Poly-Lactic Acid: Production, Applications, Nanocomposites, and Release Studies

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Abstract: Environmental, economic, and safety challenges have provoked packaging scientists and producers to partially substitute petrochemical-based polymers with biodegradable ones. The general purpose of this review is to introduce poly-lactic acid (PLA), a compostable, biodegradable thermoplastic made from renewable sources. PLA properties and modifications via different methods, like using modifiers, blending, copolymerizing, and physical treatments, are mentioned; these are rarely discussed together in other reviews. Industrial processing methods for producing different PLA films, wrappings, laminates, containers (bottles and cups), are presented. The capabilities of PLA for being a strong active packaging material in different areas requiring antimicrobial and antioxidant characteristics are discussed. Consequently, applications of nanomaterials in combination with PLA structures for creating new PLA nanocomposites with greater abilities are also covered. These approaches may modify PLA weaknesses for some food packaging applications. Nanotechnology approaches are being broadened in food science, especially in packaging material science with high performances and low concentrations and prices, so this category of nano-research is estimated to be revolutionary in food packaging science in the near future. The linkage of a 100% bio-originated material and nanomaterials opens new windows for becoming independent, primarily, of petrochemical-based polymers and, secondarily, for answering environmental and health concerns will undoubtedly be growing with time.

Introduction

Today, polymers and materials used for food packaging consist of a variety of petrochemical-based polymers, metals, glass, paper, and board, or combinations hereof. The durability and degradability of packaging materials are 2 contradictory subjects; the 1st is desirable for packaging stability and protection for its contents during shelf life and the 2nd for its rapid degradation in the environment (Bohlaman 2005).

Advantages of petrochemical-based polymers, which encouraged industries to use them are: (a) low cost and high-speed production; (b) high mechanical performance; (c) good barrier properties; and (d) good heat sealability. On the other hand, several disadvantages include: (a) declining oil and gas resources; (b) increasing oil and gas prices during recent decades; (c) environmental concerns for their degradation or incineration and global warming; (d) uneconomical costs and cross-contaminations in their recycling; and (e) consumer toxicity risks about their monomers or oligomers migrating to edible materials (Amass and others 1998; Chandra and Rustgi 1998; Mohanty and others 2000; Siracusa and others 2008).

Mechanical recycling (segregated plastics, mixed plastics), biological recycling (sewage, compost, soil), and energy recovery (incineration, pyrolysis) are 3 alternative ways for plastics waste management, with each having some advantages and disadvantages as to economical, processing, and technological aspects (Scott 2000).

The above-mentioned concerns are negligible for biopolymers concerning the biodegradation process that takes place in nature. Biodegradation is defined as the degradation of a polymer in natural environments that includes changes in chemical structure, loss of mechanical and structural properties, and finally, changing into other compounds like water, carbon dioxide, minerals, and intermediate products like biomass and humic materials. The natural environments contain chemical, biological, and physical forces with impinging factors like temperature, humidity, pH, O_2 presence, and so on, which determine the rate and products of the biodegradation process (Zee 2005).

Biopolymers are produced from natural resources and crude oil. Four categories of biopolymers are recognized: (a) extracted directly from natural raw materials, such as polysaccharides like starch and cellulose; proteins like gelatin, casein, and silk; and marine prokaryotes; (b) produced by chemical synthesis from bio-derived monomers such as poly-lactic acid (PLA), also known as poly(lactic acid) in the literature; (c) produced by microorganisms or genetically modified bacteria such as polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), hydroxyl-valerate (PHV), bacterial cellulose, xanthan, and pullan; and (d) produced from crude oil like aliphatic and aromatic polyesters, polyvinyl alcohol, and modified

polyolefins, which are sensitive to temperature and light (Chandra and Rustgi 1998; Clarinval and Halleux 2005).

PLA or poly–lactide was discovered in 1932 by Carothers (at DuPont). He was only able to produce a low molecular weight PLA by heating lactic acid under vacuum while removing the condensed water. The problem at that time was to increase the molecular weight of the products; and, finally, by ring-opening polymerization of the lactide, high-molecular weight PLA was synthesized. PLA was 1st used in combination with polyglycolic acid (PGA) as suture material and sold under the name Vicryl in the U.S.A. in 1974 (Mehta and others 2005).

In comparison to other biopolymers, the production of PLA has numerous advantages including: (a) production of the lactide monomer from lactic acid, which is produced by fermentation of a renewable agricultural source corn; (b) fixation of significant quantities of carbon dioxide via corn (maize) production by the corn plant; (c) significant energy savings; (d) the ability to recycle back to lactic acid by hydrolysis or alcoholysis; (e) the capability of producing hybrid paper-plastic packaging that is compostable; (f) reduction of landfill volumes; (g) improvement of the agricultural economy; and (h) the all-important ability to tailor physical properties through material modifications (Dorgan and others 2000).

Briefly, PLA is based on agricultural (crop growing), biological (fermentation), and chemical (polymerization) sciences and technologies. It is classified as generally recognized as safe (GRAS) by the United State Food and Drug Administration (FDA) and is safe for all food packaging applications (Conn and others 1995; FDA 2002).

Production steps, general properties, applications, processing technologies, modifications, and biodegradability of PLA are presented in this review. Consequently, migration and release studies of active compounds and PLA abilities making it a potential active food packaging are also discussed; finally, recent different types of nanocomposites used for improving PLA applications are reviewed.

PLA Production

Lactic acid (2-hydroxy propionic acid), the single monomer of PLA, is produced via fermentation or chemical synthesis. Its 2 optically active configurations, the L(+) and D(−) stereoisomers are produced by bacterial (homofermentative and heterofermentative) fermentation of carbohydrates. Industrial lactic acid production utilizes the lactic fermentation process rather than synthesis because the synthetic routes have many major limitations, including limited capacity due to the dependency on a by-product of another process, inability to only make the desirable L-lactic acid stereoisomer, and high manufacturing costs (Datta and Henry 2006).

The homofermentative method is preferably used for industrial production because its pathways lead to greater yields of lactic acid and to lower levels of by-products. The general process consists of using species of the *Lactobacillus* genus such as *Lactobacillus delbrueckii, L. amylophilus, L. bulgaricus, and L. leichmanii*, a pH range of 5.4 to 6.4, a temperature range of 38 to 42 °C, and a low oxygen concentration. Generally, pure L-lactic acid is used for PLA production (Mehta and others 2005).

PLA has a variable molecular weight and only its high molecular weight polymer is used in the packaging industry. Three ways are possible for the polymerization of lactic acid; (a) direct condensation polymerization; (b) direct polycondensation in an azeotropic solution (an azeotrope is a mixture of 2 or more chemical liquids in such a ratio that its composition cannot be changed by simple distillation. This occurs because, when an azeotrope is boiled, the

resulting vapor has the same ratio of constituents as the original mixture); and (c) polymerization through lactide formation. The 1st method is based on esterification of monomers by the aid of some solvents and exudated water is removed using progressive vacuum and high temperatures. Obtaining high molecular weight polyesters with good mechanical properties via this method is not easy, although precondensates may be of interest for the preparation of biodegradable glues or lacquers, since the −OH and −COOH end groups allow cross-linking with suitable inorganic or organic multivalent additives (Hartmann 1998).

Producing high molecular weight PLA polymers by direct polycondensation in an azeotropic solution and also application of some catalysts is more practicable. The azeotropic solution helps to decrease the distillation pressures and facilitates PLA separation from the solvent by application of molecular sieves. The variety and content of catalysts, solvent volume percentages, and the reaction time on the preparation of PLA have been studied. The results identified by using improved experimental equipment, the proper complex catalyst, and solvent volume ratio, in order to obtain a molecular weight of PLA of 6.6×10^4 (Li and others 2006).

Polymerization through lactide formation is being industrially accomplished for high molecular weight PLA production. Lactide is a cyclic dimer formed by removing water under mild conditions and without solvent. L-lactide, meso (L,D) lactide, and D-lactide are products of L-lactic acid and D-lactic acid. The terms poly lactide and poly (L-lactide) have been used in many references instead of PLA.

Lactide purification is accomplished by vacuum-distillation of high temperatures. After the vacuum-distillation of L-lactide, high molecular weight PLA with a controlled optical and crystal purity is formed by ring-opening polymerization. Ring-opening polymerization of lactide can be carried out in melt or solution by cationic, anionic, and coordination mechanisms, depending on the initiator utilized. The most considered active initiator for the L-lactide ring-opening polymerization is stannous octoate (bis 2-ethyl hexanoate, $SnOct_2$), which causes a low degree of racemization at high temperature. It has a low toxicity and is accepted by FDA (Puaux and others 2007).

A kinetics study for ring-opening polymerization of L-lactide with stannous octoate has been done and a correlated mathematical modeling developed for that (Mehta and others 2007).

The choice of initiator system, co-initiator as chain control agent, catalyst concentration, monomer-to-initiator ratio, and polymerization temperature and time significantly affect the polymer properties. Properties such as molecular weight, degree of crystallinity, and residual monomer content, in turn affect the physico-mechanical properties of polylactide and its copolymers (Vink and others 2004).

Figure 1 shows PLA production steps by ring-opening polymerization using stannous octoate as an initiator.

New ideas for decreasing PLA final price and making production processes more eco-friendly, in comparison to earlier production process, include usage of crop residue (stems, straw, husks, and leaves) from corn or, potentially, other crops, and use of unfermentable residues as a heat source, as well as substituting some part of electricity energy by wind power energy. These approaches decrease the consumption of fossil fuels and corn starch as raw materials and also diminish polluting air, water, and waste emissions to the environment (Vink and others 2003).

