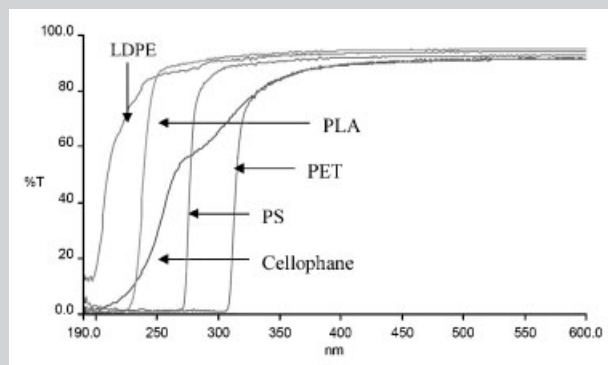


Summary: Polylactide polymers have gained enormous attention as a replacement for conventional synthetic packaging materials in the last decade. By being truly biodegradable, derived from renewable resources and by providing consumers with extra end-use benefits such as avoiding paying the “green tax” in Germany or meeting environmental regulations in Japan, polylactides (PLAs) are a growing alternative as a packaging material for demanding markets. The aim of this paper is to review the production techniques for PLAs, summarize the main properties of PLA and to delineate the main advantages and disadvantages of PLA as a polymeric packaging material. PLA films have better ultraviolet light barrier properties than low density polyethylene (LDPE), but they are slightly worse than those of cellophane, polystyrene (PS) and poly(ethylene terephthalate) (PET). PLA films have mechanical properties comparable to those of PET and better than those of PS. PLA also has lower melting and glass transition temperatures than PET and PS. The glass transition temperature of PLA changes with time. Humidity between 10 and 95% and storage temperatures of 5 to 40 °C do not have an effect on the transition temperature of PLA, which can be explained by its low water sorption values (i.e. <100 ppm at $A_w = 1$). PLA seals well at temperatures below the melting temperature but an appreciable shrinking of the films has been noted when the material is sealed near its melting temperature. Solubility parameter predictions indicate that PLA will interact with nitrogen compounds, anhydrides and some alcohols and that it will not

interact with aromatic hydrocarbons, ketones, esters, sulfur compounds or water. The CO_2 , O_2 and water permeability coefficients of PLA are lower than those of PS and higher than those of PET. Its barrier to ethyl acetate and D-limonene is comparable to PET. The amount of lactic acid and its derivatives that migrate to food simulant solutions from PLA is much lower than any of the current average dietary lactic acid intake values allowed by several governmental agencies. Thus, PLA is safe for use in fabricating articles for contact with food.



Percent transmission versus wavelength for PLA(98% L-lactide), PS, LDPE, PET and cellophane films.

An Overview of Polylactides as Packaging Materials

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Received: April 8, 2004; Revised: June 18, 2004; Accepted: June 28, 2004; DOI: 10.1002/mabi.200400043

Keywords: barrier; biodegradable; diffusion; permeability; polylactides

Introduction

Polylactide (PLA), a polymer derived from lactic acid (2-hydroxy propionic acid), has been widely studied for use in medical applications because of its bioresorbable and biocompatible properties in the human body.^[1–16] Due to its higher cost, the initial focus of PLA as a packaging material has been in high value films, rigid thermoforms, food and beverage containers and coated papers. PLA may have packaging applications for a broader array of products^[17–22] as modern and emerging production technologies lower its production costs.^[17,18,23,24] The production of PLA presents numerous advantages: (1) it can be

obtained from a renewable agricultural source (corn);^[25–27] (2) its production consumes quantities of carbon dioxide;^[4] (3) it provides significant energy savings;^[28] (4) it is recyclable and compostable;^[23,29,30] (5) it can help improve farm economies and (6) the physical and mechanical properties can be manipulated through the polymer architecture.^[31–38] Figure 1 shows a life cycle model for polylactide polymers.

Early economic studies showed that PLA is an economically feasible material to use as a packaging polymer.^[24,27,28] Medical studies have shown that the level of lactic acid (LA) that migrates to food from packaging containers is much lower than the amount of LA used in common food

ingredients.^[40] Therefore, polymers derived from lactic acid may be good candidates for packaging applications.^[3,4,17,18]

By providing consumers with extra end-use benefits, such as avoiding paying a “green tax” in Germany or meeting environmental regulations in Japan, PLA has become a growing alternative as a packaging material for demanding markets.^[41] Currently, PLA is being used as a food packaging polymer for short shelf life products with common applications such as containers, drinking cups, sundae and salad cups, overwrap and lamination films and blister packages.^[42–44] Moreover, new applications include thermoformed PLA containers being used in retail markets for fresh fruit and vegetables.^[44,45]

Poly lactide Production

The basic constitutional unit of PLA, lactic acid, can be manufactured by carbohydrate fermentation or chemical synthesis. Lactic acid (2-hydroxy propionic acid) is the

simplest hydroxyl acid with an asymmetric carbon atom and it exists in two optically active configurations, the L(+) and D(−) isomers. The L(+) and D(−) isomers are produced in bacterial systems. Mammalian systems produce only the L(+) isomer which is easily assimilated. Scheme 1 shows the chemical structure of the L and D lactic acids.

The majority of lactic acid is made by bacterial fermentation of carbohydrates. The fermentation processes to obtain lactic acid can be classified according to the type of bacteria used. In the *Heterofermentative* method less than 1.8 moles of lactic acid per mole of hexose is produced along with significant levels of other metabolites such as acetic acid, ethanol, glycerol, mannitol and carbon dioxide. In the *Homofermentative* method an average of 1.8 moles of lactic acid per mole of hexose and minor levels of other metabolites are produced. This conversion yields 90+ g lactic acid per 100 g glucose. Since homofermentative pathways lead to greater yields of lactic acid and lower levels of byproducts, homofermentative pathways are



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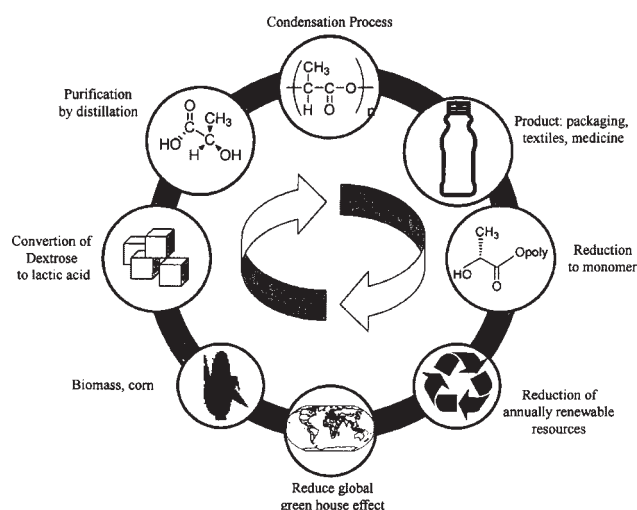
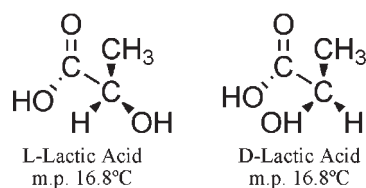


Figure 1. Life cycle for polylactide polymers, adapted from Hartmann.^[39]

mainly used by industry.^[46] The majority of the fermentation processes nowadays use a genus of *Lactobacilli* which yields a high rate of lactic acid. These bacteria are classified as homofermentative, and the general processing conditions include a pH of 5.4–6.4, a temperature of 38–42 °C and a low oxygen concentration. In general, sources of simple sugars such as glucose and maltose from corn or potato, sucrose from cane or beet sugar and lactose from cheese whey are used. In addition to carbohydrates, other nutrients such as B vitamins, amino acids and nucleotides are provided by rich corn steep liquor. Generally, batch processes produce 1 to 4.5 g · L⁻¹ · h⁻¹ of lactic acid while continuous processes produce 3 to 9.0 g · L⁻¹ · h⁻¹ of lactic acid, and cell recycle reactors produce near to 76 g · L⁻¹ · h⁻¹.

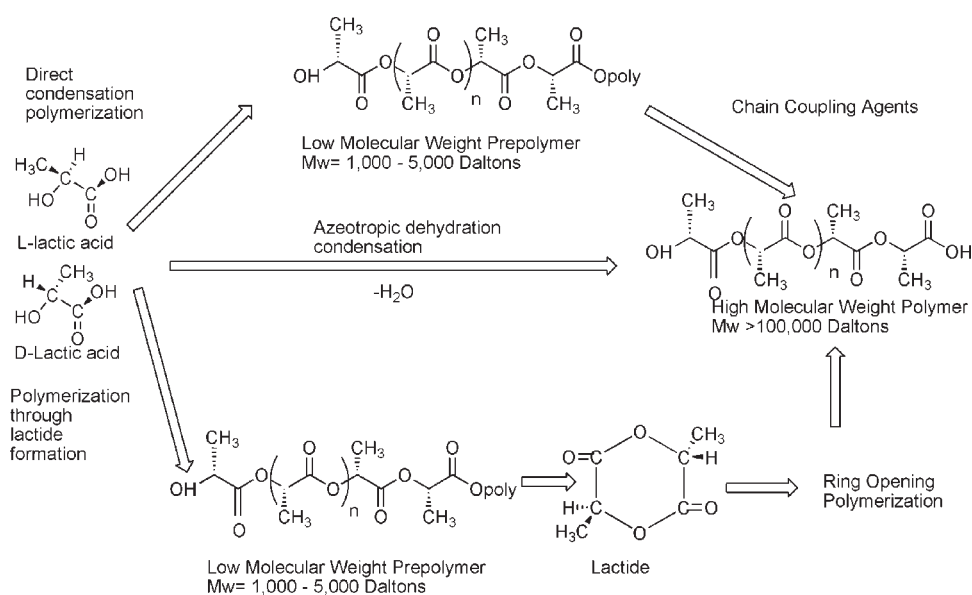


Scheme 1. Chemical structure of L and D-lactic acid (m.p. is melting point).

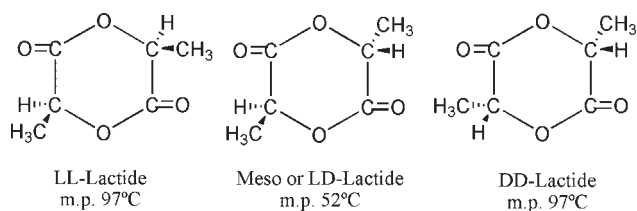
h⁻¹. If the lactic acid is used in pharmaceutical and food derivative products, it should be purified via distillation.

High molecular weight PLA can be obtained using different routes (see Scheme 2). The chemical synthesis route can be used to produce large scale quantities of racemic lactic acid^[47] but it is economically unviable. As a consequence, the production of L-lactic acid by fermentation is gaining acceptance. In general, there are three methods which can be used to produce high molecular mass PLA of about 100 000 Daltons: (a) direct condensation polymerization; (b) azeotropic dehydrative condensation and (c) polymerization through lactide formation. Polymerization through lactide formation, patented by Cargill Inc. in 1992,^[23,48] is by and large the current method used for producing PLA. Direct condensation polymerization is the least expensive route. However, it is very difficult to obtain a solvent-free high molecular weight poly(lactic acid). Therefore, the use of chain coupling agents and adjuvants adds cost and complexity to the process.^[47,49–53]

Azeotropic dehydrative condensation of lactic acid can yield high molecular weight poly(lactic acid) without the use of chain extenders or adjuvants. The general procedure consists of reducing the distillation pressure of lactic acid for 2–3 h at 130 °C. The majority of the condensation water



Scheme 2. Synthesis methods for obtaining high molecular weight PLA, adapted from Hartmann.^[49]

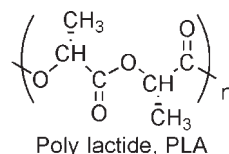


Scheme 3. Chemical structures of LL-, *meso*- and DD-lactides (m.p. is melting point).

is then removed. Catalyst is added along with diphenyl ester. A tube packed with 3 Å molecular sieves is attached to the reaction vessel and the solvent returned to the vessel via the molecular sieves for an additional 30–40 h at 130 °C. Finally, the polymer is isolated as is or dissolved and precipitated for further purification. Details of this technique can be found elsewhere.^[49]

Polymerization through lactide formation is the current method used by Cargill Dow LLC to obtain polylactide polymers of high molecular weight for commercial applications. From dextrose fermentation, either D-lactic acid, L-lactic acid or a mixture of the two are pre-polymerized to obtain an intermediate low molecular mass poly(lactic acid), which is then, under lower pressure, catalytically converted into a mixture of lactide stereoisomers.^[54] Lactide, the cyclic dimer of lactic acid, is formed by the condensation of two lactic acid molecules as follows: L-lactide (two L-lactic acid molecules), D-lactide (two D-lactic acid molecules) and *meso*-lactide (an L-lactic acid and an D-lactic acid molecule) (see Scheme 3).

After vacuum distillation of the lactide, high molecular mass PLA with controlled optical purity and a constitutional



Scheme 4. Constitutional unit of polylactide.

unit of $-\text{[OCH(CH}_3\text{)CO-O-CH(CH}_3\text{)-CO]}-$ is formed by ring-opening polymerization of the lactides.^[23,46,49,55] The ring-opening polymerization can be cationic, initiated by methyl trifluoromethanesulfonic acid or trifluoromethanesulfonic acid (triflic acid),^[54–56] or anionic, initiated by the nucleophilic reaction of the anion with the carbonyl, with subsequent acyl-oxygen cleavage.^[54,55,57,58] Extensive research on the different methods to initiate the ring opening polymerization has been reported elsewhere.^[49,54–56,58–75] Scheme 4 shows the constitutional unit of PLA polymers.

Figure 2 shows a schematic presentation of the current Cargill Dow LLC PLA production process in Blair, Nebraska.

Poly lactide Properties

The properties of high molecular weight PLA are determined by the polymer architecture (i.e. the stereochemical makeup of the backbone) and the molecular mass, which is controlled by the addition of hydroxylic compounds. The ability to control the stereochemical architecture permits

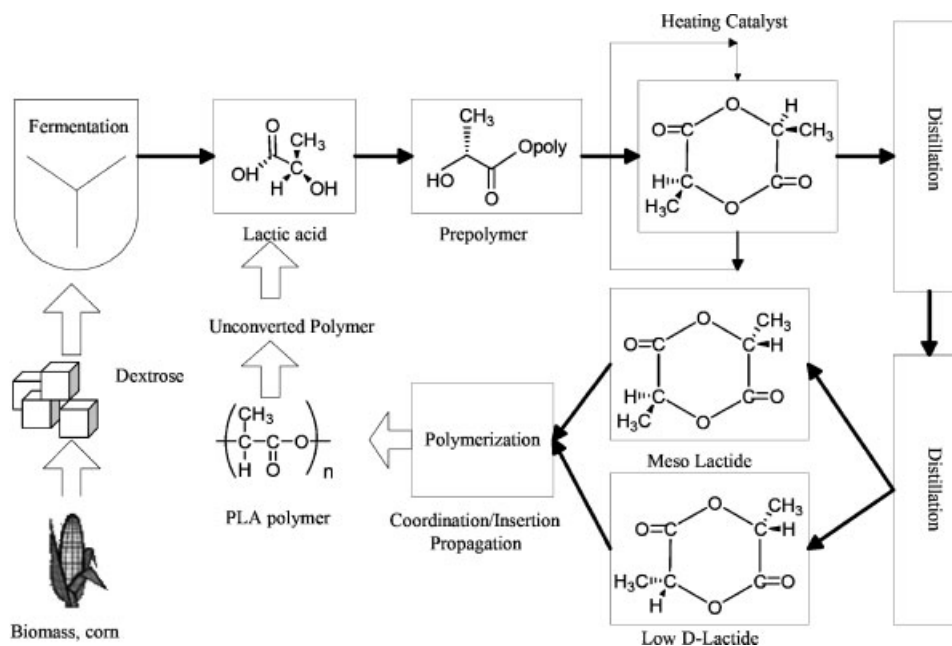


Figure 2. Current production process for PLA, adapted from Gruber.^[48]

precise control over the speed of crystallization and finally the degree of crystallinity, the mechanical properties and the processing temperatures of the material. In addition, the degradation behavior strongly depends on the crystallinity of the samples. In this section, the PLA polymer structure, optical, physical, mechanical, rheological, processing, solubility, barrier, and degradation properties are reviewed. The advances achieved in the last few years are reviewed and research on PLA blends and composites is briefly described.

Structure

Unmodified polylactides are linear macromolecules having a molecular architecture that is determined by their stereochemical composition. The repeat unit of PLA ($72 \text{ g} \cdot \text{mol}^{-1}$) contains one stereocenter that is either L(*S*) or D(*R*) in configuration. Microorganisms mainly produce L-lactic acid, and no major sources of D-lactic acid are available, although some lactobacilli are reported to produce D-lactic acid.^[46] The repeat units are either added as dimers during the ring-opening lactide polymerization or are added to the final polymer as lactic acid monomers via direct condensation polymerization, as explained in the previous section. Both mechanisms involve acyl cleavage of the ester bond with preservation of chirality. *meso*-Lactide possesses a two-fold axis of improper rotation and is therefore optically inactive. Lactide can be obtained as L,L or D,D enantiomers, commonly called L-lactide and D-lactide (which in the Cahn-Ingold-Prelog system are called the (*S,S*) and (*R,R*) enantiomers, respectively), the *meso* compound (*R,S*), and a racemic or equimolar mixture of the L and D enantiomers, *rac*-lactide, commonly referred to as DL-lactide (Scheme 3). The literature sometime confuses *meso*- and *rac*-lactides, and refers to them as DL-lactide.

In the ring polymerization technique, the lactide stereoisomers are produced from the depolymerization of low molecular weight poly(lactic acid) using tin catalysis and stereoselective initiators to enhance the rate and selectivity of the intramolecular cyclization reaction. The molten lactide is produced in proportions close to statistical expectations from the initial lactic acid isomers (equal reactivity), $w_{\text{L-lactide}} = S^2$, $w_{\text{D-lactide}} = R^2$, $w_{\text{meso-lactide}} = 2RS$ where *S* and *R* are the original fractions of L-lactic acid and D-lactic acid, respectively, and *w* is the weight fraction. Since the initial distribution of lactide isomers determines the potential for polylactide crystallization, lactide is purified by vacuum distillation. PLA derived from greater than 93% L-lactic acid can be semicrystalline whereas PLA from between 50 and 93% L-lactic acid is strictly amorphous. Both *meso*- and D-lactide induce twists in the otherwise very regular poly(L-lactide) molecular architecture. Molecular imperfections are responsible for the decrease in both the rate and extent of poly(L-lactide) crystallization. Since polylactide production always contains some amount of *meso*-lactide impurities, practically

all PLAs are made up of L- and D,L-lactide copolymers.^[76] It is known that poly(L-lactide) and poly(D-lactide) form an equimolar stereocomplex crystalline structure (i.e., *rac*-lactides) having a significantly higher melting temperature (230 °C) than the homopolymers.

Dimeric polymerization imparts some order to the otherwise random distribution of L- and D-stereocenters in PLA chains. Hence, the lactide ring-opening polymerization process gives a fundamentally different molecular architecture for PLA polymers derived from lactic isomeric mixtures other than 100% L- and 50/50 D,L-lactic acid. High molecular weight bulk lactide polymerization should be conducted at high temperatures (e.g. 190–200 °C) to maintain the appropriate viscosity, and at these temperatures racemization can become an important side reaction. However, a laboratory scale polymerization of lactide at low reaction temperature such as 120–140 °C gives a high molecular weight PLA.

Reactivity among the lactide isomers is slightly different. *meso*-Lactide has a higher rate of hydrolysis and a greater tendency to polymerize. The L- and D-enantiomers have identical rates. Witzke^[76] attributed this rate difference to a different configurational and conformational structure. Energy studies indicate that *meso*-lactide is about $1.7 \text{ kcal} \cdot \text{mol}^{-1}$ more stable than L-lactide. Although not perfect, the assumption of similar reactivities for lactide production and polymerization is still reasonable, resulting in a small error in final composition estimations.^[76] Nevertheless, the configurational and conformational differences between *meso*- and L-lactide result in different physical properties, such as melting point, solubility and relative volatility.

As far as polymerization is concerned, the role of *meso*-lactide is to provide amorphous polylactide when it is polymerized with L-lactide. Witzke^[76] investigated the molecular architecture of different lactides and found that poly(L-lactide) is arranged in a syndiotactic manner. Poly(*meso*-lactide) has a structural configuration of repeat units of (*RS*)-(*SR*)-(*RS*)-(*SR*), which is syndiotactic in dimers. It has also been reported as having an isotactic structure (*RS*)-(*RS*)-(*RS*)-(*RS*).

