CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Layered Inorganic Clays

3.1.1.1 Layered Silicates

Layered silicates (cationic clay) were chosen as nanofiller for the preparation of polypropylene based nanocomposites was Na-bentonite (Mac-Gel® (GRADE SAC), which was supplied by Thai Nippon Co., Ltd. Thailand. Montmorillonite (used as a reference), was supplied by Kunimine Industries, Japan. The main characteristics both layered silicate are given in Table 3.1.

Table 3.1 Physical properties of Na-bentonite as compared to Na-montmorillonite

Physical Properties	Bentonite	Montmorillonite
Cation exchange capacity (CEC), meq/100g	50	115
Swelling index, ml/2g	15-22	45
Moisture content, %	8-12	8-12
pH	9.5-11.0	9.5-11.0
Particle size, µm	45	45

3.1.1.2 Layered Double Hydroxides

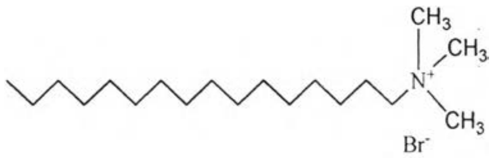
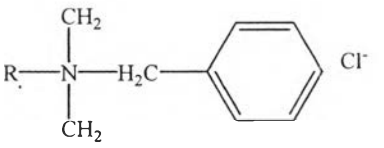
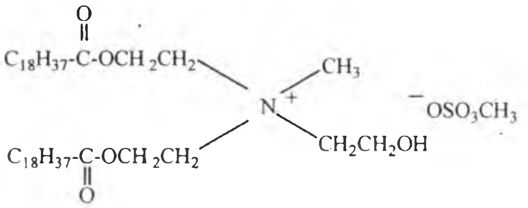
Layered Double Hydroxides (anionic clay) used in this work was synthetic aluminum-magnesium hydroxide carbonate (PURAL MG63HT) which was supplied by Sasol Germany. The mass ratio of Al_2O_3:MgO was reported as 38:62. The chemical formula was $Mg_4Al_2(OH)_{12}CO_3 \cdot nH_2O$, the basal spacing was 0.77 nm and the anionic exchange capacity (AEC) was reported to be approximately 340 meq/100g clay (Coiai *et al.* 2009).

3.1.2 Surfactants

3.1.2.1 Cationic Surfactants

Three different cationic surfactants were used for layered silicates modification with the objective of a better compatibility at the interface between polymer and layered clay. The choice of surfactants was made based on quaternary ammonium salt with different in structure and alkyl chain length. Their chemical name and structure are given in Table 3.2.

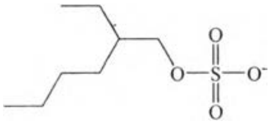
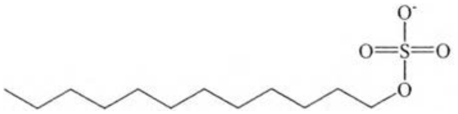
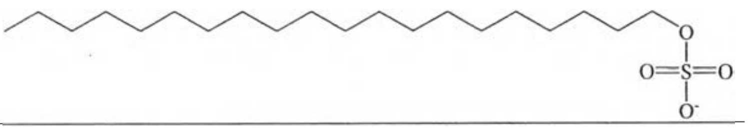
Table 3.2 Chemical structure of the cationic surfactants

Name and company/designation	Chemical structure
Hexadecyltrimethylammonium bromide salt from A.C.S. Xenon Limited Partnership/ CTAB (one alkyl tail, C16)	
N-alkyl dimethyl ammonium chloride from from Sunny World Co., Ltd/ BTC (one alkyl tail (mixed C14-C16) and one benzyl group)	 R = 50%C_{14}, 40%C_{12},10%C_{16}
Methyl di-[(partially hydrogenated) tallow carboxyethyl]-2 dihydroxyethyl ammonium methyl sulfate from Union Compound Co., Ltd/ DOEM (two alkyl tails, 2C18)	

3.1.2.2 Anionic Surfactants

Three different anionic surfactants were used for surface modification of LDH. The surfactants are based on sodium alky; sulfate with different alkyl chain length. All surfactants were purchased from Sigma-Aldrich chemical company, Germany. The chemical name and structure are given in Table 3.3.

