CHAPTER V
THE EFFECT OF MODIFIED EVA CONTENTS ON MORPHOLOGY, THERMAL, AND MECHANICAL PROPERTIES OF PLA BLENDS

5.1 Abstract

The modified EVA (mEVA) synthesized from the previous chapter was blended with PLA at various of mEVA contents of 10, 20, 30, and 40 wt%. The PLA/mEVA blends were prepared in a co-rotating twin-screw extruder with screw speed of 30 rpm. The increasing of mEVA loading in the PLA/mEVA blends caused a decrease in glass transition temperature (T_g) (from 58 °C to 55 °C) however, the elongation at break of the blends increased from 5 to 9%. Morphological interpretation through FE-SEM revealed the phase separation of the PLA/mEVA blends in the presence of mEVA.

Keywords : Catalytic reactive extrusion, Ethylene (vinyl acetate) (EVA), Poly(lactic acid) (PLA)

5.2 Introduction

Poly(lactic acid) (PLA), produced from renewable resources (e.g., wheat, rice, sugar or corn), is one of the most important bio-based and biodegradable polymers. It can be biodegraded within 4-5 weeks by heat. Although PLA has several favorable properties such as, high strength and stiffness at room temperature, the limitation of PLA is brittleness. In recent years, there are several methods to improve PLA properties such as plasticization, copolymerization and blending with various biodegradable and non- biodegradable polymers. For these methods, blending PLA with other polymers is the most effective and convenient way to improve PLA properties. However, phase separation of PLA and other polymers can

occur due to thermodynamical incompatibility, resulting in the limitation of toughness improvement.

Ethylene (Vinyl Acetate) (EVA) is the copolymer of ethylene and vinyl acetate. For Vinyl Acetate (VA), it is an extremely elastic material that can be sintered to form a porous material similar to rubber. Therefore, softness and flexibility of EVA can improve properties of PLA and its blend can be processed like other thermoplastics. There are many researches focusing on the improvement in the properties of PLA. Ma et al. (2012) studied compatibility between poly(lactic acid) (PLA) and Ethylene (Vinyl Acetate) (EVA). They found that PLA is miscible with poly(vinyl acetate) (PVAc) but not miscible with polyethylene (PE). As a result, the optimum toughening effect of EVA on the PLA (impact and tensile properties) was obtained at a VA content of 50-60%. This suggests that introduction of hydroxyl groups to EVA chains via catalytic reactive extrusion makes EVA more polar and miscible with polar polymers.

This chapter studied the effect of mEVA contents on morphology, thermal, and mechanical properties by using thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), dynamic mechanical analyzer (DMA), field emission scanning electron microscope (FE-SEM), the universal testing machine, melt flow indexer, and biodegradability testing.

5.3 Materials

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

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

5.4 Methodology

5.4.1 Preparation of PLA/ Modified EVA blends

PLA/mEVA blends with different blend ratios in Table 5.1, 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, DSC, DMA, TGA and tensile testing.

Table 5.1 The blend compositions of PLA/Modified EVA blends

PLA (wt%)	mEVA (wt%)
100	0
90	10
80	20
70	30
60	40
0	100

5.4.2 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.
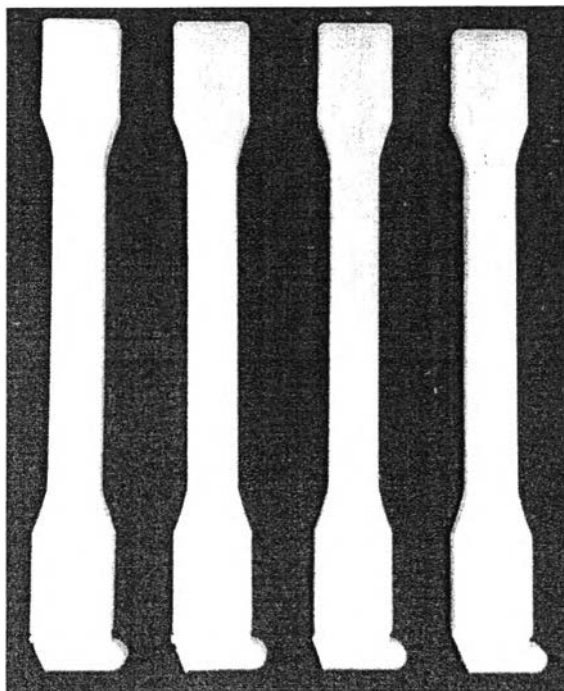
Figure 5.1 Dumbbell-shape samples by injection molding.

