

CHAPTER II

LITERATURE REVIEW

2.1 Reactive Extrusion (REX)

REX is polymer processing technique that uses a single or twin-screw extruder as a chemical reactor. It refers to the deliberate performance of chemical reactions during continuous melt extrusion of polymers and/or polymerizable monomers. REX is used more and more for chemical modification of polymers because it provides the advantages when compared with a classical batch process in solution. (Vergnes *et al.*, 2006)

- An extruder can ability to work with very viscous products, not for the case of batch reactor.
- Conditions of processing (e.g., mixing conditions, high temperatures and modular geometry) are much wider and flexible in an extrusion.
- The reaction is no solvent.
- The reaction can remove or recycle unreacted components because devolatilization of the reaction product in an extruder.

However, some drawbacks are also to be mentioned:

- The resident time should be very short in an extrusion.
- The reactions with high exothermicity could be difficult to manage in reaction extrusion because of capacity of cooling in an extruder.

2.1.1 Types of reaction in reactive extrusion (Brown *et al.*, 1991)

The types of chemical processes divided into five categories

2.1.1.1 *Graft and functionalizing reactions*

Grafting reactions are mixture of monomers that can form grafts to the polymer main chains. But functionalizing reactions are introduction of functional groups into polymer backbone, end group or side chain. As a result of

longer side chains, the viscosity of polymer during functionalizing reactions is lower than the viscosity of polymer during grafting reactions.

2.1.1.2 Interchain copolymerizations

There are reactions of two or more polymers to form graft, random, or block copolymer. Monomer do not participate in these reactions.

2.1.1.3 Coupling/crosslinking reactions

There are reactions of homopolymer with polyfunctional coupling or branching agent to increase molecular weight by chain extension, or reactions of homopolymer with crosslinking agent to increase molecular weight by crosslinking.

2.1.1.4 Bulk polymerizations

There are polymerization reactions of monomer or low molecular weight prepolymer by addition reactions (chain reactions) or condensation reactions (step reactions) to form high molecular weight polymer. These reactions have limitation of mixing and heat transfer.

2.1.1.5 Degradation reactions

There are reactions resulting in lower molecular weight polymers because of simple shear heating or addition of chemical substances (e.g., peroxide).

2.1.2 Literature review regarding of Reactive Extrusion

Moura *et al.* (2012) studied, morphology and mechanical properties of EVA-g-PLA grafted copolymers which synthesized by reactive extrusion, through tranesterification reaction between ethylene vinyl acetate copolymer (EVA) and polylactide (PLA), using titanium propoxide ($\text{Ti}(\text{OPr})_4$) and titanium phenoxide ($\text{Ti}(\text{OPh})_4$) as catalysts.

The copolymer amount increased the elongation at break. The similar trend was observed for Young's modulus. Elongation at break and Young's modulus as a function of copolymer amount are depicted in Figure 2.1.

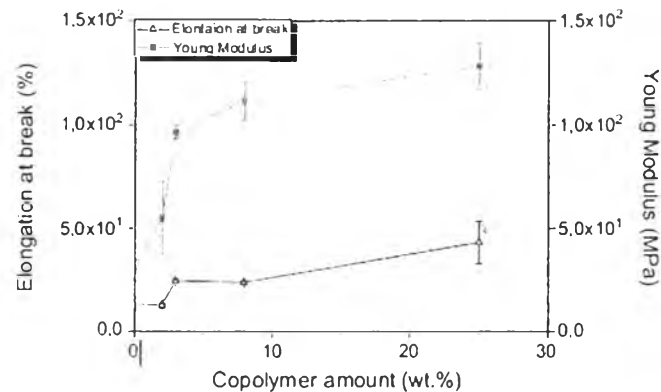


Figure 2.1 Young's modulus and elongation at break as a function of copolymer amount (Moura *et al.*, 2012).

Kim *et al.* (1994) studied transesterification of EVA in an extruder by using a modular intermeshing corotating twin-screw extruder with different screw configurations. The transesterification agent and catalyst were used 1-hexadecanol and dibutyltin dilaurate (DBTDL), respectively. The temperature of the twin-screw was set at 170 °C. The research studied various screw speeds and feed rates. The results showed the conversion was increased by reducing screw speeds and feed rates. Increasing the number of left-handed screw elements and kneading disc blocks increased resident time within the extruder and enhanced the conversion up to 31.8%.

2.2 Poly(lactic acid) or Polylactide (PLA)

Poly(lactic acid) or polylactide (PLA) is a bio-based, biodegradable, thermoplastic, linear aliphatic polyester produced from renewable resources, such as wheat, rice, corn, or sugar. Chemical structure of PLA is shown in Figure 2.2.

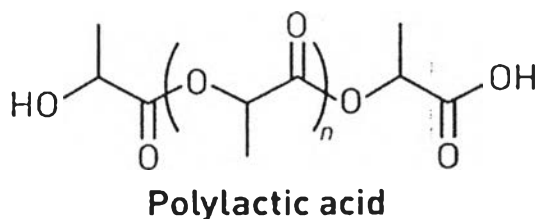


Figure 2.2 Chemical structure of PLA.

2.2.1 Synthesis of Poly(lactic acid)

PLA cannot be generated by directly condensation reaction starting from lactic acid to get high molecular weight, because water produced during the polymerization has to be removed during the polymerization process. Then it can produce via ring-opening polymerization starting from the cyclic dimer of lactic acid. Although dimerization also generates water, it can be separated prior to polymerization (Jacobsen *et al.*, 1999). Polymerization of PLA is shown in Figure 2.3.

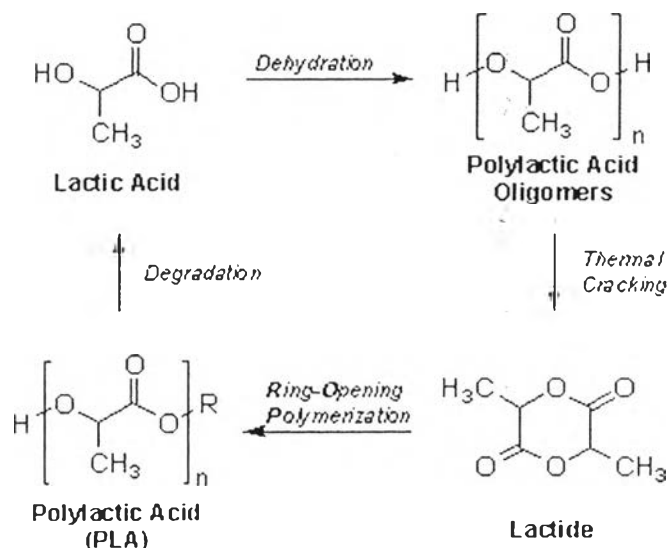


Figure 2.3 Polymerization of PLA.

2.2.2 Poly(lactic acid) Properties

Lactic acid has two optical isomers, L- and D-lactic acid. Fermentation derived lactic acid exists almost exclusively in the L form (99.5% of the L-isomer and 0.5% of the D-isomer). Due to the optical activity of lactic acid, lactide can be found in three different versions such as, D,D-lactide, L,L-lactide and D,L-lactide (meso-lactide). The mechanical and thermal properties of the poly(lactic acid) can refer from the stereochemical composition of lactide monomer for example, amorphous poly(lactic acid) has glass transition temperature (T_g) and melting temperature about 58 °C and 148 °C, respectively but semi-crystalline poly(lactic acid) has glass transition temperature (T_g) and melting temperature about 62 °C and 151 °C, respectively. Moreover, transition temperature (T_g) and melting temperature depend on structure of polymer too (Fang et al., 1999).

Products of PLA have several drawbacks such as, stiff, brittle and expensive. Then, there are several methods to improve mechanical properties and reduce cost of PLA by adding some polymer molecules.

