

CHAPTER II

LITERATURE REVIEW

2.1 Polylactide (PLA)

Polylactide or polylactic acid (PLA) is a versatile, biodegradable, hydrophobic aliphatic polyester. PLA is produced from a renewable resource such as sugarcane, corn, sugar beets and tapioca products. PLA has good mechanical and thermal properties that can be comparable with the commodity plastics (e.g. PET and PS). Moreover, PLA requires low energy to produce and save the environmental process. The synthesis methods of PLA are shown in Figure 2.1 (Avérous, 2008).

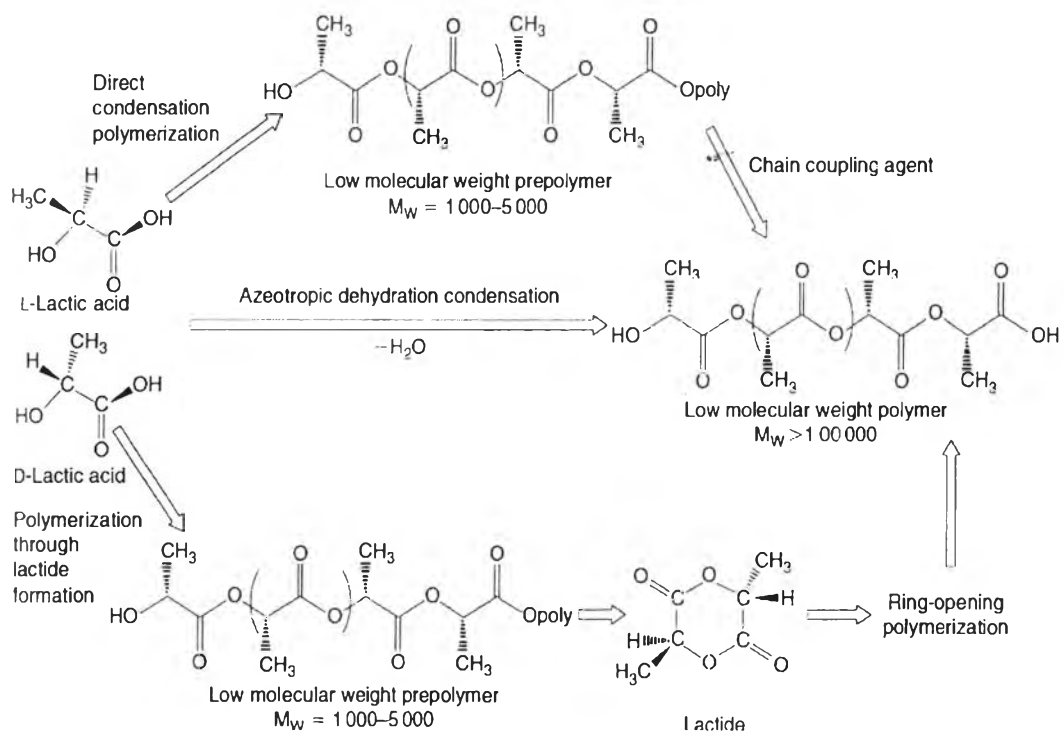


Figure 2.1. Synthesis methods of PLA (Avérous, 2008).

2.1.1 Ring-opening polymerization of PLA via catalyst initiation.

The Ring-opening polymerization of PLA is the way to get high molecular weight of PLA. There are many catalysts that used for ring-opening polymerization but among them stannous (II) octoate ($\text{Sn}(\text{Oct})_2$) is usually preferred because it provides high molecular weight, high conversion rate and high reaction rate more than another catalyst (Schwach *et al.*, 1997). The structure of stannous (II) octoate is shown in Figure 2.2. (Storey *et al.*, 2002) and the mechanism of ring-opening polymerization of PLA via stannous (II) octoate is shown in Figure 2.3 (Singh, 2008).

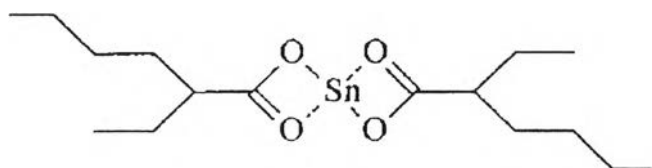


Figure 2.2. Chemical structure of stannous (II) octoate (Storey *et al.*, 2002).

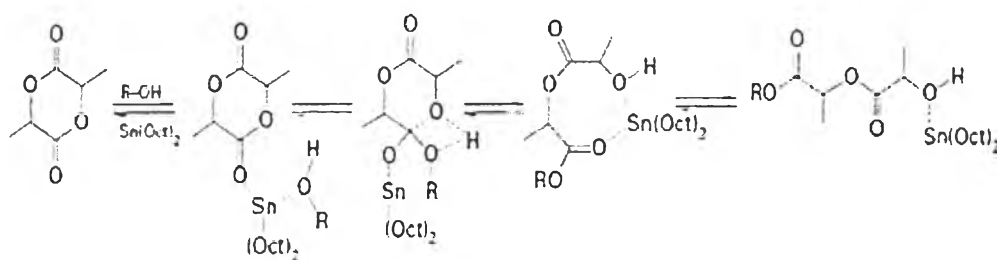


Figure 2.3. Generalized mechanism of lactide to PLA (Singh, 2008).

In 1997, Scwach *et al.* polymerize of lactides monomer to PLA in the presence of stannous (II) octoate ($\text{Sn}(\text{Oct})_2$) and hydroxytin(II) lactate (HTL) initiation. They have been studying about catalyst that polymerized high molecular weight of PLA. Moreover, they studied the effect of time to polymerize PLA. The mechanism of polymerization of PLA by using stannous (II) octoate and HTL as catalyst is shown in Figure 2.4 and Figure 2.5, respectively. The concluding of study, PLA was synthesized by ring-opening polymerization via stannous (II) octoate gave higher conversional rate and molecular weight than ring-opening polymerization via HTL. Furthermore, the increasing of reaction time was resulting in the increasing of molecular weight and %conversion of PLA. The result of this study is shown in the Table 2.1 (Scwach *et al.*, 1997).

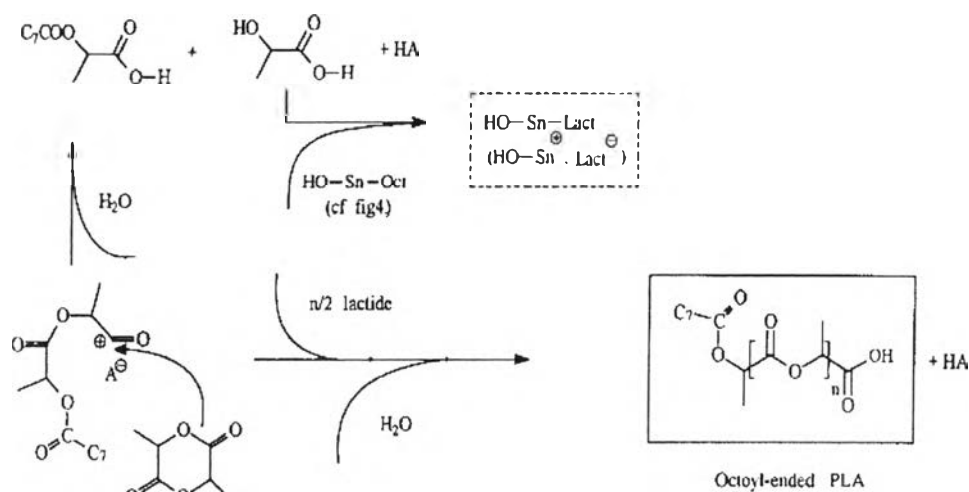


Figure 2.4 $\text{Sn}(\text{Oct})_2$ route polymerization (Scwach *et al.*, 1997).

