CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipment

Materials:

Isotactic Polypropylene used in this work was produced and supplied by HMC Polymers Company Limited. Some physical properties of the resin are summarized in Table 3.1.

Table 3.1 Physical properties of isotactic polypropylene

Properties	Moplen HP550R	ASTM Method
Melt flow rate, dg/min	22	D 1238
Density, g/cm^3	0.90	D 792B
Tensile strength at yield, Mpa	34	D638
Elongation at yield, %	9	D638
Flexural modulus, Mpa	1480	D790A
Notched izod impact strength at 123°C , J/m	22	D256A
Deflection temperature at 455 kPa, °C	97	D648

TiO_2 particles from two sources were used, the first was a commercial grade supplied by JJ-Degussa Thailand and the other was synthesized via sol-gel process. Surface area, pore volume, and pore size were measured by BET autosorb one and the average particle size was measured by laser particle size analyzer. The data of TiO_2 are summarized in Table 3.2 and Table 3.3.

Table 3.2 Surface area of TiO_2

Type of TiO_2	Surface area (m^2/g)	Pore volume (cc/g)	Pore size (nm)
Commercial grade	56.9	1.84×10^{-1}	12.9
Synthesis via sol-gel	3.31	2.02×10^{-2}	24.4

Table 3.3 Particle size of TiO_2

Types of TiO_2	Average particle size D [4,3] (μm)	Particle size D(v,0.1) (μm)	Particle size D(v,0.5) (μm)	Particle size D(v,0.9) (μm)
Commercial grade	2.95	0.77	2.25	6.24
Synthesis via sol-gel	72.95	9.26	56.48	161.03

Equipment:

Twin Screw Extruder

Compression Molding Machine

Injection Molding Machine

Differential Scanning Calorimeter (DSC)

X-ray Diffractometer (XRD)

Dynamic Mechanical Analyzer

Thermogravimetrical Analysis (TGA)

Instron Universal Tester

Scanning Electron Microscope (SEM)

BET Surface Area Analyzer

Laser Particle Size Analyzer

3.2 Production of Titanium Dioxide

3.2.1 Production of Titanium Dioxide (Commercial grade supplied by JJ-Degussa Thailand)

The precursor titanium tetrachloride ($TiCl_4$), a colourless liquid (boiling point 138°C) from the carbochloronation of natural rutile or ilment, is evaporated and mixed with air and hydrogen. In the burner (Figure 3.1), the gases are subsequently reacted at temperatures between 1000°C and 2400°C which leads to the formation of TiO_2 by:

$$TiCl_4 + 2H_2O + O_2 \rightarrow TiO_2 + 4HCl$$

In the flame tube, particle growth takes place. It can be divided into three zones: the first is the reaction and nucleation zone, where primary particles with a mean diameter of about 21 nm originated. In the second zone, melted spherical primary particles collide. Here, aggregates are formed due to delayed fusion. In the third zone, aggregates interact leading to the formation of larger agglomerates. Finally, the particles are seperated from the off-gas in a cyclone or cartridge filter. The generated HCl is recycled for production of the raw material $TiCl_4$. TiO_2 particles were observed to be the anatase structure by XRD.

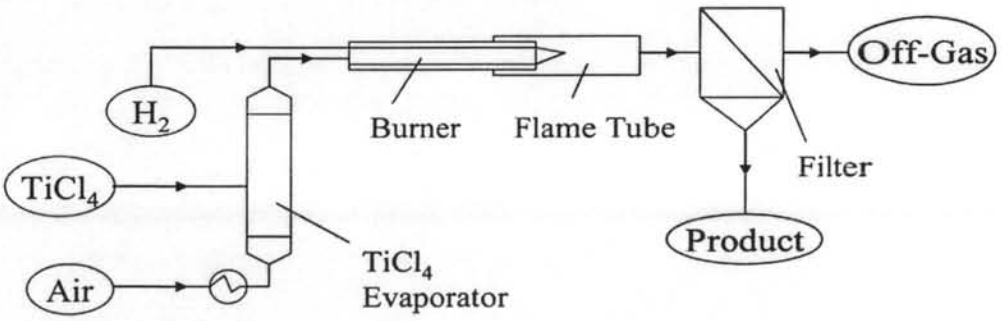

Figure 3.1 Process for the production of fumed Titanium Dioxide

3.2.2 Synthesis of Titanium Dioxide (via sol-gel process)

TiO_2 particles were prepared via sol-gel method using starting materials titanium diisopropoxide bis(acetylacetonate) 75 wt% solution in 2-propanol and tetraol (Pentaerythritol) as a linking agent, the reaction was carried out at 70°C

for 3 hours. The mole ratio between titanium diisopropoxide bis(acetylacetonate) and tetraol was 2:1. After the reaction was completed, the titanium sol was obtained. Then HCl and H_2O (1:10) were added and heated at 70°C until they were homogeneous to obtain the optimized colloidal sol. The size of the obtained sol could be checked by shining a laser light through the solution. Results from the test indicated that the size of the obtained sol was in the range of nanometer. The obtained sol was dried under vacuum and was ground before calcination. Finally, the dried titanium compound (dried gel) was calcined at 650°C for 3 hours to remove any remaining organic residues to obtain TiO_2 particles. Both sources TiO_2 particles were also observed to be the anatase structure.