2.2.3 Modification of poly(lactic acid) (Rasal *et al.*, 2010)

PLA is a glassy polymer that has elongation at break less than 10%, is suitable for applications which need high toughness. There are several methods to improve mechanical properties (mainly toughness), processibility, and crystallinity of PLA.

2.2.3.1 *Plasticization*

PLA is a glassy polymer that has elongation at break less than 10%. Different biodegradable as well as non- biodegradable plasticizers have been used to lower the glass transition temperature, increase ductility, and improve processibility.

Lactide is a natural choice to plasticize PLA. Lactide plasticized PLA showed a significant increase in elongation at break but got stiffening when low molecular weight of lactide migrated toward the surface.

Oligomeric plasticizers would not tend to migrate toward the surface because of high molecular weight.

2.2.3.2 Copolymerization

PLA has been copolymerized with other monomers by 2 methods, polycondensation copolymerization and ring opening copolymerization.

- Polycondensation copolymerization

Polycondensation of lactic acid with other monomers, producing low molecular weight copolymers ($M_w < 10$ kDa). However, these low molecular weight pre-polymers have been further polymerization to produce high molecular weight. Advantage of condensation copolymerization can control over polymer end groups. Lactic acid has been condensation copolymerized with diols and diacids that the resulting copolymer has either hydroxyl or acid end groups and a particular molecular weight.

- Ring opening copolymerization (ROC)

ROC of L-lactide is a common approach for synthesizing PLA copolymerization, initiated with hydroxyl groups such as, alcohol or polyol. The ring opening copolymerization gives precise chemistry control and resulting favorable copolymer properties. The transition metal compounds of tin, aluminum, lead, zinc, bismuth, iron and yttrium have been reported to catalyze the ROC of lactide monomers.

2.2.3.3 Blending

Blending is the most extensively used methodology to improve PLA mechanical properties. PLA has been blended with other polymers (biodegradable and non- biodegradable) to achieve better mechanical properties which is suitable for several applications.

Blending of PLA and other polymers need to concern compatibility between them which can improve by adding compatibilizer into polymer blend. It can improve PLA mechanical properties such as, increasing elongation at break, elastic modulus and tensile strength.

2.2.4 Literature review regarding of poly(lactic acid)

Bhatia *et al.* (2007) studied the compatibility and mechanical properties of biodegradable poly(lactic acid) (PLA) and poly(butylene succinate) (PBS). The extruder was set at 180 °C of temperature profile and 60 rpm of screw speed for compounding all of the blends. The DSC showed two melting peak of the PLA/PBS blend with 80/20 composition indicating incompatibility between the two polymers. However, compositions 90/10 and 80/20 (PLA/PBS) were compatible. Tensile strength, Young's modulus and percentage (%) of elongation at break of the blends decreased with increasing PBS content.

Park *et al.* (2003) studied the miscibility and morphology of poly(L-lactic acid) and poly(vinyl acetate-co- vinyl alcohol) which were prepared by acidic hydrolysis of poly(vinyl acetate). Thermal characteristic values of PLA/PVAc blends are shown in Table 2.1.

Table 2.1 Thermal characteristics of PLA/PVAc blends (Park *et al.*, 2003)

Mixing ratios of PLA/PVAc	T_g (°C)	T_m (°C)	ΔH_f (J/g)
100/0	62.8	176.1	27.1
90/10	58.1	171.0	26.3
80/20	49.4	168.0	19.0
70/30	46.5	166.7	14.3
60/40	44.9	166.4	9.0
50/50	42.9	166.6	4.8
30/70	38.9	166.0	-
0/100	35.3	-	-

The DSC thermograms of PLA/P(VAc-co-VA) are presented in Figure 2.4.

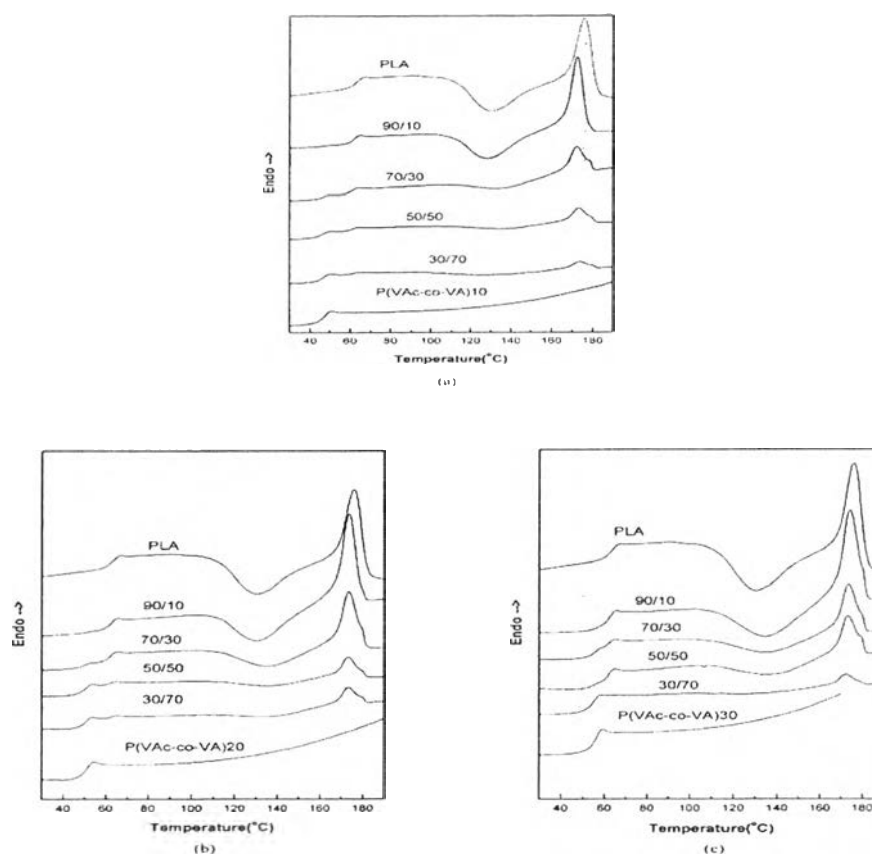


Figure 2.4 DSC thermograms of (a) PLA/P(VAc-co-VA)10 blend, (b) PLA/P(VAc-co-VA)20 blend and (c) PLA/P(VAc-co-VA)30 blends (Park *et al.*, 2003).

In the case of the PLA/P(VAc-co-VA)10 blend (Figure. 2.4(a)), a single glass transition was observed at 90/10 composition, suggesting that PLA and P(VAc-co-VA)10 were miscible at these compositions. But when increased P(VAc-co-VA) content more than 10%, double T_g were clearly observed, suggesting that PLA and P(VAc-co-VA)10 were immiscible at these compositions. In conclusion, the introduction of vinyl alcohol groups into PVAc led to immiscible blends with PLA.

Kim *et al* (2004) studied compatibilization of poly(l-lactic acid) (PLA) and polyethylene (LDPE) blends with and without reactive compatibilizer (acrylic acid (EAA), ethylene-glycidyl methacrylate copolymer (PE-GMA8 and PE-GMA25)). The SEM micrograph showing PLA/EAA blend was immiscible, indicating that AA units in EAA did not affect the compatibility with PLA. On the other hand, PE-GMA acted as a reactive compatibilizer for miscible PLA/LDPE blends but the higher GMA content in PE-GMA was not always desirable for compatibilizing PLA/LDPE blends.

The tensile properties of PLA/LDPE/PE-GMA blends are summarized in Table 2.2.

Table 2.2 Tensile properties of PLA/LDPE blends compatibilized with PE-GMA (Kim *et al*, 2004)

Blends	Stress at maximum (kgf/mm ²)	Strain at break (%)
PLA/LDPE/PE-GMA8		
80/20/0	0.80	6.6
80/20/5	0.94	77.9
20/80/0	0.72	16.4
20/80/5	1.17	50.5
PLA/LDPE/PE-GMA25		
80/20/5	3.26	4.0
20/80/5	0.76	29.5

The addition of PE-GMA was effective in enhancing the tensile properties of PLA/LDPE blends. The 80/20 PLA fracture /LDPE blend without PE-GMA8 showed typical brittle fracture behavior, while the behavior changes from brittle to ductile fracture when PE-GMA8 was added.

