CHAPTER II
LITERATURE REVIEW

2.1 Bioplastic

2.1.1 Definition

Plastics are generally defined as materials based on polymers, which are long chain molecules, usually containing strings of carbon atoms, together with various additives (such as stabilizers and lubricants) which give them useful processing and performance characteristics. Bioplastics are primarily composed of biopolymers (Eco product agency, 2009). Bioplastics have two definitions according to European Bioplastics. First, plastics based on renewable resources and second, biodegradable polymers which meet all criteria of scientifically recognized norms for biodegradability and compostability of plastics and plastic products (Source: http://www.european-bioplastics.org). Examples of bioplastics are polylactic acid (PLA), polycaprolactone (PCL), polyhydroxybutyrate-covalerate (PHBV), and polyesteramide. They can be made from plants such as canola, soybean, corn and potatoes. Like biomass plastics, bioplastics can also be made from wastes of the food industry, making food production processes more sustainable. Bioplastics are also used to make many different commercial products. Because they eventually degrade, the biopolymers used to make bioplastics have a special role in medicine, as they are used to make sutures as polyesteramide (Phillips, About.com Guide).

Biopolymers or Natural biodegradable polymers are polymers that can be either naturally produced or synthesized from renewable resources, are often biodegradable, and not toxic to produce. Some biopolymers are used as structural materials, food sources, or catalysts. Others have evolved as entities for information storage and transfer. Well-known biopolymers include starch, proteins and peptides, DNA, and RNA (ExcelPlas Australia, 2002).

2.1.2 Type of Biodegradable Polymers

Biodegradable polymers are chemically synthesized or biosynthesized during the growth cycles of all organisms. They are classified into four categories, depending on the synthesis as shown in Figure 2.1. Only three categories are obtained from renewable resources or bio-based resources. Remainder category is produced from fossil resources petroleum-based resources.

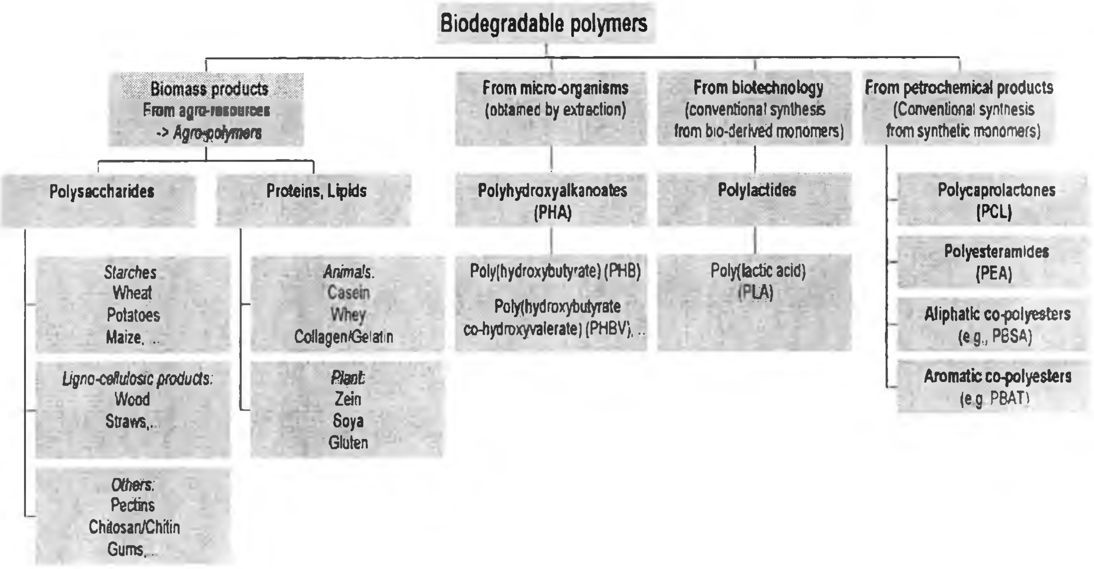


Figure 2.1 Classification of the biodegradable polymers (Bordes *et al.*, 2009).

2.1.2.1 Polymers from Biomass Products

Polymers from biomass or from agro-resources are generally classified into three groups as follows (Bordes *et al.*, 2009).

- Polysaccharides

Polysaccharides are polymeric carbohydrate structures, formed of repeating units (either mono- or di-saccharides) joined together by glycoside bonds. These structures are often linear, but may contain various degrees of branching. Polysaccharides are often quite heterogeneous, containing slight modifications of the repeating unit. Depending on the structure, these macromolecules can have distinct properties from their monosaccharide building blocks. They may be amorphous or even insoluble in water.

When all the monosaccharide in a polysaccharide is the same type the polysaccharide is called a homopolysaccharide, but when more than one type of monosaccharide is present they are called heteropolysaccharide (Varki *et al.*, 2008).

Examples include storage polysaccharides such as starch and glycogen, and structural polysaccharides such as cellulose and chitin.

2.1.2.2 Polyesters Produced by Micro-organism or by Plants

Some polyester is synthesized by certain bacteria such as metabolites which in this way ensure energy stock. Certain bacteria can accumulate up to 80% of their dry weight before auto-hydrolysis (Braunegg, 2002). In this category are found polyhydroxyalkanoate (PHA), polyhydroxybutyrate (PHB), and poly(hydroxy-butyrate-hydroxyvalerate) (PHB/HV). These polymers are polyesters (Smith, 2005).

2.1.2.3 Polyesters Synthesized from Bio-derived Monomers

Polylactic acids or Polylactide (PLA) are terms used to indicate the same biodegradable aliphatic polyester (Moore and Saunders, 1997). The difference in terminology indicates simply the synthesis method chosen to produce the polymer from lactic acid (Smith, 2005).

2.1.2.4 Polyesters Synthesized from Fossil Resources

A large number of biodegradable polyesters are based on petroleum resources, obtained chemically from synthetic monomers. The polymers are divided in this section into four groups as follows.

- Polycaprolactones

Poly (ε-caprolactone) (PCL) is usually obtained by the ring-opening polymerization (ROP) of ε-caprolactone in the presence of metal alkoxides (aluminium isopropoxide, tin octoate, etc.). PCL is widely used as a PVC solid plasticizer or for polyurethane applications, as polyols, but it finds also some applications based on its biodegradable character in domains such as biomedicine (e.g., drugs controlled release) and environment (e.g., soft compostable packaging) (Bordes *et al.*, 2009).

- Polyesteramides

Polyesteramide (PEA) is industrially obtained from the statistical co-polycondensation of polyamide (PA 6 or PA 6-6) monomers and adipic acid. The production process is solvent and halogen frees (Rudnik, 2007).

- Aliphatic Co-polyesters

One of the most promising polymers in this family is poly(butylene succinate) (PBS), which is chemically synthesized by the polycondensation of 1,4-butanediol with succinic acid. High molecular weight PBS is generally prepared by a coupling reaction of relatively low molecular weight PBS in the presence of hexamethylene diisocyanate as a chain extender. Poly(butylene succinate adipate) (PBSA) is obtained by addition of adipic acid (Smith, 2005).

- Aromatic Co-polyesters

Aromatic polyesters are formed by the polycondensation of aliphatic diols and aromatic dicarboxylic acids. The aromatic ring gives the polymer an excellent resistance to hydrolysis and to chemical agents. They are difficult to hydrolyses and therefore not biodegradable. For example, polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) are well-known polyesters obtained by polycondensation of aliphatic glycols and terephthalic acid. They can be modified by the addition of hydrolysis sensitive monomers (ether, amide or aliphatic groups) giving a family of biodegradable polyesters. Aliphatic-aromatic polyesters are formed by the polycondensation of aliphatic diols and a mix of aliphatic and aromatic dicarboxylic acids. Commercially available polyesters obtained by modification of PBT (polybutylene terephthalate) with aliphatic dicarboxylic acids areformed polybutylene succinate terephthalate (PBST) (Rudnik, 2007).

2.1.3 Application of Bioplastics

Bioplastics are used in many fields such as biomedical, agricultural, and consumer goods packaging. The packaging field (e.g. plastic bag, film, food container, and straws) trends to be increasing because of their biodegradability. The application of bioplastics (based on types of biopolymer) is shown in Table 2.1.

Table 2.1 Application of bioplastics

Group of biopolymers	biopolymers	Application
Polysaccharides	Starch	Foams (for the loose-fill foam market), films (for agriculture, e.g. mulch films), shopping bags, and mouldable products (pots, cutlery, fast food packaging) (Rudnik, 2007).
	Cellulose	Widely use in form of cellulose esters. For example; enteric coatings, hydrophobic matrices, and semi permeable membranes for applications in pharmacy, agriculture, cosmetics, thin films, containers, handles, optical applications, automotive applications, toys, writing instruments, electric insulation films, lights and casings (Rudnik, 2007).
	Chitin	Biomedicine, waste water treatment, functional membranes and flocculation (Rudnik, 2007).

Proteins	Gelatine	Gelling agent in food, pharmaceuticals, photography, and cosmetic manufacturing. (Smith, 2005).
	Casein	The manufacture of adhesives and the packaging industry for breweries, wineries and refrigerated products (Smith, 2005).
	Wheat gluten	Adhesives, coatings, cosmetics (Rudnik, 2007).
Lipids	Plant oils including castor oil and animal fats	Produce polyolefins, polyurethane, polyesters, polyethers or polyamide resins (Smith, 2005).
Polyesters produced by micro-organism or by plants	Poly-3-hydroxybutyrate (PHB)	Films and paper coatings; other possible markets include biomedical applications, therapeutic delivery of worm medicine for cattle, and sustained release systems for pharmaceutical drugs and insecticides (Garthe, 2009).
	Polyhydroxyalkanoates (PHA)	Cosmetics containers, disposable articles, medical implants, paper coating (Rudnik, 2007).
Polyesters synthesized from bio-derived monomers	Polylactic acid (PLA)	Packaging and paper coatings; other possible markets include sustained release systems for pesticides, mulch films, and compost bags (Garthe, 2009).

2.2 Polylactic Acid (PLA)

2.2.1 History

PLA was first synthesized over 150 years ago but due to its instability in humid conditions, no immediate application was found and it was not until the 1960s that its usefulness in medical applications became apparent.

Efforts to develop PLA as a commodity plastic were first made in the late 1980s and early 1990s by DuPont, Coors Brewing (Chronopol) and Cargill. All three companies ran large research and development programs to explore the possible bulk applications for lactic acid, lactide and PLA. While DuPont and Chronopol terminated their efforts, Cargill went on to develop a continuous process for high purity lactide production based on reactive distillation.

The development of PLA for bulk applications began in 1994 when Cargill first produced PLA in its 6000 t.p.a. semi-works plant in Savage, Minnesota, U.S. In 1997, Cargill and Dow Chemical formed a joint collaboration agreement to explore the market potential for PLA. In January 2000 the joint venture Cargill Dow LLC was formed for the purposes of reaching commercial-scale production of PLA and developing the market for PLA products (Wolf, 2005). A plant recently built in North America with a capacity of 1.4 million tons per year. It is sold under the trade name Natureworks^{TM} (Vink *et al.*, 2002). A much lower capacity of PLA production can be found at Boehringer, Galactic and Shimadzu (Smith, 2005).

2.2.2 Raw Material

PLA is prepared from lactic acid. Lactic acid (2-hydroxypropionic acid) is one of the simplest chiral molecules and exists as two stereo isomers, L- and D-lactic acid as shown in Figure 2.2.

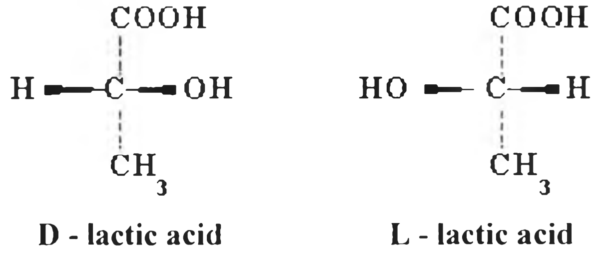


Figure 2.2 L - and D - lactic acid. (Source: http://www.lactospore.com/back.htm).

Lactic acid used in the preparation of PLA is annually derived from renewable resources. Cargill Dow uses sugar from corn as feedstock, due to its low cost and abundance, but it is envisaged to use local plant sources containing starch, or sugar, such as wheat, sugar beets or agricultural waste (Rudnik, 2007).

2.2.3 Production

2.2.3.1 Cassava Starch Production

- Starch Content of Cassava

The International Starch Institute has demonstrated for the first time on the industrial scale, that tapioca starch can be produced with the same purity and yield as that used by the potato starch industry. Both potato and tapioca starches are tuber starches, and their properties are excellent as food starches. The manufacture of identical quality specifications can be produced and thus new opportunities for the application of tapioca starch in high-end foods is now possible. Cassava harvest can take place most of the year with less manufacturing and reduced storage costs. These results of tapioca starch give a competitive advantage over the use of potato starch in many applications.

- The Occurrence of Starch

Starch makes up the nutritive reserves of many plants. During the growing season, the green leaves collect solar energy. In plants with tuberous roots, this energy is transported as a sugar solution down to the tubers, and it is down there, that the sugar is converted to starch in the form of tiny granules occupying most of the cell interior.

The conversion of sugar to starch takes place by means of enzymes. Then, the following spring, enzymes are also responsible for the re-conversion of starch to sugar, which is transported upwards as energy for the growing plant.

- Cassava Roots

The cassava plant is cultivated in most equatorial regions and is known by many names as shown in Table 2.2.

Table 2.2 Various names of cassava in different region

Region	**Name**
Indonesia	Ubi kettella Kaspe
South America	Manioca Yucca Mandioca Aipim
Africa	Manioc Cassava
India	Tapioca
Thailand	Cassava

The plant grows to a height of 1 – 3 m and several roots may be found on each plant. Manioc prefers a fertile sandy-clay soil. There are many varieties of cassava, but they fall into two main categories, namely bitter and sweet cassava (Manihot yanohy and Manihot aipi), depending on their content of yanohydrins. For industrial purposes bitter varieties are most frequently used because of their higher starch content. Sweet cassava is preferred for food because of its taste and dough forming ability. It pounds well. A typical composition of the root is presented in Table 2.3.

Table 2.3 Composition of cassava

Content	% weight
Moisture	70
Starch*	24
Fibre	2
Protein	1
Other	3

*Starch content may be as high as 32%.

- Starch Production

Fresh tubers are processed during season and dry chips during the off-season in some countries. Extraction of starch from fresh cassava roots (Figure 2.3) can be divided into five main stages: preparation (peeling and washing), rasping/pulping/grating, purification (starch washing), dewatering and drying, and finishing (milling and packaging).

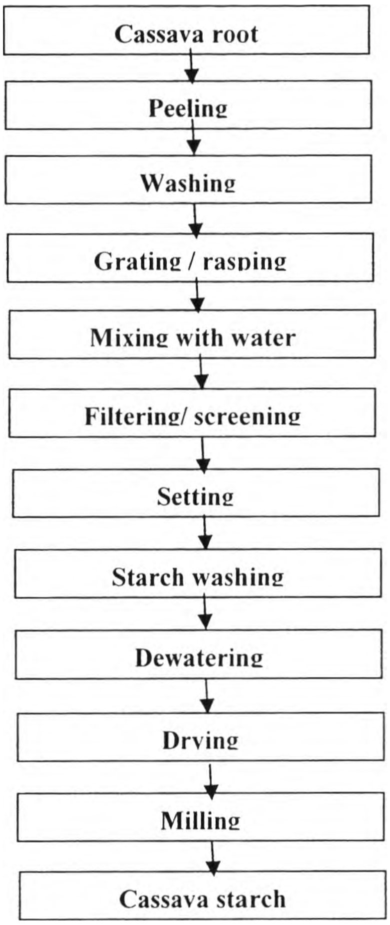


Figure 2.3 A simple process for cassava starch production.

