

As the direct polycondensation produces water molecules as by-products, degradation may occur by a reaction of hydroxyl group of water and oligo(polylactic acid) end groups. This reduces molecular weight of the resulting PLA ($M_w = 1000$ - 5000 g/mol), as shown in Figure 2.3.

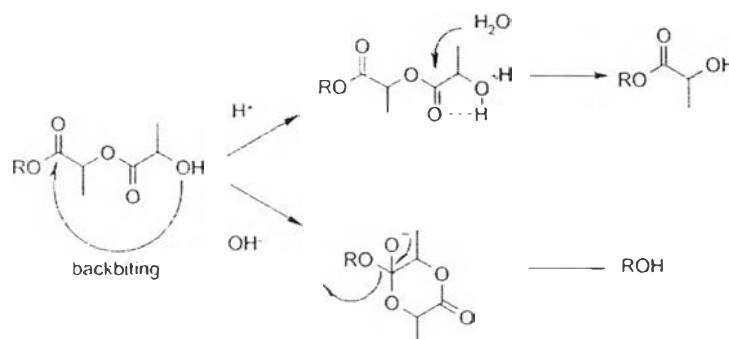


Figure 2.3 Degradation of oligo (polylactic acid) by chain-end scission (back-biting) [15].

High-molecular weight PLA is typically synthesized by a ring-opening polymerization of lactide, as shown in Figure 2.4. This reaction requires high purity of lactide monomer, obtained by dimerization of lactic acid monomer. PLA is prepared by using a catalyst, e.g. stannous octoate, with the monomer under vacuum or an inert atmosphere. By controlling the residence time and the temperatures in combination with the catalyst type and concentrations, it is possible to control the ratio and sequence of D- and L-lactic acid units in the polymer chains [16].

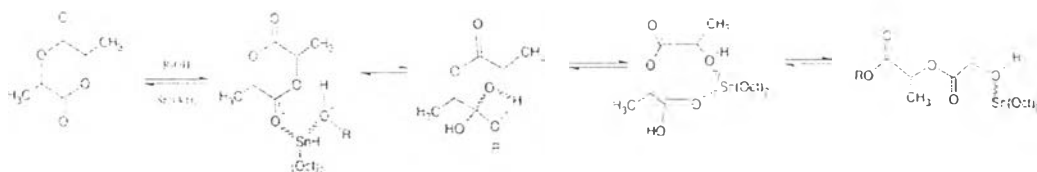


Figure 2.4 Ring-opening polymerization of lactide [16]

Alternately, high-molecular weight PLA can be synthesized through an azeotropic dehydration condensation of lactic acid, or a chain linking polymerization, as illustrated in Figure 2.5. Azeotropic dehydration procedure consists of reducing the

distillation pressure of lactic acid for 2–3 h, at 130 °C. The majority of the condensed water molecule is then removed. However, the process requires complex apparatus, where catalyst and solvent are also expensive [17]. Chain-linking polymerization method produces PLA prepolymers in a first step, which are then reacted with chain coupling agents to generate high-MW PLA. Hiltunen and coworkers synthesized polylactic acid by using hexamethylene diamine as a chain coupling agent, and found that an OH/NCO ratio of 1:1 produced PLA products with the highest molecular weight [10, 18, 19]. In addition, mechanical and degradation properties of the PLA products can be further adjusted by employing chain-linking polymerization [12].

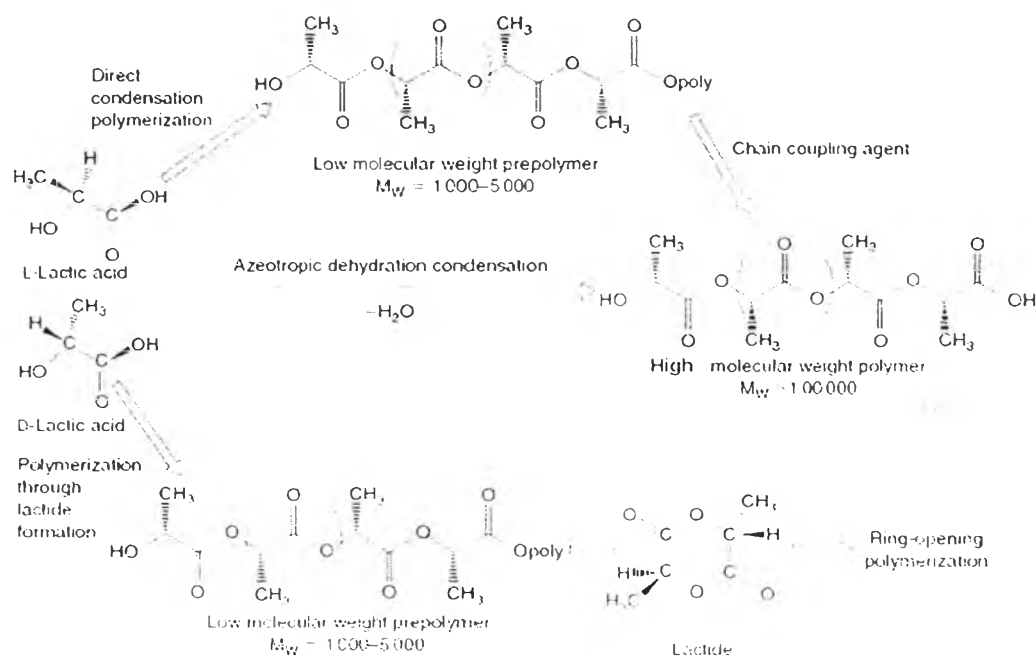


Figure 2.5 Synthesis routes of PLA [12, 20].

2.1.2. Properties of PLA

High molecular weight PLA is colorless, glossy, and has high strength and modulus, similar to polyethylene terephthalate (PET), but higher than those of high impact polystyrene (HIPS) and polypropylene (PP). The material has attracted increasing interest in various markets, such as packaging, textile, automotive, and biomedical devices, as a promising eco-friendly alternative to traditional petroleum-based commodity polymers. Table 2.1 summarizes common physical and mechanical properties of PLA compared to those of typical commodity plastics. Tensile strength and tensile modulus of PLA are similar to those of PET and polystyrene (PS). In contrast, PLA has lower elongation at break (20 times), compared to those of PP, and quite lower impact strength than HIPS.

Table 2.1 Comparison of typical properties of PLA and several petroleum-based commodity plastics [16].

Properties	PLA	PET	PS	HIPS	PP
T _g (°C)	55	75	105	N/A	-10
Tensile strength (MPa)	53	54	45	23	31
Tensile modulus (GPa)	3.4	2.8	2.9	2.1	0.9
Elongation at break (%)	6	130	7	45	120
Notched Izod IS (J/m)	13	59	27	123	27 (LDD)

Physical and chemical properties of PLA also depend on its chain structures and conformation, as shown in Table 2.2. PLA homopolymer either poly-D-lactide; PDLA or poly-L-lactide; PLLA is white powder at room temperature, with glass transition temperature (T_g) and melting temperature (T_m) values of about 50-60°C

and 180°C, respectively. An amorphous poly-DL-lactide (PDLLA) has lower thermal stability and degradability, in comparison with its semi-crystalline counterparts.