Table 3.3 Chemical structure of the anionic surfactants

Name/designation	Chemical and Structure
2-ethylhexyl sulfate (C8)	
dodecyl sulfate (C12)	
eicosyl sulfate (C20)	

3.1.3 Polymers

3.1.3.1 Polypropylene (PP)

The polymer chosen for the preparation of polymer layered silicates based-nanocomposite is a commercial grade polypropylene (Mophen HP550R), which was supplied by HMC Polymer Co., Ltd. (Rayong, Thailand). The resin properties provided are reported in Table 3.4.

3.1.3.2 Low Density Polyethylene (LDPE)

The polymer chosen for the preparation of polymer layered double hydroxide based-nanocomposite is a commercial grade low density polyethylene (LDPE) Riblene FL34 which was purchased from Polimeri Europa. The resin properties provided are reported in Table 3.5.

Table 3.4 Resin properties of polypropylene (PP)

Properties	Moplen HP550R	ASTM Method
Melt Flow rate (230°C/2.16 kg), dg/min	22	D1238
Density, g/cm^3	0.90	D792B
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

Table 3.5 Resin properties of low density polyethylene (LDPE)

Properties	Riblene FL34	Test Method
Melt Flow index (190°C /2.16 kg), dg/min	2.1	ISO 1133
Density, g/cm^3	0.924	ISO 1183
Melting point, °C	114	PE method
Brittleness point, °C	< -75	ASTM D746
Vicat softening point (1 kg.), °C	93	ISO 306/A

3.1.4 Compatibilizers

Polypropylene functionalized with maleic anhydride (PP-g-MA) Polybond®3200 by Chemtura (Thailand), having a melt flow index of 115 g/10 min (190°C/2.16 kg) and an amount of maleic anhydride grafted groups of 1 wt%, was used as the compatibilizer for the preparation of PP/layered silicates system.

Polyethylene functionalized with maleic anhydride (PE-g-MAH) UL EP Compoline® by Auserpolimeri, having a melt flow index of 2.5 g/10 min (190°C/ 2.16 kg) and an amount of maleic anhydride grafted groups of 0.5–1.0 wt%, was used as compatibilizer for the preparation of PE/layered double hydroxides system.

3.2 Organic Modification

3.2.1 Organic Modification of Layered Silicates

Na-Bentonite (Mac-Gel, Grade SAC) having a cation exchange capacity (CEC) of 50.0 meq/100 g, was first purified in order to remove impurities before modification with different cationic surfactants. Briefly, Na-bentonite was stirred in distilled water for 1 day and introduced into a separating funnel and settled for 12 h to remove the impurities, which had higher density than the swelling part. In order to obtain the higher purity and higher CEC, the centrifugation was applied. The swelling parts of Na-bentonite from the first step were centrifuged at a speed of 6000 rpm for 20 min. The bottom parts of the centrifuged Na-bentonite were removed and only the upper part which is the white gel-like substance was collected. The collected white gel-like part was dried overnight at 100°C under vacuum, crushed by agate mortar and stored in a desicator. Then, 30 g of purified clay was put in a container and swollen in 900 ml of distilled water for 24 h. After that it was heated at 80°C for 30 min and, in another container, the various cationic surfactants with 1.5 equivalents of CEC was dissolved in 200 ml of distilled water at 80°C for 30 min. Then, the solutions of two containers were mixed and vigorously stirred for 2 h at 80°C and homogenized at the same temperature for 30 min. The resulting organoclays were filtered and washed with hot water several times to remove the excess surfactant. After that, the product was dried overnight at 100°C and was ground into very fine powder, and finally screened through a 325 mesh sieve and stored in a desicator.