Depending on the preparation conditions, poly(L-lactide) crystallizes in three forms (α , β and γ). The stable α -form exhibits a well-defined diffraction pattern.^[77] Recently, Sasaki and Asakura^[78] analyzed the α -form of poly(L-lactide) using linked-atom least squares refinements for X-ray fiber diffraction data, and found that the α -form has an orthorhombic P2₁2₁2₁ space group, with a unit cell containing two antiparallel chains. “The chain conformation was the 2-fold ($15 \cdot 2/7$) helix distorted periodically form of the regular $s(3 \cdot 10/7)$ helix”.^[78] The lattice parameters were $a = 10.66 \text{ \AA}$, $b = 6.16 \text{ \AA}$, and c (chain axis) = 28.88 \AA , with a crystal density of $1.26 \text{ g} \cdot \text{cm}^{-3}$.^[78]

The β -form can be prepared at a high draw ratio and high drawing temperature. The chain conformation is a left-handed 3-fold helix.^[77,78] The β form of poly(L-lactic acid)

has an orthorhombic unit cell (containing 6 chains) containing a 3₁ (3 Å rise/1 monomeric unit) polymeric helix. The unit cell dimensions are as follows: $a = 10.31$ Å, $b = 18.21$ Å, $c = 9.0$ Å.^[77] The α -structure is more stable than the β -structure, with a melting point of 185 °C compared to 175 °C for the β -structure.^[77] Chain packing in the β -form has recently been termed a frustrate structure where the crystal structure rests on a frustrated packing of three three-fold helices in a trigonal unit-cell of parameters $a = b = 10.52$ Å, $c = 8.8$ Å, space group $P3_2$.^[79]

The γ -form, found by epitaxial crystallization, contains two antiparallel s(3/2) helices in the pseudoorthorhombic unit cell ($a = 9.95$ Å, $b = 6.25$ Å, $c = 8.8$ Å) and it assumes the known three-fold helix of polylactides.^[80] Table 1 shows the unit cell parameters for non-blended PLLA.

Zell et al.^[84] and Thakur et al.^[85] used ¹³C solid-state NMR spectroscopy as a tool to determine PLA optical purity, crystallinity, morphology and LA isomer distribution. Thakur et al.^[85] developed a method to deconvolute the NMR spectral data and extract information about the percent of crystallinity and identify the morphology of PLLA. Kasperczyk^[86] also used ¹³C NMR to determine the composition of a series of glycolide/lactide copolymers.

Nuclear magnetic resonance data for PLA was reported by Spinu et al.^[87] and L-PLA showed five peaks at 169.27, 169.31, 169.42, 169.49 and 169.66 ppm. The signal at 169.666 ppm was assigned to the carbonyl carbon of successive L-lactic acids. The other four signals are due to the carbonyl carbons in the polymer chain. In L,D-PLA six peaks were reported at 169.136, 169.301, 169.342, 169.400, 169.548 and 169.569 ppm. The extra peak is attributed to the way that PLA polymers are produced (i.e. by condensation or ring opening polymerization, since in condensation the L- or D-lactic acid are introduced randomly, while in ring opening polymerization, they are introduced in pairs).

PLLA crystals have been grown in different solvents to study the morphology and the rate of crystallization. PLLA crystals are highly dependent on the L-concentration. The rate and extent of crystallization also depend on the presence of nucleating agents as well as on the time and temperature.^[11,57,88–91] Long annealing times at temperatures higher than the glass transition temperature (T_g)

produce more perfect crystals and higher-melting crystals.^[92] In addition, the composition of the PLA (i.e. the presence of D- and meso-lactide) can increase the rate of crystallization. PLA is a slowly crystallizing polymer. Vasanthakumari and Pennings^[93] reported that the rate of crystal formation increased with a decrease of the molecular weight. Also, Kolstad,^[94] working with poly(L-lactide-co-meso-lactide) in the range of 0 to 9% meso-lactide, found that the crystallization half-time (i.e. the time taken for half of the lactide to crystallize) increased by around 40% for every one percent of meso-lactide in the polymerization mixture. In addition, he reported that the crystallization rate was driven mainly by the reduction in melting point of the copolymers. Furthermore, talc in the mix acted as a nucleating agent, increasing the nucleation density term and decreasing the crystallization half-time and the time to complete crystallization.^[94] Quenching also decreases the half-time crystallization.^[95] Research carried out on blends of PLLA/PDLA containing low concentrations of PDLA have shown it to be more effective as a nucleating agent than talc. A maximum nucleation efficiency of 66% was observed at 15 wt.-% PDLA.^[96] Tsuji and Ikada^[97] investigated the effect of the molecular weight of atactic poly(LD-lactide) (PDLA) on the crystallization behavior and morphology of isotactic poly(L-lactide) (PLLA). They found that the spherulite structure became more disordered as the molecular weight of PDLA increased.^[97] They also reported that a significant depression of the melting temperature (T_m) was seen as PLLA was blended with PDLA, due to the presence of D-lactide. Also, Baratian et al.^[98] reported that the presence of random copolymers containing 1.5 to 6% of D-lactide decreased the degree of crystallinity and spherulite growth rates.^[98,99] Ikada et al.^[100] studied the crystallization of the stereocomplex crystallites (racemic crystallites) of PDLA and PLLA. When these crystallites have a stoichiometric ratio of 1:1 (L-lactyl unit: D-lactyl unit), an increase in the melting temperature of 50 °C is observed compared to homocrystallites of either PLLA or PDLA.^[60] The eutectic crystallization of PLLA with pentaerythrityl tetrabromide was studied by Vasanthakumari^[90] and epitaxial crystallization was investigated by Cartier et al.^[80]

Table 1. Unit cell parameters for non-blended PLLA and stereocomplex crystals, adapted from Tsuji.^[11]

	Space Group	Chain Orientation	N. of helices/ unit cell	Helical conformation	a nm	b nm	c nm	α deg	β deg	γ deg
PLLA α -form ^[81]	Pseudo-orthorhombic	—	2	10 ₃	1.07	0.645	2.78	90	90	90
PLLA α -form ^[77]	Pseudo-orthorhombic	—	2	10 ₃	1.06	0.61	2.88	90	90	90
PLLA α -form ^[82]	Orthorhombic	Parallel	2	10 ₃	1.05	0.61	—	90	90	90
PLLA β -form ^[77]	Orthorhombic	—	6	3 ₁	1.031	1.821	0.90	90	90	90
PLLA β -form ^[79]	Trigonal	Random up-down	3	3 ₁	1.052	1.052	0.88	90	90	120
PLLA γ -form ^[80]	Orthorhombic	Antiparallel	2	3 ₁	0.995	0.625	0.88	90	90	90
Stereo complex ^[83]	Triclinic	Parallel	2	3 ₁	0.916	0.916	0.870	109.2	109.2	109.8

Optical

Visible and Ultraviolet Range

The absorption of visible and UV light by polymers is one of the main factors affecting food quality. The protection of light sensitive foods such as juices, vitamin and sports drinks, dairy products and edible oils from UV radiation when packaged in plastic containers has been widely investigated.^[101–105] For example, light has been found to affect the flavor and, to a lesser degree, the nutritional content of milk.^[106] Milk is mainly affected by the 400–550 nm wavelengths^[102] but researchers have also reported that other wavelengths (i.e. UV-B, UV-C and visible) also damage the quality of milk.^[106] Similar results have been found for juices and edible oils. Therefore, the material used to produce the primary package is critical in minimizing product damage.

The transmission of visible and ultraviolet light are important parameters in designing the right packaging to preserve and protect products until they reach the consumer. The primary wavelengths of interest in packaging applications are those that fall between 200 and 2200 nm. This section of the electromagnetic spectrum can be divided into three components: Ultraviolet (UV) band (100–400 nm); visible spectrum (400–700 nm); near infrared band (700–2200 nm). Ultraviolet radiation accounts for only 3% of the total radiation that reaches the earth, but it is energetic enough to cause chemical reactions, weathering of polymers, fading of certain dyes and even eye damage. UV light is subdivided into three distinct wavelength regions. UV-A (400–315 nm), often referred to as “blacklight”, is the longest wavelength region and lowest in energy. It represents the largest portion of natural UV light and it is responsible for tanning and pigmentation of the human skin.^[107] UV-B (315–280 nm) is partially blocked by the ozone layer and is the most energetic component of natural UV light. It causes the most photochemical degradation of plastics. UV-C (280–100 nm) is generally created from artificial light sources. The UV-C generated by the sun is totally absorbed by the earth’s atmosphere and never reaches the earth’s surface. The amount of UV light absorption and transmission is used to characterize polymer samples.

PLA light barrier properties have been studied and compared with the visible and ultraviolet light transmission rates of standard commercial polystyrene, poly(ethylene terephthalate), low density polyethylene and cellophane films in the range 190–800 nm.^[108] Figure 3 shows the profiles for PLA and other standard commercial films.

PLA shows almost no UV transmission in the lower range of UV-C (190–220 nm). However, at 225 nm the amount of UV light transmitted by PLA increases significantly. At 250 nm, 85% of the UV light is transmitted. At 300 nm, 95% of the UV light is transmitted. Thus, while UV-C is not transmitted, nearly all the UV-B and UV-A light passes

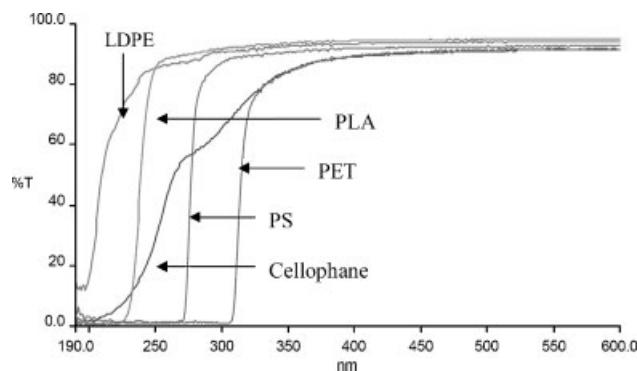


Figure 3. Percent transmission versus wavelength for PLA(98% L-lactide), PS, LDPE, PET and cellophane films. (PLA samples were obtained from Cargill Dow LLC).

through the films. Therefore, the application of transparent PLA films to, for example, dairy products may require additives to block UV light transmission. Effective UV stabilizers are able to absorb UV light and thus prevent damage to light sensitive packaged foods, resulting in retention of taste and appearance, extension of shelf life and improvement of product quality. PLA transmits less UV-C light than LDPE (Figure 3), but PET, PS and cellophane transmit less UV-B and UV-A than PLA and LDPE. Moreover, PET does not transmit UV-C and UV-B wavelengths, which are the most damaging for food.

The visible light band ranges from 400–700 nm. Within this band, colors range from violet to blue, green, yellow, orange and red. Each wavelength in the visible light band causes a particular sensation of color. The eye is not equally sensitive to light emitted at all wavelengths. It is most sensitive to the light in the yellow and green areas of the spectrum. When a light beam strikes a material, some light is transmitted, some reflected and the rest is absorbed. Light transmission depends on the reflectance at both surfaces of the material and the absorption of light into the material. Many different systems are used to characterize visible light transmission and color. According to ASTM D1746-03,^[109] the transparency of plastic sheeting is defined as the transmission of visible light in the range 540–560 nm. The average transparency is around 95%. One of the most common systems used to characterize color is the $L^*a^*b^*$ system, also referred to as the CIELAB system, which is used to determine and to compare sample colors. The CIELAB system can be visualized as a cylindrical coordinate system in which the axis of the cylinder is the lightness variable L^* , ranging from 0% to 100% and the radii are the chromaticity variables a^* and b^* . Variable a^* changes from green (negative) to red (positive) and variable b^* changes from blue (negative) to yellow (positive). Variables L , a and b are stated in different norms, ASTM D 6290-98^{e1[110]} and DIN 6176-03.^[111] Various standard parameters can be calculated from the $L^*a^*b^*$ system variables, such as the color difference between two points: $\Delta E^*_{ab} = [(\Delta L^*)^2 +$

Table 2. $L^*a^*b^*$ values for PLA (98% L-lactide) and commercial polymer samples.

	L^*	a^*	b^*	ΔE^* ^{c)}	YI
PLA ^{c)}	90.64 ^{a)} ± 0.21	−0.99 ^{b)} ± 0.01	−0.50 ^{b)} ± 0.04	—	4.67
Cellophane	88.94 ^{b)} ± 0.07	−0.83 ^{b)} ± 0.12	1.45 ^{b)} ± 0.03	2.59	6.30
Polystyrene	89.80 ^{a)} ± 0.67	−0.72 ^{b)} ± 0.02	0.49 ^{b)} ± 0.05	1.33	4.32
LDPE	89.73 ^{b)} ± 0.09	−0.92 ^{b)} ± 0.01	−0.68 ^{b)} ± 0.02	0.93	4.67
PET	88.10 ^{b)} ± 0.22	−1.07 ^{b)} ± 0.02	0.08 ^{b)} ± 0.03	2.61	5.71

^{a)} Indicates that the values are not significantly different at the $\alpha = 0.05$ level ($P > 0.01$).

^{b)} Indicates that the values are significantly difference at the $\alpha = 0.05$ level ($P < 0.01$).

^{c)} PLA crystallinity is 40%, and it was provided by Cargill-Dow LLC.

$(\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$. In addition, the yellowness index can be calculated using the tristimulus values, X and Y ; $YI = 100(C_x X \sim C_z Z)/Y$, where $C_x = 1.2769$ and $C_z = 1.0592$, according to ASTM D 6290-98^{e1}.^[110] $L^*a^*b^*$ values for PLA and other standard commercial polymers are shown in Table 2.^a

The higher PLA L value is an indicator of a slightly increased lightness. The negative value of a is indicative of a green tone in the film, and the negative b value indicates more blue color than cellophane, PS or PET. If we compare the ΔE^* values, cellophane and PET films are not very different from each other, but they are the ones most different from PLA. The yellowness index is a number calculated from spectrophotometric data that describes the change in color of a test sample from clear or white toward yellow. PLA, PS and LDPE have the same yellowness index, while cellophane and PET have higher values. The light yellow color of PLA bottles and trays could create a consumer perception that the package is old so the consumer perception of PLA container color should be determined.

Refractive Index

All polymers have a refractive index that is characteristic of the polymer structure. The refractive index can be calculated by different theoretical methods based on the molecular weight and molecular volume of the monomer or constitutional unit, the density of the polymer and the chemical structure of the polymer. The refractive index of PLA polymer and of common commercial polymers was calculated by the Lorentz and Lorentz, Gladstone and Dale and Vogel methods.^[108] Table 3 shows the experimental and calculated refractive indices for PE, PS, PVC, PET and PLA.

Light refraction is directly correlated with the isotropy of the polylactide. Tsuji et al.^[113] measured the optical

rotation of poly(D-lactic acid) and poly(L-lactic acid). The specific optical rotation, $[\alpha]$, of the polymers was measured in chloroform at a concentration of $1 \text{ g} \cdot \text{dl}^{-1}$ at 25°C , using a polarimeter at a wavelength of 589 nm. Values of -156° and $156 \text{ deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{cm}^3$ were reported for PLLA and PDLA.

Infrared

Infrared radiation refers broadly to that portion of the electromagnetic spectrum between the visible and the microwave region (i.e. 2500–15 000 nm). The infrared spectrum of commercial PLA was determined by Fourier Transform Infrared (FT-IR).^[108] For PLA polymers, maximum absorbance occurs at 240 nm and is attributed to the ester group present in the backbone. The principal PLA absorption bands in the infrared range are summarized in Table 4. The strong IR bands at 2997, 2946 and 2877 cm^{-1} are assigned to the CH stretching region, $\nu_{\text{as}}\text{CH}_3$, $\nu_{\text{s}}\text{CH}_3$ and νCH modes. The C=O stretching region is observed as a large band at 1748 cm^{-1} . The region between 1500 and 1360 cm^{-1} is characterized by the 1456 cm^{-1} CH_3 band. The CH deformation and asymmetric bands appear at 1382 cm^{-1} and 1365 cm^{-1} , respectively. The bands that appear at 1315 cm^{-1} and 1300 cm^{-1} are due to the CH bending modes. In the region of 1300 cm^{-1} to 1000 cm^{-1} , it is possible to observe the C–O stretching modes of the ester groups at 1225 cm^{-1} and the $\nu\text{O–C}$ asymmetric mode at 1090 cm^{-1} . Between 1000 cm^{-1} and 800 cm^{-1} , peaks can be observed at 956 cm^{-1} and 921 cm^{-1} which can be attributed to the characteristic vibrations of the helical backbone with CH_3 rocking modes. Two bands related to the crystalline and amorphous phases of PLA were found at 871 cm^{-1} and 756 cm^{-1} . The peak at 871 cm^{-1} can be assigned to the amorphous phase and the peak at 756 cm^{-1} to the crystalline phase. Similar findings have been reported in the literature.^[57,114,115] Finally, the peaks below 300 cm^{-1} correspond mainly to CH_3 torsion modes and to the skeletal C–C torsions. Infrared spectroscopy data and a more detailed table of PLA Raman spectroscopy frequencies can be found elsewhere.^[114,115] Absorption is reported in the

^a P-value, also known as the observed or exact level of significance, or the exact probability of committing a Type I error. P-value is defined as the lowest significance level at which the null hypothesis can be rejected.

Table 3. Theoretical and experimental refractive index for standard commercial polymers. PLA samples were obtained from Cargill-Dow LLC.

Polymer	$n_{\text{exp.}}$	$n_{\text{calculated}}$		
		Lorentz and Lorentz ^{b)}	Gladstone and Dale ^{c)}	Vogel ^{d)}
Polyethylene	1.490 ^{a)}	1.479	1.478	1.469
Polystyrene	1.591 ^{a)}	1.603	1.600	1.590
Poly(vinyl chloride)	1.539 ^{a)}	1.544	1.543	1.511
Poly(ethylene terephthalate)	1.63–1.68 ^{a)}	1.581	1.580	1.560
Poly(98% L-lactide)	— ^{e)}	1.482	1.492	1.500

^{a)} Values obtained from Van Krevelen.^[112]

^{b)} Values calculated according to Lorentz and Lorentz.^[112]

^{c)} Values calculated according to Gladstone and Dale.^[112]

^{d)} Values calculated according to Vogel.^[112]

^{e)} Experimental value was not obtained.

range of 60 to 2995 cm⁻¹ for both infrared and Raman spectroscopy.

Physical

Physical properties of PLA polymers, as well as other polymers, depend on their molecular characteristics as well as ordered structures such as crystalline thickness, crystallinity, spherulite size, morphology and degree of chain orientation. The physical properties of polylactide are related to the enantiomeric purity of the lactic acid stereocopolymers. The homopolymers poly(D-lactide) or poly(L-lactide) and high D- or L-lactide copolymers have very regular structures and develop a crystalline phase. High molecular weight polylactides are either amorphous or semicrystalline at room temperature, depending on the amounts of L, D and *meso*-lactide in the structure. PLA can be produced totally amorphous or up to 40% crystalline. PLA resins containing more than 93% of L-lactic acid are

semicrystalline^[35,76] while PLA with 50–93% L-lactic acid is strictly amorphous. The presence of both *meso*- and D-lactide forms produces imperfections in the crystalline structure, reducing the percent crystallinity. For amorphous PLA, the glass transition temperature (T_g) is one of the most important parameters since dramatic changes in polymer chain mobility take place at and above T_g . For semicrystalline PLA, both the T_g and melting temperature (T_m) are important physical parameters for predicting PLA behavior. The glass transition temperature is also determined by the proportion of different lactides. A representative case of high molecular weight amorphous polylactide is shown in Figure 4. Below the β -relaxation temperature, T_β , PLA polymers are completely brittle. Between T_β and T_g the amorphous polylactide undergoes physical aging and can show brittle or ductile fracture. In the transition between 110–150 °C, PLA changes from rubbery to viscous and is mainly dependent on the molecular weight and the shear stress. Finally, amorphous PLA decomposes between 215 and 285 °C. The commercial applications of amorphous PLA are related to the temperature at which the polylactide will be used. Amorphous PLA properties depend in part on how far below T_g the article is used or stored.

For semicrystalline polylactide, the melting temperature is a function of the processing conditions and the stereochemistry of the polymer. Figure 5 shows a typical high molecular weight semicrystalline PLA. The crystalline melting temperature, T_m , depends on the presence of *meso*-lactide in the structure which produces a depression of the melting temperature as follows: T_m (°C) \approx 175 °C–300 W_m , where W_m is the fraction of *meso* lactide and 175 °C is the melting temperature of PLA made of 100% L-lactide.^[76] For semicrystalline PLA, T_g indicates the transition between brittle and ductile fracture. The maximum practically obtainable melting point of stereochemically pure polylactide (either L- or D-) is around 180 °C with an enthalpy of 40–50 J · g⁻¹. A reduction in the melting temperature of between 20 and 50 °C can be obtained by the addition of

Table 4. Infrared spectroscopy data – peak band assignments for PLA (98% L-lactide) infrared spectra.