Oyama *et al.* (2008) studied the improvement in the mechanical properties of PLA by blending with poly(ethylene-glycidyl methacrylate). Two kinds of PLA were used in the study, PLA-L was lower molecular weight, whereas PLA-H was higher molecular weight. L80-200 (PLA-L80%/EGMA20% prepared with screw rotation speed of 200) showed a good distribution of the EGMA, so modulus of L80-200 turned lower than that of L80-30 (PLA-L80%/EGMA20% prepared with screw rotation speed of 30). Although most of the mechanical properties were similar in both L80-200 and H80-200 blends, the elongation at break was higher for L80-200 than that for H80-200. The mechanical properties of PLA blends with EGMA are shown in Table 2.3.

Table 2.3 Mechanical properties of neat PLAs and PLA/EGMA blends (Oyama *et al.*, 2008)

	Sample	Tensile tests			Flexural modulus (MPa)	HDT (°C)
		Tensile modulus (MPa)	Yield strength (MPa)	Elongation at break (%)		
As-prepared	PLA-L	1860	64.3	5	2800	55.3
	PLA-H	1890	65.9	11	2750	55.8
	L95-30	-	-	-	-	-
	L80-30	1570	38.1	26	2360	-
	L80-200	1350	40.0	>200	1170	54.2
	H80-200	1310	41.5	89	1190	54.7
	Annealed	PLA-L	2560	50.4	3	3950
PLA-H		2450	68.8	5	3710	62.7
L80-200		1600	42.8	12	1920	61.0
H80-200		1760	44.5	35	1500	60.9

Lee *et al.* (2005) studied poly(L-lactic acid) (PLLA) blended with poly(ethylene-co-vinyl alcohol) (EVOH) by esterification catalyst. Tensile properties of the graft copolymer (EVOH-g-PLLA) are shown in Table 2.4. The resulting EVOH-g-PLLA retained good tensile properties up to a content of PLLA as high as 60 wt %, thereafter, %elongation at break of the EVOH-g-PLLA decreased sharply.

Elongation at break of EVOH-g-PLLA containing 40 wt % of PLLA (EVOH-g-PLLA 40) was higher than that of the EVOH/PLLA 60/40 simple blend.

Table 2.4 Tensile Properties of PLLA/EVOH Blends (Lee *et al.*, 2005)

Blend composition	Elastic modulus (MPa)	Maximum stress (MPa)	Elongation at break (%)
PLLA	-	-	-
EVOH-g-PLLA 80	1303 ± 493.3	0.55 ± 0.35	1.77 ± 0.55
EVOH-g-PLLA 60	1711 ± 385.0	1.78 ± 0.58	9.34 ± 18.9
EVOH-g-PLLA 50	1661 ± 412.9	1.59 ± 0.72	12.2 ± 8.12
EVOH-g-PLLA 40	1198 ± 392.3	1.16 ± 0.15	21.6 ± 5.51
EVOH-g-PLLA 20	1447 ± 355.9	1.43 ± 0.65	9.44 ± 2.97
EVOH	1067 ± 453.2	1.98 ± 0.62	16.5 ± 4.62
EVOH/PLLA 60/40	860 ± 643.1	1.73 ± 0.77	2.70 ± 1.28

Figure 2.5. showed the second scan DSC thermogram of PLLA, EVOH, EVOH-g -PLLA, and EVOH/PLLA 60/40 blend. The EVOH/PLLA 60/40 blend showed two separated melting peaks, indicating that the two polymers were phase separated. Thermal properties measured by DSC of the polymers are collected in Table 5.

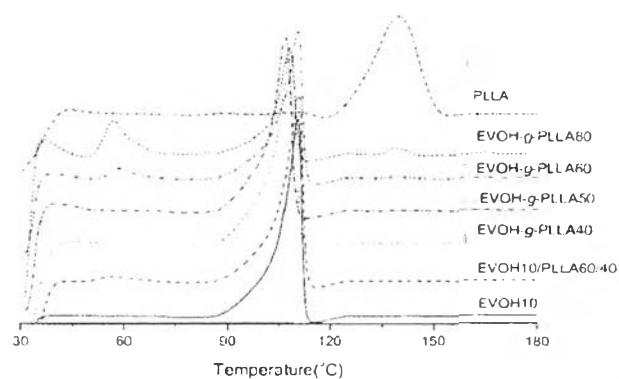


Figure 2.5 The second scan DSC thermograms of EVOH-g-PLLA and EVOH/PLLA blend (Lee *et al.*, 2005).

Table 2.5 Thermal Properties of PLLA/EVOH10 Blends (Lee *et al.*, 2005)

Sample code	T_m (°C)		T_c (°C)	ΔH_f (J/g)
PLLA	-	142	55	-
EVOH-g-PLLA 80	108	140	91	7.4
EVOH-g-PLLA 60	111	142	94	31.1
EVOH-g-PLLA 50	106	-	88	40.2
EVOH-g-PLLA 40	107	-	88	52.3
EVOH-g-PLLA 20	110	-	94	50.7
EVOH	111	-	93	80.6
EVOH/PLLA 60/40	111	142	94	52.9

2.2.5 Application of poly(lactic acid)

PLA products are used in biomedical applications, including sutures, stents, dialysis media, and drug delivery devices. Because it is biodegradable polymer, it can also be employed in the preparation of bioplastic, compost bags, food packaging and disposable tableware. In the form of fibers and non-woven textiles, PLA also has many potential uses, such as upholstery, disposable garments, awnings, feminine hygiene products and diapers. The use of PLA as a cost-effective alternative to commodity petrochemical-based plastics will increase demand for agricultural products such as corn and sugar beets, and will lessen the dependence of plastics on oil.

2.3 Ethylene (Vinyl Acetate) (EVA)

EVA is the copolymer of ethylene and vinyl acetate. The weight percentage vinyl acetate usually varies from 10 to 40, with the remainder being ethylene. It is soft and flexible like elastomeric materials, yet can be processed like other thermoplastics. With increasing vinyl acetate (VA) content, EVA copolymers change from a semi-crystalline thermoplastic material into a rubber and again into an amorphous thermoplastic material.

The chemical structure of EVA is shown in Figure 2.6.

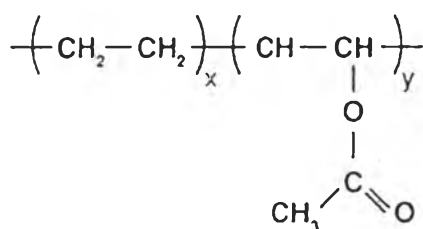


Figure 2.6 The chemical structure of EVA.

2.3.1 Ethylene (Vinyl Acetate) Properties

EVA is an extremely elastic material that can be sintered to form a porous material similar to rubber, yet with excellent toughness. It is three times as flexible as low-density polyethylene (LDPE), showing tensile elongation of 750% with a peak melting temperature of 250°F (96°C). It has good barrier properties, low-temperature toughness, stress-crack resistance, hot-melt adhesive waterproof properties, and resistance to ultraviolet radiation.