For cassava, the process of starch extraction is relatively simple as there are only small amounts of secondary substances, such as protein, in the roots. When cassava roots are harvested or selected for starch extraction, age and root quality are critical factors. Cassava roots need to be processed almost immediately after harvest, as the roots are highly perishable and enzymatic processes accelerate deterioration within 1 – 2 days. A first-rate quality starch can be obtained from cassava using only water, and this makes the processing of cassava starch and flour particularly suitable for developing countries and rural industries (Integrated Cassava Project).

2.2.3.2 Dextrose Production

Two methods for starch hydrolysis are used today for the commercial production of glucose: acid hydrolysis and partial acid hydrolysis followed by an enzyme conversion. Acidification is the conversion of starch into glucose sugar by acid hydrolysis. This operation is carried out in batches or a continuous process. In the first process, the starch slurry is mixed with hydrochloric acid (sulfuric acid is sometimes used) to bring the pH to around 1.8 – 2.0 in a steam converter and heated to about 160 °C until the desired dextrose equivalent (DE) is reached. The continuous process, which is replacing the batch process, involves feeding the mixture of starch slurry and hydrochloric acid into a tubular heat-exchanger. The time and temperature of the process are adjusted to the desired DE in the end product. In the next step, neutralization, the acidified mixture is neutralized with sodium carbonate or soda ash to remove the free acid and bring the pH value to 5.0 – 7.0. Sodium chloride is formed in the syrup in small quantities as a result of the neutralization of the hydrochloric acid by the sodium carbonate and remains in solution. Some solids include impurities, precipitated protein and coagulated fat can be removed by centrifugal separation. Impurities will depend largely on the starch used and its purity. The solution is then passed through filters (filter presses or candle type ceramic filters).The clear brown filtrate is decolorized by passing it through tanks of activated carbon, which removes colors and other impurities from the solution by surface adsorption but has no effect on the sugar. Refining can be done by ion change resins instead of activated carbon or combined with it. A recent development is to refine the converted liquor by electro dialysis, and the final glucose syrup is very superior. Concentration is the final step. The refined syrup is concentrated under vacuum in batch converters or continuous heat exchangers until the concentrated syrup reaches 80 – 85 percent solids. Commercial glucose syrups are sold according to the Beaumé standard, which is a measure of the dry substance content and specific gravity. Glucose syrup is transported in drums or in bulk road or rail tanks. It should not be stored in large quantities for long periods of time because its color may deteriorate. In the acid-enzyme process the starch slurry is treated by acidification, neutralization and filtration as in the acid hydrolysis process and then is fed into the enzyme converter. The temperature and pH are adjusted to the optimum conditions and the enzyme is added with slow agitation. The time of conversion depends on the initial dextrose equivalent obtained by acid hydrolysis, the type and strength of the enzyme and the final DE required. After the conversion has been completed, the enzyme is rendered inactive by raising the temperature and adjusting the pH, and the converted syrup is then refeed and concentrated in the same manner as in the acid-converted glucose syrup. The use of certain enzymes results in DE values as high as 98 – 99 which means a higher yield of dextrose from starch, or nearly complete conversion of starch into dextrose. When acid is used as the hydrolyzing agent, the DE of the conversion liquor, however, reaches only about 92 because a certain degree of polycondensation takes place and some of the yield of dextrose is lost owing to the acidity and high temperatures required for the conversion.

At present most of the dextrose in commerce is prepared in the form of pure dextrose monohydrate by a combined acid-enzyme process. The hot, thick glucose syrup with a concentration of 70 – 80 percent dextrose is run from the evaporator into crystallizing pans. Crystal formation is largely controlled by the quantity of dextrin left with the glucose. The separation of crystals from the syrup is carried out in centrifugal separators and the impurities are left in the mother liquor. Crystalline dextrose is then dried in rotary hot-air driers under vacuum and bagged in moisture-proof materials. Recrystallization of dextrose will yield practically 100 percent pure dextrose crystals which are used as a pharmaceutical-grade sugar. The starch used in the manufacture of glucose syrup must be as pure as possible with low protein content (particularly soluble protein). In this respect, cassava starch can be preferable to other starches. There is an increasing interest in manufacturing glucose syrup directly from starchy roots or grains rather than from the separated starch in order to save on capital investments for the production and purification of starch from such raw materials. The starch conversion industry (glucose and dextrose) is the largest single consumer of starch, utilizing about 60 percent of total starch production. Glucose syrup and crystalline dextrose compete with sucrose sugar and are used in large quantities in fruit canning, confectioneries, jams, jellies, preserves, ice cream, bakery products, pharmaceuticals, beverages and alcoholic fermentation. The functional purpose of glucose and dextrose in the confectionery industry is to prevent crystallization of the sucrose; in the bakery products industry it is to supply ferment-able carbohydrates; and in the ice-cream, fruit-preserves and similar industries it is to increase the solids without causing an undue increase in the total sweetness, thus emphasizing the natural flavor of the fruit, and also to prevent the formation of large ice crystals which mar the smooth texture. In general, glucose and dextrose are used in the food industry as a partial or complete substitute for sucrose. The use of dextrose has increased in recent years in the food-processing industries (FAO).

2.2.3.3 Lactic Acid Production

After dextrose production, lactic acid is produced by fermentation of dextrose received from wet mill process. Wet mill process combines dextrose and other media, adds microbial inoculums, and produces crude lactic acid. Various microorganisms are use to ferment starch and cellulosic materials as shown in Table 2.4.

Table 2.4 Important starchy and cellulosic materials used for the production of lactic acid (John *et al.*, 2009)

Raw material		Microorganisms	Lactic acid yield	References
Starchy	Wheat starch	*Lactococcus lactis* ssp. *lactis* ATCC 19435	0.77 to 1 g/g substrate	Hofvendahl et al., 1999
	Whole wheat	*L. lactis* and *Lactobacillus delbrueckii*	0.93 to 0.95 g/g substrate	Hofvendahl and Hahn-Hagerdal, 1997
	Barley	*Lactobacillus casei* NRRL B-441	0.87 to 0.98 g/g substrate	Linko and Javanainen, 1996
	Wheat bran	*L. amylophilus* GV 6	>0.90 g/g substrate	Vishnu et al., 2002; Altaf et al., 2006; 2007a, b
	Cassava bagasse	*L. delbrueckii* NCIM 2025, *L. casei*	0.90 to 0.98 g/g substrate	Rojan et al., 2005; John et al., 2006a,b,c; 2007
	Corn, rice, wheat starches	*Lactobacillus amylovorus* ATCC 33620	<0.70 g/g substrate	Xiaodong et al., 1997
	Potato starch	*Rhizopus oryzae*, *R. arrhizus*	0.87 to 0.97 g/g substrate	Huang et al., 2005
	Corn starch	*L. amylovorus* NRRL B-4542	0.935 g/g substrate	Nagarjun et al., 2005
	Wheat and rice bran	*Lactobacillus* sp.	129 g/1	Yun et al., 2004
	Agroindustrial starchy waste	*Enterococcus faecalis* RKY1	~0.93 g/g substrate	Oh et al., 2005;
Cellulosic	Cellulose	*L. bulgaricus* NRRL B-548	>80 g/l	Venkatesh, 1997; Abe and Takagi 1991
	Corncob	*Rhizopus* sp. MK-96-1196	90 g/l	Miura et al., 2004
	Wood	*Rhizopus oryzae* NRRL 395	>0.85 g/g substrate	Woiciechowski et al., 1999
	Waste paper	*Rhizopus oryzae*	>0.8 g/g substrate	Park et al., 1998
	Wood hydrolyzate	*Enterococcus faecalis* RKY1	~0.9 g/g	Wee et al., 2004
	Cellulose	*Lactobacillus coryniformis* ssp. *torquens* ATCC 25600	0.89 g/g cellulose	Yanez et al., 2003; 2005
	Pretreated wood	*Lactobacillus delbrueckii*	48-62 g/l	Moldes et al., 2000

Table 2.4 also shows yields of lactic acid which are provided from different microorganisms. Focus on lactic acid that is produced from cassava. Cassava gives lactic acid yield 0.90 – 0.98 g/g substrate by using L. Delbrueckii NCTM 2025 and L. casei.

2.2.3.4 PLA Production from Lactic Acid

Two main routes have been developed to convert lactic acid to high molecular weight polymer: fist, the indirect route via lactide, the product of which is generally referred to as PLA and second, direct polymerization by polycondensation, producing PLA. Both products are generally referred to as PLA.

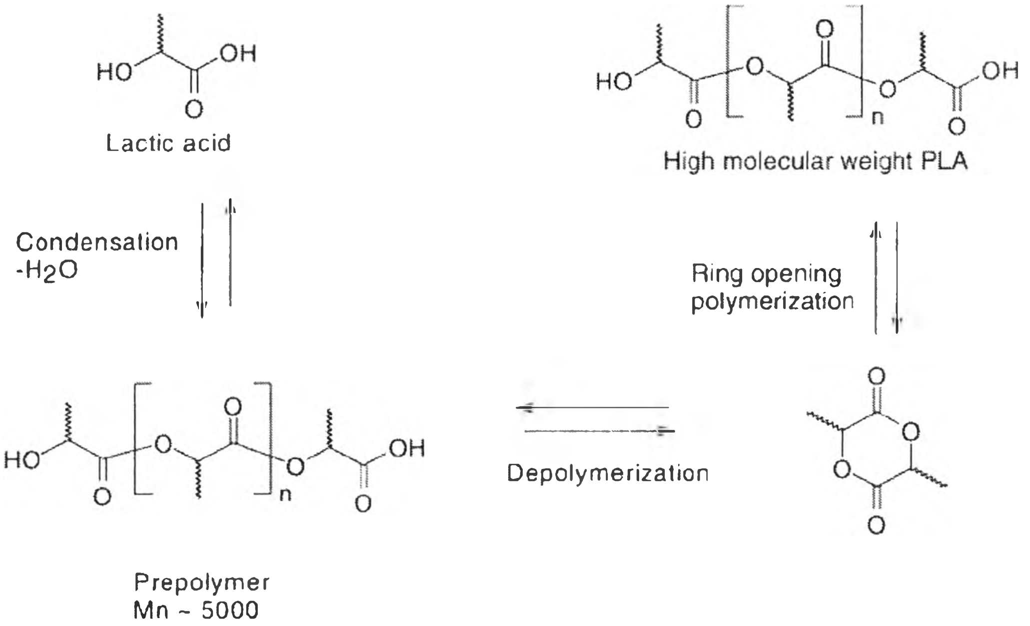


Figure 2.4 Cargill route to lactic acid (Gruber, 2004).

The first route, employed by Cargill Dow, is a continuous process using ring-opening polymerization (ROP) of lactide (Gruber and O'Brien, 2002). Condensation of aqueous lactic acid produces low molecular weight PLA prepolymer (Figure 2.4). The prepolymer is then depolymerized by increasing the polycondensation temperature and lowering the pressure, resulting in a mixture of lactide stereoisomer. An organometallic catalyst e.g. tin octoate is used to enhance the rate and selectivity of the intramolecular cyclisation reaction. The molten lactide mixture is then purified by vacuum distillation. In the final step, high molecular weight PLA (>100000 Dalton) polymer is produced by catalyzed ring-opening polymerization in the melt. Any remaining monomer is removed under vacuum and recycled to the start of the process. By controlling the ROP process chemistry, it is possible to select the stereoform of the lactide intermediate; and thereby also the properties of the resultant PLA. Usually, high purity L, L-lactide is the desired intermediate for the production of PLA (Wolf, 2005).

Figure 2.5 shows the process that is currently in operation at 6000 tons per year market development facility in Minnesota. The construction of 140,000 tons per year commercial-scale PLA plant in North America was recently announced by Cargill Dow LLC for start-up in the fourth quarter of 2001, with plans to construct an addition plant in Europe in the near future.

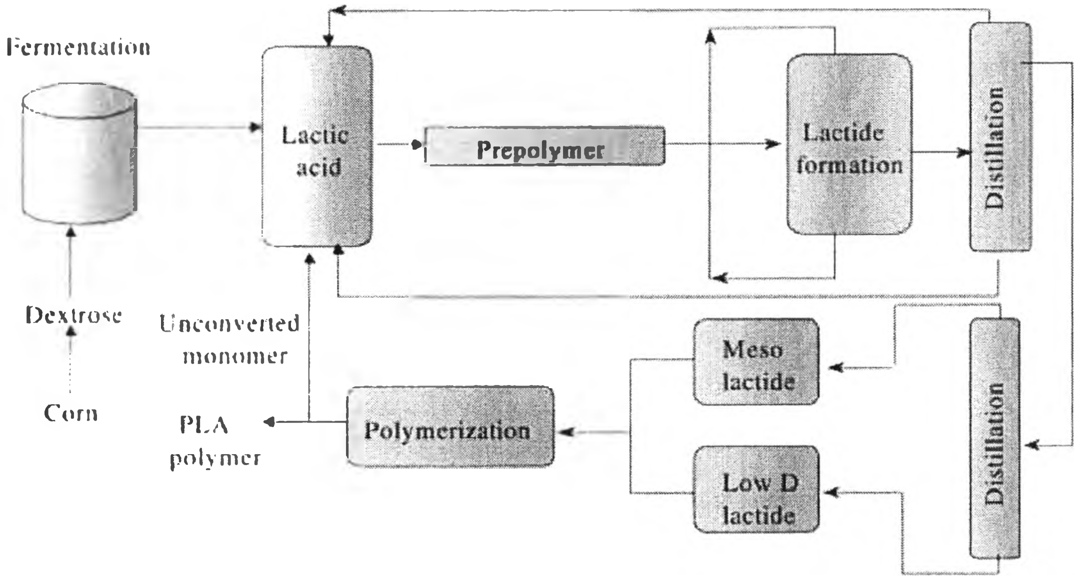


Figure 2.5 Non-solvent process to prepare PLA (Gruber, 2004).

In the second route, used by Mitsui Toatsu, lactic acid is converted directly to high molecular weight PLA by an organic solvent-based process with the azeotropic removal of water by distillation as shown in Figure 2.6 (Wolf, 2005).

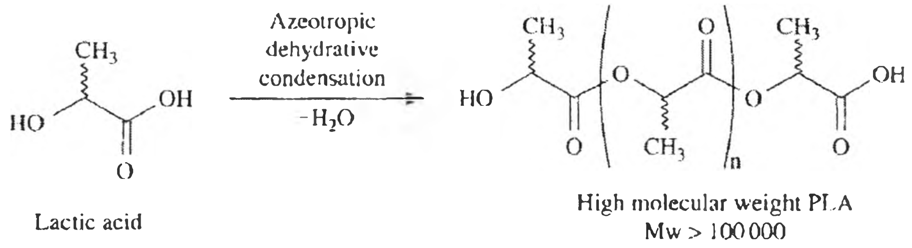


Figure 2.6 Manufacturing route to PLA according to the Mitsui process (Rudnik, 2007).

2.2.4 Applications of PLA

PLA is used in many applications such as commodity, sutures, pharmaceutical, implants, tissue engineering, etc. (Gupta *et al.*, 2007).

Commodity application: To be used in packaging such as plastic bags, bottles, film sheets, etc. and to be used in sport wear.