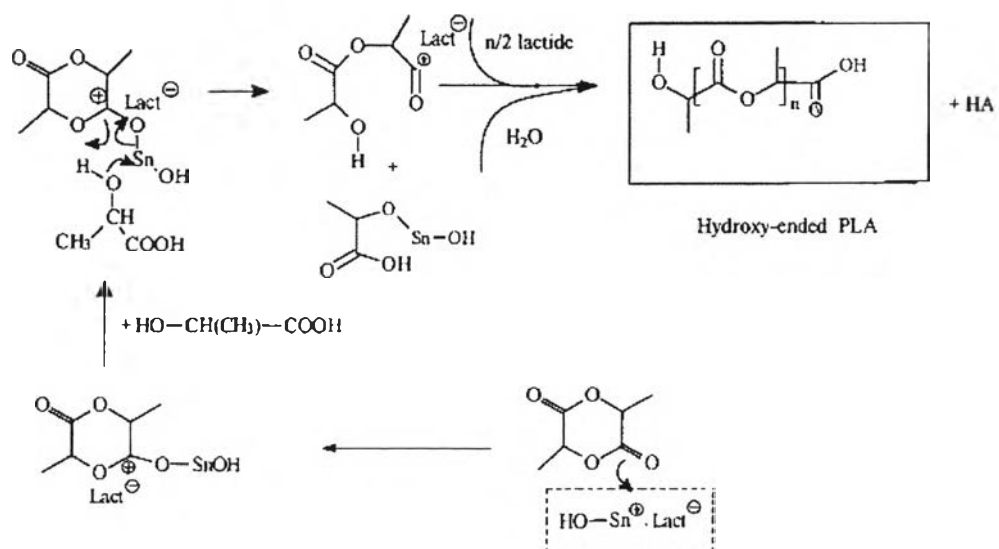


Figure 2.5 HTL route polymerization (Scwach *et al.*, 1997).

Table 2.1 Effects of time on the polymerizations resulting from Sn(Oct)₂ and HTL initiations (M/I=5000, 140 °C) (Scwach *et al.*, 1997).

Initiator	Time(h)	Conversion Rate ^a (%)	M _n ^b	I ^b
Sn(Oct) ₂	0.42	31.1	336,000	1.8
	1.08	33.6	273,000	2.3
	3.00	72.9	490,000	1.6
	5.00	83.9	415,000	2
HTL	2.25	3.3		
	4.33	13.6	3,600	1.8
	9.70	28.2	141,000	1.6
	12.92	40.0	196,000	2.2

^a As determined by H-NMR.

^b As determined by SEC.

In 1997, Hyon *et al.* synthesized PLA with different molecular weight by polycondensation and ring-opening polymerization. They focused on the effect of catalyst concentration, polymerization time and polymerization temperature on the molecular weight, polymer yield and optical rotation. They found that PLA synthesized by the conversional polycondensation gave the average molecular weight lower than 1.6×10^4 whereas, ring-opening polymerization of lactide produced polylactide with average molecular weight range from 2×10^4 to 6.8×10^4 . Moreover, the concentration of stannous (II) octoate was preferred for ring-opening polymerization of PLA is 0.05 wt%. The effect of catalyst concentration to molecular weight and conversional rate are shown in Figure 2.6 (Hyon *et al.*, 1997).

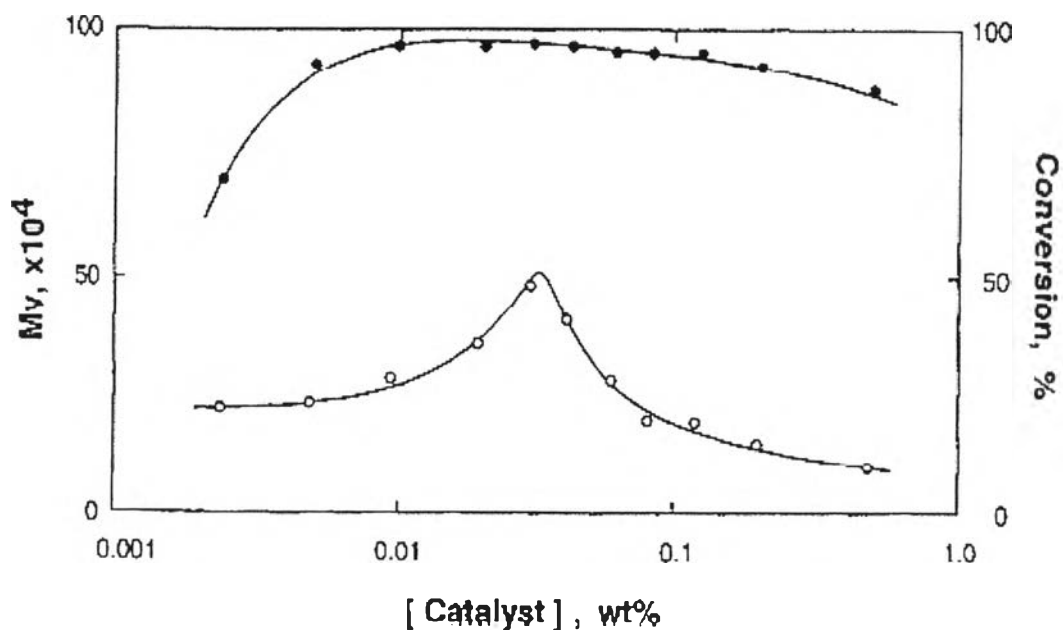


Figure 2.6 Effect of the stannous (II) octoate concentration on the viscosity average molecular weight of poly-L-lactide and the monomer conversion for bulk polymerization of L-lactide at 130°C for 72 h. ○:molecular weight, ●:conversion (Hyon *et al.*, 1997).

2.1.2 Modification of PLA

The major limitation of PLA is its poor ductility and slow degradation rate. There are several methods have been done to improve mechanical properties, degradation rate, and crystalline of PLA, for example, modified by processing, modified by plasticizer, modified by blending, and copolymerization.

2.1.2.1 Modified by processing

There are many different processes that applied to control the orientation of PLA. The parts of crystalline in PLA were oriented by drawing or stretching resulted in the increasing of strength.

In 2002, Grijpma *et al.* studied improvement of the mechanical properties of poly(D,L-lactide) by orientation. They synthesized PLA by ring opening polymerization via stannous (II) octoate. The molecules of PLA were oriented by drawing and scrim process to increase mechanical properties. After the process, tensile strength and impact strength of PLA were increasing. The results of this study are shown in Table 2.2 and Figure 2.7 (Grijpma *et al.*, 2002).

