CHAPTER IV
RESULTS AND DISCUSSION

4.1 Purification of Biopolymer

The purchased biopolymer was purified before using with NaOH solution to obtain high degree of purity (higher amine group in the structure of biopolymer). Degree of purity of purified biopolymer can be determined by two methods: titration and Fourier transform infrared (FT-IR) spectroscopy.

4.1.1 Determination of Degree of Purification of Biopolymer by Titration

A titration curve of a solution of purified biopolymer (pH of solution vs consumed volume of NaOH) is shown in Figure 4.1.

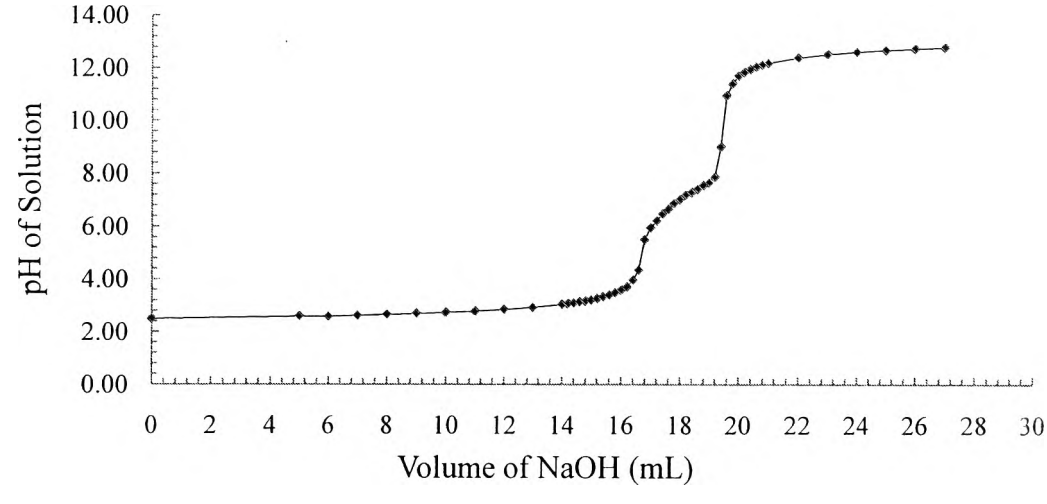


Figure 4.1 Titration curve for determining degree of purity of purified biopolymer.

The quantity of amine group in biopolymer was determined by titration of biopolymer solution with NaOH solution. Figure 4.1 shows that there are two equivalent points. The first equivalent point can be explained due to neutralization of the excess HCL. The second equivalent point can be explained due to the displacement of HCL bound to the primary amino groups in the biopolymer structure. These two equivalent points can be determined by linear extrapolation of

the adjacent portions of the titration curve. The degree of purification was calculated and the result was 96.05% with 0.066% of standard deviation (Avadi *et at.*, 2004).

4.1.2 Determination of Degree of Purification of Purified Biopolymer by Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR spectroscopy was used to another characterization method used to find degree of purification of biopolymer and was used to compare the result with titration method. Figure 4.2 shows IR spectra of original biopolymer and purified biopolymer.

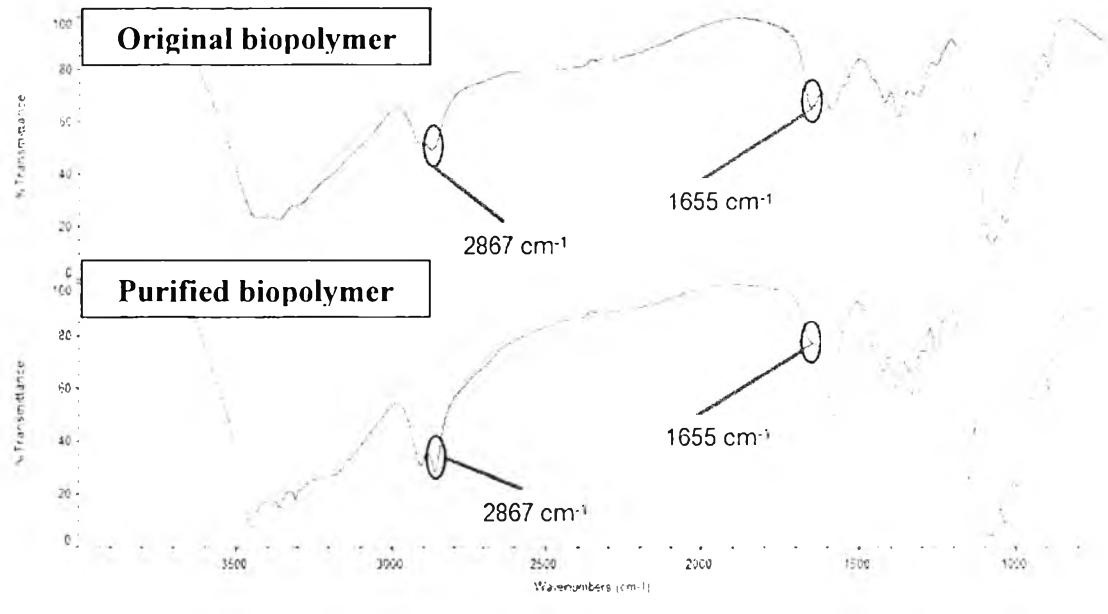


Figure 4.2 IR spectra of original biopolymer and purified biopolymer.

The FT-IR spectra of each biopolymer were very similar, but there were some different points. The noticeable difference was the decrease of characteristic peak at 1655 cm^{-1} corresponding to amide band I that should be employed for the determination of the residual N-acetylglucosamine (CONH) monomer in the highly purified biopolymer. The degree of purification of biopolymer can be determined by using the relation of the absorbance ratio of the amide band I at 1655 cm^{-1} to the CH stretching band at 2867 cm^{-1} (Miya *et al.*, 1980). The absorbance ratio can be calculated by Equation (4.1).