Assignment	Peak position
	cm ⁻¹
–OH stretch (free)	3 571
–CH– stretch	2 997 (asym), 2 946 (sym), 2 877
–C=O carbonyl stretch	1 748
–CH ₃ bend	1 456
–CH– deformation including symmetric and asymmetric bend	1 382, 1 365
–C=O bend	1 225
–C–O– stretch	1 194, 1 130, 1 093
–OH bend	1 047
–CH ₃ rocking modes	956, 921
–C–C– stretch	926, 868

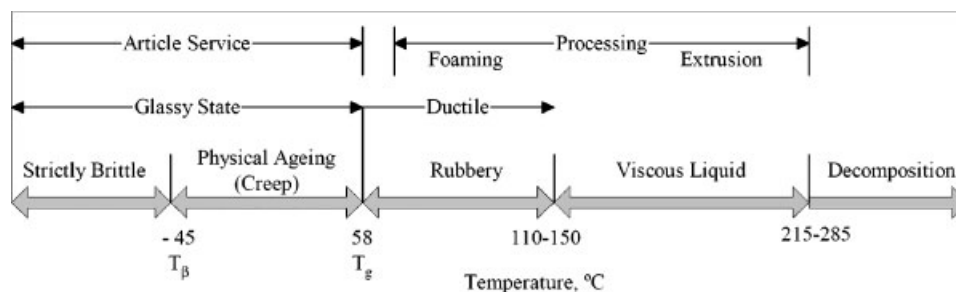


Figure 4. Metastable states of high molecular weight amorphous polylactides, adapted from Witzke.^[76]

D-lactide to the polymer structure. A qualitative and quantitative understanding of the transition temperatures as well as other polymer properties is important to identify polymer applications.

According to Ikada and Tsuji,^[3] melting temperature increases with a rise in molecular weight (\bar{M}_w) until the maximum practical value. On the other hand, the crystallinity of the samples gradually decreases with increasing \bar{M}_w . The glass transition temperature is also determined by the proportion of different lactides present. This results in PLA polymers with a wide range of hardness and stiffness values. The typical PLA glass transition temperature (T_g) ranges from 50 °C to 80 °C while the melting temperature ranges from 130 °C to 180 °C.^[3,76] PLA polymer of $\bar{M}_n = 430$ has a T_g of -8.0 °C and PLA of $\bar{M}_n = 22\,730$ has a T_g of 55.5 °C.^[116] The glass transition temperature of PLLA is higher than PDLA but this may be partly due to the difference in crystallinity between the two polymers. In general, the glass transition temperature of PLA can be represented by a Flory-Fox (Equation (1))

$$T_g = T_g^\infty - K/\bar{M}_n \quad (1)$$

where T_g^∞ is the T_g at infinite \bar{M}_w and K is a constant representing the excess free volume of the end groups of the polymer chains. Jamshidi et al.^[116] reported that $T_g^\infty = 58$ °C and $K = 5.50 \times 10^4$ for low crystallinity PLLA and that $T_g^\infty = 57$ °C and $K = 7.30 \times 10^4$ for amorphous PDLA. Celli and Scandola^[117] reported that a decrease in the molecular weight increased the enthalpy of relaxation at the glass transition. Also, they reported that PLLA is sensitive to thermal degradation. Some reasons for this poor

thermal stability are (1) hydrolysis by trace amounts of water, catalysed by hydrolysed monomers (lactic acids); (2) zipper-like depolymerization, catalysed by the remaining polymerization catalyst; (3) oxidative, random main-chain scission; (4) intermolecular transesterification to monomer and oligomeric esters and (5) intramolecular transesterification resulting in the formation of monomer and oligomeric lactides of low \bar{M}_w .

Table 5 presents the glass transition and melting temperatures and the enthalpy of fusion for two PLA, PS and PET films.^[108] Tests were carried out according to ASTM D 3418-97 and ASTM D 3417-97. Polylactide films undergo an endothermic event superimposed on T_g which is observed during the first differential scanning calorimeter (DSC) heating. This endothermic relaxation, with an average enthalpy of 1.4 J · g⁻¹ (Table 6), results from a secondary molecular reordering in the amorphous phase of semi-crystalline polymers. The endothermic peak is eliminated as the sample is heated above T_g .

The thermal history of PLLA films strongly affects their physical properties since it induces changes in crystallinity (i.e., long physical aging time affects the ratio of the glassy amorphous phase). This phenomenon is clearly observed as the storage temperature approaches the glass transition temperature of the films. Celli and Scandola^[117] found that the decrease in molecular weight of PLLA films increased the magnitude of the enthalpy of relaxation at the glass transition. Tsuji and Ikada^[95] prepared PLLA films which they annealed. They found that PLLA polymer morphology strongly depended on the annealing temperature and time since it alters the spherulite size and morphology. In

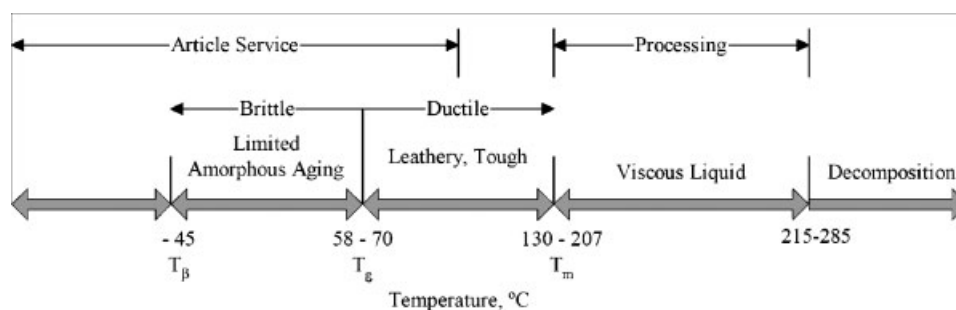


Figure 5. Metastable states of high molecular weight semicrystalline polylactide, adapted from Witzke.^[76]

Table 5. Physical properties of PLA (98% L-lactide), PLA (94% L-lactide), PS and PET.

	PLA(98% L-lactide) ^{a)}	PLA(94% L-lactide) ^{a)}	PS (atactic) ^{b)}	PET
T_g °C	71.4	66.1	100	80
Relaxation enthalpy $J \cdot g^{-1}$	1.4	2.9	N/A	N/A
T_m °C	163.4	140.8	N/A	245
Enthalpy of Fusion $J \cdot g^{-1}$	37.5	21.9	N/A	47.7
Percent Crystallinity	40	25	N/A	38

^{a)} PLA samples were provided by Cargill Dow LLC.

^{b)} PS used in packaging is atactic, so it does not crystallize. Since it is an amorphous polymer, it does not have a defined melting point, but gradually softens through a wide range of temperatures.

addition, annealing effects depend on pretreatments such as melting before annealing. Annealing studies of poly(L-lactic acid) at 448 K show an increase in melting temperature and heat of fusion with annealing time, suggesting an increase in lamellar thickness.

Crystallinity

The crystallization kinetics of polylactides have been extensively studied.^[35–38,54,73,76,77,79–81,85,89,91,118–126] Investigation of poly(L-lactide-co-meso-lactide) in the range of 0% to 9% meso-lactide showed that the crystallization kinetics are strongly dependent on the copolymer composition.^[94] Tsuji and Ikada^[122] reported that PLLA can crystallize in the presence of D-lactide. However, as the structure becomes more disordered, the size of the spherulites and the time for crystallization increases.

PLLA exhibits strong piezoelectricity when the polymer chains are highly oriented.^[3,100] Molecular orientation increases the mechanical strength of PLLA plastics. If orientation is performed at low temperature, the resulting PLLA has enhanced strength without a significant increase in crystallinity. Ou and Cakmak^[127] reported that simultaneous biaxial stretching produced PLA films with different crystalline order and orientation levels, which may have a significant impact on the final properties of the films.

Crystallization of the amorphous, but thermally crystallizable, PLA copolymers (various L- to D-contents) can be initiated by annealing at temperatures between 75 °C and the melting point. Annealing crystallizable PLA copolymers to induce crystallinity often produces two melting peaks. Yasuniwa et al.^[128] found a double melting point in PLLA polymers and attributed them to slow rates of crystallization and recrystallization. Annealing at temper-

atures close to the melting point produced only crystals with the highest melting point, longer annealing times produced more perfect, higher-melting crystals. This change in crystallization from rapidly forming, lower-melting crystals to more slowly reforming, higher-melting crystals occurred gradually as the annealing temperature progressed from 100 °C to 140 °C. Samples less than 300 000 g · mol⁻¹ developed 30–50% crystallinity. Poly(lactic acid) is a slowly-crystallizing material, similar to poly(ethylene terephthalate). More details on the crystallization kinetics of poly(lactic acid) and copolymers can be found elsewhere.^[31,33–36,57,77,89,91,93,94,116,125,126,129–133] Nucleation parameters for poly(L-lactic acid) crystallization in isothermal and non-isothermal conditions were determined using differential scanning calorimetry and electron microscopy. Equation (2) shows the nucleation parameters^[89,93,130,132]

$$K_g = \frac{4b\sigma\sigma_e T_m}{\Delta H_f k} \quad (2)$$

where K_g is the nucleation constant, σ the lateral surface energy, σ_e the fold surface energy, b the layer thickness of the crystal, ΔH_f the heat of fusion/unit volume and k the Boltzman constant. Table 6 shows the nucleation parameters from isothermal and non-isothermal kinetic analysis of PLLA.

Solving Equation (2), $T_m = 480$ K (207 °C), $T_g = 328$ K (55 °C), $\Delta H_f = 11.11 \times 10^8$ erg · cm⁻³ or 111.083×10^6 J · m⁻², $b = 5.17 \times 10^{-8}$ cm and $\sigma_e = 60.89$ erg · cm⁻² or 6.089×10^{-4} J · m⁻². The peak crystallization temperature obtained was 125 °C. In addition, Urbanovici et al.^[129] obtained isothermal DSC crystallization data for poly(lactic acid) at six temperatures between 90 and 130 °C. They used the Avrami equation which presents the degree of crystallization as a function of time and temperature.

Density

The density of amorphous poly(L-lactic acid) has been reported as 1.248 g · ml⁻¹ and for crystalline PLLA as 1.290 g · ml⁻¹.^[76] The liquid density of L-lactide, meso-lactide and amorphous polylactide can be expressed using

Table 6. Nucleation Parameters from isothermal and non-isothermal kinetic analysis for PLLA, adapted from Vasanthakumari and A. J. Pennings,^[93] Kishore^[130] and Vasanthakumari.^[132]

Parameter	Isothermal	Non-isothermal
Nucleation parameter, $k_g \times 10^5$	2.44	2.69
$\sigma\sigma_e \times 10^6$	753	830
$J^2 \cdot m^{-4}$		
Lateral surface energy, $\sigma \times 10^3$	12.0	13.6
$J \cdot m^{-2}$		

Equation (3).

$$\rho(\text{g}/\text{cm}^3) = \frac{\rho_{150^\circ\text{C}}}{1 + \alpha_l(T(^{\circ}\text{C}) - 150)} \quad (3)$$

where $\alpha_l = 7.4 \times 10^{-4} ^\circ\text{C}^{-1} \pm 0.17 \times 10^{-4} ^\circ\text{C}^{-1}$ and is the liquid thermal coefficient of expansion obtained by non-linear regression.

The density of solid polylactide was reported as $1.36 \text{ g} \cdot \text{cm}^{-3}$ for L-lactide, $1.33 \text{ g} \cdot \text{cm}^{-3}$ for meso-lactide, $1.36 \text{ g} \cdot \text{cm}^{-3}$ for crystalline polylactide and $1.25 \text{ g} \cdot \text{cm}^{-3}$ for amorphous polylactide. The density of the pure crystals can be determined by using Equation (4).

$$\rho_c(\text{g}/\text{cm}^3) = \frac{w_c}{1/\rho - (1 - w_c)/\rho_a} \quad (4)$$

where ρ_c is the density of the pure crystal, ρ is the density of semi-crystalline polylactide, w_c is the crystalline fraction and ρ_a is the density of the amorphous polylactide, so the ratio of purely crystalline and amorphous polylactide (ρ_c/ρ_a) is 1.088.

The densities of two polylactides, poly(98% L-lactide) and poly(94% L-lactide), were measured by the level to which the PLA specimen sinks in a liquid column.^[108] Poly(98% L-lactide) had a density of $1.240 \pm 0.002 \text{ g} \cdot \text{cc}^{-1}$ and poly(94% L-lactide) had a density of $1.243 \pm 0.002 \text{ g} \cdot \text{cc}^{-1}$.

Friction Coefficient

Friction is a complex summation of different factors such as internal friction and surface shear friction and it is measured in terms of the friction coefficient. Internal friction is important in cyclic processes like rolling friction. Surface friction is the interaction that takes place at the surface. Even the smoothest surfaces are rough on a sub-microscopic scale. The friction coefficient plays a very important role in film passing over free-running rolls, bag forming and the wrapping of film around a product. The upper limits of the static friction coefficients for two polylactide films, poly(98% L-lactide) and poly(94% L-lactide), were determined by an inclined plane method.^[108] Poly(98% L-lactide) had a friction coefficient equal to $\mu_s = 0.371 \pm 0.011$, and poly(94% L-lactide) equal to $\mu_s = 0.319 \pm 0.011$. The difference is due to different surface treatments. Typical friction coefficients of PS and PET films are $\mu_s = 0.4$ and $\mu_s = 0.35$, respectively.^[112]

Surface Energy

Surface energy is critically important to many converting operations and is a direct manifestation of intermolecular tension. Molecules at the surface of the polymer are not surrounded by other molecules, so the molecular forces are unbalanced and the molecules have additional energy compared with the molecules inside the liquid or solid. The surface or interfacial tension is expressed in $\text{J} \cdot \text{m}^{-2}$

($\text{N} \cdot \text{m}^{-1}$) or in $\text{erg} \cdot \text{cm}^{-2}$ ($\text{dyn} \cdot \text{cm}^{-1}$). The surface energy of polymers can be modified by flame treatment, corona discharge treatment and ozone treatment, all of which impart some oxidation to the surface of the polymer and promote adhesion in printing and converting operations. In general for films, corona treatment is chosen to increase surface tension. In this process, high-voltage electric energy is discharged on the surface of the film, which increases the surface energy. "In general, the ability of a substrate to anchor inks, coatings or adhesives is directly related to its surface energy. If the substrate surface energy does not significantly exceed the surface tension of the fluid which is to cover it, wetting will be impeded, and a poor bond will result."^[134] The surface energies of two polylactide films, poly(98% L-lactide) and poly(94% L-lactide), were measured by ACCU DYNE TEST marker pens from Diversified Enterprises, Claremont, NH according to ASTM D 2578-94^[134] and are shown in Table 7, with the surface energies of other standard polymers.

Moisture Sorption Isotherm

Moisture sorption isotherms were determined for two polylactide films, poly(98% L-lactide) and poly(94% L-lactide) in the range of $A_w = 0$ to 0.9 and at 5 , 23 and $40 ^\circ\text{C}$, where A_w is the ratio of the partial pressure of water to the saturation (vapor) pressure of water at a specified temperature.^[108] PLA films stored for more than one week at 5 , 23 , and $40 ^\circ\text{C}$ and A_w between 0.11 and 0.94 did not absorb measurable amounts of water. Previous work with PLA pellets ($\bar{M}_n = 50\,000$ – $100\,000$ Daltons) indicated very low levels of water absorption (i.e. $8\,000$ ppm at $25 ^\circ\text{C}$ and $A_w = 0.9$, with an equilibrium time no greater than 72 h).^[76] Witzke^[76] also reported that water absorption was fairly insensitive to moderate temperature changes. PLA is moderately polar with a solubility parameter (δ) of 19 – $20.5 \text{ MPa}^{0.5}$.^[1] The solubility parameter of water is $48 \text{ MPa}^{0.5}$. When the difference between the solubility parameter of water and a polymer increases, the water sorption decreases. For PET the δ is $16 \text{ MPa}^{0.5}$ and the water absorption 60 ppm at $25 ^\circ\text{C}$, with an $A_w = 0.5$.

Table 7. Experimental and calculated surface tension in $\text{dyn} \cdot \text{cm}^{-1}$ for PLA, PET, PP, PE and PS.

Polymer	γ_s experimental	γ_s calculated
	$\text{dyn} \cdot \text{cm}^{-1}$	$\text{dyn} \cdot \text{cm}^{-1}$
Poly(98% L-lactide) ^{a)}	42	45 ^{b)}
Polyethylene	35.7 ^{c)}	31.5 ^{b)}
Polypropylene	29.6 ^{c)}	32.5 ^{b)}
Poly(ethylene terephthalate)	44.6 ^{c)}	49 ^{b)}
Polystyrene	40.7 ^{c)}	43 ^{b)}

a) PLA samples were obtained from Cargill Dow LLC.

b) Calculated from $\gamma_s = (P_s/V)^{1/4}$, where P_s is the parachor in $(\text{cm}^3 \cdot \text{mol}^{-1}) \times (\text{erg} \cdot \text{cm}^{-2})^{1/4}$ and V is the molar volume.

c) Experimental values obtained from Van Krevelen.^[112]

For PS ($\delta = 19 \text{ MPa}^{0.5}$) the water absorption was 320 ppm at 25°C and $A_w = 0.5$.^[76] In PLA films water absorption is difficult to measure below 100 ppm.^[108] One reason could be that the chemical composition of the PLA films used by Auras^[108] and the chemical composition of the pellets used by Witzke^[76] was different (i.e. they contained different amounts of L- and D-lactide isomers). Another possibility is that the porous structure of the pellets trapped water.

Variation of the Glass Transition and Melting Temperature with Time, Temperature and Humidity

In polymers that absorb very low amounts of water, such as PLA and PET, the effect of water on the physical properties can be crucial to the polymer's general performance. For example, in the case of PET, water plasticizes the amorphous phase, which leads to a decrease of the T_g from about 80°C in a dry state to about 57°C in a saturated state and a consequent reduction of the elastic modulus.^[135] Besides the changes in the physical and mechanical properties, surprising changes in polymer barrier properties can occur as a result of the presence of relatively small quantities of absorbed water. Therefore, changes in the physical properties (i.e. T_g , T_m and enthalpy of fusion) as a function of the storage time at different temperatures and water activities can be used as an indicator of the change in the performance of the polymers under different environmental conditions. Variation in the glass transition and melting temperature with time, temperature and humidity for two polylactide films of rectangular shape ($5 \text{ cm} \times 1 \text{ cm} \times 25.4 \text{ }\mu\text{m}$), poly(98% L-lactide) and poly(94% L-lactide), stored for 120 d at 5, 23 and 40°C , and 0.11, 0.53 and 0.94 water activities has been reported.^[108] The glass transition and melting temperatures were monitored every week for the first month and after that every 30 d. Figure 6a, b and c show the change in the glass transition temperature for poly(98% L-lactide) as a function of time at 5, 23 and 40°C with A_w of 0.11, 0.52 and 0.94. For poly(98% L-lactide), the variation in T_g was statistically significant as a function of time ($P_{\text{value}} < 0.05$). The major reduction in T_g as a function of time was reached prior to seven days. After this no statistically significant change was recorded ($P_{\text{value}} = 0.084$). No statistically significant change of T_g as function of storage temperature was found ($P_{\text{value}} = 0.692$). Humidity had an effect on T_g , at $P_{\text{value}} = 0.05$. Figure 6d, e and f show the change in the glass transition temperature for poly(94% L-lactide) as a function of time at 5, 23 and 40°C with A_w of 0.11, 0.52 and 0.94. The reduction of T_g as a function of time was statistically significant after seven days ($P_{\text{value}} = 0.002$). The change in T_g as a function of storage temperature and the change of T_g with humidity were not statistically significant ($P_{\text{value}} = 0.124$ and 0.069, respectively).

Melting temperature was analyzed in the same way as the glass transition temperature and no significant changes were found ($P_{\text{value}} > 0.05$) for poly(98% L-lactide) and

poly(94% L-lactide). In addition, the change in the enthalpy of fusion as function of time, temperature and humidity was evaluated. For poly(98% L-lactide), no statistically significant change in the enthalpy of fusion as a function of time, temperature and humidity was found ($P_{\text{value}} > 0.05$). For poly(94% L-lactide), however, the change was statistically significant ($P_{\text{value}} < 0.05$). One reason for the change in the enthalpy was likely to be the low molecular weight sealant layer.

Heat Sealing Properties

Working with amorphous PLA sealant films, Gruber and O'Brien^[17] reported sealing temperatures of 80 and 85°C and an ultimate tensile strength of $360 \text{ g} \cdot \text{cm}^{-1}$ over a broad temperature range. They also reported a peak hot tack strength of $450 \text{ g} \cdot \text{cm}^{-1}$ in a PLA made by coextrusion.