Table 2.2 Effect of drawing on the mechanical properties of PLA (Grijpma *et al.*, 2002)

	un-oriented	Oriented	
		$\lambda = 2.5$	$\lambda = 3.4$
Modulus (MPa)	3650	4490	3740
Tensile strength, σ (MPa)	47	73.3	66.3
Elongation at break, ε (%)	1.5	48.2	21.8
Charpy (kJ m ⁻²)	12.5	35.9	No break
Izod, 0.25 mm notch (kJ m ⁻²)	1.6	5.9	52

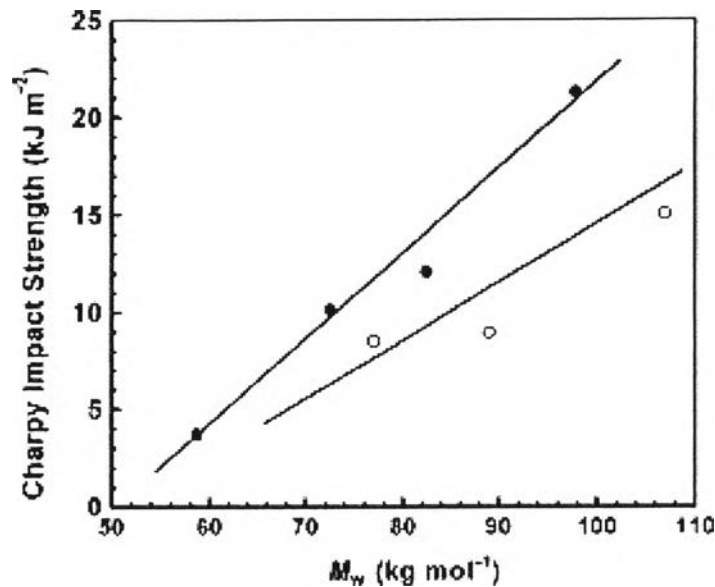


Figure 2.7. Charpy impact strength of PLA as a function of molecular weight for SCORIM processing(●) and conversional injection molding(o) (Grijpma *et al*, 2002).

2.1.2.2 Modified by plasticizer

In 1999, Jacobsen *et al.* studied the effect of different plasticizers on the mechanical properties of PLA. They studied three different type of plasticizer and compared the principal behavior of these plasticizers: poly(ethylene glycol 1500) (PEG 1500), glucosemonoesters (Dehydat) and partial fatty acid ester (Loxiol). The results of this study shown the elongation at break of PLA increased. They added 2.5 wt% of plasticizer to increase 14% of elongation at break. The best of all plasticizers from an elongation point is poly (ethylene glycol). The result of this study is shown in Figure 2.8. The impact resistance decreased when added plasticizer. But, when added more plasticizer, the impact resistance increased. The 10 wt% of PEG 1500 gave the highest impact resistance. The result of impact resistance is shown in Figure 2.9 (Jacobsen *et al.*, 1999)

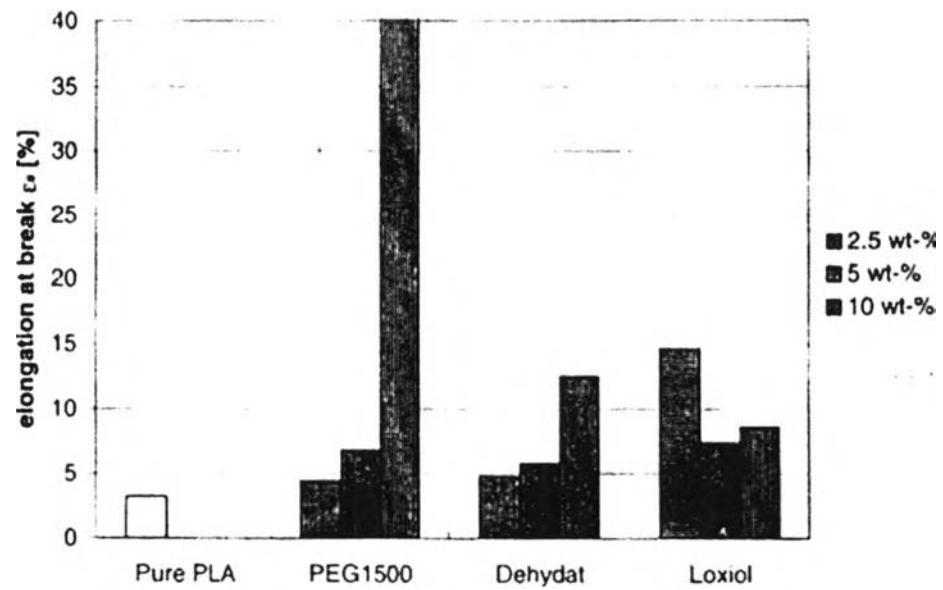


Figure 2.8. Elongation at break (%) as a function of plasticizer addition (Jacobsen *et al.*, 1999).

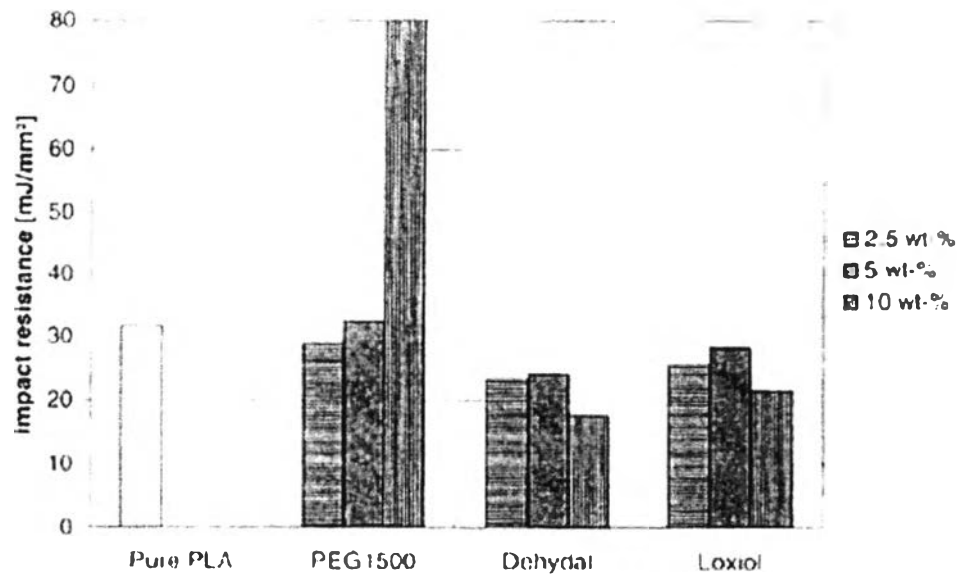


Figure 2.9. Impact resistance [mJ/mm²] as a function of plasticizer addition. (Jacobsen *et al.*, 1999).

In 2005, Ljungberg *et al.* studied PLA blended with plasticizer to enhance its flexibility and decrease problem of brittleness. They synthesized oligomeric plasticizer as called Diethyl Bishydroxymethyl Malonate Adipoyl Triethylene glycol diamine (DBMATA). After that, they blended PLA with 15% wt of plasticizer in twin screw extruder and characterized them. The results of the stress as the function of strain comparing both aged and unaged PLA film with both aged and unaged PLA/DBMATA film. They found that PLA/ DBMATA blend was very flexible with strain at break above 200% whereas the pure PLA showed strain at break only around 20%. The result of this study is shown in Figure 2.10 (Ljungberg *et al.*, 2005).