Sutures application: Surgical sutures are wound closure filaments fabricated in various shapes. The basic requirement of sutures is that they hold tissues in place until natural healing of a wound provides sufficient tissue strength.

Pharmaceutical application: The biodegradability of PLA has inspired several studies on controlled drug delivery systems.

Implants application: Poly (lactic acid) in both L and DL- forms has proved effective as implants and supports in the human body. The material characteristics of the polymer may be altered controlling the molecular weight and the L/DL composition.

Tissue engineering application: The current approach to treatment is based on transplantation. However, tissue engineering is the most fascinating domain of medical technology where patients with organ defects and malfunctions are treated by using their own cells, grown on a polymer support so that a tissue part is regenerated from the natural cells. The great advantages of tissue engineering are that a donor is not required and there is no problem of transplant rejection.

In Thailand, PLA is produced to many products such as zipper bag, carrier bag, T-shirt bag, garbage bag, mulch film, drinking straw, cup, spoon, and fork. Figure 2.7 shows the pictures of these products which are produced from Thantawan and Reangwa Co., Ltd .

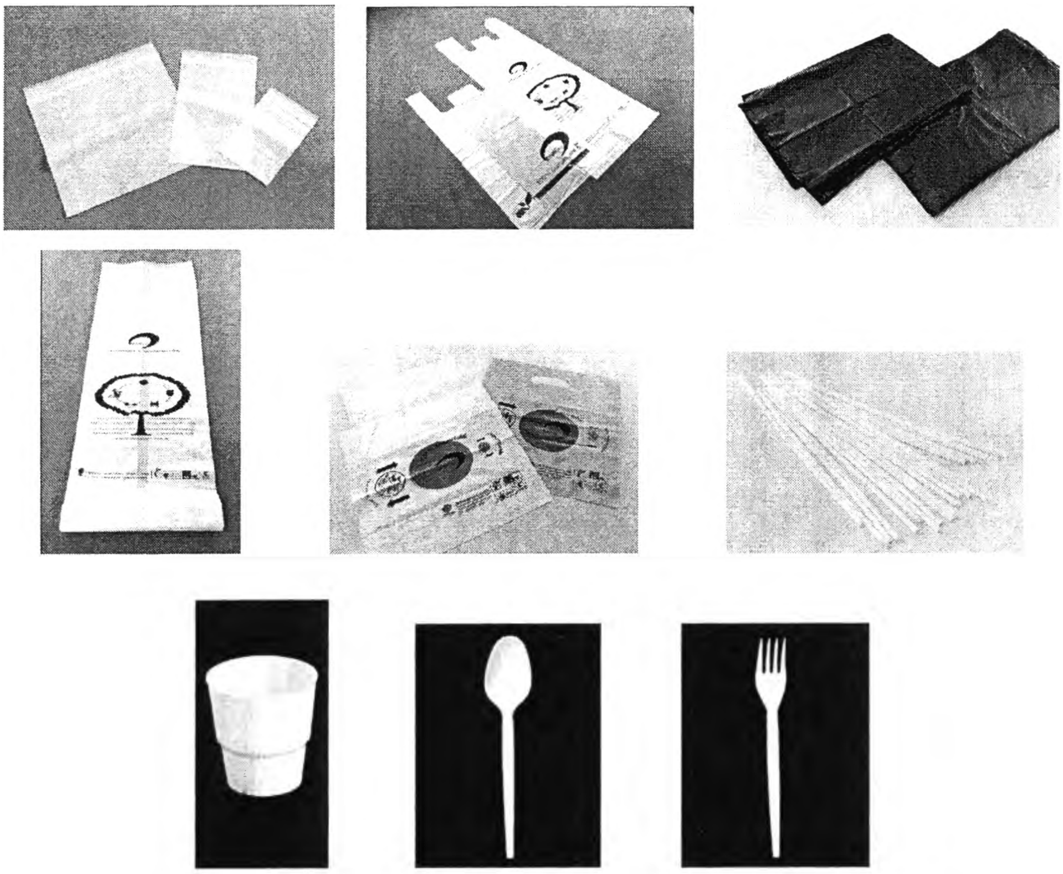


Figure 2.7 PLA products from Thatawan and Reangwa Co., Ltd..

2.3 Polybutylene Succinate (PBS)

2.3.1 History

Normally, succinic acid is used in four application areas. The first is as a surfactant, an additive as a detergent and foaming agent; the second is as an ion chelator for preventing the corrosion; the third is as an acidulate, a pH regulator and flavoring agent in food industry; and the fourth is relative to pharmaceutical products.

However, succinic acid is also a platform chemical used as a precursor of many commodity or specialty chemicals as shown in Figure 2.8.

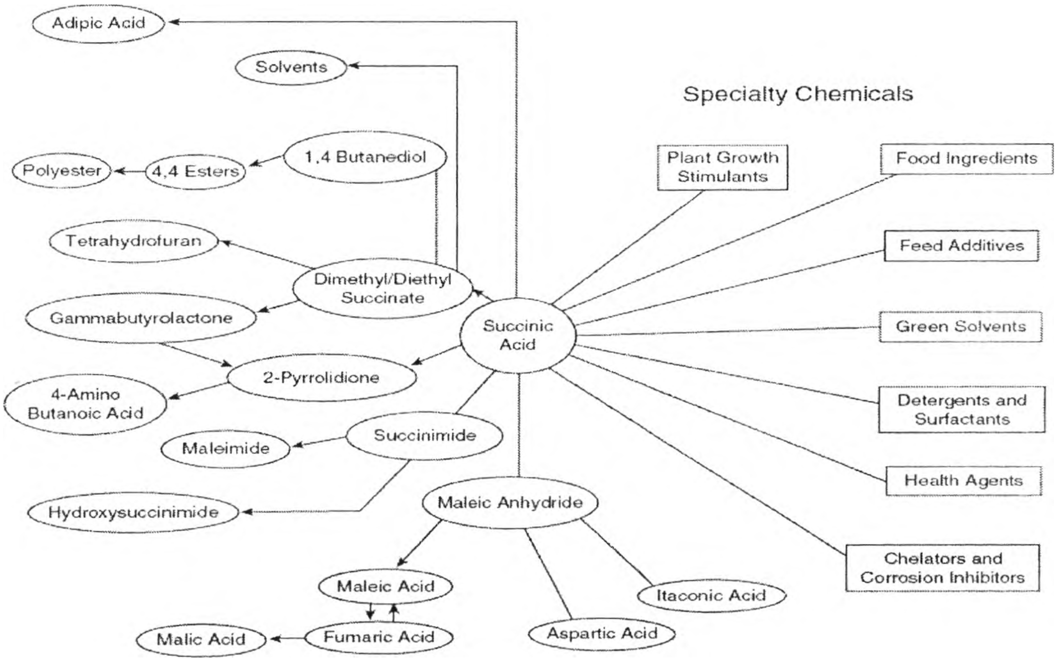
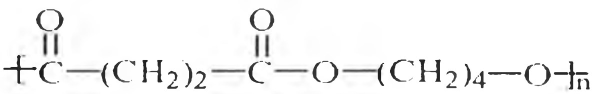


Figure 2.8 Various chemicals and products derived from succinic acid (Zeikus *et al.*, 1999).

At present, succinic acid is being focused by plastic industry to produce polybutylene succinate (PBS) by using succinic acid and 1,4 butanediol (BDO) as precursors. PBS is linear aliphatic polyester with excellent mechanical properties and biodegradability. Its molecular formula is as follows:



$$\left[\overset{\overset{O}{\|}}{C}-(CH_2)_2-\overset{\overset{O}{\|}}{C}-O-(CH_2)_4-O \right]_n$$

The pioneering work on the synthesis of PBS and other aliphatic polyesters was started by Carothers (1931). But because of poor condensation conditions at that time, the PBS obtained was of low molecular weight less than 5,000, and was weak and brittle. In 1993, Showa High Polymer constructed a semiconmercial plant with a capacity of 3,000 tons per year capable of manufacturing high molecular weight PBS under trademark Bionolle, which was synthesized via melt condensation polymerization followed by a chain-extension method. Bionolle is suitable for making films, sheet, filaments, nonwoven fabrics, laminates, molded foam products, and injection-molded products and can be applied in agriculture. Moreover, it still has other trade names from other companies. GS Pla is another trade name of PBS, which is produced by Mitsubishi Chemicals. Mitsubishi Chemicals built a 3,000 ton per year PBS production line and began the practical market in April 2003. Bioamber, a joint venture between US-based DNP Green Technology and France-based ARD (Agro-industrie Recherches et Développements), announces the successful start-up and commissioning of the world's first bio-based succinic acid plant. Since December 2009, the plant has been producing renewable succinic acid from wheat derived glucose. Built on time and on budget, this industrial scale plant has an initial annual capacity of 2,000 metric tons. Bioamber's renewable succinic acid offers higher purity than petroleum derived succinic acid, with the added benefit of consuming CO_2 gas in the production process, giving it a distinct advantage over the traditional petrochemical route.

2.3.2 Raw Materials

Raw materials of polybutylene succinic production are succinic acid and 1,4-Butanediol (BDO). Moreover, succinic acid and 1,4-Butanediol are still used in many applications.

Succinic acid: Succinate is currently used as a surfactant, an ion chelator, and as an additive in the pharmaceutical and food industries. However, this specialty chemical market is relatively small at 15,000 ton/year worldwide (Zeikus *et* *al.*, 1999). The research and development of bio-based succinate production is targeting a much larger commodity chemical market (i.e., 270,000 ton/year; Willke and Vorlop. 2004). Zeikus *et al.* (1999) described a $15 billion market of bulk chemicals that could be produced from succinate as an intermediary feedstock.

BDO: The US demand for BDO (equaling production plus imports minus exports) increased from 318,000 ton in 1999 to 408,000 ton in 2004, and it is projected to reach 479,000 ton in 2008. BDO's price has also increased from $2.20/kg (1999) to $2.76/kg (2004). Fifty-one percent of BDO is used to make tetrahydrofuran (THF); 20% is used to make γ-butyrolactone (GBL); whileanother 20% is used to make polybutylene terephthalate high-performance resins for the automotive and electronics industries. BDO can be produced from succinate in a two step process (Paster *et al.*, 2003).

2.3.3 Production of Succinic Acid

Succinic acid production can be divided in two categories: petrochemical and fermentation routes.

In term of petrochemical routes, there are several industrial processes for succinic acid production:

(1) Oxidation of paraffins forms a mixture of different carboxylic acids, followed by separation of succinic acid

(2) Catalytic hydrogenation of maleic acid or trans-maleic acid

(3) Electrochemical synthesis from maleic anhydride in a bipolar membrane or nonmembrane cell

(4) Production from acetylene, carbon monoxide, and water catalyzed by [Co $(CO)_4$] in an acid medium under a pressure of 2.94 – 49.03 MPa at 80 – 250 °C

Fermentation production of succinic acid from renewable resources has attracted intense interest in the past decades to lower the dependence on fossil resources and further reduce the price of product. Various micro-organisms have been reported to produce succinic acid such as typical gastrointestinal bacteria and rumen bacteria and some lactobacillus strains (Kaneuchi *et al.*, 1988). Among them, Actinobacillus succinogenes, Anaerobiospirillum succiniciproducens, and Mannheimia succiniciproducens are the most promising strains to produce succinic acid at high yields. A succinogenes variant can produce succinate up to 110 gl^{-1} at yield 83 – 87 wt% if the pH maintained with magnesium (Guettler *et al.*, 1996a. 1996b, 1999). A succinic acid productivity of 3.9 $gl^{-1}h^{-1}$ has been reported for M. succiniciproducens (Lee *et al.*, 2002), which is the highest value that has been reported so far.

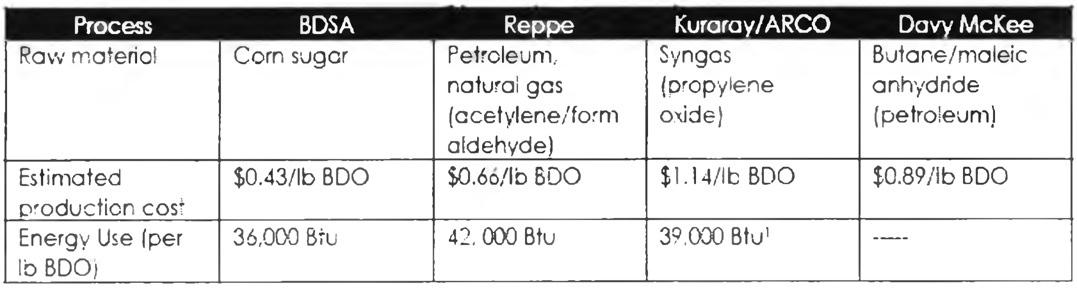
Compared with the chemical process, the fermentation process has advantages of mild condition, independence of the fossil feedstock, and fixation CO_2. Theoritically, succinate fermentation consumes 1 mol of CO_2 per mole of succinate produced: 1 mol of glucose and 2 mol of CO_2 are transformed into 2 mol of succinate. However, the fermentation process has disadvantages: large occupation space of the factory, longer fermentation time, a large demand for water and disposal of the wastewater, complicated separation and purification of the final product (Cukalovic and Stevens, 2008).

The downstream purification of succinic acid is also the key for the fermentation process, which has a cost of about 60 – 70 % of the total bioproduction process (Baniel and Eyal, 1995). The separation and purification of succinic acid from fermentation has been reviewed in the literature (Zeikus *et al.*, 1999). There are many purification ways such as liquid/liquid extraction, simultaneous fermentation and crystallization, electrodialysis acidification and crystallization technology etc. These are mention next topic.

2.3.4 Production of 1,4-Butanediol (BDO)

1,4-Butanediol is an important industrial solvent and raw material for polybutylene terephthalate resins and automotive and electrical parts. The markets for engineered, "stronger-than-steel," plastic has grown rapidly (Zeikus *et al.*, 1999). Most domestic BDO is produced by the Reppe process in which acetylene is reacted with formaldehyde. It can also be produced via propylene oxide or maleic anhydride. An economic analysis of BDO production has shown that the biologically derived succinic acid process (BDSA) has the potential to dramatically decrease production costs of BDO (Table 2.5). Added benefits include reduced materials of construction cost due to the lower corrosivity of succinic acid and lower corrosivity of succinic acid and lower energy requirements. Improvements in separations technology have further reduced process energy needs.

Table 2.5 Economic and Energy Analyses of Multiple Routes to 1,4-Butanediol (Carole *et al.*, 2004)



Process	BDSA	Reppe	Kuraray/ARCO	Davy McKee
Raw material	Corn sugar	Petroleum, natural gas (acetylene/formaldehyde)	Syngas (propylene oxide)	Butane/maleic anhydride (petroleum)
Estimated production cost	\$0.43/lb BDO	\$0.66/lb BDO	\$1.14/lb BDO	\$0.89/lb BDO
Energy Use (per lb BDO)	36,000 Btu	42, 000 Btu	39,000 Btu[1]	-----

The BDSA process produces succinic acid by fermenting glucose sugar from corn, separating and purifying the acid, and catalytically processing it as a platform chemical to produce 1,4-butanediol (BDO) and related products, tetrahydrofuran and γ-butyrolactone; n-methyl pyrrolidinone (NMP) and 2-pyrrolidinone; or other chemicals that are used to make a wide assortment of products. Existing domestic markets for such chemicals total almost 1 billion pounds, or more than \$1.3B, each year. The new process also promises to reduce reliance on imported oil and to expand markets for domestic agriculture to more than food sources.

