



CHAPTER III EXPERIMENTAL

3.1 Materials

Poly(trimethylene terephthalate) (PTT) was kindly supplied in pellet form by PTT PolyCanada LP (Corterra 9200). Its intrinsic viscosity is 0.92 dl/g. Two liquid crystalline polymers (LCPs) were used; Vectra A950 (VA950), supplied by Hoechst-Celanese. It is a copolyester of 73 mol% p-hydroxybenzoic acid (HBA) and 27 mol% 2-hydroxy-6-naphthoic acid (HNA). Another grade of LCP used is Vectra V400P (V400P), also supplied by Hoechst-Celanese. Its chemical structure has not yet been revealed. Its melt flow index is 14 g/10 min at 230°C. The poly(ethylene terephthalate) (PET) was purchased from Indorama Polymers Public Company Limited, Thailand under the trade name RAMAPET N1. Its intrinsic viscosity as measured by the ubbelohde viscometer is 0.80±0.02 dl/g. Polycarbonate (PC) (Lexan 121) was supplied by (SABIC) with a melt flow index of 17.5 g/10 min at 300°C according to ASTM D1238. All polymers were dried in a vacuum oven at 130°C for at least 12 h prior to use.

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (99.5 mol%) was purchased from Carlo Erba. Solid sodium hydroxide (NaOH) was purchased from Labscan. Multi-walled carbon nanotubes (CNTs) (diameter 13 nm, length > 1 μm) was kindly supplied by BayerMaterialScience in the form of agglomerates under the trade name Baytubes, C-150P.

3.2 Equipment

3.2.1 All Studies except for the Study on PC/ LCP/ CNTs

Melt-blending of the polymers and fillers (except for CNTs) was performed using a self-wiping, co-rotating twin-screw extruder (Collin, ZX-25). Only manual feeding was possible.

An AP-90 (Asian Plastic) injection molding machine was used to fabricate injection-molded samples for mechanical testings by an Instron 4206 tensile tester. The obtained specimens are 2.5 mm thick.

The flow properties of blended and neat materials were investigated by using a CEAST Rheologic 5000 twin-bore capillary rheometer. The inner diameter and the length of the barrel used were 15 and 250 mm, respectively, while the inner diameter and the length of the die were 1 and 20 mm (i.e. L/D ratio = 20), respectively. The temperature tolerance was set at $\pm 0.5^\circ\text{C}$.

A JEOL JSM5200 scanning electron microscope (SEM) was used to study the sample morphology. Energy dispersive X-ray (EDX) analysis was performed to evaluate the dispersion of the Zn element in the composites.

The thermal stability of the samples was evaluated by a Perkin Elmer TGA7 (TGA).

The synthesis of zinc oxide (ZnO) spherical particles was carried out in a domestic microwave oven (Samsung, M-183GN, 2.45 GHz, 850W).

A Hermle Z383 K centrifugation was used to separate the solid zinc oxide phase from the aqueous phase.

An X-ray diffractometer (XRD) (Bruker-AXS D8 Discover) was used to confirm the crystalline structure of ZnO.

Tensile testing results were obtained using an Instron 4206 tensile tester at room temperature.

3.2.2 A Study on PC/ LCP/ CNTs

Compounding of the polymer blends and polymer composites with CNTs was carried out in a twin-screw mini-compounder (Thermo Haake MiniLab).

Injection-molded samples were prepared using a mini-injection-molding machine from DSM Research Netherlands. Disks of 2.5 mm diameter and 1.1 mm thickness were used for rheological measurements. Rectangular bars (60.0 mm x 12.0 x 2.0 mm³) were also prepared for DMTA and electrical conductivity measurements.

Specimen discs with a diameter of 2.8 mm and a thickness of 0.8 mm were obtained from a compression-molder (Carver Model 3912 hydraulic unit) for contact angle measurements.

The volume conductivity of the samples were achieved using a 4 point-probe technique performed by a Keithley Sub-Femtoamp Remote SourceMeter (model 6430).

Melt rheological investigations were conducted by an ARES, TA instruments in parallel plates oscillation mode.

Contact angle measurements were performed using a Rame-Hart contact angle goniometer (model 100-00), under an atmospheric pressure and a temperature of $24\pm 2^\circ\text{C}$. Two reference liquids used were diiodomethane and water.

Sample morphologies were investigated using a scanning electron microscope (JEOL SM-71510).

Ultra-thin sectioning was performed with a diamond knife, using an ultra-microtoming device (PT-PC PowerTome) at a room temperature and deionised water was used to collect the sections.