5.5 Characterization

5.5.1 Characterizations and mechanical testing of PLA/ Modified EVA blends

5.5.1.1 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.

5.5.1.2 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

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \times w} \times 100 \qquad (5.1)$$

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.

5.5.1.3 *Dynamic Mechanical Properties Test*

The storage modulus (E′), the loss modulus (E″), and the dissipation factor (tan δ) 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 150 °C. The sample size was 10 mm × 40 mm × 4 mm in width × length × depth. The amplitude was 30.0 μm and the frequency was 1 Hz.

5.5.1.4 *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).

5.5.1.5 *Physical Properties Testing*

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

5.5.1.6 *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.

5.5.1.7 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:

Weight loss (%)   = $\{(w_0-w_i)/ w_0\} \times 100$ (5.2)

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

5.6 Results and discussion

5.6.1 Thermal stability

TGA thermograms of pure PLA, pure mEVA and PLA/mEVA blends with different blend ratios are represented in Figure 5.2. It is evident that the PLA/mEVA blends exhibit two steps of degradation as shown in Table 5.2. The first decomposition temperature of all blends is observed around 320-360 °C, corresponding to the elimination of acetic acid from the vinyl acetate sections of the modified EVA and PLA chains. The second decomposition temperature of the blends is noticed around 470-490 °C which assigned to the degradation of the ethylene backbone [1, 2]. The results also indicate that the decomposition temperatures of PLA/mEVA blends tend to decrease gradually with the increasing in mEVA contents due to the phase separation of PLA and mEVA. However, the decomposition temperatures of the PLA/mEVA blends are still higher than that of pure PLA because of a higher decomposition temperature of mEVA.
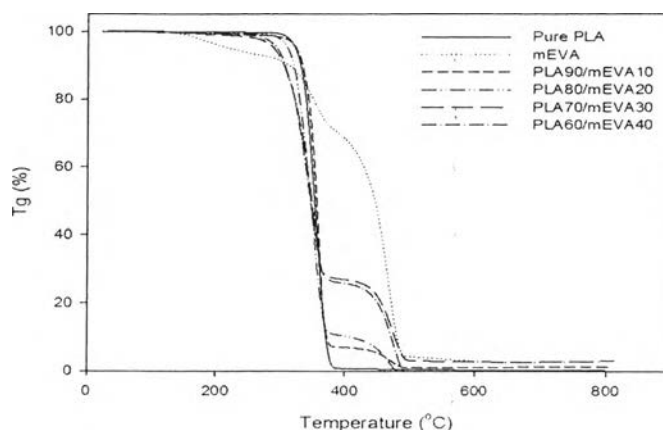
Figure 5.2 TGA thermograms of pure PLA, pure mEVA, and PLA/mEVA blends with various mEVA contents.

Table 5.2 Decomposition temperatures of pure PLA, pure mEVA and PLA/mEVA blends

Blend composition	Decomposition Temperature ($^\circ$C)	
	1st	2nd
PLA	332.8	–
mEVA	351.5	468.0
PLA90/mEVA10	351.2	471.0
PLA80/mEVA20	351.3	472.1
PLA70/mEVA30	342.9	471.0
PLA60/mEVA40	324.6	469.7

5.6.2 Thermal properties

In Figure 5.3, the melting temperature (T_m), cold crystallization temperature (T_{cc}), degree of crystallization (χ_c) and two glass transition temperature (around -25 $^\circ$C for mEVA and around 60 $^\circ$C for PLA) of PLA/mEVA blends in various blend ratios are investigated by DSC. The curves imply that the PLA/mEVA

