CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Materials Used for the Study on Isothermal and Non-Isothermal Melt-Crystallization and Subsequent Melting Behavior of Syndiotactic Polypropylene

For the study on isothermal and non-isothermal melt-crystallization and subsequent melting behavior of syndiotactic polypropylene (sPP) with different molecular characteristics, six sPP resins (i.e. internal codes: sPP#9 to sPP#14) with various molecular characteristics (see Table 3.1) were synthesized with two different metallocene catalyst systems. Resins sPP#9 to sPP#11 were synthesized with (isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride) using MMAO as the activator (with the ratio Al/Zr being 2000) in bulk monomer at 70, 50, and 30°C, respectively. Resins sPP#12 to sPP#14 were synthesized with diphenylmethylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride) using MMAO as the activator (with the ratio Al/Zr being 2000) in bulk monomer at 70. 50, and 30°C, respectively. The as-polymerized polymers were deashed via a solvent/non-solvent liquid-liquid extraction and subsequently stabilized with an antioxidant. The deashed/stabilized polymers were characterized for their molecular weight averages using size-exclusion chromatography (SEC) and their tacticity using ^{13}C-nuclear magnetic resonance (NMR) and the results are summarized in Table 3.1.

3.1.2 Materials Used for the Study on Non-Isothermal Melt-Crystallization and Subsequent Melting Behavior of Pigmented Medium-Density Polyethylene

For the non-isothermal melt-crystallization and subsequent melting behavior study of pigmented medium-density polyethylene (MDPE), the MDPE resin used had a density of 0.938 g cm^{-3} and a melt flow rate of 4.0 g/10 min. Three types of pigments used were diarylide or 'Pigment Yellow 83' (C.I.21108; hereafter denoted PY), phthalocyanine or 'Pigment Blue 15' (C.I.74160; hereafter denoted

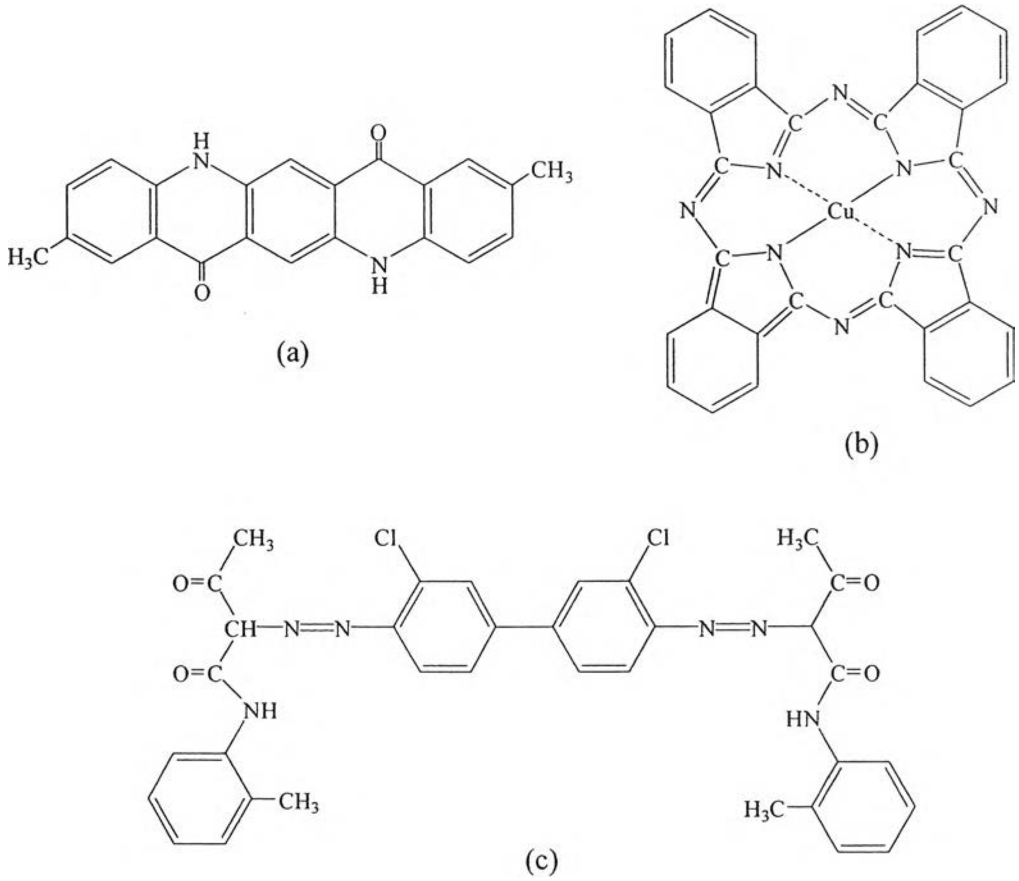
PB), and quinacridone or 'Pigment Red 122' (C.I.73915; hereafter denoted PR), respectively. The chemical structures of these pigments are illustrated in Fig. 3.1.

