



CHAPTER III EXPERIMENTAL

3.1 Materials

In this study, syndiotactic polypropylene (s-PP) was produced commercially in the pellet form by using a metallocene catalyst from Ato-Fina Oil (La Porte, Texas). This s-PP was used as the matrix.

Molecule characterization of this material was carried out by Dr. Roger A. Phillips of Basell USA, Inc. (Elkton, Maryland, USA). The results showed the following molecular weight information: the weight-molecular weight (M_w) was 153,000 and the polydispersity (M_w/M_n) was 3.83. In addition, the syndiotacticity measured by ^{13}C -NMR showed the racemic triad content (%*orr*) to be 86.07%, the racemic pentad content (%*orrrr*) to be 73.71%, with the presence of ethylene defects of less than 0.5 wt%. Some physical properties of this s-PP are shown in Table 3.1.

Table 3.1 Physical properties of s-PP

Property	Unit	Value	ASTM method
Density	g/cm^3	0.87	D 1505
Melt Index	g/10 min	10	D 1238
Tensile Strength	Mpa	16	D 638
Tensile Modulus	Mpa	490	D 638
Elongation at Break	%	310	D 790
Flexural Modulus	Mpa	379	D 638
Izod Impact	J/m	640	D 256A

Five types of calcium carbonate (CaCO_3), kindly supplied by Calcium Products Co., Ltd., were used as fillers. The properties of these filler particles with density 2.7 g/cm^3 were listed in Table 3.2.

Table 3.2 Characteristic of CaCO₃ used in this study

Trade name	Specific surface area (cm ² /g)	Average particle size (micron)	Surface modification
CALOFIL 400	13000	1.9	Uncoated
CALOFIL 100	10500	2.8	Uncoated
CALOFIL 50	5000	10.5	Uncoated
HICOAT 410	13000	1.9	Stearic acid-coated
HICOAT P-400	13000	1.9	Paraffin-coated

3.2 Methodology

3.2.1 Sample Preparation

CaCO₃ was dried in a hot-air oven at 80°C for 14 hrs. The compounds of s-PP with various CaCO₃ particles ranging in weight percent from 0 to 40 were pre-mixed in a tumble mixer for 10 min and then melt-mixed in a Collin co-rotating twin screw kneader ZK 25 (25mm x 30D) with the screw speed of 50 rpm.

All processing passes were carried out using the processing condition as shown in Table 3.3.

Table 3.3 Processing condition used in this study

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6
145°C	155°C	165°C	175°C	185°C	195°C

The extrudate was cooled in water and cut into pellet form by a Planetrol 075D2 pelletizer.

3.2.2 Compression

The pellets were pressed using a picture-frame mold in a Wabash V50H compression press machine. The molding was first pre-heated in the compression press for 5 minutes at 190°C and then was compressed with 15 ton-

force at 190°C for another 5 minutes. The molding was then cooled down to 40°C under pressure. The samples were cut into films and specimens for each test.

3.2.3 Thermal Analysis

3.2.3.1 *Crystalline structure*

The X-ray diffraction technique was employed to determine the crystalline structure of neat s-PP and CaCO₃-filled s-PP samples. The X-ray diffraction patterns were collected on a Rigaku Rint2000 diffractometer equipped with a graphite monochromator and a Cu tube for generating a CuK α radiation (1.5046 Å). First, each film samples was put on a glass slide specimen holder using vasaline as the binder. The sample was scanned between the 2 θ angle of 5° to 40° at a scanning rate of 2° per minute with 0.02° increment. The X-ray source was operated at 40 kV and 30 mA. The digital output of the proportional X-ray detector and the goniometer angle measurement was sent to an online microcomputer for data storage and analysis.

3.2.3.2 *Crystallization behavior*

The crystallization behavior of s-PP and CaCO₃-filled s-PP samples was investigated using a Perkin-Elmer Series7 Differential Scanning Calorimeter (DSC-7) under both isothermal and non-isothermal conditions. Temperature calibration was performed using an indium standard ($T_m^o = 156.6^\circ\text{C}$ and $\Delta H_f^o = 28.5 \text{ Jg}^{-1}$). A sample of 3-6 mg was sealed in champed closed aluminum sample pans. Nitrogen gas was used as a purge gas.

a) *Isothermal condition*

In the isothermal crystallization experiment, samples were heated up to a fusion temperature, T_f ranging from 127°C to 230°C and then held at that temperature for 5 minutes to erase previous thermal history. After that, the samples were rapidly cooled at 200°C/min from fusion temperature, T_f to 87.5, 90 and 92.5°C, where it was held until the crystallization process was completed (approximately 10 min).

b) Non-isothermal condition

In the non-isothermal crystallization experiment, the samples were heated up to 190°C where they were held 5 minutes, and then cooled down at rate ranging from 5 to 20°C/min to -5°C in nitrogen atmosphere. During cooling process, the crystallization patterns were recorded and crystallization enthalpy were measured. After the samples were crystallized, the samples were subsequently heated at a rate of 20°C/min to the melt state, while the melting endotherms were recorded.

