CHAPTER IV
RESULT AND DISCUSSION

4.1 Non-Isothermal Melt-Crystallization of Poly (3-hydroxybutyrate) Blends

4.1.1 Non-Isothermal Melt-Crystallization and Subsequent Melting Behavior

The non-isothermal melt-crystallization exotherms of PHB and its blends at eight different cooling rates ranging from 5 to $30^\circ C.min^{-1}$ are presented in Figure 1.a. In all graphs, the crystallization exotherms become wider and shift to a lower temperature with increasing cooling rates which would be expected because of the crystallization in a nucleation-controlled region. In order to obtain the kinetic information, the experimental data had to be converted to the relative crystallinity function of temperature, θ (T), using Equation (5). The converted θ (T) curves are shown in figure 2.a. Based on these curves, some kinetics data [e.g. the temperature 1% relative crystallinity $T_{0.01}$, the temperature at 99% relative crystallinity $T_{0.99}$ and the temperature at the maximum crystallization rate (i.e. peak temperature) T_p] were obtained and summarized in Table 1.a. Both $T_{0.01}$ and $T_{0.99}$ values represent the apparent onset and ending temperature of the non-isothermal melt-crystallization process, respectively. By increasing the heating rates, all values shift to lower temperature.

Then the data were analyzed by converting the temperature scale of the θ (T) function into the time scale, using $t = (T_0-T)/\phi$, to obtain the relative crystallinity function of time $\theta(t)$. According to figure 3.a, the faster the cooling rate, the shorter the time required for the completion of the crystallization process. It is important that all of the $\theta(t)$ curves shown do not include the apparent incubation period Δt_{inc}, which can be defined as a time period (viz. $\Delta t_{inc} = (T_f-T_{onset})/\phi$, where T_f is the fusion temperature or the temperature that a polymer sample is brought to melt, T_{onset} is the actual temperature where the sample begins to crystallize and ϕ is the cooling rate),during which polymer is still in its molten state. The Δt_{inc} values were calculated based on the T_f value of 190°C and are summarized in Table 2.a.the Δt_{inc} parameter decrease by increasing the cooling

rate.

In order to quantity the bulk kinetics of the non-isothermal melt-crystallization process, the crystallization time at an arbitrary relative crystallinity(i.e. t_θ) can be derived from the $\theta(t)$ functions shown in figure 3.a.The t_θ values (after exclusion of the apparent incubation period Δt_{inc}) for different relative crystallinities θ(i.e. at the θ values of 0.01,0.1,0.3,0.5,0.7,0.9 and 0.99,respectively)are plotted as a function of cooling rate in figures 4.a and 5.a.The $t_{0.01}$ and $t_{0.99}$ values are qualitative measure of the beginning and the ending of the crystallization process, respectively. From these values, the apparent total crystallization period Δt_c can be calculated (i.e. $\Delta t_c = t_{0.99} - t_{0.01}$) which the results are summarized in Table 2.a. The non-isothermal melt-crystallization is faster at higher cooling rates because the Δt_c values and t_θ values for a fixed θ decrease by increasing the cooling rate. In an another analysis, plots of $\ln(\Delta t_c)$ against $\ln(\theta)$ and of $\ln(t_\theta)$ against $\ln(\phi)$ were carried out for all compositions. Linear relationships with similar slopes are observed on these plots.

The subsequent melting thermograms for PHB and its blends which were recorded with a heating rate 10°C min^{-1} after non-isothermal melt-crystallization in DSC at different cooling rates were shown in Figure 6. Clearly, double melting exotherms are observed in all cooling rates. Peak I can be found to explain the melting of primary crystallites formed at a crystallization temperature and peak II show the melting of recrystallized crystallites which were formed during a heating scan. The positions of peak I and II do not seem to be affected by different cooling rates. The intensities of these peaks show that the primary crystals are not stable and, upon subsequent heating, these primary crystallites melt and recrystallized during further heating.