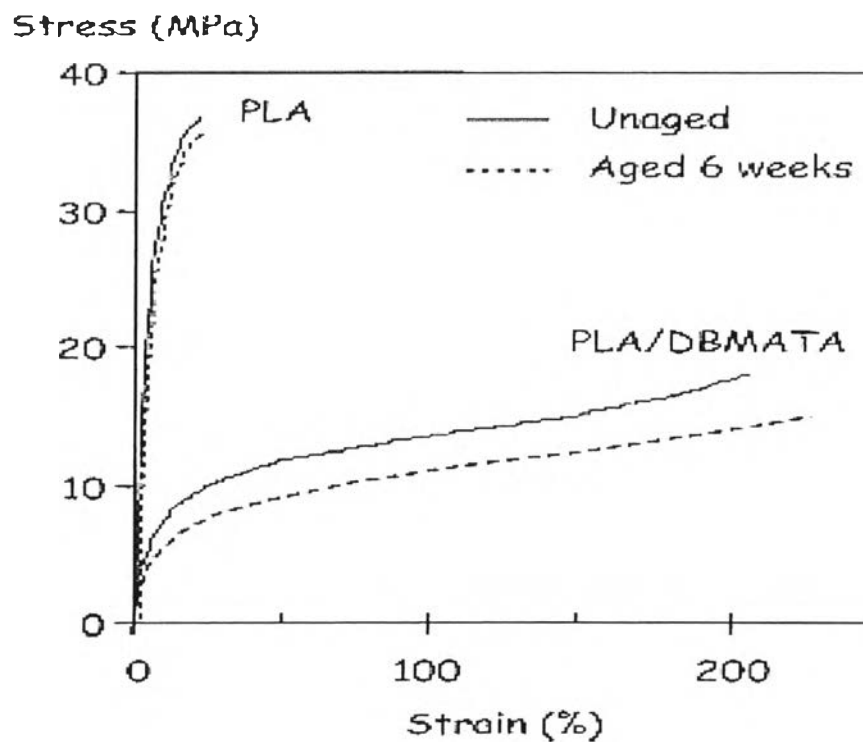


Figure 2.10. Stress/strain curves comparing aged and unaged films of PLA/DBMATA and pure PLA (Ljungberg *et al.*, 2005).

2.1.2.3 Modified by blending

Blending is the most popular methodology to improve the limitation properties of PLA. PLA has been blended with several polymers: biodegradable and non-biodegradable polymer to get preferred properties of PLA. Moreover, blend PLA with biodegradable polymer for increasing the degradation rate such as polyhydroxybutyrate (PHB), rubber etc. Non-biodegradable polymers that usually blend with PLA are low density polyethylene (LDPE), poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA) etc.

In 2009, Ishida *et al.* studied on melt-blending between PLA and four rubber components: ethylene-propylene copolymer (EPM), ethylene-acrylic rubber (AEM), acrylonitrile-butadiene rubber (NBR) and isoprene rubber (IR). They studied the effect of blending of various rubber components into PLA on the mechanical properties and morphologies. The content of rubbers was fixed at 10 and 20 wt%. The mechanical properties and morphologies of pure PLA and PLA/rubber blend were investigated. They found that PLA/NBR blend showed the highest impact strength. The result of this study is shown in Figure 2.11. Moreover, the tensile properties effected by type of rubber. The elongation decreased when blended with EPM and AEM. The blending between PLA and NBR, the elongation at break increased slightly. The highest elongation was around 2 times or more when blended with IR. The results of elongation value is shown in Figure 2.12 (Ishida *et al.*, 2009).

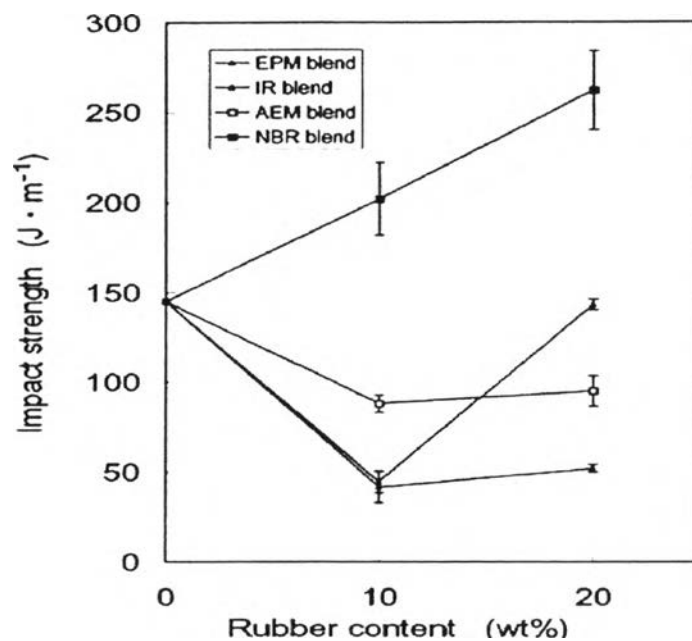


Figure 2.11. Impact strength of pure PLA and PLA/rubber blends. Error bars represent one standard deviation obtained from the testing of five specimens (Ishida *et al.*, 2009).

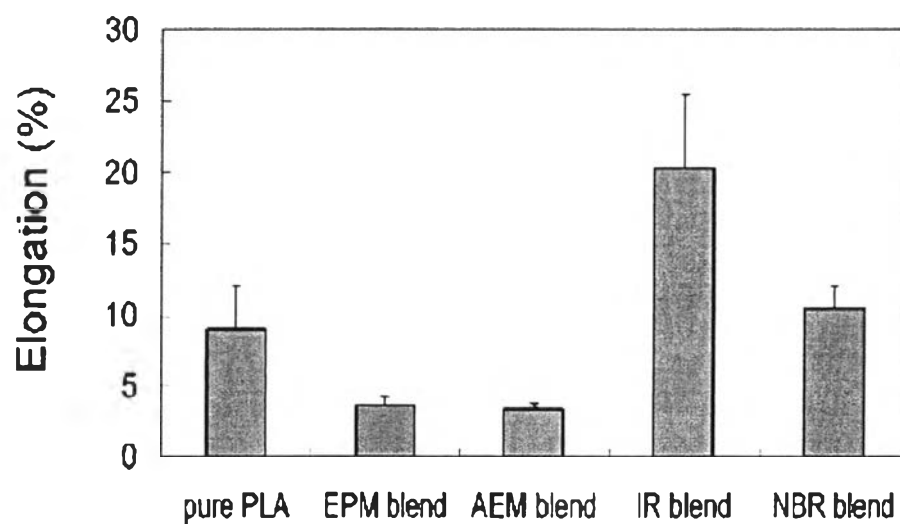


Figure 2.12. The elongation of pure PLA and PLA/rubber blends (Ishida *et al.*, 2009).