TEM images were obtained from ultra-thin sections using a Tecnai 12 TEM.

The dynamic mechanical analyzer (TA Instruments model RSA III) was used to determine the dynamic moduli of the samples in tension mode—single point bending with a fixed strain of 0.2% and a vibration frequency of 1 Hz.

3.3 Methodology

3.3.1 Preparation of PTT/VA950 Blends and Their Characterization

PTT and VA950 pellets were premixed in a dry mixer to prepare PTT/VA950 blends at VA950 contents ranging from 10 to 70 wt% . The dry-mixed blends were then melt-mixed in a self-wiping, co-rotating twin-screw extruder. The temperature of the barrel section from the feeding zone to the die was set at 80, 230, 250, 275, 285, and 265°C . The rotor was operated at a speed of 30 rpm. The extrudates were cooled by water and then pelletized.

The dried polymers were injected into dumbbell-shaped specimens at the temperatures of 250, 265 and 280°C. These injection-molded specimens were tested in an Instron 4206 tensile tester at a gauge length of 25 mm and a cross-head speed of 50 mm min⁻¹ at a room temperature. A load cell used was 100 N. The mechanical properties (tensile modulus, tensile strength, and elongation at break) were determined from the stress–strain curves. At least seven specimens were tested for each reported value.

The samples collected directly from a twin screw extruder were used for a thermal stability test by a TGA, calorimetry measurements by DSC and a rheological study by a capillary rheometer. The thermal stability measurements were carried out under nitrogen atmosphere at a heating rate of 10°C min⁻¹ from 30 to 800°C. The DSC analysis was performed with samples of comparable quantity (8±0.5 mg). The experiments started with removing the thermal histories of the sample by annealing them at 300°C for 5 min then they were removed and immediately quenched in liquid nitrogen to achieve a completely amorphous state. Then the samples were subjected to a heating scan at a rate of 5°C/min from 25°C to 300°C and then cooled to 30°C at a cooling rate of 10°C min⁻¹. The second heating and cooling traces were recorded. From the rheological data, the viscosity ratio of VA950 to PTT and flow activation energies were determined. After being extruded through a capillary die at four different temperatures (250-280°C) and varied shear rates ranging from 60 to 2000 s⁻¹, the polymer extrudate was cryogenically fractured in liquid nitrogen in the transverse direction to provide a cross-sectional view. Then they were immersed in 1,2-dichlorophenol at 80°C for 2 h to eliminate the PTT phase followed by repeated washing of the residue for a clear VA950 phase. The fractured surfaces and the VA950 residue were sputtered with a thin layer of gold prior to SEM observation. The diameter distribution of the VA950 domains were calculated from the VA950 residue of at least 200 particles.

3.3.2 An Investigation on the Non-Isothermal Crystallization Behaviors of PTT/VA950

The non-isothermal crystallization behaviors of the neat PTT and its blend with VA950 were studied using a Mettler-Toledo DSC822 differential scanning calorimeter (DSC). Samples were obtained from twin-screw extruder as stated in Section 3.31. Each sample was tested at a comparable weight of 6 ± 0.5 mg. The experiments were performed under nitrogen starting with heating each sample from 25°C at a heating rate of 80°C/min to a temperature of 310°C for 5 min in order to ensure complete melting. Then, each sample was cooled at various cooling rates ranging from 10 to 30°C/min, to 120°C. The non-isothermal melt crystallization exotherms, the initial crystallization temperature, the peak crystallization temperature, the final crystallization temperature, the half-time of crystallization ($t_{0.5}$), and the heat of crystallization (ΔH_c) were recorded. ΔH_c values were then normalized by the weight percent of a certain component to yield ΔH^*_c . The conclusions on the influences of VA950 on the non-isothermal crystallization kinetics of PTT were drawn from the parameter $F(T)$ in the combined Avrami and Ozawa equation, the $t_{0.5}$ values and the Ozawa rate constant. The crystallization activation energy of PTT, VA, and their blends were evaluated with the help of the Takhor model.

3.3.3 Microwave-Assisted Synthesis of ZnO Particles

$Zn(NO_3)_2 \cdot 6H_2O$ and solid NaOH were separately dissolved in 50 ml of deionized water and stirred by a magnetic stirrer for 30 min at room temperature. The two solutions were then mixed together with an additional 100 ml of deionized water. A domestic microwave oven was used to heat the solutions in air for 5 min. The solid fraction was obtained by centrifugation, then washed three times with deionized water and finally dried at 70°C under atmospheric pressure. The resulting white powder was characterized by XRD and SEM.

