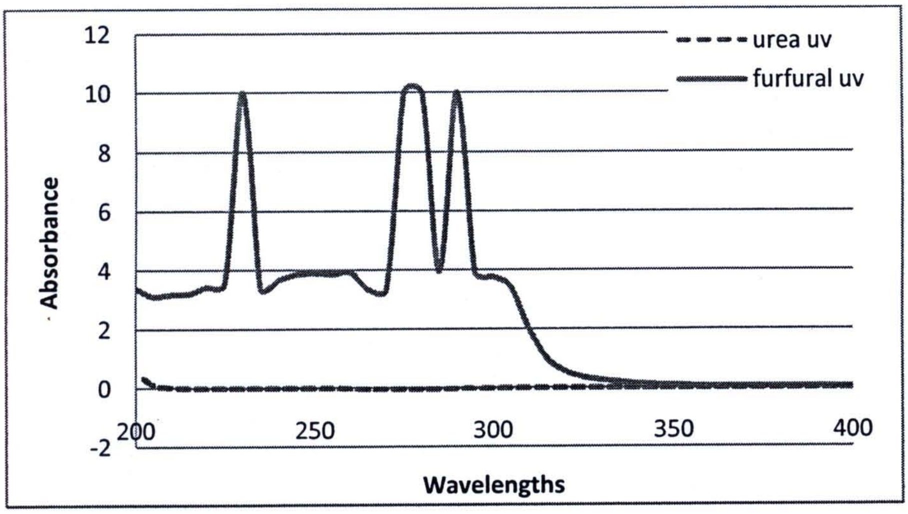


Figure 4.20 Absorption of furfural and urea dissolved in water in UV region

The results in Figures 4.19 and 4.20 show that there is no absorption for urea in either visible or UV region. On the other hand, furfural well absorbs in the UV region. In fact, the release of furfural-urea complex can be determined by measuring the release rate of either furfural or urea because the chemical structure of the complex molecule consists of both furfural and urea structure. Similarly, the release rate of the substance in a polymer complex can be determined by the properties of polymer itself as mentioned in Mogul et al. [24]. Therefore, the release rate of furfural-urea complex on extruded film can be determined by considering only the furfural release rate. Since 3 peaks of furfural absorbance in UV region hit the maximum absorbance that could be recorded by UV-vis spectrometer. In order to determine which wavelength the furfural can absorb the best, the concentration of furfural needs to be decreased to reduce the absorbance of furfural in the UV range. The previous furfural sample was diluted a hundred times and ten thousand times before being tested again. Figure 4.21 shows the absorbance of different furfural concentrations. The best concentration should be 0.364 mg of furfural in 100 ml of water because the maximum absorbance corresponding to 280 nm of wavelength is close to 1.

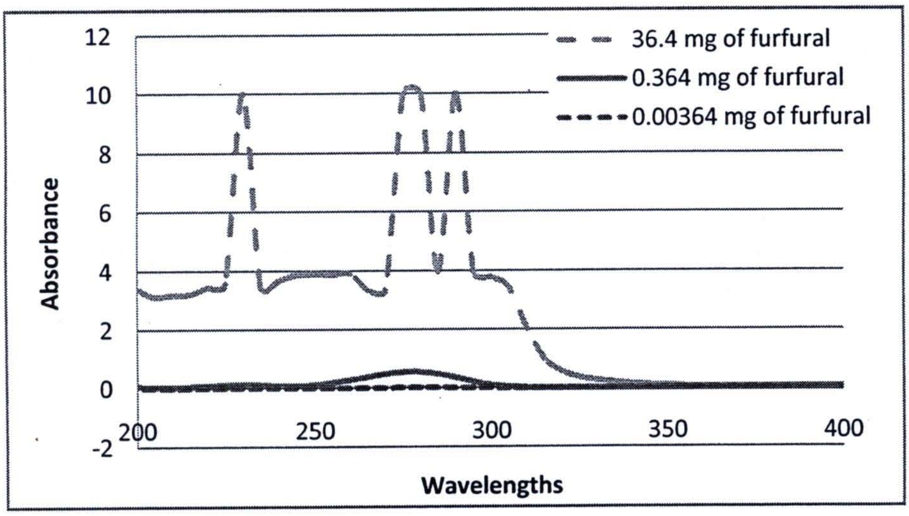


Figure 4.21 Absorption of furfural with different amounts of furfural in 100 ml water

