

CHAPTER IV

TRANSESTERIFICATION OF ETHYLENE(VINYL ACETATE) VIA CATALYTIC TRANESTERIFICATION REACTIVE EXTRUSION

4.1 Abstract

The aim of this study is to synthesize the transesterification of ethylene(vinyl acetate) or EVA via catalytic reactive extrusion in a co-rotating 20 mm diameter twin-screw extruder with 40:1 L/D ratio and screw speed at 10 rpm. The conversion of mEVA was determined by using Soxhlet extractor. The functional group was investigated by using Fourier Transform Infrared Spectroscopy (FTIR). The mEVA was further examined for thermal properties and thermal mechanical properties by using Thermogravimetric analysis (TGA), Differential Scanning calorimeter (DSC) and Dynamic mechanical analyzer (DMA). The results from FTIR and dynamic mechanical test revealed that the increment of hydroxyl groups to EVA chains was successfully obtained via catalytic reactive extrusion.

Keywords: Catalytic reactive extrusion, Ethylene(vinyl acetate) (EVA), Transesterification

4.2 Introduction

Ethylene (Vinyl Acetate) (EVA) is the copolymer of ethylene and vinyl acetate. Generally, Vinyl Acetate (VA) it is an extremely elastic material that can be sintered to form a porous material similar to rubber. Therefore, the traditional blend between PLA and EVA leads to the improvement in softness and flexibility properties of PLA.

Transesterification reaction of EVA by catalytic reactive extrusion in order to increase the hydroxyl groups in EVA chains, occurred inside the twin-screw extruder

with the incorporation of catalyst, is preferable methods to obtain more polar EVA and also miscible blend with other polar polymers.

In this work, the synthesis of transesterification of EVA via catalytic reactive extrusion was done. Moreover, %conversion, functional group, thermal properties and dynamic mechanical properties of mEVA were determined by using Soxhlet extractor, FTIR, TGA, DSC, and DMA respectively.

4.3 Materials

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

4.3.2 1-Dodecanol (Molecular Formula $\text{CH}_3(\text{CH}_2)_{11}\text{OH}$) 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.

4.3.3 Dibutyltin Dilaurate (DBTDL, $\text{C}_{32}\text{H}_{64}\text{O}_4\text{Sn}$ 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.

4.3.4 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.

4.4 Methodology

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 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.

4.5 Characterization

4.5.1 Twin-screw extruder

The 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, 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.

4.5.2 Compression molding

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

4.5.3 %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

$$\% \text{yield} = [\text{Wt. of insoluble product (g)} / \text{Wt. of crude product (g)}] \times 100 \quad (4.1)$$

4.5.4 Chemical Structure Analysis

The functional groups along mEVA backbone were studied by using Fourier Transform Infrared Spectroscopy (FTIR). For sample preparation, the blends were compressed into films. Then they were checked the declining of acetate groups at 1739 cm^{-1} corresponding to C=O and the internal standard peak at 958 cm^{-1} corresponding to C-H bending (out of plane).

4.5.5 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.

4.5.6 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

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times w} \times 100 \quad (4.2)$$

ΔH_m is the enthalpy of melting, ΔH_{cc} is the enthalpy of cold crystallization, ΔH_m^0 is the enthalpy of the perfect crystalline PE is 293 J/g (Xiao, H., *et al.*, 2009), w is the weight fraction of vinyl acetate group in the chain.

4.5.7 Dynamic Mechanical Properties Test

The storage modulus (E'), the loss modulus (E''), and the dissipation factor ($\tan \delta$) of the modified EVA were 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 was 10 mm × 40 mm × 4 mm in width × length × depth. The amplitude was 30.0 μ m and the frequency was 1 Hz.

4.6 Results and discussion

4.6.1 Extrusion

Table 4.1 shows the retention time and the throughput rate of modified EVA (mEVA).