3.3 Nanocomposites and Specimen Preparation

3.3.1 PP/TiO_2 Nanocomposites

PP and TiO_2 nanoparticles were dried at 60°C for 4 hours before melt compounding. The master bacth of 10 wt% TiO_2 was prepared by using a Collin ZK25 self-wiping, co-rotating twin-screw extruder with screw speed 50 rpm. The as-prepared master batch was blended with the required amount of PP, using the operating temperature for each zone of twin screw extruder as shown in Table 3.4, to give 1, 2, 3, 4, and 5 wt% of TiO_2 in PP. For TiO_2 from sol-gel process, due to the small amount of TiO_2 prepared, only 5wt% of TiO_2 in PP master batch was prepared. Then the as-prepared master batch was blended with the required amount of PP to give 1 and 3 wt% of TiO_2 of PP composites.

Table 3.4 Operating temperature for each zone of twin-screw extruder barrel for PP/TiO_2 nanocomposites

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6
80°C	160°C	160°C	170°C	170°C	180°C

3.3.2 Specimen Preparation

A film of each sample was prepared from compression-molded sheet with a V50H compression press (Wabash). The obtained pellets were placed between a pair of stainless steel platens, and the mold was preheated at 200°C for 5 min between the plates without any applied pressure to allow complete melting. After that, the mold was compressed under a force of 10 tons with a residence time of 5 minutes and this specimen was cooled at 50°C under pressure. 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 3.5. Tensile specimens were prepared according to ASTM D638-91 standard test methods.

Table 3.5 Operating settings of the injection molding machine for preparing specimens for mechanical testing

Barrel Temperature	180-190°C
Nozzle temperature	200°C
Mold clamp force	25 kN
Injection pressure	1000 bar

3.4 Testing and Characterizations

3.4.1 Differential Scanning Calorimetry

Non-isothermal melt-crystallization and the subsequent melting behavior of neat PP and PP filled with various contents of TiO_2 were investigated on a Perkin-Elmer Series 7 differential scanning calorimeter (DSC). A temperature calibration was performed on every other run using a pure indium standard (T_m = 156.6°C and ΔH_f = 28.45 $J.g^{-1}$). A sample of 5.0 ± 1.0 mg in weight, was sealed in an

aluminium sample holder. The experimental procedure started with heating each sample from 50 to 250°C at a heating rate of 10°C.min^{-1} in order to set a similar thermal history for all the samples studied. To ensure complete melting, the sample was kept at 250°C for a holding period of 5 min, after which each sample was cooled down at a cooling rate of 10°C.min^{-1} to 50°C in order to observe non-isothermal melt crystallization behavior. As soon as the program temperature reached 50°C, the sample was immediately reheated at a heating rate of 10°C.min^{-1} to 250°C in order to observe the subsequent melting behavior. Both the non-isothermal melt-crystallization exotherm and subsequent melting endotherm were recorded for further analysis.

3.4.2 X-ray Analysis

A Rigaku Rint 2000 wide-angle X-ray diffractometer (WAXD) was used to determine the crystal structure and degree of crystallinity of all composites which were non-isothermally melt-crystallized at a cooling rate of 10°C.min^{-1} in DSC. Wide angle X-ray diffractometer equipped with a graphite monochrometor and a Cu tube for generating CuKα radiation (1.5046 A°). The samples were examined between 5°-90° 2θ at a scanning rate of 5° 2θ/min in 0.02° 2θ increments. CuKα radiation with $\lambda = 0.514$ nm was used as the X-ray source, operated at 40 kV and 30 mA. The digital output of the proportional X-ray detector and goniometric angle measurements were sent to an online micro computer for storing the data. Percent crystallinity was calculated using Crystallinity Multipeak Method.

3.4.3 Dynamic Mechanical Analysis

Dynamic mechanical of these composites were studied using a Solid Analyzer RSA Π (Rheometric scientific). The storage modulus (E') and loss modulus (E") were measured as a function of temperature. The three point bend fixture was used to mount the samples and temperature step of 4K intervals. All experiments were performed at 1Hz frequencey and 0.025% syrain amplitude using static force tracing dynamic force.

3.4.4 Thermogravimetric Analysis

Thermogravimetric and derivative thermogravimetric tests were carried out using TG-DTA analyzer. The experiment was done at a temperature in the range of 30-600°C under ambient atmosphere. The values of degradation temperatures were reported.

3.4.5 Mechanical Property Measurements

Tensile tests were performed with an Instron Universal testing machine, Model 4206, at room temperature following the procedure describe in ASTM D638-91. A crosshead speed of 40 $mm.min^{-1}$ and 100 kN load cell was used for all measurements. The value of tensile strength at yield, percentage of elongation at yield and Young's modulus for all composites were investigated. The results from the tests were reported as an average of the data taken from 5 specimens.

3.4.6 Morphological Observertion

Energy dispersive X-ray spectrometer (EDS), OXFORD (link ISIS series 300) composition distribution map was used to analyze and confirm Ti element in composites. Scanning electron microscope (SEM), JEOL (JSM-6400) was used to observe the dispersion and size of TiO_2 of the fractured surface of selected specimens which were fractured in liquid nitrogen. The samples were sputtered with gold before viewing under a Scanning electron microscopy (SEM) operating at 15 kV.

3.4.7 Surface Area Analyzer

The surface area, pore volume and pore size data of TiO_2 were determined by using a BET (Autosorp 1).

3.4.8 Particle Size Analyzer

The particle size of TiO_2 was determined by using a Laser particle size analyser, Malvern (Masterizer X).