Table 3.1 Molecular characteristics of sPP#9 to sPP#14

Resin	Mw	Mw/Mn	Racemic dyad [%r]	Racemic pentad [%rrrr]	Triad Analysis of Data		
					%isotactic	%atactic	%syndiotactic
sPP#9	99,000	2.1	90.8	78.0	3.3	8.3	88.4
sPP#10	136,000	2.2	91.9	80.3	2.2	7.9	89.9
sPP#11	188,000	2.3	92.5	83.0	2.3	7.3	90.4
sPP#12	407,000	3.3	91.4	78.9	2.6	7.7	89.7
sPP#13	606,000	3.2	92.8	83.4	2.2	7.0	90.8
sPP#14	952,000	2.5	95.1	87.8	1.2	5.2	93.6

3.1.3 Materials Used for the Study on Non-Isothermal Melt-Crystallization and Subsequent Melting Behavior of Titanium(IV)oxide Nanoparticle-Filled Isotactic Polypropylene

The commercial general purpose grade of iPP (HP 400K) used in this study was supplied by HMC Polymers Co., Ltd. (Rayong, Thailand). Certain properties of the resin, provided by the manufacturer, are as follows: MFR (2.16 kg at 190°C) = 4g· (10 min)$^{-1}$, density = 0.9 g cm^{-3}, tensile strength at yield = 33MPa, elongation at yield = 10%, flexural modulus = 1400MPa and notched Izod impact strength at 23°C = 30 J m^{-1}. TiO_2 nanoparticles with different surface characteristics (i.e. neat, SiO_2-coated, and stearic acid-coated) were supplied by Advanced Nanotechnology Co., Ltd. (Samutprakarn, Thailand). Some specific properties of the three grades are summarized in Table 3.2. Hereafter, CYU201, CYU202, and CYU203 were used to denote the neat, the SiO_2-coated and the stearic acid-coated TiO_2 nanoparticles, respectively.



(a)

(b)

(c)

Figure 3.1 Chemical structure of the three pigments investigated: (a) quinacridone or ‘Pigment Red 122’, (b) phthalocyanine or ‘Pigment Blue 25’, and (c) diarylide or ‘Pigment Yellow 83’.

Table 3.2 Specific properties of the TiO_2 nanoparticles

Property	CYU 201	CYU 202	CYU 203
Average particle size (nm)	50	50	50
Crystal type	Rutile	Rutile	Rutile
Content of TiO_2 (%)	98	95	92
Specific surface area (m^2/g)	>35	>35	>35
Surface properties	Hydrophilic	Hydrophilic	Hydrophobic
Surface treatment agent	no	SiO_2	Fatty acid

3.2 Sample Preparation

3.2.1 Sample Preparation for the Study on Isothermal and Non-Isothermal Melt-Crystallization and Subsequent Melting Behavior of Syndiotactic Polypropylene

The as-polymerized resins were compressed into films by placing the resins between a pair of transparency films, which were later sandwiched between a pair of stainless steel platens in a Wabash V50H compression press. After pre-heating at 190°C for 2 min, the films were melt-pressed at 190°C for another 2 min under an applied clamping force of 5 tons. The compression-molded films were then cooled to 40°C in the compression press. The cooling rate of the platens was fitted well by an exponential decay with a time constant of 3 min by running cold water through channels in the press platens.