2.3.2 Literature review regarding of Ethylene (Vinyl Acetate)

Burt *et al.* (1995) studied, controlled delivery of taxol from microspheres composed of a blend of ethylene-vinyl acetate copolymer (EVA) and poly(d,l-lactic acid) (PLA). PLA/EVA blends were prepared using the solvent evaporation method. Encapsulation efficiencies were between 95-100% for taxol in 50:50 EVA:PLA blend microspheres. When PLA having 50% or more than in the EVA:PLA blend decreased the extent of coalescence of the microspheres. Different size ranges of microspheres depend on the concentration of the emulsifier. The small microspheres were produced at higher PLA concentration, whereas large microspheres were produced at lower PLA concentration. Blends of EVA and PLA have been shown to be immiscible over a range of 30-70% EVA in PLA. PLA hydrolyzed and eroded from the EVA: PLA polymer blend matrix in phosphate-buffered saline (PBS) buffer at 37°C, leading to an inactive sponge-like structure. Although the induction period and rate of PLA degradation depended on the proportion of PLA in the matrix and on process history, there was consistently little or no loss of PLA until after 40-50 days.

Ma *et al.* (2011) studied, the effect of vinyl acetate contents in ethylene-co-vinyl acetate copolymer to compatibility of the PLA/EVA blends. The compatibility between PLA and EVA was improved with increasing the vinyl acetate (VA) content, since PLA was miscible with PVAc (no phase separate) but not miscible with PE. For low VA contents, EVA has a poor compatibility with PLA, resulting in a weak interface adhesion and large particle sizes, As a consequence, the

PLA/EVA (80/20) blends with a low VA content have a brittle behavior. As a result, the optimum toughening effect of EVA on the PLA was obtained at a VA content of 50-60%.

Yoon *et al.* (1999) investigated, miscibility, and mechanical properties of poly(L-lactic acid) with poly(ethylene-co-vinyl acetate) containing 70 and 85wt% of vinyl acetate. The blend of PLLA with EVA70, that contained 70 wt% of vinyl acetate, was immiscible. On the other hand, the PLLA with EVA85 blend was miscible. The results were determined by Rheovibron that PLLA-EVA70 blend showed two single glass transition peaks. On the contrary, PLLA-EVA85 blend showed one single glass transition peak. When the EVA85 content was increased, the breaking strength and modulus decreased rapidly. Whereas the strain at break was gradually increased up to 70 wt% of EVA85 and then suddenly increased at 90 wt% of EVA85.

2.3.3 Application of Ethylene (Vinyl Acetate)

EVA is widely used for many purposes such as, sports equipment (e.g., ski boot, boxing, hockey and mixed martial arts), drug delivery device, flexible packaging, footwear, hot melt adhesives and electrical cable sheathing industry.

2.4 Ethylene-glycidyl methacrylate copolymer (E-GMA)

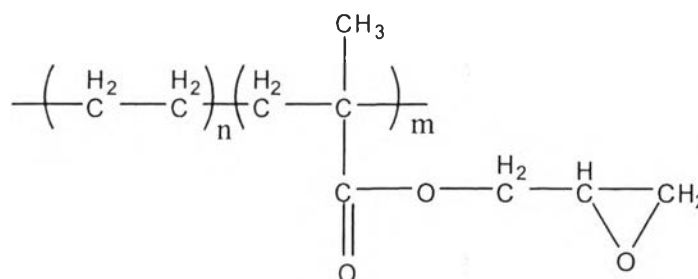


Figure 2.7 The chemical structure of E-GMA.

2.4.1 Mechanism between PLA/modified EVA and E-GMA

PLA used in this study having the $-OH$ and $-COOH$ groups at the chain ends can form interchain linkages with the GMA units in E-GMA by the following reactions:

- GMA react with $-OH$ groups of PLA

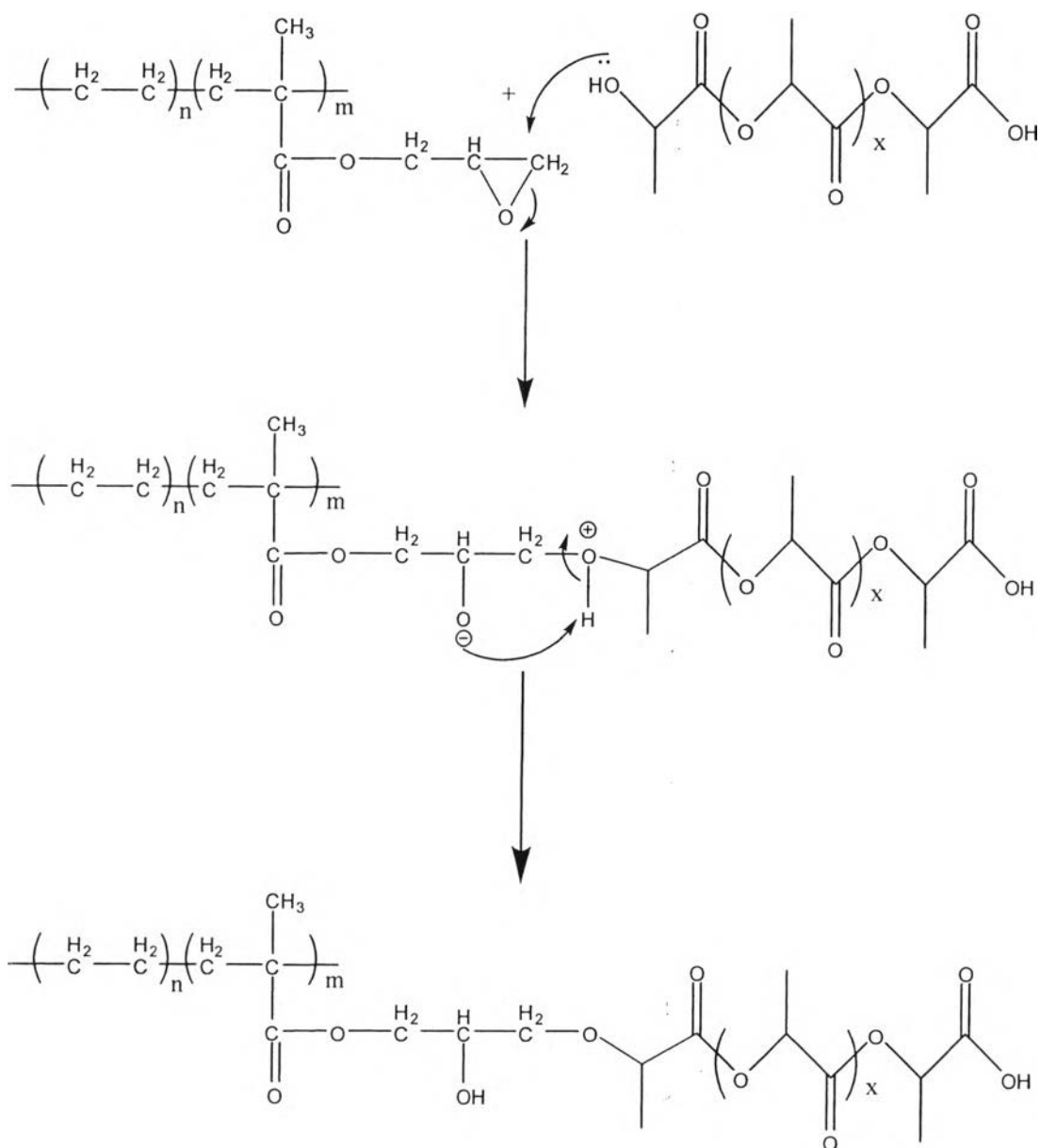


Figure 2.8 Reaction of -OH groups of PLA with GMA unit.

