CHAPTER III
EXPERIMENTAL

3.1 Materials

Materials used in this study are as follow:

1. Poly(ethylene terephthalate) (PET) used in this study was a commercial product from Indo PET (Thailand) Ltd. in the form of pellets (N1 grade).

2. Poly(trimethylene terephthalate) (PTT) was obtained from Shell Chemical Company (USA) Ltd. in the form of pellets (CP509201 grade).

3. Poly(buthylene terephthalate) (PBT) was supplied in a commercial grade by LG Chem (Korea) Ltd. (LUPOX GP-2000 grade) in the form of pellets.

Table 3.1 The characteristics of PET, PTT, and PBT

Properties	PET	PTT	PBT
Mn (g mol^{-1})	34030	25840	27380
Mw (g mol^{-1})	59140	47680	42580
PD	2.25	2.05	1.97
$T_m(^oC)$	247.02	226.83	223.17
$T_g(^oC)$	76.57	43.12	34.76

Molecular weight characterization of these resins were carried out by Dr. Hoe Chuah and his co-workers of Shell Chemicals (USA) based on size-exclusion chromatography (SEC) technique.

3.2 Experimental Procedure

3.2.1 Polymer Blend Preparation

The pellets of these three polyesters (PET, PTT, and PBT) were dried in a vacuum oven at 140°C for 5 hours before mixing to avoid significant

degradation caused by moisture at high temperature. Blends of PTT/PET and PTT/PBT were prepared at ratio of 0/100, 10/90, 25/75, 60/40, 50/50, 40/60, 25/75, 10/90, and 100/0.

A series of blends were premixed in a dry mixer and then melt-blended using a Collin co-rotating twin screw kneader ZK 25 (25mm x 30D) with the screw speed of 70 rpm. All processing passes were carried out using the processing condition as shown in **Table 3.2**

Table 3.2 Processing conditions of twin screw extruder

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6
210°C	250°C	260°C	270°C	280°C	280°C

The extrudate was cooled in the water (~25°C) and cut into pellet form by a Planetrol 075D2 pelletizer.

3.2.2 Specimens Preparation

The polymer blends obtained were pressed using a picture-frame mold in a Wabash V50H compression molding machine. The molding was preheated for 1 min at different temperature for different polyesters (i.e., at 280°C for PET and at 260°C for PTT and PBT) and then pressed at the same temperature, pressure 10 DIV for another 4 minutes. The molding was then cooled down to 40°C under pressure. The samples were cut into films and different testing specimens for each test.

3.2.3. Characterization

3.2.3.1 Thermal Analysis

The thermal properties of these three polymers and its blends were investigated using a Perkin-Elmer Series7 Differential Scanning Calorimetry (DSC-7). Temperature calibration of the instrument was carried out using a pure indium standard ($T^{\circ}_m = 156.6°C$ and $\Delta H^{\circ}_f = 28.5$ J g^{-1}) on every other run to ensure accuaracy and reliability of the data obtained. Each sample pan was loaded with

8.0 ± 0.5 mg of polymer, this is to minimize thermal lag between the samples and DSC furnace, each sample holder was loaded which weighed around 8.0 ± 0.5 mg. It is worth noting that each sample was used only once and all runs were carried out under nitrogen atmosphere to prevent extensive thermal degradation.

For the glass transition temperature (T_g) measurement, the test started with heating each sample from 40°C at a heating rate 80°C min^{-1} to a fusion temperature T_f (i.e., at 280°C for PTT/PET blends and 260°C for PTT/PBT blends, respectively), and maintained at T_f for 5 min. After that each sample was immediately quenched by liquid nitrogen, held for 10 min. In order to keep the polymer chains relax, the sample was kept at 25°C for 10 min. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), and the apparent melting temperature (T_m) were obtained by reheating the sample from 25 to 280°C at a cooling rate of 10°C min^{-1}. Finally, the sample was cooled from 280 to 40°C at a heating rate of 10°C min^{-1}, in order to observe the crystallization temperature from the melt state (T_c).