4.1.2 Non-Isothermal Melt-Crystallization Kinetics

4.1.2-1 Avrami Analysis

Data analysis based on the Avrami macrokinetic equation was done by directly fitting $\theta(t)$ functions shown in figure 3.a to equation 2.The Avrami kinetic parameters(i.e. K_A and n_A) along with r^2 parameters, indicating the goodness of

the data fitting, were obtained from the best fits. These parameters are summarized in table 4.a for all compositions. The Avrami exponents n_A was found to range from 2.93 to 3.97 with the average value of 3.58 and the standard deviation of 0.997.The Avrami crystallization rate constant K_A is found to increase with increasing heating rate in all compositions which shows increasing of crystallization rate with increasing cooling rate.

4.1.2-2 Tobin Analysis

Data analysis based on the Tobin macrokinetic equation was done by directly fitting $\theta(t)$ functions shown in figure 3.a. to equation 3.The Tobin kinetic parameters(i.e. K_T and n_T) along with r^2 parameters, indicating the goodness of the data fitting, were obtained from the best fits. These parameters are summarized in table 5.a.The Tobin exponent n_T is found to range from 4.71 to 6.82 with the average value of 5.77 and the standard deviation of 0.995 .The Tobin crystallization rate constant K_T is found to increase with increasing heating rate which shows increasing of crystallization rates with increasing heating rates for all compositions.

4.1.2-3 Comparison between Results Obtained from Avrami and Tobin Analysis

A direct comparison between the results obtained from these two models shows that the Avrami and the Tobin crystallization rate constants (i.e. K_a and K_T, respectively) are comparable. On the other hand, for a given cooling rate, the Avrami exponent n_a is always lower than Tobin .The best way to test the efficiency of both models in describing the non-isothermal melt-crystallization kinetics of PHB is to reconstruct the $\theta(t)$ functions from the result for both models. This shows that the Avrami model provides a much better prediction of the experimental data than does the Tobin model.

4.1.2-4 Ozawa Analysis

Ozawa was able to extend the Avrami model to describe the kinetics of non-isothermal crystallization. In this approach, the raw data was the relative crystallinity function of temperature $\theta(T)$ such as those shown in figure 3.a. Data

analysis according to this model could be accomplished by performing a double logarithmic plot of $\ln[-\ln(1-q(T))]$ versus $\ln(\phi)$ for a fixed temperature, where n_O was taken as the negative value of the slope and K_O was taken as the antilogarithmic value of the ratio of the y-intercept and n_O [i.e. $K_O=\exp(\text{y-intercept}/n_O)$]. Figure 7.a. shows typical Ozawa plot from the raw data shown in figure 3.a for PHB within the temperature range of 76 to 98°C,while Table 6.a summarizes the Ozawa kinetic parameters(i.e. K_O and n_O),including the r^2 parameter for all compositions. Qualitatively, the Ozawa model was satisfactory in describing the non-isothermal melt-crystallization data of PHB and its blends. The Ozawa exponents, n_O, increases by increasing temperature, because the temperature ranges are in the nucleation-controlled region. It can be explained due to the fact that the number of the athermal nuclei increases tremendously with decreasing temperature and makes the nucleation mechanism more instantaneous in time which caused the decrease of no. The Ozawa crystallization rate constant K_O decreases with increasing temperature when the crystallization is in the nucleation-controlled region which causes a slower cooling rate at higher temperature. These trends were seen in all compositions.

4.1.2-5 Effective Energy Barrier for Non-Isothermal Melt-Crystallization Process

Analysis based on the differential iso-conversional method of Freidman started with the conversion of a $\theta(T)$ function into a $\theta(t)$ function. The converted $\theta(t)$ function was then differentiated with respect to time to obtain the instantaneous crystallization rate function of time $\theta_\theta(t)$.A plot could then be performed for various values of relative crystallinity θ using the data obtained from the $\theta_\theta(t)$ and the $\theta(T)$ function and finally the effective energy barrier for non-isothermal melt-crystallization process for a given θ(i.e. ΔE_θ) could be determined, as a result, from the slope of the plot[i.e. $\Delta E_\theta=-(\text{slope})(R)$].The ΔE_θ values were derived from various values of θ ,ranging from 0.1 to 0.9 with 0.1 increment ,are summarized in table 7.a. The ΔE_θ parameter is found to increase which shows that when crystallization progressed, it is more difficult for polymer to crystallize.