In 2009, Klinklai *et al.* studied on natural rubber/ polylactic acid/ epoxidized natural rubber (NR/PLA/ENR) blending. They were varying a composition of NR/PLA/ENR as 100/100/0, 100/90/10, 100/70/30, 100/50/50, 100/30/70, 100/10/90 and 100/0/100 wt%. The characteristic peak of NR was found at 1664 cm^{-1} attributed to $>\text{C}=\text{CH}$ -stretching and 836 cm^{-1} attributed to $=\text{CH}$ -bending. After modified NR to ENR, the new peak around 870 cm^{-1} and 1250 cm^{-1} were occurred which corresponding to epoxide group. The FT-IR spectrum is shown in Figure 2.13. The mechanical properties of polymer blends were determined by tensile and impact testing machine. Moreover, thermal properties were investigated by DSC and TGA. The result of this study was found that tensile strength of the NR/PLA was the highest increasing with adding ENR 30 wt%. In addition, the effect of ENR content on the mechanical properties was the best at 30 wt%. The result of this study is shown in Table 2.3 (Klinklai *et al.*, 2009).

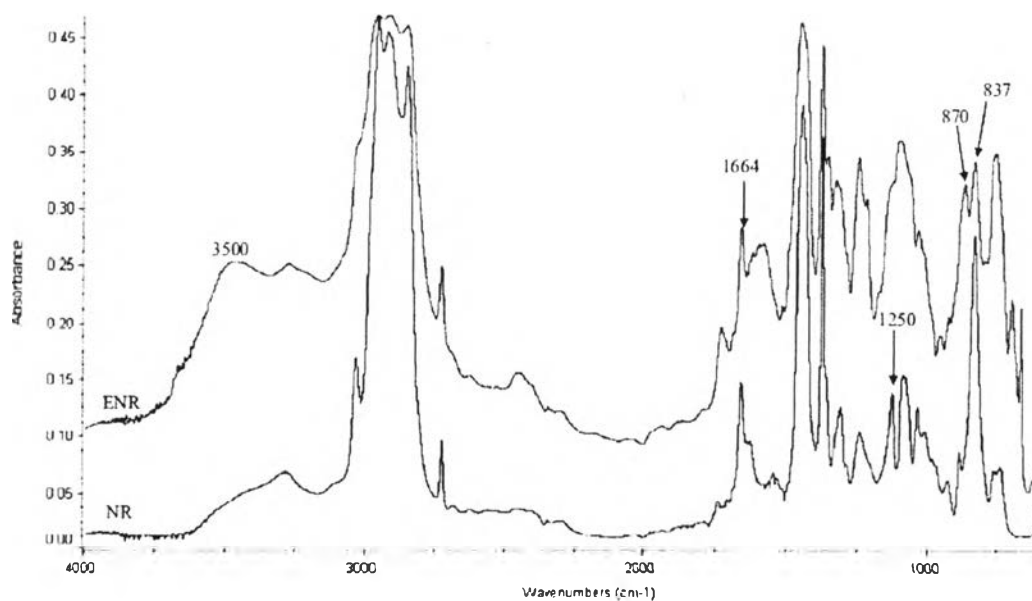


Figure 2.13. FTIR spectrum of natural rubber (NR) and epoxidized natural rubber (ENR) (Klinklai *et al.*, 2009).

Table 2.3 Mechanical properties of blending as a function of blending ratio of PLA/NR/ENR (Klinklai *et al.*, 2009)

sample	NR (wt%)	PLA (wt%)	ENR (wt%)	Tensile strength (MPa)	Impact strength (kJ/m ²)	Density (g/cm ³)
1	100	100	0	8.61	5.5	1.108
2	100	90	10	11.32	9.0	1.050
3	100	70	30	19.60	17.2	1.029
4	100	50	50	14.36	14.6	1.007
5	100	30	70	15.23	12.0	0.994
6	100	10	90	12.65	7.6	0.964
7	100	0	100	10.50	-	0.960

In 2012, Chunmei Zhang *et al.* studied on thermal, mechanical and rheological properties of polylactide toughened by epoxidized natural rubber (ENR). They studied the effect of type of ENR with epoxidation content at 20 mol% (ENR20) and 50 mol% (ENR50) and studied the effect of PLA and ENR content from 1 to 20 wt%. The TGA thermogram showed the one-stage weight loss during the decomposition. The thermal stability increased because the intense molecular interaction and crosslinking between chain of ENR. The TGA thermogram is shown in Figure 2.14. The blending of PLA/ENR20 and the blending of PLA/ENR50 gave the elongation at break increase from 9.3% to 32% and 27% respectively. Moreover, the blending of PLA/ENR50 showed lower elongation at break than the blending of PLA/ENR20. The result of this study is shown in Figure 2.15. (Chunmei Zhang *et al.*, 2012).

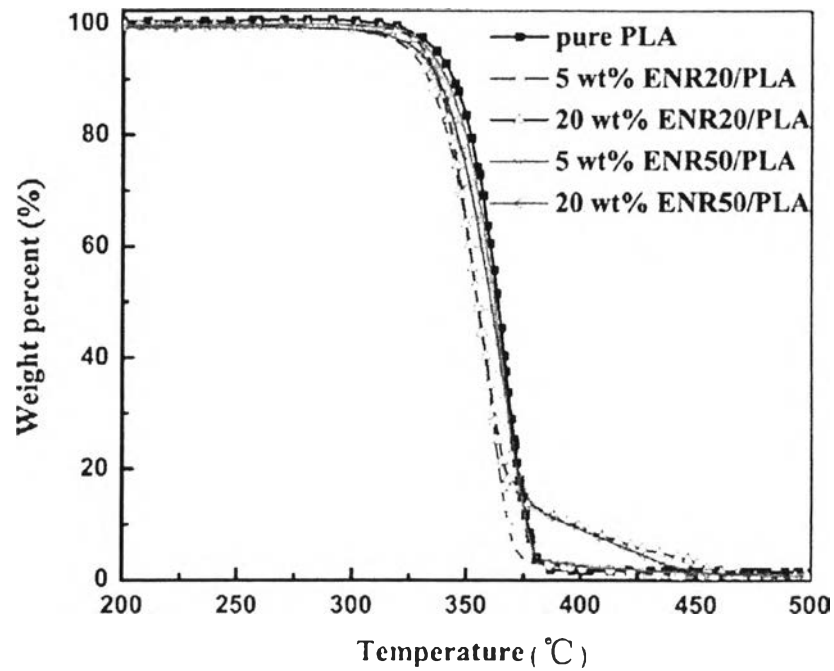


Figure 2.14. TGA curves of pure PLA, ENR20/PLA and ENR50/PLA blends.

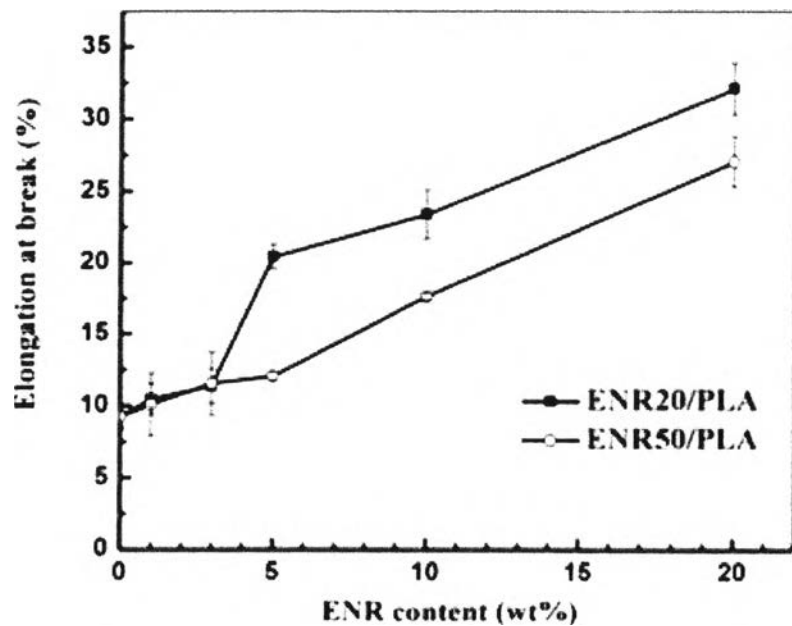


Figure 2.15. The elongation at break of pure PLA, ENR20/PLA and ENR50/PLA blends (Chunmei Zhang *et al.*, 2012).