3.2.2 Organic Modification of Layered Double Hydroxide

The Mg/Al layered double hydroxide with the empirical formula $[Mg_{0.66}Al_{0.34}(OH)_2](CO_3)_{0.17}\cdot 0.62H_2O$, denoted as LDH-$CO_3$ was used as a precursor. The nitrate form with the formula $[Mg_{0.66}Al_{0.34}(OH)_2](NO_3)_{0.34}\cdot 0.46H_2O]$, named as LDH-$NO_3$ was obtained by the titration, at room temperature, of the LDH-CO_3 dispersed in a 1M $NaNO_3$ aqueous solution (mass/volume = 2 g/100 mL) with a 1M HNO_3 until risk a constant pH 5. After titration, the white solid was washed several times with CO_2-free deionized water and dried overnight at 60 °C in vacuum oven (Tammaro *et al.* 2005). The calculated anion-exchange capacity was 3.81 mmol of NO_3^-/g obtained from TGA analysis.

The organo-LDHs were synthesized via anion-exchange reaction. Firstly, each anionic surfactant, the amount corresponding to 1.5 AEC (anion exchange capacity) of the LDH-NO_3, was dissolved in 100 ml of CO_2-free deionized water and heated at 70 °C until clear solution was obtained. The pH of solution was maintained at 10 by using 1M NaOH. Secondly, 1 g of LDH-NO_3 was added to the surfactants solution, following by ultrasonic for 15 min. The mixture was magnetically stirred for 24 h at 70 °C in nitrogen atmosphere. Then the resulting organomodified LDHs were first separated by centrifugation at 6000×g for 10 min, washed several times with CO_2-free deionized water until the pH of 7, and finally dried at 60°C under N_2 atmosphere till constant weight. The obtained organomodified LDHs were labeled as LDH-C8, LDH-C12, and LDH-C20 when the interlayer anionic surfactants were 2-ethylhexyl sulfate, dodecyl sulfate, and eicosyl sulfate, respectively (see Chapter VII).

3.3 Melt Compounding

3.3.1 Preparation of PP/Layered Silicate Nanocomposites

PP/layered silicate nanocomposites were prepared by melt intercalation using a Model T-20 co-rotating twin-screw extruder (Collin) with L/D=30 and D=25 mm. The operating temperatures of the extruder were maintained at 80, 160, 170, 180, 190, and 200°C in that order from hopper to die (shown in Figure 3.1). The screw speed was maintained at 50 rpm. A master batch containing 25 wt% of organobentonite with PP-g-MA was prepared in order to obtain a good dispersion of clay particles in the PP matrix. The master batch was then added to PP and PP-g-MA (the weight ratio of the latter was fixed at 15% irrespective of the clay content) in an appropriate amount to obtain a nominal content of 1, 2, 3, 5, and 7wt% OBTN in the nanocomposites (Table 3.6). Each composition was initially mixed by a tumble mixer for 20 min before being introduced to the extruder. Single strands of the PP/organobentonite nanocomposites were solidified by cool water, pelletized, and then dried in a vacuum oven at 80°C before characterization.

Test specimens were prepared using a Wabash V50H 50 ton compression molding machine. Pellets are placed in a picture frame mold and the mold is preheated at 200°C for 10 minutes in the press without application of pressure. The mold is then compressed under a force of 20 tons for a further 3 minutes after which the mold is cooled to 40°C under pressure. Test specimens were cut from the molded sheets using a die cutter. These specimens were further used for studying morphology and thermal behavior.