One of the most positive points of PLA production in comparison with the other hydrocarbon-based polymers is the decrease of CO_2 emission. Carbon dioxide is believed to be the most
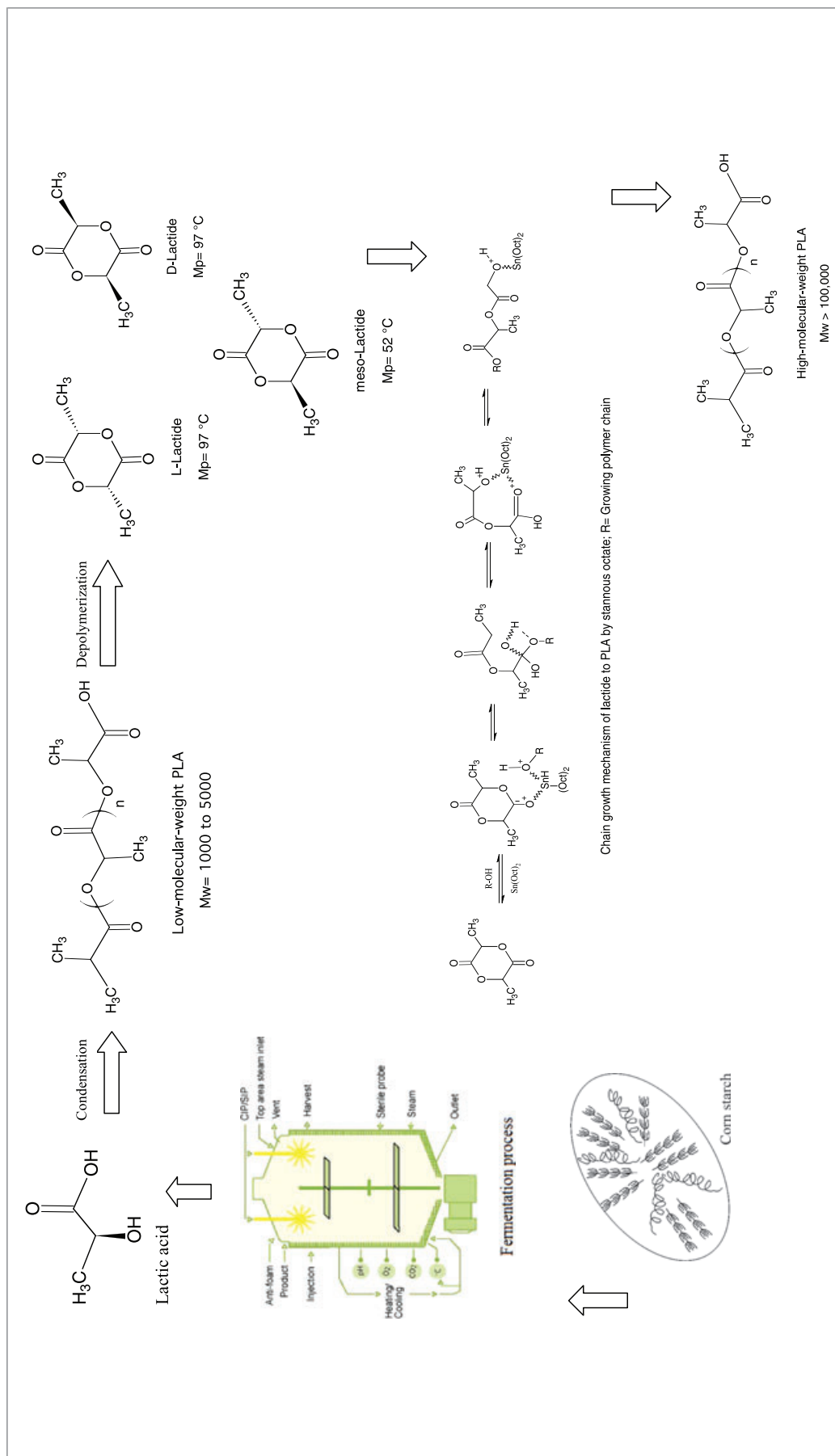
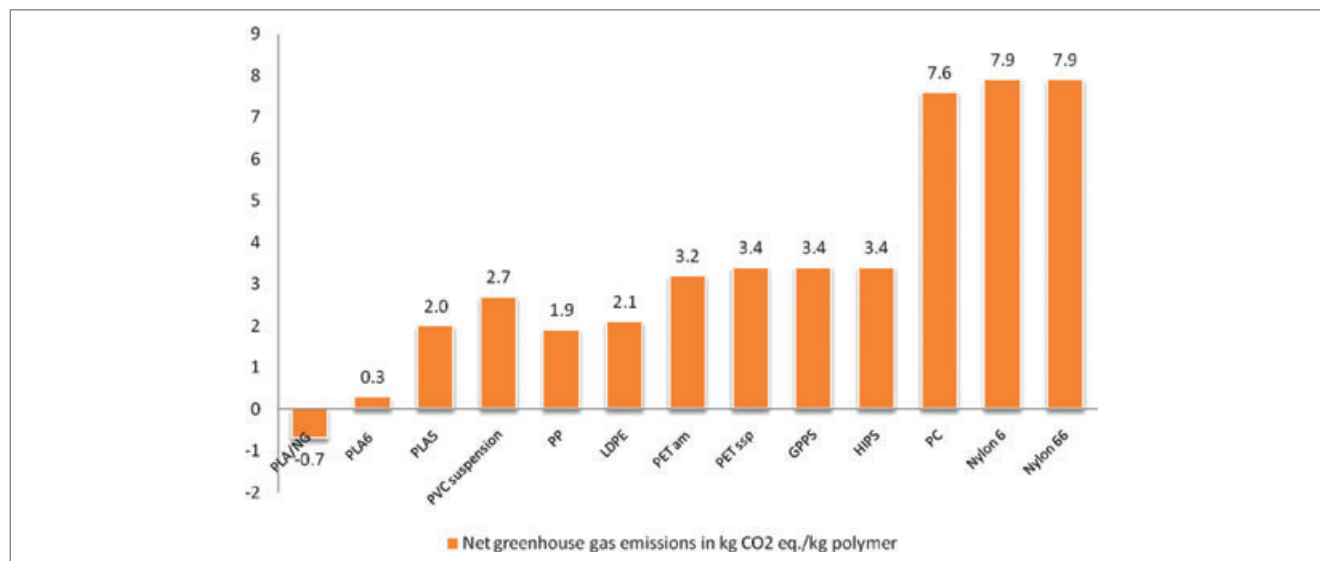**Figure 1–Current production steps for PLA.**

Figure 2–Net greenhouse gas emission of commercial PLAs and other polymers. PLA/NG = NatureWorks® PLA next generation, PLA5 = NatureWorks® PLA in 2005, PLA6 = NatureWorks® in 2006, HIPS = high impact poly(styrene), PC = poly(carbonate), GPPS = general purpose poly(styrene), PET am = PET amorph, PET ssp = PET solid sate polycondensed.

important contributor to global climate change and its warming. Because, carbon dioxide is absorbed from air when corn is grown, use of PLA has the potential to emit fewer greenhouse gases compared to competitive hydrocarbon-based polymers. "Net" or "residual" emissions are calculated as total emissions from the cradle to the factory gate minus carbon dioxide uptake that occurs during corn production. This amount is negative for present PLA production. It means the total CO_2 consumption from the cradle to factory is more than its emission to the environment (Bogaert and Coszach 2000). Vink and others (2003) concluded if all produced PLA articles enter into composting process which emits CO_2 in atmosphere; Nevertheless, their net CO_2 emission is less than for other polymers. Vink and others (2007) showed the net greenhouse gas emissions of NatureWorks® PLA polymers decreased from 2 kg CO_2 eq./kg polymer in 2003 to 0.3 kg in 2006. The authors also estimated the −0.7 kg of CO_2 for next PLA generation using wind energy in the near future. By this opportunity, PLA can even become a greenhouse gas sink by the implementation of a new process technology combined with the use of green power to drive the production processes (Figure 2).

NatureWorks® LLC, the present leader in PLA technology, has a 50 to 50 joint venture between Cargill incorporated and Dow Chemical Co. and was formed in November 1997. In 2002, they started the world's first full-scale PLA plant in Blair, Nebraska, U.S.A., capable of producing 140,000 metric tons per year. NatureWorks® entered into a joint venture between Cargill and Teijin Limited of Japan in December 2007 (www.natureworksllc.com).

Other major companies involved in PLA manufacturing are Toyobo, Dai Nippon Printing Co., Mitsui Chemicals, Shimadzu, NEC, Toyota (Japan), PURAC Biomaterials, Hycail (The Netherlands), Galactic (Belgium), Cereplast (U.S.A.), FkuR, Biomer, Stanelco, Inventa-Fischer (Germany), and Snamprogetti (China) (Wolf 2005; Platt 2006).

Sources for lactic acid fermentation

NatureWorks® exclusively uses corn starch as raw material for lactic acid production via lactic fermentation. Many studies have been conducted to find other sources of carbohydrates for lac-

tic acid production. The use of a specific carbohydrate feedstock depends on its price, availability, and purity. Some agricultural byproducts, which are potential substrates for lactic acid production include, cassava starch, lignocellulose/hemicellulose hydrolysates, cottonseed hulls, Jerusalem artichokes, corn cobs, corn stalks, beet molasses, wheat bran, rye flour, sweet sorghum, sugarcane press mud, cassava, barley starch, cellulose, carrot processing waste, molasses spent wash, corn fiber hydrolysates, and potato starch (Reddy and others 2008).

Other sources of carbohydrate for lactic acid production include kitchen wastes (Kim and others 2003; Zhang and others 2008), fish meal wastes (Huang and others 2008), and paper sludge (Budhavaram and Fan 2007). By using kitchen wastes, concerns about waste management in crowded cities could be automatically eased. Additionally, some parts of carbohydrates from wastes will return to the production cycle of lactic acid and, as a result, decrease a large amount of corn consumption. By using other carbohydrate sources rather than corn, the criticisms and debates about utilizing a food source as packaging material will be defused (Zhang and others 2008).

PLA Processing Technologies for Food Applications

The methods of manufacture for biopolymers are all established polymer-manufacturing techniques, but the control and application of these methods must be varied to cope with certain factors associated with exploiting the advantages of biopolymers. The manufacturing routes all show certain fundamental similarities, with the major differences depending on whether a thermoset or thermoplastic biopolymer is to be processed.

The conditions in biopolymer processes such as injection molding are least damaging to polymer melts, and most problematic in continuous processes like extrusion, particularly in processes where the extrudate is stretched, such as film blowing. The limiting factors for processing conditions for biopolymers are the same as for petrochemical-based ones: degradation at the upper limits of temperature and shear, and lack of homogeneity at the lower limits. However, these limits are somewhat more tightly drawn at the upper limits for biopolymers. The results of exceeding these upper limits are degradation of the polymer, resulting in molding

Table 1–Processing possibilities of typical commercial biodegradable polymers (Clarinval 2002; Clarinval and Halleux 2005, NatureWorks® datasheets).

	Injection molding	Extru-sion	Extrusion blow molding	Cast film extrusion	Blow mold-ing	Fiber spinn-ing	Thermo-forming
Starch	×	×	×	×			
Cellulose	×	×			×		
PHB	×	×	×	×	×		×
PHB-PHV	×	×	×	×	×	×	×
PLA	×	×		×	×	×	×
PBS	×	×					
PCL	×	×	×		×	×	×
PBST	×	×		×			×
PBAT		×	×	×			
PTMAT		×	×	×		×	
PVA	×	×		×		×	×
PP,PE + additives	×	×	×	×	×	×	×
Starch + PVA	×	×		×	×	×	
Starch + cellulose acetate	×	×	×		×		×

PHB = Poly(3-hydroxybutyrate); PHV = Poly(hydroxyl valerate); PBS = Poly(butylenes succinate); PCL = Poly(ε-caprolactone); PBST = Poly(butylene succinate terephthalate); PBAT = Poly(butylene adipate terephthalate);
PTMAT = Poly(tetramethylene adipate terephthalate); PVA = Poly(vinyl alcohol).

Table 2–Commercial Ingeo™ PLA resins adapted by NatureWorks® data sheets.

Product code	Applications	Usages
2002D	Extrusion, thermoforming	Dairy containers, food serviceware, transparent food containers, blister packaging, cold drink cups
3001D 3051D	Injection molding for applications with heat deflection temperatures lower than 55 °C (130 °F)	Cutlery, cups, plates, and saucers, and outdoor novelties
3251D	Injection molding, having higher melt flow capability than other PLA resins for easier molding of thin-walled parts	Injection molding applications, both clear and opaque, requiring high gloss, UV resistance, and stiffness
4032D	Biaxially oriented films with use temperatures up to 150 °C (300 °F), barrier to flavor and grease, and oil resistance	Laminations, printed films with higher curing temperatures, other packaging applications
4042D	Biaxially oriented films with use temperatures up to 130 °C (265 °F), barrier to flavor and grease, and superior oil resistance	Candy twist-wrap, salad, and vegetable bags, window envelope film, lidding film, label film, other packaging applications
4060D	Heat sealant with a seal initiation temperature of 80 °C	Can be coextruded with other PLA resin to form a sealant layer for biaxially-oriented PLA film
7000D	Injection stretch blow molding, for 1:2 stage operations	Fresh dairy, edible oils, fresh water
7032D	Injection stretch blow molding, for 1:2 stage operation	Fruit juices, sports drinks, jams, and jellies

defects such as weld lines, discoloration, or a strong odor in the final product (Johnson and others 2003).

Processing possibilities of typical commercial biodegradable polymers are presented in Table 1.