Table 4.1 Retention time and throughput rate of mEVA

Retention time (min)	Throughput rate (g/hr)
10.27	177.89

4.6.2 Soxhlet Extraction of mEVA

According to the separation of an insoluble substance to investigate the conversions of mEVA, soxhlet extractor 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 (4.3). The conversion and % Yield of mEVA are shown in Table 4.2.

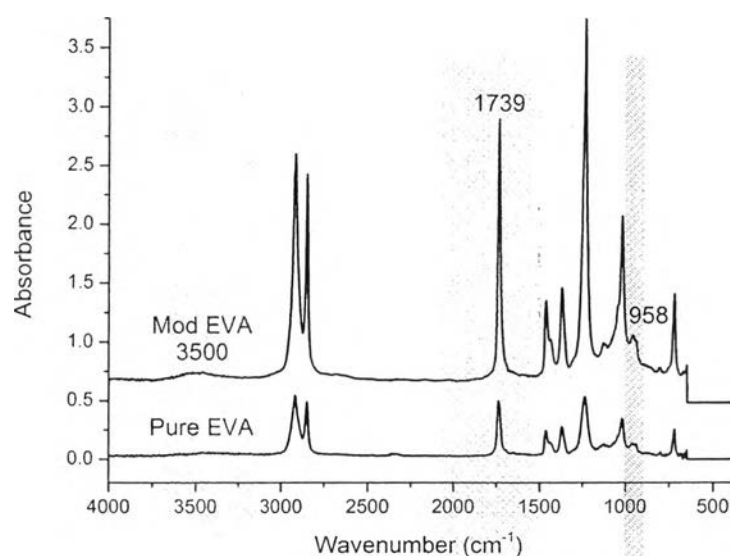
$$\% \text{Yield} = [\text{Wt. of insoluble product (g)} / \text{Wt. of crude product (g)}] \times 100 \quad (4.3)$$

Table 4.2 Conversion and %Yield of mEVA at screw speed of 10 rpm

Sample	Crude product (g)	Insoluble product (g)	%yield	%unreacted alcohol	Conversion (mol%)
1	3.0424	2.7448	90.22	9.78	32.47
2	3.0868	2.7955	90.56	9.44	33.14
3	3.1063	2.8013	90.18	9.82	31.71
Average			90.32	9.68	32.44

4.6.3 FTIR Analysis of mEVA

The FTIR spectrum of pure EVA is shown in Figure 4.1 which is composed of C=O stretching at 1739 cm^{-1} corresponding to acetate group and C-H bending (out of plane) at 958 cm^{-1} . Otherwise, the FTIR spectrum of mEVA demonstrates the weak band absorption of hydroxyl groups at about 3500 cm^{-1} . The result reveals that the increment of hydroxyl groups to EVA chains is successfully obtained via catalytic reactive extrusion.

**Figure 4.1** FTIR spectra of pure EVA and mEVA.

4.6.4 Thermal stability

TGA is commonly used to determine the thermal stability of mEVA. The TGA thermograms indicate the significant difference between pure EVA and mEVA in Figure 4.2. Moreover, pure EVA and mEVA exhibit two steps of degradation as shown in Table 4.3. The first decomposition temperature of the EVAs is observed around 350 °C which corresponding to the elimination of acetic acid from the vinyl acetate sections of the EVAs. The second decomposition temperature of the EVAs is noticed around 470 °C which assigned to the degradation of the ethylene backbone [1, 2].