blends are two-phase system or immiscible blends. Furthermore, the glass transition temperatures of the binary blends decrease with increasing mEVA contents suggested that the flexibility of PLA phase occurs due to the additional mEVA. The cold crystallization temperature and degree of crystallization also decrease with increasing the amount of mEVA caused from the supplement of vinyl acetate which is amorphous region of mEVA [3].
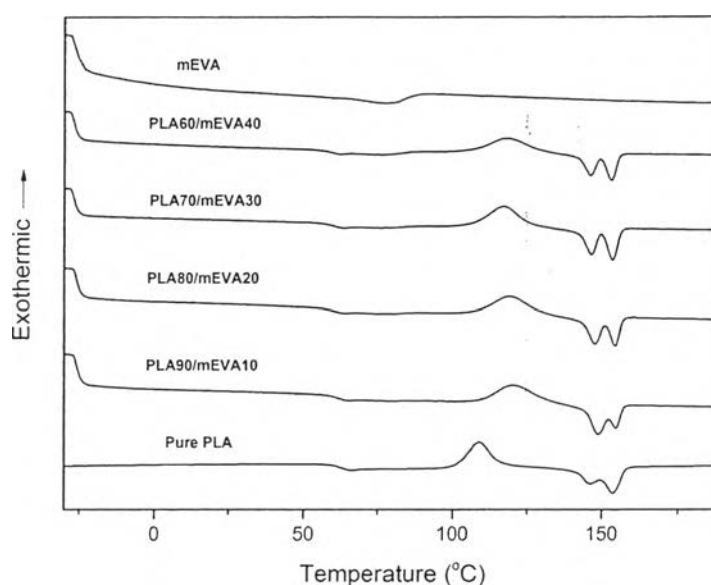

Figure 5.3 DSC thermograms of pure PLA, pure mEVA, and PLA/mEVA blends with various mEVA contents.

Table 5.3 Thermal properties of pure PLA and PLA/mEVA binary blends

Sample	T_{g1} ($^{\circ}$C)	T_{g2} ($^{\circ}$C)	T_{cc} ($^{\circ}$C)	T_{m1} ($^{\circ}$C)	T_{m2} ($^{\circ}$C)	ΔH_{cc} (J/g)	ΔH_{m} (J/g)	$\%\chi_{c}$
Pure PLA	-	59.9	103.0	146.8	153.7	19.4	24.5	5.45
PLA90/mEVA10	-26.8	58.6	120.3	148.9	154.8	26.9	28.3	1.72
PLA80/mEVA20	-26.6	57.0	119.3	147.8	154.4	26.9	27.9	1.34
PLA70/mEVA30	-27.7	56.4	117.0	146.6	153.7	27.2	27.9	1.15
PLA60/mEVA40	-27.8	55.9	118.3	146.2	159.2	22.3	22.9	1.06

5.6.3 Dynamic mechanical properties

The storage modulus (E′) and loss modulus (E″) of pure PLA, pure mEVA and PLA/mEVA blends with different blend ratios shown in Figures 5.4-5.6 and Table 5.4 are used to identify the thermal mechanical properties. At room temperature (30 °C), the results reveal that the storage modulus of PLA/mEVA blends decrease with the increasing of mEVA contents as shown in Table 5.4. This is probably due to the presence of soft elastomeric phase [4].

Generally, Tan δ in dynamic mechanical properties is used in order to determine the glass transition temperature (T_g) of the materials. The variation of tan δ as a function of temperature is showed in Figure 5.6. The glass transition temperatures (T_g) of PLA and mEVA are at around 70.1 °C and -20 °C, respectively. The results show that T_g of PLA/mEVA blends with various blend ratios shifts to a lower value compared to that of pure PLA. According to the T_g from DSC results, it is similar to that of DMA which is able to explain the flexibility of PLA phase owing to the increasing in mEVA contents.
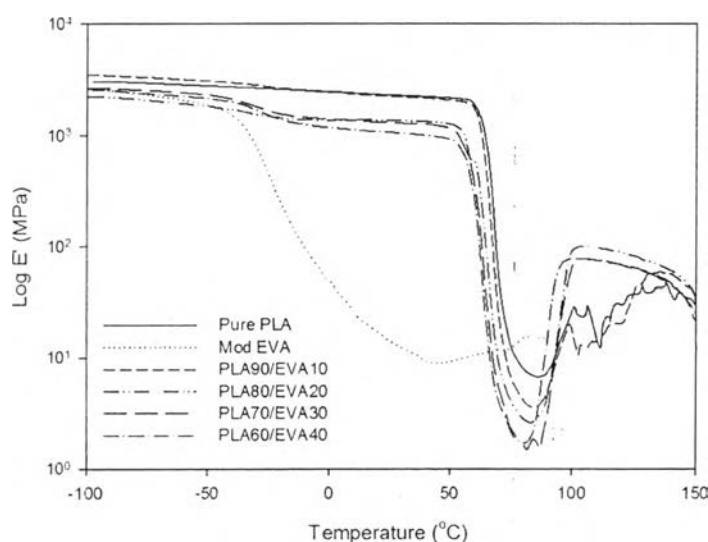

