CHAPTER III
EXPERIMENTAL

3.1 Materials

Ethylene (vinyl acetate) or EVA, MV1055 from TPI POLENE Public Co., Ltd., Thailand.

Polylactide or PLA, 2002D from NatureWorks LLC was purchased from Fresh Bag Co., Ltd., Thailand.

Lactide monomer was purchased from Bio Invigor Inc., China.

1-dodecyl alcohol was purchased from Sigma-Aldrich Co., Ltd., Thailand.

Dibutyl tin dilaurate or DBTDL was purchased from Sigma-Aldrich Co., Ltd., Thailand.

Tin (II) octoate or $Sn(Oct)_2$ was purchased from Sigma-Aldrich Co., Ltd., Thailand.

Irganox® 1076 was purchased from Sigma-Aldrich Co., Ltd., Thailand.

Table 3.1 Physical and thermal properties of EVA and PLA

Properties	**EVA**	**PLA**
Molecular weight, g/mol	-	74000
Form	pellet	Pellet
Color	clear	light yellow
Melting point, °C	(70±5)°C	(160±8)°C
Melt Flow Rate, g/10min (2.16g, 190°C)	8.00	4.00
Degradation temp, °C	~429.5°C	~332°C
Density, g/ml	0.953	1.24

3.2 Equipments

3.2.1 Twin Screw Extruder

Transesterification of EVA, graft copolymerization of EVA/PLA, and modification of EVA-g-PLA, were prepared by specific twin screw extruder from LabTech with L/D ratio of 20:1 (40-cm length and 2-cm diameter) for the screw speeds of 30 and 40 rpm; and SHJ-36 from Nanjing Giant Machinery Co., Ltd. with screw diameter of 36 mm and L/D ratio of 40:1 for 150 rpm; respectively. The processing conditions for the process are shown in Table 3.2.

Table 3.2 Processing conditions of reactive extrusion for transesterification of EVA, and graft copolymerization of EVA/PLA twin-screw extruder

Type	Temperature (°C)										Screw speed (rpm)
	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Die	
Transesterification of EVA	145	165	175	180	185	185	185	185	185	190	10, 20, 30, and 40
EVA-g-PLA, (0.1, 0.3, and 0.5% wt $Sn(Oct)_2$)	140	150	160	165	165	165	165	165	165	160	30 and 40
EVA-g-PLA, (0.1, 0.3, and 0.5%wt $Sn(Oct)_2$)	155	190	200	209	209	209	209	209	209	225	150

3.2.2 Fourier Transform Infrared Spectrophotometer (FTIR)

FTIR Nexus 670, Thermo Nicolet, was used to investigate functional groups of modified EVA and EVA-g-PLA via ATR mode with ZnSe window, scan wavelength from 4000 cm^{-1} to 650 cm^{-1} with 64 scans at a resolution of 4 cm^{-1}.

3.2.3 Nuclear Magnetic Resonance (NMR)

The structure of EVA-g-PLA was confirmed by H^1NMR (AVANCE300) at frequency of 300 Hz. in $CDCl_3$.

3.2.4 X-ray Diffractometer (XRD)

The characteristic peaks of EVA-g-PLA, and modified EVA-g-PLA were observed by XRD Shidamatsu, Dmax 2002. According to the Bragg's law:

$$n\lambda = 2d\sin\theta , \quad (3.1)$$

where λ is the wavelength of the X-ray radiation used

d is the space between the diffractional lattice planes (d-spacing)

θ is the measure diffraction angle or glancing angle

3.2.5 Differential Scanning Calorimeter (DSC)

The crystallization and melting behaviors (T_m, T_c, and %crystallinity) of modified EVA, EVA-g-PLA, and modified EVA-g-PLA were measured with Mettler Toledo model DSC822. 25 ml/min of nitrogen gas was consistly purged into the equipment during the measurement in order to prevent specimens from thermal degradation.

