CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Poly(lactic acid) (PLA) was purchased from BC Polymer. It is an extrusion grade with CAS Number 9002-97-5.

3.1.2 Ethylene(vinyl acetate) (EVA) was purchased from Sigma-Aldrich. It has 18 wt% of vinyl acetate with CAS Number 24937-78-8.

3.1.3 Ethylene-glycidyl methacrylate, or E-GMA(CAS Number 26061-90-5) was purchased from Sigma-Aldrich.

3.1.4 Ethylene-acrylate ester-glycidyl methacrylate terpolymer, or T-GMA (CAS Number 51541-08-3) was purchased from Sigma-Aldrich.

3.1.5 Ethylene-acrylic acid copolymer, or PE-AA (CAS Number 9010-77 – 9) was purchased from Sigma-Aldrich.

3.1.6 Poly(2-ethyl-2-oxazoline), or Oxa (CAS Number 25805-17-8) was purchased from Sigma-Aldrich.

3.1.7 1-Dodecanol (Molecular Formula $CH_3(CH_2)_{11}OH$) with CAS Number 112-53-8 was purchased Sigma-Aldrich. Its molecular weight is 186.33 g/mol and the melting point is 22 - 26 °C.

3.1.8 Dibutyltin Dilaurate (DBTDL, $C_{32}H_{64}O_4Sn$ with CAS Number 77-58-7) was purchased Sigma-Aldrich. Its molecular weight is 631.55 g/mol and the melting point is 22 - 24 °C.

3.1.9 Acetone (CH_3COCH_3) with CAS Number 67-64-1 was purchased RCI Labscan. Its molecular weight is 58.08 g/mol, the boiling point is 56.2 °C, and density is 0.790.

3.2 Equipment

3.2.1 Twin-Screw Extruder

The modified EVA (mEVA) was prepared in the co-rotating twin-screw extruder (Labtech types LTE-20-32 & LTE-20-40) 20 mm diameter with 40:1 L/D ratio and screw speed at 10 rpm and the temperature profiles along the extruder barrel were 145, 165, 175, 180, 185, 185, 185, 185, 185 and 190 °C from feed zone to die.

The PLA/mEVA blends were prepared in a co-rotating 20 mm diameter twin-screw extruder (Labtech types LTE-20-32 & LTE-20-40) with 40:1 L/D ratio. The ratio of PLA/mEVA blends were 90/10, 80/20, 70/30 and 60/40 w/w. The PLA/mEVA blends with various compatibilizer contents of 5, 10 and 15 phr were then prepared at a screw speed of 30 rpm. The temperature profiles along the extruder barrel were 140, 150, 160, 165, 165, 165, 165, 165, 165 and 160 °C from feed zone to die.

3.2.2 Compression Molding

The mEVA obtained from twin-screw extruder were prepared into thin film with Labtech compression molding machine (maximum force was 150 kg, size of mold was 20x20 cm^2) with preheating 15 minutes and heating for 5 minutes with force 10 kN. The operating temperature was 120 °C and cool down to room temperature.

The blends obtained from twin-screw extruder were prepared into thin film with Labtech compression molding machine (maximum force was 150 kg, size of mold was 20x20 cm^2) with preheating 25 minutes and heating for 5 minutes with force 10 kN. The operating temperature was 190 °C and cool down to room temperature.

3.2.3 Injection Molding

The blends obtained from twin-screw extruder were prepared into specimen of dumbbell-shape by using Battenfeld BA 250 CDC Injection molding

with 88/22 L/D, the operating temperature was 130 °C, pressure 95 bar and cool down at room temperature in dumbbell-shape mold. After that, the samples were used for investigating the tensile properties.

3.2.4 Soxhlet Extractor

According to the separation of an insoluble substance to investigate the conversions of mEVA, soxhlet extractor (VELP SCIENTIFICA, SER 148) was typically used. Acetone at 160 °C was used to wash out an excess 1-dodecanol. The insoluble part was vacuum dried at 60 °C overnight, and then % yield of mEVA was calculated by the following equation (3.1).

