

CHAPTER III EXPERIMENTAL

3.1 Materials

The materials used in this work are as follows:

3.1.1 Calcium Carbonate (CaCO₃)

Calcium carbonate (CALOFIL1000, 1.2 μm average particle size) and stearic acid-coated calcium carbonate (HICOAT1010, 1.2 μm average particle size) were kindly supplied by Calcium Products Co., Ltd.

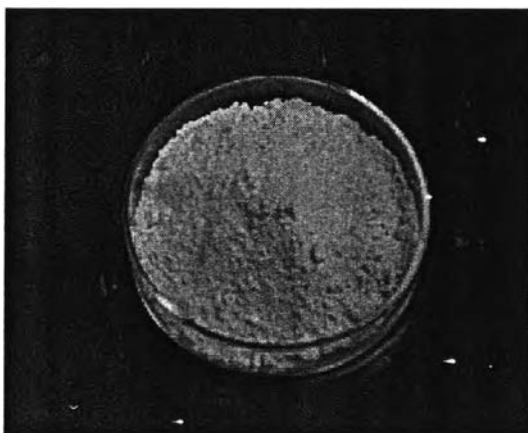


Figure 3.1 Calcium carbonate (CALOFIL1000).

3.1.2 Isotactic Polypropylene (iPP)

Commercial grade of isotactic polypropylene (iPP) (HP500N) was courteously supplied by HMC Polymers Co., Ltd. (Thailand). HP500N was a homopolymer grade with density and melt-flow rate (MFR) values of about 0.90 g·cm⁻³ and 12 dg·min⁻¹, respectively.

3.1.3 Propylene Gas

Polymerization grade propylene (purity 99.5%) was purchased from Linde Gas Singapore Ltd. and was used as the monomer.

3.1.4 Sodium Dodecyl Sulfate (SDS)

Sodium dodecyl sulfate (purity 94-98%) purchased from Carlo Erba Reagenti (Italy) served as a surfactant to form the surfactant template or bilayer for polymerization.

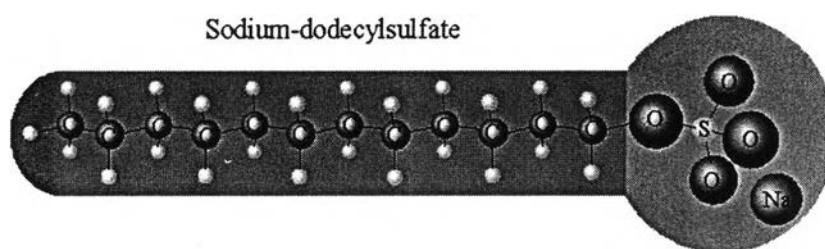


Figure 3.2 Chemical structure of sodium dodecyl sulfate (SDS).

3.1.5 Initiator

Sodium persulfate (purity 99.0%+) purchased from Fluka (USA) acted as a water-soluble initiator.

3.1.6 Solvent

Xylene (AR-grade) purchased from Lab-Scan (Asia) (Thailand), was used as extracting solvent.

3.1.7 Other Chemicals

Sodium chloride (purity 99.9%+) was purchased from Carlo Erba Reagenti (Italy). Both sodium hydroxide (AR-grade) and hydrochloric acid 37% (AR-grade) were purchased from Lab-Scan (Asia) (Thailand). The surfactant and all chemicals were used as received.

3.2 Instrumentation

3.2.1 Zeta Potential Meter

The electrophoretic mobility of the CaCO_3 particles was observed with a Zeta potential meter 3.0.



Figure 3.3 Zeta potential meter 3.0.

3.2.2 Tensiometer

The interfacial tension was measured by calculating drop shape of solution by using a KRÜSS DSA10 Mk2 drop shape analysis system.

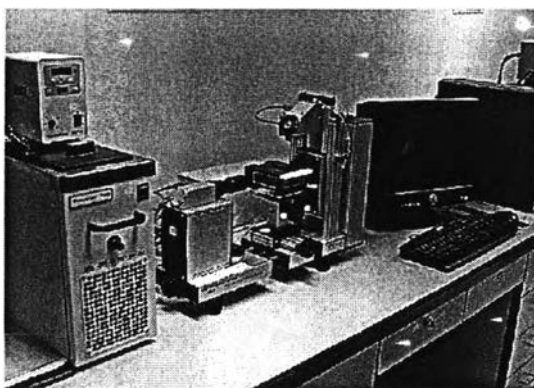


Figure 3.4 KRÜSS DSA10 Mk2 drop shape analysis system.