- GMA react with -COOH groups of PLA

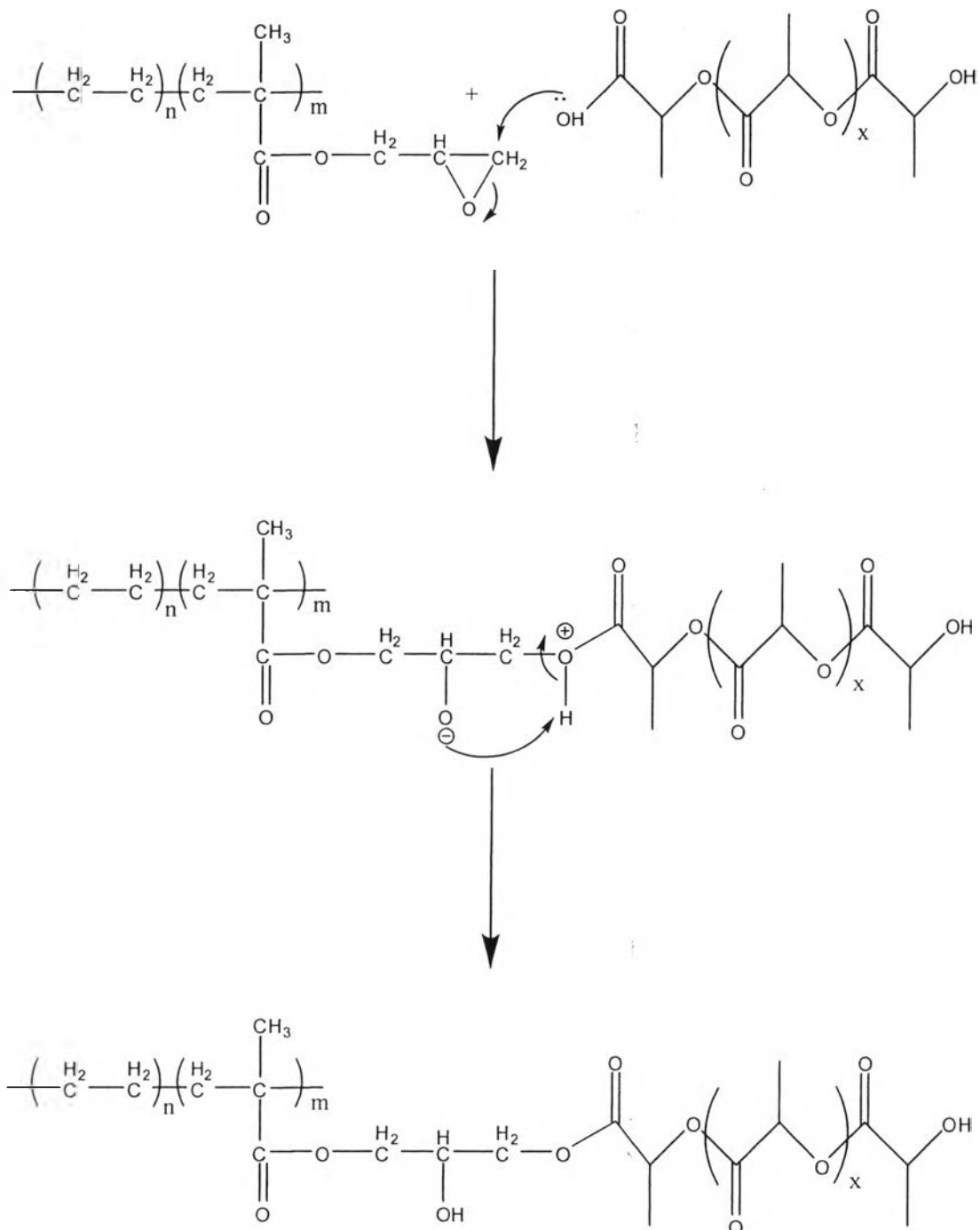


Figure 2.9 Reaction of –COOH groups of PLA with GMA unit.

And the ethylene units in EVA can complete with the ethylene units in E-GMA because they have same structure.

2.4.2 Literature review regarding of Ethylene-glycidyl methacrylate copolymer

Kumar *et al.* (2010) studied, effect of glycidyl methacrylate (GMA) on the thermal, mechanical and morphological property of PLA/PBAT. The tensile and impact properties of virgin PLA and PLA/PBAT blends at variable ratios were represented in Table 2.6.

Table 2.6 Tensile and impact properties of virgin PLA, PBAT, PLA/PBAT blend with GMA and blend nanocomposites (Kumar *et al.*, 2010)

Compositions	Tensile strength (MPa)	Tensile modulus (MPa)	Impact strength (J/m)	Elongation at break (%)
PLA virgin	48.71	1254	21.09	4.5
PBAT virgin	11.03	39.06	54.28	521.6
PLA/PBAT (85/15)	31.26	900.2	25.72	5.1
PLA/PBAT (80/20)	32.02	903.5	43.35	5.7
PLA/PBAT (75/25)	29.47	808.15	50.44	6.75
PLA/PBAT/GMA (72/25/3)	22.75	1314.23	63.85	6.6
PLA/PBAT/GMA (70/25/5)	30.52	1746.4	76.56	6.5
PLA/PBAT/C20A/GMA	19.36	1841.40	41.58	2.8

(67/25/5/3)				
PLA/PBAT/C20A/GMA (65/25/5/5)	26.55	2106.66	46.90	2.4

PLA/PBAT blend prepared at a ratio of 75:25 exhibits a decrease in tensile strength of 62.8% and tensile modulus of 55.1% as compared with the virgin PLA matrix but increase of impact strength value from 21.09 J/m in virgin PLA to 50.00 J/m. In case of PLA/PBAT blend prepared using 5 wt.% GMA, the tensile modulus increased from 1254 MPa (PLA matrix) to 1746 MPa.

From SEM micrographs of the impact fractured surface of the blend matrix with and without GMA and blend nanocomposite, the blends of PLA and PBAT have better miscibility with the addition of GMA into the blends.

The melting and crystallization behaviour of virgin PLA, PBAT, PLA/PBAT blend and PLA/PBAT blend nanocomposites shown in Table 2.7.

Table 2.7 Melting and crystallization behaviour of virgin PLA, PBAT, PLA/PBAT blend and PLA/PBAT blend nanocomposites (Kumar *et al.*, 2010)

Compositions	T _g (°C)	T _m (°C)		T _c (°C)	ΔH _c (J/g)	ΔH _m (J/g)
		PBAT	PLA			
PLA virgin	66.0	-	151.0	128	9.12	0.7193
PBAT virgin	-39.69	119.0	-	66.1	-3.90	12.47
PLA/PBAT (75/25)	61.0	117.9	155.3	136.0	-4.01	1.08
PLA/PBAT/GMA (70/25/5)	56.0	117.3	150.3	134.5	-3.43	2.27

PLA/PBAT/C20A/GMA (65/25/5/5)	55.9	119.3	150.0	122.7	-5.21	12.39
----------------------------------	------	-------	-------	-------	-------	-------

2.5 Ethylene-methyl acrylate-glycidyl methacrylate terpolymer (T-GMA)

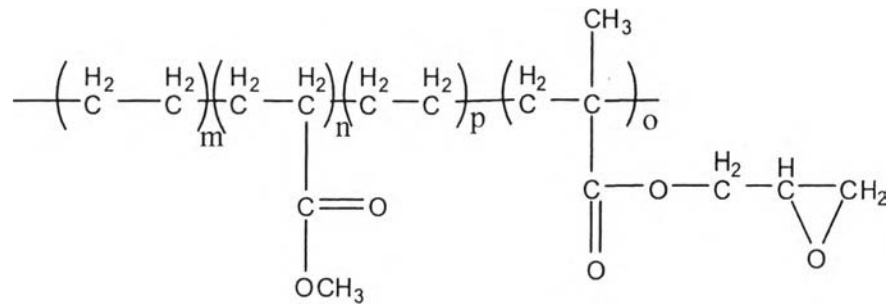


Figure 2.10 The chemical structure of T-GMA.