The crystallization behavior of these three polyesters and its blends were also investigated using a DSC-7 under both isothermal and non-isothermal crystallization conditions.

(a) *Isothermal Crystallization Condition*

To study the isothermal crystallization, each sample was heated from 40°C at a heating rate of 80°C min^{-1} to a desired fusion temperature T_f (i.e., at 280°C for PET and 260°C for PTT and PBT respectively). To ensure complete melting, the sample was kept at the respective T_f for a holding period of 5 min. After this period, each sample was rapidly cooled (i.e., ca. 200°C min^{-1}) from T_f to a desired crystallization temperature, where it was held until crystallization process was considered complete (when no significant change in the heat flow as a function of time was further observed). Both the isothermal crystallization exotherms and subsequent melting endotherms were recorded for further analysis. The heating rate used was 10°C min^{-1}. The kinetics of the isothermal crystallization process was carried out by directly fitting the experimental data to the aforementioned macrokinetic models.

(b) *Nonisothermal Crystallization Condition*

For determining nonisothermal crystallization, each sample was heated from 40°C at a heating rate 80°C min^{-1} to a desired fusion temperature T_f, at 300°C for PET and 280°C for PTT and PBT, respectively. In order to minimize the number of variable parameters, the time interval of the sample was kept at each specified T_f (i.e. the holding time t_h) was fixed at 5 min. After this period, each sample was cooled down at a desired constant cooling rate, ϕ (in the range of 5 to 50°C min^{-1}) to 30°C. The cooling exotherms were recorded and analyzed accordingly. The analysis of the experimental data was carried out using modified Avrami, Tobin, Ozawa, and Ziabicki equations to directly fit the experimental data to the respective macrokinetic models.

3.2.3.2 *Thermogravimetric Analysis*

The determination of decomposition temperature of the pure polymers and its blends was performed on a DuPont Instrument model 2950 from 30°C to 600°C under a nitrogen atmosphere with a heating rate of 10°C min^{-1}.

3.2.3.3 *Crystal Structure and Crystallinity*

The crystal modification and apparent degree of crystallinity of these three polyesters and their blends were investigated by using Wide-angle X-ray diffraction (WAXD) technique. The sample was prepared at the same conditions (i.e., nonisothermal crystallization condition at cooling rate of 10°C min^{-1}) set forth in DSC measurements. Each sample was then removed of the DSC sample holder and was pasted onto a glass X-ray sample holder, using vasaline as adhesive. The sample was scanned between the 2θ angle of 5° to 40° at a scanning rate of 2° minute^{-1} with 0.02° increment. The X-ray source was operated at 40 kV and 30 mA. The WAXD intensity pattern of each sample was then collected on a Rigaku Rint 2000 diffractometer, equipped with a computerized data collection and

analytical tools. The X-ray source (CuKα radiation, λ = 1.54 Å) was generated with an applied voltage of 40 kV and a filament current of 30 mA.

3.2.4 Tensile Properties

Tensile strength of the blends were determined using an Instron Universal Testing Machine Model 4206 according to ASTM D638-91 test method. The tests were carried out using a 100 kN load cell and 5 mm min^{-1} cross-head speed. Dumbbell shape specimens were cut from the as-prepared sheets using a plastic sample cutting machine, and the specimen dimensions, were as follow: width of narrow section was 13 mm and the gauge length was 50 mm. The results were obtained from a mean value of five specimens.

3.2.5 Rheological Measurement

The shear viscosity of these blends was determined in a series of two different modes, steady and dynamic shear rheological modes. These measurements were carried out on ARES (Rheometrics Scientific) with cone-and-plate geometry. Pellets of the blends were compressed into circular disk of 1 mm thickness and 25 mm diameter. Before the measurement was taken, the rheometer was heated up to 260°C, and the gap was set to 0.052 mm. For the steady rate sweep test, shear viscosity was determined as a function of shear rate. In case of dynamic measurements, the strain (γ) values were chosen in order to perform the experiments in the linear viscoelastic region i.e., the limiting strain under which the rheological parameters (G', G'', η^*, etc.) remained constant.