3.2.3 The High Pressure Reactor

Polymerization reactions were carried out in a 2 liters Parr reactor (Parr Instrument Company), equipped with a pitch-blade turbine impeller, a speed controller, external heating jacket, thermowell, and pressure transducer (Figure 3.5). The impeller speed, internal reactor temperature, and pressure reading are digitally displayed on the front panel.

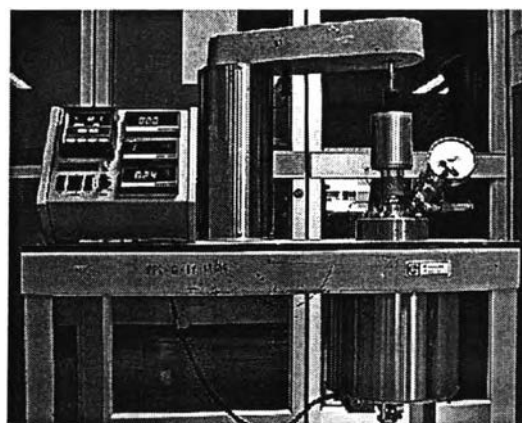


Figure 3.5 High pressure Parr reactor.

3.2.4 Twin-Screw Extruder

Each type of CaCO_3 was mixed with iPP in Collin ZK25 self-wiping, co-rotating twin-screw extruder and cut into pellet form by a Planetrol 075D2 pelletizer.

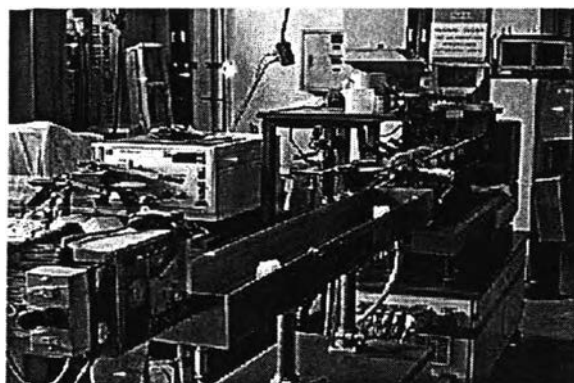


Figure 3.6 Collin ZK25 self-wiping, co-rotating twin-screw extruder.

3.2.5 Injection Molding

Test specimens of the CaCO₃-filled iPP composite samples were prepared by an ARBURG Allrounder® 270M injection molding machine.



Figure 3.7 ARBURG Allrounder® 270M injection molding machine.

3.2.6 Instron Universal Testing Machine

Tensile and flexural tests of the CaCO₃-filled iPP composite samples were carried out on an Instron 4260 universal testing machine.

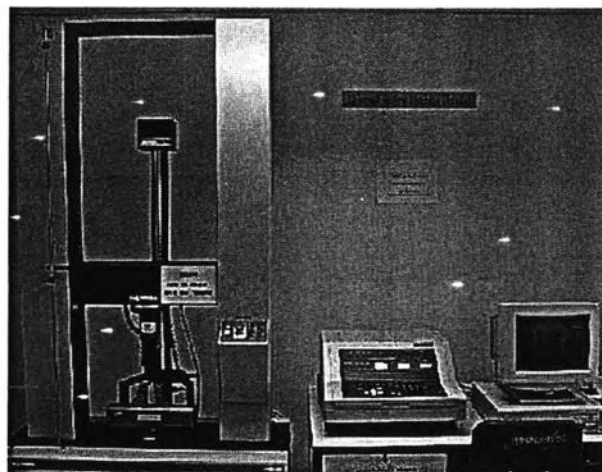


Figure 3.8 Instron 4260 universal testing machine.

3.2.7 Zwick Pendulum Impact Tester

Impact tests of the CaCO_3 -filled iPP composite samples were performed on a Zwick 5113 pendulum impact tester.

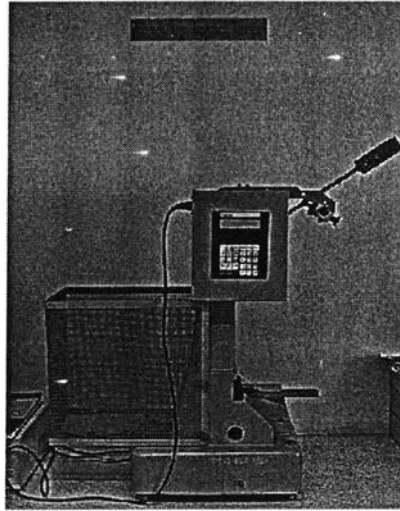


Figure 3.9 Zwick 5113 pendulum impact tester.