2.5.1 Mechanism between PLA/modified EVA and T-GMA

PLA used in this study having the $-\text{OH}$ and $-\text{COOH}$ groups at the chain ends can form interchain linkages with the GMA units in T-GMA by the following reactions:

- GMA react with $-\text{OH}$ groups of PLA

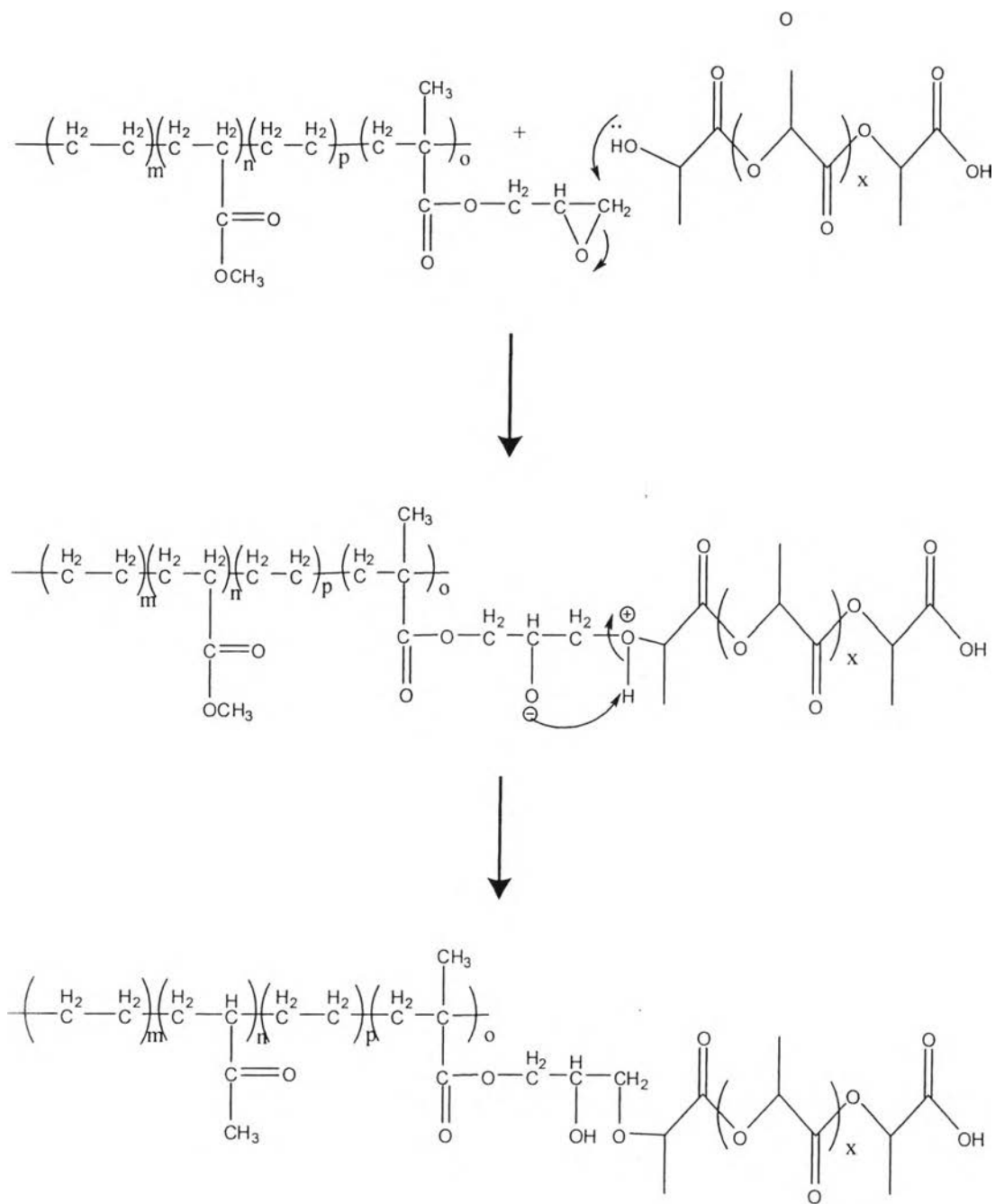


Figure 2.11 Reaction of $-OH$ groups of PLA with GMA unit.

- GMA react with $-COOH$ groups of PLA

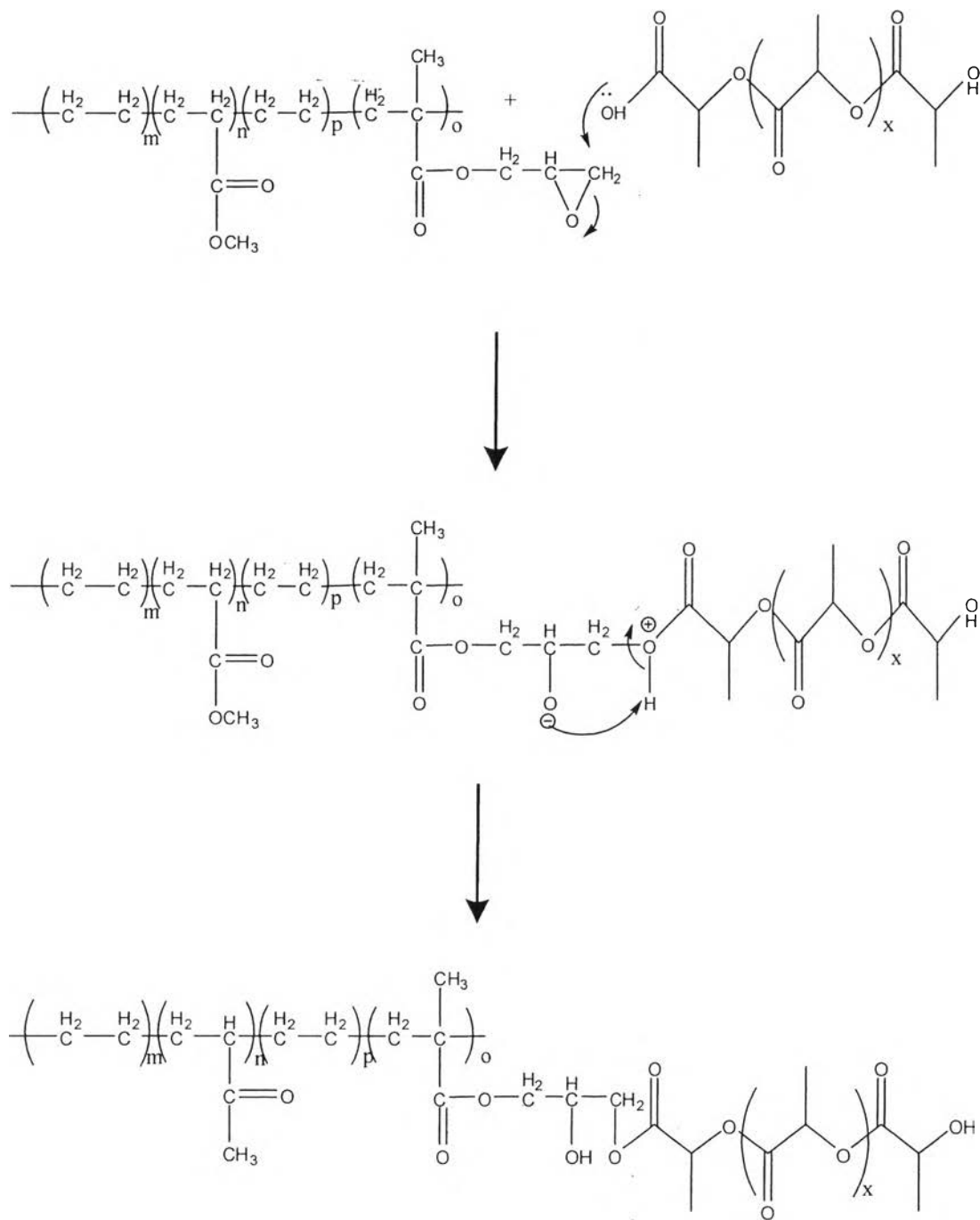


Figure 2.12 Reaction of $-\text{COOH}$ groups of PLA with GMA unit.

Also, the ethylene vinyl acetate units in EVA can complete with the acrylate ester units in T-GMA because they have same structure.