Commercial PLA resins are packaged in crystalline and amorphous pellet forms. Crystalline and amorphous pellets look significantly different. Semicrystalline pellets are opaque and amorphous pellets are transparent. Different types of PLA resins with different application ranges are being produced and each customer should specify packaging demands and match them with PLA data sheets. In Table 2, available commercial PLA resins for food packaging applications are characterized.

The processing technologies for producing different packaging applications with PLA resins are mentioned here.

Drying

As PLA is sensitive to high-relative humidity and temperature conditions, and for minimizing the risk of its molecular degradation, it is necessary to be dried less than 0.01% w/w. This value is expressed as 0.025% w/w or below in NatureWorks® data sheets. PLA resins normally are packaged with moisture content below 0.04% w/w in moisture-resistant foil liners to maintain that moisture level, and so the drying process is essential. Drying conditions are dependent on temperature, time, air flow rate, and dew point. Amorphous pellets must be dried below the T_g (43 to 55 °C) to prevent the resin pellets from sticking together, which can bridge and plug the dryer (Lim and others 2008).

For crystalline types, the recommended temperatures and times range between 80 to 100 °C and 4 to 2 h, respectively. Typical drying conditions are 4 h at 80 °C (175 °F) or to a dew point of −40 °C (−40 °F), with an airflow rate greater than 0.032 m^3/ min per kg (0.5 cfm/lb) of resin throughout (NatureWorks® PLA processing guide for biaxially oriented film 2005b). PLA is a hygroscopic thermoplastic and readily absorbs moisture from the atmosphere; so its resins should not be exposed to atmospheric

conditions after drying and the packages should be kept sealed until ready to use and promptly be dried and resealed if not entirely used.

Extrusion

The 1st major step in the conversion of plastic resin into films, sheets, containers and so on, is to change the pellets from solid to liquid or molten phase in an extruder.

Extrusion is a common way for melting thermoplasts and it is the 1st step for extrusion coating, cast film extrusion, blown film extrusion, and other polymer processes.

Screw extruders are typically used in the polymer industry. They consist of an electrically heated metal barrel, a hopper for feeding the resin, a motor for rotating a screw, and a die where the polymer melt exists. So, the combination of thermal energy generated by a heater and frictional heat due to friction between the plastic and the screw and barrel provide sufficient heat to melt the pellets.

The L/D ratio, which is the ratio of flight length of the screw to its outer diameter, determines the shear and residence time of the melt. Screws with a large L/D ratio provide greater shear heating, better mixing, and longer melt residence time in the extruder. Another important screw parameter is the compression ratio, which is the ratio of the flight depth in the feed section to the flight depth in the metering section. The greater the compression ratio a screw possesses, the greater the shear heating it provides (Giles and others 2005).

Recommended extrusion conditions for PLA pellets include general purpose screws with L/D ratios from 24:1 to 30:1 and compression ratio of 2.5:1 to 3:1, melt temperature of 200 to 220 °C, and also smooth barrels (NatureWorks® PLA 4042 data sheet 2006a).

Injection molding

Injection molding involves melting a thermoplastic by extrusion, injecting the polymer melt into a mold, cooling the part, and finally ejecting the part. Most polymers can be injection molded so long as they can flow and fill the mold cavity easily. The commonly used polymers are Poly(ethylene terephthalate) PET, Poly(styrene) (PS), Poly(propylene) (PP), high-density poly(ethylene) (HDPE), Low-density poly(ethylene) (LDPE), nylon, and Poly(vinyl chloride) PVC.

An injection molding machine is similar to an extruder and the main difference between 2 machines is in their screw operation. In an extruder, the screw rotates continuously providing output of continuous and long product (pipe, rod, sheet), but the screw of an injection molding machine, which is called reciprocating screw, does not only rotate but also moves forward and backward according to the steps of the molding cycle. The mold is equipped with a cooling system providing controlled cooling and solidification of the material. Injection molding may be used to manufacture a wide variety of parts such as bottle caps, food trays, containers, and preforms for blow molding (Rosato and others 2000).

Injection mold-grade PLA is injection molded on most conventional equipment, but there could be some torque limitations if the screw design has a high compression ratio. Compression ratios of 2.5 to 3 should be adequate and the recommended melting temperature is 200 to 205 °C. Since PLA has a lower glass transition temperature (about 58 °C) than PS or PET, it might take a little longer time to set up in the mold (NatureWorks® PLA injection molding guide for 3051D 2006b).

Physical aging occurs when a polymer is in a nonequilibrium state and is caused by molecular relaxations that are biased in the direction required to drive the material closer to equilibrium. This phenomenon is very common and is encountered in thermoplastics moldings that have been cooled rapidly from an elevated temperature during the shaping operation such as injection molding process (White 2006). Physical aging significantly affects the physical properties of the amorphous phase in glassy or partly glassy polymers. The effect of aging takes place around T_g and can be noticed by shrinkage of specific volume, decreases in specific enthalpy and entropy, and a decrease in molecular mobility. These effects are associated with decrease of free volume, which controls the mobility of large segments of the polymer chains and affects the mechanical properties of polymers such as shrinkage, stiffness, brittleness, and decrease in damping (Ke and Sun 2003b; Acioli-Moura and Sun 2008).

Injected molded PLA articles are relatively brittle, which caused by rapid physical aging of polymer since ambient temperature is approximately 25 °C below the T_g. Cai and others (1996) studied physical aging behavior of PLA in different times and temperatures by DSC. The results confirmed the augmentation of endothermic peak at T_g by increasing the aging time, which is related to the increase of the excess enthalpy of relaxation. The rate of physical aging was very fast initially and decreased as time increased. They also showed that the aging temperature of 37 °C had the maximum enthalpy of relaxation, but by increasing the temperature above 60 °C the enthalpy of relaxation was greatly reduced. However, storage conditions for injected molded PLA articles that are especially intended for further processing (like preforms) should be carefully controlled.

Shear-controlled orientation in injection molding (SCORIM) is a nonconventional injection molding technique that allows for the enhancement of the mechanical properties of semicrystalline polymers and has additional degrees of freedom over conventional injection molding. SCORIM technique manipulates the structure development of a solidifying polymer melt through an in-mold shearing action, thereby tailoring the morphology and hence controls the mechanical properties of polymers (Grossman 1995). Ghosh and others (2008) investigated the effect of operative parameters of SCORIM on Poly(L-lactic acid) (PLLA). They showed some modifications in energy at break and maximum stress of all the SCORIM processed PLLA. The overall increments in maximum stress and energy at break were 134% and 641%, respectively.

Blow molding

Blow molding is a process of blowing up a hot thermoplastic tube (called parison or preform, a term derived from the glass industry) with compressed air to conform to the shape of a chilled mold and releasing the finished product form the mold. The most widely used materials for blow molding are LDPE, HDPE, PP, PVC, and PET (Lee and others 2008).

There are 3 common types of blow molding: extrusion blow molding, injection blow molding, and injection stretch blow molding (ISBM).

Extrusion blow molding. Extrusion blow molding begins with extruding a polymer melt into a parison. The chilled mold is then closed, followed by blowing air through a blow pin to inflate the parison to conform to the shape to the mold cavity. After cooling the plastic, the mold is opened, and the part is ejected. Containers produced by extrusion blow molding must meet minimum stiffness requirements to undergo filling on automated lines. They must avoid, or limit, unsightly bulging under weight of their contents, both alone or when stacked. They must also withstand normal impacts of handling, transport, and accidental dropping. Such impact must be absorbed by the container walls, weld lines (pinch-off and handle areas), and screw cap closure threads, often under extremes of temperature. Basic polymers for extrusion blow molding are HDPE, PP, and PVC. These polymers are sometimes coextruded with Ethylene vinyl alcohol (EVOH) or nylon to provide a better gas barrier (Lee 2006).

PLA containers are not produced by this method, because of a lack of the required physical and mechanical properties; and PLA resins for this application have not been yet produced.

Injection blow molding. Injection blow molding is a 2-step process for making plastic containers. This method produces a molded parison called a preform. This method is preferred over extrusion blow molding for making small parts that require high-production volumes and closer quality dimensions. Injection blow molding consists of injecting a thermoplastic material into a cavity and around a core rod producing a hollow test tube like shape (preform). The molded preform still on the core rod is transferred to the blow mold. The mold is clamped around the preform and air is blown into it to shape to the cavity. The preform is injected onto a support pin or core, which forms a neck with threads to their required dimensions. The preform is then blown against the cavity wall to its final shape (Lee 2006; Lee and others 2008).

The use of preform allows the manufacture of bottles with more precise detail in the neck and finish (threaded) area than extrusion blow molding.

Injection blow molding requires lower degree of melt strength than extrusion blow molding and its tooling costs are higher. Common polymers for this method are PS, LDPE, Linear low-density poly(ethylene) (LLDPE), HDPE, PP, PVC, and PET (Lee and others 2008).

This process is typically limited to the production of relatively small bottles and PLA pellets are rarely recommended to be processed by this method.

Injection stretch blow molding. Injection stretch blow molding (ISBM) is an extension of injection blow molding with 2 modifications: (a) the preform is significantly shorter than the bottle and (b) a stretch rod is used to stretch the preform in the axial direction. This process became known in the blow molding industry with the introduction of plastic or PET soft drink bottles.

While all blow molding processes involve blowing air to stretch the parison or preform in some fashion, ISBM is designed to achieve and retain biaxial orientation to significantly improve gas barrier properties, impact strength, transparency, surface gloss, and stiffness. Biaxial orientation is achieved by elongating the preform with the stretch rod and blowing air to stretch the preform in a direction perpendicular to the axis of the preform, while precisely controlling a temperature warm enough to allow rapid inflation and molecular orientation, but cool enough to retard relaxation of its molecular structure once oriented (Rosato and others 2000)

PET bottles for carbonated soft drinks are the most common food packaging applications of this process. The combination of stretching by rod and blowing air at high pressure (about 4 MPa) induces biaxial molecular orientation, thereby making the bottles a better barrier to carbon dioxide and stronger to withstand the internal pressure (Rosato and others 2000; Lee and others 2008).

ISBM-grade PLA resins are accessible and they are generally used for bottles for different foods like fresh dairy liquids, fruit juices, sport drinks, edible oils, and so on.

ISBM-grade PLA resin is typically run at lower processing temperatures than bottle-grade PET and the blow molding conditions include: preform temperature at 80 to 100 °C, stretch rod speed 0.8 to 1.2 m/s, and blow mold temperature at 100 to 120 °C. In fact, the heating of the preforms is critical in getting a container with good clarity and material distribution. Normal preform temperatures for running on a 2-step process have been between 80 and 100 °C. This temperature may be lower or higher depending on the preform design, bottle design, and reheating equipment that is being used (NatureWorks® PLA ISBM bottle guide 2005a).

Preform design is critical in getting a container with good clarity and physical properties. Designing a preform for use as a PLA container is specific to the blow mold equipment, bottle design, and mold tooling.

Cast film extrusion

The cast film process involves extruding a molten polymer through a slit die and drawing it around 2 or more highly polished high-speed rolls, typically chrome-plated and water-cooled. In less than 1 revolution, the chill roll solidifies the product as it draws it down to the correct thickness. Cast film is used in packaging, food wrap, substrate for coating, protective film, agricultural film for weed control, general purpose polyethylene film as a protective barrier to prevent scratching of parts during shipment, and many other applications (Giles and others 2005).

Due to rapid cooling by the chilled rolls, cast films typically have a low degree of crystallinity and transparent appearance. Besides providing good optical properties, cast film extrusion has the advantages of high production rate, good control of film thickness and uniformity, and little or no additive is required for processing.

