CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Polymer

- Ethylene vinyl acetate (EVA) [TPI Polene Public Co., Ltd.]
- Polycaprolactone (PCL) [Perstorp UK Ltd.]

3.1.2 Monomer

- ε-Caprolactone [Fluka]

3.1.3 Catalyst

- Tin (II) 2-ethylhexanoate ($Sn(Oct)_2$)[Sigma]

3.1.4 Clay Mineral

- Bentonite (BN) [Thai Nippon Chemical Industry Co., Ltd.]

3.1.5 Surfactant

- Stepantex SP-90 [Sunny World Co., LTD.]

3.1.6 Solvent

- Toluene, A.R. grade [Lab Scan]
- Chloroform, A.R. grade [Lab Scan]
- Methanol, commercial grade [Lab Scan]
- Ethyl acetate, A.R. grade [Lab Scan]
- Tetrahydrofuran, HPLC grade [Burdick & Jackson]

3.2 Equipment

3.2.1 X-ray Diffractometer (XRD)

X-ray diffractometer (XRD) was used to observe the d-value of organoclay and to investigate the crystal structure of synthesized PCL , PCL nanoclay nanocomposites, and graft copolymer. X-ray diffraction patterns were measured on a a Bruker AXS Model D8 Advance with Ni-filtered Cu K_α radiation operated at 40 kV and 30 mA. Both film and powder examples were observed on the 2θ range of 5 – 30 degree with scan speed 1 degree/min and scan step 0.01 degree.

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of EVA, modified EVA, PCL, and EVA-g-PCL film were obtained using a Nicolet Nexus 670 FTIR spectrometer in the frequency range of 4000-400 cm^{-1} with 32 scans at a resolution of 2 cm^{-1}.

3.2.3 Gel Permeation Chromatography (GPC)

The different molecular weights of synthesized PCL were examined by GPC Shimadsu Model in THF solvent as the mobile phase, Waters Styragel THF Column, and RID-10A detector. The THF solvent was filtrated with MN 615 ∅ 155 mm filter paper under the vacuum. The crude polymers were dissolved in THF at the concentration 0.5 wt% and filtrated with 0.45 mm diameter of cellulose acetate filter before injecting into the column. The conditions of this machine were 40°C column temperature, 1 ml/min flow rate, and 30 min run time. Molecular weight and molecular weight distribution of PCL were calculated in reference to a polystyrene calibration.

3.2.4 Thermogravimetric Analysis (TGA)

TG-DTA curves were collected on a TGA Q50 TA instrument. Each specimen was loaded on the platinum pan and heated from 30 to 600°C at a heating rate of 10°C/min under flow of N_2 90 ml/min.

3.2.5 Differential Scanning Calorimetry (DSC)

DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The sample was first heated from -20 to 130°C, cooled down from 130 to 0°C, and second heat from -20 to 130°C at a rate of 10°C/min under N_2 atmosphere with a flow rate of 10ml/min.

3.2.6 Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on JEOL JSM-6400 Scanning Microscope to observe surface morphology of different molecular weight PCL, PCL nanoclay nanocomposites, and EVA-g-PCL. The specimens were coated with gold under vacuum before observation to make them electrically conductive.

3.2.7 Twin Screw Extruder

PCL nanoclay nanocomposites were prepared using a Colin D-8017 Model T-20 corotating twin-screw extruder with L/D=30 and D=25 mm. The operating temperatures of extruder were maintained at 80, 90, 100, 100, 100, and 95°C from hopper to die, respectively. The screw speed was maintained at 20 rpm.

3.2.8 Compression Molding

The compression molding was performed by using a Wabash V50H Press, at 100°C for 5 minutes and 15 tons compression force for 5 minutes, then cooled down to 30°C.

3.2.9 Tensile Testing

Tensile tests were performed using Instron tensile testing machine. The specimens were prepared according to the ASTM D638 standard. The grips moved apart at a constant speed of 250 mm/min, then the tensile stress, modulus, and strain were tested at least five samples of each condition.

3.2.10 Izod Impact Testing

The sheets of sample were cut into the specimen shape following the ASTM D256 (notched IZOD type), then tested the impact strength by the ZWICK 5113 Pendulum Impact Tester with the pendulum load of 21.6 J. At least five samples were tested of each condition.

3.2.11 Dynamic Mechanical Analysis (DMA)

DMA analyses were carried out by using a dynamic mechanical analyzer NETZSCH DMA 242 instrument. The specimen was 10 × 60 × 3 mm^3 (width × length × thickness). The testing temperature was -120 to 55°C, heating rate at 3°C/min, and frequency 1 Hz under a dual-cantilever bending mode.

3.3 Methodology

3.3.1 Synthesis of Different Molecular Weight PCL

ε-CL, stannous octoate (monomer/catalyst mole ratio = 2000, 4000, 6000, 8000, and 10000) were weighed into flask with toluene as solvent. The reaction was done under nitrogen atmosphere at 120°C for 24 h. After the reaction was completed, the product was dissolved in chloroform and then precipitated in cold methanol, and dried under vacuum at 40°C. The yield can be calculated by the following equation.

$$\%\text{Yield} = \frac{\text{wt. of PCL}}{\text{wt. of } \varepsilon - \text{CL}} \times 100$$

3.3.2 Preparation of Organoclay

300 g of Na-Bentonite was swollen in water for 24 h. Stepantex SP-90 was dissolved in methanol at 80°C for 30 min. The swollen clay was mixed with Stepantex SP-90 solution and kept at 80°C for 2 h with vigorously stirring. After that the mixture was homogenized at 80°C for 1 h. The sediment was filtrated and washed with hot water several times to remove the excess salts and surfactant. Dry in a vacuum oven at 100°C overnight. Ground into powder and screen through a mesh $^{\#}$325.

3.3.3 Preparation of Nanocomposites

PCL and 7 wt% organoclay, prepared for masterbatch were melt blended in a Model T-20 co-rotating twin-screw extruder (Collin) with L/D=30 and D=25 mm; the processing conditions were the following: temperature (°C): 80, 90, 100, 100, 100, and 95°C from hopper to die, respectively and the screw rotation is 20 rpm. PCL and 7 wt% organoclay were premixed in a tumble mixer before introducing into the twin-screw extruder then extruded through a single strand die, followed by solidified with cold water and pelletized. The obtained pellets were dried in oven. After the preparation of masterbatch, it was dilute to 1, 3, and 5 wt% organoclay PCL nanocomposites.

3.3.4 Transesterification of EVA

EVA copolymer was partially hydrolyzed in a homogeneous medium. In a typical reaction, 10 g of EVA was solubilized in 100 ml of toluene at 70°C under stirring. 10 ml of a 2 wt% solution of sodium hydroxide in methanol was added and the reaction was carried out under reflux for 60 min. The polymeric material was precipitated into methanol and dried in a vacuum oven at 60°C for 24 h.

3.3.5 Synthesis of EVA-g-PCL

ε-CL, stannous octoate (monomer/catalyst mole ratio = 2000) and modified EVA as initiator were weighed into flask. Modified EVA was dissolved in toluene then ε-CL and stannous octoate were added into flask. The reaction was done under nitrogen atmosphere at 120°C for 24 h. After the reaction was completed, the product was dissolved in chloroform and then precipitated in cold methanol, and dried under vacuum at 40°C. The yield can be calculated by the following equation.

$$\%\mathrm{Yield} = \frac{\mathrm{wt.of\ EVA - g - PCL}}{\mathrm{wt.of\ Modified\ EVA + wt.of}\ \varepsilon - \mathrm{CL}} \times 100$$