Table 2.2 Physical, thermal properties and degradability of PLAs [20].

Properties	PDLA	PLLA	PDLLA
Solubility	soluble in benzene, chloroform, acetonitrile, THF, dioxane insoluble in ethanol, methanol, and aliphatic hydrocarbons		
Crystalline structure	Semi-crystalline	Semi-crystalline	Amorphous
T_m (°C)	~180	~180	Varies
T_g (°C)	50-60	55-60	Varies
Decomposition temperature (°C)	~200	~200	185-200
Half-life in normal saline (37°C)	4-6 months	4-6 months	2-3 months



2.1.3. Advantages of PLA

Sustainability and environmentally-friendly

PLA is considered a sustainable material, as its lactic acid monomer is derived from renewable resources, e.g., corn, wheat, or cassava, via bacterial fermentations. The material is environmental friendly, because PLA products can be biodegraded, recycled, and composted [21]. The degraded lactic acid is finally digested into carbon dioxide and water, which are important for plant growing and photosynthesis system, as shown in Figure 2.6. These sustainability and eco-friendly characteristics make PLA an attractive biopolymer.

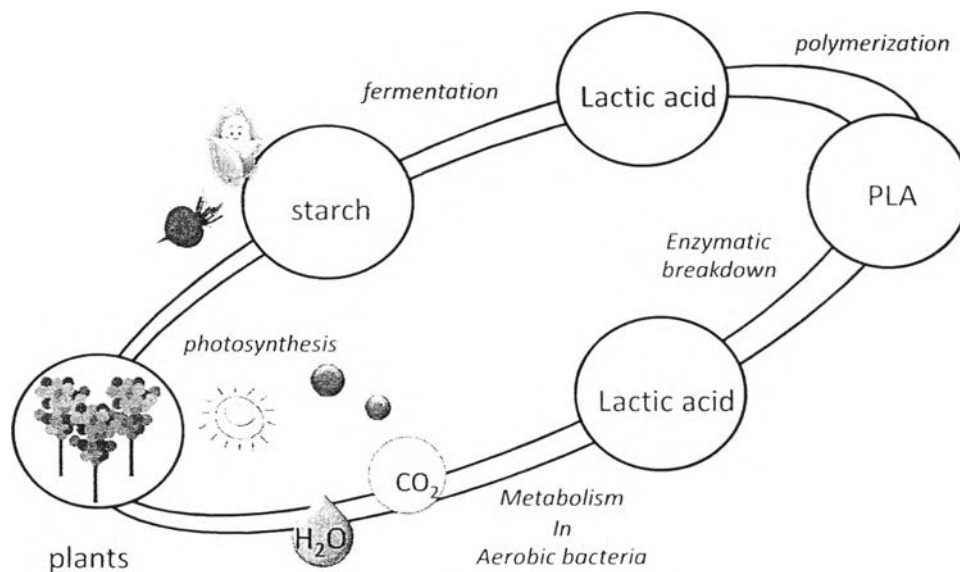


Figure 2.6 Life cycle of PLA [11].

Biodegradability and biocompatibility

The most attractive property of PLA in biomedical applications is its *biodegradability and biocompatibility*. In addition, this does not produce toxic or carcinogenic effects in local tissues, when being used in biomedical applications. Therefore, the degraded products do not interfere with tissue healing [22].

PLA degradability is dependent on several factors, such as molecular weight, crystallinity, purity, degradation conditions, (temperature and pH), a presence of terminal carboxyl or hydroxyl groups. In addition, additives that act catalytically, e.g. enzymes, bacteria or inorganic fillers, also imposes strong effect on PLA degradation. Importantly, water permeability is a major factor to determine PLA degradability, because the degradation mechanism is predominated by the uptake of water, followed by hydrolysis of ester bonds [17]. In hydrolysis reaction, PLA is degraded both in alkaline and acidic conditions, as detailed in Figure 2.7 -2.8 [23].

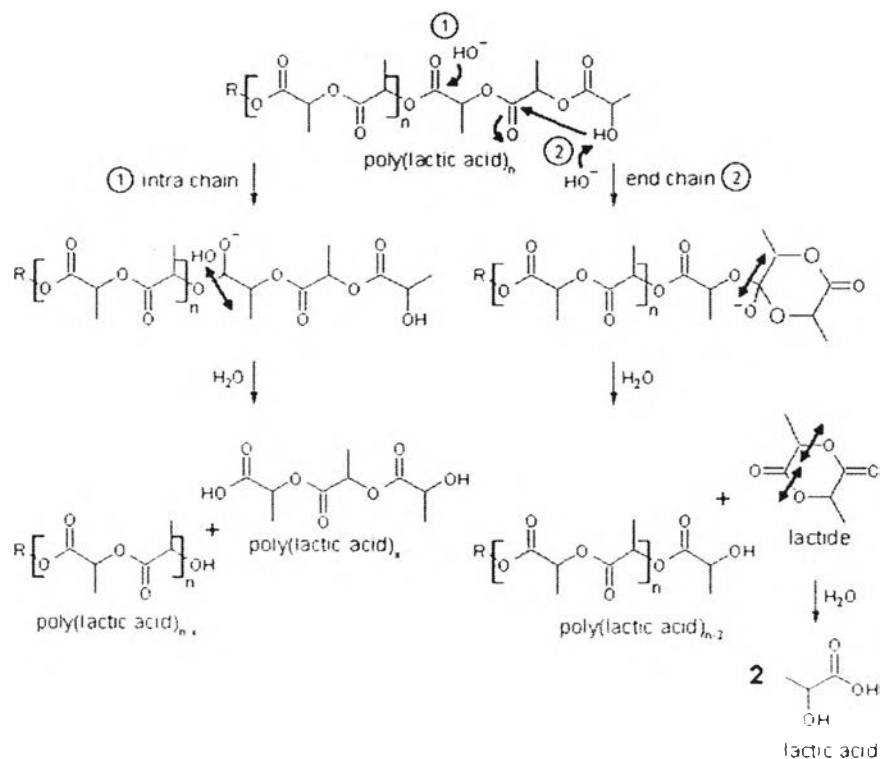


Figure 2.7 PLA hydrolysis in alkaline conditions [23].