2.3.5 Synthesis of PBS

2.3.5.1 Tranesterification Polymeriztion

In the transesterification polymerization method, PBS is synthesized by melt polymerization starting from stoichiometric amounts of dimethyl succinate and 1,4-butanediol, or using an excess of 1,4-butanediol not above 10%, in the presence of a catalyst such as tetra-n-butyl-titanate or tetraisopropyl titanate, as shown in Figure 2.9. In this reaction is operated at a temperature ranging from 150 to 190 °C under the nitrogen atmosphere. After most of the methanol and water produced by tranesterification have been distilled off, the polycondensation is operated under a vacuum at high temperature to remove the butanediol formed in the reaction and finally, polymerize the oligomer via tranesterification, PBS with M_n of 59,500 and M_w of 104,100 (Xu and Guo, 2009).

$$HO(CH_2)_4OH + CH_3OOC(CH_2)_2COOCH_3 \rightleftharpoons H[O(CH_2)_4OOC(CH_2)_2CO]_nO(CH_2)_4OH + CH_3OH$$

Figure 2.9 Reaction formula showing polymerization of PBS from dimethyl succinate and 1,4-butanediol.

2.3.5.2 Direct Polymerization of Succinic Acid and Butanediol to Synthesize PBS

Direct melt polymerization can be produce in two ways: one is where the polymerization is finished in the melt of succinic acid and butanediol, which is called "direct melt polymerization" the other method is where the polymerization is finished in the solution of raw materials, which is called "solution polymerization".

In direct melt polymerization, PBS is prepared by using a two-step process. In the first step, esterification takes place at 150 – 200 °C under atmospheric pressure of in a low vacuum. In the second step, polycondensation is followed under a high vacuum at a higher temperature around 220 – 240 °C. To avoid oxidation, both esterification and polycondensation should be conducted in a nitrogen atmosphere.

The keys to obtaining high molecular weight PBS are as follows:

- During the esterification stage, the water formed must be removed from the system
- Esterification must be carried out at the proper temperature.
- A sufficiently high vacuum is required to remove the butanediol and the small amount of water formed in the polycondensation stage.

- Catalysts with high reactivity and that are resistant to hydrolysis must be chosen to improve the molecular weight of PBS and to shorten the reaction time.

Solution polymerization of succinic acid and butanediol to PBS Solution polymerization is a modified method of direct melt polymerization, which dissolves the raw materials in a solvent such as xylene or decahydronaphthalene. The esterification reaction and the condensation reaction in the solvent improve the removal of the small molecular material formed in the reaction process, sp the reaction can be conducted at lower temperature, which can avoid oxidation of PBS, but at the cost of a longer reaction time (Xu and Guo, 2009).

2.3.5.3 Condensation Polymerization Followed by Chain Extension

Chain extension is another method to produce high molecular weight PBS. In this process, the polycondensation conditions are not so critical as those for the direct melt polycondensation. On the other hand, the disadvantage is that incorporation of the chain extender will reduce the biosafety and will affect the biodegradability of the PBS obtained. Consequently, chain-extended PBS cannot be applied as a food-contacting material. The M_w of PBS can reach nearly 300,000 and the M_n can reach nearly 200,000 at the optimal conditions. It was reported by Showa Denko (Japan) (Xu and Guo, 2009).

2.3.5.4 Lipase-Catalyzed Synthesis of PBS

Lipase-catalyzed synthesis of PBS is a recently developed method, which is fulfilled at milder conditions without remnant metal salt. In 2006, Azim *et al.* (2006) reported Candida antarctica lipase B catalyzed synthesis of PBS from the monophasic reaction mixtures of diethyl succinate and 1,4-butanediol. The reaction temperature played an important role in determining the molecular weight of PBS. After polymerization for 24 h in diphenyl ether, PBS with Mn of 2,000, 4,000, 8,000, and 7,000 was produced at 60, 70, 80, and 90 °C, respectively. The low molecular weight was due to precipitation after polymerization for 5 – 10 h, limiting the growth of the polyester chain length. Increasing the polymerization temperature from 80 to 95 °C can result in the maintenance of a monophasic reaction mixture after 21 h, which led to production of PBS with Mw of 38,000 and polydispersity index of 1.39. PBS synthesized by lipase catalyzation has a narrower polydispersity index than that synthesized by the methods described above and has no residual metal. However, at present the former has a lower molecular weight than the latter. In addition, the remaining lipase may cause a problem in the following thermal processing. The future trend will focus on further improvement of the molecular weight and utilize immobilized lipase as a catalyst. Ring-opening polymerization of cyclic monomers, succinic anhydride and tetrahydrofuran, can also be applied for PHB synthesis. Catalyzed by aluminum triflate at 100 °C for 48 h, PBS with M_n of 12,400 was obtained at a yield of 49% (Wang and Kunioka, 2005).

2.3.6 Applications of PBS

PBS decomposes naturally into water and CO_2. In this era of increasing environmental awareness, it is thus attracting attention as a promising eco-friendly alternative to common plastics. The scope of the application fields is growing. So far, PBS has found applications in agriculture, fishery, forestry, civil engineering, and other fields in which recovery and recycling of materials after use is problematic. For example, PBS is actually used as packaging materials, vegetation nets, mulching film, compost bags, *e*tc (Xu and Guo, 2009). Figure 2.10 shows various PBS products.

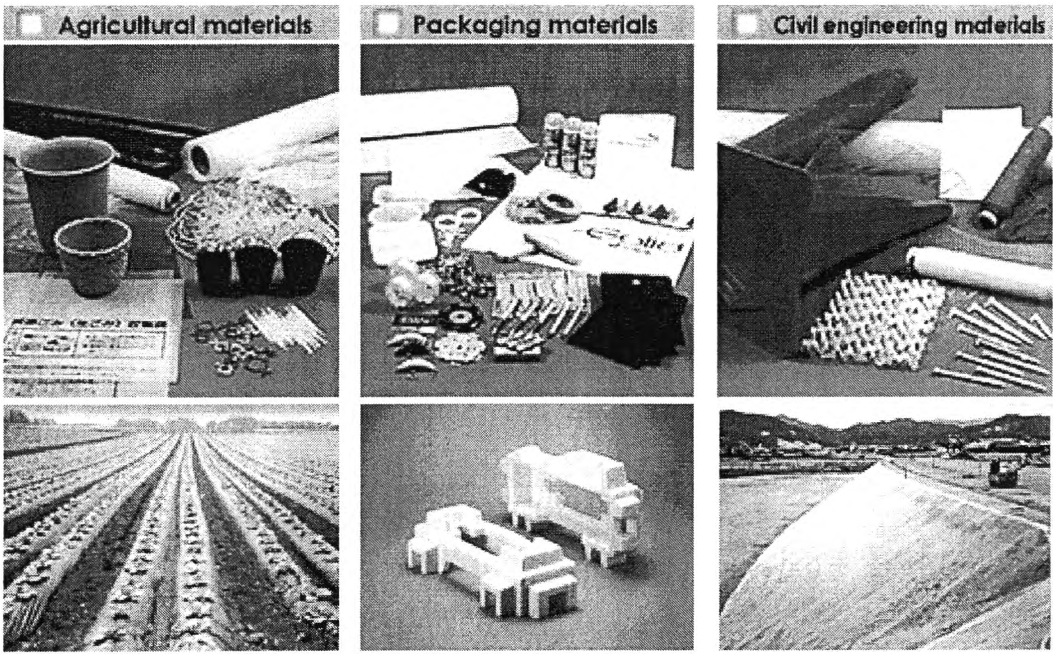


Figure 2.10 PBS products in many applications
(Source: http://www.shp.co.jp/en/bionolle.htm).

2.4 Current Situation of Bioplastics in Thailand

2.4.1 Introduction

The amount of garbage produced in Thailand is constantly increasing, with over 14.4 million tons created in 2003. The main elimination process is landfill-only 11% is recycled. With the situation driving research into developing environmentally friendly new products, there is an increasing interest in biodegradable plastics as one of the potential solutions. This chapter focuses on government and private sector activities in the area of bioplastics, the potential for Thailand's materials and plastic industry, and the current government policy (NIA Roadmap, 2008).

2.4.2 Status of Bioplastics in Thailand

With increasing concern over the amount of garbage produced, both government and private organizations are beginning to support the development of Thailand's bioplastics sector. The National Innovation Agency (NIA) supports the investment, technology acquisition and assessment in bioplastics, The Pollution Control Department has enacted laws to alleviate the garbage problem; The National Metal and Materials Technology (MTEC) supports testing laboratory for biodegradable plastics; and the Thai Bioplastics Industry Association (TBIA) – which was recently initiated to stimulate development of the sector- serves as a national focal point for negotiations with other industrial countries on issues such as collaboration on drafting standards for biodegradable plastics.

In particular, since 2003 NIA has been active in promoting bioplstics, compiling technology and business information on bioplastics from leading countries as well as coordinating with all stakeholder organizations to drive the support infrastructure and policy for the establishment bioplastics industry in Thailand (NIA Roadmap, 2008).

2.4.2.1 Trend of Bioplastic Industry and Production in Thailand

The Thai Bioplastics Industry Association (TBIA) is urging the government to draw up manufacturing standards and assistance measures aimed at promoting the development of more innovative products. So far, there are two types of bioplastics: biodegradable and compostable. Both types are made from a combination of petrochemical and agricultural materials. However, the TBIA reported that Thailand should focus more on bioplastics are made from agricultural materials. For example, Thailand is the world's biggest exporter of cassava, an ingredient in products that help alleviate climate change, such as biofuels. The TBIA mention that the government should encourage the bioplastics industry to become more export-oriented, in order to take advantage of a potentially market. Worldwide bioplastic production is growing rapidly, by an average of 70-80 percent per annum. Moreover, rising oil prices have increased bioplastic consumption, because regular plastic is made mainly from petrochemicals. Global bioplastic consumption is expected to reach 5 million tonnes in 2015, up from 900,000 to 1 million tonnes this year (Insea, 2010). Although oil prices still increase continuously but conventional plastic's price is still lower than bioplastics' price. That is the reason why people still use conventional plastic. The National Innovation Agency (NIA) is to propose a plan to the Finance Ministry that would introduce an environmental tax on oil-based plastics by 2010 in an attempt to encourage consumers to use more biodegradable plastics. The move is a part of the National Road Map for the Development of the Bioplastics Industry, which covers the five years from 2008 to 2012. The measure is designed to boost bioplastics demand in Thailand in line with practices in Japan and several European countries. The government will have to set clear goals and take serious action if it is to encourage the replacement of oil-based plastics with bioplastics and establish a bioplastics industry in the country. The way, that encourage consumer to use bioplastic, is called green tax. Green tax is the environmental tax that will make the price of oil-based plastics higher, plus the trend of environmental concern, manufacturers and consumers will shift to biodegradable plastics instead (Ekvitthayavechnukul, 2009). As previous mention, Thailand has the potential to compete and become a leader in bioplastic production but legislation and funding are needed to boost the scale of production. The data from NIA show that an investment of 70 billion baht across the bioplastic production chain could be a yearly return of 200 billion baht. If compared to other applications, making bioplastic from agricultural products is the most profitable. Cassava can be made into bioplastic with a return of more than 20 baht per kilogram, compared to 25 satang for cassava ethanol. Then Thailand should be exporting finished products, not raw materials. Domestically, building the production facilities requires a large amount of investment while the demand for bioplastics in Thailand is still small (Source: www.bangkokpost.com).

At present, Thailand has LA production plant which belongs to Purac of the Netherland. However, Thailand lacks PLA production plant (PLA is polymerized from LA). This company has realized awareness of Thailand, especially our biomass resources. This includes NatureWorks Company which is interested to build PLA production plant in suitable area such as Thailand, Malaysia, and China (Ekvitthayavechnukul, 2009). Thailand also has policy to expand bioplastic market in Japan which is the major importer of plastic pellets and plastic products. Japan imports goods and plastic products from Thailand at the value of 513.07 million dollar (6.48 percent) so it is possible to expand market to Japan. Thailand has to accelerate the development of bioplastic industry to reach the needs of customers, both domestic and international, and to have measures and policies of environmental management to support the use of products which are environmental friendly.

Since there are currently no bioplastics factories in Thailand, many companies have started importing bioplastics compounds to use the existing plastics processing machinery to produce finished bioplastics products as pilot production for both domestic and export markets. Moreover, some companies have started developing their business to produce bioplastics products as shown in Table 2.6.

Table 2.6 Companies carrying on business relating to bioplastics (NIA, 2008)

Company	**Location**	**Product**	**Technology**
1. Advance Packing Co., Ltd. (Special Tech Group)	Phranakorn Sri-Ayutthaya	Plastic bags for plants	- produced from corn starch - import raw plastic from USA and process in Thailand
2. M.S.V. Trading Ltd., Part	Bangkok	Food container such as plate, bowl, spoon and fork	
3. Bio Green World Co., Ltd. (BGW)	Samut Prakarn	Food container such as Plates, bowls, spoons and cups	- produced from PLA or PLA / starch blend - PLA pellets imported from Taiwan

4. BIOFOAM Jazzy Creation Co., Ltd.	Bangkok	Heat-resistant food packaging (single-use) such as disposable plates, bowls and food trays	- Produced from cassava starch, hot-molded into finished products - Own proprietary technology
5. Biodegradable Packaging for Environment Co., Ltd. (BPE)	Bangkok	Single use food packaging such as disposable plates, bowls and spoons	- Produced from bagasse
6. KU-GREEN: Biodegradable Package	Bangkok	Single use food packaging such as disposable plates, bowls, trays and glasses	- Produced from cassava starch, hot-moulded into finished products - Own proprietary technology
7. Thantawan Industry Public Co., Ltd.	Bangkok	Bag, film	- Import raw plastic from USA and process in Thailand - Development compounding

8. PURAC Thailand	Rayong	Lactic acid	- Produced from molasses or cassava

2.4.3 NIA Pilot Project at Sa-med Island

According to environmental issue, bioplastic is interesting more and more. NIA has also set up a pilot project at Sa-med island in Rayong province to promote the use of bio- plastics in Thailand.

2.5 Disposal Phase

2.5.1 Waste Situation in Thailand

Thailand is currently producing 41,240 ton of waste daily (or about 15 million ton per year). Among this is the plastics waste, making up 20% of the mix, and only 22% of this plastics waste can be recycled or transformed into fuel. As a result, the remaining 2.2 million ton of plastics waste needs to be disposed each year (Pollution Control Dept., 2009). However, bio-plastics will not create such a problem as they can be degraded naturally in the suitable condition, leaving no other residues but carbon dioxide and water. Therefore, bioplastics can be a potential solution to tackle the problem of the overwhelming plastics waste.

2.5.2 Waste Treatment Technology

The main treatment technologies currently used for MSW management were landfill, incineration and anaerobic digestion. About 35% of MSW is sent to sanitary landfill sites whereas only 2% is being treated by other means such as incineration, composting or anaerobic digestion to produce fertilizers or biogas.

2.5.2.1 Sanitary Landfill

Sanitary landfills as shown in Figure 2.11 involve well-designed engineering methods to protect the environment from contamination by solid or liquid wastes. The three basic procedures that are carried out in sanitary landfills are: spreading the solid waste materials in layers, compacting the wastes as much as possible, and covering the material with dirt at the end of each day. This method reduces the breeding of rats and insects at the landfill, reduces the threat of spontaneous fires, prevents uncontrolled settling of the materials, and uses the available land efficiently.