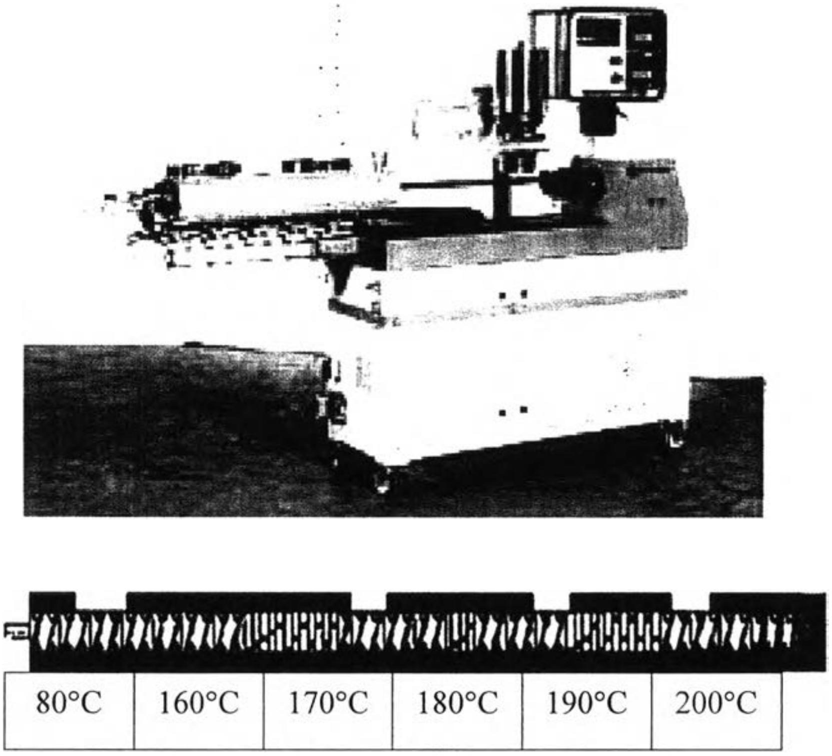


Figure 3.1 The co-rotating twin-screw extruder (Collin) and the operating temperatures of the extruder.

Table 3.6 Designing formula for preparing PP/layered silicate nanocomposites

Sample	**Concentration (wt%)**		
	PP	**PP-g-MA**	**Organoclay**
PP	100	-	-
PP/PP-g-MA	85	15	-
			CTAB-clay
PP1CTAB	84	15	1
PP2CTAB	83	15	2
PP3CTAB	82	15	5
PP5CTAB	80	15	5
PP7CTAB	78	15	7
			BTC-clay
PP1BTC	84	15	1
PP2BTC	83	15	2
PP3BTC	82	15	5
PP5BTC	80	15	5
PP7BTC	78	15	7
			DOEM-clay
PP1DOEM	84	15	1
PP2DOEM	83	15	2
PP3DOEM	82	15	5
PP5DOEM	80	15	5
PP7DOEM	78	15	7

3.3.2 Preparation of LDPE/Layered Double Hydroxide Nanocomposites

LDPE nanocomposites containing different alkyl sulfate surfactants modified LDH were prepared in a Brabender Plastograph PL2100 (30 mL chamber, Figure 3.2) at 180 °C using a screw speed of 80 rpm. In the first step, the mixture of LDPE and PE-g-MAH was melted in the mixing chamber for 4 min in order to achieve the constant torque, then a desired amount of organomodified LDHs were added into the mixing chamber and compounded future for 16 min. It should be note that the weight ratio of PE-g-MA and organomodified LDHs was fixed in 1:1. The LDPE/LDH-C12 nanocomposite with 5 wt% clay concentration was also prepared using the same method. The designing formulation for each set of nanocomposites is given in Table 3.7.

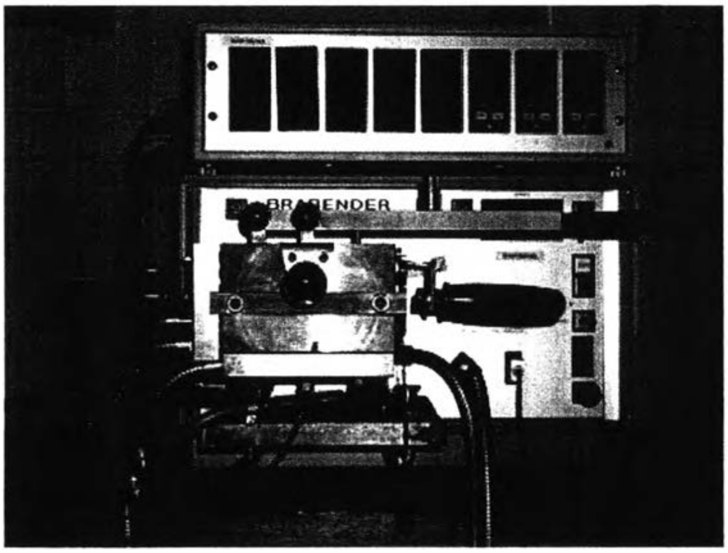


Figure 3.2 The Brabender Plastograph (PL2100) mixer.