4.2 Non-Isothermal Cold-Crystallization of Poly (3-hydroxybutyrate) Blends

4.2.1 Non-Isothermal Cold-Crystallization and Subsequent Melting Behavior

The non-isothermal cold-crystallization exotherms of PHB and its blends at eight different cooling rates ranging from 5 to 30°C.min^{-1} are presented in Figure 1.b.

In all graphs, the crystallization exotherms become wider and shift to a higher temperature with increasing cooling rate which would be because of the crystallization in a diffusion-controlled region. In order to obtain the kinetic information, the experimental data had to be converted to the relative crystallinity function of temperature ,θ (T), using Equation (5). The converted θ (T) curves are shown in figure 2.a.Based on these curves, some kinetics data [e.g. the temperature 1% relative crystallinity $T_{0.01}$, the temperature at 99% relative crystallinity $T_{0.99}$ and the temperature at the maximum crystallization rate (i.e. peak temperature) T_p] could be obtained and summarized in Table 1.b. Both $T_{0.01}$ and $T_{0.99}$ values represent the apparent onset and ending temperature of the non-isothermal cold-crystallization process. By increasing the heating rates, all values shifted to higher temperatures for all compositions.

Then the data were analyzed by converting the temperature scale of the θ (T) function into the time scale, using t= $(T_0-T)/\phi$, to obtain the relative crystallinity function of time $\theta(t)$. According to figure 3.b, the faster the heating rate, the shorter the time required for the completion of the crystallization process. It is important that all of the $\theta(t)$ curves shown do not include the apparent incubation period Δt_{inc}, which can be defined as a time period (viz. $\Delta t_{inc} = (T_{onset}-T_{ini})/\phi$, where T_{onset} is the actual temperature where the sample begins to crystallize, in this case $T_{ini}=25^0C$ and ϕ is the cooling rate),during which polymer is still in its molten state. The Δt_{inc} values were calculated based on the T_f value of 190°C and are summarized in Table 2.b.the Δt_{inc} parameter decrease by increasing the heating rate for all compositions.

In order to quantity the bulk kinetics of the non-isothermal cold-crystallization process, the crystallization time at an arbitrary relative crystallinity(i.e. t_θ) could be

derived from the $\theta(t)$ functions shown in figure 3.b.The t_θ values (after exclusion of the apparent incubation period Δt_{inc}) for different relative crystallinities θ(i.e. at the θ values of 0.1,0.1,0.3,0.5,0.7,0.9 and 0.99,respectively)are plotted as a function of cooling rate in figures 4.b and 5.b.The t $_{0.01}$ and $t_{0.99}$ values are qualitative measure of the beginning and the ending of the crystallization process. From these values, the apparent total crystallization period Δt_c can be calculated(i.e. $\Delta t_c = t_{0.99} - t_{0.01}$) which the results are summarized in Table 2.b. Decreasing the Δt_c values and t_θ values for a fixed θ by increasing cooling rate show that, non-isothermal cold-crystallization is faster with increasing the heating rate. In an another analysis, plots of $\ln(\Delta t_c)$ against $\ln(\theta)$ and of $\ln(t_\theta)$ against $\ln(\phi)$ were carried out for all compositions. Linear relationships with similar slopes are observed on these plots.

The subsequent melting thermograms for PHB and its blends, double melting exotherms are observed in higher heating rates (i.e. $\geq 20°C.min^{-1}$) which were shown in Figure 1.b. It suggests that the primary crystallites the primary crystallites formed during this crystallization are very unstable which melted during further heating

4.1.2 Non-Isothermal Cold-Crystallization Kinetics

4.1.2-1 Avrami Analysis

Data analysis based on the Avrami macrokinetic equation is done by directly fitting $\theta(t)$ functions shown in figure 3.b to equation 2.The Avrami kinetic parameters(i.e. K_A and n_A) along with r^2 parameters, indicating the goodness of the data fitting, were obtained from the best fits. These parameters are summarized in table 4.b for all compositions. The Avrami exponents n_A is found to range from 3.03 to 4.47 with the average value of 3.80 and the standard deviation of 0.998.The Avrami crystallization rate constant K_A is found to increase with increasing cooling rate in all compositions which shows increasing of crystallization rate with increasing cooling rate .