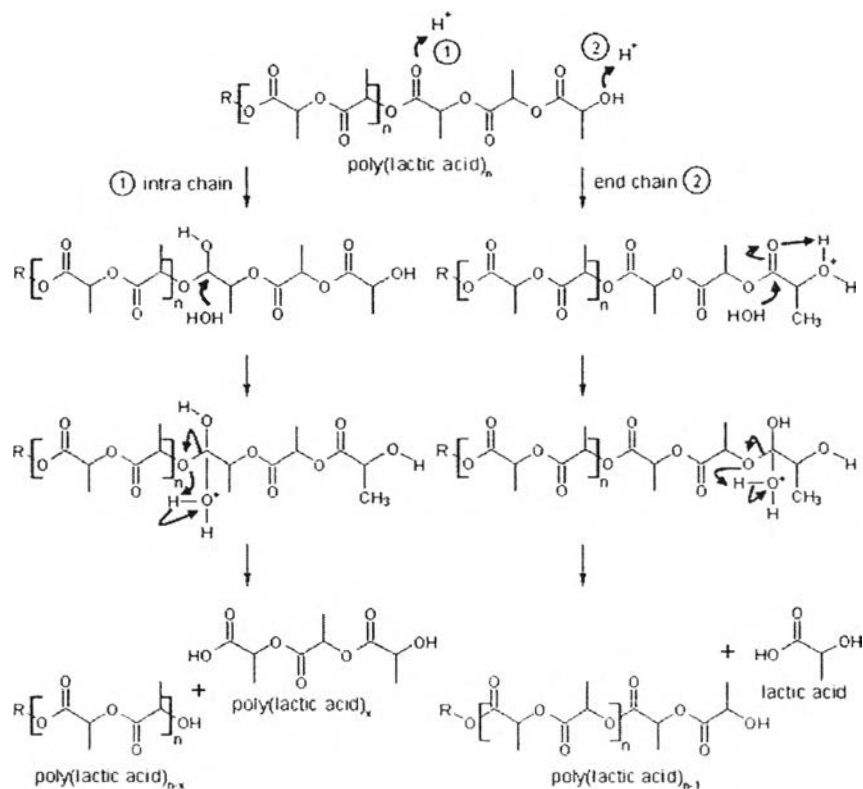


Figure 2.8 PLA hydrolysis in acidic conditions [23].

Recycle ability

As the majority of petroleum-based plastics is non-degradable, post-consumer plastic bottles, e.g., PET, PE and PP need a recycling process to relieve their harm to the environment. Most thermoplastic waste can be reprocessed or physical recycled, whereas some plastics, such as polyester and polyamide, can react with chemical reagents to convert to small molecules which is called a chemical recycle process. Although PLA is biodegradable, non-suitable environmental conditions or composting facilities may limit its degradation. Similar to PET, PLA is a thermoplastic polyester, which can be recycled by both physical and chemical processes [10, 12, 24]. Therefore, chemical recycling process of PLA products have been developed. This makes PLA even more sustainable [21]. Since PLA is degradable and has low thermal stability, the material is especially vulnerable

to mechanical degradation during extrusion. Therefore, after every reprocessing cycle the resulting products have lower quality than the starting material, and so its market value decreases [25].

Low energy consumption and low carbon processes

PLA can be processed by various techniques, e.g. injection molding, film extrusion, blow molding, thermoforming, fiber spinning, and foaming processes. The production and processing of PLA require lower energy consumption (25–55%), compared to those of petroleum-based polymers [26]. Moreover, the carbon dioxide release from the production of PLA products is much lower than those of other conventional polymers.

2.1.4. Properties enhancement of PLA

Toughness enhancement

Despite its excellent properties, PLA has some disadvantages in terms of mechanical properties. Similar to polystyrene, PLA has less than 10% elongation at break. This is not suitable for demanding mechanical performance applications, where a plastic deformation at higher stress levels is needed, such as, screws and fracture fixation plates [27].

Toughness is an ability of a material to absorb energy and plastically deform without fracturing. Efficiency of toughness enhancement is typically obtained from increasing of ductility, e.g., impact strength (amount of energy per volume that a material can absorb before rupturing), elongation at break and breaking energy (calculated from area under tensile stress-strain curve) of the polymer, as shown in Figure 2.9. However, toughness enhancement usually leads to a small loss in stiffness and without a harmful effect on thermal stability [28].



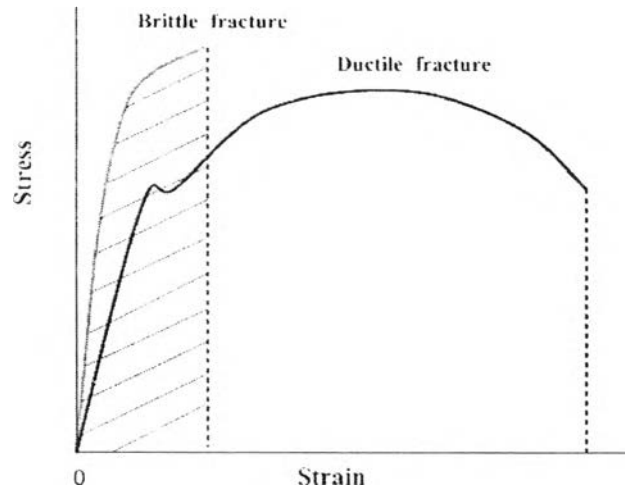


Figure 2.9 Stress-strain curve of brittle and ductile polymers [29].

PLA is typically toughened by plasticization [1, 2], Copolymerization [3], and melt blending with flexible polymers [4]. Among those, plasticization method is the most simplified and convenient to conduct. Small amount of plasticizers can be incorporated as processing aid, during plastic formation. The plasticizing efficiency of a plasticizer is evaluated by the decrease in T_g (T_g of the plasticizer should be lower than PLA) and enhancement in tensile toughness. This is dependent on miscibility of the plasticizer and PLA matrix, molecular weight, and content of the plasticizer. In recent years, various biodegradable monomers and oligomers have been used as plasticizers for PLA, due to environmental concerns. Martino and coworkers [1] studied effect of molecular weight and concentration of dioctyl adipate (DOA) plasticizer on elongation at break of PLA. The results exhibited that enhancement of elongation at break of PLA was achieved when the concentration of plasticizer reached 10 wt %. However, incorporation of DOA plasticizers decreased its tensile strength and elastic modulus. The small DOA molecules showed some migration at the concentrations higher than 10 wt %. On the other hand, high molecular weight polyadipate (Glyplast® G206/7) is a less efficient plasticizer, as phase separation occurs because of its lower compatibility with PLA matrix. Most importantly, migration of plasticizers not only contaminates the food or beverage in contact with plasticized PLA, but also causes plasticized PLA to regain the brittleness of neat PLA

[4]. Miscibility of PLA matrix and secondary phases have been enhanced by chemical bonding, e.g. copolymerization.

D. Cohn and coworkers [3] developed toughened PLA by copolymerization with poly(ϵ -caprolactone; PCL) (Figure 2.10) and studied the effect of chemical composition on tensile properties of the copolymers. The results showed that, tensile modulus of PCL/PLA copolymers were increased with increasing of PLA molecular weight, in the same way, their elongation at break were decreased. This result can be concluded that mechanical properties of PCL/PLA copolymers depended on chemical composition, higher rigidity observed in higher DP of PLA segment. This research informs that chemical bonding of copolymer enhances mechanical properties for PLA. It is also noted that, PLA-containing block copolymers show a potential for used as plasticizer for miscibility enhancement with the PLA matrix.