The absorbance ratio $= \frac{(A)_{amide\ 1655\ cm^{-1}}}{(A)_{CH\ stretching\ 2867\ cm^{-1}}}$ Equation. (4.1)

The result is 96.80 % degree of purification with 0.358% of standard deviation. The degree of purification of purified biopolymer is higher than that of original biopolymer which is 87.6 %.

4.2 Preparation of PolyHIPE

4.2.1 Effect of Biopolymer

In this part of the experiment, the condition for the preparation of polyHIPE was 10 vol% of organic phase and 90 vol% of aqueous phase. 20 wt% of mixed surfactant was used to stabilize the emulsion condition so the amount of biopolymer solid (≤ 62 microns) was varied 0, 7, 11, 16 and 23 wt% related to weight of monomer. When aqueous phase was added into the organic phase, biopolymer solid was dispersed well in the emulsion. However, dispersion of biopolymer became more difficult at 16 and 23 wt% because the emulsion was observed to be very viscous. When the addition of biopolymer was more than 23wt%, the phase separation occurred clearly because the amount of mixed surfactant was insufficient to keep the same emulsion form. Biopolymer is solid particle when added into the emulsion, it served as the mechanical barrier to prevent coalescence of the aqueous phase droplets. In the same way, at high viscosities, the shear stress of mixing was insufficient to break up all the large droplets of aqueous phase in the emulsion if the biopolymer solid was greater than 23 wt%.

4.2.1.1 Morphology and Surface Area of PolyHIPE with Solid Biopolymer

SEM micrographs of PolyHIPEs in Figure 4.3 show porous foams with an open porous network structure and the dispersion of biopolymer are compared with original polyHIPE.

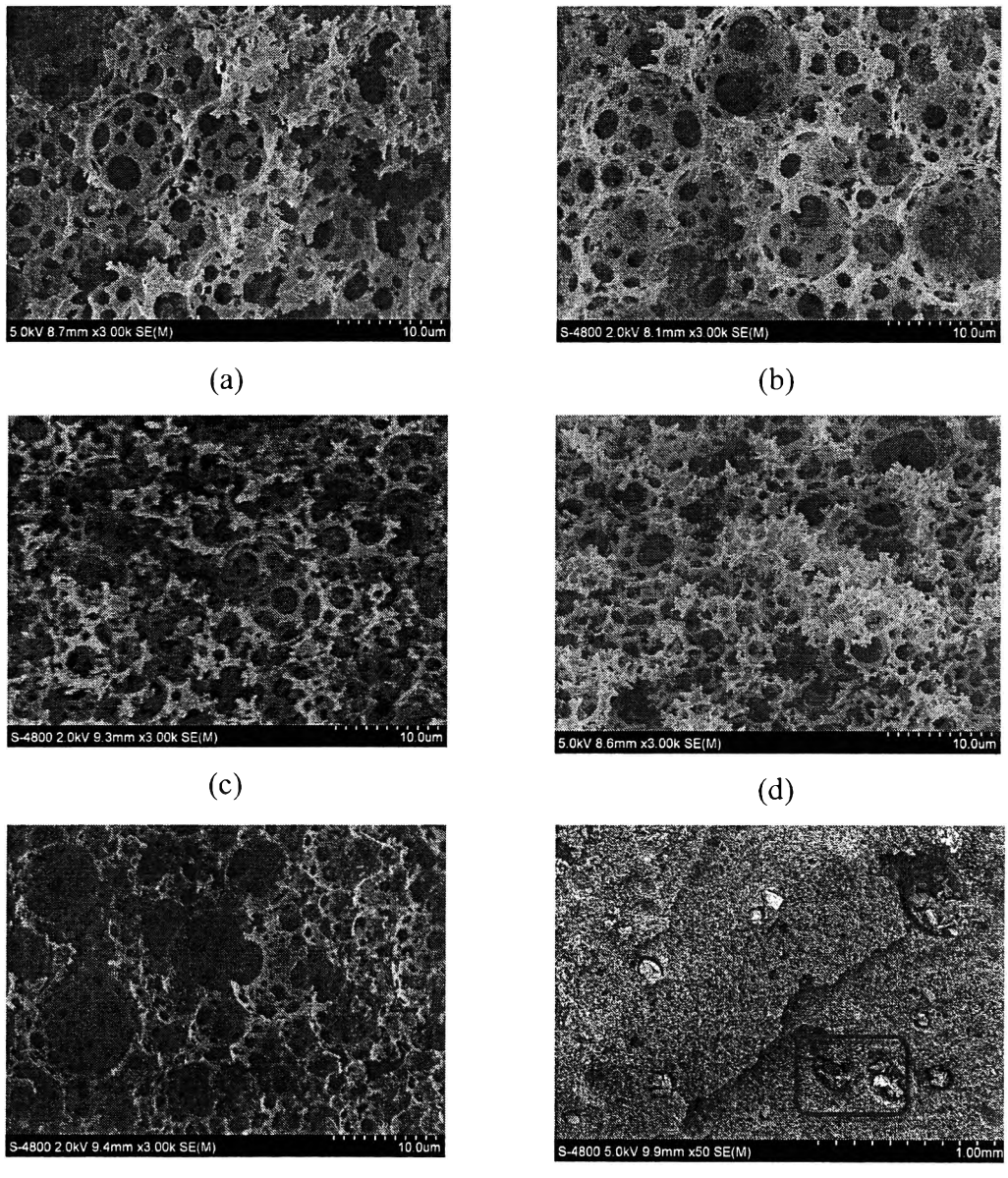
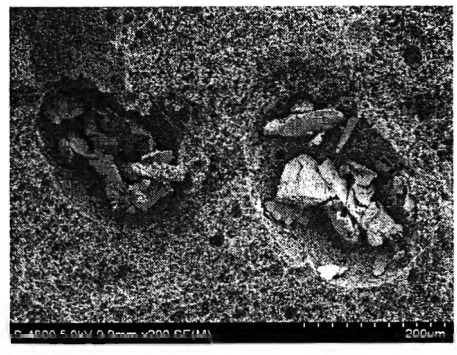


Figure 4.3 SEM micrographs of polyHIPE filled with different amount of biopolymer content; (a) 0 wt% at 3000x, (b) 7 wt% at 3000x, (c) 11wt% at 3000x, (d) 16 wt% at 3000X, (e) 23 wt% at 3000x, (f) 16wt% at 500x and (g) High magnification of marked section in picture (f).