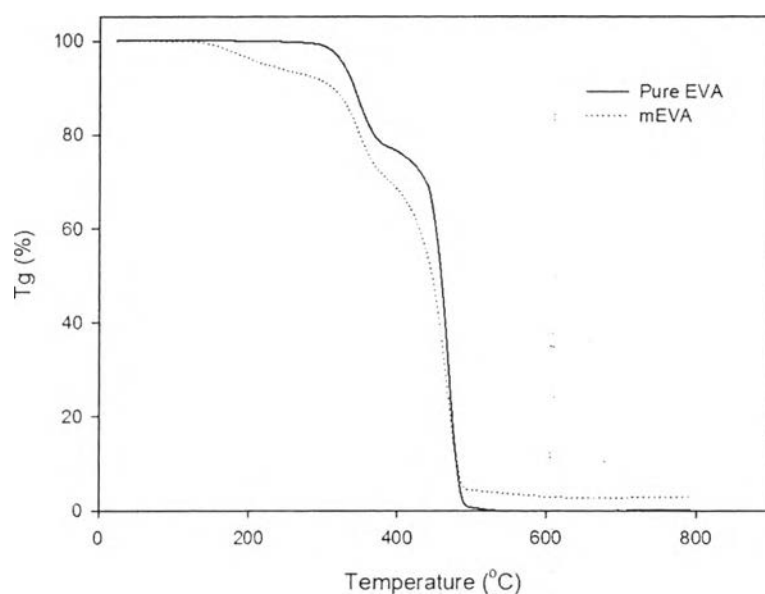


Figure 4.2 TGA thermograms of pure EVA and mEVA.

Table 4.3 Decomposition temperature ($^{\circ}\text{C}$), weight loss (%) and char residue (wt%) of pure EVA and mEVA

Sample	Decomposition Temperature ($^{\circ}\text{C}$)		Weight Loss (%)		Char Residue (wt%)
	1 st peak	2 nd peak	1 st decomposition	2 nd decomposition	
Pure EVA	351.5	468.0	23.5	76.1	-
mEVA	352.7	471.0	21.6	65.6	4.8

4.6.5 Thermal properties

DSC curves of pure EVA and mEVA are shown in Figure 4.4. Moreover, the melting temperature (T_m), crystallization temperature (T_c), degree of crystallization (χ_c), and glass transition temperature (T_g) are exhibited in Table 4.4. The results show that the glass transition temperature of mEVA higher than that of pure EVA because hydrogen bonding obstructs the mEVA chain motion. The melting temperature and degree of crystallization of mEVA are slightly higher than those of pure EVA.

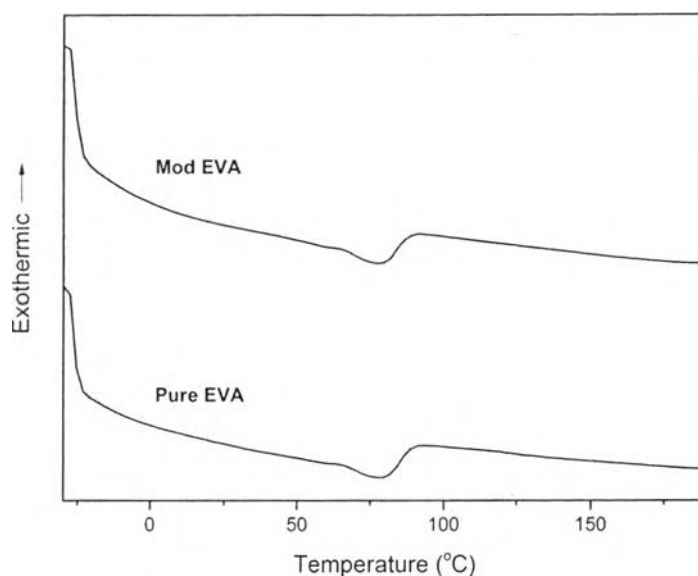


Figure 4.3 DSC thermograms of pure EVA and mEVA.

Table 4.4 Thermal properties of pure EVA and mEVA

Sample	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔH_c (J/g)	$\% \chi_c$
Pure EVA	-27.7	78.8	56.6	20.7	0.09
mEVA	-27.0	79.0	56.9	23.7	0.10

4.6.6 Dynamic mechanical properties

Storage modulus (E') and loss modulus (E'') of pure EVA and mEVA are shown in Figures 4.4-4.6, respectively. Likewise, a prominent peak in phase angle curve ($\tan \delta$), appears at the glass transition temperature (T_g) of the materials as shown in Table 4.5. The result implies that the storage modulus and the loss modulus of mEVA are lower than those of pure EVA probably due to the plasticization effect of an excess 1-dodecanal. However, the glass transition temperature (T_g) of mEVA is

higher than that of pure EVA that confirm the existing of hydrogen bonding along the mEVA chains, resulting in the obstruction of mEVA chain motion.