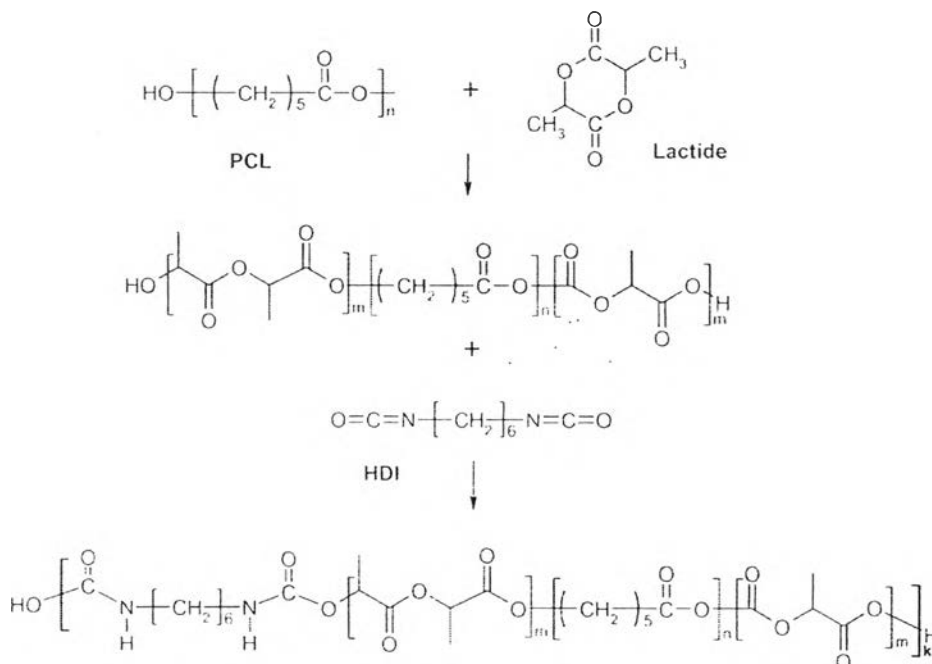


Figure 2.10 Synthesis and structure of PCLA multiblock copolymers [3].

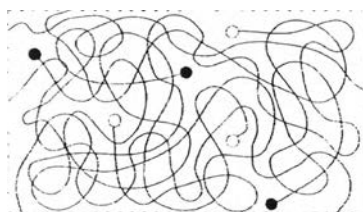
The most popular method for toughness enhancement is blending with more flexible polymers. Regarding to biomedical applications, biocompatible polymers,

such as poly(vinyl alcohol: PVA), poly(ϵ -caprolactone: PCL), poly(ethylene glycol: PEG), poly-hydroxyalkanoate (PHA), and poly(butylene succinate: PBS) have generally been used as second-phase polymers. Many publications reported an incorporation of rubber into PLA. Mechanical properties of the rubber/PLA blends can be controlled by varying types, contents, and modification of the rubber phase [4].

PLA degradation rate

Degradation rate of PLA is dependent on crystallinity, molecular weight, morphology, and water diffusion rate into the polymer [30]. Degradability is considered an important selection criterion of polymers for biomedical applications [31]. In drug delivery system, degradable polymers are employed to delay drug dissolution. Drug release rate can be controlled by varying the polymer matrix structures [32, 33].

Completely amorphous PLA film



Crystallized PLA film

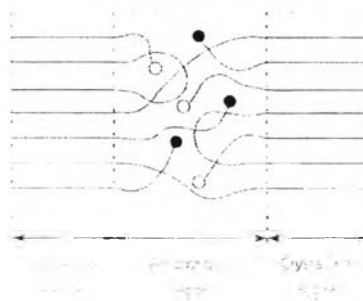


Figure 2.11 Schematic representation of structure of a complete amorphous PLA film and a crystallized PLA film [34].

Effect of crystallinity of PLA on hydrolysis mechanism of PLA film in alkaline solution was studied H. Tsuji [34]. The authors found that degradation mechanism of PLA involved by hydrolysis, which proceeded homogeneously along the film cross section, mainly via the bulk-erosion mechanism. Increasing of water diffusion rate of PLA is depended on content of loose chain packing in the amorphous region between the lamellae, led to high content of end groups, as shown in Figure 2.11.

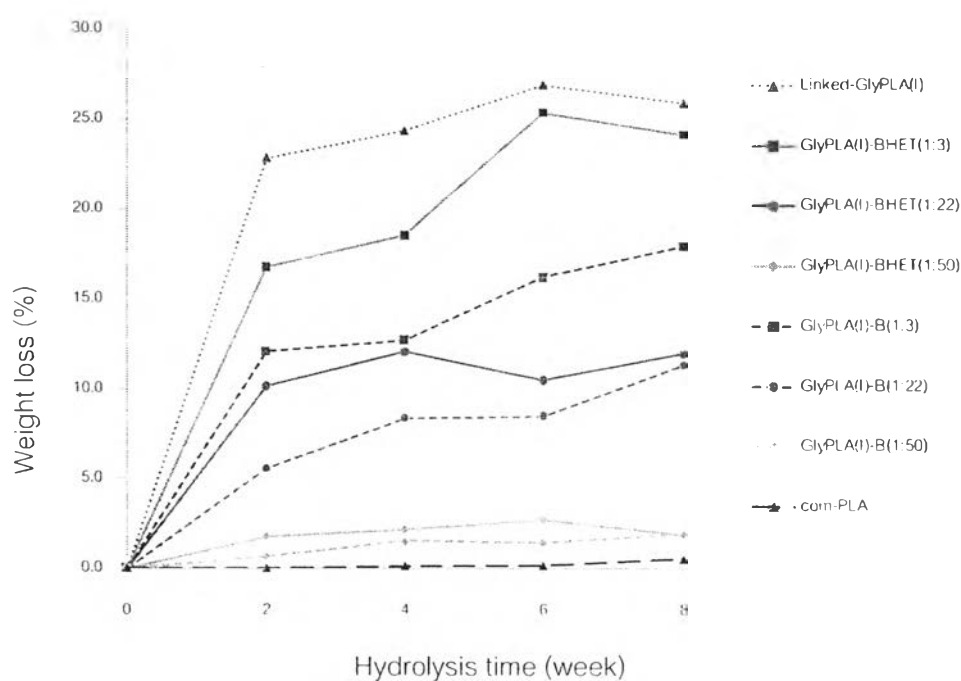


Figure 2.12 Hydrolysis rate of linked-GlyPLA(I), compared to copolymer of GlyPLA-B-ET (—) copolymer of GlyPLA-B (---), with aliphatic/aromatic composition of 1:3 (■) 1:22 (○), and 1:50 (◇) [11].

It had been reported in our previous works [11, 35] that the co-monomer content and its arrangement in copolymer chains plays significant roles in the degradation rate of PLA copolymers. Poly(lactic acid-co-ethylene terephthalate) was developed and its hydrolytic degradation in a phosphate buffer solution (pH 7.4) was examined at room temperature. Bis-hydroxy ethyl terephthalate (BHET) and dimer of

BHET were chain-linking copolymerized with OH-terminated PLA glycolysates (GlyPLA) by using various chemical compositions. The results showed that the degradation rates of the copolymer decreased when BHET content increased. The use of longer aromatic sequences (B) exhibited slower hydrolysis characteristic, as shown in Figure 2.12. This indicates that tailor-made hydrolysis behaviors can be obtained by copolymerization PLA and PET with different chemical compositions and microstructures.