(g)

Figure 4.3 (Cond't) SEM micrographs of polyHIPE filled with different amount of biopolymer content; (a) 0 wt% at 3000x, (b) 7 wt% at 3000x, (c) 11wt% at 3000x, (d) 16 wt% at 3000X, (e) 23 wt% at 3000x, (f) 16wt% at 500x and (g) High magnification of marked section in picture (f).

All of them were polymerized at the same condition. Figure 4.3(a) shows open porous structure of the polyHIPE without adding biopolymer, which was used as a reference. Figure 4.3(b) – 4.3(e) show morphology of polyHIPE that contain biopolymer solid at 7 wt%, 11 wt%, 16 wt% and 23 wt%, respectively. They also show high porous and high interconnected pore structure. In Figure 4.3(f), biopolymer (16 wt%) dispersed well in the porous structure, however Figure 4.3(g), enlargement of highlighted area of Figure 4.3(f) show agglomeration of biopolymer particles due to high hydrophilicity of biopolymer in hydrophobic structure of polyHIPE.

The surface area of the polymer foams was determined from nitrogen adsorption isotherms applying the Brunauer-Emmet-Teller (BET) model. Table 4.1 shows that surface area was decreased with increasing the amount of biopolymer in polyHIPE due to agglomeration of biopolymer particles as obviously seen in SEM of Fig 4.3 (g) that lead to block pore in the structure of polyHIPE and result in decreased the surface area.

Table 4.1 Surface area of polyHIPE prepared by addition of biopolymer solid particle into the emulsion polymerization

wt% biopolymer in polyHIPE	Surface Area (m^2/g)
0	303.00
7	278.40
11	270.20
16	210.00
23	87.30

4.2.1.2 Thermal Properties

The characterization was carried out to measure the thermal stability of the biopolymer, original polyHIPE and polyHIPE that contained biopolymer. TGA thermograms presenting percentage of weight loss against temperature and derivative thermograms are shown in Figure 4.4 and Figure 4.5, respectively. There were two steps of degradation of biopolymer. First step at 76.20 °C was due to desorped water in the structure of biopolymer and second step at 300.68 °C indicated the degradation of biopolymer. The original polyHIPE (0 wt% biopolymer) showed degradation temperature at 439.31 °C. For polyHIPE with 7, 11, 16 and 23 wt% biopolymer, there were two steps of degradation. First step indicated to degradation of desorped water in the structure of polyHIPE at about 127 °C and second step was due to degradation of polyHIPE at 448.13 °C, 449.84, 450.48 and 451.23 °C, respectively. The thermal decomposition temperatures (T_d) are summarized in Table 4.2.

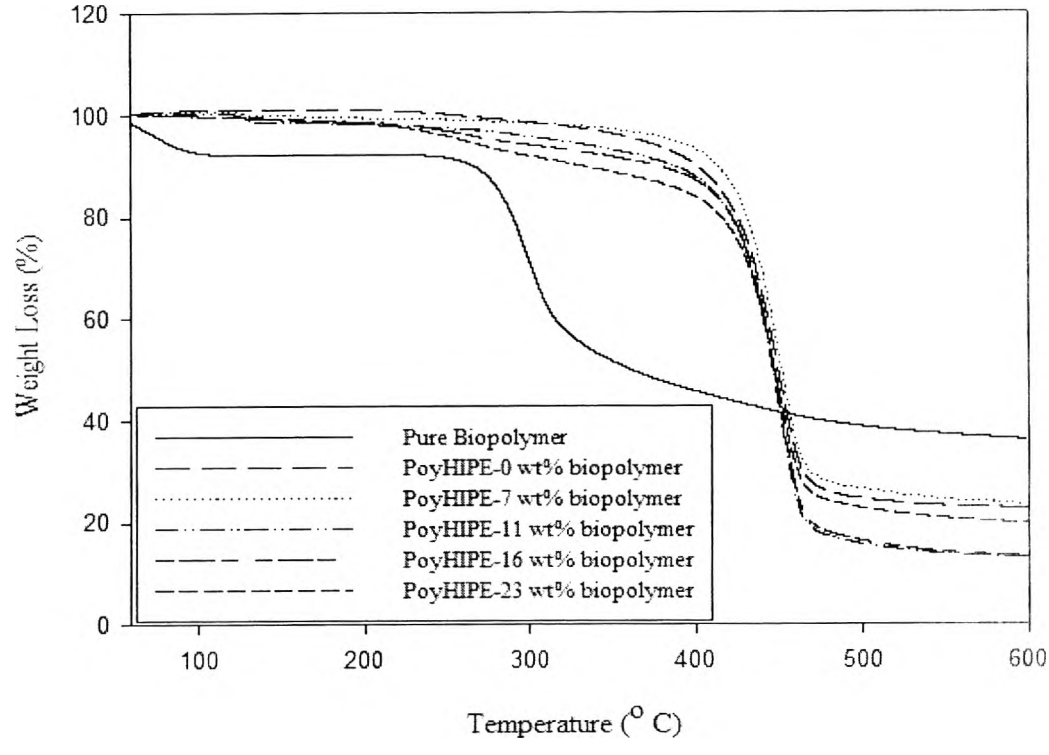


Figure 4.4 TGA thermograms of biopolymer, original polyHIPE and polyHIPE- biopolymer.

