CHAPTER III
EXPERIMANTAL

3.1 Materials and Sample Preparation

Materials used in this study are as follow:

1. Poly (3-hydroxybutyrate), PHB, (Mw = 300,000) was purchased from Sigma-Aldrich (SM chemical, Thailand) in fine powder form.
2. Poly (lactic acid), PLA in granule form.

PHB and PLA were dried in a vacuum oven at 120°C for 5 hours and then the blends were prepared by precipitation. Chloroform was used as the solvent. PHB and PLA were mixed in different weight ratios, PHB90/PLA10, PHB92.5/PLA7.5, PHB95/PLA5, PHB92.5/PLA7.5 and PHB100%. Solutions of PHB and PLA were prepared by dissolving them in chloroform at 50°C to obtain 2 g/ml solutions. The mixtures were stirred for 3 hours. The solutions were poured in non-solvent (water) in order to have precipitate. Finally the blends were derived by filtering following by drying at 50°C for 3 days.

Films of approximately 200μm thickness were obtained by melt-pressing at 190°C in a Wabash V50H compression molding machine under an applied force of 15 ton-force. The residence time of the film moldings in the press was about 2 min.

3.2 Non-Isothermal Crystallization Kinetics of PHB and Its Blends

3.2.1 Bulk Crystallization Kinetics

3.2.1.1 Differential Scanning Calorimetry Measurement

The Differential Scanning Calorimeter apparatus, DSC 822, was used to observe glass transition temperature, equilibrium melting temperature and overall crystallization kinetics based on both isothermal and non-isothermal melt- and cold-crystallization of PHB/PLA blends.

Calibration for the temperature scale was carried out using a pure indium standard (T^0_m=156.6 and ΔH^0_f =28.5jg^{-1}) on every run to ensure accuracy and

reliability of the data obtained. To minimize thermal lag between polymer sample and DSC furnace, each sample holder was loaded with a disc-shape sample weighing around 0.8±0.5 mg which was cut from the prepared films and assume the thermal lag will be the same for both heating and cooling scan. To prevent any thermal degradation, each sample was used just one time and all the runs were done under a nitrogen atmosphere.

The samples were heated from 30°C at a heating rate of 80°C min^{-1} to 190°C and kept there for 5 minutes to ensure complete melting and after that the samples were taken out and immediately quenched in liquid nitrogen in order to reach the amorphous state of the samples.

3.2.1.2 Method

For glass transition temperature (T_g) measurement, the experiment was started by heating each sample from 30°C to a fusion temperature of 190°C at a rate of 10°C min^{-1}.

For non-isothermal crystallization from the melt state, after heating the samples to 190°C and be sure about complete melting, they were cooled down with a desired constant cooling rate in the range of 5 to 30°C min^{-1} to 30°C. After that, the samples were heated at a rate of 10°C min^{-1} to observe the subsequent melting behavior.

For non-isothermal crystallization from the glassy state, after heating and quenching, each sample were transferred to the DSC cell and heated from 30 to 190°C at a desired cooling rate ranging from 5 to 30 min^{-1} to observe crystallization and subsequent melting behavior.

3.3 Isothermal Crystallization Kinetics of PHB and Its Blends

3.3.1 Differential Scanning Calorimetry Measurement

To study overall isothermal crystallization from the melt state, PHB and its blends were heated from 30°C at a heating rate of 80°C min^{-1} to 190°C and held there for 5 min to ensure complete melting. After that, they were rapidly cooled to a desired temperature T_c ranging from 55 to 80°C and held until crystallization process is considered complete (when there is no significant change in the heat flow

as a function of time). The crystallization exotherms were recorded for analysis with different macrokinetic models.

3.3.2 Morphological Characterization

To study the morphology and radius growth of PHB and the blends, the polarized light microscope (Leica DMRXP) was used. It had a hot stage and a temperature control system was used. Samples were prepared by melting on a glass slide on a hot stage and then the melted sample was pressed with a piece of cover glass and maintained for 5 minutes at this temperature to remove any previous thermal history. The temperature of hot stage for PHB/PLA was 190°C. Then the samples were transferred to the hot stage of microscope and were cooled to a desired isothermal crystallization temperature T_c. The subsequent growth of spherulite was viewed between crossed polars and recorded by a CCD camera at appropriate time intervals. The images of spherulites were analyzed on a computer using the Scion image software. By plotting spherulitic radius as a function of time, the slope of the line or the spherulite growth rate at desired crystallization temperature was obtained to give the growth rate.