Similar to PP, PET, and PS films, the physical properties of PLA films can be enhanced through orientation. Uniaxial orientation of PLA is achieved with conventional machine direction orientation (MDO) rolls. Since PLA tends to neck in (neck in happens by contacting the melt film with the 1st point of the die; the hot film shrinks on its way down so its width from the die to the chill roll is reduced. At the same time, beading or thickening of the edges occurs) during drawing, nipped rolls are usually required. It is possible to improve both the thermal resistance and impact resistance of PLA films or sheets by drawing, orientation, and crystallization to the same level of strength and stiffness as oriented polypropylene (OPP) or PET, while maintaining its high transparency. An oriented film is obtained by stretching it to 2 to 10 times its original length at 60 to 80 °C, and further annealing it at temperatures between the stretching temperature and melting point. An oriented film may be either processed for dry lamination, printing, and heat seal or other applications including various types of packaging (Kawashima and others 2002).

Thermoforming

Thermoforming is a generic term encompassing many techniques for producing useful plastic articles from flat sheets. Thermoforming is a process that deals with the pressing or drawing of pliable plastic into final shape by vacuum or air pressure. A wide range of thermoplastics, including PP, LDPE, LLDPE, HDPE, PET, PS, and nylon, may be thermoformed. Food packaging is the largest application for thermoformed containers, trays, cups, and tubs. Typical thermoforming steps are clamping, heating, shaping, cooling, and trimming (Throne 1996)

PLA sheet can be thermoformed with vacuum, compressed air/vacuum, or only compressed air assistance. The radiant heater of the thermoforming line for PLA must be adjusted to very low temperatures. Preheating is not absolutely necessary; however it has the general advantage that the sheet is homogeneously preheated.

PLA sheet is quite brittle at room temperature and requires some special handling and storage considerations. There is a greater risk of cracking and breaking during transporting compared with Oriented poly(Styrene) (OPS) or PET. Neither the sheet nor the finished product can be stored at temperatures above 40 °C or greater than 50% relative humidity. These conditions minimize moisture uptake and consequently sheet blocking, and resistance to unwinding. Exposure to high temperatures or humidity, even for a short period, can cause the material to deform and eventually break down. Sheet and formed products must be transported in cooled trucks and stored in a climate-controlled warehouse. The toughness of PLA increases with orientation, and therefore, thermoformed articles are less brittle than PLA sheet, particularly in the regions that have been highly stretched during the forming operations rather than flanges and lips. So, flange or lip areas that receive less orientation tend to be more brittle than the rest of the thermoformed part (NatureWorks® processing guide for thermoforming articles 2005c; Patey 2010).

PLA is frequently thermoformed using forming ovens, molds, and trim tools designed for PET or polystyrene. Because of higher shrinkage of PP than PLA, the molds and trim tools designed for PP are less optimally used for PLA.

PLA has a lower softening temperature than PET or PS. Typically oven settings are about 55 °C (100 °F) or lower than PS and about 40 °C (75 °F) or lower than PET oven settings. The sheet should be about 90 to 110 °C (190 to 230 °F) entering the mold. Aluminum molds are recommended for thermoforming PLA. PLA thermal properties indicate that the cooling time in the mold will be greater for PLA than either PS or PET (NatureWorks® processing guide for thermoforming articles 2005c).

Patey (2010) discussed some essential factors for PLA thermoforming process. According to his suggestions, optimizing a

conventional polymer thermoforming line for PLA just needs some minor modifications in tools and equipments.

PLA crystallinity diminishes its shrinkage after thermoforming process. Uradnisheck (2009) showed the shrinkage of PLA thermoformed articles is minimized by longer dwell times and crystallinity of polymer. He concluded that the crystallinity in a thermoformed article dwelling in the heated mold raised to a higher level due to supplemental crystallinity generated in the preheat step and forming or stretching step.

PLA Thermal Stability

PLA is thermally unstable and exhibits rapid loss of molecular weight as the result of thermal treatment at processing temperatures. The ester linkages of PLA tend to degrade during thermal processing or under hydrolytic conditions. PLA undergoes thermal degradation at temperatures lower than the melting point of the polymer, but the degradation rate rapidly increases above the melting point. It has been postulated that thermal degradation mainly occurs by random main–chain scissions. Several reactions such as hydrolysis, depolymerization, oxidative degradation, and inter- and intramolecular trans–esterification reactions to mononmer and oligomeric esters, are suggested to be involved in the degradation process during thermal treatments (Taubner and Shishoo 2001; Södergård and Stolt 2002).

Taubner and Shishoo (2001) studied 3 parameters on thermal degradation of PLA during extrusion processing, including processing temperature (210 and 240 °C), residence time in the melt (1.75 and 7 min), and the inherent moisture content of polymer. Their results confirmed higher polymer degradation by increasing processing temperature and time. In a temperature of 210 °C, the loss in M_n (Number-average molecular weights) was less dependent on the residence time in the melt compared to when processed at a temperature of 240 °C. The presence of moisture in the material affected the loss in M_n to a great extent when processing was done at 210 °C. The rate of degradation at 240 °C and 7 min was so high that they concluded the moisture content in the polymer probably does not contribute further to the degradation process.

Different factors like particle size and shape of polymer, temperature, moisture, crystallinity, % D-isomer, residual lactic acid concentration, molecular weight, molecular weight distribution, water diffusion, and metal impurities from the catalyst will affect the polymer degradation rate. Yu and others (2003) have developed a mathematical model to describe the molecular weight and polydispersity index (Q) in PLA thermal degradations. They claimed model ability to predict changes of the molecular weight and poly dispersity index in the PLLA thermal degradation. Their model was based on the random chain scission mechanism, effects of temperature, and time on the molecular weight and polydispersity index.

PLA Properties

PLA has unique properties like good appearance, high mechanical strength, and low toxicity; and good barrier properties have broadened its applications. Numerous researchers have studied the different properties of PLA alone and in combination with other polymers as blend or copolymer; and here some of them will be introduced.

Auras and others (2003) studied mechanical, physical, and barrier properties of 2 PLA films by the names of 4030–D, which was made with nominally 98% L-lactide, and 4040–D, which was made with nominally 94% L-lactide resins. Finally, the data from these 2 PLA film samples were compared to those of polystyrene (PS) and polyethylene terephthalate (PET). PLA films showed good tensile strength with higher values than PS but lower than PET. Both 4030-D and 4040-D had lower T_m (melting point) and T_g (glass transition temperature) than PET and PS, which makes PLA better for heat-sealing and thermal processing. In terms of barrier properties of PLA, the permeability coefficients of CO_2 and O_2 were lower than those of PS and comparable to those of PET.

For tensile modulus and flexural modulus, PLA has the highest value in comparison to PS, PP, and HDPE. For notched izod impact (izod impact strength testing is an American society for testing and materials [ASTM] standard method [D256 − 06ae1] of determining impact strength. A notched sample is generally used to determine impact strength. An arm held at a specific height is released. The arm hits the sample and breaks it. From the energy absorbed by the sample, its impact strength is determined), PLA has the lowest one between PS, PP, and HDPE. The elongation at break is low and nearly 4% that is just higher than that of PS (Dorgan and others 2000).

Low glass transition temperature of PLA limits its usages in thermally processed packages. Because of its deformation and its low melting temperature, it is better to use it for heat-sealing and thermoforming applications.

Five major properties of typical biodegradable polymers are compared with LDPE, PS, and PET in Table 3. It is approximately possible to predict the application fields of a polymer by these properties and barrier properties.

The other important property of polymers is their rate of crystallinity. Crystallinity is the indication of amount of crystalline region in the polymer with respect to amorphous content. Crystallinity influences many polymer properties including hardness, modulus, tensile strength, stiffness, crease point, and melting point. So, while selecting a polymer for a required application its crystallinity plays the foremost role.

PLA crystals can grow in 3 structural positions called α, β, and γ forms. They are characterized by different helix conformations and cell symmetries, which develop upon different thermal and/or mechanical treatments. The α form grows upon melt or cold crystallization, the β form develops upon mechanical stretching of the more stable α form, and the γ form, which only recently has been reported to develop on hexamethylbenzene substrate (Di Lorenzo 2005).

Di Lorenzo (2005) measured crystallization rates of PLA over a wide temperature range, using both isothermal and nonisothermal methods. He determined that the crystallization rate of PLA at temperatures between 100 and 118 °C is very high. He concluded that the high crystallization rate of PLA below 120 °C has to be ascribed to the high rate of radial growth of the spherulites (spherical semicrystalline regions inside nonbranched linear polymers).

By modification of the chain architecture through the introduction of branching, different melt flow properties will be obtained. Thermal and rheological properties of 2 commercial types of PLA, linear and branched, were investigated by Dorgan and others (2000). The crystallization kinetic of the branched polymer was faster than that of the linear analog. Longer relaxation times in the terminal region of the branched material introduced it as a higher zero shear rate viscosity. They concluded that by utilizing the structure modifications through polymer branching the ability of using PLA in many processing operations will be extended.

Optical properties of PLA are important in dyeing operations for textiles and in various packaging applications where clarity is desirable. Hutchinson and others (2006) determined the optical

Table 3–Comparison of typical biodegradable polymer properties with LDPE, PS, and PET adapted from Clarinval and Halleux (2005).

	T_g (°C)	Tm (°C)	Tensile strength (MPa)	Tensile modulus (Mpa)	Elongation at break (%)
LDPE	−100	98 to 115	8 to 20	300 to 500	100 to 1000
PCL	−60	59 to 64	4 to 28	390 to 470	700 to 1000
Starch	–	110 to 115	35 to 80	600 to 850	580 to 820
PBAT	−30	110 to 115	34 to 40	–	500 to 800
PTMAT	−30	108 to 110	22	100	700
PS	70 to 115	100	34 to 50	2300 to 3300	1.2 to 2.5
Cellulose	–	–	55 to 120	3000 to 5000	18 to 55
PLA	40 to 70	130 to 180	48 to 53	3500	30 to 240
PHB	0	140 to 180	25 to 40	3500	5 to 8
PHA	−30 to 10	70 to 170	18 to 24	700 to 1800	3 to 25
PHB-PHV	0 to 30	100 to 190	25 to 30	600 to 1000	7 to 15
PVA	58 to 85	180 to 230	28 to 46	380 to 530	–
Cellulose acetate	–	115	10	460	13 to 15
PET	73 to 80	245 to 265	48 to 72	200 to 4100	30 to 300
PGA	35 to 40	225 to 230	890	7000 to 8400	30
PEA	−20	125 to 190	25	180 to 220	400

PGA = Poly(glutamic acid); PEA = Poly(ester amide).

properties of PLA with different amounts of stereoisomer proportions by ellipsometric measurements. They developed an equation for index of refraction of PLA with a wide range of stereoisomer proportions (L-content) within the range of wavelengths from 300 to 1300 nm by using Cauchy coefficients.

There are many PLA resins for different applications with different properties; the general characteristics of a commercial amorphous PLA, injection mold grade and having a 96:4 L:D ratio content, are summarized in Table 4.

PLA barrier properties

One of the most important factors in food packaging polymers is their barrier or permeability performance against transfer of gases, water vapor, and aroma molecules. Gas permeation properties of PLA (L:D ratio 96:4) have been studied by Lehermeier and others (2001) and these values have been reported: at 30 °C, N_2 permeation in PLA was 1.3 (10^{-10} cm^3cm/cm^2scm Hg), and the activation energy was 11.2 kJ/mol. For oxygen, the corresponding values were 3.3 (10^{-10} cm^3cm/cm^2scm Hg) and 11.1 kJ/mol. The values for carbon dioxide permeation were 1.2 (10^{-10} cm^3cm/cm^2scm Hg) and 6.1 kJ/mol. For methane, a value of 1.0 (10^{-10} cm^3cm/cm^2scm Hg) and an activation energy of 13.0 kJ/mol were found.