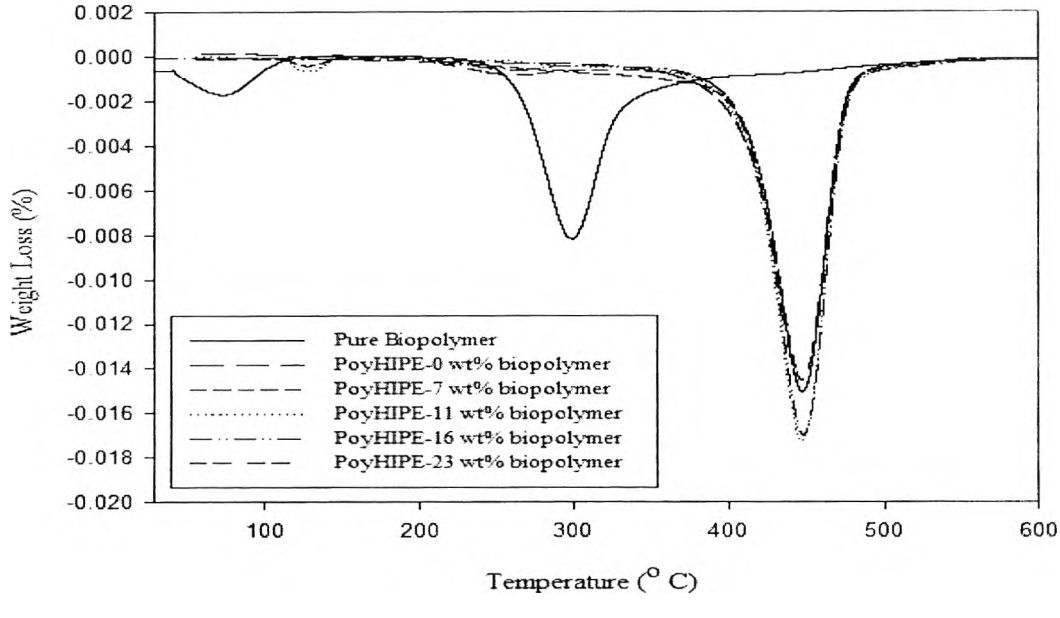


Figure 4.5 Deriverative thermograms of biopolymer, original polyHIPE and polyHIPE- biopolymer.

Table 4.2 Thermal decomposition temperature (T_d) of biopolymer, original polyHIPE, polyHIPE containing biopolymer

Sample	Decomposition Temperature, T_d* (°C)
Purified biopolymer	298.96
0 wt% biopolymer in polyHIPE	439.31
7 wt% biopolymer in polyHIPE	448.13
11 wt% biopolymer in polyHIPE	449.84
16 wt% biopolymer in polyHIPE	450.48
23 wt% biopolymer in polyHIPE	451.23

* Inflection Point

The decomposition of polymer foams shifted to a high temperature with adding of biopolymer. This means that the incorporation of biopolymer into polymer foam offers a stable structure against decomposition; therefore, the decomposition temperature slightly increases.

For the extraction of biopolymer, polyHIPE that contained biopolymer was immersed in acetic acid (1%v/v) and then biopolymer would be dissolved and come out. This SEM micrograph in Figure 4.6 shows the structure of polyHIPE after extraction biopolymer. There are some cracking of the pore because of the extraction. Before biopolymer was extracted, biopolymer used to attach in this pore; therefore after extraction it's normally that the cracking will occur.

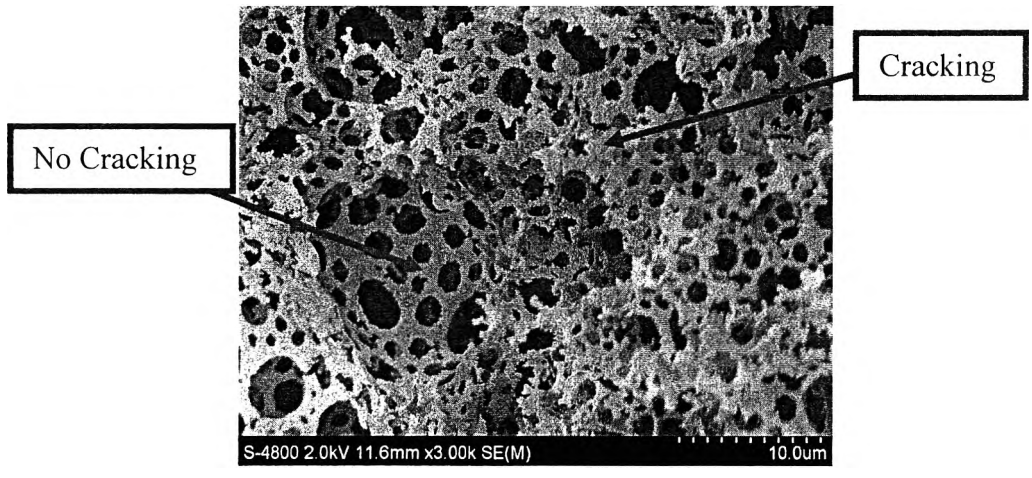


Figure 4.6 SEM micrograph shows the structure of polyHIPE at 3000x after biopolymer (23 wt%) extraction.

4.2.2 Effect of Mixed Surfactant

The second part of the synthesis of polyHIPEs was to increase the amount of each surfactant for adding more biopolymer in the emulsion. The amount of mixed surfactant was increased to 20 wt%, 23 wt% and 25 wt% to find the suitable condition. The results are presented in Table 4.3.

Table 4.3 The amount of mixed surfactant on addition of biopolymer in the emulsion

Amount of mixed surfactant (wt %)	Amount of biopolymer (wt %)	Characteristic of Emulsion
20	23	Emulsion Formation
	26,30	Phase separation
23	30	Emulsion Formation
	38	Phase separation
25	38	Emulsion Formation
	47	Phase separation

When the amount of mixed surfactant increased, the higher amount of biopolymer could be added into the emulsion. High amount of mixed surfactants could stabilize more biopolymer, but still there was a limit of adding in

each percentage of mixed surfactant, otherwise the phase separation would occur. At 25 %wt of mixed surfactant, the polymer foam started to shrink after soxhlet extraction and drying. This formation depended on high surfactant concentration (related to monomer content) that resulted in weak unconnected porous material (Cameron, 2005) as shown in Figure 4.7.