The thermal scans consisted of three steps with heat-cool-heat which strat from -30°C to 190°C at heating rate of 10°C/min, corresponding to the melting behavior investigations.

The crystallinity of polymer can be determined by using ΔH of the melting curve and then %crystallinity can be calculated from the equation below;

$$\text{Crystallinity (\%)} = \frac{\Delta H \text{ of sample}}{\Delta H \text{ of standard sample}} \times 100, \quad (3.2)$$

where ΔH of standard sample means that of perfect crystalline sample (100% crystallinity). The crystallinity of the EVA-g-PLA is contributed by both of EVA and PLA, so ΔH of the perfect crystalline PE is 293 J/g (Salamone, J.C., 1996) and PLA is 93 J/g (Xiao, H., *et al.*, 2009), respectively.

3.2.7 Thermogravimetric Analysis (TGA)

The samples were analyzed by TGA using a Mettler (TG-DTA) instrument under N_2 flow of 100 ml/min. The heating process was conducted from 30-800°C at heating rate of 10°C/min to investigate thermal stability of samples.

3.2.8 Tensile Testing Machine

The tensile test was performed using Lloyd Universal Testing Machine. The tensile specimens were prepared according to the ASTM D 882-91 standard with 500N load , a 100 mm/min crosshead speed and a gauge length 50 mm. The samples were cut into stripes of 10 mm × 150 mm (width × length) and thickness in the range of 0.1-0.25 mm. Then the tensile stress at break, Young's modulus, and %strain at break were collected for at least five samples of each condition.

3.2.9 Scanning Electron Microscope

The morphology of EVA-g-PLA was observed by Hitachi S-4800. The measurement was carried out at 5-15 kV. The cryogenic-fracture specimens were coated by Pt prior to investigation.

3.3 Methods

3.3.1 Transesterification of EVA in a Twin-screw Extruder

A mixture of EVA (TPI POLENE), 1-dodecanol and DBTDL purchased from SM Chemicals (Sigma Aldrich), were mixed together in a container then fed into a twin-screw extruder (LabTech), with 2 die exits (3-mm diameter). The operating temperatures of 10 zones from hopper to die were 145-165-175-180-185-185-185-185-185-190 °C. The screw rotating speeds were varied, i.e. 10, 20, 30, and 40 rpm. The throughput was collected and dried. Then the throughput was extracted by acetone to get rid of excess 1-dodecanol and dried in vacuum oven at 30°C for several hours before shaped into thin film by compression moulding (Wabash) at 120°C (preheat 10 minutes and compress 5 minutes), in order to examine the conversion of EVA to EVA-co-EVOH (or modified EVA) by FTIR (Nexus 670, Thermo Nicolet). The thermal properties by DSC (Mettler Toledo, DSC822) were carried out using samples being heated from -30 °C to 130 °C and cooled to -30 °C,

then heated again from -30 °C to 130 °C with heating rate 5 °C/min while TGA (Perkin Elmer, Pyris Diamond) providing thermal stabilities of the modified EVAs ran in temperature range of 30-900 °C with heating rate 10 °C/min. Dynamic mechanical properties of the modified EVAs were also investigated using NETZSCH DMA 242, penetration mode from -100 °C to 40 °C, sample size 5mm × 5mm × 3mm (width×length×depth), amplitude 30.0 μm, and frequency 1 Hz.

3.3.2 Preparation of Ethylene(vinyl acetate)-g-Polylactide by Catalytic Reactive Extrusion in an Intermeshing Co-Rotating Twin-Screw Extruder

The preparation of EVA-g-PLA was done by catalytic reactive extrusion process in the twin-screw extruder from LabTech with L/D ratio of 20:1 (40-cm length and 2-cm diameter) and 2 die exits (3-mm diameter). The experiment will be done as follow: A mixture of transesterified EVA and PLA (the EVA to PLA ratio 40:60) was mixed with $Sn(Oct)_2$ catalyst (0.1, 0.3 and 0.5 wt%) and 0.5 wt% of Irganox®1076. The barrel temperatures were set as shown in Table 3.2. Throughput was melt mixed again with the same extruder and the same condition in order to increase retention time. Then the throughput was dry in vacuum oven overnight at 60°C before characterizations.