3.2.8 Scanning Electron Microscope (SEM)

Scanning electron micrographs were taken to identify the morphology of the CaCO_3 -filled iPP composite samples. Samples were characterized using a JEOL JSM-5200 scanning electron microscope at a magnification of 3500.



Figure 3.10 JEOL JSM-5200 scanning electron microscope.

3.2.9 FTIR Spectrometer

The extracted polymer from admicellar-treated CaCO_3 was characterized by Thermo Nicolet Nexus 670 FT-IR spectrometer.



Figure 3.11 Thermo Nicolet Nexus 670 FT-IR spectrometer.

3.2.10 Particle Size Analyzer

Malvern MastersizerX particle size analyzer was used to measure particle size of CaCO_3 particles.

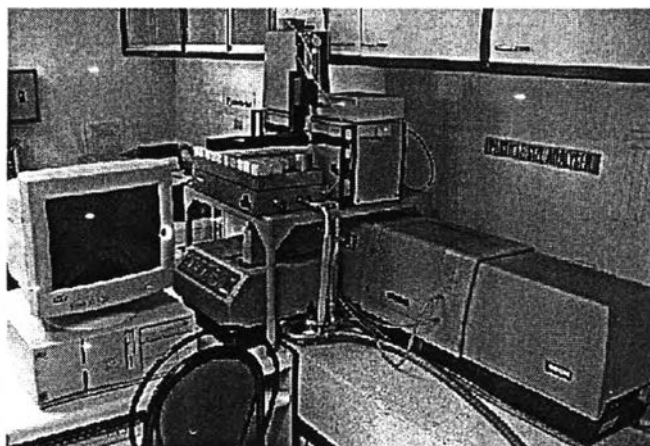


Figure 3.12 Malvern MastersizerX particle size analyzer.

3.2.11 Differential Scanning Calorimetry

Non-isothermal crystallization and melting behavior of CaCO₃-filled iPP samples were investigated on a Perkin-Elmer Series 7 differential scanning calorimeter (DSC).

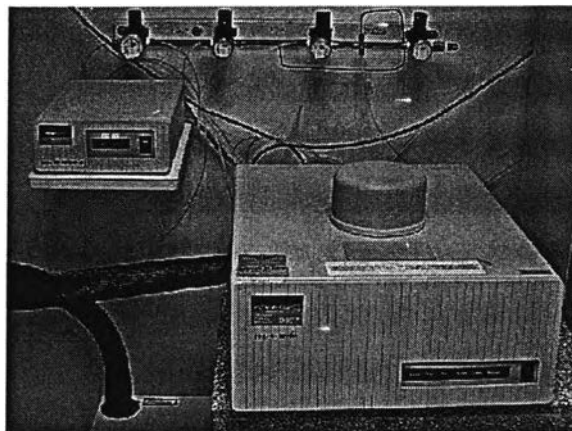


Figure 3.13 Perkin-Elmer Series 7 differential scanning calorimeter.

3.2.12 X-Ray Diffractometer

A wide-angle X-ray diffraction (WAXD) technique was used to determine the crystal structure and the apparent degree of crystallization of CaCO₃-filled iPP samples.

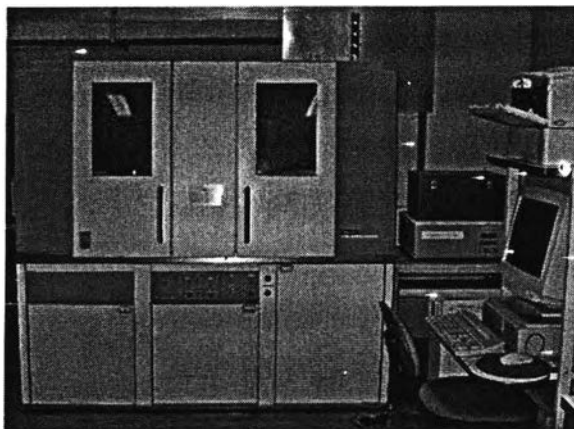


Figure 3.14 Rigaku Rint2000 diffractometer.