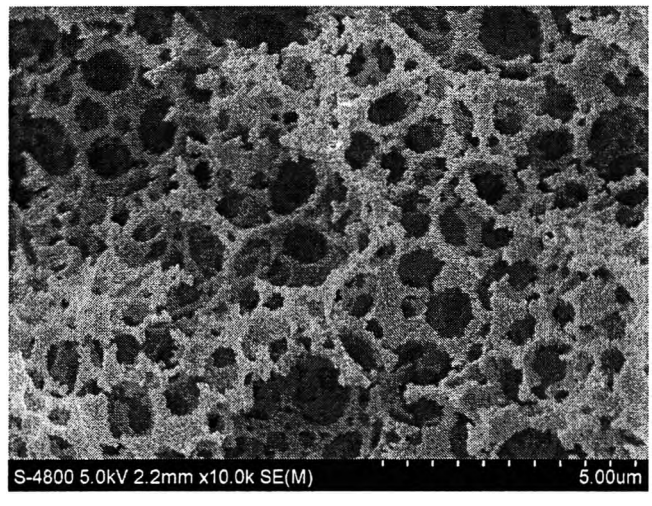


Figure 4.7 SEM micrograph (10000x) of polyHIPE (38 wt% of biopolymer) at 25 %wt of mixed surfactant.

4.2.3 Effect of Biopolymer Solution

Due to the agglomeration of biopolymer solid in polyHIPE, biopolymer in solution form was used. Biopolymer solid was dissolved in acetic acid and added in aqueous phase. The amount of mixed-surfactant was also 20 wt%. Percentage of biopolymer related to weight of monomer added in emulsion is shown in Table 4.4.

Table 4.4 Amount of biopolymer and volume of acetic acid for adding in the emulsion

Biopolymer (wt%)	Volume of acetic acid (mL)	pH	%v/v of acetic acid	Emulsion Formation
30	9	~ 5	1	Yes
50	12.5	~ 5	1	Yes
70	17	~ 5	1	Yes
100	9	~ 5	5	Yes
120	13	~ 5	5	Yes
150	14	~ 5	5	Yes, (exceed aqueous phase occurred)

The highest possible amount of biopolymer for loading was 150 wt% related to weight of monomer. At biopolymer of 150 wt%, there was excess water separated after polymerization. As the result, dissolving more biopolymer was not suitable because of instability of the emulsion. It could be concluded that the highest percentage of biopolymer loading was 150 wt%.

4.2.2.1 Characterization of PolyHIPE Containing Biopolymer

This characterization was used to determine if the polyHIPE contained biopolymer. The IR spectra of polyHIPE without biopolymer and polyHIPE containing biopolymer were similar but there were the noticeable differences. The characteristic peaks at 3455 cm^{-1}, 1153 $cm^{-1}$and 1077 cm^{-1} were corresponded to N-H stretching, C-N stretching and N-H wagging, respectively. Therefore, it can confirm that the biopolymer solution can be added into the polyHIPE. The IR spectra are shown in Figure 4.8. From the result of FTIR, it shows the functional group of amines so it means that biopolymer can be loaded in the structure of polyHIPE.

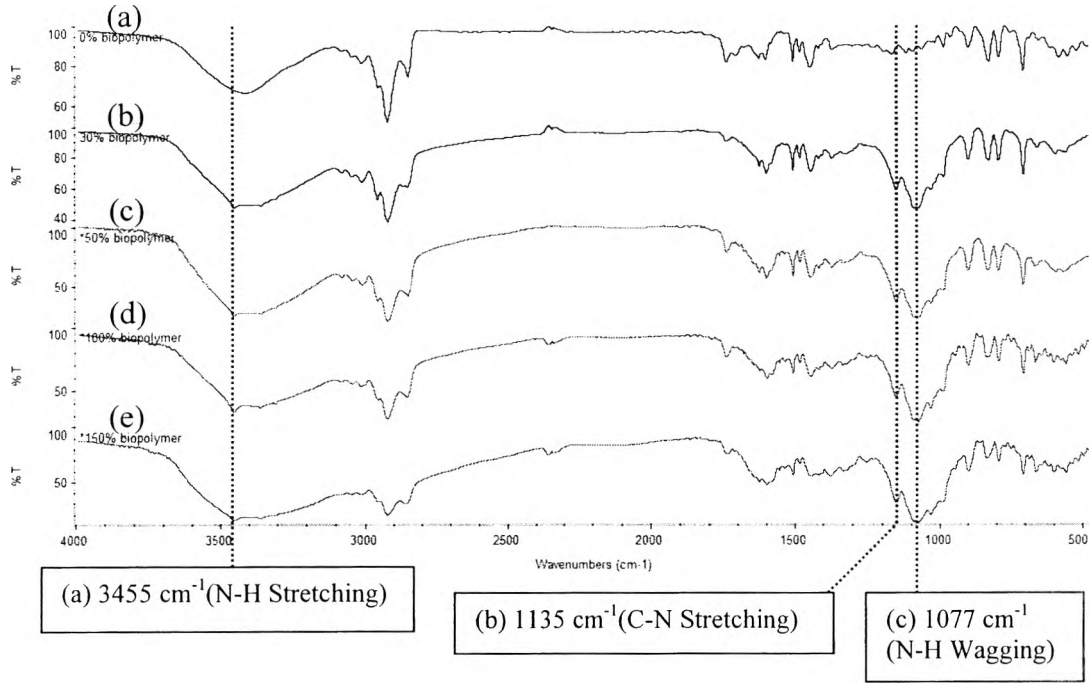


Figure 4.8 IR spectra of original polyHIPE and polyHIPE containing biopolymer prepared by adding biopolymer solution, a) 0 wt%, b) 30 wt%, c) 50 wt%, d) 100 wt% and e) 150 wt%.

When increases percentage of addition of biopolymer in the solution, the nitrogen in polyHIPE increases simultaneously as shown in Table 4.5, where the amount of nitrogen (N) in structure of polyHIPE was measured by using CHNS analyzer and %loading of biopolymer can be calculated from the amount of nitrogen (N). The amount of biopolymer was better dispersed in the emulsion by stirring, so % loading increased when increased the amount of biopolymer. When loading of biopolymer solution was compared with solid, the biopolymer solution loading was higher in polyHIPE.