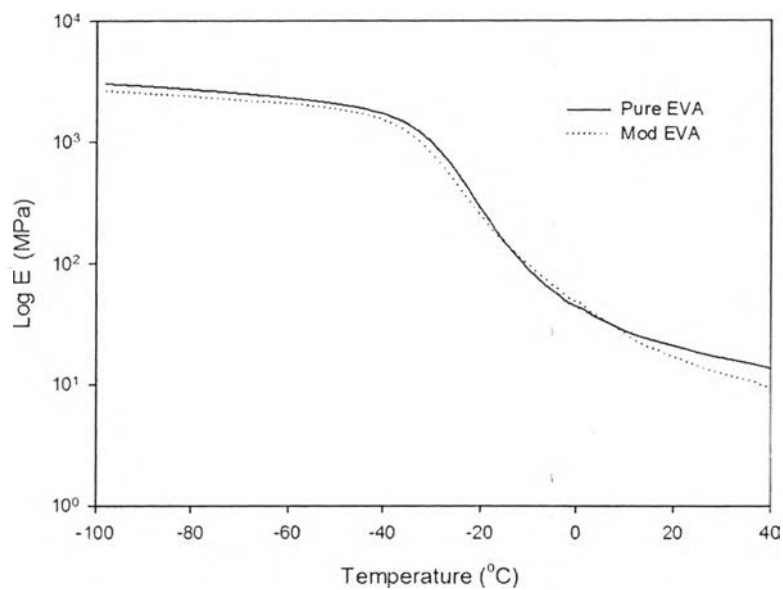


Figure 4.4 Storage Modulus of pure EVA and mEVA.

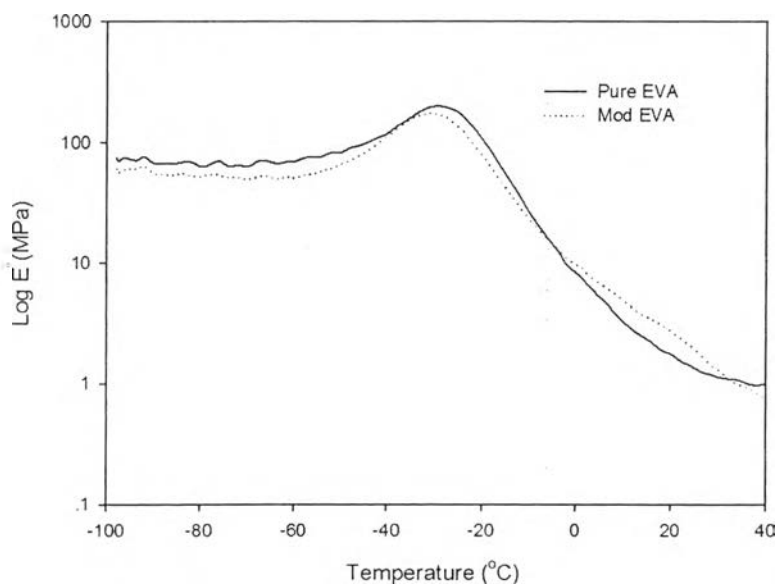


Figure 4.5 Loss Modulus of pure EVA and mEVA.