Auras^[108] determined the best sealing conditions for poly(94% L-lactide) films. Figure 7 shows the peel force as a function of the sealing temperature. The type of failure and the amount of shrink that the film exhibits when sealed at each temperature is also shown. Poly(94% L-lactide) had a constant peel force until the sealing temperature exceeds 115°C . At 120°C the peeling force increased by 25%, though the material failed before seal failure. The maximum and minimum peel forces did not differ much from the average values, which indicates uniform sealing of the PLA samples. When the heating temperatures exceeded 110°C , the shrinkage of the sample increased to 10% and then 20% at a temperature of 120°C . The best sealing condition for poly(94% L-lactide) was a temperature of around 110°C for one to five seconds. The strongest peel seal can be achieved at temperatures near the melting point of the inner sealant layer of the polymer film. Sealing at a temperature above the fusion temperature resulted in a weld seal and a high shrinkage percentage. The dwell time for sealing did not result in any considerable difference in seal strength once the temperature at the interface reached the set temperature. Sufficient pressure is required to bring the sealing surfaces together at the sealing temperature. Once achieved, however, a higher pressure did not add to the seal strength. The combination of the delamination failure mode shown in PLA with this peel strength value may indicate the potential for PLA to be incorporated into an "easy-open" package.

Heat Deflection Temperature

Poly(98% L-lactide) lost 50% of its modulus and storage modulus at 80°C and 87% of the storage modulus at 100°C . Figure 8 shows DMA curves for poly(98% L-lactide). The use of poly(98% L-lactide) at a temperature higher than the glass transition resulted in an almost complete loss of the film strength. For poly(94% L-lactide), 50% of the storage modulus was lost at 82°C and a total loss of the storage modulus was found at 90°C (not shown). The increased loss rate of the biaxially oriented poly(94% L-lactide) film is

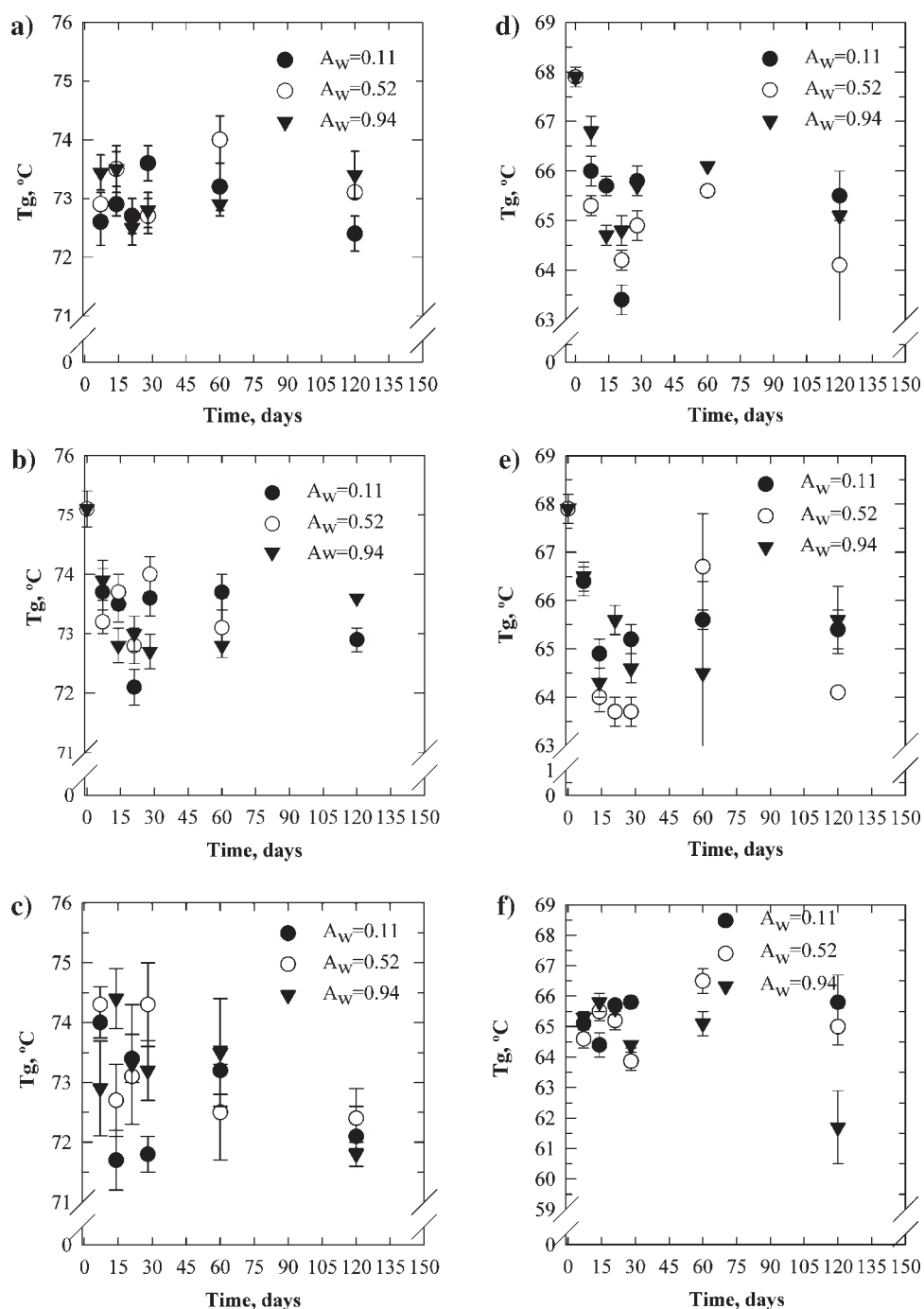


Figure 6. a, b, c represent the variation in the glass transition as a function of time for poly(98% L-lactide) storage at 5, 23, and 40 °C with A_w of 0.11, 0.52 and 0.94, and d, e, f represent the variation in the glass transition variation as a function of time for glass transition variation for poly(94% L-lactide) storage at 5, 23, and 40 °C with A_w of 0.11, 0.52 and 0.94.

attributed to a lower percent crystallinity ($\chi_c = 25\%$) than the poly(98% L-lactide) ($\chi_c = 40\%$) and a lower melting temperature.

Rheological

The shear viscosity of PLA polymers affects thermal processing, such as injection molding, extrusion, film

blowing, sheet forming, fiber spinning and thermoforming. Polylactide melt behavior is similar to polystyrene. Melt viscosities of high molecular weight PLA were reported as 5 000 to 10 000 poise (500–1 000 Pas) at 10 to 50 s⁻¹.^[57] The weight average molecular weight of PLA used for injection molding is around 100 000 Daltons and approximately 300 000 for cast-extruded film grades. The amount

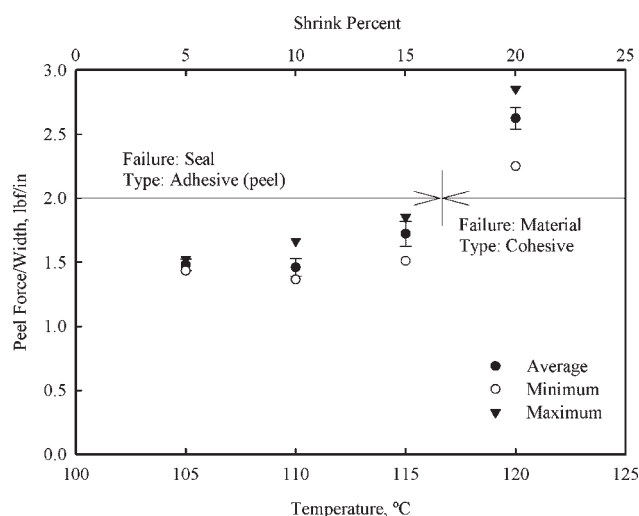


Figure 7. Peel force and shrink percentage as a function of sealing temperature.

of plasticizer plays an important role in the melt viscosity. The PLA working temperature is dependent on its melt viscosity, which depends on the weight-average molecular weight, the L/D ratio, the amount of plasticizer, the shear rate, the type of melt processing and the amount of energy put into the polymer.^[136] A number of dilute-solution experiments have been performed with polylactide, the data from which have been used to create a number of Mark-Houwink equations. The Mark-Houwink equation represents the relationship between η , the intrinsic viscosity, and the molecular number or weight and is a function of the type of polylactide, the solvent used and the temperature of the solution. Table 8 shows the Mark-Houwink constants for various polylactide polymers.

Semicrystalline PLA has a higher shear viscosity than amorphous PLA. However, as the temperature increases, the shear viscosity decreases for both amorphous and semicrystalline PLA.^[143] The PLA melt is a pseudoplastic,

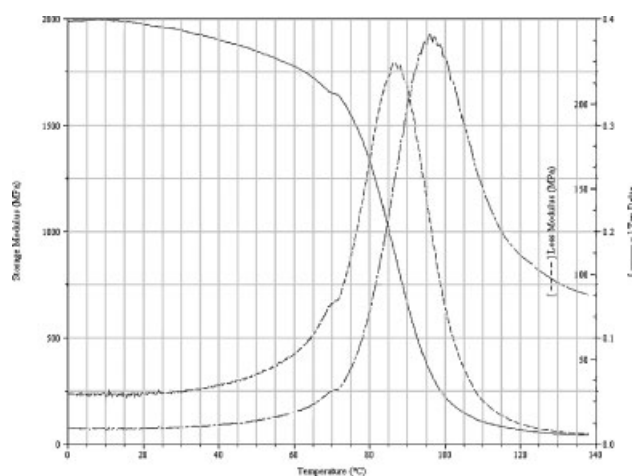


Figure 8. DMA curves of poly(98% L-lactide) ($\chi_c = 40\%$) showing E' , E'' and $\tan \delta$ as a function of temperature at a frequency of 1 Hz.

non-Newtonian fluid with behavior adequately described using a power law equation.^[143] On the other hand, Dorgan et al.^[144] working with PLAs with a wide range of optical compositions found that the melt properties were not dependent on the optical composition of the polymers. Witze investigated the linear viscoelastic properties and the lactide-polylactide mixture viscosities occurring during polymerization for different polylactide polymers with different monomeric compositions (L-, *meso*-, D-lactide) between 68 and 151 °C.^[76] He concluded that the zero-shear viscosity of amorphous polylactide depended on its isomeric makeup, weight average molecular weight and the temperature, between T_g and $T_g + 100$ °C.^[76] Cooper-White and Mackay^[145] reported that PLLA melts have a critical molecular weight for entanglement of $16\,000\text{ g} \cdot \text{mol}^{-1}$ and an entanglement density of $0.16\text{ mmol} \cdot \text{cm}^{-3}$ at 25 °C. In addition, the terminal viscosity (η_0) was found to be dependent on chain length to the fourth power. For

Table 8. Mark-Houwink constants for poly(lactic acid) in selected solvents ($K = \text{dl} \cdot \text{g}^{-1}$), adapted from Garlotta,^[57] Schindler^[136] and Sinclair.^[137] PDLLA provided by Cargill-Dow LLC is insoluble in ethyl acetate.

Poly(lactic acid)	Mark-Houwink constant	Solvent
PLLA	$[\eta] = 5.45 \times 10^{-4} M_v^{0.73}$	25 °C in chloroform ^[33,97]
PDLLA	$[\eta] = 2.21 \times 10^{-4} M_v^{0.77}$	25 °C in chloroform ^[33,97]
PDLLA	$[\eta] = 1.29 \times 10^{-5} M_v^{0.82}$	25 °C in chloroform ^[138]
Linear PLLA	$[\eta] = 4.41 \times 10^{-4} M_v^{0.72}$	25 °C in chloroform ^[139]
“Star” PLLA (6 arms)	$[\eta] = 2.04 \times 10^{-4} M_v^{0.77}$	25 °C in chloroform ^[139]
PDLLA	$[\eta] = 2.59 \times 10^{-4} M_v^{0.689}$	35 °C in THF ^[140]
PDLLA	$[\eta] = 5.50 \times 10^{-4} M_v^{0.639}$	31.15 °C in THF ^[140]
PLLA (amorphous)	$[\eta] = 6.40 \times 10^{-4} M_v^{0.68}$	30 °C in THF ^[87]
PLLA (amor./semicryst.)	$[\eta] = 8.50 \times 10^{-4} M_v^{0.66}$	30 °C in THF ^[87]
PLLA (semicryst.)	$[\eta] = 1.00 \times 10^{-3} M_v^{0.65}$	30 °C in THF ^[87]
PDLLA	$[\eta] = 2.27 \times 10^{-4} M_v^{0.75}$ (one point method)	30 °C in benzene ^[141] Tuan-Fuoss viscometer
PDLLA	$[\eta] = 6.06 \times 10^{-4} M_v^{0.64}$	25 °C in chloroform ^[136]
PLLA	$[\eta] = 5.72 \times 10^{-4} M_v^{0.72}$	25 °C in chloroform ^[136]
PDLLA	$[\eta] = 1.58 \times 10^{-4} M_v^{0.78}$	25 °C in ethyl acetate ^[142]
PDLLA	$[\eta] = 1.63 \times 10^{-4} M_v^{0.73}$	25 °C in ethyl acetate ^[142]

branched PLLA, the entanglement happens at a molecular weight about four-fold that of linear PLLA and the terminal viscosity (η_0) was dependent on chain length to the 4.6 power.^[146]

The melt flow index is indicative of the extrudability of thermoplastic materials. Values of 8.51 ± 0.19 g/10 min and 7.83 ± 0.15 for poly(98% L-lactide) and poly(94% L-lactide), respectively, were found at 200 °C and 5 kg of weight.^[108]

Processing

PLA can be processed by injection molding, sheet extrusion, blow molding, thermoforming and film forming. Cargill Dow LLC commercialized PLA polymer under the name of Natureworks for extrusion, thermoforming, cast film, blown film and injection stretch blow molded bottles and containers.^[17,147] Mitsubishi Plastics in Japan also commercialized PLA polymers for different applications under the brand name of LACEA.^[18]

Hartmann^[49] reported that the molecular weight for polymers used in extrusion and injection molding is usually reduced over the virgin material. PLA quickly loses its thermal stability when heated above its melting point. Significant molecular weight degradation occurred when PLA was held 10 °C above its melting point for a substantial period of time.^[49,57] Migliaresi et al.^[148] measured the reduction in molecular weight due to thermal degradation and attributed it to chain splitting and not to hydrolysis as had been previously reported. They did not observe oxidation of PLA. The degradation of PLA is not only a consequence of the thermal degradation of the PLA, but the amount of residual monomer in the resin also has an important effect in inducing early degradation of the polymer.

PLLA polymers have a narrow processing window (12 °C) although a 90/10 L- to D-copolymer has a much wider window of processing conditions (40 °C) due to its lower melting temperature.^[57] PLA can be plasticized with lactides, oligomeric lactic acid and a wide variety of conventional plasticizers. In general, PLA plasticizing agents are low molecular weight lactide and glycol acids. However, Bechtold et al.^[149] found that a copolymer made from lactic acid and ethylene oxide could be used as a macromolecular plasticizing agent for commercial PLA. Other biocompatible plasticizers such as glycerol, citrate ester, polyethylene glycol, PEG monolaurate and oligomeric lactic acid have also been used to improve the brittle behavior of PLA.^[150] Glycerol is the least efficient of these plasticizing agents, and polyethylene glycol is the most efficient. A reduction in the glass transition temperature from 58 °C to 12 °C was found when plasticizers were used.^[150] No reduction in the melt temperature was observed.

PLA polymers start to thermally degrade at 300 °C and completely decompose at 400 °C when tested under dried conditions by thermal gravimetric analysis (TGA) with a

heating ramp of 10 °C · min⁻¹ and purged with nitrogen at 50 ml · min⁻¹. Zero-order kinetics are followed between 40 and 80% volatilization, which are consistent with a depolymerization phenomenon. Further details of this process can be found elsewhere.^[76] Thermal decomposition is independent of initial lactide isomer distribution. The activation energy for PLA weight loss is 139 kJ · mol⁻¹ between 186 °C and 257 °C. Polylactide has a similar thermal stability to PVC but is considerably less stable than PS, PP, PE and PET.

Mechanical

The mechanical properties of poly(lactic acid or lactide) have been studied by many investigators.^[11,17,18,22,32,33,39,57] Results for polylactides produced and processed under different conditions are shown in Table 9.

The variation shown in Table 10 is due to the degree of orientation in the samples and the stereochemical composition of various poly(lactic acid) samples. Annealing L-PLA increased the tensile strength due to the increase in the stereoregularity of the chain and increased the impact resistance due to the crosslinking effects on the crystalline domains.^[57,151]

In general, the modulus and tensile strength were greatest for PLA polymers with a viscosity-average molecular weight above 55 000 g · mol⁻¹.^[49,57] The impact strength and the Vicat softening temperature increased with molecular weight and crystallinity.^[49,57]

Perego et al.^[33] who worked with PLLA having molecular weights of 35 000 and 55 000 Daltons found an increase of almost 20% in the modulus of elasticity for poly(L-lactide) compared with poly(D,L-lactide). In addition, they demonstrated that the impact resistance was strongly influenced by crystallinity.^[33]

The tensile strength and the elastic modulus values for poly(98% L-lactide and 94% L-lactide), PS and PET were measured and are presented in Table 10. The higher content of L-lactide in the films contributes to a higher tensile strength. Although poly(98% L-lactide) has greater elongation at yield than poly(94% L-lactide), the latter has an elongation at break 7 times greater than poly(98% L-lactide), which indicates that poly(94% L-lactide) is more plastic. The tensile strength values obtained for both polylactides are within the range of values reported in the literature for PS under the same testing conditions. However, when compared to PET, both PLA films had lower values. The impact resistance of poly(98% L-lactide) films is around 360 g.

Solubility

According to Kharas et al.^[46] polylactides are soluble in dioxane, acetonitrile, chloroform, methylene chloride,

Table 9. Mechanical properties of poly(L-lactide), adapted from Perego et al.^[33] and Garlotta.^[57] The specimens were obtained by injection molding at a temperature of 195 °C.

	L-PLA ($M_v = 66\,000$) ^{a)}	Annealed L-PLA ($M_v = 66\,000$)	D,L-PLA ($M_v = 114\,000$)
Tensile strength	59	66	44
MPa			
Elongation at break	7.0	4.0	5.4
%			
Modulus of elasticity	3 750	4 150	3 900
MPa			
Yield strength	70	70	53
MPa			
Flexural strength	106	119	88
MPa			
Unnotched izod impact	195	350	150
J · m ⁻¹			
Notched izod impact	26	66	18
J · m ⁻¹			
Rockwell hardness	88	88	76
Heat deflection temperature	55	61	50
°C			
Vicat penetration	59	165	52
C			

^{a)} M_v is the molecular weight.

1,1,2-trichloroethane and dichloroacetic acid. Ethyl benzene, toluene, acetone and tetrahydrofuran only partly dissolve polylactides when cold, though they are readily soluble in these solvents when heated to boiling temperatures. Crystalline poly(L-lactide) is not soluble in acetone,

Table 11. Solubility parameters for polylactides, adapted from Garlotta.^[57]

Determination method	Solubility parameter cal ^{0.5} × cm ^{-1.5}
Density in solution ^[152]	10.25 ± 0.16
Density in solution ^[153]	10.29 ± 0.13
Limiting viscosity number, $[\eta]$ ^[152]	10.00 ± 0.20
Limiting viscosity number, $[\eta]$ ^[153]	10.00 ± 0.23
<i>Group Contribution Methods</i>	
Small ^[154]	9.7
Hoy ^[154]	9.9
Van Krevelen ^[154]	9.4
Fedors ^[154]	11.1

ethyl acetate or tetrahydrofuran. All polylactides are insoluble in water, some alcohols and alkanes. Solubility parameters were measured and reported to be around 10.3 cal^{1/2} · cm^{-1.5} for amorphous poly(D,L-lactide). Solubility parameters from the literature are reported in Table 11.^[57] Tsuji and Sumida^[11] found that lactides in phosphate, acid and alkaline solutions had solubility parameter (δ_s) values of 4.0–6.2 cal^{0.5} · cm^{-1.5}.

The relative affinity of a polymer and a solvent can be assessed using solubility parameters. Auras^[108] estimated the affinity between a number of different solvents (alkenes, aromatic hydrocarbons, halohydrocarbons, ethers, ketones, aldehydes, esters, nitrogen compounds, sulfur compounds, acid halides and anhydrides, alcohols, acids, phenols and polyhydric alcohols) and polylactide, as well as PET and PS. The Hansen^[153] extension of the Hildebrand (1916) enthalpy of mixing between a solvent and a polymer was used to determine the interaction between PLA and the different solvents. Figure 9 and 10 show two-dimensional plots of the affinity between nitrogen compounds, alcohols and polylactide, as well as poly(ethylene terephthalate) (PET) and polystyrene (PS). A detailed study of other solvent interactions with PLA can be found elsewhere.^[108] The solubility regions of PLA, PET and PS can be approximated by a circle with a radius of about 2.5 δ units with centers at $\delta_v = 19.01$; $\delta_h = 10.01$ for PLA, $\delta_v = 19.77$;

Table 10. Mechanical properties of poly(98% L-lactide), poly(94% L-lactide), PS and PET films.^[108]

	Poly(98% L-lactide) ^{a)}		Poly(94% L-lactide) ^{a)}		PS Biaxial	PET
	MD	CD	MD	CD		
Tensile yield stress	72	65	84	74	55–82	275
MPa (kpsi)	(10.5)	(9.5)	(12.2)	(10.7)	(8–12)	(40)
Percent elongation at yield	5	4	3	4	–	~6
Percent elongation at break	11	5	78	97	3–40	60–165
Elastic modulus	2.11	2.54	2.31	2.87	3.2	2.8–4.1
GPa (kpsi)	(306.4)	(368.3)	(335.4)	(416.3)	(464)	(400–600)

^{a)} PLA samples were provided by Cargill Dow LLC.