Hydrophobicity

Hydrophilicity/hydrophobicity is a key of characteristic to determine the application of polymer as biomedical materials. PLA surface has low cell affinity, because of its strong hydrophobic property (water contact angle about 80°) [36]. In tissue engineering, it was found that PLA can elicit an inflammatory response from the living host upon direct contact with biological fluids [37, 38]. Uhrich and coworkers [32] studied PLA-PEG copolymerization and found that a decrease of hydrophobic behaviors of PLA was mainly due to hydrophilicity of the incorporated PEG blocks. The inclusion of PEG in copolymer systems imparts extremely beneficial surface properties within the body because of its ability to repel proteins within aqueous environments. This repulsion inhibits the adsorption of proteins to the polymer surface and, therefore, prevents many polymer-cell interactions. Paul and coworkers [39] prepared PLA/nanoclay composites. It was found that biodegradation of PLA in compost increased with the addition of nanoclays. This was attributed to the high relative hydrophilicity of the clays, allowing an easier permeability of water into the polymer matrix and activating the hydrolytic degradation process.

Gas barrier enhancement

Gas barrier properties are governed by a permeation and diffusion of gas molecules through the polymer membrane. In packaging and membrane applications, gas permeability through PLA membrane was enhanced by decreasing the polymer crystallinity, since crystallite domains were impermeable to small



molecules. In contrast, gas barrier properties of PLA was improved by creating tortuous pathways, such as, adding nanofillers, or cellulose nanowhiskers, and forming multilayers of silicates [26]. Gas selectivity behavior is also an interesting characteristic for polymers membrane. In our previous works, CO₂/O₂ selectivity of PLA/PEG crosslinked ENR was studied. The results exhibited that the presence of PEG segments increase selectivity of CO₂ gas of the membrane due to enhancing penetrant diffusion coefficient of PEG with sour gas [4, 9].

2.1.5. Glycolysis of PLA

Glycolysis reaction is well known as one of the most efficient chemically-recycling process of thermoplastic polyester such as PET. It was found that BHET and its oligomers are obtained when PET are glycolysed with ethylene glycol (Figure 2.13). Research work on developing the glycolysed products of PET into other useful materials had been conducted in the last decade [24]. Therefore, it has introduced ideas to our research group to in-depth study the glycolysis reaction of PLA [10-13, 40]. It was proven that hydroxyl-terminated lactic acid prepolymers (Figure 2.14) are major products from glycolysis of PLA resins with ethylene glycol [13].

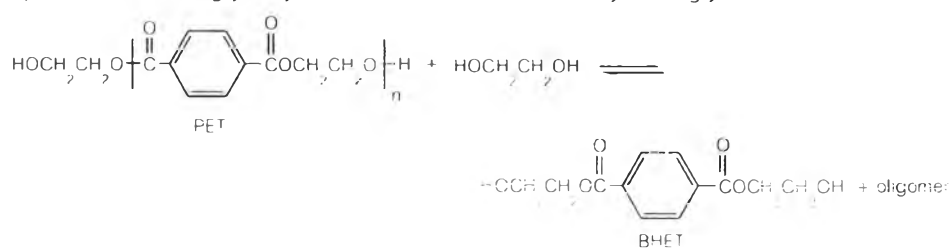


Figure 2.13 Glycolysis reaction of PET.

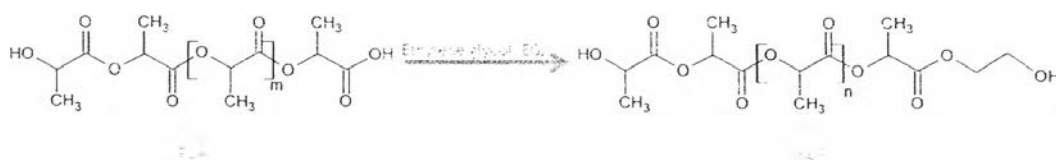


Figure 2.14 Glycolysis reaction of polylactic acid and ethylene glycol [12].

Tounthai et. al. summarized that the molecular weight (MW) of glycolysed products (GlyPLAs) can be optimized by adjusting glycolysis conditions and EG content. An increase in the EG content and glycolysis time and temperature leads to a reduction in MW of the products. Moreover, the decrease in MW of GlyPLAs leads to a reduction in their T_g and T_m . Chemical structure of the GlyPLAs was revealed by ^{13}C -NMR (Figure 2.15). The original PLA shows signals due to carbonyl ($\text{OC}=\text{O}$), methine ($-\text{O}-\text{C}(\text{H})\text{CH}_2\text{COO}-$), and methyl ($-\text{CH}_3$) carbons of LA repeating units at 169.5, 68.95, and 16.58 ppm, respectively. The resonances at 66.6 and 69.5 ppm are assigned to methine carbons of the OH-terminated LA end-groups, and LA units located next to the LA terminals. Signals at 67.1 and 60.6 ppm are due to methylene carbons of EG, i.e., $\text{OCO}-\text{CH}_2\text{CH}_2\text{OH}$ located at the other end of GlyPLA [13]. Moreover, these products possess high feasibility for use as starting materials in the development of other PLA-based thermoplastics [10, 12] and thermosets [13].

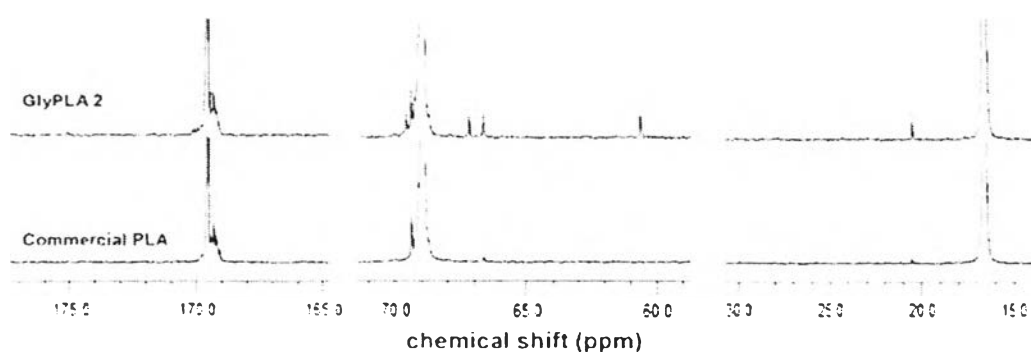


Figure 2.15 ^{13}C -NMR spectra of commercial PLA and GlyPLA2

(obtained from PLA:EG is 1:1, 195°C, for 210 min) [13].

2.2. Epoxidized Natural Rubber (ENR)

2.2.1. General characteristic of ENR

Natural rubber (NR) is an interesting material, whose commercial success is due not only to its excellent physical properties (i.e., strength, low heat buildup, excellent flexibility, high impact and tear resistance), but also its renewability. NR is applied in wide applications, ranging from household to industrial products, such as gloves (medical, household and industrial), toy balloons, rubber bands, tires, tube and replacement of synthetic-rubber.

However, their disadvantages are low thermal resistance, poor oil and ozone resistance. It is essential to develop processes for NR in order to improve its properties and wider its applications. Blending of NR with other polymers is among a popular process, because of its simple and economical procedures [41]. Modification of NR chemical structure also provides various opportunities for applications. Increasing of NR's polarity is achieved by converting part of carbon-carbon double bonds on the NR molecular chains to more polar groups (such as epoxide), as shown in Figure 2.16. This is called Epoxidized Natural Rubber (ENR).