2.5.2 Literature review regarding of Ethylene-acrylate ester-glycidyl methacrylate terpolymer

To improve the compatibility between PBAT and PLA, Zhang *et al.* (2009) used a random terpolymer of ethylene, acrylate ester and glycidyl methacrylate (referred as “T-GMA”) as a reactive compatibilizer in poly(lactic acid)/poly(butylene adipate-co-terephthalate) blend. Blends of PLA with 10, 20, 30, and 40 wt% of PBAT and T-GMA were added at 1.0–10.0 wt% to the PLA/PBAT blends. The ultimate strain of PLA/PBAT (90/10 wt%) blend was higher in the presence of T-GMA than in its absence. However, addition of T-GMA beyond the optimum amount had opposite effect on tensile ultimate strain as embrittlement. The impact strength at PBAT 10, 20, and 30 wt% in PLA which added T-GMA showed in Figure 2.13.

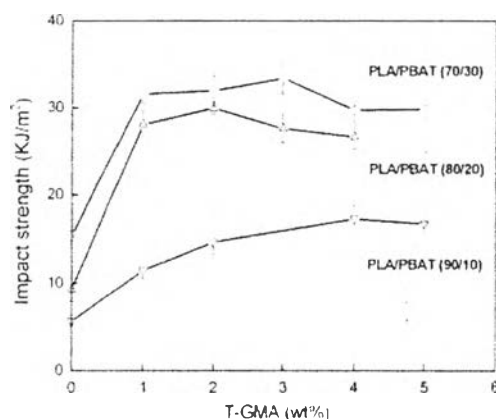


Figure 2.13 Effect of T-GMA concentration in the PLA/PBAT blends (PLA/PBAT = 90/10, 80/20, 70/30 wt%) on impact strength (Zhang *et al.*, 2009).

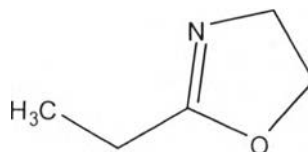
SEM images shows PLA/PBAT (70/30 wt%) blend with 0 and 5 wt% T-GMA. The blend without T-GMA showed a kind of immiscible, namely, two-phase structure with PBAT dispersing in PLA matrix. As a comparison with the

presence of T-GMA (5 wt%), the blend of PLA and PBAT showed better miscibility. The thermal properties of PLA/PBAT blending are shown in Table 2.8.

Table 2.8 Thermal properties of PLA in blends at different T-GMA contents(Zhang *et al.*, 2009)

T-GMA content (%)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
0	106.5	8.021	148.2	12.06
2	108.5	6.688	146.9	11.93
5	109.2	7.512	147.6	10.67
10	110.6	6.374	148.2	11.49

2.6 POLY(2-ETHYL-2-OXAZOLINE)

**Figure 2.14** The chemical structure of Poly(2-ethyl-2-oxazoline).

2.6.1 Mechanism between PLA/modified EVA and Poly(2-ethyl-2-oxazoline)

PLA used in this study having the –OH and –COOH group at the chain ends can form interchain linkages with the oxazoline group of Poly(2-ethyl-2-oxazoline) by the following reaction:

- oxazoline group of Poly(2-ethyl-2-oxazoline) react with –OH groups of PLA

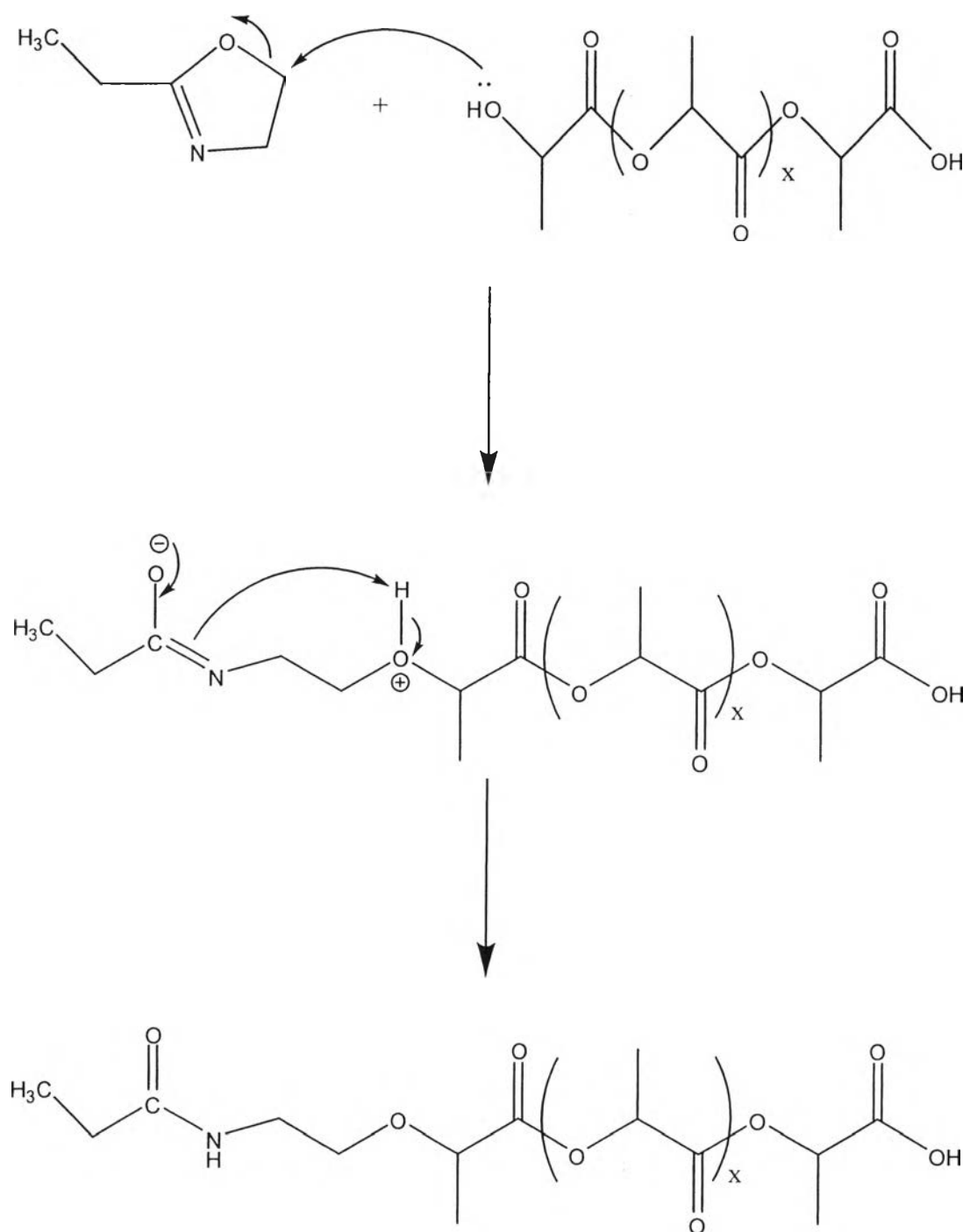
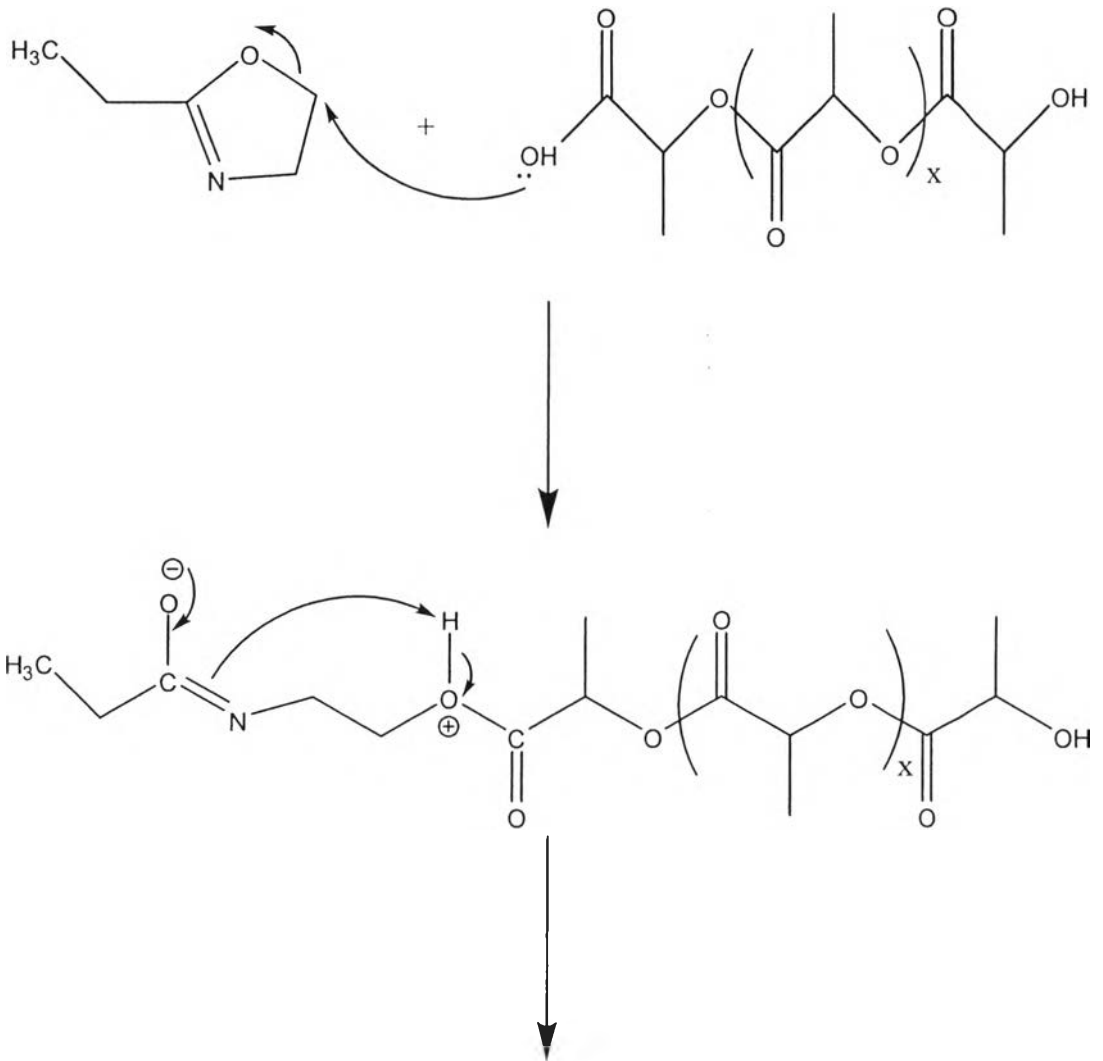