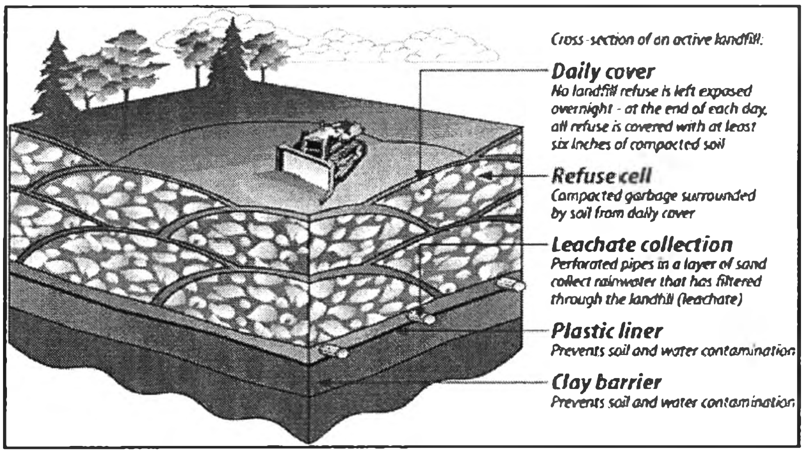


Figure 2.11 The sanitary landfill
(Source: http://www.blueenvironmental.com/landfill.html).

2.5.2.2 Incineration

Incineration is the thermal destruction of waste. It can be adapted to the destruction of a wide variety of wastes. This includes but is not limited to household wastes, often referred to as municipal wastes, industrial wastes, medical wastes, sewage, Superfund soils and liquids, and the hazardous wastes (liquids, tars, sludges, solids, and vent fumes) generated by industry. The major benefit of incineration is that the process actually destroys most of the waste rather than just disposing of or storing it. Figure 2.12 shows waste incineration, which involves the application of combustion processes under controlled conditions to convert waste materials to inert mineral ash and gases.

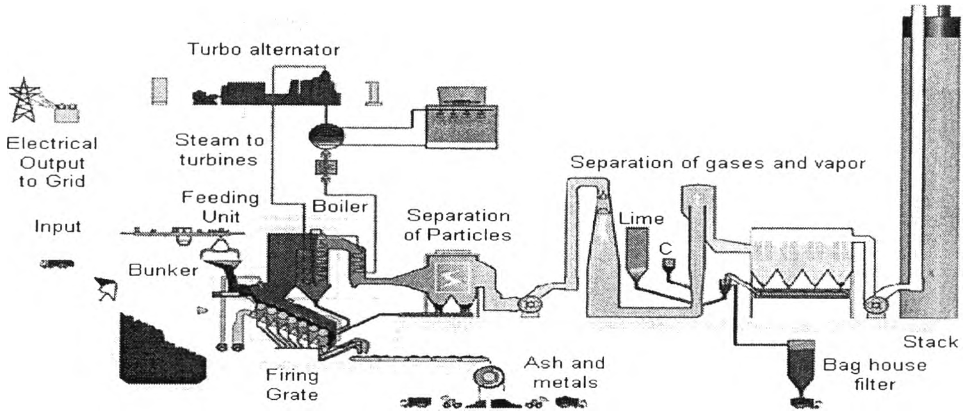


Figure 2.12 Incineration process
(Source: http://www.wtert.eu/default.asp?ShowDok=13).

2.5.2.3 Composting

Composting process as illustrated in Figure 2.13 is a natural biological process, carried out under controlled aerobic conditions (requires oxygen). In this process, various microorganisms, including bacteria and fungi, break down organic matter into simpler substances. The effectiveness of the composting process is dependent upon the environmental conditions present within the composting system i.e. oxygen, temperature, moisture, material disturbance, organic matter and the size and activity of microbial populations. Figure 2.14 shows biodegradation of bioplastic in real composting conditions.

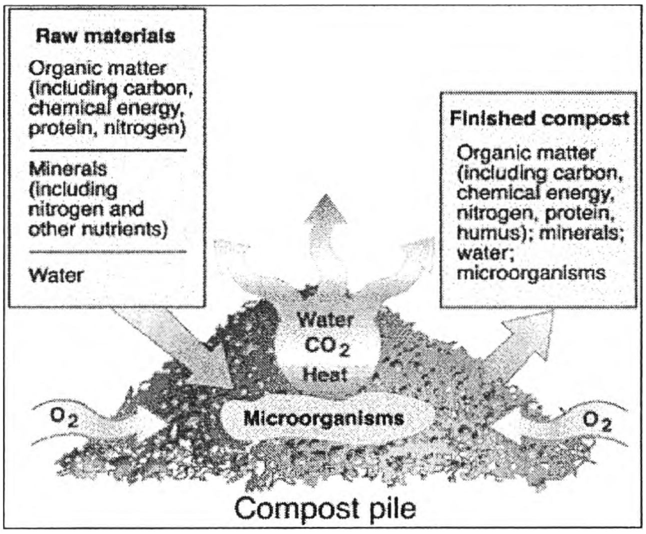


Figure 2.13 Composting process
(Sorce:http://ellerbruch.nmu.edu/classes /cs255students/mboks/p5/page1.html).

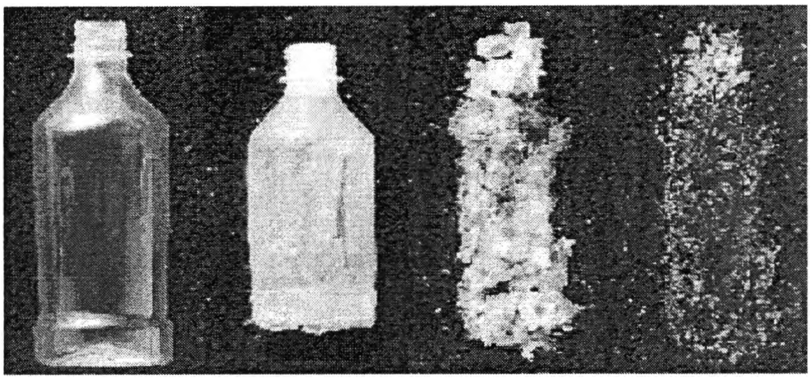
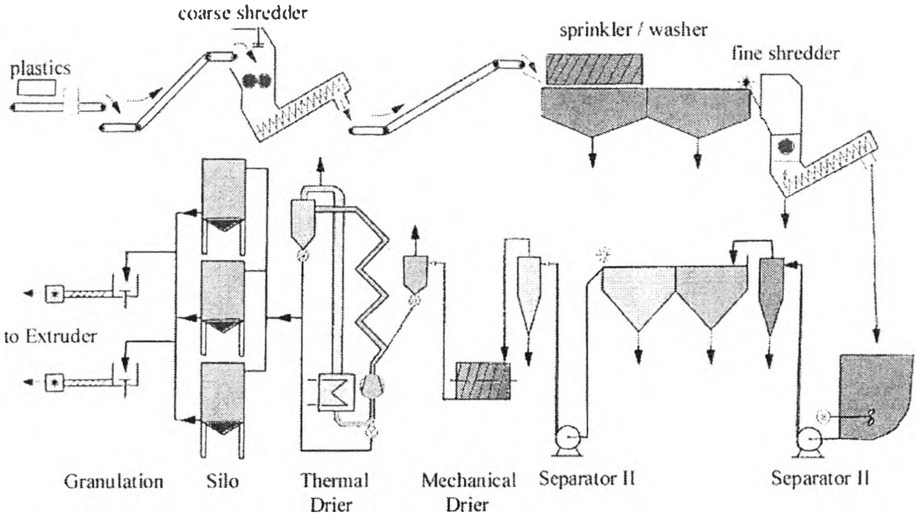


Figure 2.14 Biodegradation of bio-plastic in real composting conditions
(Source: http://www.treehugger.com/files/2008/08/bioplastics-recycling-consortium-forms.php).

2.5.2.4 Recycling

Recycling involves processing used, unwanted materials (waste) into new products to prevent waste of potentially useful materials, reduce the consumption of fresh raw materials, reduce energy usage, reduce air pollution (from incineration) and water pollution (from landfill) by reducing the need for "conventional" waste disposal, and lower greenhouse gas emissions as compared to virgin production. Figure 2.15 illustrates processing plant of recycled plastic.

Recyclable materials include many kinds of glass, paper, metal, plastic, textiles, and electronics. Although similar in effect, the composting or other reuse of biodegradable waste–such as food or garden waste–is not typically considered recycling. Materials to be recycled are either brought to a collection center or picked up from the curbside, then sorted, cleaned, and reprocessed into new materials bound for manufacturing.



Processing Plant of Recycled Plastic

Figure 2.15 Processing plant of recycle plastic
(Source: http://www.sbg.ac.at/ipk/avstudio/pierofun/waste/plastic.htm).

2.6 Life Cycle Assessment (LCA)

2.6.1 Overview

The history of LCA goes back almost 40 years and started with energy and material budgets to which complementary pollution aspects were progressively added. With the two oil crises in the 1970s, interest in LCA was boosted, but mostly for the energy efficiency part. With the growing solid-waste issues at the end of the 1980s, the development of the methodology accelerated and in 1992 the first formal framework for the impact assessment phase was proposed. The purpose of this phase, based on scientific knowledge and models, is to convert inventory data into potential impacts on ecosystems and human health. The refining of this phase remains one of the key scientific challenges of the methodology for many research teams around the world (Mens, 2007).

2.6.2 Definition of LCA

Life Cycle Assessment is a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and materials used and releases to the environment; and to identify and evaluate opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process or activity, encompassing, extracting and processing raw materials; manufacturing, transportation and distribution; use, re-use, maintenance; recycling, and final disposal. The general categories of environmental impacts needing consideration include resource use, human health, and ecological consequences (SETAC, 1993).

Life Cycle Assessment (LCA) is used as a tool to assess the environmental impacts of a product, process or activity throughout its life cycle; from the extraction of raw materials through to processing, transport, use and disposal. In its early days it was primarily used for product comparisons, for example to compare the environmental impacts of disposable and reusable products. Today its applications include government policy, strategic planning, marketing, consumer education, process improvement and product design. It is also used as the basis of eco-labeling and consumer education programs throughout the world.

2.6.3 Methodology

A framework for LCA has been standardized by the International Organization for Standardization (ISO) in the ISO 14040 series. It consists of 4 elements: Goal and Scope Definition, Inventory Analysis, Impact Assessment, and Interpretation as illustrated in Figure 2.16.

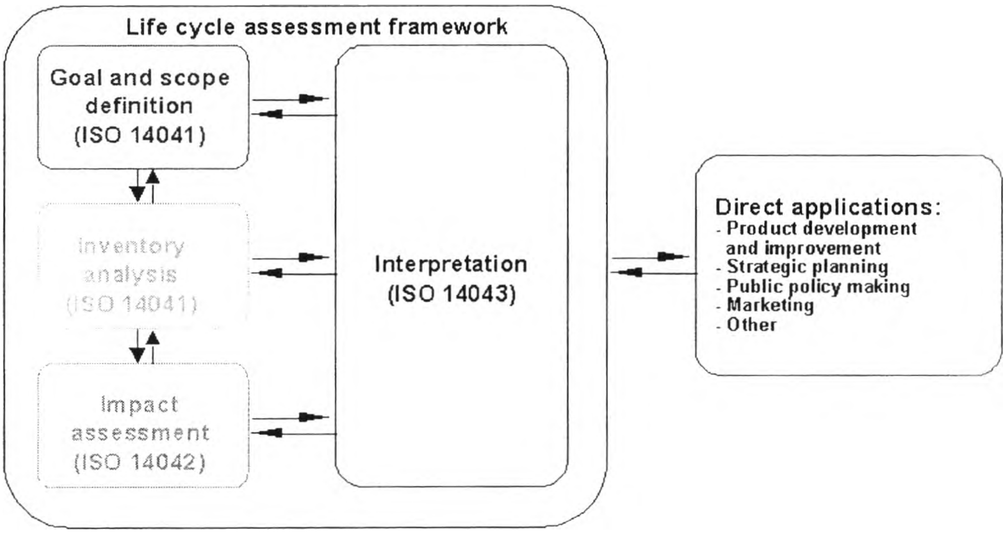


Figure 2.16 Life-cycle assessment framework as laid down in ISO 14040:1997 (Source: http://www.boustead-consulting.co.uk).

2.6.3.1 Goal and Scope Definition

Goal and scope definition is the first phase in a life cycle assessment containing the following main issues (Jensen, 1997):

- Goal

The goal of an LCA study shall unambiguously state the intended application, including the reasons for carrying out the study and the intended audience, i.e. to whom the results of the study are intended to be communicated.

- Scope

The scope describes the breadth, the depth and the detail of the study. It is important to define a functional unit and the system boundaries. The data quality requirements should be carefully specified.

- Functional unit

One of the main purposes for a functional unit is to provide a reference to which the input and output data are normalized. A functional unit of the system shall be clearly defined and measurable. The result of the measurement of the performance is the reference flow.

- System boundaries

The initial system boundary defines the unit processes which will be included in the system to be modeled. Ideally, the product system should be modeled in such a manner that the inputs and outputs at its boundary are elementary flows. However, as a practical matter, there typically will not be sufficient time, data, or resources to conduct such a comprehensive study. Decisions must be made regarding which unit processes will be modeled by the study and the level of detail to which these unit processes will be studied.

2.6.3.2 Inventory Analysis

Life Cycle Inventory (LCI) is the phase of the LCA involving the compilation and quantification of inputs and outputs; it comprises data collection and data calculation. Data collection consists of the identification and quantification of the relevant input and output flows for the whole life cycle of a product.

Basically three types of flows can be differentiated: elementary flows (emissions, resources) that are emitted into the environment or extracted from it, product flows (goods, services), that come from or go to the technosphere, and waste flows (a sub-type of product flows). The use of resources and the use of land, raw materials, fabricated products, auxiliary materials, energy carriers and electricity are recorded as inputs. Emissions to air, water and land as well as wastes and by-products are outputs in an inventory analysis. In the later stage of the impact assessment, the quantitative information on the product system's elementary flows (and in some methods the waste flows) is used to analyze the product's impacts.

The most important steps of life cycle inventory work are determination of the reference quantity (e.g. functional unit, reference flow), description of system in flow diagrams, identification of unit processes to be modeled separately in LCI model, qualitative determination of inputs and outputs, quantitative determination of inputs and outputs, documentation of the type of data survey, inventory data collection, inventory data collection of transport, and Calculation of the inventory, including allocations and covering the inventories of the background data sets (Jensen, 1997).

2.6.3.3 Impact Assessment

The impact assessment is carried out on the basis of the inventory analysis data. It is the third phase in a life cycle assessment containing the following main issues (Bianchi, 2008):

- Category definition

The impact assessment categories should link the potential impacts and effects on what is referred to as the "areas of protection" of the LCA, i.e. the entities that we want to protect by performing and using the LCA. Today, there is acceptance that the protection areas of life-cycle assessment are:

- ➢ natural resources
- ➢ natural environment
- ➢ human health
- ➢ and often also: man-made environment

- Classification

In the classification step the inventory data are assigned to categories according to their impact. For instance, carbon dioxide emissions contribute to the greenhouse effect and are hence assigned to the impact category Climate change. If a substance contributes to several impact categories, it has to be taken into account in all of these categories. Such a case is, for example, nitrogen oxide that causes both eutrophication and acidification.

- Characterization

Classification is followed closely by characterization. Every substance is assigned a potential impact in the impact category under study. The potential impact of a substance is given relative to a dominant factor in the category, e.g. for the Climate change potential this is typically 1 kg of carbon dioxide emissions. These relative impacts (the characterization factors of a substance) are than multiplied with the amount of each emission and the resulting impact values are summed for the respective impact category.