Table 3.7 Designing formula for preparing LDPE/Organo-LDHs nanocomposites

Sample	**LDPE (g)**	**PE-g-MA (g)**	**Organo-LDHs (g)**
LDPE	20	-	-
LDPE/PEMAH (97.5/2.5)	19.5	0.5	-
LDPE/LDH-C8 (2.5wt%)	19.5	0.5	0.5
LDPE/LDH-C12 (2.5wt%)	19.5	0.5	0.5
LDPE/LDH-C20 (1.5wt%)	19.7	0.3	0.3
LDPE/LDH-C20 (5.0wt%)	19.7	0.3	0.3

3.4 Characterizations

3.4.1 Characterization of PP/Layered Silicate Nanocomposites

3.4.1.1 X-ray Diffractometer (XRD)

X-ray Diffractometer (XRD; D/MAX2200, Rigaku) was used to determine the structure of the layered clays, organoclays, and nanocomposites. The X-ray beam was nickel-filtered Cu $K\alpha_1$ (λ = 1.504 nm) radiation operated at 40 kV and 30 mA. Corresponding data were collected from 2θ range of 1.2-40° at a scanning rate of 2° min^{-1}.

3.4.1.2 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM; JEOL, JEM-2010) was used to clarify the nanostructure and the dispersion level of the layered clay. The ultrathin sections (~75 nm) were prepared by cryo-ultramicrotome with a glass knife cooled at -110°C. The samples were operated with acceleration voltage of 200 kV.

3.4.1.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM), JEOL (JSM-5800 LV), was used to observe the dispersion of clay particles in the PP matrix. An energy dispersive X-ray spectrometer (EDS), OXFORD (link ISIS series 300), with mapping mode was used to analyze and confirm the dispersed clay particles, especially Si and Al elements. The selected samples were dipped and fractured in liquid nitrogen. Then the samples were sputtered with gold before viewing under a scanning electron microscope (SEM) operating at 15 kV.

3.4.1.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used to investigate the thermal stability of the nanocomposites as compared to pure polymers. The samples were heated from 30–700°C at a rate of 10°C min^{-1} in a nitrogen atmosphere of 200 ml/min.

3.4.1.6 Crystallization Behaviour

Wide-Angle X-ray Diffraction (WAXD) D8 Discover system from Bruker, was used to study the crystallinity of PP based nanocomposites. The samples were scan at a scanning rate of 2° min^{-1} under the diffraction angle 2θ in the range of range 3–40°. The crystallinity was estimated from WAXD profiles after a liner background subtraction and deconvolution of the profile into crystalline and amorphous fractions, using a Gaussian lineshape for the peaks.

Differential scanning calorimetry (DSC) A TA Instruments Q1000 (New Castle, Delaware) with liquid nitrogen cooling, was used for this study and was routinely calibrated with four different standards (cyclopentane, biphenyl, indium, and tin) at a 10°C/min heating rate. Film samples were cut from the same sheet used to cut samples for tensile testing, placed in aluminum DSC pans, and scanned at a rate of 10°C/min. The melting and crystallization temperature of the samples were investigated in the temperature range from 30°C to 200°C from the second heating scan and first cooling scan, respectively. The fractional crystallinity was determined by integration of the area under the respective melting exotherms and conversion of these enthalpies to fractional crystallinities with a melting enthalpy of polypropylene. Crystallinities were calculated by using following equation:

$$\chi_c = \frac{\Delta H_m}{(f * \Delta H_m^0)} * 100$$

where χ_c is % wt. fraction crystallinity, ΔH_m is the experimental melting enthalpy, f is the polypropylene fraction by weight in the composite, and $\Delta H_m{}^0$ is the melting enthalpy of infinite polypropylene crystal (207.1 J/g) (Bu *et al.* 1988).