3.3 Methodology

3.3.1 Determination of Point of Zero Charge (PZC) of CaCO₃

The change in the surface charge of CaCO₃ particles with pH is important to determine the surfactant adsorption. Electrophoretic mobility was used to determine the surface charge of the CaCO₃ particles at various solution pH's. The CaCO₃ colloidal dispersion was diluted in 100 ml distilled water. The pH in the solution was adjusted by 0.1 M NaOH or HCl, and was left to equilibrate for 1 day. The electrophoretic mobility of the CaCO₃ particles was observed at room temperature with a Zeta potential meter 3.0.

3.3.2 Determination of Amount of SDS Adsorbed on CaCO₃

A solution of SDS of the desired concentration, pH (<pH at PZC), and salt concentration (0.00-0.50 M) was first prepared. A 10 ml aliquot of the solution was then pipetted into a 24-ml vial containing a 1 g of CaCO₃. The pH of the solution was adjusted with HCl or NaOH aqueous solutions. The sealed vial was shaken at 150 rpm at room temperature for a set time (equilibrium adsorption). The adsorbed SDS on CaCO₃ was calculated by taking the difference between the initial and the final concentration of SDS. The SDS concentrations were determined using a KRÜSS DSA10 Mk2 drop shape analysis system to measure the surface and interfacial tension of pendant drops of the sample solutions. The SDS concentration was determined by using a calibration curve between the interfacial tension versus SDS standard concentration.

3.3.3 Determination of Adsorption Isotherm of SDS on CaCO₃

The adsorption isotherms of SDS on CaCO₃ were obtained by exposing 1 g of CaCO₃ to 10 ml of SDS solution of known initial concentration. The mixture equilibrated at room temperature for a set time in a sealed 24-ml vial. The pH of the solution was pre-adjusted and NaCl pre-added as in the above experiments. The amount of SDS in the supernatant was measured by drop shape analysis using the same procedure as described above. The initial SDS concentration in this

experiment was varied from 40 to 20,000 μM , which covered the regions below and above the CMC of SDS.

3.3.4 Admicellar Polymerization of Propylene onto CaCO_3

3.3.4.1 *Pressure Drop of Propylene Gas During The Adsolubilization and Polymerization*

Before determining the pressure drop for adsolubilization and polymerization, the amount of propylene dissolved in water was first determined by means of a “blank” in order to find out the exact amount of propylene solubilized into the surfactant bilayers. 1,200 ml water containing pre-added NaCl and pre-adjusted pH as in the above experiments was poured into the Parr reactor which was then closed and sealed. After vacuuming the reactor, propylene gas was introduced into the reactor and adjusted to a desired pressure at 30°C to 70°C (corresponding to adsolubilization and admicellar polymerization conditions) and the pressure decrease with time was recorded.

3.3.4.2 *Admicellar Polymerization Process*

Polymerization of propylene onto CaCO_3 was carried out using sodium persulfate as initiator. A 120 g of CaCO_3 was put into the Parr reactor. A 1,200 ml aqueous solution of SDS with desired initial concentration was fed into the reactor and the mixture was adjusted for pH and NaCl was added as in the above experiments. The desired amount of initiator used in the polymerization experiment was 3:1 initiator to surfactant ratios. The reactor was sealed and vacuumed. After this, propylene gas monomer was introduced into the reactor and the pressure adjusted to 140 psi. For the adsolubilization process, the mixture was stirred at 150 rpm for a set time at 30°C. If a pressure drop was observed, the reactor was then repressurized with propylene gas to 140 psi before proceeding to the admicellar polymerization. To initiate polymerization, the temperature of the mixture was raised to 70°C and the stirrer speed is adjusted to 150 rpm for a further hours to ensure complete polymerization and the pressure decrease with time was recorded. When equilibrium was established, i.e. the pressure remains constant, the reactor was cooled down to room temperature. The supernatant liquid was carefully decanted from the reactor and the CaCO_3 was washed several times with distilled water to

remove surfactant and initiator. Lastly, the CaCO_3 was dried in a vacuum oven at 80°C overnight.

3.4 Characterization and Testing

3.4.1 Characterization of Coated Film

FT-IR was used to characterize the polypropylene film. The coated film on treated CaCO_3 was extracted by xylene extraction. After the solvent was evaporated, the remaining polymer was coated on a silicide disk for further analysis on a Thermo Nicolet Nexus 670 FT-IR spectrometer.

3.4.2 Particle Size Analysis of CaCO_3 Particles

A Malvern MastersizerX Particle size analyzer was used to measure particle size of as-received, untreated, and admicellar-treated CaCO_3 particles.