3.2.4 Mechanical Testing

3.2.4.1 Tensile properties

Tensile strength and Young's modulus were measured on an Instron Universal Testing Machine model 4206 according to ASTM D 638-91 test method using 100 kN load cell and 50 mm/min crosshead speed. Dumbbell shape specimens were cut from the as-prepared sheets using a pneumatic puncher. The specimen dimensions were as follow: width of narrow section being 13 mm and the gauge length being 50 mm. Five specimens were tested for each condition.

3.2.4.2 Impact resistance

Izod impact resistance values were determined on a Swick model 5113 impact tester according to ASTM D 256-90b test method with 2.7-Joule pendulum and 124.4 degrees release angle. The specimen size was 3x12.7x63.5 mm. Each specimen was machined to produce a V-shape notch having a 45 degree angle and 2.5 mm depth. Five specimens were tested for each condition.

3.2.5 Rheological Measurement

3.2.5.1 Steady shear measurement

The shear viscosity of the compound was determined in a series of two different rheometers.

a) Capillary rheometer

A capillary rheometer (Instron model 3213) was used to study the steady state shear behavior of these compounds at high shear rate. The capillary was a tapered type having 45° entrance angle. The diameter of barrel was 9.525 mm. The capillary die number 1860 with 1.25 mm in diameter and 50.19 mm in length and L/D ratio of 40.15 was used in this study.

Procedure: Test temperature used was 200°C and plunger speed schedules were set. The materials were poured into the barrel through a funnel and packed down with a plunger until the first extrudate appeared at the capillary exit. The sample was allowed to reach the set temperature then forced through the capillary by the plunger at pre-selected velocities. The next velocity in the measurement schedule begun when the load versus extension curve reached a slope closed to zero. The loads, together with the corresponding plunger speed, were used to calculate the shear stress and the shear strain for the sample under test.

Calculation:

It was assumed that the melt was incompressible, the flow was laminar and fully developed, and there was no slippage at the wall.

The load on the plunger and the plunger speed were converted into apparent shear stress and shear rate at the wall respectively by using the following equations involving the geometry of the capillary and the barrel.

$$\tau_w = \frac{FD_c}{4A_pL_c} \quad (3.1)$$

where τ_w = apparent shear stress at the wall
 F = the force acting on the plunger
 A_p = cross sectional area of the plunger
 D_c = diameter of the capillary die
 L_c = length of the capillary die

$$\dot{\gamma}_w = \frac{2V_p D_b^2}{15D_c^3} \quad (3.2)$$

where $\dot{\gamma}_w$ = apparent rate at wall
 V_p = plunger speed
 D_b = barrel diameter

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} \quad (3.3)$$

where η_a = apparent viscosity

The true shear rate was determined by using the Rabinowitch correction,

$$\dot{\gamma}_{tr} = \frac{3n+1}{4n} \dot{\gamma}_w \quad (3.4)$$

where $\dot{\gamma}_{tr}$ = true shear rate
 n = Power law index

Thus, 'n' was the slope of the plot of $\log \tau_w$ versus $\log \dot{\gamma}_w$.

In this study, the Bagley correction was not applied because the L/D ratio was 40.15, which was significantly long to neglect end effect. So the true viscosity was determined from

$$\eta_{tr} = \frac{\tau_w}{\dot{\gamma}_{tr}} \quad (3.5)$$

b) Parallel plate rheometer

The Rheometer ARES using 8 mm in diameter with parallel plate geometry was used to study the steady state shear behavior of these compounds at low shear rate (0.25-25 rad/s).

Procedures: Before the measurement was taken, the rheometer was heated up to 200°C, and the gap was calibrated. Then the compound was loaded. As the compound melted, the gap was set to 0.2 mm. The measurement

was performed on the steady rate sweep test, shear viscosity was determined as a function of shear rate.

3.2.5.2 *Oscillatory shear measurement*

Pellets of CaCO₃-filled s-PP samples were compressed into disc-shape. The dynamic viscoelastic properties were carried out on Rheometer ARES using 8 mm diameter with parallel plate geometry.

Procedures: Before the measurement was taken, the rheometer was heated up to 200°C, and the gap was calibrated. Then the compound was loaded. As the compound melted, the gap was set to 0.2 mm. At the first step, the dynamic strain sweep test was used to find the linear viscoelastic regime at frequency equal to 1 rad/s. After that the dynamic frequency sweep test was used to measure the storage (G') and loss modulus (G'') covered the range of frequency from 0.05 to 100 rad/s starting with the highest frequency.

3.2.6 Microstructure Characterization

The impact fractured surfaces obtained from impact testing were cut about 2 mm below the fractured surface and stuck onto aluminium stubs. The samples were then coated with gold by vapour deposition and examined under Scanning Electron Microscope (JEOL 5200-2AE).