3.2.2 Sample Preparation for the Study on Non-Isothermal Melt-Crystallization and Subsequent Melting Behavior of Pigmented Medium-Density Polyethylene

MDPE and each pigment were pre-mixed in a paint mixer. Each pigment was added into MDPE at a content of 0.1, 0.2, 0.3, or 0.4 phr. Both neat MDPE and the pre-mixed formulations were then fed into a Collin ZK25 self-wiping, counter-rotating twin screw extruder, operating at a screw speed of 30 rpm and die temperature of 180°C. All of the samples were then compressed into thin films between a pair of transparency films, which were later sandwiched between a pair of stainless steel platens in a Wabash V50H compression press at 180°C under an applied clamping force of 10 ton-force for 2 min.

3.2.3 Sample Preparation for the Study on Non-Isothermal Melt-Crystallization and Subsequent Melting Behavior of Titanium(IV)oxide Nanoparticle-Filled Isotactic Polypropylene

Each type of TiO_2 nanoparticles was first dried in an oven at 80°C for 24h and then pre-mixed with iPP pellets in a tumble mixer for 20 min to achieve dry blends in various contents of TiO_2 nanoparticles (i.e. 5, 10, 20, and 30 wt%). The as-prepared dry blends were then fed into a Collin ZK25 self-wiping, co-rotating twin screw extruder operating at a screw speed of 80 rpm and a temperature profile of 185°C (die zone), 190°C (zone 5), 185°C (zone 4), 180°C (zone 3), 175°C (zone 2), and 100°C (feed zone). The extrudate was cooled in a water bath and later cut into pellets by a Planetrol 075D2 pelletizer.

Each of the as-prepared compounds was dried in an oven at 60°C overnight, prior to being shaped into film and mechanical test specimens. A part of each sample was then compressed into thin films between a pair of transparency films set between a pair of stainless steel platens in a Wabash V50H compression press, at 190°C. After 2 min holding at 190°C, the film moldings were allowed to cool at ambient condition between the transparency films and the stainless steel platens. Another part of the sample was injection-molded into mechanical test specimens according to the ISO 527-1 (for tensile test specimens), ISO 180 (for impact test specimens), and ISO 178 standard test methods, using an ARBURG Allrounder® 270M injection molding machine. The temperature settings (from the feed zone to the nozzle) were 150, 160, 170, 180, and 190°C, respectively. The injection pressure was 1000 bar and the dwelling pressure was 700 bar. Prior to the mechanical tests, all of the test specimens were conditioned under ambient condition for 7 days.

3.3 Differential Scanning Calorimetry Measurements

3.3.1 For the Study on Isothermal and Non-Isothermal Melt-Crystallization and Subsequent Melting Behavior of Syndiotactic Polypropylene

A Perkin-Elmer Series 7 differential scanning calorimeter (DSC) was used to record isothermal melt-crystallization exotherms and subsequent melting endotherms for these resins. Calibration for the temperature scale was carried out using a pure indium standard ($T_m^\circ = 156.6°C$ and $\Delta H_f^\circ = 28.5$ J·g-1) on every other run to ensure accuracy and reliability of the data obtained. To minimize thermal lag between the polymer sample and the DSC furnace, each sample holder was loaded with a disc-shaped sample, cut from the as-prepared films, and each one was weighed around 3.6 ± 0.4 mg. Each sample was used only once and all the runs were carried out under nitrogen atmosphere to minimize thermal degradation.

The experiment started with heating each sample from 25°C to 190°C at a heating rate of 80°C·min-1, in order to nullify previous thermal history of the sample and to set a standard thermal history to all of the samples studied. To ensure complete melting each sample was melt-annealed at 190°C for 5 min before being quenched to a specified crystallization temperature Tc at a prescribed cooling rate of 200°C·min^{-1}. The sample was held at the specified Tc until the crystallization process was complete (viz. when no significant change in the heat flow was further observed). The sample was later heated up again to 165°C at a heating rate of 20°C·min^{-1} in order to observed its subsequent melting behavior. Both the recorded melt-crystallization isotherms and the subsequent melting endotherms were further analyzed accordingly.