Life Cycle Impact Assessment uses generally the following categories:

- *Greenhouse effect (or global warming potential)*

Global warming is called the greenhouse effect because the gases that are gathering above the earth make the planet comparable to a greenhouse. By trapping heat near the surface of the earth, the greenhouse effect is warming the planet and threatening the environment. The climate changes that will result from global warming are extremely difficult to predict. If temperatures do indeed rise significantly, the most important result would be that some portion of the polar icecaps would melt, raising global sea levels. The Global Warming Potential (GWP) is the potential contribution of a substance to the greenhouse effect. This value has been calculated for a number of substances over periods of 20, 100 and 500 years because it is clear that certain substance gradually decompose and will become inactive in the long run.

- *Ozone layer depletion*

The ozone layer is essential to life on earth, as it absorbs harmful ultraviolet-B radiation from the sun. Every time 1% of the ozone layer is depleted, 2% more UV-B is able to reach the surface of the planet. The increasing of ultraviolet-B is one of the most harmful consequences of ozone depletion because it can cause skin cancer. Ozone Depletion Potential (ODP) values have been established mainly for hydrocarbons containing combined bromine, fluorine and chlorine, or CFCs. Here too, one of the substances (CFC-11) has been adopted as a reference.

- *Acidification*

The Acidification Potential (AP) is expressed relative to the acidifying effect of SO_2. Other known acidifying substances are nitrogen oxides (NO_x), sulfuric acid (H_2SO_4), and hydrogen chloride (HCl).

- *Eutrophication*

Eutrophication is an increase in the concentration of chemical nutrients (nitrogen (N) and phosphorus (P)) in water bodies, often leading to changes in animal and plant populations and degradation of water and habitat quality. The Nutriphication Potential (NP) is expressed as kg phosphate (PO_4) equivalents. Other emissions also influence eutrophication, notably nitrogen oxides and ammonium.

2.6.3.4 Interpretation

Within the framework of an evaluation, the results from the impact assessment and the inventory analysis are analyzed and conclusions and recommendations are established. A further aspect is the transparent presentation of the LCA results. The ISO standards comprise three interpretation elements (Bianchi, 2008):

- Significant issues

In order to determine the significant issues the main contributions of each impact category have to be identified (which emissions and/or which processes are dominant within each category). The relevant inventory data which cannot be recorded through impact categories must also be integrated into the study. Following the scope definition, the main contributions can be grouped by the individual process step, individual life phases and the entire life cycle. Together with these results, the significant issues can now be established, since it is now also clear which processes or life phases are dominant.

- Results evaluation

To evaluate the results according to the ISO standard, a completeness check, a sensitivity check, and a consistency check of the identified processes or life phases must be carried out. Completeness is checked by e.g. a mass and energy data analysis and considering experts' know-how of the modeled processes. Sensitivity is determined by calculating scenarios for different processes or different parameters (e.g. varying yield of processes and emission factors). The effects of the different assumptions on the total result show the sensitivity.

It must be ensured that all necessary information and data relevant to the interpretation are available and complete; for confidentially needs or process operators the ISO standards foresee to establish respective agreements. It is also important to check to what extent uncertainties, for example through the estimation of data due to data gaps, may influence the result. The consistency check should ensure that the procedure is consistent with the goal and scope definition and that the methodology and other rules have been accurately and consistently applied for the whole product system.

- Conclusions and recommendations

The aim of this third step of the interpretation is to reach conclusions and recommendations for the report of the LCA study or life cycle inventory study.

This step is important to improve the reporting and the transparency of the study. Both are essential for the readers of the LCA report.

The results of the critical review of the study shall also be included when presenting the conclusions and recommendations.

2.6.4 Applications of LCA

The applications of LCA can be included into decision making in various fields, examples are (Bianchi, 2008):

- Product development and improvement
- Process and service operation

- Strategic planning
- Technological impact assessment
- Public policy making
- Marketing

2.7 LCA Studies on Bioplastics

In 2010, Groot and Borén investigated the Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand. The LCA of this paper was carried out for L-lactide, D-lactide, PLLA, and two PLLA/PDLA blends made from cane sugar in Thailand, and were compared with that of fossil-based polymers. The LCA complies with ISO standards, and is a cradle-to-gate analysis including sugarcane cultivation, sugarcane milling, auxiliary chemicals production, transport, and production of lactide and PLAs. In the analysis, process data were taken from the designs of full-scale plants for the production of lactic acid, lactides, and PLA. The data were combined with ecoprofiles of chemicals and utilities and recalculated to the following environmental impacts: primary renewable and non-renewable energy, non-renewable abiotic resource usage, farm land use, global warming, acidification, photochemical ozone creation, human toxicity, and eutrophication. A schematic of the production chain from agriculture to lactide and PLA is given in Fig. 2.17.

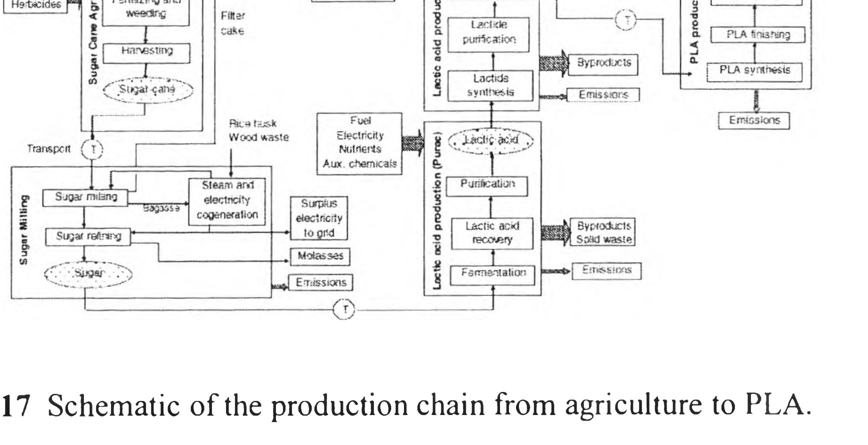


Figure 2.17 Schematic of the production chain from agriculture to PLA.

From their study, it was shown that on a weight-by-weight basis, PLLA results in significantly lower emissions of greenhouse gasses, and less use of material resources and nonrenewable energy, compared to fossil-based polymers. With the present calculations, the Global Warming Potential (GWP) in L-lactide production is 300–600 kg CO2 eq./tonne and for PLLA 500–800 kg CO2 eq./tonne. The range indicates the sensitivity of the GWP to the energy credit for electricity production from bagasse in the sugar mill. The GWP of PLLA/PDLA blends with increased heat resistance is also lower compared to fossil based polymers with similar durable character. Being based on an agricultural system the biobased PLA gives rise to higher contributions to acidification, photochemical ozone creation, eutrophication, and farm land use compared to the fossil polymers. Figure 2.18 shows that the global warming potential of PLLA is much lower than for fossil based polymers, and this is one of the main drivers today for producing biopolymers.

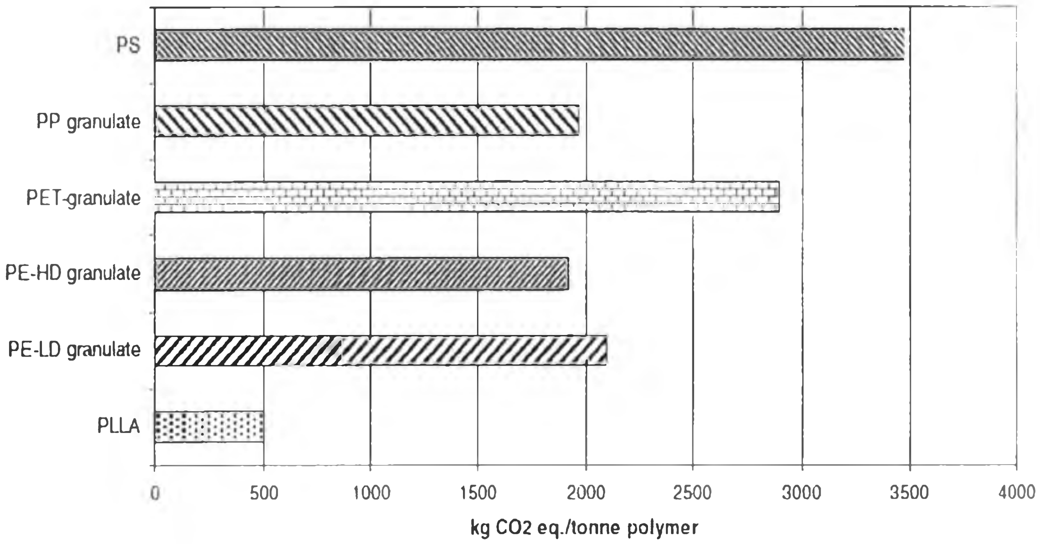


Figure 2.18 GWP involved with the production of PLLA and other polymers.

A second way of comparing the ecoprofile of biopolymers and fossil-based polymers is to address the gross energy demands. This energy demand is the combination of the energy used in the process and the feedstock related energy; for PLA the feedstock is the sugar plant, and for fossil-based polymers it is oil. The feedstock-related energy represents the energy of fuel-type materials that are fed in the system, but used as carbon based building blocks rather than fuels. Figure 2.19 shows the comparison on the gross energy demand for PLLA and fossil-based polymers. A further division into renewable and non-renewable energy now splits the total into four parts.

– The feedstock related renewable energy. This number reflects the average energy content of the sugar substrate.

– The process-related renewable energy. This number is high for PLLA as it represents the energy in the bagasse (excludes energy equivalents for coproduced power fed to the grid). For fossil-based polymers, this number is very small and represents, e.g., the use of wood in addition to natural gas or oil in national energy based economy.

– The process related non-renewable energy used to make the polymer (recovery of crude oil, transportation, refining for steam, and electricity production to make the polymer)

– The feedstock related non-renewable energy. This number is zero for biopolymers. In case of fossilbased polymers, this number reflects the average energy content of the feedstock.

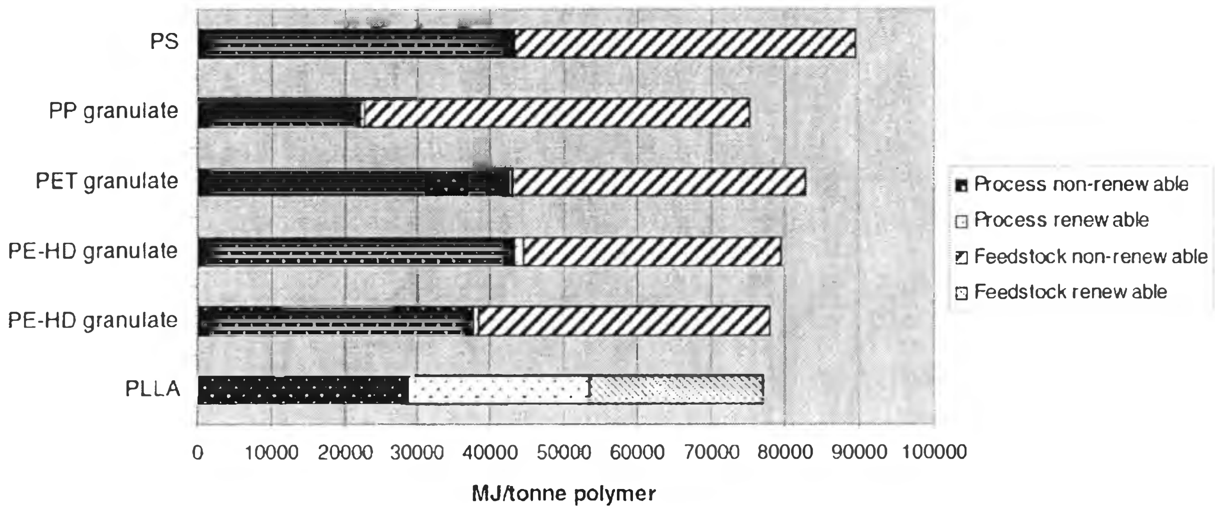


Figure 2.19 Primary energy demand involved with the production of PLLA and other polymers.

In 2010, Vink *et al.* investigated the eco-profile for current Ingeo® polylactide production. This paper gave the latest life cycle inventory data based on new lactic acid production technology that was implement in December 2008. Further, the use of Renewable Energy Certificate was no longer included in the reported eco-profile. The objective of this paper is to provide detailed inventory data sufficient for use by LCA practitioners interested in the use of Ingeo resin for specific products. Figures 2.20 and 2.21 show nonrenewable energy use and greenhouse gas emission which are less than Ingeo since 2005 reported by Vink *et al.* (2010). They are also illustrated Ingeo target in the near-future of both energy use and greenhouse gas emission.

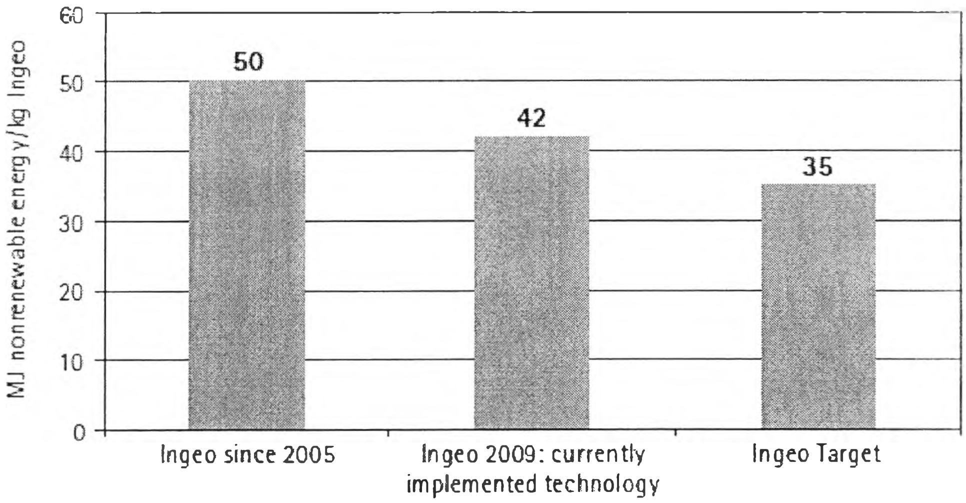


Figure 2.20 Cradle to polymer factory gate nonrenewable energy use for the various Ingeo production systems.

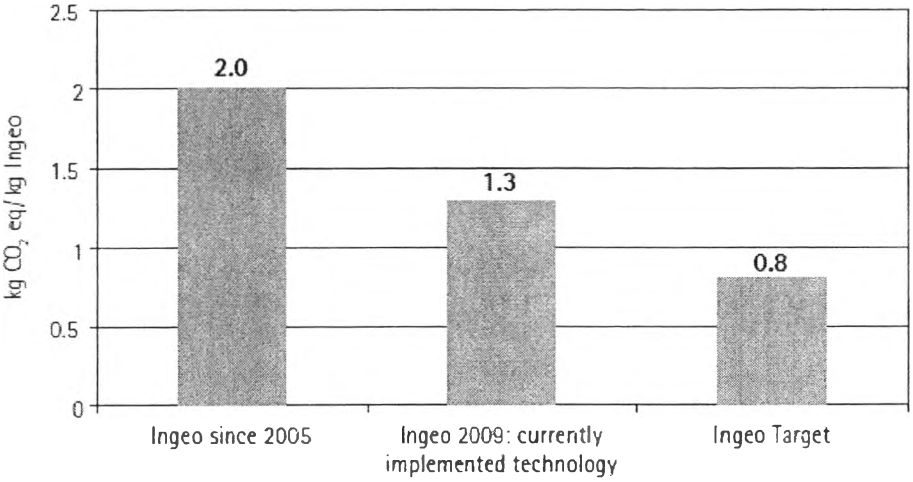


Figure 2.21 Cradle to polymer factory gate greenhouse gas emissions for the various Ingeo production systems.

