CHAPTER III
EXPERIMENTAL

3.1 Materials

Syndiotactic polypropylene (sPP) used in this work was produced and supplied by AtoFina Petrochemicals (USA) based on a metallocene technology. Some physical properties of the resin are summarized in Table 3.1.

Table 3.1 Physical properties of sPP

Property	Unit	v alue	ASTM method
		s-PP	
Density	g/cm_3	0.88	D 1505
Melt Index	g/10 min	2	D 1238
Melting Point	°C	130	DSC
Tensile Strength	Mpa	15	D 638
Tensile Modulus	Mpa	480	D 638
Elongation at break	%	11	D 790
Flexural Modulus	Mpa	340	D 638
Izod Impact (Notched)	J/m	640	D 256A Non-break

Inorganic fillers used in this work are kaolin [$Al_2Si_2O_5(OH)_4$; Engelhard Corporation (USA)], talcum [$Mg_3Si_4O_{10}(OH)_2$, Pacific Commo Trading (Thailand)], marl [$CaSiO_3$; Pacific Commo Trading (Thailand)], titanium dioxide [TiO_2; Pacific Commo Trading (Thailand)], and SiO_2 [PPG Siam Silica (Thailand)]. Organic fillers are some sorbitol derivatives such as 1,3:2,4-dibenzylidene sorbitol [DBS; Ciba Specialty Chemicals (Switzerland)], 1,3:2,4-di-*p*-methyldibenzilidene sorbitol [MDBS; Ciba Specialty Chemicals (Switzerland)], and 1,3:2,4-di-*m,p*-methylbenzylidene sorbitol [DMDBS; Milliken Asia (Singapore)]. The average particle size of these fillers was measured by a Malvern Instruments Masterizer X particle size analyser was summarized in Table 3.2.

3.2 Methodology

3.2.1 Sample Preparation

All of the fillers used were first dried in a hot-air oven at 60°C for 14 hrs and then cooled down to room temperature. Each filler was then dry-mixed with sPP pellets in a tumble mixer for 10 min and later compounded in a Collin ZK25 self-wiping, co-rotating twin-screw extruder, operating at a screw speed of 50 rpm and the die temperature of 190°C. Due to the limitation on the amount of sPP resin and fillers in possession, only 5 percent by weight (wt.%) of each inorganic filler or 1 wt.% of each organic filler was added to the sPP resin. Table 3.3 summarizes the temperature settings for all of the heating zones in the kneading extruder. The extrudate was water-cooled before being pelletized by a Planetrol 075D2 pelletizer into pellets.

Table 3.2 Characteristics of organic and inorganic fillers used

Filler	Average Particle Size (μm)
DBS	26.83 ± 1.0
MDBS	5.26 ± 0.6
DMDBS	6.69 ± 0.6
kaolin	15.11 ± 1.5
talcum	13.85 ± 1.8
marl	42.47 ± 2.0
TiO_2	5.29 ± 1.0
SiO_2	36.44 ± 0.7

Table 3.3 Temperature settings of all the heating zones in the kneading extruder

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6
120°C	155°C	165°C	175°C	185°C	190°C

3.2.2 Preparation of Testing Specimens

A film of each compound was prepared by melt-pressing sliced pellets between a pair of transparency films, which, in turn, were sandwiched between a pair of stainless steel platens in a Wabash V50H compression press. The temperature of the platens was set at 190°C. The molding was pre-heated for 5 min, before compressing under an applied clamping force of 10 tons for another 5 min. Later, the film was cooled down while still in the compression machine until the temperature of the platens read 40°C. Each film specimen was used for studying non-isothermal crystallization and subsequent melting behavior.

An ARBURG Allrounder® 270M injection molding machine was used to prepare specimens for mechanical tests. The operating settings of the machine are summarized in Table 3.4. Tensile and impact specimens were prepared according to ASTM D638-91 and ASTM D256-90b standard test methods, respectively. Prior to corresponding mechanical tests, both of the tensile and impact specimens were conditioned at ambient condition for 3 days.