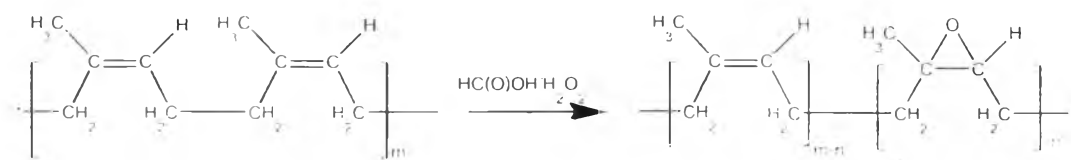


Figure 2.16 Epoxidation reaction of natural rubber latex.

Degree of epoxidation is controlled by temperature, reaction time and content of acid and peroxide. Saendee and Tangboriboonrat [17] prepared ENR from reaching NR latex, with 85% formic acid and 30% aqueous solution of hydrogen peroxide at 50°C and studied effect of reaction time on degree of epoxidation in a range from 4 to 24 hr. They found that mole percent of epoxide in the synthesized ENR was increased with increasing reaction time, as shown in Figure 2.17.

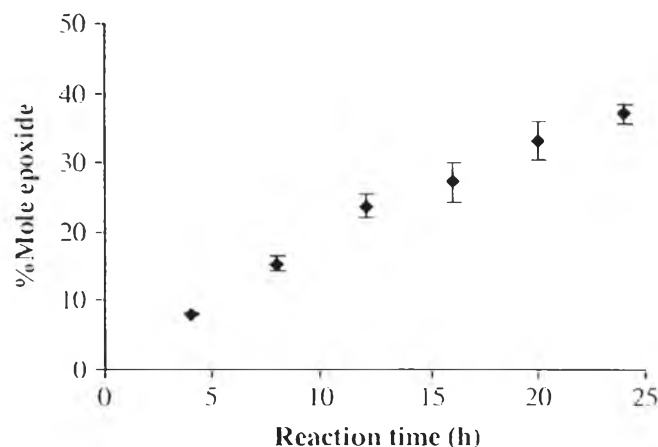


Figure 2.17 Mole percentage of epoxide in synthesized ENR at various reaction times [7].

The nature of the ring-opening products depends on an initial degree of epoxidation. At low modification levels, the majority of epoxy groups are isolated, due to the randomness of the epoxidation reaction. The major ring-opening products are those expected from simple olefin chemistry, e.g., hydroxyl-acetates, diols and inter-molecular ethers [42]. The free volumes of chain phases are decreased whereas the density and polarity of the derivative are increased, which provides ENR with high thermal properties, oil and organic solvent resistance. Johnson and Thomas [6] studied effect of degree of epoxidation on transportation of aliphatic hydrocarbons in ENR with 25 mol% of epoxide (ENR25), and 50 mol% of epoxide (ENR50), in comparison with NR. They found that the maximum solvent uptake value decreased in order NR>ENR25>ENR50, due to decreasing of chain flexibility. This reflects an improvement of solvent resistance with the increase of degree of epoxidation. It is note that the transportation behavior of small molecules in ENR is adjusted by chain flexibility, which leaded to mole percent of epoxide.

2.2.2. Crosslinking of ENR

To improve mechanical properties of rubber materials for commercial applications, the rubber chains are crosslinked to generate a network structure with strong mechanical properties. NR is commonly cured by a chemical vulcanization using sulfur [43]. In addition, curing of NR are possibly initiated by dicumyl peroxide [44] and radiations, such as electron beam [45], γ rays [46], UV radiation, and ultrasonic wave [47].

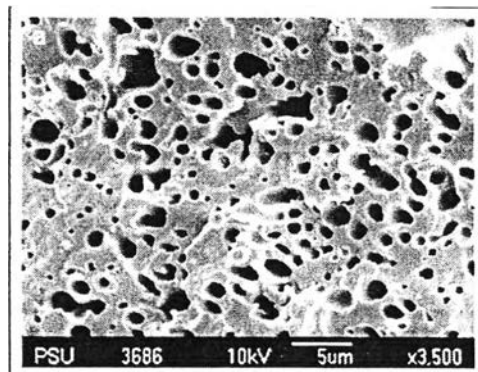
Similar to NR, sulfur or peroxide formulations can be employed to crosslink ENR by reacting with the double bonds. However, the residual acidity of ENR should be neutralized (pH about 10) to optimize scorch time, caused by acid group presents possibility of crosslinking with the epoxide group while mixing [47]. Crosslinking of ENR can be achieved by various crosslinking agents that can react with its epoxide group, such as amines [48, 49], phosphorus [50], carboxylic acids [51], and alcohol derivatives [52, 53]. Effects of crosslinking agents, i.e. 2-ethylhexyl acrylate (EHA), 1,6-hexanediol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA) and aliphatic polyurethane acrylate, on mechanical properties of PVC/ENR blends were revealed by Ratnam and Zaman [54]. The authors showed that multifunctional acrylates and oligomers of acrylated PU provided excellent enhancement in mechanical properties of radiation-crosslinked PVC/ENR blends. The highest tensile strength was achieved in PVC/ENR blends with a presence of TMPTA, as a result from miscibility improvement between PVC and ENR phases. Elongation at break of PVC/NBR blends was also improved drastically by the introduction aliphatic polyurethane acrylate, because its chain flexibility enhances toughness of the PVC/NBR blends.

Tanrattanakul et.al. [5] examined the use of neat ENR and crosslinked ENR as toughening agents for Nylon 6 (PA6), in comparison with unmodified NR. It was found that the introduction of NR and uncrosslinked ENR led to a decrease in tensile strength, but a slight increase in elongation at break of PA6. The ENR/PA6 blend exhibited a six-fold improvement of impact strength, compared to that of pure-PA6. In contrast, this property slightly decreased by incorporation of NR. This phenomenon could be explained in terms of blend morphology. Large-sized



particles of NR in PA6 matrix was the cause of its premature failure. Because of the significant improvement in toughness of polymer is compromised with a great loss in strength and stiffness. This can be developed by using crosslinked ENR with phenolic resin as the toughening agent of PA6. The results indicated that the incorporation of the phenolic resin-cured ENR increased tensile properties, but decreased impact strength of the blends, probably because the morphology of ENR was changed from small particles to large patches of rubber after crosslinking, led by fully crosslinking of ENR (Figure 2.18).

Un-crosslinked ENR/PA6



Crosslinked ENR/PA6

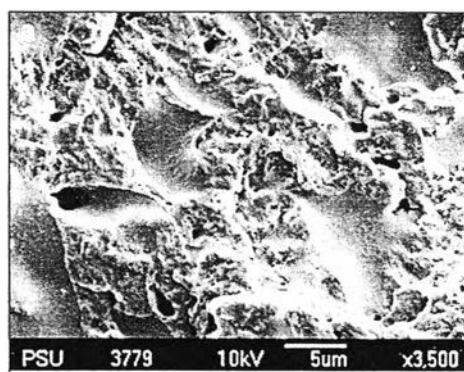


Figure 2.18 SEM micrograph of un-crosslinked ENR/PA6 and crosslinked ENR/PA6 [5].

Flexibility of crosslinked ENR domains can be enhanced by using long chain aliphatic structure (polymer) as its crosslinker. This was verified by Nguyen and

coworkers [9]. The authors used hydroxyl-terminated block-copolymers of poly(lactic acid) and poly(ethylene glycol) as macromolecular crosslinker for ENR, as summarize in Figure 2.19.