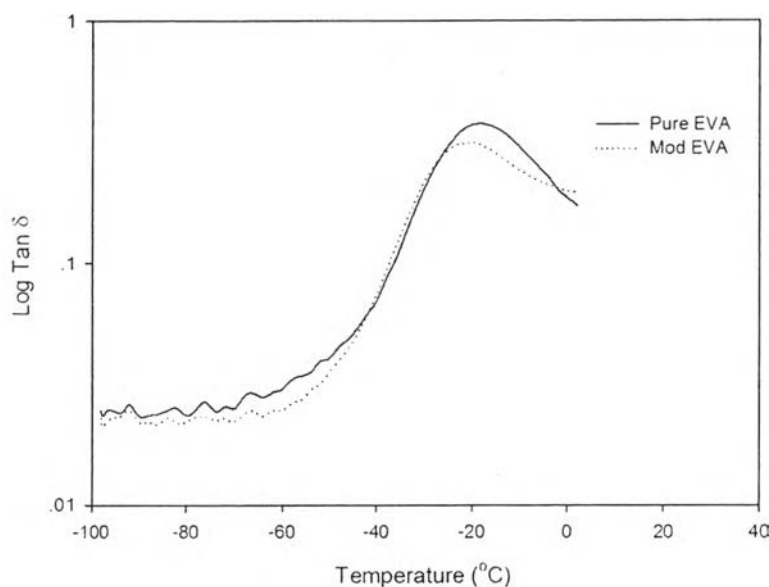


Figure 4.6 Tan δ of pure EVA and mEVA.

Table 4.5 Dynamic mechanical properties of pure PLA and mEVA

Blend composition	Tan δ_{max} (T_g , °C)	30 °C	
		E' (MPa)	E'' (MPa)
Pure EVA	-21.2	16	1.28
mEVA	-20.0	12	1.12

4.7 Conclusion

Transesterification of EVA was done in a 20 mm diameter co-rotating twin-screw extruder with 40:1 L/D ratio and screw speed at 10 rpm. %yield and conversion of EVA to EVA-co-EVOH (or modified EVA) were 90.32 and 32.44. The result from FTIR revealed that the increment of hydroxyl groups to EVA chains was successfully obtained via catalytic reactive extrusion. The storage and loss modulus of mEVA were lower than pure EVA. However, its glass transition

temperature was slightly higher than pure EVA as a result of intermolecular hydrogen bonding.

4.8 Acknowledgements

This research is funded from National Research Council of Thailand (NRCT), the Petroleum and Petrochemical College

The author would like to gratefully acknowledge the help of TPI POLENE.Co.Ltd, for the material support.

Finally, I would like to thank the help of Assoc. Prof. Dr. Rathanawan Magaraphan, Asst. Prof. Dr. Manit Nithitanakul and Asst. Prof. Dr. Suparat Rukchonlatee for their suggestion of the experiment.

4.9 References

[1] Varghese, H., Bhagawan, S. S., and Thomas, S. (2001). Thermogravimetric analysis and thermal ageing of crosslinked nitrile rubber/poly(ethylene-co-vinyl acetate) blends. Journal of Thermal Analysis and Calorimetry , 63, 749-763.

[2] Fernandez, M. D., and Fernandez, M. J. (2008). Thermal decomposition of copolymer from ethylene with some vinyl derivatives. Journal of Thermal Analysis and Calorimetry , 91, 447-454.

[3] Kim, P.J., and White, J.L. (1994). Transesterification of ethylene vinyl acetate copolymer in a modular intermeshing corotating twin screw extruder with different screw configurations. Journal of Applied Polymer Science , 54 (1), 33-45.

[4] Moura, I., Nogueira, R., Bounor-Legare, V., and Machado, A.V. (2012). synthesis of EVA-g-PLA copolymer using transesterification reactions. Materials Chemistry and Physics.

[5] Pattanaponganun, B. (2010). Catalytic reactive extrusion of ethylene(vinyl acetate)-g-poly lactide bioplastic. Bangkok: Petroleum and Petrochemical College.

[6] Vergnes, B., and Berzin, F. (2006). Modeling of reactive systems in twin-screw extrusion: Account / Revue, 9, 1409-1418.