Table 3.4 Operating settings of the injection molding machine for preparing specimens for mechanical testing

Barrel temperature	180-195°C
Nozzle temperature	200°C
Mold clamp force	25 kN
Mold temperature	RT-50°C
Injection pressure	1,000 bar

3.2.3 Characterization

3.2.3.1 Crystallization and subsequent melting behavior

Non-isothermal melt-crystallization and subsequent melting behavior of neat sPP and sPP filled with various organic or inorganic filler was investigated on a Perkin-Elmer Series7 differential scanning calorimeter (DSC). Temperature calibration was carried out using a pure indium standard (T_m^o = 156.6°C and ΔH_f^o = 28.5 $J \cdot g^{-1}$) on every other run to ensure accuracy and reliability of the obtained data. To minimize thermal lag between the polymer sample and the

furnace, each sample holder was loaded with a disc-shaped specimen weighing around 6 ± 0.5 mg in weigh, cut from the as-prepared film, was sealed in an aluminium sample holder. 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.

The experimental procedure started with heating each sample from 25°C at a scanning rate of 80°C·min^{-1} to 190°C. To ensure complete melting, the sample was kept at 190°C for holding period of 5 min. After this period, each sample was cooled at a desire cooling rate ϕ, ranging from 2.5 to 20°C min^{-1}, to 25°C in order to observe the nonisothermal crystallization behavior. The sample was then subjected to heating to observe the subsequent melting behavior (recorded using a heating rate of 20°C min^{-1}). Both the nonisothermal crystallization exotherms and subsequent melting endotherms were recorded for further analysis. The analysis of experimental data, according to the nonisothermal crystallization exotherms, was carried out using modified Avrami, Ziabicki equations to directly fit the experimental data to respective macrokinetic models.

3.2.3.2 Crystal structure and crystallinity

The crystal modification and apparent degree of crystallinity of sPP compounds were investigated on a Rigaku Rint 2000 wide-angle X-ray diffractometer (WAXD). The sample was prepared at the same conditions (i.e. non-isothermally crystallized at a cooling rate of 10°C min^{-1}) set forth in DSC measurements. Each sample was then removed from 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 angles 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 and copper target was used (CuK_α radiation, λ = 1.54 Å).

3.2.4 Mechanical Properties

3.2.4.1 Tensile properties

The yield s trength, percentage of elongation at yield, and Young's modulus for both neat and filled sPP samples were measured on an Instron 4206 universal testing machine according to ASTM D638-91 standard test method using 100 kN load cell and 50 $mm \cdot min^{-1}$ crosshead speed. In order to obtain reliable data, the dimension of each testing specimen was carefully measured using a digital caliper. Ten specimens for each formulation were tested, from which the mean value as well as the standard deviation were reported.

3.2.4.2 Impact strength

The Izod impact strength was performed on a Swick 5113 impact tester according to ASTM D256-90b standard test method using 2.7 Joule pendulum and 124.4° release angle. In order to obtain reliable data, the dimension of each testing specimen was carefully measured using a digital caliper. Ten specimens for each formulation were tested, from which the mean value as well as the standard deviation were reported.

3.2.4.3 Hardness

The Hardness was measured on a Rockwell Hardness Tester (Matsuzawa, DXT-3) according to ASTM D785 standard test method using scale-R. Ten specimens for each formulation were tested, from which the mean value as well as the standard deviation were reported.

3.2.5 Microstructure Characterization

A JEOL 520-2AE scanning electron microscope (SEM) was used to observe the topography of the fractured surface of selected specimens which were fractured in liquid nitrogen. Each selected specimen was cut about 2 mm below the fractured surface and the cut piece was adhered onto an aluminum stub. The sample was coated with gold to enhance the conductivity of the surface before being subjected to observation under SEM.

3.2.6 Particle Size Measurement

The particle size of particulate filler studies was determined by using a particle size analyzer (Malvern Instruments Ltd., Masterizer X). This instrument measures the average particle size as summarize in Table 3.2.