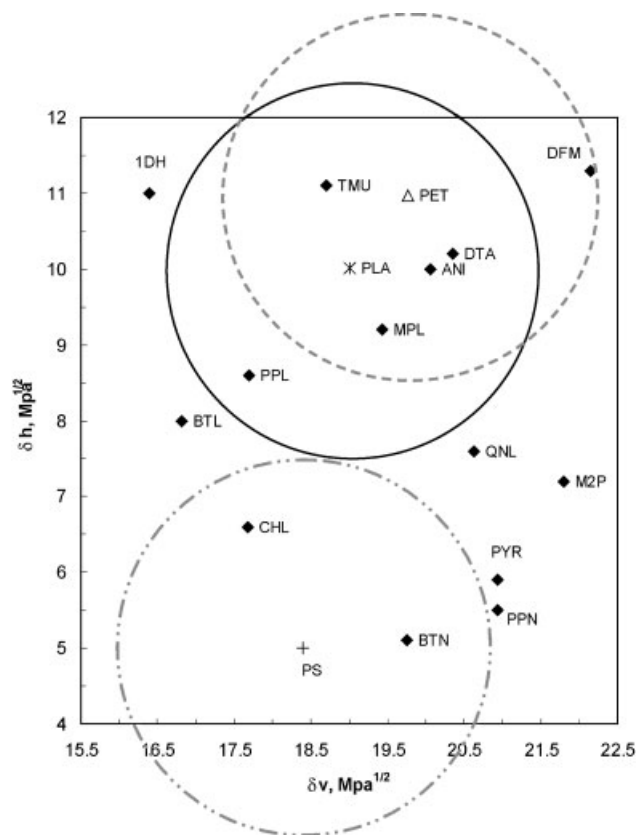


Figure 9. Volume dependent cohesion parameter (δ_v) versus Hansen hydrogen bonding parameter for polylactide and nitrogen compounds. Values indicated for solvents with $\Delta\delta < 5 \text{ MPa}^{1/2}$ (PPN, propionitrile; BTN, butyronitrile; 1DH, 1,1-dimethylhydrazine; PYR, pyridine; PPL, propylamine; MPL, morpholine; ANI, aniline; M2P, *N*-methyl-2-pyrrolidone; BTL, butylamine; CHL, cyclohexylamine; DFM, *N,N*-dimethylformamide; DTA, *N,N*-dimethylacetamide; TMU, tetramethylurea).

$\delta_h = 10.97$ for PET and $\delta_v = 15.90$; $\delta_h = 5.00$ for PS and are the corresponding solubility parameters.^[108,152,155] The solvents inside the circle show interaction with PLA and the other polymers. Note that the distortions from perfect circles are due to the differing scales used for the y and x axes.

Barrier

Carbon Dioxide

PLA carbon dioxide barrier properties have been measured by different investigators. Carbon dioxide permeation of $1.76 \times 10^{-17} \text{ kg} \cdot \text{m/m}^2 \cdot \text{s} \cdot \text{Pa}$ with an activation energy of $6.1 \text{ kJ} \cdot \text{mol}^{-1}$ was reported by Lehermeier.^[5] Auras^[108] determined the carbon dioxide barrier properties of two PLA films. Table 12 presents CO_2 permeability coefficient values as a function of temperature in the range $25\text{--}45^\circ\text{C}$ at 0% RH. The activation energy was calculated according to the Arrhenius equation. In the range of 25°C to 45°C ,

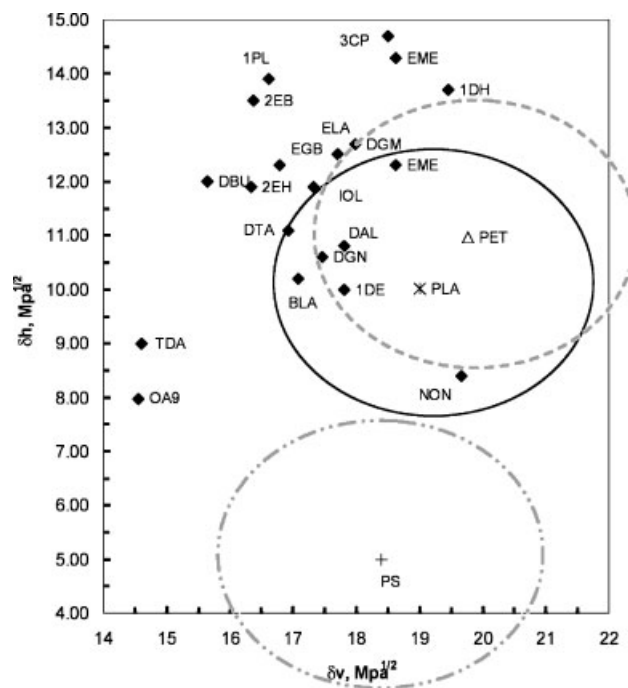


Figure 10. Volume dependent cohesion parameter (δ_v) versus Hansen hydrogen bonding parameter for polylactide and alcohol. Values indicated for solvents with $\Delta\delta < 5 \text{ MPa}^{1/2}$ (3CP, 3-chloropropanol; BEA, benzyl alcohol; CHL, cyclohexanol; 1PL, 1-pentanol; 2EB, 2-ethyl-1-butanol; DAL, diacetone alcohol; DBU, 1,3-dimethyl-1-butanol; ELA, ethyl lactate; BLA, butyl lactate; EME, ethylene glycol monoethyl ether; DGM, diethylene glycol monoethyl ether, methyl; DGE, diethylene glycol monoethyl ether, EGB, ethylene glycol mono-butyl ether; 2EH, 2-ethyl-1-hexanol; IOL, 1-octanol; 2OL, 2-octanol; DGN, diethylene glycol mono-butyl ether; 1DE, 1-decanol; TDA, 1-tridecanol; NON, nonyl; OA9, oleyl alcohol).

poly(98% L-lactide) film had a higher CO_2 permeability coefficient than poly(94% L-lactide). The permeation activation energy was lower for poly(98% L-lactide) resin.

The CO_2 permeability coefficients for PLA resins are lower than the reported value for crystalline PS at 25°C and 0% RH ($1.55 \times 10^{-16} \text{ kg} \cdot \text{m/m}^2 \cdot \text{s} \cdot \text{Pa}$),^[156] but higher than that for PET (1.73 and $3.17 \times 10^{-18} \text{ kg} \cdot \text{m/m}^2 \cdot \text{s} \cdot \text{Pa}$ at 0% RH at 25°C and 45°C , respectively).

Oxygen

Lehermeier^[5] reported an oxygen permeation coefficient for PLA of $3.3 \times 10^{-17} \text{ kg} \cdot \text{m/m}^2 \cdot \text{s} \cdot \text{Pa}$ and an activation energy of $11.1 \text{ kJ} \cdot \text{mol}^{-1}$. Auras^[157] determined and compared the diffusion, solubility and permeability coefficients (D , S , P) of PET and two PLA films by using an isostatic technique at 1 and 0.21 atmosphere pressure at three temperatures (5 , 23 and 40°C) and four water activities (0 , 0.3 , 0.6 and 0.9). Figure 11 shows the oxygen permeability coefficient for poly(98% L-lactide) film as a function of the

Table 12. CO₂ permeability coefficients and activation energy for PLA resins.^{a)}

Resin	$P \times 10^{17}$					E_p
	$\text{kg} \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$					$\text{kJ} \cdot \text{mol}^{-1}$
	Temperature					
	$^{\circ}\text{C}$					
	25	30	35	40	45	
Poly(98% L-lactide)	2.77 ± 0.05	3.12 ± 0.05	3.42 ± 0.06	3.78 ± 0.06	4.18 ± 0.15	15.65 ± 0.63
Poly(94% L-lactide)	1.99 ± 0.06	2.29 ± 0.06	2.52 ± 0.06	2.87 ± 0.04	3.35 ± 0.06	19.44 ± 0.90

^{a)} PLA samples were provided by Cargill Dow LLC. Poly(98% L-lactide) has 40% crystallinity and Poly(94% L-lactide) has 25% crystallinity.

water activity. A significant increase in the oxygen permeability coefficient was observed as temperature increased. PLA shows an increase in the oxygen permeability coefficient from 3.5×10^{-18} kg · m/m² · s · Pa at 5 °C to 11×10^{-18} kg · m/m² · s · Pa at 40 °C in the absence of moisture. At higher water activity levels ($A_w = 0.9$), the oxygen permeability coefficient decreases slightly to 8.5×10^{-18} kg · m/m² · s · Pa at 40 °C. Reduction in the oxygen permeability coefficient as water activity increases (at a constant temperature) is shown in Figure 11 for the three temperatures tested. This reduction is most pronounced at 40 °C.

The difference between the values obtained by Auras^[157] and the values from Lehermeier^[5] can be explained by differences in the crystallinity and processing conditions used to produce the films.

The enthalpy of sorption, ΔH_s , the activation energy of diffusion, E_D , the apparent activation energy of permeation, E_P , and the values of P_0 , S_0 and D_0 are presented in Table 13. Further details can be found elsewhere.^[157]

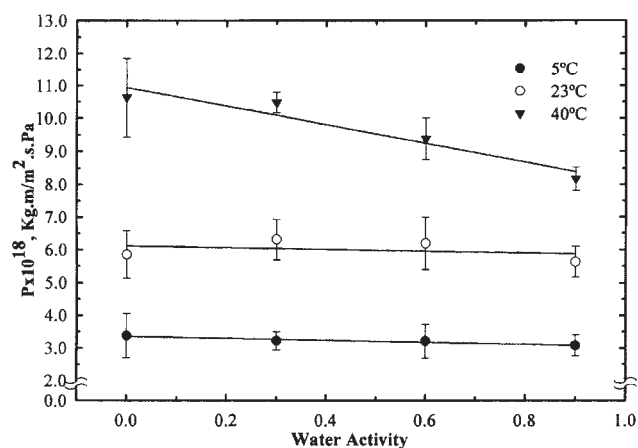


Figure 11. Oxygen permeability coefficient as a function of water activity for poly(98% L-lactide).

Poly(98% L-lactide) has higher crystallinity than poly(94% L-lactide), which generates a more tortuous path for the permeation of oxygen molecules. Since the crystallization of polymers tends to decrease the amorphous volume available for diffusion, the diffusion coefficient and the solubility of more amorphous polymers are higher than those of glassy crystalline polymers. PET and PLA are both hydrophobic films that absorb very low amounts of water and show similar barrier property behavior.

Water

Water vapor permeability coefficient (WVPC) values were determined at 10, 20, 30 and 37.8 °C in the range of 40% to 90% RH.^[108,158] Figure 12 shows that, surprisingly, the permeability for 98% L-lactide polymers is practically constant over the range studied, despite PLA being a polar polymer.

WVPC of PET films showed no significant change as a function of relative humidity. The average WVPC for PET was $1.1 \pm 0.1 \times 10^{-15}$ kg · m/m² · s · Pa at 25 °C in the 40% to 90% RH range. The reported WVPC of PS is 6.7×10^{-15} kg · m/m² · s · Pa at 25 °C.^[156] The activation energy for the water vapor permeation process is $E_P = -9.8$ kJ · mol⁻¹ for 98% L-lactide and $E_P = -10.1$ kJ · mol⁻¹ for 94% L-lactide. Both activation energies are negative.

Water vapor permeation was also measured in some NatureWorks™ PLA polymers from Cargill Dow LLC.^[29] A water vapor transmission rate of 340 g · mL/(m² · day) was reported, but the conditions under which this test was performed are not clear. Shogren^[159] measured the water vapor transmission rate of crystalline and amorphous PLLA and reported an activation energy of 5 kJ · mol⁻¹ for amorphous PLLA and a negative activation energy of -0.1 kJ · mol⁻¹ for crystalline PLLA. Siparsky et al.^[160] reported a permeability coefficient of 9.63×10^{-14} kg · m/m² · s · Pa, a solubility coefficient of 4×10^{-4} m³/m³ · Pa and a diffusion coefficient of 4×10^{-12} m² · s⁻¹ at 20 °C and a water activity of $A_w = 0.5$ in PLA films. They reported an

Table 13. Pre-exponential terms, enthalpy of sorption, activation energy for diffusion and permeation in the oxygen mass transport through PET and PLA films at different water activity conditions.

Material	Water Activity	$P_0 \times 10^{14}$	E_p	$D_0 \times 10^{12}$	E_D	$S_0 \times 10^3$	ΔH_s
		kg · m/m ² · s · Pa	kJ · mol ⁻¹	m ² · s ⁻¹	kJ · mol ⁻¹	kg/m ³ · Pa	kJ · mol ⁻¹
PET	0.0	6.2	30.3	6.6	11.8	9.6	18.5
	0.3	3.0	28.6	2.9	9.5	10.2	19.1
	0.6	4.7	29.9	10.1	11.6	4.6	18.3
	0.9	2.4	28.4	38.9	14.2	0.6	14.1
Poly(98% L-lactide)	0.0	9.0	23.6	300	1.0	2 667	22.6
	0.3	12.4	24.4	981	3.2	1 264	21.2
	0.6	4.9	22.2	34.2	5.0	141	17.2
	0.9	2.0	20.2	27.8	3.3	72.0	16.9
Poly(94% L-lactide)	0.0	3.0	21.1	0.0004	12.1	N/A ^{a)}	N/A
	0.3	0.9	18.7	14.9	12.5	N/A	N/A
	0.6	3.1	21.6	0.9	5.0	N/A	N/A
	0.9	2.0	20.6	17 202	28.0	N/A	N/A

^{a)} N/A: not applicable.

enthalpy of sorption of $-40 \text{ kJ} \cdot \text{mol}^{-1}$ and activation energy of diffusion of $49 \text{ kJ} \cdot \text{mol}^{-1}$. Yoon et al.^[161] found approximately the same enthalpy of sorption ($-48.4 \text{ kJ} \cdot \text{mol}^{-1}$) when working with semicrystalline PLA.

Water sorption and diffusion in polymer membranes follow complex mechanisms due to the nature of the water molecule. Water molecules are particularly small and have a strong tendency to form hydrogen bonds between themselves and with other polar groups. Yoon et al.^[161] and Siparsky et al.^[162] reported that water molecules found in a PLA matrix followed the water-cluster model rather than the solution-diffusion model. They did not observe variation of the diffusion coefficient with an increase in the crystallinity of PLLA, which means that the water molecules were associated with each other and formed clusters through preferential binding via hydrogen bonding. The water molecules are not highly soluble in the polymer and

diffuse in cluster form. On the other hand, some researchers have shown that clusters of water are not present in the polymer matrix.^[76,163,164] The water permeation model in PLA is not yet completely understood.

Nitrogen

Nitrogen barrier properties of PLA films have also been investigated.^[5] The value reported at 30°C was $1.21 \times 10^{-17} \text{ kg} \cdot \text{m/m}^2 \cdot \text{s} \cdot \text{Pa}$, with an activation energy of $11.2 \text{ kJ} \cdot \text{mol}^{-1}$.

Organic Compounds (Ethyl Acetate and D-Limonene)

Permeability, diffusion and solubility coefficients of D-limonene in PLA were reported for NatureWorksTM PLA.^[165] The permeability coefficient for D-limonene was lower than $1 \times 10^{-18} \text{ kg} \cdot \text{m/m}^2 \cdot \text{s} \cdot \text{Pa}$. Auras^[108] also reported similar values at 45°C , with a partial pressure of 258 Pa. A diffusion coefficient and a permeability coefficient lower than $10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$ and $10^{-18} \text{ kg} \cdot \text{m/m}^2 \cdot \text{s} \cdot \text{Pa}$, respectively, were found. PLA is a very good barrier to D-limonene and is comparable to PET and Nylon-6.

In addition, Auras^[108] studied the barrier of PLA to ethyl acetate. A representative plot of the weight gain as a function of time for the sorption of ethyl acetate by PLA films is presented in Figure 13.

To reach equilibrium sorption required more than 30 d. The diffusion, solubility and permeability coefficients obtained from gravimetric experiments at 45°C and 30°C are presented in Table 14.

As was predicted using the solubility parameters, ethyl acetate is outside the solubility region of PLA. The solubility coefficients for ethyl acetate in PLA can be considered very low and are comparable to those of PET.

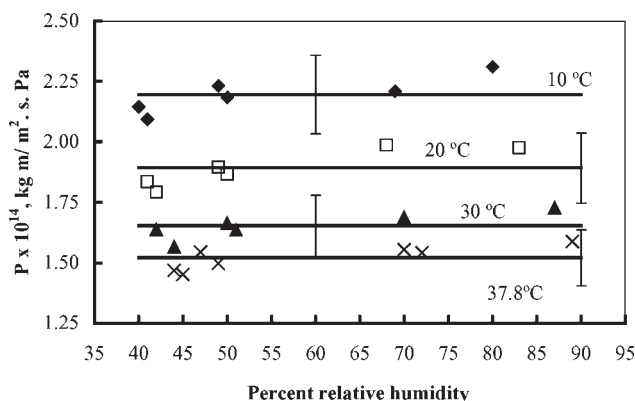


Figure 12. Water vapor permeability coefficient of poly(98% L-lactide) as a function of %RH. Error bars represent cumulative imprecision in measurements.

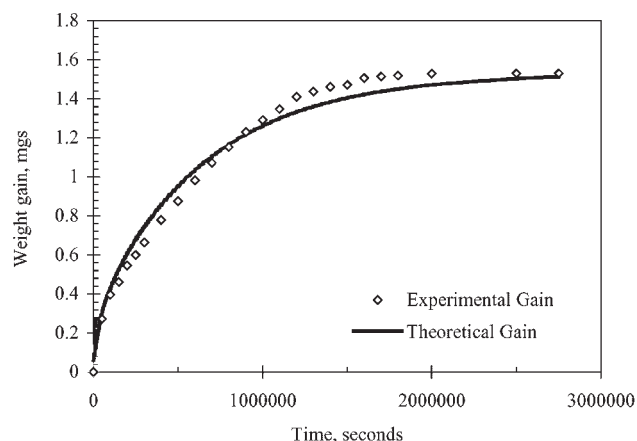


Figure 13. Sorption profile for ethyl acetate in PLA at 30 °C, $p = 3\,030\text{ Pa}$. PLA initial weight 150 mg.

Grease Resistance

Gruber and O'Brien^[17] reported a higher resistance to aliphatic molecules such as oils and terpenes in papers coated with PLA films. Paper coated with PLA did not fail by grease penetration after 120 h of testing at 55 °C, although paper coated with LDPE failed in just 10 h.^[17] Table 15 indicates the resistance of PLA coated paper to different compounds.

Migration

Migrants from PLA may include lactic acid, lactoyllactic acid, other small oligomers of polylactide and lactide. Lactic acid is of primary interest because the other species are expected ultimately to hydrolyse to lactic acid. Scheme 5 shows the chemical equilibria between lactic acid, its linear dimer, trimer and lactide.

Table 14. Ethyl acetate permeability, diffusion and solubility coefficients for poly(98% L-lactide) at 45 °C and 30 °C.