2.1.2.4 Modified by copolymerization

There are many monomers that copolymerized with PLA to improve the weak properties of PLA. A polycondensation of lactic acid copolymerized with other monomers, produced low molecular weight copolymer. Monomers were used in polycondensation copolymerization such as D,L-mandelic acid and other α -hydroxy acids, etc. Moreover, ring-opening copolymerization of lactide monomer with cyclic monomer produced high molecular weight copolymer. Cyclic monomers were used in ring-opening copolymerization such as glycolide, trimethylene carbonate, ϵ -caprolactone, etc. (Sodergard, 2002).

In 2000, Hiki *et al.* studied L-lactide block copolymerization with hydroxy-terminated [RS]-poly(3-hydroxybutyrate) ([RS]-PHB) by the catalyst of tin (II) octoate. They studied the effect of L-lactide and [RS]-PHB content from 44 to 69% and studied the effect of increase reaction temperature. The result of yield of copolymer was very high and molecular weight was around 11,900-30,000 Da. The feed ratio of L-lactide affected the molecular weight. The molecular weight distribution was very low. The result of block copolymerization of [RS]-PHB and L-lactide is shown in Table 2.4. Furthermore, they studied on mechanical properties of block copolymerization of [RS]-PHB and L-lactide. The polymer films were made from the PLLA-[RS]-PHB-PLLA gave the Young's modulus increased from 30 to 160 MPa when increase the composition of PLLA. In contrast, the elongation at break was increasing from 200 to 86%. The result of mechanical properties of this study is shown in Table 2.5. (Hiki *et al.*, 2000).

Table 2.4 Results of block copolymerization of the telechelic [RS]-PHB and l-lactide (polymerized with Sn(Oct)₂ as catalyst for 40 min at 160°C in bulk) (Hiki *et al.*, 2000)

Run No.	Telechelic [RS]-PHB M _a ^b (10 ³ Da)	[M]/[I] ^a	Unit ratio 3HB/LA ^c	Yield (%)	M _a (10 ⁴ Da)		Mw/Mn ^b
					GPC ^b	Calcd. ^d	
1	5.4	28.1	42/58	87	1.2	1.25	1.3
2	5.4	42.0	32/68	79	1.5	1.49	1.2
3	5.4	64.5	22/78	87	2.1	2.16	1.3
4	10.1	31.8	56/44	83	1.6	1.77	1.2
5	10.1	51.6	47/53	82	2.0	2.23	1.2
6	10.1	83.6	31/69	90	3.0	3.22	1.2

^a The monomer (M) ratio in feed relative to the total end group (I) of the prepolymer.

^b Determined by GPC calibrated with polystyrene standard (chloroform eluent).

^c Determined by ¹H NMR spectra.

^d Calculated from the yield.

Table 2.5 Mechanical properties of the polymer films of PLLA-[RS]-PHB-PLLA ([RS]-PHB: M_n 10; 100; M_w=M_n . 1:18 (Hiki *et al.*, 2000)

Run No.	Composition (3HB/LA) ^a	Modulus (MPa)	Strength (MPa)	Elongation (%)	x ^b (%)
1	100/0 ^c	24	15	610	-
2	56/44	30	10	200	9
3	47/53	130	14	150	10
4	31/69	160	15	86	23
5	0/100 ^d	800	39	7.2	37

^a Determined by ¹H NMR spectra.

^b The degree of crystallinity of PLLA was calculated by DSC.

^c For a preferentially syndiotactic [RS]-PHB homopolymer (M_n = 95,000, M_w/M_n=1.70).

^d For PLLA homopolymer (M_n=99,000, M_w/M_n=1.86, T_m= 173 °C).

In 1997, Chen *et al.* synthesized [L]-Lactide/ethylene oxide ([L]-LA/EO) ring-opening copolymerization by using the various catalysts including isobutyl- aluminoxane (IBAO) and Sn-Al bimetallic catalysts. They studied the effect of reaction temperature on multiblock segment length and molecular weight of copolymer. They found that the increasing of reaction temperature resulted in shorter segment block length. DSC thermogram showed two melting peaks that corresponded to [L]-PLA and PEO crystalline phase. The composition between two phases and the block length affected the melting temperature and enthalpy of fusion. The DSC thermogram is shown in Figure 2.16 and the values of thermal properties are shown in Table 2.6. Moreover, they compared the properties between L-LA/EO and L-LA/PEG based on modulus and yield strength. The modulus and yield strength of L-LA/EO were higher than L-LA/PEG. The result of this study is shown in Table 2.7. (Chen *et al.*, 1997).

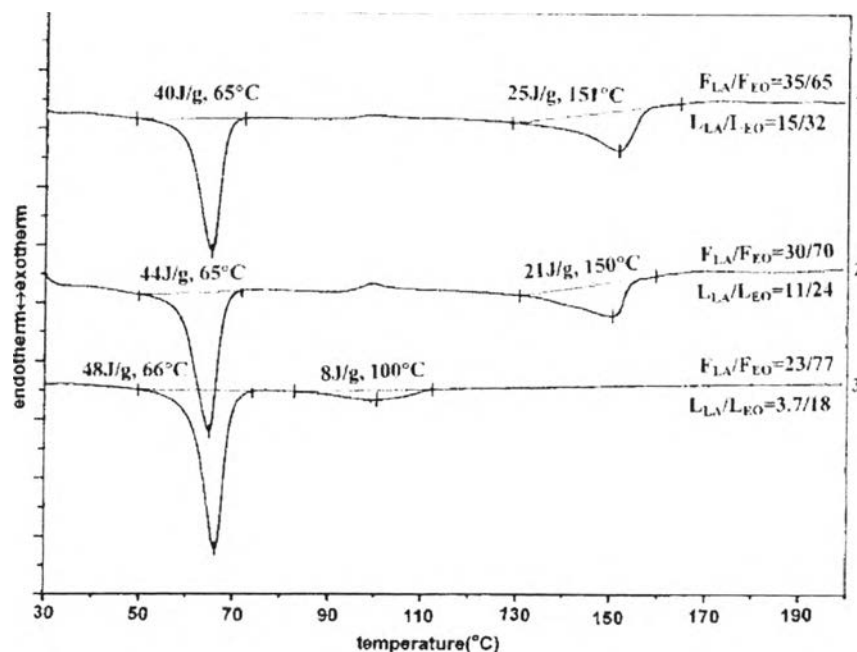


Figure 2.16. DSC thermograms recorded during the first heating scan of the following copolymer MeOH-i fractions: (1) entry 5, (2) entry 6, and (3) entry 10 (Chen *et al.*, 1997).