The authors concluded that polymer chain branching and small changes in L:D stereochemical content have no effect on permeation properties, but film crystallinity profoundly impacted of the permeation of mentioned gases. For example, due to higher crystallinity of biaxially oriented PLA film, CH_4 permeation is 4.5 times lower than that of the other films. The permeation properties of PLA for all gases studied were very similar to polystyrene.

In research done by Bao and others (2006), different results for pure gas permeation of PLA were obtained, which disagreed with those of previous work. They used a time–lag method for the determination of PLA permeation to pure gases and also determined diffusivity and solubility of N_2, CO_2, and O_2 in PLA film. For example, at 30 °C, N_2 permeability, diffusivity, and solubility in PLA (98.7% L, 1.3% D) were 0.05 (10^{-10} cm^3cm/cm^2scm Hg), $2.4 \times 10^{-8} cm^2/s$, and $2.2 \times 10^{-4} cm^3/cm^3$(polymer) cm Hg, respectively. The measured activation energy of N_2 permeation was 34.6 kJ/mol.

Sorption of nitrogen, oxygen, carbon dioxide, and water in PLA has also been studied at 293.2, 303.2, and 313.2 °K (Oliveira and others 2004).

Shogren (1997) reported that the water vapor transmission rate of crystalline and amorphous PLA in 6, 25, and 49 °C as 27, 82, and 333 g/m^2 per day for the crystalline form and 54, 172, and 1100 g/m^2 per day for the amorphous form, respectively. He reported activation energies of 5 and − 0.1 kJ/mol for amorphous and crystalline PLA, respectively.

Siparsky and others (1997) used a "solution-diffusion" model to determine the water vapor permeability parameters of different PLA films, PLA copolymers with caprolactone, and blends with polyethylene glycol. These parameters included the solubility coefficient S, which is a measure of the equilibrium water concentration available for hydrolysis and the diffusion coefficient D, which characterizes the rate of water vapor diffusion into the film under specific conditions. They calculated the permeability coefficient by the equation of P = SD. They studied S and D for PLA films by different percent of L and D Lactide. They found the degree of crystalline had little influence on the measured permeability parameters.

In a more detailed research done by Tsuji and others (2006), the effects of D-Lactide content, degree of crystallinity (% Xc), and molecular weight of PLA films on water vapor transfer rate (WVTR) were studied. They observed the WVTR of PLA films decreased monotonically with increasing Xc from 0% to 20%, while leveled off for Xc exceeding 30%; so they suggested this change due to the higher resistance of restricted amorphous regions to water vapor permeation compared with that of the free amorphous regions. They also concluded that changes in M_n of PLA films in the range of 9×10^4 to 5×10^5 g/mol and D-lactide unit content of PLA films in the range of 0% to 50% have insignificant effects on their WVTR values.

Some aforementioned PLA permeability parameters are summarized in Table 5.

Orientation changes the barrier properties. In a study done by Auras and others (2005), oriented PLA (OPLA) was investigated with PET and oriented polystyrene (OPS) with regard to physical, mechanical, and barrier properties. They concluded, in terms of water vapor barrier, that PET gave the best performance, followed by OPS and OPLA. In the case of oxygen barrier properties, PET showed the lowest oxygen permeability coefficients, followed by OPLA and OPS that showed very poor oxygen barrier performance.

According to these results, the barrier properties of PLA are remarkable and better than those of OPS. As a consequence, PLA

Table 4–General characteristics of commercial amorphous poly L-lactid acid film, injection mold grade, 96:4 L:D, produced by NatureWorks® Co.

Characteristics	Unit	Amount	Reference
Physical:			
Molecular weight	g/mol	66000	Garlotta (2001)
Specific gravity	–	1.27	
Solid density	g/cm^3	1.2515	
Melt density	g/cm^3	1.0727	
Glass transition temperature	°C	55	Mehta and others (2005)
Melting temperature	°C	165	
Specific heat (Cp)	J/Kg °C		
190 °C		2060	
100 °C		1955	
55 °C		1590	
Thermal conductivity	W/m °C		
190 °C		0.195	www.nature worksllc.com (technical data sheet)
109 °C		0.197	
48 °C		0.111	
Optical:			
UV light transmission:			Auras and others (2004)
190 to 220 nm		<5%	
225 to 250 nm		85%	
>300 nm		95%	
Visible light transmission		95%	
Color			
L*		90.64 ± 0.21	
a*		−0.99 ± 0.01	
b*		−0.50 ± 0.04	
Mechanical:			
Tensile strength	MPa	59	
Elongation at break	%	7.0	
Elastic modulus	MPa	3500	
Shear modulus	MPa	1287	
Poissons ratio	–	0.3600	www.nature works.com (technical data sheet)
Yield strength	MPa	70	
Flexural strength	MPa	106	
Unnotched izod impact	J/m	195	
Notch izod impact	J/m	26	
Rockwell hardness	HR	88	
Heat deflection temp.	°C	55	
Vicat penetration	°C	59	
Ultimate tensile strength	MPa	73	
Percent of elongation	%	11.3	
Young's modulus	MPa	1280	
Rehological:			
Cross WLF Viscosity Model:			
n		0.2500	
Tau	Pa	1.00861e + 005	www.nature worksllc.com (technical data sheet)
D1	Pa-s	3.31719e + 009	
D2	K	373.15	
D3	K/P	0	
A1		20.194	
A2	K	51.600	

Table 5–PLA permeability parameters.

		L:D, 96:4 (30 °C) (Lehermeier and others 2001)	L:D, 98.7:1.3 (30 °C) (Bao and others 2006)
CO_2	10^{-10} cm^3 cm/ cm^{2}scm Hg	1.2	1.1
O_2		3.3	0.26
N_2		1.3	0.05

		Water vapor permeation property		
(Shogren 1997)		**6 °C**	**25 °C**	**49 °C**
Crystalline, 66% crystallinty	g/m^2/day	27	82	333
Amorphous		54	172	1100
(Siparsky and others 1997)		**20 °C**	**40 °C**	**50 °C**
L:D (100:0), 39% crystallinity	cm^{3}cm/cm^{2}sPa	1.6	1	2
L:D (100:0), Amorphous		1.9	0.8	2.1
L:D (95:5)		1.4	2.2	2.1
L:D (50:50)		2.2	8.7	6.1

and oligomers that will be subsequently hydrolyzed in aqueous systems to lactic acid. Based on these findings, they concluded that PLA is safe and GRAS for its intended uses in fabricating articles intended for use in contact with food. The authors also mentioned that the projected intake of lactic acid from PLA is approximately 700 times less than the estimated daily lactic acid intake of a breast-fed infant.

Mutsuga and others (2008) determined the PLA migration products for 4 different PLA sheets, which are used in lunch boxes in Japan. They applied 3 food simulants such as water, 4% acetic acid, and 20% ethanol at temperatures of 40, 60, and 95 °C for different periods of time. They concluded that the rate of migration is augmented by high temperatures. The total migrated levels, including lactic acid, lactide, and oligomers, at 40 °C after 180 d were 0.28 to 15 μg.cm^{-2} and 0.73 to 2840 μg.cm^{-2} for 60 °C after 10 d. The migration test at 95 °C for 30, 60, and 120 min mimicked the use of lunch boxes in a microwave oven at 100 °C or above, and the total migrated levels for 120 min were 2.04 to 49.63 μg.cm^{-2}.

So, for a PLA much of the concerns about migrations of potential dangerous materials, which exist for petrochemical-based polymers are resolved. These results are only for pure PLA polymer and more studies are needed for its blends and copolymers, also for all the compounds that are applied or added for improving physical, mechanical, and barrier properties of PLA.

PLA Applications

PLA has potential for use in a wide range of applications; Table 6 shows an overview of NatureWorks^{TM} PLA and Ingeo^{TM} fibers, PLA opportunities, and examples of commercially available products. As be seen, PLA food packaging applications are ideal for fresh products and those whose quality is not damaged by PLA oxygen permeability.

PLA is a growing alternative as a "green" food packaging polymer. New applications have been claimed in the field of fresh products, where thermoformed PLA containers are used in retail markets for fruits, vegetables, and salads. The market capacity of these products packaged in PLA is unlimited.

The major PLA application today is in packaging (nearly 70%); the estimation for 2020 shows the increase of other applications especially in fibers and fabrics (Table 7).

is suitable for packaging a wide range of foods that are mentioned in the section of PLA applications.

Studies on Migration from PLA

Lactic acid is the lone monomer in the PLA structure and so, migrated agents are lactic acid monomers, dimmers, and oligomers. Conn and others (1995) investigated the safety of PLA as a food contact polymer under different conditions and studied the migration of most probable species from PLA. They concluded: (1) Very limited migration can be expected from PLA into foods that it contacts during the intended conditions of use. (2) The small amount of any material that might migrate from PLA into food will be lactic acid, or its dimers (lactoyl lactic acid and lactide)

Table 6–Business segments for products based on Ingeo[TM] plastic and Ingeo[TM] fibers PLA (NatureWorks®) adapted from Vink and others (2004).

Business segment	Commercially available applications
1- Ingeo plastic applications	
Rigid thermoforms	Clear fresh fruit and vegetable clamshells
	Deli meat trays
	Opaque dairy (yogurt) containers
	Bakery, fresh herb, and candy containers
	Consumer displays and electronics packaging
	Disposable articles and cold drink cups
Biaxially oriented films	Candy twist and flow wrap
	Envelope and display carton windows
	Lamination film
	Product (gift basket) overwrap
	Lidding stock
	Die cut labels
	Floral wrap
	Tapes
	Shrink sleeves
	Stand-up pouches
	Cake mix, cereal, and bread bags
Bottles	Short shelf-life milk
	Edible oils
	Bottled water
2- Ingeo fiber applications	
Apparel	Casual (sports-), active, and underwear fashion item
Nonwovens	Wipes, hygiene products, diapers, shoe liners, automotive head and door liners, and paper reinforcement
Furnishings	Blankets and panel, upholstery, and decorative fabrics
Industrial carpets	Agricultural and geotextiles[a]
	Residential/institutional broadloom and carpet tiles
Fiberfill	Pillows, comforters, mattresses, Duvets, and furniture

[a]Geotextiles are permeable fabrics which, when used in association with soil, have the ability to separate, filter, reinforce, protect, or drain. Usually geotextiles are placed at the tension surface to strengthen the soil.

Table 7–Main applications of PLA in 2003 and the estimation for 2020 (Wolf 2005).

	Percent of total production (2003)		Estimated percent of total production (2020)	
	Cargill Dow	Hycail	Cargill Dow	Hycail
Sector				
Packaging	70	70	20	55
Building				
Agriculture	1	12		6
Transportation			20	2
Furniture				
Electric appliance and electronics	1	1	10	10
Houseware		12		6
Other (fibers and fabrics)	28	3 to 5	50	21
Other (analytics)				
Total	100	100	100	100

Table 8–PLA functional properties for packaging (Kawashima and others 2002).

Functional property	Packaging improvement	Comment
Dead fold, twist, and crimp[a]	Improved folding and sealing	OPLA has excellent dead fold and twist retention
High gloss, and clarity	Package aesthetics	Comparable with PET and cellophane, 3 times more than nylon and PP, 10 times more than LDPE
Barrier properties	Grease and oil resistance	Good resistant to oils and terpens
Renewable resource	Made from CO_2 and H_2O	
Flavor and aroma properties	Reduced taste/odor issues	
Low temperature heat seal	Stronger seals at lower temperatures	PLA can provide an "easy-open" package
High tensile and modulus	Wet paper strength, ability to down guage coating	
Low coefficient of friction, polarity	Printability	Excellent printability, metallizable, antifogging ability
GRAS status	Food contact approved	

[a]The ability to hold a crease or fold, or the ability to retain a twist that is imparted in order to close the edges of the film around a small object.