Figure 5.4 Storage Modulus of pure PLA, pure mEVA and PLA/mEVA blends at various mEVA contents.
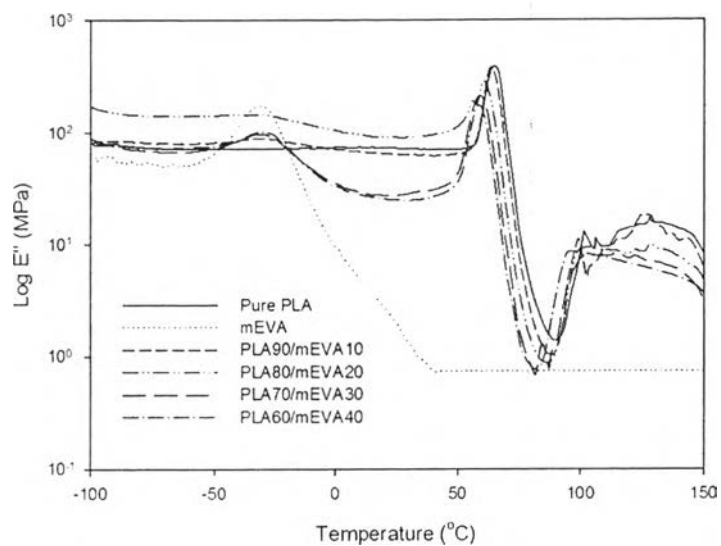
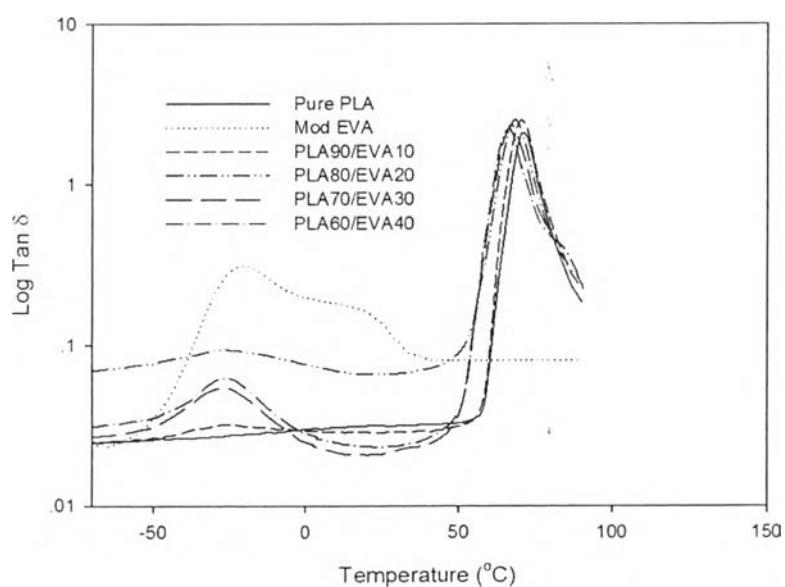**Figure 5.5** Loss Modulus of pure PLA, pure mEVA and PLA/mEVA blends at various mEVA contents.

Figure 5.6 Tan δ of pure PLA, pure mEVA and PLA/mEVA blends at various mEVA contents.

Table 5.4 Dynamic mechanical properties of pure PLA, pure mEVA and PLA/mEVA blends

Blend composition	Tan $\delta_{max,1}$ (Tg₁, °C)	Tan $\delta_{max,2}$ (Tg₂, °C)	30 °C E' (MPa)
PLA	-	70.1	2280
mEVA	-20.0	-	12
PLA90/mEVA10	-26.9	70	2208
PLA80/mEVA20	-27.8	68.2	1364
PLA70/mEVA30	-27.8	66.6	1290
PLA60/mEVA40	-28.6	66.4	1048

