CHAPTER III
EXPERIMENTAL

3.1 Materials

Materials used in this study are as follow:

1. Poly(trimethylene terephthalate) (PTT) used in this study was supplied in pellet form by Shell Chemicals Company (USA) (Corterra CP509201). The weight- and number-average molecular weights of this resin were determined to be ca. 78,100 and 34,700 Daltons, respectively. Molecular weight characterization was carried out by Dr. Chuah at Shell Chemical Company based on size-exclusion chromatography (SEC).

2. Poly(ethylene 2,6-naphthalate) (PEN) used in this study was obtained in pallet form by BP Chemicals Company (USA).

3.2 Non-Isothermal Crystallization Kinetics of PTT

3.2.1 Sample Preparation

PTT pallets were dried in a vacuum oven at 140°C for 5 hours prior to further use. Films of approximately 200 μm thickness were obtained by melt-pressing at 260°C in a Wabash V50H compression molding machine under an applied pressure of 4.62×10^2 MNm^{-2}. After 5 min holding time, the films were taken out and allowed to cool down to room temperature, under the ambient condition, between the two metal platens. This treatment assumes that the previous thermo-mechanical history was essentially erased and provides a standard crystalline memory condition for our experiments.

3.2.2 Bulk Crystallization Kinetics

(a) Differential scanning calorimetry measurement

In this study, a Perkin-Elmer Series 7 DSC (DSC-7) was used to study the kinetics of non-isothermal crystallization of PTT. Temperature calibration was carried out using an indium standard (T_m^o = 156.6°C and ΔH_f^o = 28.5 J g^{-1}). The

consistency of the temperature calibration was checked every other run to ensure the 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 8.0 ± 0.5 mg, which was cut from the sample films. It is worth noting that each sample was used only once and all the runs were preformed under nitrogen atmosphere to prevent extensive thermal degradation.

(b) Method

For non-isothermal crystallization from the melt state, the experiment started with heating the sample from 30°C at a heating rate of 80°C min^{-1} to 275°C, where it was held for 5 min to ensure complete melting [Supaphol et al. (accepted)]. After this period, the sample was cooled down with a desire constant cooling rate ϕ_c, ranging from 5 to 30°C min^{-1}, to 25°C. The sample was then heated with a constant scanning rate of 10°C min^{-1} to observe the subsequent melting behavior.

For non-isothermal crystallization from the glassy state, each sample was first heated at a heating rate of 80°C min^{-1} to 275°C and maintained at this temperature for 5 min to ensure complete melting [Supaphol et al. (accepted)], before being quenched in liquid nitrogen. After submergence in liquid nitrogen for 10 min, each sample was transferred to the DSC cell and then heated from 25°C to 275°C with a desire heating rate ϕ_h, ranging from 5 to 30°C min^{-1} for observing crystallization and subsequent melting behavior.

3.3 Crystallization Kinetics and Morphology of PTT and PTT/PEN Blends

3.3.1 Samples Preparation

PTT and PEN pallets were dried in a vacuum oven at 140°C for 5 hours and then were pre-mixed in a dry mixer to produce PTT/PEN pre-blends of 3, 6, 9 % wt of PEN, respectively. The pre-blends were then melt-mixed in a self-wiping, co-rotating twin-screw extruder (Collin, ZK 25), operating at a screw speed of 40 rpm and using extrusion temperature of 150, 270, 280, 290, 300, 280°C for Feeding Zone, Zone 1, Zone 2, Zone 3, Zone 4, Die, respectively. The extrudate

were cooled in water and were pelletized using a pelletizer (Planetrol, 075D2). The resulting blends were hereafter denoted (1-*x*)PTT/*x*PEN, where *x* is the weight percentage of PEN in blends. Films of approximately 200 μm thickness for neat resins and their blends were obtained by melt-pressing at 300°C in a compression molding machine (Wabash V50H) under an applied pressure of 3 ton-force. After 2 min holding time, the films were removed and allowed to cool down to room temperature, under the ambient condition, between the two metal platens. This treatment assumes that the previous thermo-mechanical history was essentially erased and provides a standard crystalline memory condition for our experiments.

3.3.2 Differential Scanning Calorimetry Measurement

A Perkin-Elmer Series 7 DSC (DSC-7) was used to observe glass transition temperatures, equilibrium melting temperatures and study the overall crystallization kinetics of isothermally melt-crystallized PTT, PEN and their blends. Temperature calibration was carried out using an indium standard (T_m^o = 156.6°C and ΔH_f^o = 28.5 J g^{-1}). The consistency of the temperature calibration was checked every other run to ensure the 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 8.0 ± 0.5 mg, which was cut from the sample films. It is worth noting that each sample was used only once and all the runs were preformed under nitrogen atmosphere to prevent extensive thermal degradation.

(a) Determination the glass transition temperature

The experiment started with heating PTT, PEN and their blends from 30°C to a fusion temperature of 300°C at a heating rate 80°C min^{-1} for a melt-annealing period of 5 min in order to remove previous thermal histories, after which the samples were taken out and immediately quenched in liquid nitrogen to attain the completely amorphous state of the samples. In order to observe the glass transition temperature, each sample was reheated again in DSC from 25 to 300°C at a rate of 10°C min^{-1}.

(b) Study overall isothermal melt-crystallization kinetics and determination of equilibrium melting temperature

For the study of overall isothermal crystallization from the melt state, the experiment started with heating PTT and the blends from 30°C at a heating rate of 80°C min^{-1} to 300°C, where it was held for 5 min to ensure complete melting. After this period, each sample was rapidly cooled (i.e., at a cooling rate 200°C min^{-1}) to a desired crystallization temperature T_c ranging from 190 to 205°C (in case of PEN samples, they were crystallized isothermally between 237.5 and 250°C), where it was held until crystallization process was consider complete (when no significant change in the heat flow as a function of time was further observed). The crystallization exotherm was recorded for analysis with Avrami, Malkin and Urbanovici-Segal macrokinetic model. Then the sample was heated with a constant scanning rate of 10°C min^{-1} to observe the subsequent melting endotherm, where the melting temperature of isothermally crystallized samples were recorded to calculate equilibrium melting temperatures based on the Hoffman-Weeks theory.

3.3.3 Polarized Light Microscopy Measurement

The morphology and radius growth of PTT and the blends crystallite under isothermal crystallization were investigated using a polarized light microscope (Leica DMRXP) equipped with a hot stage (Mettler Toledo FP82HT), a temperature control system (Mettler Toledo FP90), and a CCD camera (Cohu 4910). Specimen was prepared by melting the sample on a glass slide on a hot stage at 300°C, followed by pressing of the melted sample with a piece of cover glass and maintained for 5 min at this temperature to remove previous thermal history. The specimen was then rapidly transferred to another hot stage which lies on the stage of polarized light microscope and the temperature was already set at desired crystallization temperature ranging from 185 to 210°C. The subsequent growth of particularly selected spherulite was viewed between crossed polarizers and recorded by a CCD camera at appropriate time intervals. The images of spherulitic radius were analyzed on a computer using the Scion image software. By plotting spherulite radius as a function of time, the slope of the line or the spherulite growth rate at desired crystallization temperature ranging from 185 to 210°C were obtained.