Table 9– Some commercialized PLA products (Platt 2006; www.nature worksllc.com).

Product	Company name[a]
Packaging	
Films and trays for biscuits, fruit, vegetables, and meat	Treophan, Natura, IPER, Sainsburys, Sulzer, Ecoproducts, RPC
Yogurt cup	Cristallina/Cargill Dow
Rigid transparent packaging of batteries with removable printed film on back side	Panasonic
Trays and bowls for fast food	McDonalds
Envelope with transparent window, paper bag for bread with transparent window	Mitsui, Ecocard
Agriculture and horticulture	
Mulching films	Novamont, Cargill Dow
Long life consumer good	
Apparel (T-shirt, socks)	FILA/Cargill Dow, Kanebo Gosen
Blanket	Ingeo
Casing of walkman	Sony
CD (compact disk)	Sanyo Marvic Media/Lacea
Computer keys	Fujitsu
Small component of laptop housing	Fujitsu/Lacea
Sapre wheel cover	Toyota

[a]List is not exhaustive.

In the field of packaging, 2 specific areas have received close attention, namely high-value films and rigid-thermoformed containers. PLA brings a new combination of attributes to packaging, including stiffness, clarity, deadfold and twist retention, low-temperature heat sealability, as well as an interesting combination of barrier properties including flavor, and aroma barrier characteristics. The functional properties and benefits of PLA in these areas are presented in Table 8.

Commercialized PLA products demonstrate this fact that PLA is not being used solely because of its degradability, nor because it is made from renewable resources; it is being used because it functions very well and provides excellent properties at a competitive price. There are many commercialized PLA products in today's market and their variety and consumption are increasing rapidly (Table 9). The reader can find the partners and consumers of PLA from the NatureWorks® Co. website (www.natureworksllc.com).

PLA is also used in biomedical applications, with various uses as internal body components mainly in the of restricted load for example, interference screws in ankle, knee, and hand; tacks and pins for ligament attachment; rods and pins in bone, plates and screws for craniomaxillofacial bone fixation (Lim and others 2003); and also for surgical sutures, implants, and drug delivery systems (Furukawa and others 2005; Mills and others 2006).

PLA as an Active Packaging Material
Release studies from PLA

Active packaging is defined as an intelligent or smart system that involves interactions between package or package components and food or internal gas atmosphere and complies with consumer demands for high quality, fresh-like, and safe products (Labuza and Breene 1989).

Active packaging is an innovative approach to change the condition of the packaging to extend shelf-life or improve safety or sensory properties while maintaining the quality of the food. Traditional packaging concepts are limited in their ability to prolong shelf-life of food products. The most important active packaging concepts are O_2 and ethylene scavenging, CO_2 scavengers and emitters, moisture regulators, antimicrobial packaging concepts, antioxidant release, release or adsorption of taste, and aroma molecules (Vermeiren and others 1999; Lopez-Rubio and others 2004; Kerry and others 2006).

As a GRAS and biodegradable material, and also because of its biosorbability and biocompatible properties in the human body, PLA and its copolymers (especially poly-glycolic acid) is attractive to pharmaceutical and medical scientists as a carrier for releasing various drugs and agents like bupivacaine (Sokolsky-Papkov and others 2009), rapamycin (Miao and others 2008), melittin (Cun and others 2008), 5-fluorouracil (Liu and others 2008), amoxicillin (Xu and Czernuszka 2008), human nerve growth factor (rhNGF) (Gu and others 2007), and gentamicin (Schnieders and others 2006) and many others.

In food domains, little research has been done studying the ability of PLA as an active packaging material. PLA is a relatively new polymer and needs time to become an acceptable and an effective active packaging in the market.

Antioxidants have been added to food packaging material for the intentional purpose of migration into food, because prooxidant effects are often seen to a high extent and could be reduced by antioxidants. Van Aardt and others (2007) studied the release of antioxidants from loaded poly (lactide-co-glycolide) (PLGA) (50:50) films, with 2% α-tocopherol, and a combination of 1% butylated hydroxytoluene (BHT) and 1% butylated hydroxyanisole (BHA), into water, oil (food simulant: Miglyol 812), and milk products at 4 and 25 °C in the presence and absence of light. They concluded that in water medium PLGA (50:50) showed hydrolytic degradation of the polymer and release of BHT into water. In Miglyol 812, no degradation or antioxidant release took place, even after 8 wk at 25 °C. Milk fat was stabilized to some extent when light-exposed dry whole milk and dry buttermilk were exposed to antioxidant-loaded PLGA (50:50). The authors also suggested potential use of degradable polymers as a unique active packaging option for sustained delivery of antioxidants, which could be a benefit to the dairy industry by limiting the oxidation of high-fat dairy products, such as ice cream mixes.

PLA and antimicrobial packaging trends

The innovative strength of PLA antimicrobial packaging has a direct impact on consumer health by creating safer and more wholesome packaged foods. Active packaging realizes certain extraordinary and vital functions other than providing an inert barrier between product and external conditions.

Active substances that are important and considered for novel bioactive packaging include antimicrobials, vitamins, phytochemicals, prebiotics, marine oils, and immobilized enzymes (Lopez-Rubio and others 2006).
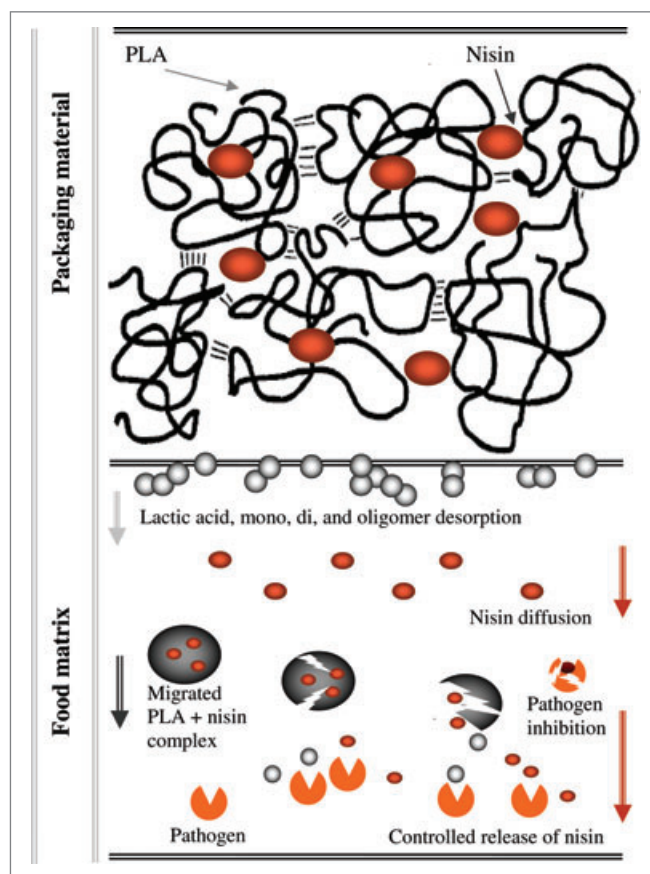

Figure 3–Schematic representation of PLA film with nisin as an active agent incorporated and release thereof.

A whole range of active additives, including silver-substituted zeolite, organic acids and their salts, bacteriocins such as nisin and pediocin, enzymes such as lysozyme, a chelator like ethylenediaminetetraacetic acid (EDTA), lactoferrin, and plant extracts have already been successfully incorporated in antimicrobial active packaging (Joerger 2007).

The most widely used bacteriocin in active food packaging is nisin due to its GRAS status (FDA 2001). Successful introduction of a new active packaging requires careful attention to the interactions in the active agent, packaging, and food triangle.

Notion of controlled release. In particular for active packaging, the major complexity emerges for migration/diffusion as either slow release of package component itself or as an active agent being incorporated. In both contexts, the evaluation of materials compliance with regulations includes migration monitoring for package component (monomer) and additives (active agent). A schematic representation is showed in Figure 3 for release of an active agent (nisin) alone and in conjunction with packaging material. Recently, the predictive mathematical modeling for active agent-controlled release and its various approaches were excellently reviewed by Poças and others (2008).

On the contrary, to study an additive's release from a package, active agent desorption from the multilayer biodegradable film and diffusion in agarose gels were monitored. The data attained after 2 or 6 d of contact between antimicrobial films and agarose gels were employed to find out nisin mass transfer by numerical modeling following Fick's 2nd law. The values were in the range from 0.87×10^{-3} m/s to 4.30×10^{-3} m/s and 6.5×10^{-11} m²/s to 3.3×10^{-10} m²/s, for nisin apparent desorption and diffusion

coefficients, respectively. The diffusion process was governed by interactions between nisin, package, and food matrix simulant (Chollet and others 2009).

Mode of incorporation. The customized direct incorporation of active agents may result in a loss of activity due to interactions with food components, thus showing from a diminution of active concentration and dilution into bulk foods (Kim and others 2002; Coma 2008). The incorporation of antimicrobial agents into PLA packaging material slows down their release and helps to maintain high concentrations of the active compounds against pathogenic bacteria like *Listeria monocytogenes* (Jin and others 2009).

In the last decade, the above-mentioned slow release approach has been used for PLA. In this regard, major antimicrobial agents include bacteriocins, predominantly nisin (Ariyapitipun and others 1999; Jin and others 2009), lactic acid (Ariyapitipun and others 1999), lysozyme (Del Nobile and others 2009), and chitosan (Torres-Giner and others 2008).

Novel PLA active packaging potential approaches

Although the above-mentioned PLA systems reduced resistant bacterial strain development and guaranteed a higher level of microbial protection for certain food products, their casting and preparation was complicated and inactivation of the active proteins was observed. Active agent modification by attachment to a polymer did not yield biologically active derivatives. Up till now, a literature study reveals that relatively low attention has been given to micro-encapsulated active agents in foods. Active agent-loaded polymeric micro-/nanoparticles give the impression of being promising formulations to achieve long-lasting antimicrobial activity (Salmaso and others 2004; Sanchez-Garcia and others 2007).

Thus, this particular controlled release concept can be enlarged to the applications of other active agents like antioxidants for oil-rich foods and antisticking/antifogging agents for cheese slices and fresh fruits, respectively.

PLA Modifications

The special characteristics of PLA can make it a good fit for some applications but may also require modifications for some others. For example, the oxygen and moisture permeability of PLA is much higher than for most other plastics, such as PE, PP, and even PET. However, the applications of PLA are limited by several factors such as low glass transition temperature, weak thermal stability, and low toughness and ductility (Harada and others 2007).

For extending PLA applications, the properties like impact strength or flexibility, stiffness, barrier properties, thermal stability, and production costs must be improved. Generally, modifiers have been studied to improve stiffness at elevated temperatures, reduce cost, or increase the degradation rate of PLA.

Some efforts of PLA modifications in the field of packaging are presented in Table 10.

A large number of investigations have been performed on the blending of PLA with various polymers, for example, thermoplastic starch, poly (ethylene oxide), poly (ethylene glycol), poly (ε-caprolactone), poly (vinyl acetate), poly (hydroxy butyrate), cellulose acetate, poly (butylene succinate), and poly (hexamethylene succinate). Low molecular weight compounds have also been used as plasticizers for PLA, for example, oligomeric lactic acid, glycerol, triacetine, and low molecular weight citrates (Ljungberg and others 2005).

The choice of polymers or plasticizers to be used as modifiers for PLA is limited by the requirements of the application. For packaging and hygiene applications, only nontoxic substances approved for food contact and personal care can be considered as plasticizing agents. The plasticizer should be miscible with PLA, thus creating a homogeneous blend. The plasticizer should not be too volatile, because this would cause evaporation to occur at the high temperature used during processing. Furthermore, the plasticizer should not be prone to migration into the materials in contact with the plasticized PLA. It would also cause the blended materials to regain the brittleness of pure PLA (Ren and others 2006).