Temperature	45	30	
°C			
Temperature Generated	25	15	0
°C			
Partial pressure	12 654	7 560	3 030
Pa			
P	1.22×10^{-17}	1.18×10^{-18}	5.34×10^{-19}
$\text{kg} \cdot \text{m}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa})$			
D	2.63×10^{-15}	2.81×10^{-16}	8.66×10^{-17}
m^2/s			
S	4.62×10^{-3}	4.27×10^{-3}	6.17×10^{-3}
$\text{kg}/(\text{m}^3 \cdot \text{Pa})$			

Table 15. Grease resistance of PLA coated paper according to TAPPI T507, adapted from Gruber and O'Brien.^[17]

Grease or Oil	23 °C no press	55 °C with press
Mineral Oil	>120 h	>24 h
Olive Oil	>120 h	>24 h
Oleic Acid	>120 h	>24 h
Butter	>120 h	>24 h

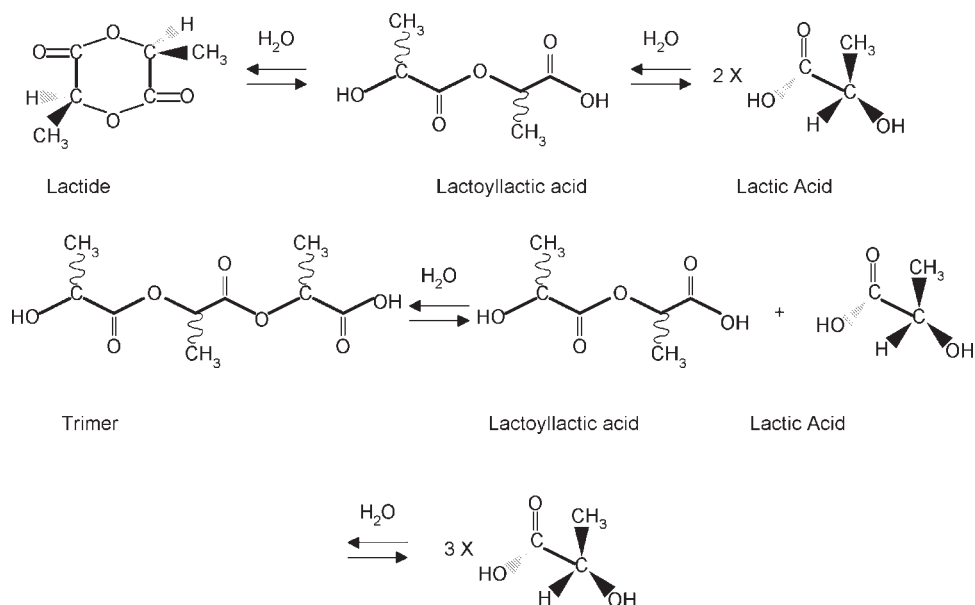
Studies of total and specific migration have been carried out by Conn et al.^[40] and Auras.^[108] Poly(98% L-lactide) stored for 15 d at 40 °C with two different food simulants, 10% ethanol and 95% ethanol, showed that the total amount of food contact substances (FCS) that migrate from PLA polymer in simulant is lower than the average daily intake of lactic acid from all proposed uses as indirect food additives (22 mg per day).^[108] Total migration from the PLA is $12.9\text{ mg} \cdot \text{kg}^{-1}$ of food in contact with the film. This total migration value is lower than the amount of lactic acid present in a kilogram of yogurt (10 g/kg) or beef (9 g/kg) and it is less than the average dietary intake of lactic acid by infants. A related study of lactic acid migration can be found elsewhere.^[40] The amount of lactic acid and its derivatives that migrates to ethanol solutions from PLA polymers was much lower than any of the current average dietary lactic acid intake values reported by the Food and Drug Administration, the US Department of Agriculture, the European Community's Scientific Committee on Food and the Japanese Standards of Food Additives. PLA polymers can be considered safe for their intended use in fabricating articles for contact with food. Any intake of potential migrants from PLA other than lactic acid will be in very small amounts and these will hydrolyze to lactic acid.

Degradation of PLA

Biodegradation

PLA degrades primarily by hydrolysis, after several months exposure to moisture. Polylactide degradation occurs in two stages. First, random non-enzymatic chain scission of the ester groups leads to a reduction in molecular weight. This step can be accelerated by acids or bases and is affected by both temperature and moisture levels.^[23] Embrittlement of the polymers occurs in this step with a reduction of the molecular weight to around 40 900 Daltons. Second, low molecular weight PLA can diffuse out of the bulk polymer and be used by microorganisms, yielding carbon dioxide, water and humus.^[30]

In the first step, PLA degradability is driven by the hydrolysis and cleavage of the ester linkages in the polymer backbone (Scheme 6), which is autocatalyzed by the carboxylic acid end groups. The process follows first order kinetics.^[166]



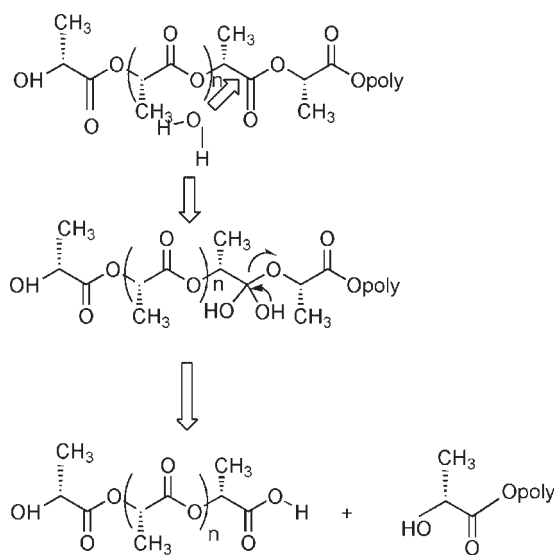
Scheme 5. Chemical structure of lactic acid and lactide, lactoyllactic acid and its trimer, adapted from Conn et al.^[40]

In the second step, the molecular weight is reduced until the lactic acid and low molecular weight oligomers are naturally metabolized by microorganisms to yield carbon dioxide and water (Figure 14).

Although the degradation process in PLA is a simple hydrolysis, the degradation rate can be affected by many factors due to the complexity of the solid-liquid reaction system. The polymer degradation rate is mainly determined by polymer reactivity with water and catalysts. Any factor which affects the reactivity and the accessibility, such as particle size and shape, temperature, moisture, crystallinity, % isomer, residual lactic acid concentration, molecular weight, molecular weight distribution, water diffusion and

metal impurities from the catalyst, will affect the polymer degradation rate.^[1,3,15,21,23,39,95,119–121,123,137,141,166–216] In general, high temperatures and humidity (50 to 60 °C) will cause PLA to degrade rapidly. For a detailed description of the degradation process, see Snook.^[30]

Tsuji and collaborators^[95,199,200] studied the hydrolysis of PLLA films at 37 °C in alkaline solution (pH 12)^[199] acid solution (pH 2.0)^[120] and phosphate-buffered solutions (pH 7.4).^[198] They reported that the hydrolysis of PLLA films proceeds mainly via a surface erosion mechanism in dilute alkaline solution^[199] and mainly via a bulk erosion mechanism in a phosphate-buffered solution.^[198] In acid solution, the hydrolysis of PLLA proceeds homogeneously along the film cross section mainly by the bulk erosion mechanism. The durability of PLLA films in an acid



Scheme 6. PLA hydrolysis and molecular weight loss.

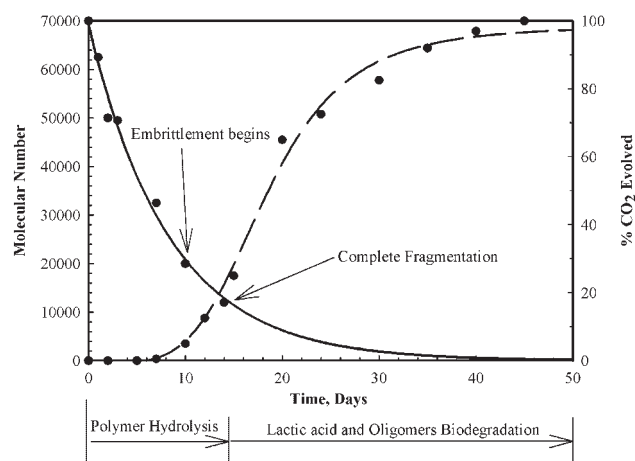


Figure 14. Biodegradation of PLA in 60 °C compost, adapted from Hartmann.^[39]

medium is similar to that in a neutral medium. The hydrolytic scission of PLLA chains occurs mainly in the amorphous area between the crystalline regions, irrespective of the hydrolysis medium. They also reported that the overall hydrolysis rate of PLLA films decreases with increasing initial crystallinity in alkaline solution and increases with increasing crystallinity in phosphate-buffered solution. High-temperature hydrolysis was studied by Tsuji et al.^[121] They found that the high temperature hydrolysis of PLLA films proceeds homogeneously along the film cross-section mainly via bulk erosion. PLLA hydrolysis at high temperature takes place mainly in the amorphous region.^[121] Tsuji and Ishida^[217] reported that enzymatic and alkaline hydrolyses are strong enough to enhance the practical surface hydrophilicity of the PLLA films because of their surface-erosion mechanisms. Gonzalez et al.^[201] also studied the *in vitro* degradation of PLA microspheres under humid environments at 37 °C. They found that the initial smooth-surface microspheres were transformed into porous particles during degradation at pH 7 and 37 °C, by a heterogeneous bulk degradation process, which accompanied a reduction in molecular weight and an increase in crystallinity. On the other hand, studies done with bulk PLLA^[31] showed that the hydrolysis proceeds in two modes – slow hydrolysis at the specimen surface and hydrolysis accelerated by formed and accumulated catalytic oligomers.

Composting studies were carried out by Weber^[183] by storing PLA samples in biodegradation chambers. As a result, they recommended that a maximum of 10% PLA be used in compost piles to prevent pH reduction of the pile. In addition, Gartiser et al.^[187] compared the anaerobic degradation of eight commercially available biodegradable polymers according to different standards and found that carbon dioxide is essential to the degradation process since it enhances the growth of various anaerobic bacteria.^[187]

Comparisons between laboratory and field exposure degradation have been done by Pometto and collaborators.^[189–191] They exposed PLA films in banana fields in Costa Rica and found that these PLA plastic films lost their mechanical properties faster than during exposure under simulated conditions in the laboratory.^[190] They also found that degradation of PLA is enhanced by an increase in temperature and relative humidity.^[191] Finally, they predicted that PLA with an initial molecular weight of 180 000 Daltons would be visibly degraded in around 6 months at between 29.6 °C and 23.4 °C and at a humidity of around 80%.^[189]

A comparative study of the degradation of PLA and starch-based materials was done by Gattin et al.^[218] They reported that the nature of the degradation strongly depends on the experimental conditions. A comparison between the earthworm-induced degradation of two lactic acid stereocopolymers, 50/50 and 96/4/L/D poly(L-lactic-co-D-lactic acid), was carried out by Alauzet et al.^[186] They found that high molar mass poly(lactic acid)s could be ingested by earthworms provided they were disintegrated first. How-

ever, the worms cannot bioassimilate the polymer before the hydrolytic degradation process is completed and reduced the polymer to oligomers.

PLA monolayer and PLA trilayer plastic films exposed to long wavelength UV (365 nm) at 55 °C and 10% RH for 8 weeks had an increase in the degradation rate compared to non-UV-treated samples. In addition, loss of physical properties was observed two weeks earlier than for the non-UV-treated samples.^[188] UV light has an enhancing effect on the degradation of PLA plastic films.

Studies with PLA blends have been carried out by a number of researchers,^[187,218,219] who found that the physical and morphologic properties of the blend play an important role its degradation.

The preparation and degradation of PLA nanocomposites was studied by Sinha Ray et al.^[193] They found that a PLA-layered silicate nanocomposite produced by simple melt extrusion was biodegradable and that nanocomposites enhance biodegradability. During the first month, both the extent of molecular weight reduction and weight loss were almost the same for PLA and PLACN4, where CN4 indicates the presence of 4% nanocomposite particles. After a month there was a sharp weight loss for PLACN4 compared to that of PLA. They attributed the enhanced biodegradation to the presence of the terminal hydroxylated edge groups on the silicate layers.^[193,220] The authors also attribute the enhancement in the biodegradability to the incorporation of organically modified synthetic fluorine mica.^[194]

Enzymatic

Enzymes such as proteinase K, pronase and bromelain have been used to bring about hydrolysis of polylactide *in vivo*. However, enzymes are large molecules and are unable to diffuse through the crystalline regions. As expected, little enzymatic degradation occurs at the beginning of the degradation process. Enzymatic involvement can produce pores and fragmentation, making more polymer regions accessible to the enzymes.

in vivo and *in vitro*

The *in vivo* and *in vitro* degradation have been evaluated for polylactide surgical implants. *In vitro* studies showed that the pH of the solution does play a role in the *in vitro* degradation and that an *in vitro* study can be used as a predictor of the *in vivo* degradation of PLA.^[196] Further studies of *in vitro* and *in vivo* degradation of PLA can be found elsewhere.^[3,6,9,11,13,177,182,196,197,211,214,221–226]

Burning

Burning of plastics materials with a high calorific value to obtain energy is an essential part of an overall waste

management scheme. Tight control of the burning plant is pursued to achieve efficient combustion of the polymers with low gas emissions to ensure that no toxic gases are released. Therefore, polymers which have low gas emissions are preferred. Upon incineration, PLA burns with a clean blue flame, without generating any poisonous or corrosive gases.^[137]

Recycling

Few studies regarding the recycling of PLA have been carried out. Both PLA and oriented PLA (oriented lactic acid) can be hydrolyzed with boiling water or steam to lactic acid, which can be recycled back to the monomer. This could lead to molecular recycling and would allow the recycling of both manufacturing plant materials and post-consumer packaging.^[137] Tsuji et al.^[195] showed that PLLA could be hydrolyzed at 180 °C to 350 °C for up to 30 min, obtaining L-lactic acid as the final product.

Release

Back in 1973, lactic acid and glycolic acid were proposed as degradable matrices for the sustained release of bioactive substances. PLA has many advantages for this purpose, which are that the polymeric matrix disappears innocuously, that degradation can be tailored by varying the copolymer composition and that controlled release devices are easily fabricated. Several publications^[227–230] have proposed different sustained-release devices, including pellets, microspheres, microcapsules and cylinders. Substance release is done via zero or first order kinetics, depending on design, diffusion or erosion and crystallinity. The release of the substance is complete in between one week to several months, depending on the copolymer composition and crystallinity, molecular weight, surface-to-volume ratio and the service environment. Recently, Ahola et al.^[228] investigated the release of ibuprofen from a PLA copolymer with ϵ -caprolactone. They found that the release of ibuprofen varied with the initial shape and load of the specimen, and that the release of this material followed Fickian diffusion. Also, release of leuprolide have been carried out from D-PLA and L-PLA.^[229] A linear release of leuprolide was obtained between day 6 and 25, with a continuous release for over 100 d. The molecular weight of PLA, and the D-PLA and L-PLA complex ratios have an effect on the release ratio.

Copolymers, Blends, Composites and Nano-Composites

Poly(lactide) blends are mixtures of different compositions of poly(L-lactide) and poly(D-lactide). Much research has been done in this area and nearly all commercially available PLAs are a blend of stereoisomers. In addition, poly(lactides) have

been blended with many different biodegradable polymers such as polymers obtained from glycolic acid,^[3,203,231–234] starch^[57] and ϵ -caprolactone.^[3,60,66,118,160,168,177,235–243]

Investigations with starch polymers have been carried out by many researchers.^[244] Park et al.^[245] reported that the glass transition temperature of both L-PLA and star-PLA/cornstarch composites remained almost unchanged although the crystallization was influenced. They found an increase in the crystallization rate and in the enthalpies of crystallization and melting for PLA with starch contents above 5%.^[245] Starch plays a role as a nucleating agent in PLA. Kim et al.^[246] showed that PLA is incompatible with starch granules. However, maleated PLA develops an interfacial adhesion with native corn starch.^[244] Martin and Averous^[150] reported better mechanical and physical properties with a different plasticizer than with thermoplastic starch, although they encouraged more research with starch due to its lower cost. The biodegradation of starch and PLA based materials was studied and it was found that temperature and relative humidity play a very important role in the degradation process.^[218] Wang et al.^[219] found that methylenediphenyl diisocyanate improves the interfacial interaction between PLA and granular starch. Ke and Sun^[247] added poly(vinyl alcohol), PVOH, to the starch due to its compatibility and then blended it with PLA. The final result was that the tensile strength of the starch/PLA blends increased as the PVOH concentration increased up to 40% and decreased as PVOH molecular weight increased.^[247] Both Wang^[219] and Ke^[247] found that gelatinized starch was responsible for an increase in tensile strength. Since gelatinized starch absorbs water, the tensile strength and the elongation of the blend decreased as the starch moisture content increased.^[219,247] Further studies of starch-PLA plastic foams indicated that the addition of PLA improved the mechanical properties of the foams and reduced their bulk densities and compressibilities.^[248] The blends with 40% PLA and 19% moisture produced a loose fill foam with the best physical characteristics and mechanical properties.^[248]

Polymers made from ϵ -caprolactone (CL) are excellent drug permeation products. However, mechanical and physical properties need to be enhanced by copolymerization or blending.^[243] Ibuprofen release from polymers made from ϵ -caprolactone has proved successful due to their excellent drug permeation properties.^[228] The addition of PLLA to CL decreased the number densities of spherulites in PLLA and PCL films.^[118] Moreover, the melting temperature of PLLA and PCL blends decreased by 3 and 0.5 °C, respectively.^[249] Liu et al.^[184] found that the degradation of PLA blends with poly(ϵ -caprolactone) was selective, which shows that the polymer blends exhibited well separated crystalline domains.

Blends of PLLA and poly(vinyl alcohol) were studied by Tsuji and Muramatsu.^[122] They showed that the tensile strength and Young's modulus decreased with increase in the composition of PLLA.

Blends of poly(ethylene glycol), PEG, and poly(lactic acid) showed an increase in the melting temperature of around 40 °C for the PLA.^[250] The molecular weight of the PEG affects the polymer morphology due to the enhanced crystallinity of the longer PEG chains.^[231]

Calcium phosphate composites with PLA showed an increase in the flexural modulus and yield strength.^[2] Poly(L-lactide)-clay blends made from a solvent-cast blend showed a poor dispersion of clay in the mix. However, the Young's modulus of the blend increased with a small amount of clay.^[251]

Poly(lactide)/layered silicate nanocomposites were investigated by Sinha Ray et al.^[193,194,220,252–254] They successfully prepared a series of biodegradable PLA nanocomposites using simple melt extrusion of PLA and organic modified layered silicate^[220] and they reported the mechanical, physical and rheological properties of the nanocomposites.

Finally, a number of researchers investigated the use of PLA blends and composites in comparison to commercial biodegradable polymers for medical applications. A detailed discussion of these investigations can be found elsewhere.^[3,9,16,32,70,124,170,173,202,215,231,233,234,238,255–284]

Current Applications of Polylactides

Polymers made of lactic acid achieved their first commercial success as fiber materials for resorbable sutures. After this, a number of different prosthetic devices were developed. PLA has been widely studied for use in medical applications because of its bioresorbability and biocompatible properties in the human body.^[1–6,8,11,12,14,16,32,54,196,224,225,260,285–288] Since PLA manufacturing processes are lowering its production costs,^[23,24] PLA may find use in different applications for a broad array of products.

The new Cargill Dow LLC polylactide plant in Blair, NB, USA, which was inaugurated in April, 2002 promises to help lower the cost and to encourage the use of PLA, bringing to the market 140 000 tons of PLA per year.^[289] The low-cost continuous process commercialized under the tradename of NatureworksTM guarantees the production of PLA for commercial applications.^[17] NatureworksTM polymers can be found in a variety of configurations (i.e. L-, D-, and *meso*-isomers) for a variety of applications.^[147] NatureworksTM functional properties include improved folding and sealing properties, high gloss and clarity, good grease resistance, low heat sealing temperature and approval for food contact.

Mitsui Chemical is conducting PLA business development under the commercial name of LACEA. LACEA polymers can be used for a variety of forming operations (i.e. injection molding, film forming, spinning, blow molding, foaming and blown film).^[18] These processing conditions can be used with different polymer resins and by controlling the resin temperature.

Economic studies show that PLA is an economically feasible material to use as a packaging polymer.^[24] However, due to its higher cost, the initial use of PLA as a packaging material has been in high value films, rigid thermoforms, food and beverage containers and coated papers. Two of the pioneer companies in using PLA as a packaging material were Dannon and McDonald's in Germany in yoghurt cups and cutlery, respectively.^[42,290] In the last five years, the use of PLA as a packaging material has increased all across Europe, Japan, and the USA, mainly in the area of fresh products where PLA is being used as a food packaging polymer for short shelf life products such as fruit and vegetables and package applications include containers, drinking cups, sundae and salad cups, overwrap and lamination films, and blister packages.^[42,43,45,289,291–296]

Currently, PLA is used in compostable yard bags^[297] to encourage recycling and composting programs. In addition, new applications such as fibers,^[22,77,113,298,299] textiles,^[298,300] foamed articles^[220,248,301] and paper coatings^[29] are being pursued. Commercial brands like Ingeo concentrate on commercializing fabrics made from polylactide polymers.^[298,302,303]

Commercially available PLA films and packages can provide better mechanical properties than polystyrene (PS) and have properties comparable to those of poly(ethylene terephthalate) (PET). The new, commercially available, PLA polymers promise to reduce the cost and to encourage the use of PLA.^[304] In the next ten years, PLA production and consumption is expected to increase substantially.^[24,43,44,291,305–307]

Perspectives

PLA polymers are becoming a cost-effective alternative to commodity petrochemical-based materials. The introduction of PLA will encourage the use and expansion of agricultural based materials. As the PLA price drops and new facilities produce higher volumes of PLA, new applications will be pursued. Although PLA is a relatively new polymer, it is possible to manipulate its physical, mechanical and barrier properties by changing its chemical composition, and varying its molecular characteristics. It is also possible to blend PLA with other polymers, making it a good biodegradable alternative for use in plastic packaging.

Acknowledgement: The authors thank Kraft Foods for partially supporting this project and Cargill Dow LLC for the polymer samples.

[1] H. Tsuji, K. Sumida, *J. Appl. Polym. Sci.* **2001**, 79, 1582.