Table 2.6 DSC Analysis of Methanol Insoluble [L]-LA-EO Copolymers (Chen *et al.*, 1997)

entry	M_w/M_n	$L_{[L]-LA}/L_{EO}$	$F_{[L]-LA}/F_{EO}$	T_m^a (°C)	ΔH_f^a obsrvd (calcd ^c) (J/g)	T_m^b (°C)	ΔH_f^b obsrvd (calcd ^c) (J/g)
4	44 100/12 300	11/25	47/53	60	25 (36)	136	35 (47)
5	118 000/21 100	25/42	30/70	60	25 (59)	147	23 (37)
6	162 000/26 100	9/44	22/78	64	64 (73)	142	18 (30)
10	121 000/23 700	17/83	17/83	63	63 (84)	127	14 (25)
15	110 000/30 600	18/39	33/67	65	40 (53)	151	25 (39)
17	86 400/37 000	13/39	31/69	65	42 (56)	150	22 (38)
18	46 400/17 500	10/32	31/69	66	47 (56)	100	8 (38)

^a Melting transition of PEO blocks. ^b Melting transition of PLA blocks. ^c Calculated assuming that the PEO and PLA chain segments are long and do not interact in amorphous or crystalline domains; using ΔH_f values for PEO (M_n) 4 _ 106) and [L]-PLA (M_n) 12 900) of 140 and 63 J/g, respectively; using the equations ϕH_f (calcd) = $w_{PEO} \phi H_f(PEO)$ or $w_{[L]-PLA} \Delta H_f([L]-PLA)$ where w_{PEO} and $w_{[L]-PLA}$ are the weight fractions of PEO and [L]-PLA segments, respectively.

Table 2.7 Tensile Properties of [L]-PLA/PEG and [L]-PLA/[L]-LA-co-EO Blend (Chen *et al.*, 1997)

Blend	Modulus (MPa)	Yield stress (MPa)	Elongation at yield(%)	Break stress (Mpa)	Elongation at break(%)
[L]-PLA/PEG MW (PEG)=18,500 (89/11 w/w)	423 \pm 20	14.5 \pm 2.8	6.0 \pm 0.1	25.5 \pm 2.8	240 \pm 21
[L]-PLA/[L]- LA-co-Eo ^b (80/20 w/w) $w_{[L]-LA}/W_{EO}$ =89/11	710 \pm 21	24.1 \pm 3.1	6.0 \pm 0.1	26.2 \pm 2.6	204 \pm 18

In 2002, Frick *et al.* synthesized polylactide-b-polyisoprene-b-poly lactide (PLA-PI-PLA) triblock copolymers. The contents of triblock copolymer were 5.1-35-5.1 kg/mol as called S, 9.0-33-9.0 kg/mol as called C and 14-33-14 kg/mol as called L. They investigated dynamic mechanical and tensile testing based on Young's modulus and ultimate tensile strength. For dynamic mechanical analysis, all triblock (S,C, and L) showed the decreasing of the elastic modulus around the T_g of PLA. The independent plateau of triblocks C and L demonstrated that there are free of significant diblock contamination. In contrast, triblock S had the negative slope for the plateau region that attributed to the short chain of PLA resulting in weaker point. The result of DMA of triblock is shown in Figure 2.17. They found that the increasing in volume fraction of PLA sample was resulting in the increasing of Young's modulus, Yield stress and ultimate tensile strength. The result of this study is shown in Table 2.8 and Figure 2.18 (Frick *et al.*, 2002).

Table 2.8 Tensile data for Triblock Copolymers (Frick *et al.*, 2002)

Triblock	Young's modulus $E_{\pm sd}$ (MPa)	Yield strain $\epsilon_{Y\pm sd}$ (%)	Yield stress $\sigma_{Y\pm sd}$ (MPa)	Strain at break $\epsilon_{B\pm sd}$ (%)	Ultimate tensile strength $\sigma_{B\pm sd}$ (MPa)
S	6.7 \pm 0.6	55 \pm 9.1	1.5 \pm 0.4	200 \pm 40	3.1 \pm 0.9
C	3.8 \pm 1.1	5 \pm 0.8	2.9 \pm 0.7	650 \pm 70	9.2 \pm 1.9
L	150 \pm 26	4 \pm 0.5	5.5 \pm 1.0	450 \pm 60	10.1 \pm 1.8

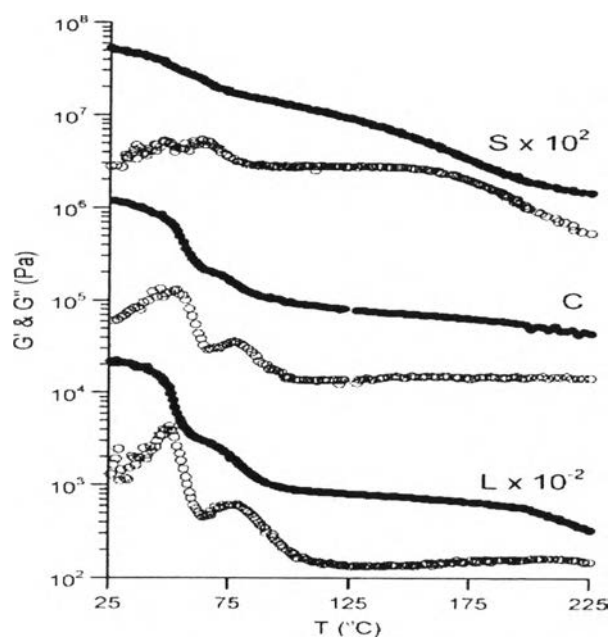


Figure 2.17. DMS temperature sweeps for triblocks S, C, and L (temperature ramp rate = 2 °C/min, frequency (ω) = 0.5 rad/s, strain (ϵ) = 1%): G' , filled circles; G'' , open circles (Frick *et al.*, 2002).

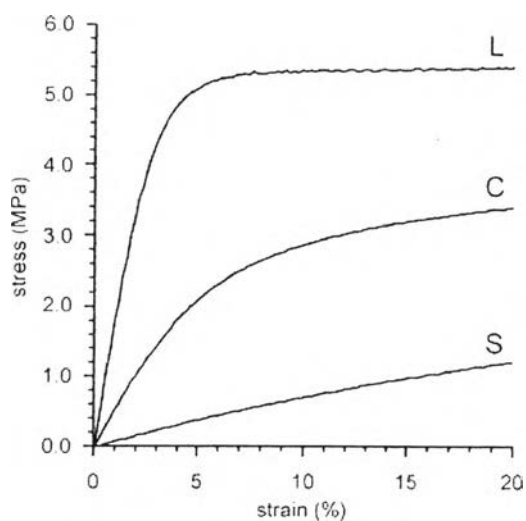


Figure 2.18. Representative stress-strain curves for triblocks S, C, and L pulled to 20% strain (ASTM D178).