Table 4.5 Amount of nitrogen in polyHIPE at various biopolymer addition

Addition of biopolymer (wt%)*	N(mg) per 1g of PolyHIPE		% biopolymer in polyHIPE
	Theory	Experiment	
30	20.07	10.91	54.36
50	28.99	17.25	59.51
70	35.81	24.67	68.89
100	43.48	30.79	70.81
120	47.43	35.24	74.29
150	52.17	40.35	77.32

* Related to weight of monomer (DVB)

4.2.2.2 Morphology Properties and Surface Area

The SEM micrographs of polyHIPE prepared by adding the biopolymer solution are presented in Figure 4.9(a) – 4.9(f) which shows the interconnected pore network structures. The structures were similar to polyHIPE reference in Figure 4.3(a), but the noticeable difference was secondary pore. The amount of secondary pore of polyHIPE – biopolymer was lower than that of polyHIPE reference as the comparison is shown in Figure 4.10(a) and 4.10(b). Due to the biopolymer in solution form combining with monomer (DVB), it can increase the amount of polyHIPE texture and decrease the amount of secondary pore lead to decrease the total pore volume.

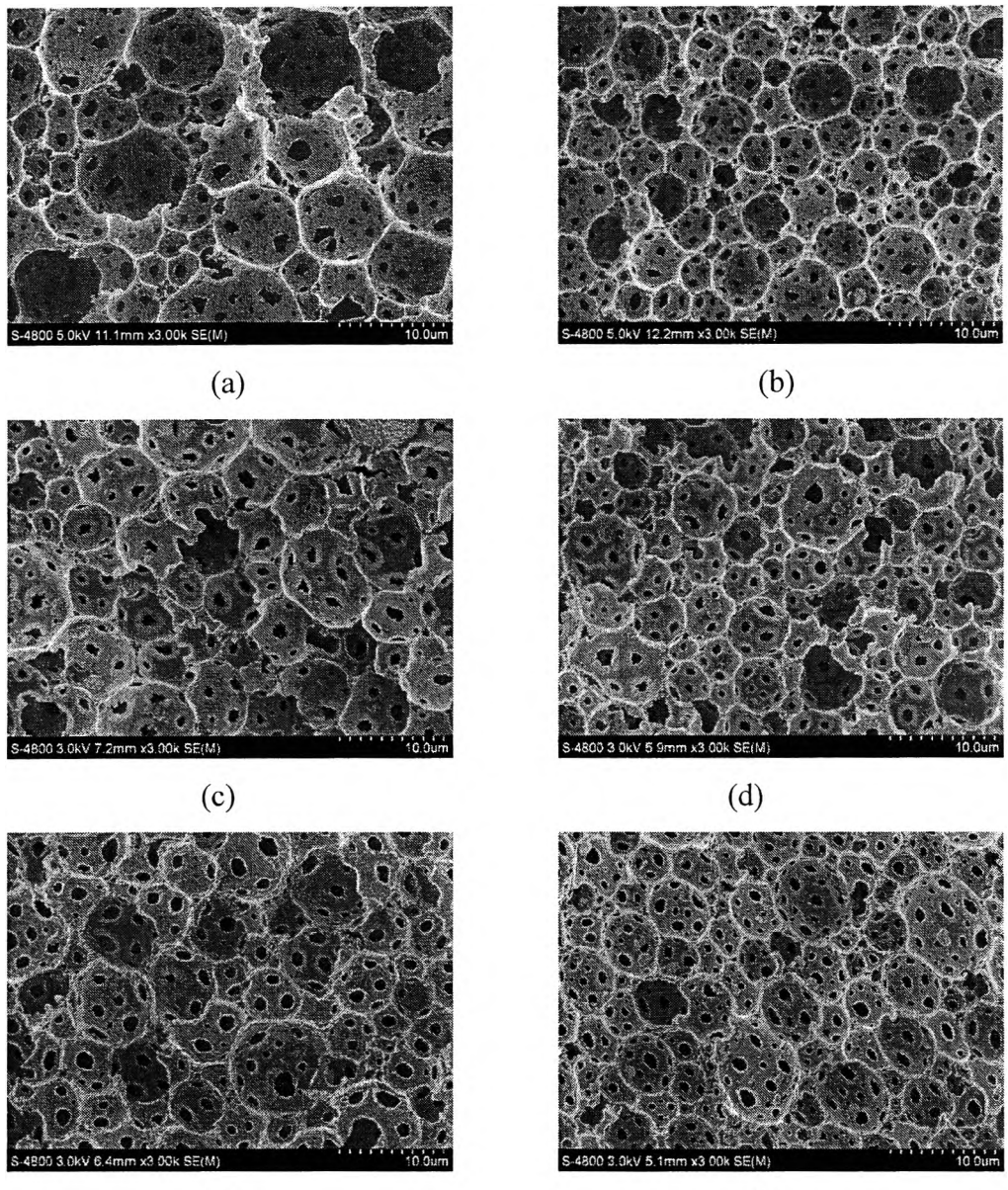
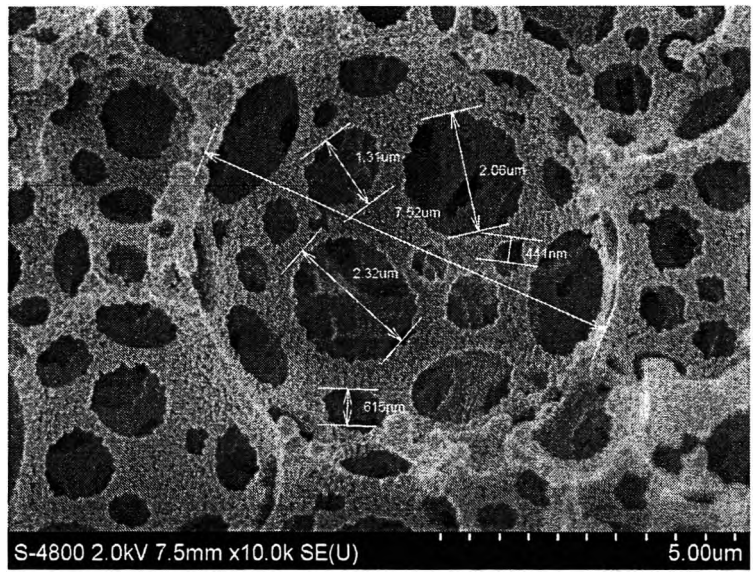
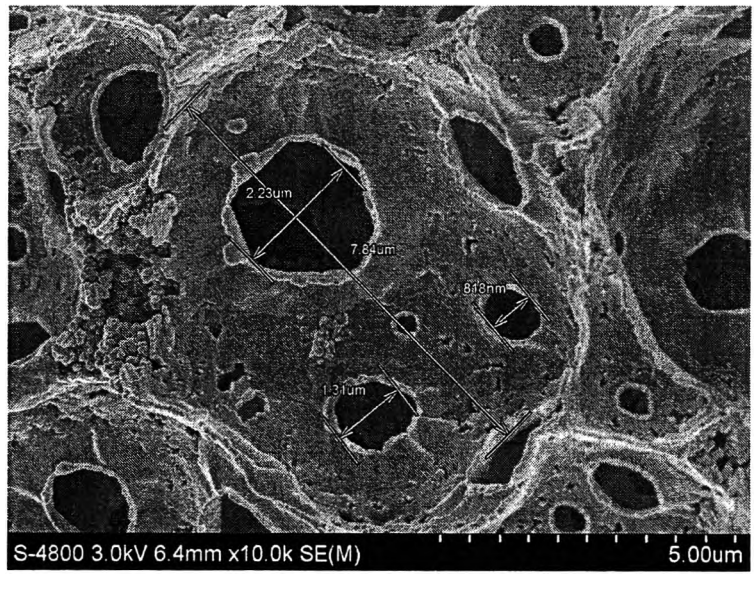