5.6.4 Morphology

FE-SEM micrographs of the cryogenic fracture of Pure PLA and the PLA/mEVA blends with various blend ratios are shown in Figure 5.7a.-5.7e. In Figure 5.7b-5.7e, the binary blend exhibits two-phase structure of both mEVA domain and PLA matrix. The spherulites are occurred from the mEVA in the PLA/mEVA blend [5]. Due to the phase separation of the blends, the mEVA domain size increases with increasing in the mEVA contents. The bigger sizes of mEVA phase effect to mechanical properties of PLA/mEVA blends that shown in decreasing of Young's modulus, tensile strength, and elongation at break of the blends.
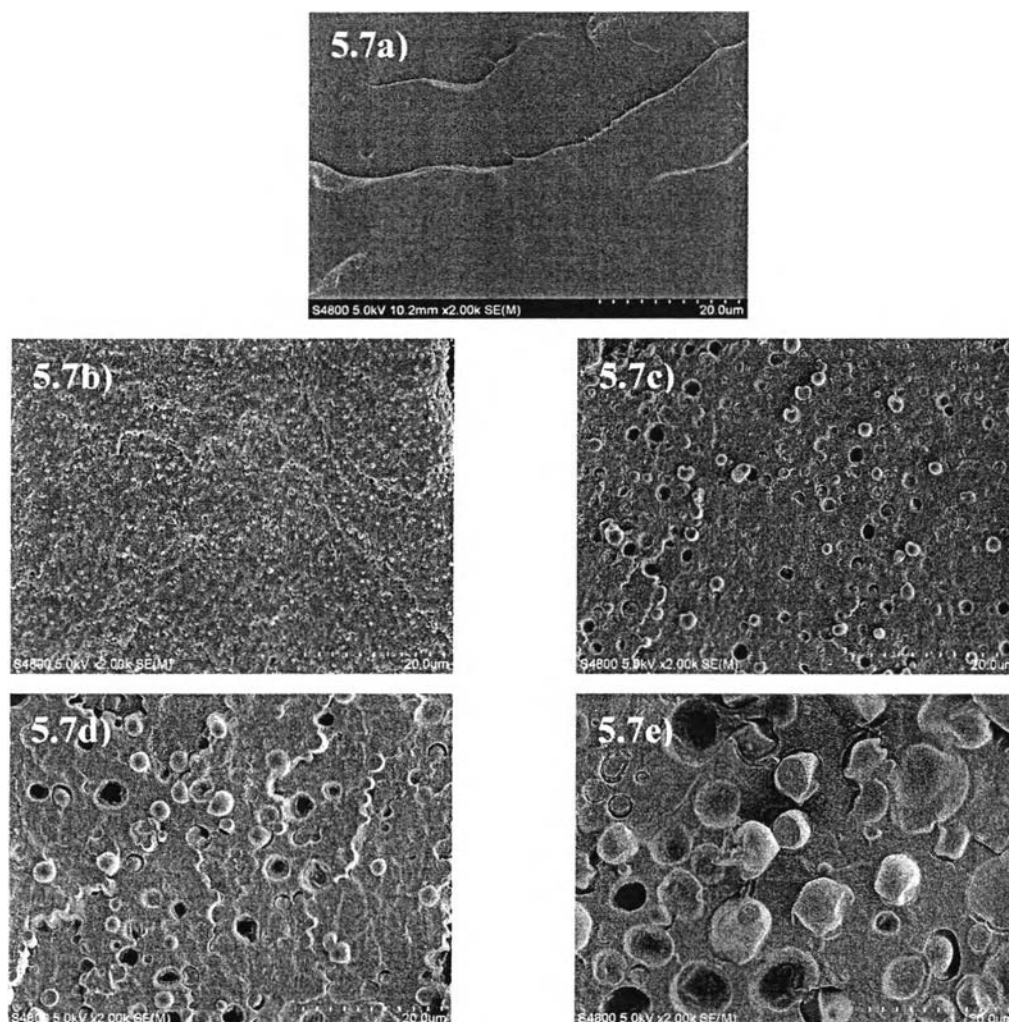
Figure 5.7 FE-SEM images of the fracture of the blend (a) Pure PLA (b) PLA/mEVA (90/10 wt%) blend (c) PLA/mEVA(80/20 wt%) blend (d) PLA/mEVA(70/30 wt%) blend (e) PLA/mEVA (60/40 wt%) blend.