3.4.3 Gravimetric Analysis (Percentage of Weight Loss)

This characterization method was based on the difference in weight of the surface-modified CaCO_3 before and after burning in a furnace at 600°C for 1 h to remove the polypropylene-coated film from the CaCO_3 surface. The percentage of coating was equal to the percent of weight loss which was determined using this equation:

$$\% \text{ weight loss} = \frac{\text{weight of } \text{CaCO}_3 \text{ (before burning)} - \text{weight of } \text{CaCO}_3 \text{ (after burning)}}{\text{weight of } \text{CaCO}_3 \text{ (before burning)}} \times 100$$

CaCO_3 particles were dried in oven at 60°C for 24 h and weighted before calcination.

3.4.4 Polymer Composite Preparation

The compounds of iPP and CaCO_3 particles of various surface characteristics at a fixed 30 wt.% loading were carried out by first pre-mixing in a tumble mixer for 10 min and then melt-mixed in a Collin ZK25 self-wiping, co-rotating twin-screw extruder operating at a screw speed of 80 rpm and a temperature profile of 190 (die), 190 (zone 4), 180 (zone 3), 170 (zone 2), 160 (zone 1), and 70°C

(feed zone). The composite extrudates were water-cooled pelletized using a Planetrol 075D2 pelletizer. The composite pellets were dried at 60°C overnight, prior to being shaped into specimens for mechanical tests using an ARBURG Allrounder[®] 270M injection molding machine. The temperature settings (from the feed zone to the nozzle) were 160, 170, 175, 185, and 190°C, respectively. The injection pressure was 1,000 bars and the dwelling pressure was 700 bars. Prior to the mechanical tests, all of the test specimens were conditioned under ambient conditions for 7 days.

3.4.5 Differential Scanning Calorimetry Measurements

Non-isothermal crystallization and melting behavior of CaCO₃-filled iPP samples was investigated on a Perkin-Elmer Series 7 differential scanning calorimeter (DSC). Temperature calibration was performed using an indium standard ($T_m^\circ = 156.6^\circ\text{C}$ and $\Delta H_f^\circ = 28.5 \text{ J/g}$). Each sample of 3 to 6 mg in weight, cut from the prepared compressed films, was sealed in an aluminum sample holder. The experimental procedure started with melting each sample at 200°C for 5 min and then cooling it to 30°C at a rate of 10°C/min. After that, the sample was immediately subjected to heating at a rate of 20°C/min to 190°C. Both the crystallization exotherm and the melting endotherm were recorded for further analysis. All measurements were carried out in a nitrogen atmosphere.

3.4.6 Crystal Structure and Crystallinity Measurements

A wide-angle X-ray diffraction (WAXD) technique was used to determine the crystal modification and the apparent degree of crystallinity for both neat and CaCO₃-filled iPP samples prepared according to the conditions set forth for DSC measurements but without a subsequent heating step. Each sample was removed from the DSC sample holder and pasted onto a glass sample holder. The WAXD intensity patterns of the sample were then collected on a Rigaku Rint2000 diffractometer (CuK_α radiation, $\lambda = 1.54 \text{ \AA}$), equipped with computerized data collection and analytical tools. The X-ray source was operated at a voltage of 40 kV and a filament current of 30 mA.

3.4.7 Mechanical Properties Measurements

3.4.7.1 Tensile Testing

The tensile strength of the CaCO₃-filled iPP composites were determined using an Instron universal testing machine. Tests were carried out according to ASTM D638-91 using a 100 kN load cell and 50 mm/min crosshead speed. 10 specimens were determined for each sample and the results were averaged to obtain a mean value.

3.4.7.2 Flexural Testing

The flexural strength of the composites was measured using an Instron universal testing machine according to ASTM D790-92 in three-point bending mode. Measurements were carried out using a 5 kN load cell, 11.52 mm/min crosshead speed and a 43.2 mm support span. 15 specimens were tested for each sample and the results were averaged to obtain a mean value.

3.4.7.3 Impact Testing

Izod impact strength was measured using a Zwick pendulum impact tester instrument with 2.7 joules pendulum according to ASTM D256-90b test method. The results were reported by evaluating a mean value from 15 specimens.

3.4.8 Morphology Observation of Fracture Surface

The morphological appearance of the fractured surface of selected impact test specimens for iPP filled with 30 wt.% of various types of surface-treated CaCO₃ particles was investigated using a JOEL JSM-5200 scanning electron microscope (SEM). Each sample was coated with a thin layer of gold using a JEOL JFC-1100E ion sputtering device before observation under SEM. The average percentage of area of CaCO₃ on iPP matrix was measured by Semafore 4.0 software from SEM images.