3.3.3 Modification of Ethylene(vinyl acetate)-g-Polylactide

The modification of EVA-g-PLA was done inside the twin-screw extruder, the experiment will be done as follow: A mixture of transesterified EVA, PLA and LA (the EVA: PLA: LA ratio 40:20:40) was mixed with $Sn(Oct)_2$ catalyst (0.1, 0.3 and 0.5 wt%) and 0.5 wt% of Irganox®1076. The barrel temperatures were set as shown in Table 3.2.

3.4 Characterizations

3.4.1 Characterizations and Testing of The Modified EVA at Various Screw Rotating Speeds (10, 20, 30, and 40 rpm)

3.4.1.1 Chemical Analysis

The partially modified EVA at each screw rotating speed was studied on its change in functional groups along the backbone by FTIR technique

(Nexus 670, Thermo Nicolet). The samples were compressed into films, then checked the declining of acetate groups at 1739 cm^{-1} corresponding to C=O, with an internal standard peak at 958 cm^{-1} corresponding to C-H bending (out of plane).

3.4.1.2 Thermal Properties and Crystallization Behavior Observation

The melting temperature (T_m), the crystallization temperature (T_c) and ΔH were observed for studying the crystallization behavior, including the investigation of transesterification by using DSC. The samples were scanned with the rate of 5°C/min by heated-cooled-heated from -30°C to 190°C.

3.4.1.3 Thermal Stability Analysis

TGA was used to investigate compositions at any degradation temperatures (T_d) of the samples. 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 Dynamic Mechanical Properties Testing

The study of dynamic mechanical properties of the modified EVA was done by NETZSCH DMA 242, penetration mode with compression holder from -100 °C to 40 °C, sample size 5mm × 5mm × 3mm (width×length×depth), amplitude 30.0 μm, and frequency 1 H_z .

3.4.2 Characterizations and Testing of EVA-g-PLA and Modified EVA-g-PLA at Various Catalyst Contents (0.1wt%, 0.3wt%, and 0.5wt%)

3.4.2.1 Chemical Analysis

Functional groups and structure of EVA-g-PLA were examined by FTIR Nexus 670, Thermo Nicolet from 4000 cm^{-1} to 650 cm^{-1}, and H^1NMR at frequency of 100.32 Hz, samples were dissolved in $CHCl_3$-d_6 .

3.4.2.2 Physical Properties Testing

The physical properties such as tensile testing were measured according to the ASTM D 882-91. The tensile specimens were prepared in a form of thin sheet by compression moulding machine with teflon mould at 190°C, preheated for 10 min and compressed for 5 min with compression pressure of 5 tons, the

specimens were cut into strip form of 10mm × 150mm × 0.5mm (width × length × depth).

3.4.2.3 Crystallization Behavior and Thermal Properties Observation

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

3.4.2.4 Thermal Stability Analysis

TGA (Perkin Elmer, Pyris Diamond) was used to investigate the degradation temperature (T_d). The samples were analyzed at temperature of 30-800°C with the heating rate of 10°C/min under the nitrogen gas atmosphere.

3.4.2.5 Dynamic Mechanical Properties Testing

The study of dynamic mechanical properties of the modified EVA was done by NETZSCH DMA 242, penetration mode from -30 °C to 100 °C. The specimens were prepared by compression moulding machine with teflon mould at 120°C, 10 min preheat, and 5 min compress with compression pressure of 15 tons. Then, the specimens were cut into a dimension of 5mm × 5mm × 3mm (width × length × depth).

3.4.2.6 Morphology

The cryogenic-fracture surface of samples were coated by Pt and then the phase compatibilization of samples were observed by SEM (Hitachi S-4800) with 5-15 kV and 1000x magnification.