5.6.5 Mechanical properties

The tensile properties of pure PLA and PLA/mEVA at various mEVA contents are represented in Figures 5.8-5.10. Pure PLA behaves strong and stiff but brittle, as reflected by the high Young's modulus, tensile strength and low elongation at break. It is evident that the Young's modulus and tensile strength of the binary blends dramatically decrease. For elongation at break, the results show the increasing

of elongation at break with the increase in mEVA contents up to 30 wt% [3]. This behavior is attributed to the toughening and elastomeric effect of mEVA that reduce the crystallinity of the blends as shown in DSC result. However, a high content of mEVA (40 wt%) causes the decreasing of elongation at break of PLA/mEVA (60/40 wt%) blend. This is due to incompatibility between PLA and mEVA, leading to phase separation on blend with high mEVA contents.
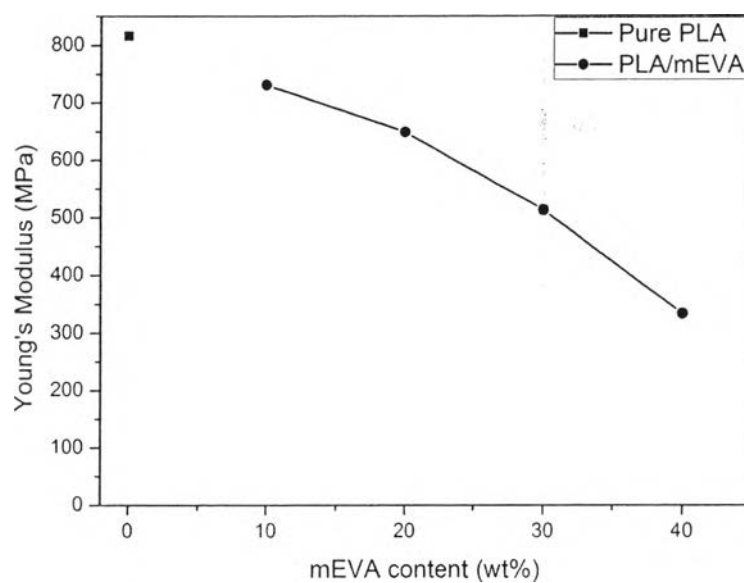

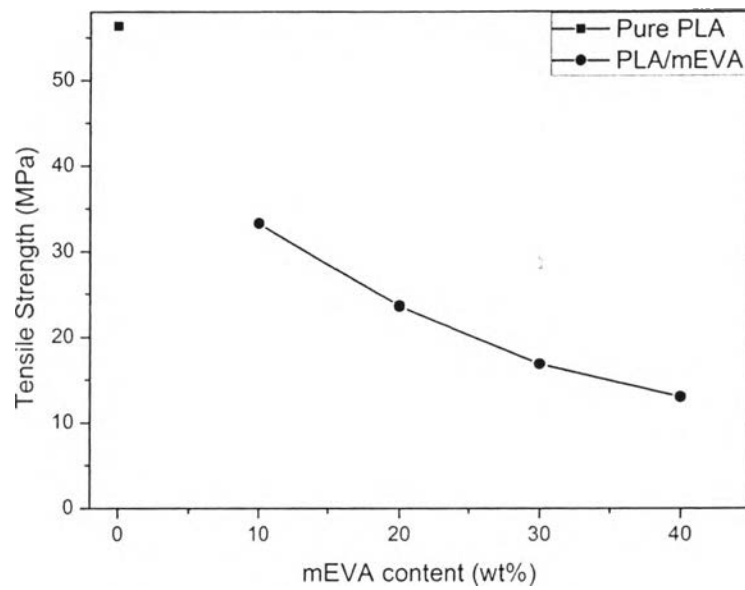**Figure 5.8** Young's modulus of PLA/mEVA blends at various mEVA contents.

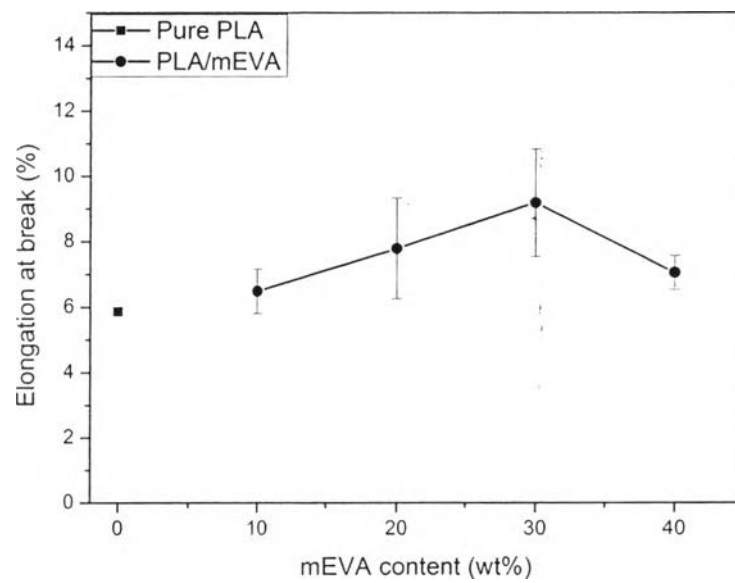**Figure 5.9** Tensile strength of PLA/mEVA blends at various mEVA contents.