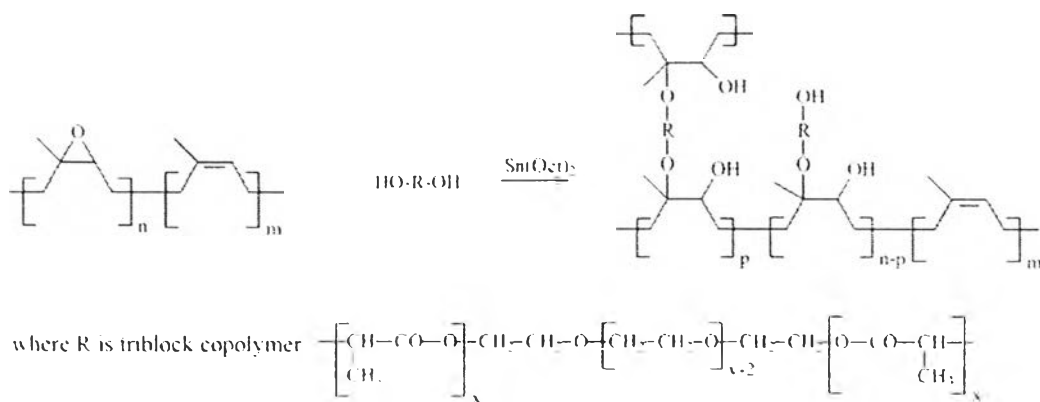


Figure 2.19 Crosslinking reaction of ENR and triblock PLA/PEG copolymers [9].

The cured products exhibited improvement in tensile strength and elongation at break, compared to those of uncured-ENR. Chemical structure and crosslink efficiency of the cured ENR products was investigated by sequential solvent extraction. The three possible structures are obtained, shown in Figure 2.20. The crosslinked structure (Toluene insoluble fraction) is shown in the range of 40 to 60 %.

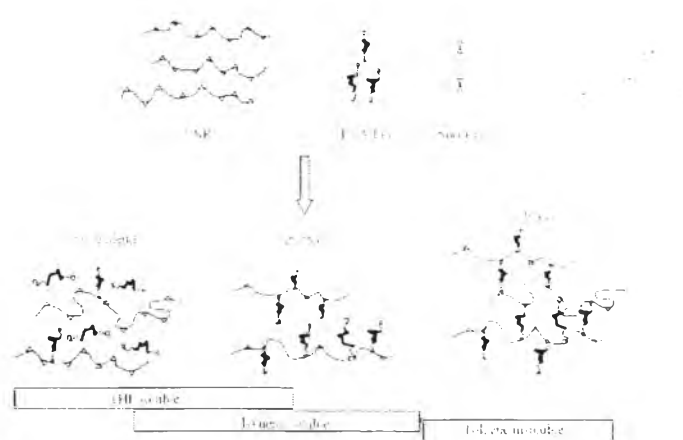


Figure 2.20 Proposed crosslinking reaction of ENR by OH-capped PLA/PEG copolymers, and the possible structures of the products and their solvent solubility.

In addition, gas permeability and selectivity behaviors of the cured ENR were adjustable, where water vapor and carbon dioxide permeability increased with an increase in the copolymer feed content. The opposite trend is observed for oxygen permeability. These cured materials with tunable properties showed high potential for use in membrane applications and as toughening agent for PLA.

2.3. Rubber toughened PLA

Toughness enhancement of PLA is important for many practical applications. In this context, the terms “toughness” and “fracture toughness” denote the physical absorption of energy during a deformation that ends in fracture. In general, the deformation of rubber toughened polymers involves three important stages. [55]

1. elastic deformation, resulting in the generation of stress concentrations around the rubber particles, and (in some cases) cavitation in the rubber particles.
2. plastic strain softening, characterised by local yielding of the matrix, through multiple crazing, extensive shear yielding.
3. strain hardening of the yield zone, a process to which stretching of the rubber phase to very high strains makes a significant contribution, especially when the rubber content is high in specimens containing sharp notches or cracks, strain hardening causes crack blunting and consequent expansion of the yield zone.

Toughening efficiency of polymer are determined by tensile and impact testing. After increasing of rubber, elongation at break and impact strength should be increased. High toughness polymer also determine by SEM micrograph. The incorporation of dispersed rubber particles into a brittle polymer is known to improve its toughness. Toughening mechanism of polymer depends not only on mechanical of polymer matrix, but also type of rubber, dispersion of the rubber (particle size is less than 1 μm), and interfacial adhesion between rubber and PLA matrix. The interfacial adhesion generated from compatibility or miscibility between

rubber and polymer phase. It is generally influenced by several morphological parameters, such as the particle size, particle size distribution, particle volume fraction, particle configuration in the matrix, and matrix ligament thickness (surface-to-surface interparticle distance). However, some of the morphological parameters are interrelated.

Ishida and coworkers [4] studied effect of rubber types, i.e., ethylene-propylene copolymer (EPM), ethylene-acrylic rubber (AEM), acrylonitrile-butadiene rubber (NBR), and isoprene rubber (IR) on tensile properties and impact strength of PLA. Tensile strength of PLA decreased 52% with the incorporation of rubbers (Figure 2.21), where NBR and IR blends exhibited high ability to improve elongation at break of PLA, with 2 times increase for IR. In addition, Izod impact test results exhibited that only NBR can improve the impact strength of PLA, due to the good compatibility between PLA and NBR, which was confirmed by an existence of the smallest rubber particle size (3-4 μm), compared to other 3 rubbers (Figure 2.22-2.23).

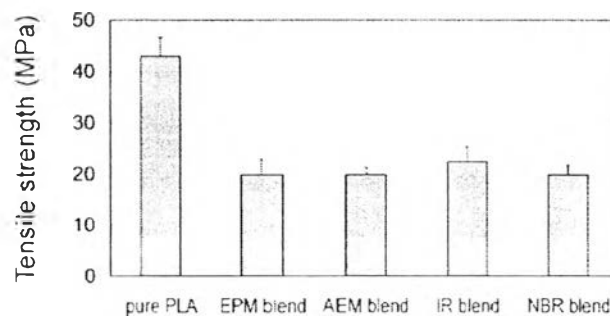


Figure 2.21 Tensile strength of PLA and the blend of EPM/PLA, AEM/PLA, IR/PLA, and NBR/PLA (10%wt rubber content).

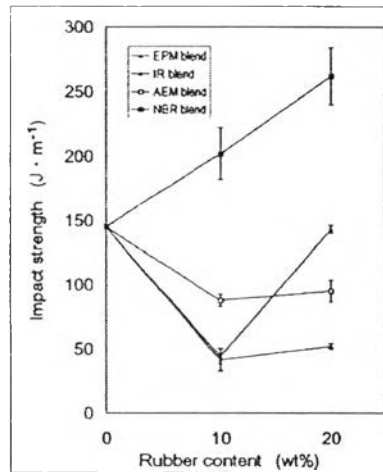


Figure 2.22 Izod impact strength of PLA and the blend of EPM/PLA, AEM/PLA, IR/PLA, and NBR/PLA by various of rubber content.