3.4.1.7 Mechanical Testing

Lloyd universal testing machine (Model LRX) was used to measure the tensile strength, percentage of elongation, and Young's modulus of the nanocomposites. The samples were prepared as rectangular film (10 x 1 cm) with the thickness of 200–400 μm. A strain rate of 25 mmmin^{-1} and gauge length of 50 mm was employed. At least five specimens were used for each sample to determine an average and standard deviation.

3.4.1.8 Specimen Preparation

Test specimens are prepared using a Wabash V50H 50 ton compression molding machine. Pellets are placed in a picture frame mold and the mold is preheated at 200°C for 10 minutes in the press without application of pressure. The mold is then compressed under a force of 20 tons for a further 3 minutes after which the mold is cooled to 40°C under pressure. Test specimens were cut from the molded sheets using a die cutter. These specimens were further used for studying morphology and thermal behavior.

3.4.1.9 Solvent Extraction

A series of PP/layered silicate nanocomposite based on CTAB-clay with varied concentrations of clay from 1 to 7 wt%, was selected to study the confinement effects on the macroscopic/bulk properties of these nanocomposites using solvent extraction technique. Small pieces of pure PP, PP/PPMAH blend, and nanocomposites were weighed (1.5 g) and placed in a stainless steel 120×120 wire mesh (100 μm openings). The obtained samples were extracted with boiling xylene and toluene in a Kumagawa extractor for 8 and 16 h, respectively, following our previous work (Passaglia *et al.* 2008). The xylene and toluene soluble fractions were recovered, the solvent was evaporated, and the material was dried under vacuum until reaching a constant weight. The macroscopic/bulk properties of toluene soluble and insoluble composite fractions were investigated and compared with those of the starting materials (polymers, clay, and composites). The change of polymer properties to different morphologies (confinement effects) and thermal analysis were investigated as following and the results are reported in CHAPTER V.

X-ray diffraction analysis was carried out by using a Siemens Kristalloflex 810 diffractometer D500/501 (Cu Kα radiation, λ = 0.15406 nm) at room temperature. The diffractograms were collected over 2θ range from 1.5° to 40° at the scanning rate of 0.016°/sec. The composites and residual fractions were analyzed as pressed films, whereas the soluble fractions were analyzed as powders. By analyzing the XRD patterns of PP, PP/PPMAH blend, and PP/PPMAH/OBTN nanocomposites and separating the amorphous and crystalline contribution the degree of crystallinity was calculated. The areas of Bragg reflections at 14°, 17°, 18.5°, 21°, 22°, 25.5°, and 28.5° corresponding to the indexed planes of the monoclinic crystals of isotactic PP (α-form) (110), (040), (130), (111), (131)+(041), (060), and (220), respectively as well as the area of the amorphous halo (A_a), were determined by a mathematical deconvolution of the XRD pattern profile in the range between 5° and 30°. After that, the A_c, which is the sum of all Bragg's reflection areas, was calculated. The relative crystallinity was determined according to the following equation: $x_c = \frac{A_c}{A_c + A_a} \cdot 100$ (Machado *et al.* 2005).

Transmission Electron Microscopy (TEM) (ZEISS EM 900), at an acceleration voltage of 80 kV, was used. Ultrathin sections (about 50 nm thick) of the samples were prepared by a Leica EM FCS cryoultramicrotome equipped with a diamond knife cooled at -60 °C keeping the samples at -80 °C.

Infrared spectra were recorded with a Fourier transform spectrometer, PerkinElmer 1760-X. The soluble fractions were mixed with KBr and analyzed as powders, whereas the residual fractions were analyzed as films, made with a Carver 3851-0 laboratory press.

The thermogravimetric analysis (TGA) was performed with a Mettler Toledo Star System TGA/SDTA 851^e module. Composites, soluble fractions, and residual fractions (7-10 mg) were placed in an aluminum sample pan and the analyses were carried out at the standard rate of 10 °C/min from 25 °C to 900°C under air flow (60 ml/min).