Figure 5.10 Elongation at break of PLA/mEVA blends at various mEVA contents.

5.6.6 Melt flow index (MFI)

The effect of mEVA contents on the rheological properties of the blends can be investigated from MFI values as shown in Figure 5.11. The result shows that the MFI values increase with increasing mEVA contents. This arises from the incorporation of mEVA which have higher MFI value than PLA. This proposes that mEVA facilitate processability of PLA/mEVA blends.
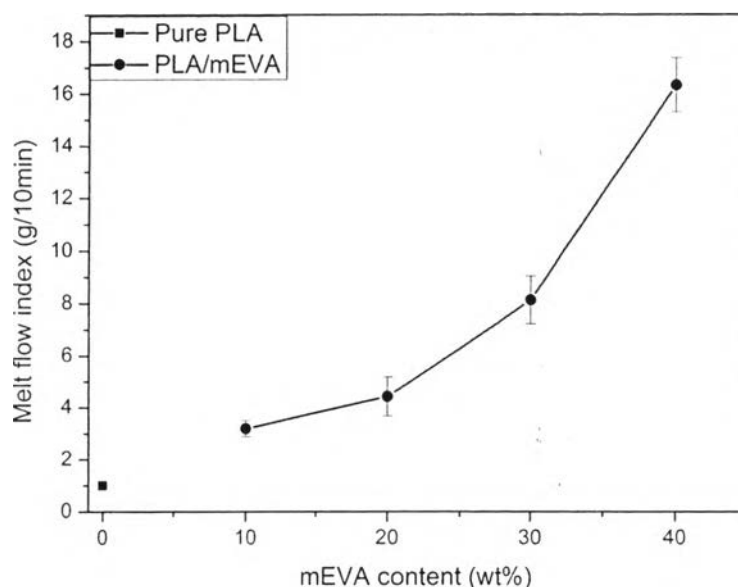

Figure 5.11 MFI values of PLA/mEVA blends at various mEVA contents.

5.6.7 Biodegradability

Figure 5.12 shows the biodegradability by evaluating weight loss of pure PLA and PLA/mEVA blends. The biodegradability of PLA/mEVA blends is lower than that of pure PLA and weight loss of PLA/mEVA blends decrease with increasing mEVA contents. This results from mEVA which is non-biodegradable polymer that more difficultly degradable than PLA itself.
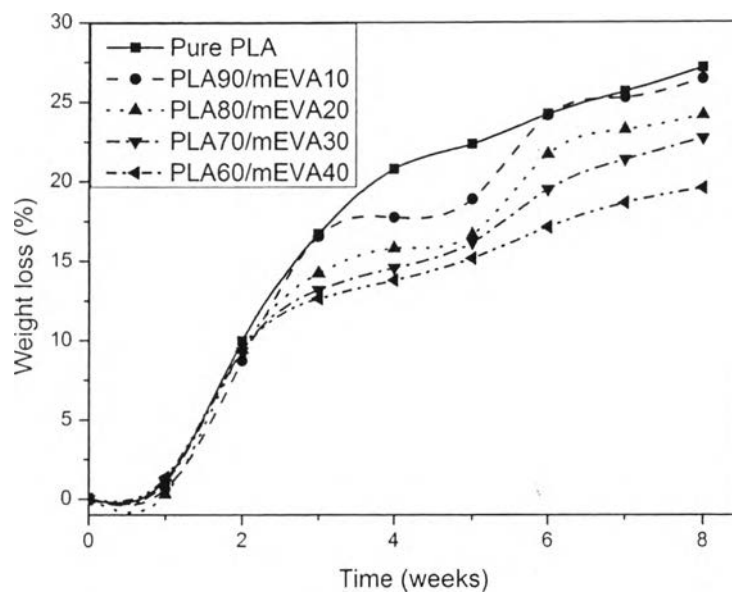
Figure 5.12 Weight loss of PLA/mEVA blends at various mEVA contents.