There is a tendency for plasticizers to migrate to the surface of a polymer. A possible way to prevent this migration would be to increase the molecular weight of the plasticizers.

However, increasing the molecular weight too much would eventually decrease the solubility causing phase separation and formation of a 2-phase system.

The final properties of these blends depend on the chemical structure of the original components, the mixing ratio of the constituent polymers, the interaction between the components, and the processing steps to which they are then subjected.

Amorphous PLA exhibits lower modulus above the glass transition temperature and poor heat resistance, which limits the wide application of PLA in the general plastic use. Thus, how to improve the crystallization behavior or enhance the degree of crystallinity (% Xc) of PLA becomes the main problem that must be solved. Decreasing the cooling rate of PLA from melt and providing an annealing process for PLA articles is believed to be the most efficient way to enhance the (% Xc) of PLA. It has been reported that the smaller the cooling rate, the higher the (% Xc). Annealing endows PLA chain segments enough activation energy and promotes the crystallization through the reorganization process. Especially, in a certain condition, the annealing process also induces the polymorphic transition in PLA (Li and others 2009).

Other kinds of modifications, such as surface modifications, are being applied in biomedical uses for improving polymer release properties (Janorkar and Hirt 2004; Koo and Jang 2008).

Nanotechnology and PLA Food Packaging

Nanotechnology and its applications in food science have recently been studied by several researchers. The use of nanoparticles, such as micelles, liposomes, nanoemulsions, biopolymeric nanoparticles, and cubosomes, as well as the development of nanosensors aimed at ensuring food safety, are some novel nanofood applications.

Nanoparticles can be used as bioactive compounds in functional foods. Bioactive compounds that can be found naturally in certain foods have physiological benefits and might help to reduce the risk of certain diseases, including cancer. Omega-3 and omega-6 fatty acids, probiotics, prebiotics, vitamins, and minerals have found their applications in food nanotechnology as bioactive compounds (Sozer and Kokini 2009).

Nanotechnology is also applicable in food packaging in the form of elementary components of food packaging. This approach includes improving packaging performances like its gas, moisture, ultraviolet, and volatile barriers, increasing mechanical strength, decreasing weight, and increasing the heat resistance and flame retardancy of the packaging material. Nanoadditives, intelligent packaging (using nanosensors), delivery and controlled release of neutraceuticals, antibacterial agents, self-cleaning packaging, and systems to monitor product conditions during transportation are other novel nano-approaches in food packaging (Ray and Bousmina 2005; Sozer and Kokini 2009).

Table 10–Summary of PLA modifications for packaging applications.

Type of modification	Treatment or added material	Effect	Reference
Modifier	Citrate esters	Lowering the Tg and improving the elongation at break	Labrecque and others (1997)
	Triacetine or tributyl citrate	Decrease in Tg and increase in crystallinity	Ljungberg and Wesslén (2002)
	Oligomeric malonate esteramides	Decrease in Tg and improvement of the strain at break	Ljungberg and others (2005)
	4,4-Methylene diphenyl diisocyanate	Tg value increased to 64 °C, tensile strength increased from 4.9 to 5.8 MPa good nucleating agent for PLA crystallization	Li and Yang (2006)
	Polyglycerol esters	Improving the elongation at break	Uyama and others (2006)
	Polyethylene glycol and acetyl triethyl citrate	Decrease in Tg and increase in crystallization rate	Li and Huneault (2007)
	Talc	Increase the ductility at more than 10%	Li and Huneault (2007)
	Bifunctional cyclic ester	Enhance PLA toughness	Jing and Hillmyer (2008)
	Poly(1,3-butylene adipate)	Decrease in storage modulus and glass transition temperature but increase in elongation at break	Wang and others (2008)
	Polycarbodiimide	Improve the thermal stability at 210 °C for up to 30 min	Yang and others (2008)
Blending with:	Polyvinyl acetate	Increase in tensile strength and percent elongation	Gajria and others (1996)
	Poly ethylene oxide (PEO)	Elongation at break of more than 500%	Nijenhuis and others (1996)
	Poly ε-caprolactone (PCL)	High improvement in mechanical properties	Tsuji and Ikada (1996)
	Poly ethylene glycol (PEG)	Enhance the crystallinity of PLA and biodegradability	Sheth and others (1997)
	Starch with different plasticizers	Lowering the price, decreasing Tg, and increasing crystallinity and biodegradability	Ke and Sun (2001); Jacobsen and Fritz (1996); Ke and others (2003)
	Polyvinyl alcohol and starch	Increase in tensile strength	Ke and Sun (2003a)
	Ethylene vinyl alcohol (EVOH)	Improvement of mechanical, thermal, and biodegradability properties	Lee and others (2005)
	Polycarbonate	Improvement of mechanical properties and biodegradation rate	Wang and others (2007)
	Poly ethylene glycidyl methacrylate (PEGMA)	Production of super-tough PLA materials	Oyama (2009)
Copolymerization of PLA and:	DL-mandelic acid	Increasing Tg and improving mechanical properties	Kylmä and others (1997)
	ε-Caprolactone	Improving the decomposition temperatures and crystallinity	Park and others (1998)
	Polyvinyl chloride	Improving strength and toughness	Lu and others (2008)
	Acrylonitrile–butadiene–styrene	Improved impact strength and elongation at break with a slight loss in modulus and tensile strength	Li and Shimizu (2009)
Physical treatment	Vacuum compression-molding and solid-state extrusion techniques	Flexural strength and flexural modulus were improved up to 221 MPa and 8.4 GPa, respectively	Lim and others (2001)
	Orientation	Significant improvement in tensile and impact properties	Grijpma and others (2002)
	Annealing	Increasing the toughness	Park and others (2004)
	Aging	Increasing the Tg	Quan and others (2004)
	Drawing	Improvement in tensile and fracture properties	Todo (2007)

Addition of different fillers to polymers for improving their performances like their strength and stiffness, barrier properties, resistance to fire and ignition, and also decreasing their price has always been a common objective in packaging technology. Traditionally, mineral fillers such as clay, silica, and talc are incorporated in film preparations in the range of 10% to 50% by weight to reduce film cost or to improve its performance in some way. However, mechanical strength of such films, in general, decreases when fillers are present. Recently, nanocomposites have received significant attention as an alternative to conventional filled polymers (Rhim 2007).

Nanocomposites

Nanocomposites are a new class of composites that are particle-filled polymers for which at least 1 dimension of the dispersed particles is in the nanometer range. Three types of nanocomposites include isodimensional nanoparticles (with 3 nano dimensions), nanotubes or whiskers (with 2 nano dimensions), and polymer-layered crystal nanocomposites (with 1 nano dimension) (Alexandre and Dubois 2000).

Although several nanoparticles have been recognized as possible additives to enhance polymer performance, the packaging industry has focused its attention mainly on layered inorganic solids like clays and silicates, due to their availability, low cost, significant enhancements, and relative simple processability (Azeredo 2009). These nanocomposites exhibit markedly improved mechanical, thermal, optical, and physicochemical properties when compared with the pure polymer or conventional (microscale) composites. The layered silicates commonly used in nanocomposites consist of 2-dimensional layers, which are 1-nm thick and several microns long depending on the particular silicate (Alexandre and Dubois 2000).

The commonly used layered silicates for the preparation of polymer-layered silicate (PLS) nanocomposites are montmorillonite (MMT), hectorite, and saponite (Sinha Ray and Okamoto 2003).

The matrix of polymer/clay nanocomposites consists mainly of synthetic polymers including thermosets such as epoxy, thermoplastics like poly (methyl methacrylate), nonpolar polymers like polyethylene and polypropylene, polar polymers like nylon, and conductive polymers like polyaniline. In addition, biodegradable polymers such as PLA and polycaprolactone (PCL) have also been tested for the manufacture of nanocomposites with layered silicate (Rhim 2007).

PLA nanocomposites

The combination of PLA and montmorillonite-layered silicate may result in a nanocomposite with good barrier properties that is suitable for film packaging material. The modulus of PLA would be increased by the addition of montmorillonite. However, the incorporation of the montmorillonite clay into PLA could decrease the toughness of the PLA composites. There are various technical approaches to achieve a balance of good strength and toughness for PLA nanocomposites. The addition of poly ethylene glycol could act as a good plasticizer in a PLA/clay systems (Shibata and others 2006).

A comprehensive review is provided by Sinha Ray and Okamoto (2003) for the preparation, characterization, materials properties, crystallization behavior, melt rheology, and foam processing of pure polylactide (PLA) and PLA/layered silicate nanocomposites. They concluded this new family of composite materials frequently exhibits remarkable improvements in its material properties when compared with those of virgin PLA. Improved properties can include a high storage modulus both in the solid and melt states, increased tensile and flexural properties, decreased gas permeability, increased heat distortion temperature, and increased rate of biodegradability of pure PLA.

In a complementary review, Sinha Ray and Bousmina (2005) presented recent developments on the above-mentioned properties for many biodegradable polymers' nanocomposites. They described 2 types of biodegradable polymers: (a) originating from renewable sources like PLA, poly (3-hydroxybutyrate), thermoplastic starch (TPS), plant-based polymers, cellulose, gelatin, or chitosan; and (b) originating from petroleum sources like poly (butylene succinate), aliphatic polyesters, poly(ε-caprolactone), or poly (vinyl alcohol).

Recent research on PLA nanocomposites

The potential applications of PLA-based nanocomposites are in food packaging, medical applications, and tissue cultures. Some research conducted on PLA nanocomposites in the field of food packaging after the year 2005 is presented here.

Biodegradability of polymers through photodegradation has been studied by using TiO_2 nanoparticles as photocatalysts that decompose various organic chemicals like aldehyde, toluene, and polymers such as PE, PP, PVC, and PS.

In a study done by Nakayama and Hayashi (2007), TiO_2 nanoparticles were prepared and the surface of TiO_2 was modified using propionic acid and n-hexylamine, with the modified TiO_2 uniformly dispersed into PLA matrixes without aggregation. They studied the PLA-TiO_2 nanocomposite's photodegradation under UV light and concluded photodegradability of nanocomposites can be efficiently promoted.

Melt intercalation is a method where the blending of polymer and silicate layers is followed by molding to form a polymer-layered silicate nanocomposite. In general, for intercalation, polymers and layered hosts are annealed above the softening point of the polymer. Chow and Lok (2009) used this method for studying the effect of maleic anhydride-grafted ethylene propylene rubber (EPMgMA) on the thermal properties of PLA/organomontmorillonite nanocomposites. They concluded that the addition of OMMT (Organo-montmorillonite) and EPMgMA did not influence much the T_g and T_m (melting temperature) of PLA nanocomposites. The degree of crystallinity of PLA increased slightly in the presence of OMMT; it had been supposed that OMMT could act as a nucleating agent to increase the crystallinity of PLA. In contrast, the addition of EPMgMA may restrict the crystallization process and crystal formation of PLA, which subsequently reduces the degree of crystallinity of PLA/OMMT nanocomposites. Finally, they claimed that the thermal stability of PLA/OMMT was greatly enhanced by the addition of EPMgMA.

Kim and others (2009) studied the effect of bacterial cellulose on the transparency of PLA/bacterial nanocomposites, since bacterial cellulose had shown good potential as reinforcement or preparing optically transparent materials due to its structure, which consists of ribbon-shaped fibrils with diameters in the range from 10 to 50 nm. They found that light transmission of the PLA/bacterial cellulose nanocomposite was quite high due to the size effect of the nanofibrillar bacterial cellulose. Additionally, the tensile strength and Young's modulus of the PLA/bacterial cellulose nanocomposite were increased by 203% and 146%, respectively, compared with those of the PLA.