The differential scanning calorimeter (DSC) analyses were performed with a PerkinElmer DSC7 calorimeter equipped with a CCA/liquid nitrogen cooling unit. Two different temperature ranges were investigated. The melting/crystallization behavior of PP (pure and/or nanocomposites) was investigated in the temperature range from 40 °C to 200 °C at the scanning rate of 10°C/min under nitrogen flow. The instrument was calibrated using the melting temperature and enthalpy of indium (T_m = 156.95 °C; ΔH_m = 28.49 J/°C) and the melting temperature of zinc (T_m = 419.50 °C) as references. The glass transition temperature of the composites and residue samples (15 ± 0.5 mg) was measured from -90°C to 60°C at the scanning rate of 50°C/min. In this case, the calibration was carried out using the melting temperature and enthalpy of indium (T_m = 155.57 °C; ΔH_m = 27.96 J/°C) and the melting temperature of mercury (T_m = -25.88 °C) as references.

3.4.1.10 Rheological and Extrudate Swell Measurements

Melt rheology and extrudate swell studies for the PP/organobentonite nanocomposite samples were carried out by using a CEAST Rheologic 500 twin-bore capillary rheometer (Figure 3.3). The inner diameter and the length of the barrel used were 15 and 300 mm, respectively, while the length-to-inner diameter (*L/D*) of the circular die was 20/1. Samples were placed in the barrel and forced through the capillary with a piston attached to the moving crosshead. Studies were done at three testing temperatures of 190, 200, and 210°C and the range of apparent shear rates varied from 50 to 8000 s^{-1}. The hold-on time and hold-on pressure for stages 1, 2, and 3 were 180 seconds at 10, 20, and 30 Pa, respectively. The results are reported in CHAPTER VI.

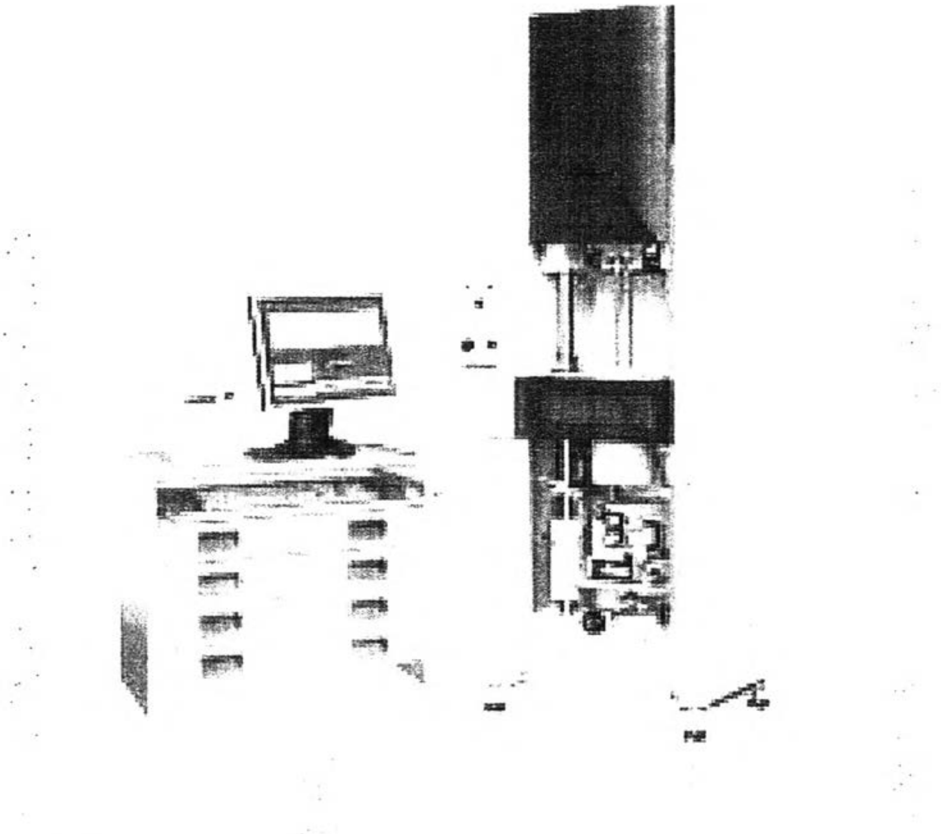


Figure 3.3 The CEAST Rheologic 500 twin-bore capillary rheometer.