3.3.4 Preparation of PET/VA950/ZnO In-Situ Hybrid Composites and Their Characterization

PET, VA resins and ZnO powder were premixed in a dry mixer to prepare PET/VA blends with 10 wt% VA950 content and 0, 0.5 and 1.0 phr ZnO loadings with respect to the total polymer weight. The melt blending was carried out in a self-wiping, co-rotating twin-screw extruder with the temperature of the barrel section from the feeding zone to the die set at 95, 250, 260, 270, 275, 265°C. The rotor was operated at a speed of 20 rpm. The extrudates were cooled by water and then pelletized. The chopped samples obtained from the extruder were used for the rheological measurements and DSC analysis. The shear viscosity of the blends was measured by using a twin-bore capillary rheometer at 260°C and a shear rate range of 200–6,400 s⁻¹. The rheometer extrudates were quenched at room and cryogenically fractured for further SEM analysis. To observe the clear morphology of Vectra A950 domains, these rheometer extrudates were immersed in 2-chlorophenol at 80°C for 2 h to dissolve the PET matrix, followed by repeated washing of the Vectra A950 residue. The fractured surfaces and the Vectra A950 residue were sputtered with a thin layer of gold prior to observation. Energy dispersive X-ray (EDX) analysis was also conducted to investigate the dispersion of the Zn element in the composites. The DSC measurements were carried out on the neat polymer and the blend pellets after twin-screw extrusion. All experiments were performed under nitrogen at a flow rate of 20 ml/min. The standard sample used was indium. Each sample holder was loaded with samples of 7±0.5 mg. All the experiments started with heating the sample at a heating rate of 200 C min⁻¹ from 25°C to 310°C and annealing there for 5 min in order to remove previous thermal histories. The samples were then cooled at a rate of 10°C/min to 25°C followed by heating to 300°C at a heating rate of 10°C min⁻¹. For the study of the isothermal crystallization behavior, after the melt-annealing, the sample was cooled from 310°C to 200°C and maintained until the crystallization of the PET matrix was complete. The neat PET and the blends, with or without ZnO, were injected into dumbbell-shaped specimens for the tensile tests. To investigate the mechanical performance of the samples, a tensile tester was operated at room temperature with an extensional speed of 5 mm/min and an initial gauge length of 25 mm. Test results were obtained by averaging the data from at least five samples.

Tensile modulus, tensile strength, and percent elongation at break were determined from the stress–strain curves.

3.3.5 Investigation on the Response of PET/VA950 In-Situ Composites to Microwave Irradiation

PET and VA950 pellets were first dried-mixed at a VA content of 10 wt%. before melt-mixing was carried out in a self-wiping, co-rotating twin-screw extruder. The temperature of the barrel section from the feeding zone to the die was set at 95, 250, 260, 270, 275, 265°C. The rotor speed was set at 20 rpm. The extrudates were cooled by water and then pelletized. The pristine PET and PET/VA blend were heated to a molten state in a disc-shaped aluminum container and then quenched to room temperature. Solidified samples were obtained in the form of a disc of 1 cm in diameter and 2 mm in thickness. They were in an amorphous state prior to microwave exposure.

Microwave irradiation was carried out using a domestic microwave oven manufactured by Samsung model M183GN. The sample was irradiated at 300 W from one to four cycles with each cycle lasting 20 min. During exposure to microwave energy, an infrared gun was used to detect the temperature of the sample with respect to time. After each cycle, the sample was taken out for the DSC characterization.

To evaluate the mechanical performance of the pristine PET and the PET/VA950 blends, the samples were injected at 260°C in an injection molding machine. Dumbbell-shaped, 2.5 mm thick specimens were obtained. They were in an amorphous state as a mold temperature used was low. The injection-molded samples were treated by microwave energy in the same manner as the disc-shaped samples. Then mechanical testing of the treated and untreated samples was carried out in an Instron tensile tester at room temperature with an extension speed of 5 mm/min and an initial gauge length of 25 mm. The mechanical properties, i.e., tensile modulus, tensile strength, and percent elongation at break were determined from the stress–strain curves. Test results were reported as the average values from at least five samples.