Carbon nanotubes (CNTs) have been the subject of much attention because of their outstanding performance including excellent mechanical, electrical, and thermal properties. The most promising area of nanocomposite research involves the reinforcement of polymers using CNTs as reinforcing filler (Kim and others 2007).

Li and others (2009) introduced functionalized multiwalled carbon nanotubes (f–MWCNTs) into PLA to investigate the effect of such filler on the crystallization behavior of PLA. They concluded that the addition of f–MWCNTs accelerates the crystallization of PLA dramatically and induces formation of homogeneous and very small spherulites. The results of polarized optical microscopy showed that the average spherulite diameter is about 200 μm, but for nanocomposites it was very difficult to differentiate the spherulites one by one.

Numerous studies have also been done on PLA nanocomposites in medical science regarding drug delivery systems, tissue engineering, and bone fixation (Jo and others 2004; Sakata and others 2006; Chen and others 2007).

PLA Degradability, Biodegradability, and Recyclability

Almost all the conventional plastics such as PE, PP, PS, and PVC are resistant to microbial attack; on the contrary aliphatic polyesters like PLA are readily degraded by microorganisms present in the environment. According to ASTM D6400–04, a biodegradable plastic is ''a plastic that degrades because of the action of naturally occurring microorganisms such as bacteria, fungi, and algae,'' and a compostable plastic is ''a plastic that undergoes degradation by biological processes during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues.

PLA degradation was studied in animal and human bodies for medical applications like implants, surgical sutures, and drug delivery materials (Vainionpaa and others 1989). In these environments, PLA is initially degraded by hydrolysis and the soluble oligomers formed are metabolized by cells. PLA degradation upon disposal in the environment is more challenging because PLA is largely resistant to attack by microorganisms in soil or sewage under

ambient conditions. The polymer must 1st be hydrolyzed at elevated temperatures (about 58 °C) to reduce the molecular weight before biodegradation can commence. No degradation was observed on PLA sheets after 6 wk in soil, thus PLA will not degrade in typical garden compost (Brandrup and others 1999; Ohkita and Lee 2006). Urayama and others (2002) reported that the molecular weight of PLA films with different optical purity of the lactate units (100% L and 70% L) decreased by 20% and 75%, respectively, after 20 mo in soil.

Kale and others (2007) studied the degradation of PLA bottles in a real composting condition (compost containing cow manure, wood shavings, and waste feed) at 65 °C for 30 d. They observed major fragmentation, which produces decomposition of the polymer chain into shorter oligomer chains and monomers since the 4th day, and on the15th day, the bottles were already in pieces and mostly consisted of parts from cap threads, and neck (bottle parts having higher thickness) and finally on the 30th day the bottles were completely degraded.

Microbial and enzymatic degradation of PLA have recently been studied by many researchers because these types of degradations usually do not need the high temperatures to be accomplished. Williams (1981) 1st reported the degradation for PLLA by proteinase K from *Tritirachium.album.,* afterward many studies were done for finding different enzymes corresponding PLA degradation. Reported enzymes that enable to degrade PLA in different scale include, alkaline protease (Oda and others 2000), serine proteases such as subtilisin, trypsin, elastase, and α-chymotrypsin (Lim and others 2005), Cutinase-like enzyme (Masaki and others 2005). Lipase could hydrolyze low molecular weight PLLA and some copolymers such as PDLLA (poly D,L-lactic acid) and, poly(D-lactid-co-glycolide) but not PDLA (poly D-lactic acid) and high molecular weight PLLA (Fukuzaki and others 1989). Pranamuda and others (2001) found an enzyme from *Amycolatopsis* sp. cultures and named it PLLA depolymerase. The optimum pH and temperature for this enzyme were 6.0 and 37 to 45 °C, respectively. PLLA depolymerase can also hydrolyze casein, silk fibroin, succinyl-*p*-nitroanilide, but not PHB and PCL. The enzymatic degradation of aliphatic polyesters by hydrolysis is a 2-step process. The 1st step is adsorption of the enzyme on the surface of the substrate through surface-binding and the 2nd step is hydrolysis of the ester bond (Tokiwa and Calabia 2006).

Pranamuda and others (2001) 1st isolated a PLA-degrading microorganism of *Amycolatopsis* strain from soil environment, which was capable of degrading 60% of the PLA film after 14 d. Suyama and others (1998) reported that PLA-degrading microorganisms are not widely distributed in the natural environment and, thus, PLA is less susceptible to microbial attack in the natural environment than other synthetic aliphatic polyesters like PHB, PCL, and Poly(butylenes succinate) (PBS). Several PLA-degrading microorganisms, their enzymes, and substrate specificities are reported in Table 11. Upon disposal in the environment, PLA is hydrolyzed into low molecular weight oligomers and then mineralized into CO_2 and H_2O by the microorganisms present in the environment.

Microbial degradation of PLA should be studied for packaging of foods containing microorganisms including lactic acid bacteria, and fungi for their probable abilities of PLA degradation. Torres and others (1996) reported the ability of assimilation of lactic acid and racemic oligomer products of PLA for 2 strains of *Fusarium moniliforme* (widely distributed in soil) and on strain of *Penicillium roqueforti* (the main fungus in blue cheese, and can be isolated from soil).

Recycling diverts material from alternative waste streams such as land filling or incineration, as well as conserves natural resources and energy. PET and HDPE make up a large percentage of the plastic bottles that get recycled. Sorting PLA in recycling facilities is difficult due to low volumes and in many cases, the PLA container looks like PET. Because of this, the possibility of mixing the different materials together exists. As a result, there is concern in the recycling community that PLA bottles, at high enough levels, would contaminate the PET recycle stream due to chemical and thermal property differences. The National Association for PET Container Resources (NAPCOR) recently announced its concern for potential contamination of the PET recycling stream associated with PLA bottles. This trade association for the PET plastic industry in the U.S. and Canada cited its concerns involving cost of separation, increased contamination, yield loss, and impact on recycled PET (RPET) quality and processing (www.napcor.com).

Consequently, NatureWorks® and Primo Water Corp. conducted a commercial scale bottle recycling evaluation to demonstrate that automated systems being used today in the recycling industry are capable of separating PLA bottles from PET bottles with good accuracy and efficiency (93%). In this evaluation, near-infrared equipment was used since it is a common sorting technology in large recycling operations and can accurately identify many different types of polymers (NatureWorks® 2009).

Recycled bottles crushed, chopped into flakes, and pressed into bales. They enter to final recycling step and are changed to PLA monomers; L-lactic acid or L-lactide. There are 2 methods for PLA recycling, primarily hydrolysis or solvolysis to L-lactic acid or L-lactic acid-based compounds and, 2nd, depolymerization to the cyclic dimer, L-lactide. Both methods have problems with low yield of monomers in a short period and require the removal of catalysts and additives used for hydrolysis, solvolysis, or depolymerization (Tsuji and others 2003).

High-temperature hydrolysis, normally above the melting point, is an effective way to hydrolyze PLA rapidly to L-lactic acid without the aid of catalysts. The highest maximum yield of L-lactic acid (about 90%) in a high temperature and high pressure water was attained at 250 °C for 10 to 20 min (Tsuji and others 2001).

Conclusion

In previous years, the most negative point of PLA was its price in comparison with petrochemical-based polymers. Today, by using other sources of dextrose, optimizing lactic acid production processes and its costs, substituting electricity energy by wind and solar energy for PLA production, optimizing PLA production processes, and increasing PLA demands, reduction of its price can be attained. The present PLA price is much lower than in previous years, but it is not fixed and it even will be considerably lower in the future because, according to expert forecasts, beyond 2010 the global demand for biodegradable plastics will continue to increase by 30% each year and PLA will take a large part of this market because of its valuable properties (Bastioli 2005).

The linkage of a 100% bio-originated material and nano-materials opens new windows for becoming independent from petrochemical-based polymers and also free of environmental and health concerns.

Substituting PET with PLA in food packages, which require high-barrier properties, is not feasible unless some modifications are applied to develop its permeability. Also, the brittleness of PLA may also limit its applications where toughness and impact resistance are critical. However, with the help of nanotechnology

Table 11–PLA-degrading microorganism, their enzymes substrate specificities, and detection methods used in degradation tests.

Microorganism	Enzyme	Substrate specificity	Detection method for PLA degradation
Amycolatopsis sp. strain HT 32	Protease	L-PLA	Film-weight loss; monomer production (lactic acid)
Amycolatopsis sp. strain 3118	Protease	L-PLA	Film-weight loss; monomer production
Amycolatopsis sp. strain KT-s-9	Protease	Silk fibroin, L-PLA	Clear-zone method
Amycolatopsis sp. strain 41	Protease	L-PLA, silk powder, casein, Suc-(Ala)3-pNA	Film-weight loss; monomer production
Amycolatopsis sp. strain K104−1	Protease	L-PLA, casein, fibrin	Turbidity method
Lentzea waywayandensis (formerly Saccharothrix waywayandensis)	Protease	L-PLA	Film-weight loss; monomer production
Kibdelosporangium aridum	Protease	L-PLA	Film-weight loss; monomer production
Tritirachium album ATCC 22563	Protease	L-PLA, silk fibroin, elastin	Film-weight loss; monomer production
*Brevibacillus (formerly Bacillus brevis)**	Protease	L-PLA	Change in molecular weight and viscosity
*Bacillus stearothermophilus**	Protease	D-PLA	Change in molecular weight and viscosity
*Geobacillus thermocatenulatus**	Protease	L-PLA	Change in molecular weight and viscosity
*Bacillus sinithii strain PL 21**	Lipase (Esterase)	L-PLA, pNP-fatty acid esters	Change in molecular weight
Paenibacillus amylolyticus strain TB-13	Lipase	DL-PLA, PBS, PBSA, PES, PCL, triolein, tributyrin	Turbidity method
Cryptococcus sp. strain S-2	Lipase (Curtinase)	L-PLA, PBS, PCL, PHB	Turbidity method

Adapted from Tokiwa and Calabia (2006).

and providing safe PLA nanocomposites, many of its weakness compared to petrochemical-based polymer will be resolved.

According to its safety, biodegradability, and ability for being improved in a tailor–made fashion, the authors predict the substituting of many petrochemical-based polymers by PLA for almost all pharmaceutical and direct food contact packaging materials in the near future.

Nomenclature

ASTM = American society for testing and materials;
EVOH = Ethylene vinyl alcohol;
GPPS = General purpose poly(styrene);
HDPE = High-density poly(ethylene);
HIPS = High-impact poly(styrene);
LDPE = Low-density poly(ethylene);
LLDPE = Linear low–density poly(ethylene);
MMT = Montmorillonite;
MWCNT = Multiwalled-carbon nanotube;
OMMT = Organo-montmorillonite;
OPLA = Oriented poly(lactic acid);
OPP = Oriented poly(propylene);
OPS = Oriented poly(Styrene);
PBAT = Poly(butylene adipate terephthalate);
PBS = Poly(butylenes succinate);
PBST = Poly(butylene succinate terephthalate);
PC = Poly(carbonate);
PCL = Poly(ε–caprolactone);
PEA = Poly(ester amide);
PEG = Poly(ethylene glycol);
PEGMA = Poly(ethylene–glycidyl methacrylate);
PEO = Poly(ethylene oxide);
PET = Poly(ethylene terephthalate);
PGA = Poly(glutamic acid);
PHB = Poly(3-hydroxybutyrate);
PHV = Poly(hydroxyl valerate);
PLLA = Poly(L-lactic acid);
PP = Poly(propylene);
PS = Poly(styrene);
PTMAT = Poly(tetramethylene adipate terephthalate);
PVA = Poly(vinyl alcohol);
PVC = Poly(vinyl chloride);
TPS = Thermoplastic starch.

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