5.7 Conclusion

The PLA/mEVA blends were produced by a 20 mm diameter co-rotating twin-screw extruder with 40:1 L/D ratio and screw speed at 30 rpm with various mEVA contents. According to DSC results, PLA/mEVA blends exhibited the two glass transition temperatures that result from the PLA/mEVA blends were two-phase system or immiscible blends. The increment of mEVA loading in the PLA/mEVA blends caused a decrease in glass transition temperature (T_g) (from 58 $^\circ$C to 55 $^\circ$C). Moreover, the cold crystallization temperature, degree of crystallization, storage modulus, and Young's modulus were decrease due to the presence of soft amorphous phase. However, the elongation at break of the blends enhanced with the increasing in mEVA and indicated the optimum elongation at 30wt% of mEVA. Morphological interpretation through FE-SEM reveals the phase separation of the PLA/mEVA blends in the presence of mEVA. As a result of MFI value, mEVA can facilitate processability of PLA/mEVA blends. However, mEVA retarded biodegradability of PLA.

5.8 Acknowledgements

5.9 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] Lee, C.M., Kim, E.S., and Yoon, J.S. (2005). Reactive Blending of Poly(L-lactic acid) with Poly(ethylene-co-vinyl alcohol). Journal of Applied Polymer Science , 98, 886-890.

[4] Yoon, J.S., Oh, S.H., Kim, M.N., Chin, I.J., and Kim, Y.H. (1999). Thermal and mechanical properties of poly(l-lactic acid)–poly (ethyleneco-vinyl acetate) blends. Polymer , 40, 2303-2312.

[5] Takayama, T., and Todo, M. (2006). Improvement of impact fracture properties of PLA/PCL polymer blend due to LTI addition. J Mater Sci , 41, 4989-4992.

[6] Ma, P., Hristova-Bogaerds, D.G.,Goossens, J.G.P., Spoelstra,A.B., Zhang, Y., and Lemstra, *P.J. (2012). Toughening of poly(lactic acid) by ethylene-co-vinyl acetate copolymer* with different vinyl acetate contents. European Polymer Journal , 48, 146-154.

[7] Oyama, H. (2009). Super-tough poly(lactic acid) materials: Reactive blending with ethylene copolymer. Polymer , 50, 747-751.

[8] Park, J.W., and Im, S.S. (2003). Miscibility and morphology in blends of poly(L-lactic acid) and poly(vinyl acetate-co-vinyl alcohol). 44, 4341-4354.

[9] Li, Yanli., Liu, Li., Shi, Y., Xiang, F., Huang, T., Wang, Y., and Zhou, Z. (2010). Morphology, Rheological, Crystallization Behavior, and Mechanical Properties of Poly(L-lactide)/Ethylene-co-Vinyl Acetate Blends with Different VA Contents. Journal of Applied Polymer Science , 121, 2688-2698.

[10] Gajria, A.M., Dave, V., Gross, R.A., and McCarthy, S.P. (1995). Miscibility and biodegradability of blends of poly(lactic acid) and poly(vinyl acetate). 37, 437-444.

[11] Bhatia, A., Gupta,R.K., Bhattacharya, S.N., and Choi, H.J. (2007). Compatibility of Biodegradable Poly (lactic acid) (PLA) and Poly (butylene succinate) (PBS) Blends for Packaging Application. Korea-Australia Rheology Journal , 19 (3), 125-131.

[12] Burt, H. M., Jackson, J.K., Bains, S.K., Liggins, R.T., Oktaba, A.M.C., Arsenault, A.L., and Hunter, W.L. (1995). Controlled delivery of toxol from microspheres composed of a blend of ethylene-vinyl acetate copolymer and poly(d,l-lactic acid). Cancer Letters , 88, 73-79.

[13] Fang, Q., and Hanna, M.A. (1999). Rheological properties of amorphous and semicrystalline. Industrial Crops and Products , 47-53.

[14] Feldmam, D. (2005). Polyblend Compatibilization. Journal of Macromolecullar Science , 42, 587-605.

[15] 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.