4.1.2-2 Tobin Analysis

Data analysis based on the Tobin macrokinetic equation is done by directly fitting $\theta(t)$ functions shown in figure 3.b. to equation 3.The Tobin kinetic

parameters(i.e. K_T and n_T) along with r^2 parameters, indicating the goodness of the data fitting, were obtained from the best fits. These parameters are summarized in table 5.b.The Tobin exponent n_T is found to range from 4.94 to 7.40 with the average value of and the standard deviation of 0.996 .The Tobin crystallization rate constant K_T is found to increase with increasing cooling rate which shows increasing of crystallization rate with increasing cooling rate.

4.1.2-3 Comparison between results obtained from Avrami and Tobin Analysis

A direct comparison between the results obtained from these two models shows that the Avrami and the Tobin crystallization rate constants (i.e. K_a and K_T, respectively) are comparable. On the other hand, for a given cooling rate, the Avrami exponent n_a is always lower than Tobin .The best way to test the efficiency of both models in describing the non-isothermal melt-crystallization kinetics of PHB is to reconstruct the θ (t) functions from the result for both models.

4.1.2-4 Ozawa Analysis

Ozawa was able to extend the Avrami model to describe the kinetics of non-isothermal crystallization. In this approach, the raw data is the relative crystallinity function of temperature $\theta(T)$ such as those shown in figure 3.b. Data analysis according to this model can be accomplished by performing a double logarithmic plot of $\ln[-\ln(1-q(T))]$ versus $\ln(\phi)$ for a fixed temperature, where n_O is taken as the negative value of the slope and K_O is taken as the antilogarithmic value of the ratio of the y-intercept and n_O [i.e. $K_O=\exp(y\text{-intercept}/n_O)$]. Figure 7.b. shows typical Ozawa plot from the raw data shown in figure 3.b for PHB within the temperature range of 36 to 56°C,while Table 6.b summarizes the Ozawa kinetic parameters(i.e. K_O and n_O),including the r^2 parameter for all compositions. Qualitatively, the Ozawa model was satisfactory in describing the non-isothermal melt-crystallization data of PHB and its blends. The Ozawa exponents, n_O, are varying from ca.1.69 to ca. 4.94 with increasing temperature. The Ozawa crystallization rate constants, K_O, decrease with increasing temperature when the crystallization is in the diffusion-controlled region which causes a

higher cooling rate at higher temperature.

4.1.2-5 Effective Energy Barrier for Non-Isothermal Cold-Crystallization Process

Analysis based on the differential iso-conversional method of Freidman starts with the conversion of a $\theta(T)$ function into a $\theta(t)$ function. The converted $\theta(t)$ function is then differentiated with respect to time to obtain the instantaneous crystallization rate function of time $\theta_\theta(t)$. A plot can then be performed for various values of relative crystallinity θ using the data obtained from the $\theta_\theta(t)$ and the $\theta(T)$ function and finally the effective energy barrier for non-isothermal melt-crystallization process for a given θ (i.e. ΔE_θ) can be determined, as a result, from the slope of the plot[i.e. $\Delta E_\theta = -(slope)(R)$]. The ΔE_θ values are derived from various values of θ, ranging from 0.1 to 0.9 with 0.1 increment, are summarized in table 7.b. The ΔE_θ parameters are found to decrease which show that when crystallization progressed, it is more difficult for polymer to crystallize.

4.3. Isothermal Crystallization of Poly (3-hydroxybutyrate) Blends

4.3.1 Glass Transition Temperature

DSC has been used to investigate miscibility in polymer blends. Essentially just one T_g was observed for all compositions in the range of studying which was located between two T_g. By increasing the amount of PLA, The T_g raises which shows miscibility between two polymers in amorphous state.

4.3.2 Melting Behavior

To determine the equilibrium melting temperature of PHB and its blends, we must know the melting behaviors of the polymers. All the blends were isothermally crystallized at various crystallization temperatures T_c ranging from 60 to 75°C in a step increment of 2.5°C to examine the changes of the melting peaks. The subsequent melting temperatures which were scanned in DSC at the same heating rate of 10°C/min which were shown in figure 8.