2.1.3 Application of PLA

PLA has good mechanical and thermal properties to use in many applications such as packaging, paper coating, fiber, film and carrier bag (Rudnik, 2008). Moreover, PLA also has bioresorbability, biocompatibility and biodegradable properties to use in biomedical application. The applications of PLA are shown in Table 2.9. (Rasala *et al.*,2010)

Table 2.9 The application of PLA

Sector	Application	Reference
Packaging	Food packaging	Vink et al., 2004
	Film	Vink et al., 2004
	Rigid thermoformed food	Vink et al., 2004
biomedical	Suture in guinea	Kulkarni et al., 1966
	Bone repair of rat	Hollinger, 1983
	Drug release in rat	Schakenraad et al., 1990
	Fracture fixation of dog	An et al., 1998
Other	Textile or non-wovens	Materials, 2000

2.2 Epoxidized Natural Rubber (ENR)

Epoxidized Natural Rubber (ENR) is the natural rubber that some part of double bonds is replaced by epoxide groups randomly along the chain. ENR has many good properties offering high strength, solvent resistance and wear resistance. ENR is now established commercial polymer which has three grades; 10, 25 and 50 mole % of epoxide contents as called ENR-10, ENR-25 and ENR-50. The chemical structure of ENR is shown in Figure 2.19 (Yoksan R., 2008).

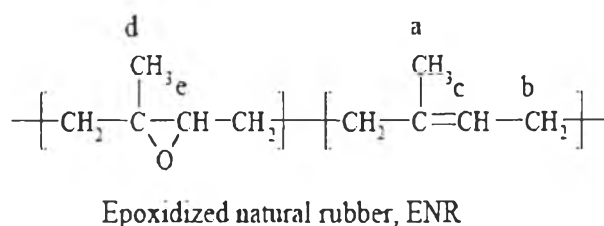


Figure 2.19. Chemical structure of ENR (Yoksan R., 2008).

2.2.1 Synthesize method of ENR.

Natural rubber (NR) is the most important economic commodities in Thailand. NR has many good physical and thermal properties such as high elasticity, stickiness, resilience, etc. Due to the double bond in its structure, NR has limitation properties such as low stability to heat, oxygen, sunlight and hydrocarbon/hydrophobic solvent. The chemical modification at double to improves those limitation properties.

Epoxidized natural rubber (ENR) is the natural rubber that has epoxide group along the chain. It reduces the number of double bond that results in hydrophilicity increasing. The mechanical and thermal properties of ENR can comparable with NR. Moreover, it can improve some limitation of NR. The synthesis method of ENR is shown in Figure 2.20 (Yoksan R., 2008).

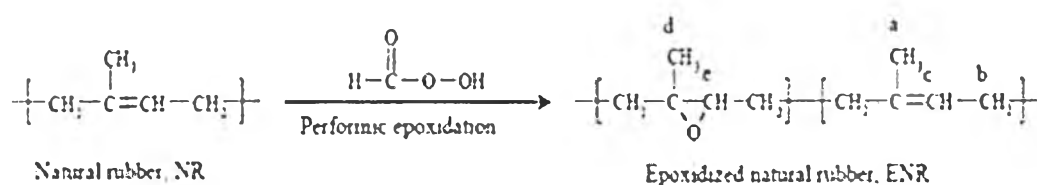


Figure 2.20. Synthesis of Epoxidized Natural Rubber (Yoksan R., 2008).

In 1992, Gelling studied the epoxidation of NR latex with peroxyacetic solution. They varied the acid concentration and temperature. They studied the effect of mole % of epoxide content on the systematic change in properties. They studied the vulcanization characteristic of ENR. Moreover, they studied the mechanical and thermal properties of ENR that compared with NR. Tensile strength of ENR increased following the content of epoxide group increasing. Moreover, the properties of ENR can comparable with NR. The result of this study is shown in Table 2.10 (Gelling, 1992).

Table 2.10 The properties of ENR (Gelling, 1992)

Property	Vulcanisate			
	NR	ENR 25	ENR 50	ENR 75
Stress at 100% extension (MPa)	0.74	0.69	0.78	0.96
Tensile strength (MPa)	25.8	24.1	30.9	28.4
Elongation at break (%)	760	789	762	622
Degree of crystallinity ^h	11	11	10	4
Unit cell volume (mm ³)	0.955	0.985	0.999	1.036

In 2011, Mishra *et al.* found polycaprolactone (PCL)/epoxidized natural rubber (ENR) blends (PCL/ENR = 70/30, 50/50 wt/wt) that were prepared by a melt mixing in an internal mixer in the presence of a small amount of dicumyl peroxide (DCP). They studied the effect of peroxide crosslinking on thermal, mechanical, and rheological properties of the blends were investigated. The crosslinked blends exhibited high elongation-at-break and fairly good elastic recovery as well as melt processibility. DCP modified blends showed higher tensile strength and elongation at break than simple blend. The result of this study is shown in Table 2.11. (Mishra *et al.*, 2011).

Table 2.11 Tensile properties of the blending (Mishra *et al.*, 2011)

Samples	Tensile strength (MPa)	100% Tensile modulus (MPa)	Elongation at-break (%)	Tension set (%)
PE5050	8.8 ± 0.4	3.9 ± 0.5	1500 ± 80	41
PE5050D0.5	9.1 ± 0.4	3.7 ± 0.5	1580 ± 80	26
PE5050D1.0	9.3 ± 0.5	3.4 ± 0.6	1650±40	23
PE7030	18.5 ± 0.9	6.4 ± 0.4	800 ± 60	37
PE7030D0.5	20.5 ± 0.7	6.3 ± 0.4	850 ± 60	31
PE7030D1.0	23.2 ± 0.8	6.2 ± 0.3	910 ± 40	28

In 2005, Yew *et al.* studied Epoxidized natural rubber/poly lactide/rice starch (ENR/PLA/RS) blending that were prepared by a twin-screw extruder and compression molding into dumbbell specimens. They studied the effect of RS and ENR contents on mechanical properties. They characterized the mechanical properties and morphology of a composite by tensile testing and SEM. They found that tensile modulus of PLA increased by the incorporation of RS. In contrasting, ENR content increasing was resulting in tensile modulus decreasing. The result of this study is shown in Table 2.12. (Yew *et al.*, 2005).

Table 2.12 Tensile properties of PLA/RS composites (Yew *et al.*, 2005)

Materials	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PLA	3.30 \pm 0.08	57.8 \pm 0.86	3.8 \pm 0.07
PLA/RS10	3.50 \pm 0.08	40.9 \pm 0.77	2.6 \pm 0.06
PLA/RS20	3.80 \pm 0.07	44.0 \pm 0.56	2.5 \pm 0.08
PLA/RS30	4.20 \pm 0.09	37.7 \pm 0.92	2.1 \pm 0.04
PLA/RS40	4.40 \pm 0.09	33.6 \pm 0.68	1.9 \pm 0.05
PLA/RS50	4.50 \pm 0.08	30.6 \pm 0.78	1.7 \pm 0.07
PLA/RS20/E2.5	3.70 \pm 0.06	47.9 \pm 0.62	2.7 \pm 0.06
PLA/RS20/E5	3.30 \pm 0.07	49.0 \pm 0.54	3.4 \pm 0.05
PLA/RS20/E7.5	3.10 \pm 0.08	41.6 \pm 0.68	2.9 \pm 0.08
PLA/RS20/E10	2.80 \pm 0.06	37.2 \pm 0.79	2.6 \pm 0.07