[2] N. C. Bleach, K. E. Tanner, M. Kellomaki, P. Tormala, *J. Mater. Sci.: Mater. Med.* **2001**, 12, 911.

- [3] Y. Ikada, H. Tsuji, *Macromol. Rapid Commun.* **2000**, *21*, 117.
- [4] J. R. Dorgan, H. J. Lehermeier, L.-I. Palade, J. Cicero, *Macromol. Symp.* **2001**, *175*, 55.
- [5] H. J. Lehermeier, J. R. Dorgan, D. Way, *J. Membr. Sci.* **2001**, *190*, 243.
- [6] B. C. Benicewicz, P. K. Hopper, *J. Bioact. Comp. Polym.* **1995**, *5*, 453.
- [7] Aluminum Association, "Tokyo Steps up to Recycling Efforts", 1999, www.mmc.co.jp/english/environment/environment1999.pdf.
- [8] M. Vert, *Macromol. Symp.* **2000**, *153*, 333.
- [9] L. Zhang, C. Xiong, X. Deng, *J. Appl. Polym. Sci.* **1995**, *56*, 103.
- [10] M. Mochizuki, "Properties and Application of Aliphatic Polyester Products", in: *Biopolymers. Polyesters III. Applications and Commercial Products*, 1st edition, Y. Doi, A. Steinbüchel, Eds., Wiley-VCH Verlag GmbH, Weinheim 2002, p. 1–23.
- [11] H. Tsuji, "Polylactides", in: *Biopolymers. Polyesters III. Applications and Commercial Products*, 1st edition, Y. Doi, A. Steinbüchel, Eds., Wiley-VCH Verlag GmbH, Weinheim 2002, p. 129–177.
- [12] Y. Ikada, *Adv. Eng. Mater.* **1999**, *1*, 67.
- [13] E. A. R. Duek, C. A. C. Zavaglia, W. D. Belangero, *Polymer* **1999**, *40*, 6465.
- [14] A. G. A. Coombes, M. C. Meikle, *Clin. Mater.* **1994**, *17*, 35.
- [15] Y. Cha, C. G. Pitt, *Biomaterials* **1990**, *11*, 108.
- [16] T. Ouchi, Y. Ohya, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 453.
- [17] P. R. Gruber, M. O'Brien, "Polylactides. "NatureWorks™ PLA"", in: *Biopolymers. Polyesters III. Applications and Commercial Products*, 1st edition, Y. Doi, A. Steinbüchel, Eds., Wiley-VCH Verlag GmbH, Weinheim 2002, p. 235–250.
- [18] N. Kawahima, S. Ogawa, S. Obuchi, M. Matsuo, T. Yagi, "Polylactic acid "LACEA"", in: *Biopolymers. Polyesters III. Applications and Commercial Products*, 1st edition, Y. Doi, A. Steinbüchel, Eds., Wiley-VCH Verlag GmbH, Weinheim 2002, p. 251–274.
- [19] B. Eling, S. Gogolewski, A. J. Pennings, *Polymer* **1982**, *23*, 1587.
- [20] H. Tsuji, R. Smith, W. Bonfield, Y. Ikada, *J. Appl. Polym. Sci.* **2000**, *75*, 629.
- [21] L. Fambri, A. Pegoretti, R. Fenner, S. D. Incardona, C. Migliaresi, *Polymer* **1997**, *38*, 79.
- [22] K. E. Perepelkin, *Fibre Chem.* **2002**, *34*, 85.
- [23] R. E. Drumright, P. R. Gruber, D. E. Henton, *Adv. Mater.* **2000**, *12*, 1841.
- [24] R. Datta, S.-P. Tsai, P. Bonsignorea, S.-H. Moona, J. R. Frank, *FEMS Microbiol. Rev.* **1995**, *16*, 221.
- [25] S. J. Holland, B. J. Tighe, "Biodegradable Polymers", in: *Advances in Pharmaceutical Sciences*, 1st edition, Academic Press London, London 1992, p. 101–165.
- [26] V. Gewin, *PLoS Biol.* **2003**, *1*, 15.
- [27] D. J. Sawyer, *Macromol. Symp.* **2003**, *201*, 271.
- [28] J.-C. Bogaert, P. Coszach, *Macromol. Symp.* **2000**, *153*, 287.
- [29] N. Whiteman, "2000 Polymers, Laminations and Coatings Conference", Chicago, IL 2000, p. 631–635.
- [30] J. B. Snook, M.Sc. Thesis, Michigan State University, East Lansing 1994, p. 130.
- [31] C. Migliaresi, A. De Lollis, L. Fambri, D. Cohn, *Clin. Mater.* **1991**, *8*, 111.
- [32] M. Hiljanen-Vainio, P. Varpomaa, J. Seppala, P. Tormala, *Macromol. Chem. Phys.* **1996**, *197*, 1503.
- [33] G. Perego, G. D. Cella, C. Bastioli, *Polymer* **1996**, *59*, 37.
- [34] H. Cai, V. Dave, R. Gross, S. P. McCarthy, *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 2701.
- [35] H. Tsuji, Y. Ikada, *Macromol. Chem. Phys.* **1996**, *197*, 3483.
- [36] J.-R. Sarasua, R. E. Prud'homme, M. Wisniewski, A. Le Borgne, N. Spassky, *Macromolecules* **1998**, *31*, 3895.
- [37] H. Tsuji, Y. Ikada, *Polymer* **1995**, *36*, 2709.
- [38] T. Miyata, T. Masuko, *Polymer* **1998**, *39*, 5515.
- [39] M. H. Hartmann, N. Whiteman, "TAPPI Polymers, Laminations, & Coatings Conference", Chicago, IL, United States 2000, p. 467–474.
- [40] R. E. Conn, J. J. Kolstad, J. F. Borzelleca, D. S. Dixler, L. J. Filer, Jr., B. N. LaDu, M. W. Pariza, *Fd. Chem. Toxic* **1995**, *33*, 273.
- [41] R. D. Leaversuch, in: *Plastics Technology*, available at: <http://www.plasticstechnology.com/articles/200306bib2.html>. Access date 8/25/2003.
- [42] J. Baillie, *Packag. Week* **1997**, *13*.
- [43] N. Whiteman, "Packexpo", Chicago, IL November 6, 2002, p. 37–42.
- [44] M. O'Brien, "Ilip Launches New Fresh Food Packaging Solution", available at: <http://www.cargilldow.com/corporate/release.asp?id=110>. Access date 2/27/2003.
- [45] "NatureWorks™ PLA Makes North American Commercial Debut in Grocery Stores Taking a Fresh Approach to Deli Packaging", available at <http://www.cargilldow.com/corporate/release.asp>. Access date 10/6/2003.
- [46] G. B. Kharas, F. Sanchez-Riera, D. K. Severson. "Polymers of Lactic Acid", in: *Plastics from Microbes*, D. P. Mobley, Ed., Hanser Publishers, Munich 1994, p. 93–258.
- [47] H. R. Kricheldorf, I. Kreiser-Saunders, C. Jurgens, D. Wolter, *Macromol. Symp.* **1996**, *103*, 85.
- [48] US 5142023 (1992), invs.: P. R. Gruber, E. S. Hall, J. H. Kolstad, M. L. Iwen, R. D. Benson, R. L. Borchardt.
- [49] M. H. Hartmann, "High Molecular Weight Polylactic Acid Polymers", in: *Biopolymers from Renewable Resources*, 1st edition, D. L. Kaplan, Ed., Springer-Verlag Berlin Heidelberg, Berlin 1998, p. 367–411.
- [50] R. Dunsing, H. R. Kricheldorf, *Polym. Bull.* **1985**, *14*, 491.
- [51] J. W. Leenslag, A. J. Pennings, *Makromol. Chem.* **1987**, *188*, 1809.
- [52] S. H. Hyon, K. Jamshidi, Y. Ikada, *Biomaterials* **1997**, *18*, 1503.
- [53] Y. Zhao, Z. Wang, J. Wang, H. Mai, B. Yan, F. Yang, *J. Appl. Polym. Sci.* **2004**, *91*, 2143.
- [54] A. C. Albertsson, I. K. Varma, *Biomacromolecules* **2003**, *4*, 1466.
- [55] S. Jacobsen, H.-G. Fritz, P. Degee, P. Dubois, R. Jerome, *Ind. Crops Prod.* **2000**, *11*, 265.
- [56] H. R. Kricheldorf, I. Kreiser, *Makromol. Chem.* **1987**, *188*, 1861.
- [57] D. Garlotta, *J. Polym. Environ.* **2001**, *9*, 63.
- [58] H. R. Kricheldorf, I. Kreiser-Saunders, N. Scharnagl, *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 285.
- [59] G. L. Baker, M. R. Smith, T. Liu, C. P. Radano, C. Wang, M. Yin, Progress Reports 2000–2001, Michigan State University, Center for Fundamental Materials Research, East Lansing, MI, 2001, p. 23–25.
- [60] H. Tsuji, A. Mizuno, Y. Ikada, *J. Appl. Polym. Sci.* **2000**, *76*, 947.
- [61] F. E. Kohn, J. W. A. Van den Berg, G. Van de Ridder, J. Feijen, *J. Appl. Polym. Sci.* **1984**, *29*, 4265.
- [62] S. I. Moon, C. W. Lee, M. Miyamoto, Y. Kimura, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1673.

- [63] M. Wisniewski, A. Le Borgne, N. Spassky, *Macromol. Chem. Phys.* **1997**, *198*, 1227.
- [64] P. Degee, P. Dubois, R. Jerome, *Macromol. Chem. Phys.* **1997**, *198*, 1985.
- [65] B. Atthof, M. Trollsas, H. Claesson, J. L. Hedrick, *Macromol. Chem. Phys.* **1999**, *200*, 1333.
- [66] C. X. Song, X. D. Feng, *Macromolecules* **1984**, *17*, 2764.
- [67] T. Serizawa, H. Yamashita, T. Fujiwara, Y. Kimura, M. Akashi, *Macromolecules* **2001**, *34*, 1996.
- [68] Y. Ohya, S. Maruhashi, T. Ouchi, *Macromolecules* **1998**, *31*, 4662.
- [69] J. Kasperczyk, *Macromolecules* **1995**, *28*, 3937.
- [70] Y. Hori, Y. Takahashi, A. Yamaguchi, T. Nishishita, *Macromolecules* **1993**, *26*, 4388.
- [71] S. J. de Jong, S. C. De Smedt, M. W. C. Wahls, J. Demeester, J. J. Kettenes-van den Bosch, W. E. Hennink, *Macromolecules* **2000**, *33*, 3680.
- [72] S. J. de Jong, W. N. E. van Dijk-Wolthuis, J. J. Kettenes-van den Bosch, P. J. W. Schuyl, W. E. Hennink, *Macromolecules* **1998**, *31*, 6397.
- [73] S. Brochu, R. E. Prud'homme, I. Barakat, R. Jerome, *Macromolecules* **1995**, *28*, 5230.
- [74] D. Brizzolara, H. J. Cantow, K. Diederichs, E. Keller, A. J. Domb, *Macromolecules* **1996**, *29*, 191.
- [75] H. Tsuji, Y. Ikada, *Polymer* **1999**, *40*, 6699.
- [76] D. R. Witzke, Ph.D. Thesis, Michigan State University, East Lansing, MI 1997, p. 389.
- [77] W. Hoogsten, A. R. Postema, A. J. Pennings, G. t. Brinke, P. Zugenmair, *Macromolecules* **1990**, *23*, 634.
- [78] S. Sasaki, T. Asakura, *Macromolecules* **2003**, *36*, 8385.
- [79] J. Puiggali, Y. Ikada, H. Tsuji, L. Cartier, T. Okihara, B. Lotz, *Polymer* **2000**, *41*, 8921.
- [80] L. Cartier, T. Okihara, Y. Ikada, H. Tsuji, J. Puiggali, B. Lotz, *Polymer* **2000**, *41*, 8909.
- [81] P. De Santis, A. J. Kovacs, *Biopolymer* **1968**, *6*, 299.
- [82] J. Kobayashi, T. Asahi, M. Ichiki, A. Oikawa, H. Suzuki, H. Watanabe, E. Fukada, Y. Shikinami, *J. Appl. Phys.* **1995**, *77*, 2957.
- [83] T. Okihara, M. Tsuji, A. Kawaguchi, K. Katayama, H. Tsuji, S. H. Hyon, Y. Ikada, *J. Macromol. Sci., Phys.* **1991**, *B30*, 119.
- [84] M. T. Zell, B. E. Padden, A. J. Paterick, K. A. M. Thakur, R. T. Kean, M. A. Hillmyer, E. J. Munson, *Macromolecules* **2002**, *35*, 7700.
- [85] K. A. M. Thakur, R. T. Kean, J. M. Zupfer, N. U. Buehler, M. A. Doscoth, E. J. Munson, *Macromolecules* **1996**, *29*, 8844.
- [86] J. Kasperczyk, *Polymer* **1996**, *37*, 201.
- [87] M. Spinu, C. Jackson, M. Y. Keating, K. H. Gardner, *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 1497.
- [88] E. W. Fischer, H. J. Sterzel, G. Wegner, *Kolloid-Z. Z. Polym.* **1973**, *251*, 980.
- [89] R. Vasanthakumari, A. J. Pennings, *Polymer* **1981**, *22*, 862.
- [90] R. Vasanthakumari, *Polymer* **1981**, *22*, 862.
- [91] B. Kalb, A. J. Pennings, *Polymer* **1980**, *21*, 607.
- [92] H. Tsuji, Y. Ikada, *Macromolecules* **1993**, *26*, 6918.
- [93] R. Vasanthakumari, A. J. Pennings, *Polymer* **1983**, *24*, 175.
- [94] J. J. Kolstad, *J. Appl. Polym. Sci.* **1996**, *62*, 1079.
- [95] H. Tsuji, Y. Ikada, *Polymer* **1995**, *36*, 2709.
- [96] S. C. Schmidt, M. A. Hillmyer, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 300.
- [97] H. Tsuji, Y. Ikada, *Polymer* **1996**, *37*, 595.
- [98] S. Baratian, E. S. Hall, J. S. Lin, R. Xu, J. Runt, *Macromolecules* **2001**, *34*, 4857.
- [99] J. Huang, J. Buehler, E. Hall, R. Kean, J. J. Kolstad, L. Wu, J. Runt, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37*, 370.
- [100] Y. Ikada, K. Jamshidi, H. Tsuji, S. H. Hyon, *Macromolecules* **1987**, *20*, 904.
- [101] P. Rappard, *Packag. Rev. S. Afr.* **1997**, *23*, 19.
- [102] K.-H. Nelson, W.-M. Cathcart, *J. Food Prot.* **1984**, *47*, 346.
- [103] K. T. H. Farrer, *Packag. News* **1983**.
- [104] M. C. Erickson, *Int. J. Dairy Technol.* **1997**, *50*, 107.
- [105] W. L. Dunkley, R. M. Pangborn, J. D. Franklin, *Milk Dealer* **1963**, *52*, 52.
- [106] R. L. Bradley, Jr., *J. Food Prot.* **1980**, *43*, 314.
- [107] M. Moehrle, M. Soballa, M. Korn, *Photodermatol. Photoimmunol. Photomed.* **2003**, *19*, 175.
- [108] R. Auras, Ph.D. Thesis, Michigan State University, East Lansing 2004, p. 268.
- [109] ASTM-D1746-03, Standard Test Method for Transparency of Plastic Sheet 8.01, p. 398–401.
- [110] ASTM-D6290-98e1, Standard Test Method for Color Determination of Plastic Pellets 8.03, p. 892–896.
- [111] DIN-6176, 2001–03, Colorimetric calculation of color differences with the DIN 99 Formula.
- [112] D. W. VanKrevelen, “*Properties of Polymers*”, Elsevier Science B.V., Amsterdam, The Netherlands 1997.
- [113] H. Tsuji, Y. Ikada, S. H. Hyon, Y. Kimura, T. Kitao, *J. Appl. Polym. Sci.* **1994**, *51*, 337.
- [114] G. Kister, G. Cassanas, M. Vert, *Polymer* **1998**, *39*, 267.
- [115] G. Kister, G. Cassanas, M. Vert, B. Pauvert, A. Terol, *J. Raman Spectrosc.* **1995**, *26*, 307.
- [116] K. Jamshidi, S. H. Hyon, Y. Ikada, *Polymer* **1988**, *29*, 2229.
- [117] A. Celli, M. Scandola, *Polymer* **1992**, *33*, 2699.
- [118] H. Tsuji, T. Yamada, M. Suzuki, S. Itsuno, *Polym. Int.* **2003**, *52*, 269.
- [119] H. Tsuji, H. Ishida, *J. Appl. Polym. Sci.* **2003**, *87*, 1628.
- [120] H. Tsuji, K. Nakahara, *J. Appl. Polym. Sci.* **2001**, *86*, 186.
- [121] H. Tsuji, K. Nakahara, K. Ikarashi, *Macromol. Mater. Eng.* **2001**, *286*, 398.
- [122] H. Tsuji, H. Muramatsu, *J. Appl. Polym. Sci.* **2001**, *81*, 2151.
- [123] T. Iwata, Y. Doi, *Macromolecules* **1998**, *31*, 2461.
- [124] C. G. Pitt, J. S. Wang, S. S. Shah, R. Sik, C. F. Chignell, *Macromolecules* **1993**, *26*, 2159.
- [125] S. Iannace, L. Nicolais, *J. Appl. Polym. Sci.* **1996**, *64*, 911.
- [126] R. J. M. Zwiers, S. Gogolewski, A. J. Pennings, *Polymer* **1983**, *24*, 167.
- [127] X. Ou, M. Cakmak, *ANTEC 2003*, Nashville, TN 2003, p. 1701–1705.
- [128] M. Yasuniwa, S. Tsubakihara, Y. Sugimoto, C. Nakafuku, *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 23.
- [129] E. Urbanovici, H. A. Schneider, H. J. Cantow, *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 359.
- [130] K. Kishore, R. Vasanthakumari, A. J. Pennings, *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 537.
- [131] T. Miyata, T. Masuko, *Polymer* **1997**, *38*, 4003.
- [132] K. Kishore, R. Vasanthakumari, *Colloid Polym. Sci.* **1988**, *266*, 999.
- [133] C. Marega, A. Marigo, V. Di Noto, R. Zannetti, A. Martorana, G. Paganetto, *Makromol. Chem.* **1992**, *193*, 1599.
- [134] ASTM-D2578-94. 94, Standard Test Method for Wetting Tension of Polyethylene and Polypropylene Films, 8.02, p. 67–69.
- [135] A. Launay, F. Thominet, J. Verdu, *J. Appl. Polym. Sci.* **1999**, *73*, 1131.