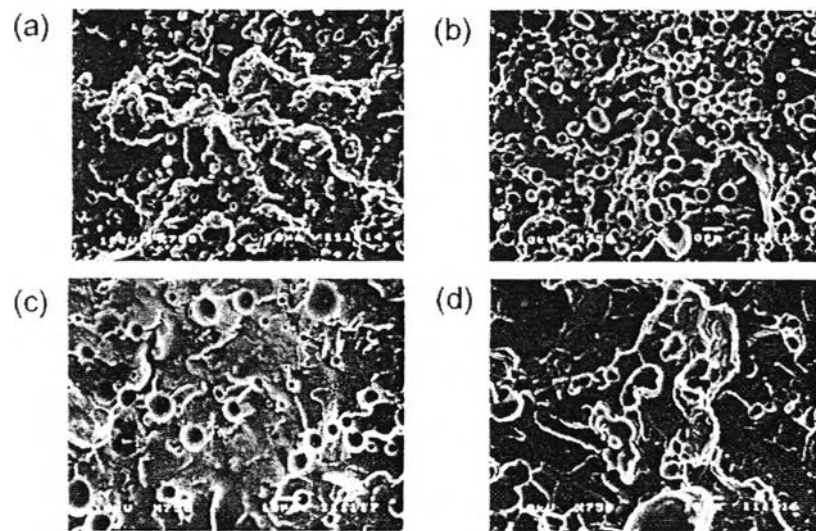


Figure 2.23 SEM micrographs of freeze-fractured surfaces of 10 wt % NBR (a), AEM (b), IR (c), and EPM (d) blends.[4]

Kumar and coworkers [56] studies effect of glycidyl methacrylate (GMA) on mechanical properties and morphology of PLA/PBAT blends. SEM micrograph showed white round particles of PBAT phase distributed within the PLA matrix. The micrographs of impact fractured surface of the blend matrix showed ductile fracture,

which was evident from the presence of more and longer fibrils being pulled out during test, as shown in Figure 2.24.

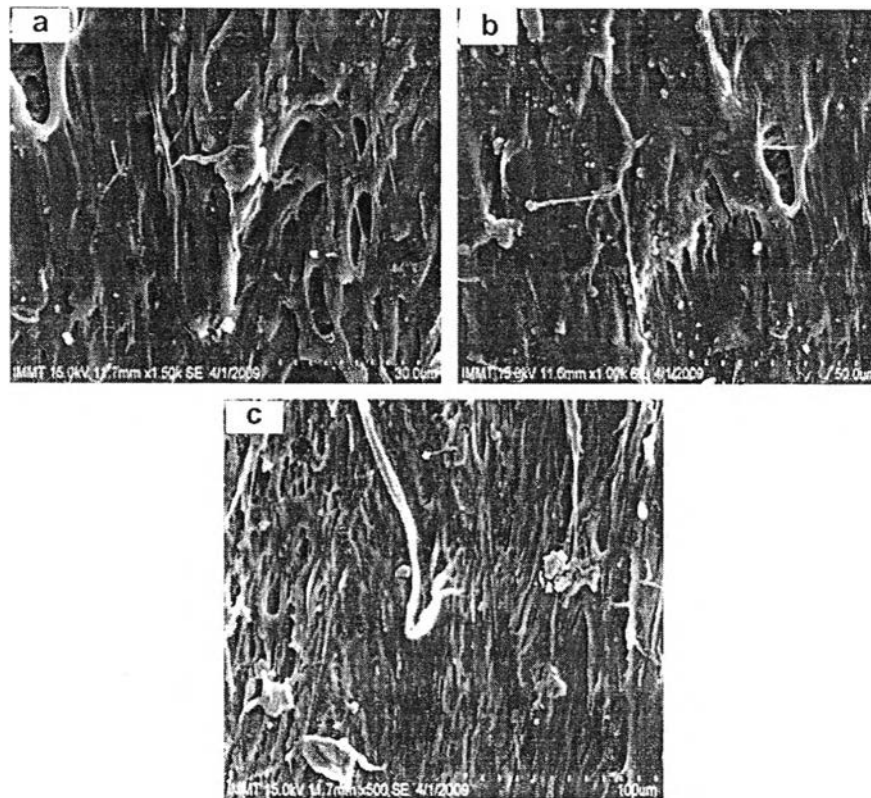


Figure 2.24 SEM micrographs of PLA/PBAT/3%GMA at different magnifications (a) 1,500 (b) 1,000 and (c) 500 X [56].

Kang et.al. [57] developed toughened PLA by compounding PLA with synthetic bioelastomer (BE). The authors suggested two main reasons for the significantly improvement in elongation at break and toughness of PLA. A uniform dispersing of BE particles in PLA, which upon loading absorbs energy, cavitates and induces matrix shear yielding. Molecular entanglements between PLA and BE chains were readily generated due to their affinity. The degree of chain entanglement between blend phases is generally determined by their molecular weight and intermolecular interaction, such as hydrogen bond. When molecules reach a specific chain length longer than a critical one, these would form a coherently entangled

physical network. Figure 2.25 shows SEM micrograph of tensile-fractured surface of a 11.5 vol% BE/PLA blend. This exhibited fibril-like morphology, due to matrix shear yielding, reflecting strong interfacial adhesion between PLA and BE phases. This led to a significant improvement in toughness of PLA. SEM micrograph of the impact-fractured surface of the blend exhibited large cavities and a certain degree of matrix deformation, corresponding to ductile fracture. Voids, randomly distributed as dark spots in the micrograph, elongate along the crack propagation.

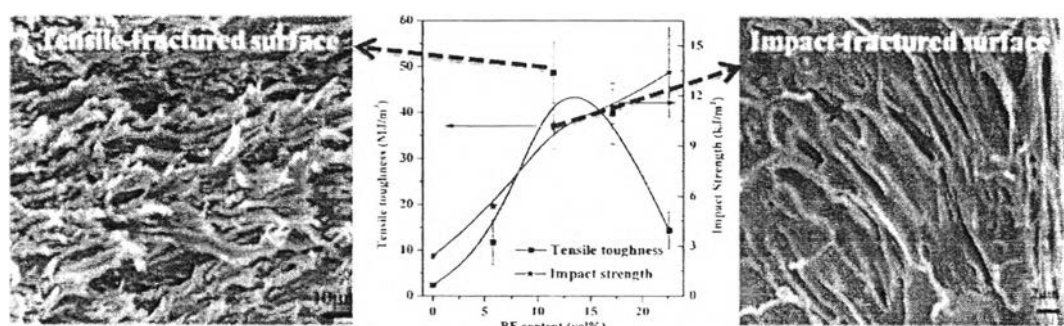


Figure 2.25 Effect of BE content in PLA/BE blends on tensile toughness and impact strength, and their SEM micrograph [57].

According to the advantages of the hydroxyl-terminated block-copolymers of poly(lactic acid) and poly(ethylene glycol) mentioned above, it is in our interest to verify whether the similar results can be achieved with the glycolysed PLA. Therefore, investigation on curing efficiency and crosslink density of ENR with the glycolysed PLA is one of the main objectives of this work. Moreover, feasibility of toughen PLA with the developed cured-ENR is examined.