%yield = [Wt. of insoluble product (g) / Wt. of crude product (g)] × 100   (3.1)

3.2.5 Fourier Transform Infrared Spectroscope, FTIR

The functional groups along mEVA backbone were studied by using Thermo Nicolet Nexus 670 FTIR spectrometer. The specimens were prepared by compression molding into film. The spectra would be record over the wave number range of 4000 - 400 cm^{-1} with 64 scans at a resolution of 4 cm^{-1}.

3.2.3 Thermogravimetric Analyzer, TGA

Thermal stability of mEVA and the blends would be determined by using Perkin-Elmer Pyris Daimond thermogravimatric analysis (maximum temperature was 1,000 °C). The weight of sample would be in the range of 5-10 mg. The blends were analyzed at temperature of 30-800 °C with the heating rate of 10 °C/min under the nitrogen gas atmosphere.

3.2.4 Differential Scanning Calorimeter, DSC

The glass transition temperature (T_g), melting temperature (T_m), and cold crystallization temperature (T_{cc}) were performed by using differential scanning calorimeter (Mettler Toledo, DSC822). The samples were heated from 30 to 190 °C with the heating rate of 10°C/min. Then they were cooled to -30 °C with the cooling rate of 10°C/min and reheated at the 190 °C at the same condition. Degree of crystallization (χ_c) was calculated by

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times w} \times 100 \qquad\qquad (3.2)$$

ΔH_m is the enthalpy of melting, ΔH_{cc} is the enthalpy of cold crystallization, ΔH_m^0 is the enthalpy of melting for 100% crystalline PLA sample, taken as 93.1 J/g (Salamone, J. C., 1996), ΔH of the perfect crystalline PE is 293 J/g (Xiao, H., *et al.*, 2009), w is the weight fraction of PLA in the composite.

3.2.5 Dynamic Mechanical Analyzer, DMA

Dynamic mechanical properties were carried out by using a dynamic mechanical analyzer (EPLEXOR 100N, GABO) in tension mode, and the sample size was 10×40×4 mm³. All DMA experiments were performed at 1 Hz with a scanning temperature range of -100 to 150 °C. The heating rate is 2 °C/min under nitrogen gas flow. Static and dynamic strains were 80% and 60%, respectively.

3.2.6 Field Emission Scanning Electron Microscope, FE-SEM

The morphology of the blends was examined by using Field Emission Scanning Electron Microscope (Hitachi, S-4800). The fracture surface of samples was coated by Pt and then the phase compatibilization of samples was examined by using FE-SEM.

3.2.7 Universal Testing Machine

The tensile properties were tested by using an Instron 4206 universal testing machine with cross-head speed of 50 mm/min. The samples were in the dumbbell-shape. The size of sample specimen was 13 mm width of narrow section, 90 mm length of narrow section, and 4 mm thickness.

3.2.8 Melt Flow Indexer

The melt flow index of the blends was tested by using Zwick, Model4105 melt flow indexer. The sample which had weight in the range of 5-8 g was melted at 160 °C. The melt was driven through a capillary die using a 1 kg piston, melt time 120 seconds, and cut time 30 seconds. Repeat the entire procedure 5 times and average the results.

3.2.9 Biodegradability Testing

The samples ($10\times40\times1$ mm^3) were test according to ASTM D5988 – 03 (Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials after Composting). During the course of this testing, weight remaining was measured every week for 8 weeks The weight loss was evaluated using the follow equation:

$$\text{Weight loss (\%)} \quad = \quad \{(w_0-w_i)/\,w_0\} \times 100 \qquad (3.3)$$

Where w_0 and w_i are the sample weight before and after the biodegradation tests, respectively.

3.3 Methodology

3.3.1 Modification of EVA via catalytic reactive extrusion

A 300 g of EVA was mixed with 40 ml of 1-Dodecanol and 0.5 wt% of Dibutyltin Dilaurate in a container then, fed into a twin-screw extruder. Temperature profiles were 145, 165, 175, 180, 185, 185, 185, 185, 185 and 190 °C from feed zone to die. Screw speed was 10 rpm. Throughput was collected and dried. Then it was mixed again by using the same condition to increase retention time. The throughput was extracted by acetone and dried in vacuum oven at 30°C for several hours in order to further prepare thin compressed film by using compression molding at 120 °C (preheat 15 minutes and compress 5 minutes), in order to examine the conversion of EVA to EVA-co-EVOH (or modified EVA) by using soxhlet extractor. The functional group was investigated by using (FTIR Nicolet Nexus 670). The thermal properties by using DSC (Mettler Toledo, DSC822) were carried out using samples being heated from 30 to 190 °C with the heating rate of 10°C/min. Then they were cooled to -30 °C with the cooling rate of 10°C/min and reheated at the 190 °C at the same condition while TGA (Perkin-Elmer Pyris Daimond)