In this case, the apparent shear stress (τ_{app}) for the capillary rheometer capillary can be expressed by the following equation:

$$\tau_{app} = \frac{\Delta PD}{2L} \quad (1)$$

Where ΔP is the total pressure drop (Pa) during die extrusion, D and L are the diameter and the length of the die (mm), respectively. No end correction (Bagley correction) was applied. The apparent shear rate γ_{app} can be expressed by the following equation:

$$\gamma_{app} = \frac{32Q}{\pi R^3} \tag{2}$$

where Q is the volumetric flow rate. According to the equation (1) and (2), the apparent shear viscosity (η_{app}) can be calculated by:

$$\eta_{app} = \frac{\tau}{\gamma_{app}} \tag{3}$$

Extrudate swell was measured using an attached KEYENCE VG laser analytical device, which comprise a laser light source and a light sensor. The extrudate swell (B) is reported as the percentage of extrudate swell (%), as can be defined in the following equation:

$$\%B = \frac{(D_e - D)*100}{D} \tag{4}$$

where D_e and D are the diameter of the extrudate and the die, respectively. Extrudates leaving from the die at particular apparent shear rates were collected in order to study surface morphology. Selected samples were sputtered with gold before viewing under a scanning electron microscope (JEOL JSM 5200) and operating at 15 kV.

3.4.2 Characterization of LDPE/layered double hydroxide nanocomposites

3.4.2.1 X-ray diffraction analysis (XRD)

X-ray diffraction analysis (XRD) of pristine LDH, LDH-NO_3, organomodified LDHs and their nanocomposites were recorded by using a Siemens Kristalloflex 810 diffractometer (CuKα radiation, λ=0.15406 nm) in the 2θ region of 1.5–40° at the scanning rate of 0.016 degree/sec.

3.4.2.2 Fourier transform infrared (FT-IR)

Fourier transform infrared (FT-IR) spectra for pristine LDH, LDH-NO_3, and organomodified LDHs were recorded over the wave number range 450–4000 cm^{-1} using Perkin Elmer FT-IR 1760-X spectrophotometer. The powdered samples were mixed with KBr and pressed in the form of pellets for measurement.

3.4.2.3 Morphological Analysis

Morphological features of the LDH-CO_3, LDH-NO_3, and the organomodified LDHs were studied using a scanning electron microscope (FE-SEM), HITASHI (S4800). The powdered samples were first spread on sample button using conducting cement while the nanocomposite samples were dipped and fractured in liquid nitrogen before putting on the sample button. Then all samples were sputtered with platinum before viewing under an electron microscope operating at 3 kV.

3.4.2.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of the pristine LDH, LDH-NO_3, organomodified LDHs and the nanocomposites was performed with a Mettler Toledo Stare System TGA/SDTA 851^e Module. Samples (~10 mg) were placed in an aluminum sample pan and runs were carried out at a standard rate of 10 °C/min from 25 °C to 900 °C under air flow (60 ml/min).

3.4.2.5 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimeter (Perkin-Elmer, DSC7) was used to measure the crystallization and melting behavior of the PP/organoclay nanocomposites. The samples were heated and cooled from 30-200°C, using a heating/cooling rate of 10°C min^{-1} in a nitrogen atmosphere. The heats of crystallization of the samples were measured after melting of the specimen in order to eliminate the thermal and mechanical history.

3.4.2.6 Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) for the nanocomposites was recorded with a Perkin-Elmer DMA7e instrument (three-point bending geometry). Thermograms were carried out at the heating rate of 5 °C/min and 1Hz frequency from the temperature range of -150–50 °C.

3.4.2.7 Specimen Preparation

Specimens of the nanocomposites for XRD, TEM and DMTA (2×1×0.2 cm) analysis were prepared by a Carver 3851-0 laboratory press at a temperature of 190 °C.