The eco-profile of current and near-future NatureWorks® polylactide (PLA) production reported by Vink *et al.* (2007). They provide the cradle–to–polymer–factory–gate life cycle inventory data (eco-profiles) for the 2006 and the near-future PLA production system and explain the use of RECs (renewable energy certification). Figure 2.22 shows the simplified flow diagram and system boundary for NatureWorks PLA production system. The cradle–to–factory–gate PLA production system is divided into five major steps:

- Corn production and transport of corn to the corn processing wet mill
- Corn processing and the conversion of starch into dextrose
- Conversion of dextrose into lactic acid
- Conversion of lactic acid into lactide
- Polymerization of lactic into polylactide polymer pellets

From their study, it was shown that PLA production in 2006 emitted 0.27 kg CO_2 eq./kg PLA, 7.7 g NO_x/kg PLA, 2.5 g SO_x/kg PLA, and used 27.2 MJ/kg PLA of fossil energy.

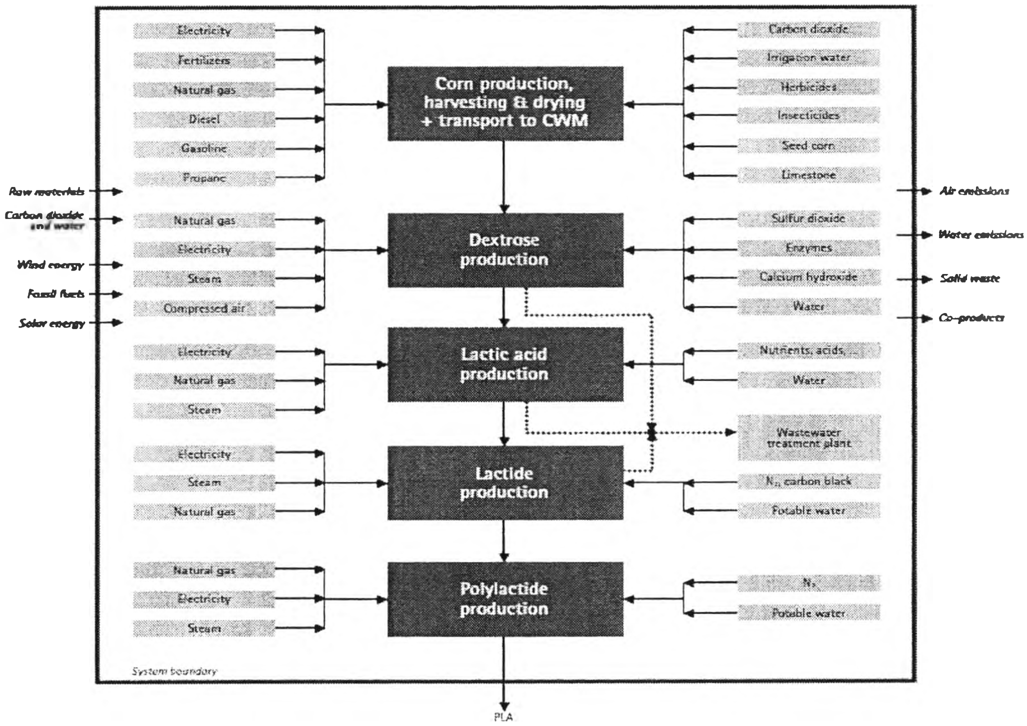


Figure 2.22 Simplified flow diagram and system boundary for the NatureWorks PLA production system.

Applications of life cycle assessment to NatureWorks^{TM} polylactide (PLA) production by Vink *et al.* (2002). They explained the role of life cycle assessment (LCA), a tool used for measuring environmental sustainability and identifying environmental performance-improvement objectives. The paper gives an overview of applications of LCA to PLA production and provides insight into how they are utilized. The first application reviews the contributions to the gross fossil energy requirement for PLA (54 MJ/kg). In the second one PLA is compared with petrochemical-based polymers using fossil energy use, global warming and water use as the three impact indicators as shown in Figure 2.23, 2.24, and 2.25, respectively. The last application gives more details about the potential reductions in energy use and greenhouse gasses. Cargill Dow's 5 – 8 year objective is to decrease the fossil energy use from 54 MJ/kg PLA down to about 7 MJ/kg PLA. The objective for greenhouse gasses is a reduction from +1.8 down to -1.7 kg CO_2 equivalents/kg PLA. Polymers from renewable resources can be significantly lower in greenhouse gas emissions and fossil energy use today as compared with conventional petrochemical-based polymers. Over the longer term, LCA demonstrates that PLA production processes can become both fossil-energy free and a source of carbon credits. This bright future will come only with significant investment of time, effort and money. A final, important benefit of LCA is that it can serve as a tool for monitoring return on these investments over time.

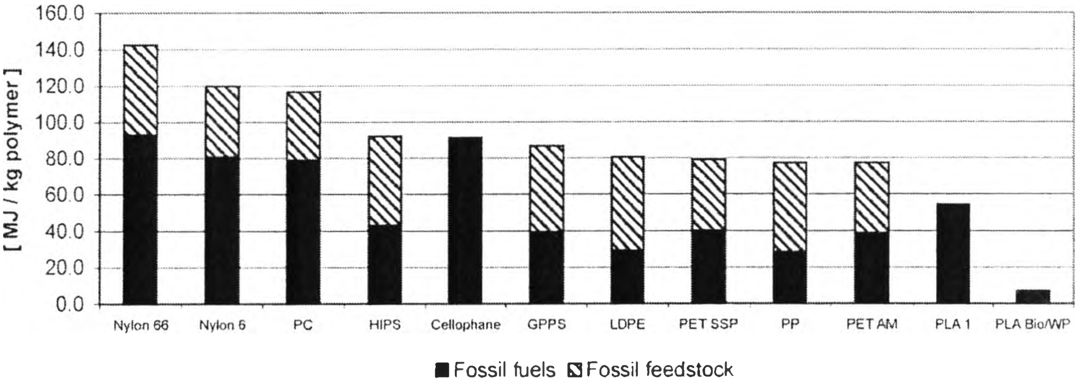


Figure 2.23 Fossil energy requirement for some petroleum based polymers and polylactide.

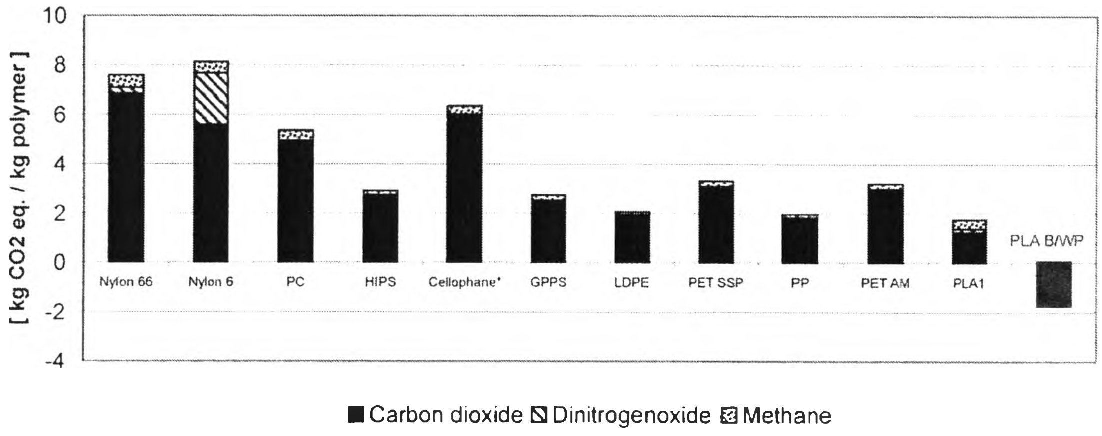


Figure 2.24 Contributions to global climate change for some petrochemical polymers and the two polylactide polymers.

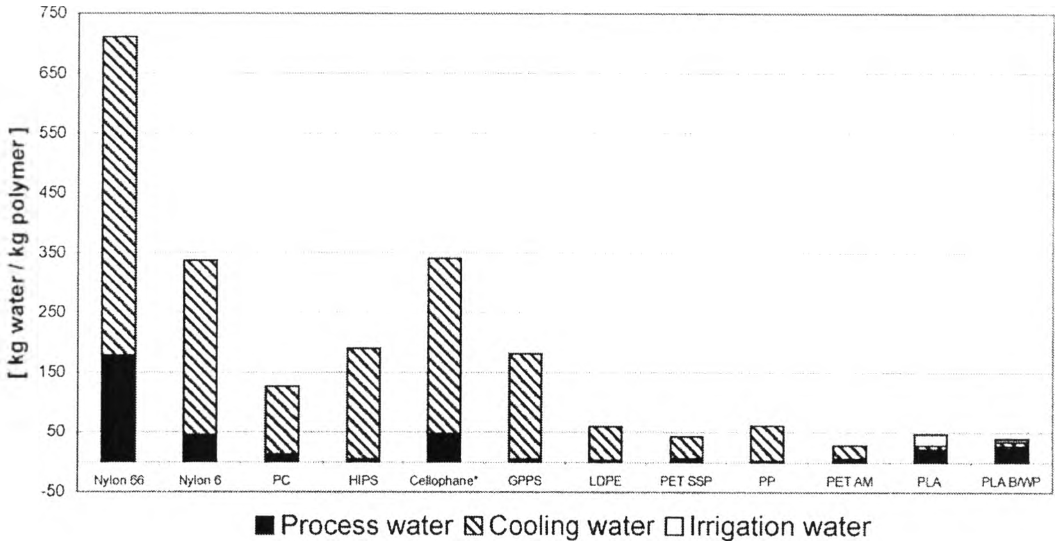


Figure 2.25 Gross water use by petrochemical polymers and the two PLA cases.

In 2008, Leng *et al.* investigated the entire life cycle of cassava-based ethanol fuel from cassava plantation, ethanol conversion, transport, fuel ethanol blending and distribution to its end use. Product system of cassava-based ethanol fuel is described and it is divided into six unit processes. The functional unit of this system is to produce 100,000 ton ethanol and cassava dry chip conversion rate of fresh cassava: 3:1. Figure 2.26 shows the unit process of cassava cultivation and treatment.

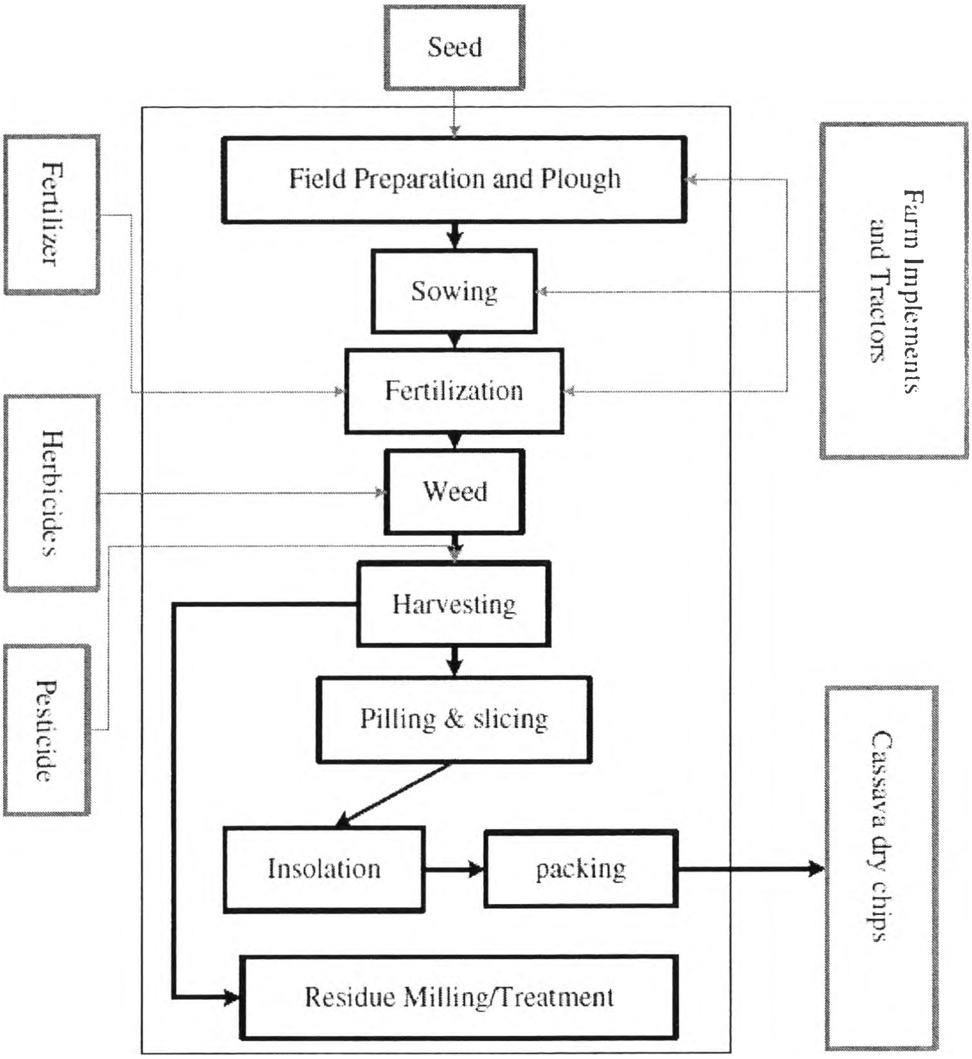


Figure 2.26 Unit of cassava cultivation and treatment.

This study also showed emission for cassava cultivation and treatment (g/ton chips) as shown in Table 2.7.

Table 2.7 Emission for cassava cultivation and treatment (g/ton chips)

	Item	VOC	CO	NO_X	PM_{10}	SO_x	CH_4	N_2O	CO_2	Solid
1	Chemical production	16	102	277	25	252	363	3	201,082	/
1.1	N	3	32	45	4	38	128	1	52,399	/
1.2	P_2O_5	3	22	83	7	93	76	0	50,573	/
1.3	K_2O	2	5	19	2	19	17	0	11,250	/
1.4	Multiple nutrient	2	13	27	2	27	50	0	23,860	/
1.5	Herbicide	6	32	102	9	75	91	1	63,000	/
2	Cassava plantation	40	144	440	24	29	58	200	−188,614[a]	/
3	Transport	0	0	2	0	0	1	0	357	/
3.1	Chemical transport	0	0	1	0	0	0	0	170	/
3.2	Stem transport	0	0	0	0	0	0	0	26	/
3.3	Fresh cassava transport	0	0	0	0	0	0	0	80	/
3.4	Haulm	0	0	0	0	0	0	0	81	/
4	Haulm burning	/	180,000	363,000	/	/	15,000	21,000	/	/
5	Cassava pre-treatment	0	0	0	0	0	0	0	97	5
	Total	56	180,246	363,717	49	281	15,421	21,203	12,565	5

[a] CO_2 is taken out of the atmosphere during growth of the cassava.

In 2008, Nguyen and Gheewala investigated the life cycle assessment of fuel ethanol from cassava in Thailand. In this paper divided the process into four main unit processes of the cassavabased E10/E85 fuel system for the life cycle inventory (LCI) are cassava production, ethanol conversion, transportation and fuel combustion in vehicles as shown in Fig.2.27.