analyzed at temperature of 30-800 °C with the heating rate of 10 °C/min under the nitrogen gas atmosphere. Dynamic mechanical properties of the mEVA was determined by using Dynamic mechanical analyzer (EPLEXOR 100N, GABO) in tension mode, and the sample size was 10×40×4 mm^3. All DMA experiments were performed at 1 Hz with a scanning temperature range of -100 to 150 °C. The heating rate is 2 °C/min under nitrogen gas flow. Static and dynamic strains were 80% and 60%, respectively.

3.3.2 Preparation of PLA/ Modified EVA blends

PLA/mEVA/compatibilizer blends with different blend ratios shown in Table 3.1, were fed into the twin-screw extruder. Temperature profiles were 140, 150, 160, 165, 165, 165, 165, 165, 165 and 160 °C from feed zone to die. Screw speed was 30 rpm. Then, the blends were dried in vacuum oven at 40°C for 24 hours before characterization by using FE-SEM, FTIR, DSC, DMA, TGA and tensile testing.

Table 3.1 The blend compositions of PLA/Modified EVA blends

PLA (wt%)	mEVA (wt%)	Compatibilizer	
		Type	Content (phr)
90 80 70 60	10 20 30 40	Ethylene glycidyl methacrylate copolymer	5
			10
			15
		Ethylene-acrylate ester-glycidyl methacrylate terpolymer	5
			10
			15
		Ethylene-acrylic acid copolymer	5
			10
			15
		Poly(2-ethyl-2-oxazoline)	5
			10
			15

3.3.3 Preparation of specimens for testing by Injection molding.

The blends obtained from twin-screw extruder were prepared into dumbbell-shape for tensile test. The operating temperature was 130 °C, molding pressure was 35 bars, holding time in the mold was 5 sec and cool down in dumbbell-shape mold.
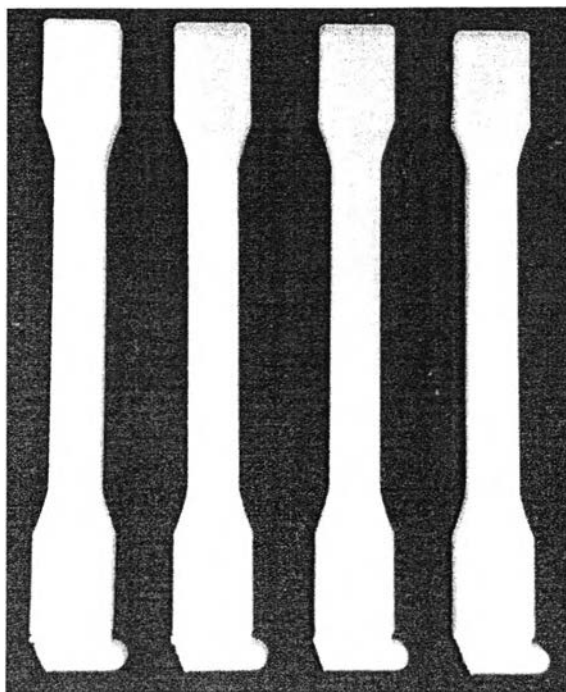
Figure 3.1 Dumbbell-shape samples by injection molding.

3.4 Characterizations

3.4.1 Characterizations and mechanical testing of modified EVA

3.4.1.1 %Yield and Conversion

According to the separation of an insoluble substance to investigate the conversions of mEVA, soxhlet extractor (VELP SCIENTIFICA, SER 148) is typically used. Acetone at 160 °C is used to wash out an excess 1-dodecanol. The insoluble part is vacuum dried at 60 °C overnight, and then % Yield of mEVA is calculated by the following equation (1).

$$\%yield = [\text{Wt. of insoluble product (g)} / \text{Wt. of crude product (g)}] \times 100 \quad (3.4)$$

3.4.1.2 Chemical Structure Analysis

The functional groups along the blends backbone were studied by using Thermo Nicolet Nexus 670 Fourier Transform Infrared Spectroscope (FTIR). For sample preparation, the blends were compressed into films. The spectra will be record over the wave number range of 4000 - 400 cm^{-1} with 32 scans at a resolution of 4 cm^{-1}.