Figure 4.9 SEM micrographs of polyHIPE filled with different amount of biopolymer solution content at 3000x; (a) 30 wt%, (b) 50 wt%, (c) 70wt%, (d) 100 wt%, (e) 120 wt% and (f) 150 wt%.



(a)



(b)

Figure 4.10 SEM micrographs (10000x) of polyHIPE that showed diameter of primary, secondary pore and size of polyHIPE texture (a) polyHIPE reference and (b) polyHIPE contained biopolymer solution 120 wt%.

Table 4.6 Surface area of polyHIPE contained biopolymer solution

wt% biopolymer in polyHIPE	Surface Area(m^2/g)
0	303.00
30	46.74
50	49.99
70	60.57
100	65.07
120	73.35
150	102.10

The result from surface area analyzer showed that surface area decreased from 303.00 m^2/g (polyHIPE reference) to 46.74 m^2/g (30 wt% biopolymer in polyHIPE) due to the increasing of amount of polyHIPE texture and lower volume of secondary pore in the structure that lead to decreasing surface area. Nevertheless, when increased the amount of biopolymer, surface area increased due to the decreasing of average void diameter that lead to increasing surface area again. The average void diameter of polyHIPE contained biopolymer 30 wt%, 50 wt%, 70 wt%, 100 wt%, 120 wt% and 150 wt% were 69.775, 69.463, 65.850, 59.838, 53.263 and 50.913 μm, respectively.

4.2.2.3 Thermal Properties

TGA thermograms of % weight loss versus temperature and derivative thermograms of polyHIPE – biopolymer are shown in Figure 4.11 and Figure 4.12, respectively. There are two steps in the decomposition of polyHIPE - biopolymer. The first step degradation of 30 wt%, 50 wt%, 70wt%, 100 wt%, 120 wt% and 150 wt% biopolymer solution adding were at 269.46, 247.76, 264.90, 255.44, 276.15 and 259.50 °C, respectively. These degradations indicated to the residue biopolymer that was not dissolved in acetic acid. This result is in agreement with SEM micrograph in Figure 4.13 that shows a few of biopolymer that remaining in the structure of polyHIPE. The second step was concluded as the decomposition of polyHIPE. The degradation occurred at 450.87, 451.86, 453.37,

451.92, 453.82 and 455.24 °C, respectively. The thermal decomposition temperatures (T_d) are shown in Table 4.7.