The concentration of a sample in solution can be determined by measuring the absorbance at the maximum wavelength and applying the Beer-Lambert Law.

$$A = ebc$$

The absorbtivity (e) of each unknown sample is constant. Normally, the path length (b) equals to1. Therefore, the absorbtivity can be determined by considering the slope of the absorbance and concentration. To obtain the slope (e), the concentration of the furfural in aqueous solution needs to be varied. The varied concentration is based on 0.36 mg of furfural in 100 ml of water. The absorbances of the lower and higher concentrations are considered to identify the standard curve. The results from different furfural concentrations are shown in Figure 4.22.

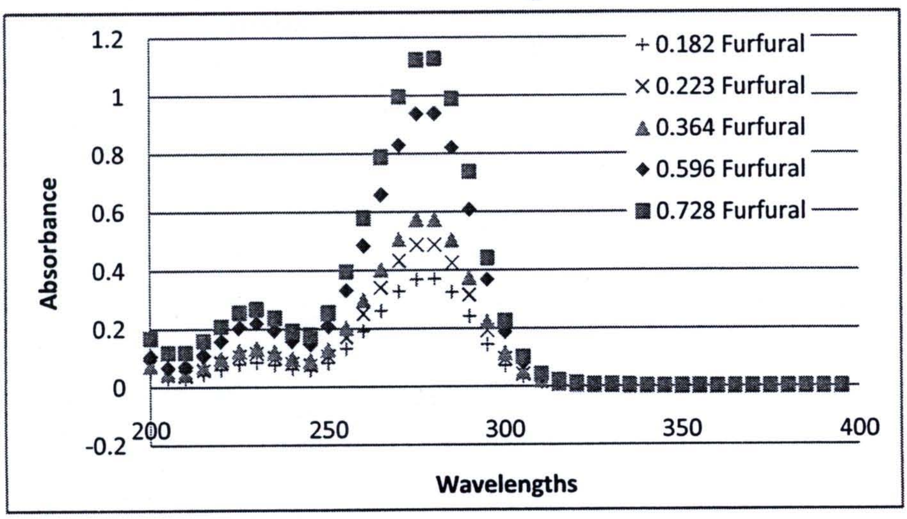


Figure 4.22 Absorption of furfural with different concentrations (mg/1,000 ml water)

According to Figure 4.22, the standard curve for furfural can be plotted. The slope of the concentration and absorbance which can be referred to as absorbtivity can be determined at the highest absorption wavelength. The results from Figure 4.25 show that the maximum absorbance is at 280 nm of wavelength. The relationship between absorbance of furfural and concentration of furfural at the highest absorption wavelength is shown in Figure 4.23.