Figure 2.15 Reaction of $-\text{OH}$ groups of PLA with oxazoline group.

- oxazoline group of Poly(2-ethyl-2-oxazoline) reacts with –COOH group of PLA



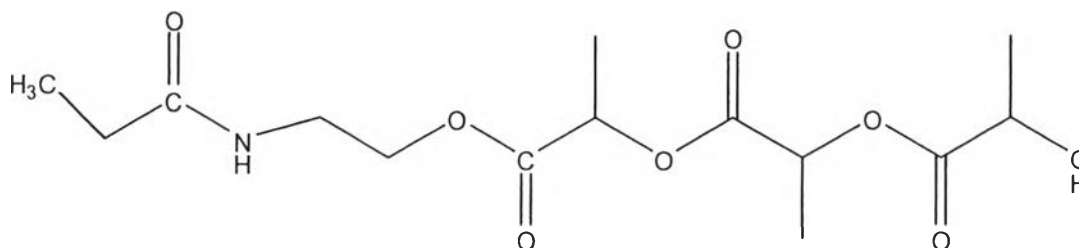


Figure 2.16 Reaction of $-\text{COOH}$ groups of PLA with oxazoline group.

And the ethylene units in EVA can complete with the ethylene units in Poly(2-ethyl-2-oxazoline) because they have same structure.

2.7 Ethylene-acrylic acid copolymer (PE-AA)

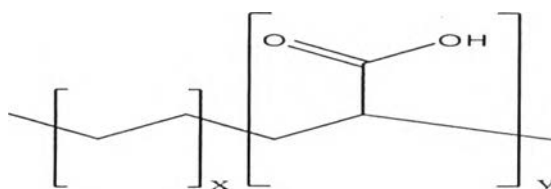


Figure 2.17 The chemical structure of PE-AA.

2.7.1 Mechanism between PLA/modified EVA and PE-AA

PLA used in this study having the $-\text{OH}$ group at the chain ends can form ester linkage with the carboxylic group of PE-AA by the following reactions:

- Carboxylic group of PE-AA react with $-\text{OH}$ group of PLA

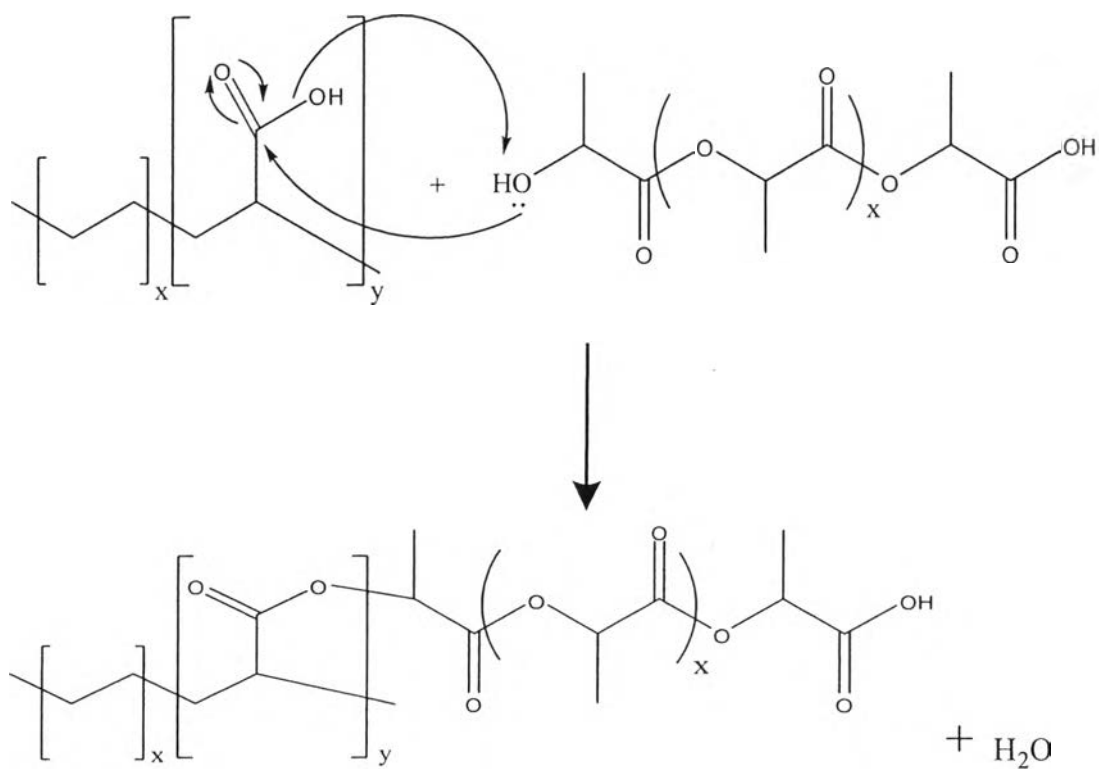


Figure 2.18 Reaction of $-\text{OH}$ group of PLA with carboxylic group.

And the ethylene units in EVA can complete with the ethylene units in PE-AA because they have same structure.