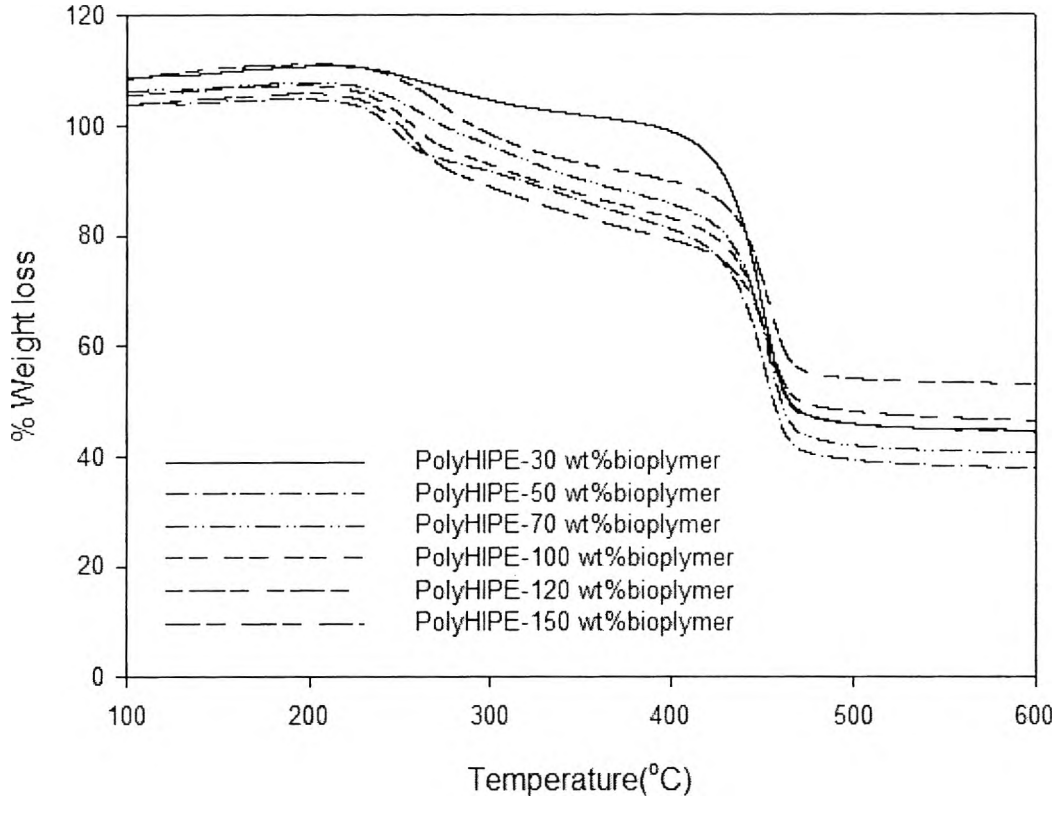


Figure 4.11 TGA thermograms of polyHIPE prepared by adding biopolymer solution at different wt% of biopolymer.

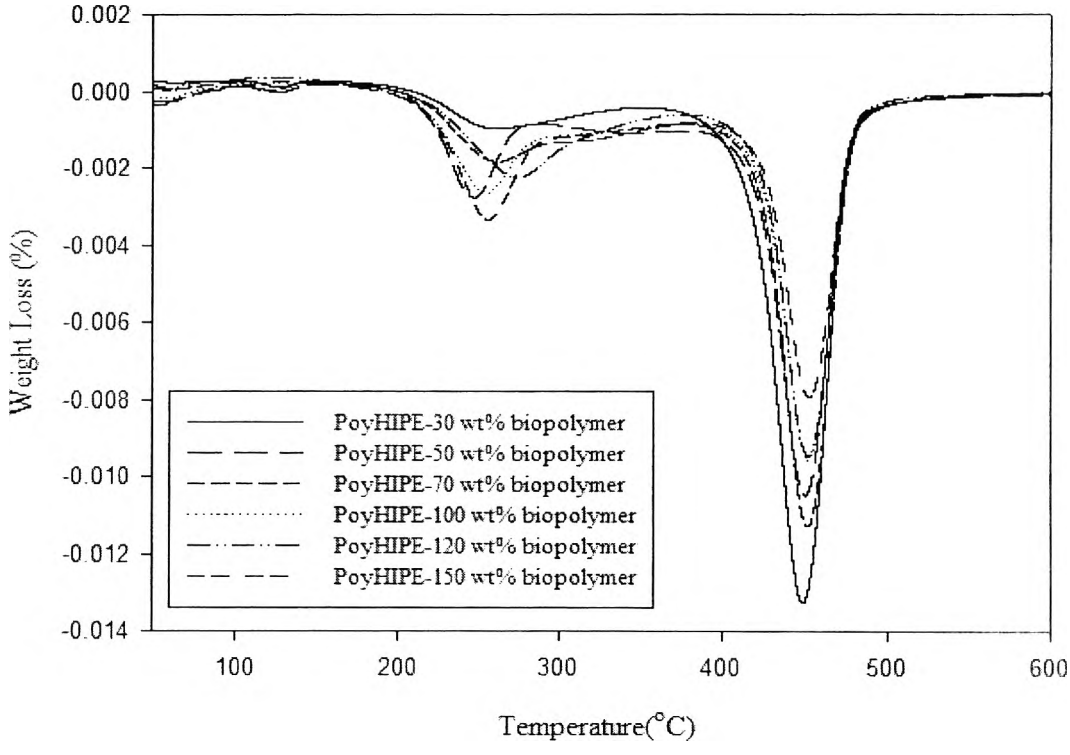


Figure 4.12 Deriverative thermograms of of polyHIPE prepared by adding biopolymer solution at different wt% of biopolymer.

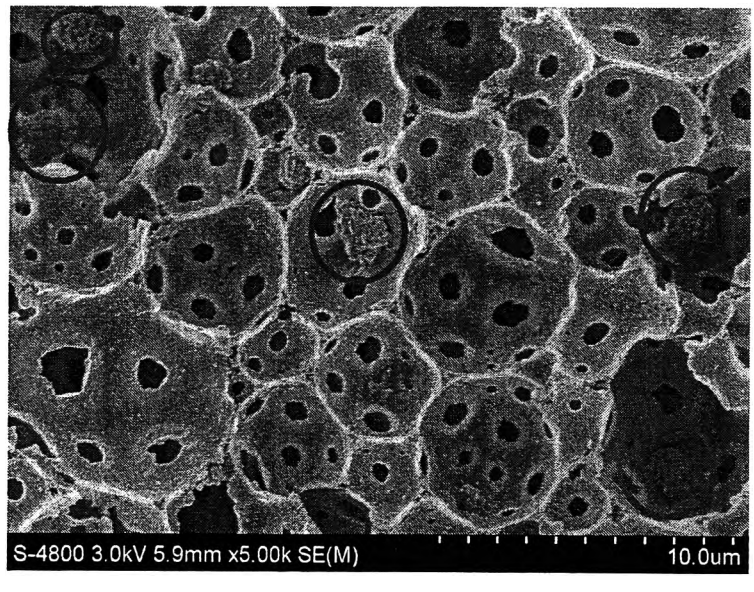


Figure 4.13 SEM micrograph (5000x) of polyHIPE that contained a few of biopolymer that was not dissolve in the structure.

Table 4.7 Thermal decomposition temperature (T_d) of polyHIPE at different wt% of biopolymer solution

wt% biopolymer in polyHIPE	Decomposition Temperature, T_d* (°C)
30	269.46, 450.87
50	247.76, 451.86
70	264.90, 453.37
100	255.44, 453.91
120	276.15, 453.82
150	259.90, 455.24

* Inflection Point

The result showed that decomposition temperature of polyHIPE increased slightly when increased wt% of biopolymer. The addition of biopolymer solution affect to the size of texture in the structure of polyHIPE that become larger as shown in Figure 4.9(b); therefore, it made the structure of polyHIPEs become more stable against decomposition.