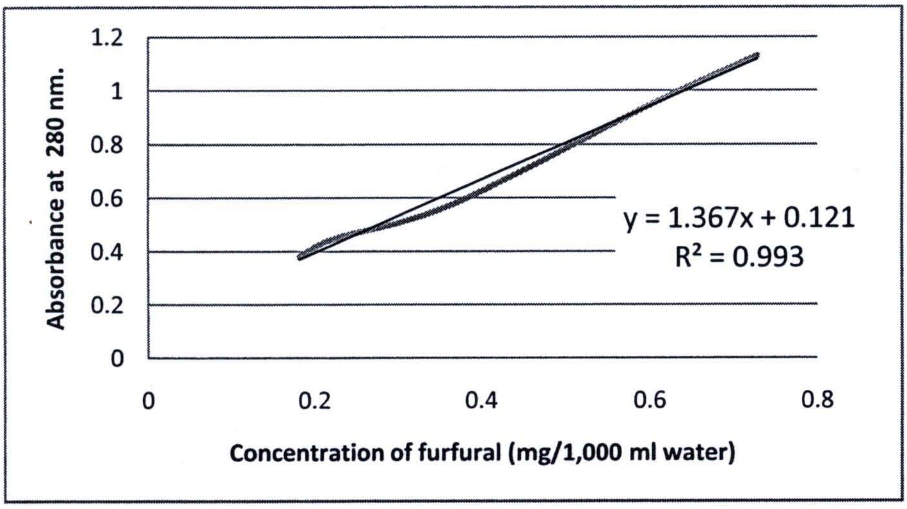


Figure 4.23 Standard plot of UV-vis for furfural

From this standard curve, the concentration of released furfural can be determined by measuring the absorbance of the sample. The released amount of the furfural from the furfural-urea complex imbedded with PBSA polymer is monitored for 4 consecutive days. The experiment uses 36.6 mg of the polymer film in 20 ml of water. Furthermore, the release rate of furfural in the polymer film is then compared to the release rate of furfural from furfural-urea complex without polymer imbedding. Since, the polymer film contains 10% of furfural-urea complex, 3.7 mg of furfural-urea complex is mixed with 20 ml of water.

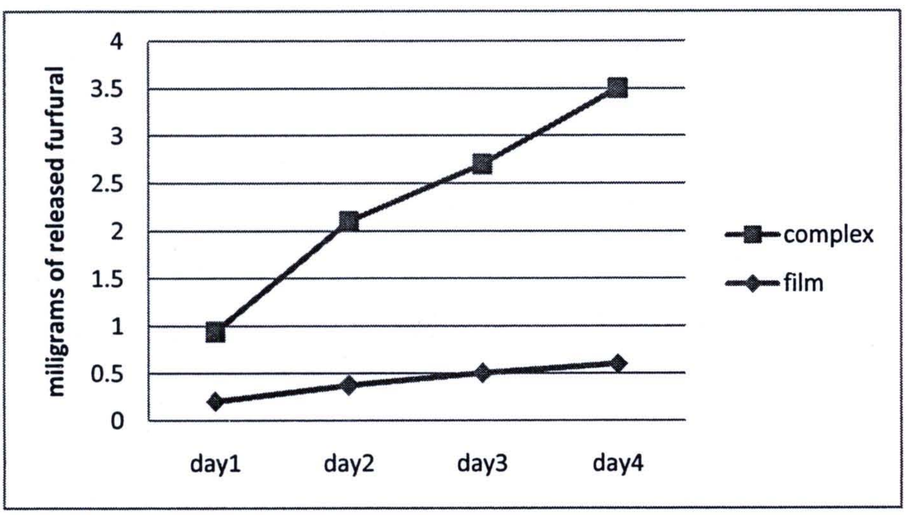


Figure 4.24 Released amount of furfural in furfural-urea complex with and without polymer

Figure 4.24 expresses the amount of furfural released from furfural-urea complex in comparison with the furfural released from furfural in the polymer film. According to the slope, the release of furfural from furfural-urea complex is faster than the complex imbedded with polymer. This could be due to the bonding between the furfural-urea complex in PBSA polymer leading to more difficulty for the complex to release. In addition, the released amount of furfural-urea complex in polymer film is dramatically less than the released amount of furfural-urea complex without polymer imbedding. This means either that the release rate of furfural-urea complex in polymer film is slower than the release rate of only furfural-urea complex or the original polymer film contains less than 10% of furfural-urea complex. Although 10% by weight of the furfural-urea complex is added into the polymer, it could result in less than 10% complex at same point in the film due to non-uniform distribution. However, despite this difference in the original amount of furfural-urea complex, the complex imbedded in polymer film has obviously slower release rate than the one without polymer imbedding.