According to figure 8, the subsequent melting exotherms for all the blends, exhibited double exothermic melting phenomena. The occurrence of the first peaks was a result of the melting of the primary crystallites and the second ones were the result of the melting of the recrystallized crystallites of different stabilities. By increasing T_c, there is a really small shift of the peak to a higher temperature for all blends. The position of the melting peaks for all the compositions are in higher temperatures in comparison to neat PHB. However, the compositions of the blends do not have obvious affect on the peaks at the same range of crystallization temperatures.

4.3.3 Determination of the Equilibrium Melting Temperature

As mentioned previously, the exothermic peaks which corresponded to the melting of primary crystal formed at a special T_c listed in table 8 are observed to determine the equilibrium melting temperature according to equation 24.

Figure 9 show the plots between the observed T_m and T_c for PHB and it blends. For each graph, it shows the linear relationship between the Observed T_m and T_c within the T_c range studied. the intersection of a least square line, fit to the data set of each composition, with the line of $T_m = T_c$ gives the values of T_m^o. The slope of the least square line, which equals $1/2 \beta$ can be used to calculate β parameter($\beta = 0.5 \times \text{slope}^{-1}$). The T_m^o, β, χ^2 values for each sample were summarized in table 9. The value of β shows that the extrapolation is valid and can get a reliable T_m^o value because the values were not greatly affected by the lamellar thickening process.

There is one other way to determine T_m^o. According to equation 25, the reduced M and X have to be calculated from a set of the observed T_m-T_C data which summarized in Table 2 and the initial guess value of T_m^o. the true is the value that results when the slope of the M-X plot of $1(\beta^m = 1)$. The T_m^o, β^m and χ^2 values are summarized in Table 9.

4.3.4 Overall Isothermal Melt-Crystallization Kinetics

Figure 9 shows the time-dependant relative crystallinity function $\theta(t)$ (after subtraction of the induction time t_0), which crystallized at different crystallization temperature for PHB and its blends. Although the time to reach the ultimate crystallinity

(complete crystallization) increased with increasing crystallization temperature T_c, there is not a significant difference between the data which shows that PHB and it blends are not really sensitive to isothermal crystallization.

Another bulk or overall kinetic parameter which can be derived directly from the $\theta(t)$ data is the half-time of crystallization $t_{0.5}$ which is defined as the elapsed time measured from the onset of crystallization until the crystallization is half-completed. Table 10 show all the half-time $t_{0.5}$ data which derived from the experimental $\theta(t)$ data. The same trend is seen for all the $t_{0.5}$ that there is a little increase by increasing the crystallization temperature T_c. For PHB-blend system considered at the same crystallization temperature T_c, The half-time of crystallization increased by increasing the amount of PLA except in the amount of PHB92.5/PLA7.5 which shows the least amount of half-time of crystallization in comparison to all compositions. It was shown in figure 11.

The plots between the half-time of crystallization $t_{0.5}$ and undercooling of PHB and its blends were shown in figure 5. For all compositions, with increasing degree of undercooling, there is a little decrease in crystallization half-time. For the same undercooling, the half-time of crystallization decreased by increasing the PLA content. PHB97.5/PLA2.5 showed the lowest amount of half-time of crystallization.

4.3.4-1 Isothermal Crystallization Kinetics Based on the Avrami Analysis

Data analysis based on the Avrami macrokinetic equation is done by directly fitting $\theta(t)$ functions shown in figure 9 to equation 2.The Avrami kinetic parameters(i.e. K_A and n_A) along with χ^2 parameters, indicating the goodness of the data fitting, were obtained from the best fits. These parameters are summarized in table 10 for all compositions. The Avrami exponents n_A is found to range from 3.03 to 4.47 with the average value of 3.80 and the standard deviation of 0.998 which according to the definition of the Avrami exponent correspond to a two dimensional growth with a combination of thermal and athermal nucleation.

According to table 10, The Avrami crystallization rate constant K_A and the reciprocal crystallization half-time $t_{0.5}^{-1}$ are found to decrease by increasing crystallization temperatures in all compositions. It means that the samples crystallize

faster with decreasing T_c, although the amounts of these changes are not really very much.

For PHB-blend system at the same T_c, the Avrami rate constant K_a and the reciprocal crystallization half-time, $t_{o.5}^{-1}$, decrease by increasing the amount of PLA and PHB97.5/PLA2.5 showed the highest amount as shown in figures 13 and 15,respectively.