3.3.2 For the Study on Non-Isothermal Melt-Crystallization and Subsequent Melting Behavior of Pigmented Medium-Density Polyethylene

A Mettler-Toledo DSC822^e differential scanning calorimeter (DSC) was used to study the non-isothermal melt-crystallization and subsequent melting behavior of neat and pigmented MDPE samples. Calibration for the temperature scale was carried out with a neat indium standard (T_m^0=156.6°C and ΔH_f^0=28.5 J g^{-1}) on every other run to ensure accuracy and reliability of the data. To minimize thermal lag between the polymer sample and the DSC oven each sample holder was loaded with a disc-shaped sample (4.0±0.8 mg) cut from the film samples. Each sample was used only once and all the runs were carried out under nitrogen atmosphere. The measurements started with heating each sample from 25 to 160°C at a heating rate of 80°C min^{-1}. This procedure was to set a similar thermal history for all of the samples investigated. To ensure complete melting, each sample was melt-annealed at 160°C for 5 min, after which time the sample was cooled at a desired cooling rate f, ranging from 5 to 30°C min^{-1}, to 25°C. The subsequent melting behavior was then observed by reheating the sample at a heating rate of 20°C min^{-1} to 160°C. Both non-isothermal melt-crystallization exotherms and subsequent melting endotherms were recorded for further analysis.

3.3.3 For the Study on Non-Isothermal Melt-Crystallization and Subsequent Melting Behavior of Titanium(IV)oxide Nanoparticle-Filled Isotactic Polypropylene

The non-isothermal melt-crystallization and subsequent melting behavior of neat iPP and iPP samples filled with TiO_2 nanoparticles with different surface characteristics were measured by a Mettler-Toledo DSC822^e differential scanning calorimeter (DSC). The calibration was carried out with an indium standard (T_m^0 = 156.6°C and ΔH_f^0 = 28.5 J 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 DSC furnace, each sample holder was loaded with a disc-shaped sample (4.2±0.8 mg) cut from the as-prepared films (0.18±0.03mm thick). Each sample was used only once and all the runs were carried out under nitrogen atmosphere (flow rate = 60 ml min^{-1}).

The measurements started with heating each sample from 25 to 190°C at a heating rate of 80°C min^{-1}. This treatment was to set a similar thermal history to all of the samples investigated. To ensure complete melting, each sample was melt-annealed at 190°C for 5 min, after which time the sample was cooled at a desired cooling rate (ϕ), ranging from 5 to 30°C min^{-1}, to 25°C. The subsequent melting behavior was then observed by reheating the sample at a heating rate of 10°C min^{-1} to 190°C. Both non-isothermal melt-crystallization exotherms and subsequent melting endotherms were recorded for further analysis.

3.4 Mechanical Testing

For the study on non-isothermal melt-crystallization and subsequent melting behavior of titanium(IV)oxide nanoparticle-filled isotactic polypropylene, tensile strength at yield, elongation at yield, and Young's modulus for both neat iPP and iPP samples filled with TiO_2 nanoparticles with different surface characteristics were measured on an Instron 4206 universal testing machine, according to the ISO 527-1 standard test method, using a 100 kN load cell, a 50 mm min^{-1} crosshead speed and a 50 mm gauge length. The Izod impact resistance for all of the samples was determined on a Zwick 5113 impact tester according to a similar procedure to that described in the ISO 180 standard test method, with the original size of each specimen being about $27 \times 62 \times 4$ mm^3 using a 2.7 J pendulum and a 124.4° release angle. Flexural strength and flexural modulus for all of the samples were determined on test specimens cut from the molded dumbbells according to the procedure described in the ISO 178 standard test method using the three-point loading fixture of the Instron 4206 universal testing machine. All of the mechanical measurements were carried out at room temperature ($26\pm1^{\circ}$C) and the results were reported as averages of the data taken from at least 10 specimens.