3.4.1.3 Thermal Stability Analysis

The degradation temperature of the samples was investigated by using Thermogravimetric analysis (TGA). The samples were analyzed at temperature of 30-800°C with the heating rate of 10 °C/min under the nitrogen gas atmosphere.

3.4.1.4 Thermal Properties and Crystallization Behavior Characterization

The glass transition temperature (T_g), melting temperature (T_m), and cold crystallization temperature (T_{cc}) were performed by using differential scanning calorimeter (Mettler Toledo, DSC822). The samples were heated from 30 to 190 °C with the heating rate of 10°C/min. Then they were cooled to -30 °C with the cooling rate of 10°C/min and reheated at the 190 °C at the same condition. Degree of crystallization (χ_c) was calculated by

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times w} \times 100 \qquad (6.1)$$

ΔH_m is the enthalpy of melting, ΔH_{cc} is the enthalpy of cold crystallization, ΔH_m^0 is the enthalpy of melting for 100% crystalline PLA sample, taken as 93.1 J/g (Salamone, J. C., 1996), w is the weight fraction of PLA in the composite.

3.4.1.5 Dynamic Mechanical Properties Test

The storage modulus (E'), the loss modulus (E''), and the dissipation factor (tan δ) of the modified EVA was determined by using Dynamic Mechanical Analyzer (DMA). The tension mode was used in the temperature range

from -100 °C to 40 °C. The sample size is 10 mm × 40 mm × 4 mm in width × length × depth. The amplitude is 30.0 μm and the frequency is 1 Hz.

3.4.2 Characterizations and mechanical testing of PLA/ Modified EVA/compatibilizer blends

3.4.2.1 Thermal Stability Analysis

Thermogravimetric analysis (TGA) was used to determine the decomposition temperature (T_d) of the blends by using the temperature range of 30-800 °C and the heating rate of 10 °C/min under nitrogen gas atmosphere.

3.4.2.2 Thermal Properties and Crystallization Behavior Characterization

The melting temperature (T_m), the crystallization temperature (T_c) and ΔH were observed for studying the crystallization behavior by using Differential Scanning calorimeter (DSC). The samples were scanned with the rate of 10°C/min by heated-cooled-heated from -30 °C to 190°C.

3.4.2.3 Dynamic Mechanical Properties Test

The storage modulus (E′), the loss modulus (E″), and the dissipation factor (tan δ) of the blends were determined by using Dynamic Mechanical Analyzer (DMA). The tension mode was used in the temperature range from -100 °C to 150 °C. The sample size is 10 mm × 40 mm × 4 mm in width × length × depth. The amplitude is 30.0 μm and the frequency is 1 Hz.

3.4.2.4 Morphology characterization

The fracture surface of samples was coated by Pt and then the phase compatibilization of samples was examined by using the field emission scanning electron microscope (FE-SEM).

3.4.2.5 Physical Properties Testing

The tensile strength, %elongation at break and Young's modulus were measured by using the universal testing machine.

3.4.2.6 Melt Flow Indexer

The melt flow index of the blends was tested by using Zwick, Model4105 melt flow indexer. The sample which had weight in the range of 5-8 g

was melted at 160 °C. The melt was driven through a capillary die using a 1 kg piston, melt time 120 seconds, and cut time 30 seconds. Repeat the entire procedure 5 times and average the results.

3.4.2.7 Biodegradability Testing

The samples ($10 \times 40 \times 1 mm^3$) were test according to ASTM D5988 – 03 (Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials after Composting). During the course of this testing, weight remaining was measured every week for 8 weeks. The weight loss was evaluated using the follow equation:

$$\text{Weight loss (\%)} = \{(w_0 - w_i)/ w_0\} \times 100 \qquad (3.3)$$

Where w_0 and w_i are the sample weight before and after the biodegradation tests, respectively.