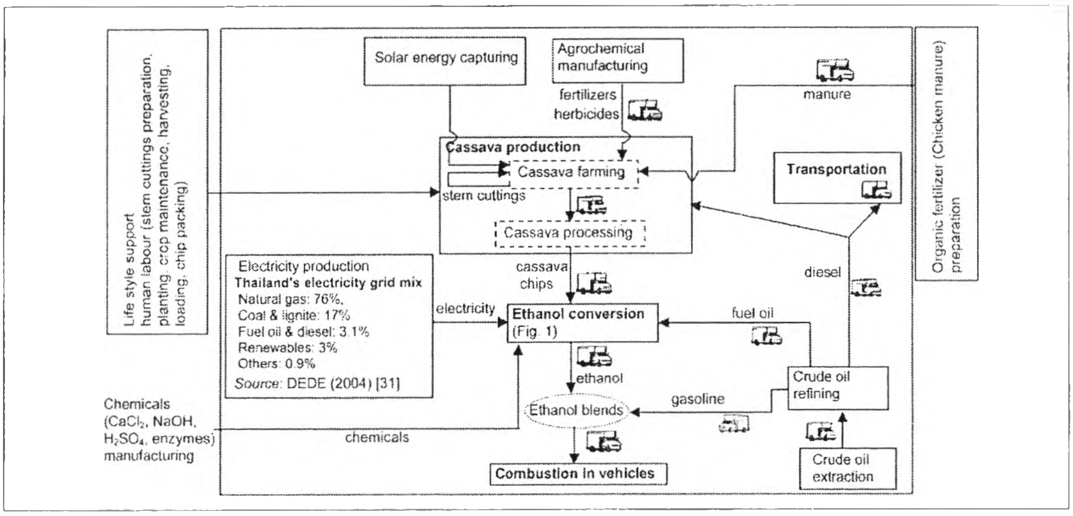


Figure 2.27 System boundary of the cassava-based E10/E85 fuel life cycle.

Cassava production is also notable for its contribution to acidification, nutrient enrichment and POCP. Acidification originates principally from SO_2 emission from the manufacturing of P fertilizer and NOx emission (direct and indirect) from diesel used to power farm tractors. This amount of NOx also contributes to nutrient enrichment. However, the largest contributor to nutrient enrichment from cassava production is N_2O soil emissions from N fertilizer application, as seen in Fig. 2.28.

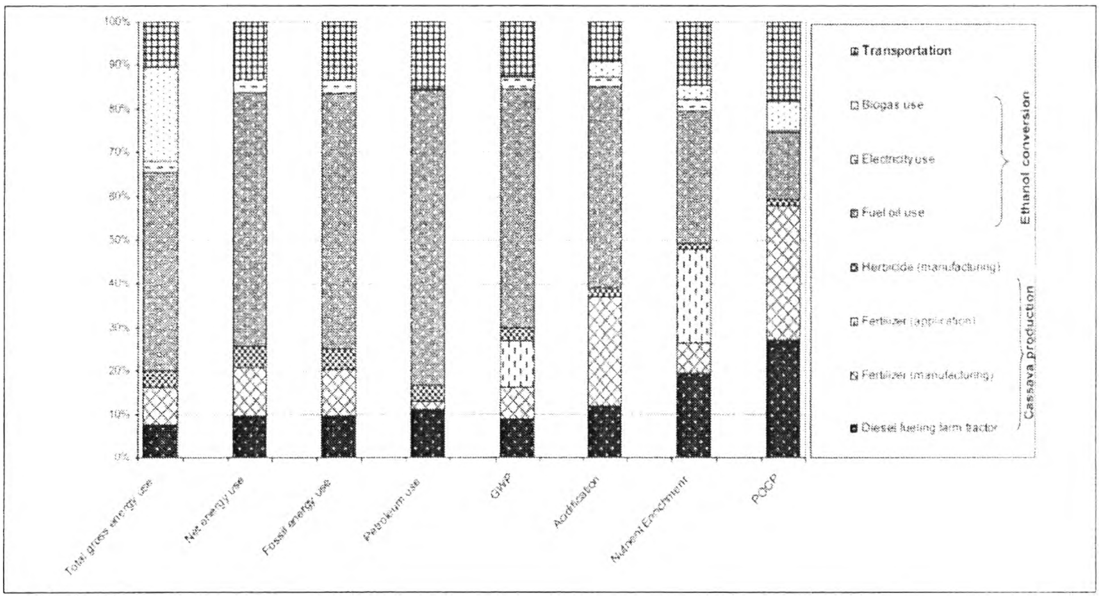


Figure 2.28 Characterization results – Contributions to the environmental impacts from ethanol production cycle.

Madival *et al.* (2009) evaluated the environmental impact of PLA, PET and PS containers used for distribution of fresh produce. PET contributed the highest in almost all the impact categories. This could be largely attributed to the higher weight of the containers. The transportation stage of PLA, PS and PET was the major contributor for global warming, ozone layer depletion and aquatic ecotoxity burdens through its life journey. This study found that the transportation stage of the resins and containers is a major contributor to most of the impact categories during the life cycle of the three clamshell containers. This finding cannot be neglected. Although the strawberry exporter and the container supplier are situated in California, the PET resin manufacturing site is in Columbia, South Carolina. Similarly for

PS, the resin production site was found to be at Joliet, Illinois. There may be PET and PS resin companies having manufacturing sites much closer to California than the ones assumed by this study. In that case, the results would change depending on the distances between the resin supplier and the converter. The only supplier for PLA resin in the U.S. is NatureWorks LLC, Nebraska. Figure 2.29 shows the normalized impact value comparing 1000 PLA, PS and PET containers from cradle to gate. PET showed the highest overall values for all the impact categories, mainly due to the higher weight of the containers. The main impacts to the environment were the resin production and the transportation stage of the resins and containers. This implies that the transportation stage of the package is an important contributor to the environmental impact of the packaging systems, and that it cannot be diminished.

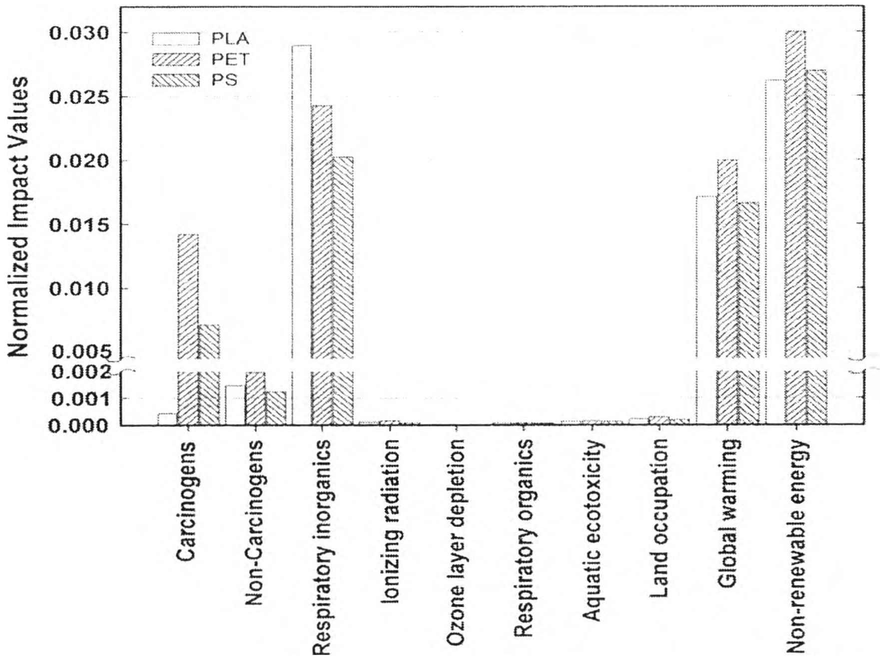


Figure 2.29 Normalized impact value comparing 1000 PLA, PS and PET containers from cradle to gate.

LCA studies comparing actual bio-based and hydrocarbon-based packaging containers specifically disposal phase are scare. Iovino *et al.* (2008) studied the aerobic biodegradation of a composite PLA/starch/natural fibre (coir) with and without the coupling agent (maleic anhydride; MA), using standard test methods designed for biodegradable plastics (ISO 14855). They used glass flasks of approximately 2 L internal volume as bioreactor. In the bioreactors, compost and test materials were mixed in the ratio of 6:1 (w:w calculated on dry mass) and then they were placed in an oven at constant temperature of 58 ±2 °C maintained throughout the 90 d of the experiment. The compost medium was prepared from the organic fraction of 2-months old mature compost obtained from vegetable refuse. After 90 d of incubation, TPS was quite completely transformed and an extreme deterioration of the initial pieces. The amount of CO_2 produced by TPS mineralization increased in the first 20 d at a degradation rate of 4:1, and then it started to decrease after roughly 40 d incubation. For PLA, the most productive phase for PLA mineralization occurred between 12 and 50 d incubation. The degradation was about 55.5% of its theoretical carbon dioxide production, having PLA a carbon content of 54.6 wt%. For the standard matrix, it is made by 75 wt% of PLA and 25 wt% of TPS. The theoretical carbon dioxide production was 170 g of CO_2 if totally mineralized having a carbon content of 53.6% by weight. The biodegradation was 61.5%. The materials have short survival time in biotic environment such as compost. and there after their use they are suitable for disposal in landfills.

Santosh *et al.* (2009) compared the environmental impact of PLA, PET and PS thermoformed clamshell containers used for the packaging of strawberries. The functional unit was 1000 containers of capacity 0.4536 g (1lb) each for the packaging of strawberries. Five different end of life scenarios in terms of landfill, incineration and recycling were: (a) scenario I – 40% recycling, 30% incineration. 30% landfill, (b) scenario II – 100% landfill, (c) scenario III – 100% recycling, (d) scenario IV – 50% incineration. 50% landfill and (e) current – 23.5% incineration, 76.5% landfill. In the five end-of-life scenario about carbon dioxide emission, the values for CO_2 emissions for PET were the highest. The CO_2 emission values for PLA, PET and PS were almost similar for scenarios I and II. One hundred percent recycling of containers has the lower CO_2 emission. Scenario IV and the current scenario V show the highest CO_2 emissions for PLA, PET and PS respectively. For energy consumption, PLA, PET and PS, scenarios II, IV and the current scenario have similar energy consumption values, indicating that increasing the incineration percent from 0 to 50 does not recover energy significantly in the overall system. To reduce the energy consumption for PLA containers, recycling should be established.

Kale *et al.* (2007) studied the biodegradation performance of polylactide (PLA) bottles under simulated composting conditions according to ASTM and ISO standards, and these results are compared with a novel method of evaluating package biodegradation in real composting conditions. Two simulated composting methods were used in this study to assess biodegradability of PLA bottles: (a) a cumulative measurement respirometric (CMR) system and (b) a gravimetric measurement respirometric (GMR) system. Both CMR and GMR systems showed similar trends of biodegradation for PLA bottles and at the end of the 58th day the mineralization was 84.2±70.9% and 77.87±10.4%, respectively. PLA bottle biodegradation in real composting conditions was correlated to their breakdown and variation in molecular weight. Figure 2.30 shows the biodegradation of PLA bottles in real composting conditions. Molecular weight of 4100 Da was obtained for PLA bottles in real composting conditions on the 30th day. The biodegradation observed for PLA bottles in both conditions explored in this study matches well with theoretical degradation and biodegradation mechanisms.

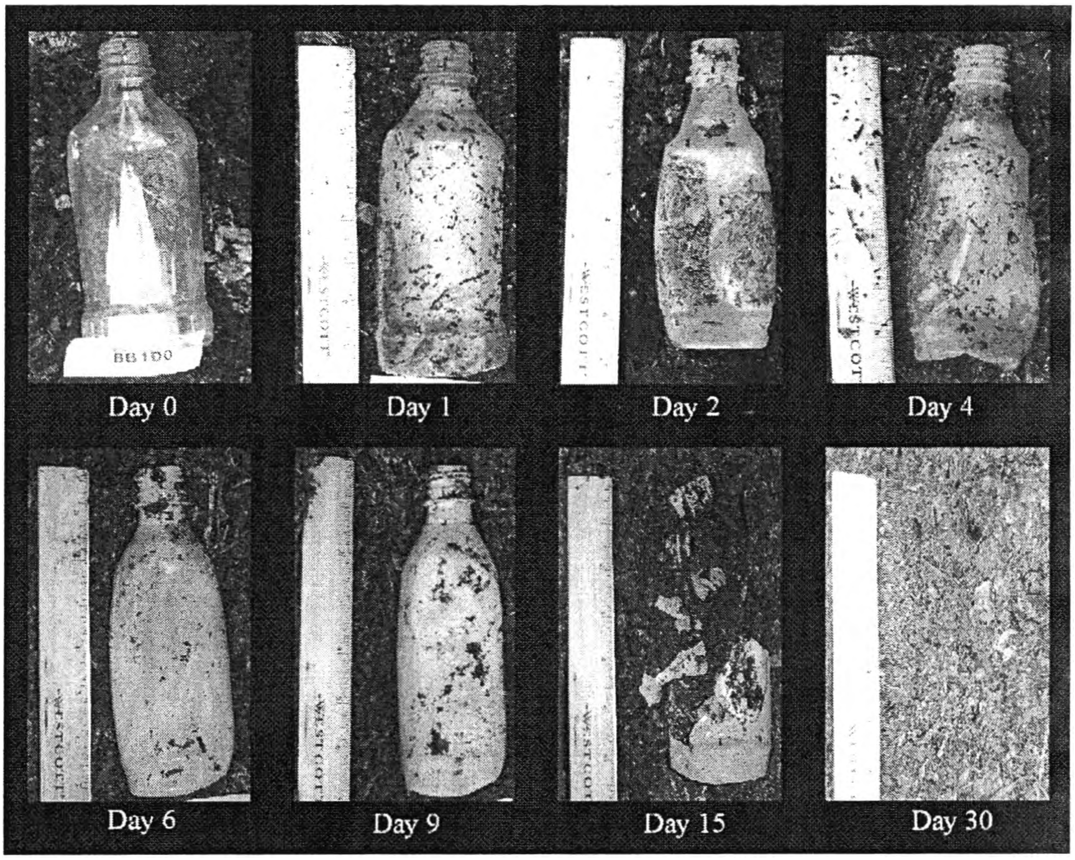


Figure 2.30 Biodegradation of PLA bottles in real composting conditions.

Smet *et al.* (1999) investigated the emission of volatile compounds during the aerobic and the combined anaerobic/aerobic composting of biowaste. In their experiments, the combined anaerobic/aerobic composting process could be considered as an attractive alternative for aerobic biowaste composting. In order to reduce the size and volume of solid waste to be disposed off, composting of the biodegradable fraction of the household waste, being 50-60% of the total mass, became a widely accepted technique in recent years. A new biowaste composting technology was the combined anaerobic/aerobic composting process. In Belgium, only one biowaste composting plant was working according to this technique up to now. In this plant, an intensive thermophilic (55-50 °C) solid state fermentation (phase I) takes place in a vertical reactor with a biowaste retention time of 3 weeks and a biogas production of ± $100m^3$ ton^{-1} biowaste. As a result of the closed fermentor design, all volatiles emitted during phase I were collected in the biogas. On-site, part of this biogas in converted into steam for process heating (7%), while the remaining gas was converted into electricity upon burning in an electricity generator. After digestion (phase I), the residue was dewatered in a press and the press cake is aerated during a 2-week period (phase II). With regard to the emission of volatiles, however, no data were found for this combined anaerobic/aerobic composting process.