Figures 14 and 16, respectively, showed that the Avrami rate constant and the reciprocal crystallization half-time $t_{o.5}^{-1}$ versus the degree of undercooling for PHB and its blends. These figures can be the representation of the bulk crystallization rate of a semi-crystalline polymer. They showed that there are increases for both K_a and $t_{o.5}^{-1}$ with increasing the degree of undercooling. At the same amount of the degree of undercooling, PHb97.5/PLA2.5 exhibited the highest amount of K_a and $t_{o.5}^{-1}$ which showed it crystallized the fastest and by increasing the amount of PLA the crystallization become slower.

4.3.4-2 Isothermal Crystallization Kinetics Based on the Malkin Analysis

Data analysis based on the Malkin macrokinetic equation is done by directly fitting $\theta(t)$ functions shown in figure 9 to equation 4.The Malkin kinetic parameters(i.e. C_1 and C_0) along with χ^2 parameters, indicating the goodness of the data fitting, were obtained from the best fits. These parameters are summarized in table 11.The Malkin exponent C_0 is found to range from 200 to 47 with the average value of 134.29 and the standard deviation of 0.995 .The Malkin crystallization rate constant C_1 is found to show a little decrease with increasing crystallization temperature in all composition which shows decreasing of crystallization rates with increasing crystallization temperature (decreasing undercooling) for all compositions. Moreover, for PHB-blend system considered at the same T_c and the same undercooling Δt, the C_1 values showed the same trend as the Avrami rate constant which shown in figure 17 and 18, respectively.

4.3.4-3 Isothermal Crystallization Kinetics based on the Urbanovici-

Segal Analysis

Data analysis based on the Urbanovici-Segal macrokinetic equation is done by directly fitting $\theta(t)$ functions shown in figure 9 to equation 5.The Urbanovici-Segal kinetic parameters(i.e. K_{us}, n_{us} and r) along with χ^2 parameters, indicating the goodness of the data fitting, were obtained from the best fits. These parameters are summarized in table 12.The Urbanovici-Segal exponent n_{us} is found to range from 3.77 to 2.78 with the average value of 3.16 and the standard deviation of 0.992 .The Urbanovici-Segal crystallization rate constant K_{us} is found to show a little decrease with increasing crystallization temperature in all composition which shows decreasing of crystallization rates with increasing crystallization temperature (decreasing undercooling) for all compositions. Moreover, for PHB-blend system considered at the same T_c and the same undercooling Δt, the K_{us} values showed the same trend as the Avrami rate constant which shown in figure 19 and 20, respectively

4.4 Isothermal Growth Rate

By measuring the spherulite radius from PLM micrographs taken during the isothermal crystallization, the growth rate was determine by a linear least square fit of the initial linear portion of growth rate curves before impingement. Figure 21 give plots of the spherulitic radius versus time for different crystallization temperatures for PHB, PHB97.5/PLA2.5, PHB95/PLA5,PHB92.5/PLA7.5 AND PHB90/PLA10, respectively. It is clear that there is a linear increase in the radius with time. The slope of the each straight line refers to the spherulitic growth rate of each crystallization temperatures. The spherulite growth rate G for PHB, PHB97.5/PLA2.5, PHB95/PLA5,PHB92.5/PLA7.5 AND PHB90/PLA10 were summarized in table 13-17, respectively. The plots of growth rate G as a function of crystallization temperature T_c are displayed in figure 22. In the range of crystallization studied, growth rate of all samples decreased by increasing the crystallization temperature, T_c. For PHB/blend system at the same T_c in the range of 65 to 85°C, the growth rate of PHB was more than the others. As the content of PLA increases, the growth rate decreases. The trend is exactly similar to the other overall crystallization rate parameters.

Figure 23 shows the plots of growth rate versus degree of undercooling for PHB and its blends. For the same undercooling; the spherulite growth rate of PHB is the highest.

Figures 25 show the LH plots of PHB and its blends according to Lauritzen-Hoffman secondary nucleation theory. All compositions were found to be in regime II. The calculated K_g and G_0 values for all samples were listed in Table 18.