3.3.6 A Study on Electrically Conductive Blends of PC/ LCP/ CNT

Melt-mixing of neat blends and blends filled with CNT was carried out in a twin-screw mini-compounder at 290°C for the neat PC and PC/V400P/CNT, and 300°C for PC/VA950/CNT, with a rotational speed of 60 rpm. For the CNT composites, mixing was done in two separate steps but under the same conditions; PC was mixed with CNT for 5 minute as the first step and then taken out, the PC/ CNT compound was then mixed with an LCP as the second step. The reversed mixing sequence was also conducted by first mixing LCP with CNT, then PC was introduced into the compound.

Injection-molded samples were prepared using a mini-injection-molding machine with the injection-molding temperature/mold temperature of 310/150°C for PC, V400P and PC/ V400P/ CNT, 300/80°C for VA950 and PC/ VA950/ CNT, and the injection pressure was kept at 6 bar for all the experiments. Injection-molded disk-shaped samples with a diameter of 2.5 mm and a thickness of 1.1 mm were used for rheological measurements. Injection-molded rectangular bars (60.0 x 12.0 x 2.0 mm³) were also prepared. The bars were cut into the dimensions of 36.0 x 12.0 x 2.0 mm³ and 30.0 x 6.5 x 2.0 mm³ for the determination of electrical conductivity and dynamic mechanical properties, respectively. A compression molder was used to prepare PC, VA400P, and VA950 discs (diameter 2.8 mm, thickness 0.8 mm) for contact angle measurements. All the compression pressures applied were set at 4000 psi. The compression molding conditions, i.e. heating time (min)/ compression time (min)/ temperature (°C) applied to PC, V400P, and VA950 were 10/ 5/ 300, 15/ 15/ 240, and 15/ 15/ 300, respectively.

Dynamic rheological measurements were carried out on the disk-shaped samples using an an ARES Rheometer. The frequency sweep measurement was performed with 25 mm parallel plate geometry, in oscillatory shear mode, at 300°C, and a fixed strain amplitude of 2%.

The contact angle measurements were performed on a Rame-Hart contact angle goniometer (model 100-00) operating at 1 atm and a temperature of 24±2°C using water and diiodomethane as reference liquids.

To measure the electrical conductivity of the samples, a 4 point-probe technique was used and the experiments were performed on a Keithley Sub-Femtoamp Remote SourceMeter. The current of 10 μA was applied to the low resistivity samples whereas the voltage of 100 V was applied for high resistivity samples (specific conductivity $< 10^{-10}$ S/cm). Copper electrodes were used. The sample geometry was shown in Fig. 3.1.

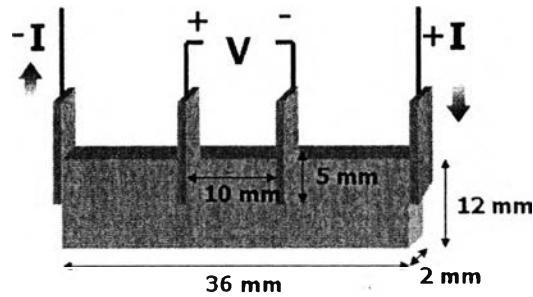


Figure 3.1 Schematic of the 4 point-probe configuration.

The specific conductivity of the materials can be computed by the following equation:

$$R = \frac{\rho \cdot l}{A} \quad (3.1)$$

where R is the resistance, ρ the electrical resistivity measured in Ohm·metre ($\Omega \cdot m$), A the cross-sectional area of the current flow measured in square metres (m^2), and l the length of the conductor measured in metres (m).

The specific conductivity (σ) is by definition the reciprocal of electrical resistivity, ρ , and has the SI units of siemens per metre.

$$\sigma = \frac{1}{\rho} \quad (3.2)$$

According to the geometry shown in Fig. 3.1, l is equal to 0.1 m, and A to $1\text{E-}5 \text{ m}^2$ (obtained from 5mm x 2mm).

The mechanical performance of the samples was investigated using a dynamic mechanical analyzer (RSA III). The temperature range of analysis was 35°C to 200°C, temperature scanning rate 4°C min^{-1} , frequency 1 Hz, strain 0.2% in single-point bending mode.

The morphology of the LCP was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The LCP residue was obtained by immersing the blends in chloroform at room temperature for 12 h, then filtrated using a PP membrane and followed by silver coating prior to observation under a scanning electron microscope (JEOL SM-71510). TEM images were obtained from ultra-thin sections using a Tecnai 12 TEM. Sectioning was performed with a diamond knife, using an ultra-microtoming device (PT-PC PowerTome). Deionized water was used to collect ultrathin sections.