- [136] A. Schindler, D. Harper, *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2593.
- [137] R. G. Sinclair, *Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 585.
- [138] J. Huang, M. S. Lisowski, J. Runt, E. Hall, R. Kean, N. U. Buehler, J. S. Lin, *Macromolecules* **1998**, *31*, 2593.
- [139] Y. Doi, K. Fukuda, in: "Biodegradable Plastics and Polymers: Proceedings of the Third International Scientific Workshop on Biodegradable Plastics and Polymers, Osaka, Japan (Studies in Polymer Science, 12)", Y. Doi, K. Fukuda, Eds., Elsevier Science, New York 1994, p. 464–469.
- [140] J. A. P. P. Van Dijk, J. A. Smit, F. E. Kohn, J. Feijen, *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 197.
- [141] M. C. Gupta, V. G. Deshmukh, *Colloid Polym. Sci.* **1982**, *260*, 514.
- [142] K. Xu, A. Kozluca, E. B. Denkbass, E. Piskin, *J. Appl. Polym. Sci.* **1996**, *59*, 561.
- [143] Q. Fang, M. A. Hanna, *Ind. Crops Prod.* **1999**, *10*, 47.
- [144] J. R. Dorgan, J. Randal, J. Janzen, D. Knauss, B. Braun, P. Gruber, "Global Plastics Environmental Conference 2004", Detroit, MI February 18–19 2004.
- [145] J. J. Cooper-White, M. E. Mackay, *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1803.
- [146] J. R. Dorgan, J. S. Williams, *J. Rheol.* **1999**, *43*, 1141.
- [147] Cargill-Dow-LLC. "PLA Polymer 4042D – A Nature-Works Product. Biaxially Oriented Films – General Purpose", available at: www.cargilldow.com/corporate/pdf/4042.pdf. Access date 01/08/03.
- [148] C. Migliaresi, D. Cohn, A. De Lollis, L. Fambri, *J. Appl. Polym. Sci.* **1991**, *43*, 83.
- [149] K. Bechtold, M. A. Hillmyer, W. B. Tolman, *Macromolecules* **2001**, *34*, 8641.
- [150] O. Martin, L. Averous, *Polymer* **2001**, *42*, 6209.
- [151] D. M. Bigg, "Annual Technical Conference – Society of Plastics Engineers", 1996, p. 2028–2039.
- [152] A. F. M. Barton, "Handbook of Solubility Parameters and Other Cohesion Parameters", CRC LLC 1999.
- [153] C. M. Hansen, K. Skaarup, *J. Paint Technol.* **1967**, *39*, 511.
- [154] G. Rocha, R. Gross, S. McCarthy, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 454.
- [155] C. M. Hansen, "Hansen Solubility Parameters: A User's Handbook", CRC Press LLC, New York 1999.
- [156] S. Pauly, "Permeability and Diffusion Data", in: *Polymer Handbook*, J. I. Brandup, E. H. Grulke, Eds., John Wiley & Sons Inc., New York 1999, p. 547.
- [157] R. Auras, B. Harte, S. Selke, *J. Appl. Polym. Sci.* **2004**, *92*, 1790.
- [158] R. Auras, B. Harte, S. Selke, R. Hernandez, *J. Plast. Film Sheet.* **2003**, *19*, 123.
- [159] R. Shogren, *J. Environ. Polym. Degrad.* **1997**, *5*, 91.
- [160] G. L. Siparsky, K. J. Voorhees, J. R. Dorgan, K. J. Schilling, *J. Environ. Polym. Degrad.* **1997**, *5*, 125.
- [161] J.-S. Yoon, H.-W. Jung, M.-N. Kim, E.-S. Park, *J. Appl. Polym. Sci.* **2000**, *77*, 1716.
- [162] G. L. Siparsky, K. J. Voorhees, J. R. Dorgan, K. J. Schilling, *J. Environ. Polym. Degrad.* **1997**, *5*, 125.
- [163] A. Polyakova, D. M. Connor, D. M. Collard, D. A. Schiraldi, A. Hiltnerand, E. Baer, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1900.
- [164] A. Polyakova, R. Y. F. Liu, D. A. Schiraldi, A. Hiltnerand, E. Baer, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1889.
- [165] N. Whiteman, P. DeLassus, J. Gunderson, "Polymers Laminations & Coatings Conference Proceeding, Polyolefins 2002, International Conference on Polyolefins", Houston, Texas, USA February 24–27, 2002.
- [166] X. Zhang, U. P. Wyss, D. Pichora, M. F. A. Goosen, *J. Bioact. Comp. Polym.* **1994**, *9*, 80.
- [167] I. Grizzi, H. Garreau, S. Li, M. Vert, *Biomaterials* **1995**, *16*, 305.
- [168] Z. Gan, D. Yu, Z. Zhong, Q. Liangand, X. Jing, *Polymer* **1999**, *40*, 2859.
- [169] H. Tsuji, S. Miyauchi, *Polym. Degrad. Stab.* **2001**, *71*, 415.
- [170] A. M. Gajria, V. Dave, R. Gross, S. P. McCarthy, *Polymer* **1996**, *37*, 437.
- [171] H. Tsuji, S. Miyauchi, *Polymer* **2001**, *42*, 4463.
- [172] S. Li, S. McCarthy, *Macromolecules* **1999**, *32*, 4454.
- [173] N. Koyama, Y. Doi, *Macromolecules* **1996**, *29*, 5843.
- [174] R. T. MacDonald, S. P. McCarthy, R. Gross, *Macromolecules* **1996**, *29*, 7356.
- [175] D. Mallarde, M. Valiere, C. David, M. Menet, P. Guerin, *Polymer* **1998**, *39*, 3387.
- [176] M. S. Reeve, S. P. McCarthy, M. J. Downey, R. Gross, *Macromolecules* **1994**, *27*, 825.
- [177] M. F. Meek, K. Jansen, R. Steendam, W. van Oeveren, P. B. van Wachem, M. J. A. van Luyn, *J. Biomed. Mater. Res., Part A* **2003**, *68A*, 43.
- [178] Y. Kumagai, Y. Kanesawa, Y. Doi, *Makromol. Chem.* **1992**, *193*, 53.
- [179] Y. Ohya, S. Maruhashi, T. Ouchi, *Macromol. Chem. Phys.* **1998**, *199*, 2017.
- [180] S. H. Hyon, K. Jamshidi, Y. Ikada, *Polym. Int.* **1998**, *46*, 196.
- [181] A. Torres, S. M. Li, S. Roussos, M. Vert, *J. Appl. Polym. Sci.* **1996**, *62*, 2295.
- [182] D. K. Gilding, A. M. Reed, *Polymer* **1979**, *20*, 1459.
- [183] R. Weber, "Industrial Agricultural Products Center", available at: <http://agproducts.unl.edu/compost.htm>. Access date 08/10/2003.
- [184] L. Liu, S. Li, H. Garreau, M. Vert, *Biomacromolecules* **2000**, *1*, 350.
- [185] M. Kanchanasopa, E. Manias, J. Runt, *Biomacromolecules* **2003**, *4*, 1203.
- [186] N. Alauzet, H. Garreau, M. Bouche, M. Vert, *J. Polym. Environ.* **2002**, *10*, 53.
- [187] S. Gattiser, M. Wallrabenstein, G. Stiene, *J. Environ. Polym. Degrad.* **1998**, *6*, 159.
- [188] G. H. Kai-Lai, A. L. Pometto III, *J. Environ. Polym. Degrad.* **1999**, *7*, 93.
- [189] G. H. Kai-Lai, A. L. Pometto III, A. Gadea-Rivas, J. A. Briceño, A. Rojas, *J. Environ. Polym. Degrad.* **1999**, *7*, 173.
- [190] G. H. Kai-Lai, A. L. Pometto III, P. N. Hinz, A. Gadea-Rivas, J. A. Briceño, A. Rojas, *J. Environ. Polym. Degrad.* **1999**, *7*, 167.
- [191] G. H. Kai-Lai, A. L. Pometto III, P. N. Hinz, *J. Environ. Polym. Degrad.* **1999**, *7*, 83.
- [192] R. Gattin, A. Copinet, C. Bertrand, Y. Couturier, *J. Polym. Environ.* **2001**, *9*, 11.
- [193] S. Sinha Ray, Y. Kazunobu, M. Okamoto, K. Ueda, *Polymer* **2003**, *44*, 857.
- [194] S. Sinha Ray, K. Yamada, M. Okamoto, A. Ogami, K. Ueda, *Chem. Mater.* **2003**, *15*, 1456.
- [195] H. Tsuji, H. Daimon, K. Fujie, *Biomacromolecules* **2003**, *4*, 835.
- [196] P. Mainil-Varlet, R. Curtis, S. Gogolewski, *J. Biomed. Mater. Res.* **1997**, *36*, 360.
- [197] L. E. Claes, *Clinical Materials* **1992**, *10*, 41.
- [198] H. Tsuji, Y. Ikada, *Polym. Degrad. Stab.* **2000**, *67*, 179.

- [199] H. Tsuji, Y. Ikada, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, 36, 59.
- [200] H. Tsuji, A. Mizuno, Y. Ikada, *J. Appl. Polym. Sci.* **2000**, 77, 1452.
- [201] M. F. Gonzalez, R. A. Ruseckaite, T. R. Cuadrado, *J. Appl. Polym. Sci.* **1999**, 71, 1223.
- [202] R. F. Storey, T. P. Hickey, *Polymer* **1994**, 35, 830.
- [203] A. M. Reed, D. K. Gilding, *Polymer* **1981**, 22, 494.
- [204] D. Cam, S. H. Hyon, Y. Ikada, *Biomaterials* **1995**, 16, 833.
- [205] A. Gopferich, "Mechanisms of Polymer Degradation and Elimination", in: *Handbook of Biodegradable Polymers*, A. J. Domb, J. Kost, D. M. Wiseman, Eds., Hardwood Academic Publishers, Amsterdam 1997, p. 451–471.
- [206] S. Karjomaa, T. Suortti, R. Lempiainen, J. F. Selin, M. Itavaara, *Polym. Degrad. Stab.* **1998**, 59, 333.
- [207] H. Pistner, H. Stallforth, R. Gutwald, J. Muhling, J. F. Reuther, C. Michel, *Biomaterials* **1994**, 15, 439.
- [208] S. Li, M. Tenon, H. Garreau, C. Braud, M. Vert, *Polym. Degrad. Stab.* **2000**, 67, 85.
- [209] H. A. von Recum, R. L. Cleek, S. G. Eskin, A. G. Mikos, *Biomaterials* **1995**, 16, 441.
- [210] S. Li, M. McCarthy, *Biomaterials* **1999**, 20, 35.
- [211] Y. Cha, C. G. Pitt, *Biomaterials* **1990**, 11, 108.
- [212] H. Pistner, D. R. Bendix, J. Muhling, J. F. Reuther, *Biomaterials* **1993**, 14, 291.
- [213] K.-L. G. Ho, A. L. Pometto III, *J. Environ. Polym. Degrad.* **1999**, 7, 101.
- [214] G. E. Karlsson, A. C. Albertsson, *Macromol. Symp.* **1998**, 127, 219.
- [215] P. Tormala, *Clin. Mater.* **1992**, 10, 29.
- [216] S. Kamei, Y. Inoue, H. Okada, M. Yamada, Y. Ogawa, H. Toguchi, *Biomaterials* **1992**, 13, 953.
- [217] H. Tsuji, T. Ishida, *J. Appl. Polym. Sci.* **2003**, 87, 1628.
- [218] R. Gattin, A. Copinet, C. Bertrand, Y. Couturier, *J. Polym. Environ.* **2001**, 9, 11.
- [219] H. Wang, X. Sun, P. Seib, *J. Polym. Environ.* **2002**, 10, 133.
- [220] S. Sinha Ray, M. Okamoto, *Macromol. Rapid Commun.* **2003**, 24, 815.
- [221] B. C. Benicewicz, P. K. Hopper, *J. Bioact. Comp. Polym.* **1991**, 6, 65.
- [222] Q. Cai, J. Bei, S. Wang, *Polym. Adv. Technol.* **2002**, 13, 534.
- [223] M. Asano, H. Fukuzaki, M. Yoshida, M. Kumakura, T. Mashino, H. Yuasa, K. Imai, H. Yamanaka, U. Kawaharada, K. Suzuki, *Int. J. Pharm.* **1991**, 67, 67.
- [224] A. G. A. Coombes, J. D. Heckman, *Biomaterials* **1992**, 13, 297.
- [225] H. Tsuji, *Polymer* **2000**, 41, 3621.
- [226] P. Van De Witte, J. W. A. Van den Berg, J. Feijen, J. L. Reeve, A. J. Mchugh, *J. Appl. Polym. Sci.* **1996**, 61, 685.
- [227] R. G. Sinclair, "The First Corn Utilization Conference", St. Louis, Missouri June 11–12, 1987, p. 1–16.
- [228] N. Ahola, J. Rich, T. Karjalainen, J. Seppala, *J. Appl. Polym. Sci.* **2003**, 88, 1279.
- [229] J. Slager, A. J. Domb, *Biomacromolecules* **2003**, 4, 1308.
- [230] J. Slager, A. J. Domb, *Biomacromolecules* **2003**, 4, 1316.
- [231] H. Younes, D. Cohn, *Eur. Polym. J.* **1988**, 24, 765.
- [232] D. K. Gilding, A. M. Reed, *Polymer* **1979**, 20, 1459.
- [233] S. E. M. Ibim, A. M. A. Ambrosio, M. S. Kwon, S. F. El-Amin, H. Allcock, C. T. Laurecin, *Biomaterials* **1997**, 18, 1565.
- [234] J.-S. Yoon, W.-S. Lee, K.-S. Kim, I.-J. Chin, M.-N. Kim, C. Kim, *Eur. Polym. J.* **2000**, 36, 435.
- [235] M. Stolt, M. Viljanmaa, A. Sodergard, P. Tormala, *J. Appl. Polym. Sci.* **2003**, 91, 196.
- [236] H. Tsuji, A. Mizuno, Y. Ikada, *J. Appl. Polym. Sci.* **1998**, 70, 2259.
- [237] C.-H. Kim, K. Y. Cho, E.-J. Choi, J.-K. Park, *J. Appl. Polym. Sci.* **2000**, 77, 226.
- [238] Y. Shen, K. J. Zhu, Z. Shen, K.-M. Yao, *J. Polym. Sci., Part A: Polym. Chem.* **1996**, 34, 1799.
- [239] E. J. Choi, J. K. Park, H. N. Chang, *J. Polym. Sci., Part B: Polym. Phys.* **1994**, 32, 2481.
- [240] C. J. Meredith, E. J. Amis, *Macromol. Chem. Phys.* **2000**, 201, 733.
- [241] S. Aslan, L. Calandrelli, P. Laurienzo, M. Malinconico, C. Migliaresi, *J. Mater. Sci.* **2000**, 35, 1615.
- [242] A. J. Nijenhuis, D. W. Grijpma, A. J. Pennings, *Polymer* **1996**, 37, 2783.
- [243] S. Wang, H. Nishide, E. Tsuchida, *Polym. Adv. Technol.* **1999**, 10, 282.
- [244] D. Carlson, L. Nie, R. Narayan, P. Dubois, *J. Appl. Polym. Sci.* **1999**, 72, 477.
- [245] J. W. Park, D. J. Lee, E. Sang Yoo, S. Soon Im, S. H. Kim, Y. H. Kim, *Korea Polym. J.* **1999**, 7, 93.
- [246] H. S. Kim, I.-J. Chin, J.-S. Yoon, S. H. Kim, J.-S. Jung, *Korea Polym. J.* **1998**, 6, 422.
- [247] T. Ke, S. X. Sun, *J. Polym. Environ.* **2003**, 11, 7.
- [248] Q. Fang, M. A. Hanna, *Cereal Chem.* **2000**, 77, 779.
- [249] H. Tsuji, Y. Ikada, *J. Appl. Polym. Sci.* **1998**, 67, 405.
- [250] W. M. Stevels, M. J. K. Ankone, P. J. Dijkstra, J. Feijen, *Macromol. Chem. Phys.* **1995**, 196, 3687.
- [251] N. Ogata, G. Jimenez, H. Kawai, T. Ogihara, *J. Polym. Sci., Part B: Polym. Phys.* **1997**, 35, 389.
- [252] S. Sinha Ray, M. Okamoto, *Macromol. Mater. Eng.* **2003**, 288, 936.
- [253] S. Sinha Ray, K. Okamoto, K. Yamada, M. Okamoto, *NanoLetters* **2002**, 2, 423.
- [254] S. Sinha Ray, P. Maiti, M. Okamoto, K. Yamada, K. Ueda, *Macromolecules* **2002**, 35, 3104.
- [255] D. W. Grijpma, E. Kroeze, A. J. Nijenhuis, A. J. Pennings, *Polymer* **1993**, 34, 1496.
- [256] D. W. Grijpma, R. D. A. Van Hofslot, H. Super, A. J. Nijenhuis, A. J. Pennings, *Polym. Eng. Sci.* **1994**, 34, 1674.
- [257] Y. Kimura, Y. Matsuzaki, H. Yamame, T. Kitao, *Polymer* **1989**, 30, 1342.
- [258] S. Higashi, T. Yamamuro, T. Nakamura, Y. Ikada, S. H. Hyon, K. Jamshidi, *Biomaterials* **1986**, 7, 183.
- [259] D. Brizzolaro, H. J. Cantow, R. Mulhaupt, A. J. Domb, *J. Comput.-Aided Mater. Des.* **1996**, 3, 341.
- [260] S.-h. Hsu, W.-C. Chen, *Biomaterials* **2000**, 21, 359.
- [261] A. Breitenbach, T. Kissel, *Polymer* **1998**, 39, 3261.
- [262] I. Arvanitoyannis, A. Nakayama, E. Psomiadou, N. Kawasaki, N. Yamamoto, *Polymer* **1996**, 37, 651.
- [263] J. L. Eguiburu, M. J. Fernandez-Berridi, J. San Roman, *Polymer* **1996**, 37, 3615.
- [264] Y. Li, J. Nothnagel, T. Kissel, *Polymer* **1997**, 38, 6197.
- [265] K. Stridsberg, A. C. Albertsson, *Polymer* **2000**, 41, 7321.
- [266] A. J. Nijenhuis, E. Colstee, D. W. Grijpma, A. J. Pennings, *Polymer* **1996**, 37, 5849.
- [267] H. Tsuji, Y. Ikada, *Polymer* **1996**, 37, 595.
- [268] Z. G. Wang, B. S. Hsiao, X. H. Zong, F. Yeh, J. J. Zhou, E. Dormier, D. D. Jamiolkowski, *Polymer* **2000**, 41, 621.
- [269] L. Zhang, C. Xiong, X. Deng, *Polymer* **1996**, 37, 235.
- [270] Y. Li, C. Volland, T. Kissel, *Polymer* **1998**, 39, 3087.
- [271] E. Blumm, A. J. Owen, *Polymer* **1995**, 21, 4077.
- [272] M. C. Davies, K. M. Shakesheff, A. G. Shard, A. J. Domb, C. J. Roberts, S. J. B. Tendler, P. M. Williams, *Macromolecules* **1996**, 29, 2205.

- [273] C. Howe, N. Vasanthan, C. MacClamrock, S. Sankar, I. D. Shin, I. K. Simonsen, A. E. Tonelli, *Macromolecules* **1994**, 27, 7433.
- [274] T. G. Park, S. Cohen, R. Langer, *Macromolecules* **1992**, 25, 116.
- [275] T. Yamaoka, Y. Takahashi, T. Ohta, M. Miyamoto, A. Murakami, Y. Kimura, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, 37, 1513.
- [276] S. Iannace, L. Ambrosio, S. J. Huang, L. Nicolais, *J. Appl. Polym. Sci.* **1994**, 54, 1525.
- [277] H. Tsuji, Y. Ikada, *J. Appl. Polym. Sci.* **1997**, 63, 855.
- [278] H. Tsuji, Y. Ikada, *J. Appl. Polym. Sci.* **1994**, 53, 1061.
- [279] M. Shibata, K. Ozawa, N. Teramoto, R. Yosomiya, H. Takeishi, *Macromol. Mater. Eng.* **2003**, 288, 35.
- [280] S. Farmaceutico, "Lactide/Glycolide Copolymers: Review on Toxicity, Biocompatibility, and Clinical Application (data up to 1999)", available at: <http://www.ghimas.it/dentale/documenti/inglese/Lactide-glycolide.PDF>. Access date 10/21/2003.
- [281] A. S. Zalusky, R. Olayo-Valles, J. H. Wolf, M. A. Hillmyer, *J. Am. Chem. Soc.* **2002**, 124, 12761.
- [282] S. Schmidt, M. A. Hillmyer, *J. Polym. Sci., Part B: Polym. Phys.* **2002**, 40, 2364.
- [283] K. S. Anderson, S. H. Lim, M. A. Hillmyer, *J. Appl. Polym. Sci.* **2003**, 89, 3757.
- [284] F. Yao, W. Chen, H. Wang, H. Liu, K. Yao, P. Sun, H. Lin, *Polymer* **2003**, 44, 6435.
- [285] C. Chaput, E. A. DesRosiers, M. Assad, M. Brochu, L. H. Yahia, A. Selmani, C.-H. Rivard, "Processing Biodegradable Natural Polyesters for Porous Soft-Materials", in: *Advances in Materials Science and Implant Orthopedic Surgery*, R. Kossowski and N. Kossowski, Eds., Kluwer Academic Publishers, Dordrecht 1995.
- [286] M. H. Hartmann, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, 40, 570.
- [287] K. Whang, C. H. Thomas, K. E. Healy, G. Nuber, *Polymer* **1995**, 36, 837.
- [288] R. A. Zoppi, S. Contant, E. A. R. Duek, F. R. Marques, M. L. F. Wada, S. P. Nunes, *Polymer* **1999**, 40, 3275.
- [289] M. O'Brien, J. Paxinos, "Cargill Dow's World-scale Manufacturing Facility Comes On Line", available at: <http://www.cargilldow.com/corporate/release.asp?id=94>. Access date 8/25/2003.
- [290] Anonymous, "Cargill Dow to Start up Giant PLA Plant", *Modern Plastic*, February, 2000.
- [291] M. O'Brien, "Biopolymer Industry Moves from Field of Dreams to Reality: Consumer Products Hitting Retail Shelves Across the Globe", available at: <http://www.cargilldow.com/corporate/release.asp?id=111>. Access date 2/27/2003.
- [292] M. O'Brien, "First North American Converter Takes Aim at Grocery Industry with NatureWorks™ PLA", available at: www.cargilldow.com/corporate/release.asp. Access date 4/23/2003.
- [293] M. O'Brien, "Unifi and Cargill Dow Provide Update on NatureWorks™ PLA Development", PR Newswire, June 2001, p. 2.
- [294] "Faerch Plast to Market Food Packaging from Nature", available at: <http://www.cargilldow.com/corporate/release.asp>. Access date 10/6/2003.
- [295] "NatureWorks™ PLA Makes North American Commercial Debut in Grocery Stores Taking a Fresh Approach to Deli Packaging", available at: <http://www.cargilldow.com/corporate/release.asp>. Access date 10/6/2003.
- [296] NatureWorks™ PLA, "Top It Off With NatureWorks™ PLA. Dairy and Delicatessen Container Lidding Solutions", available at: <http://www.cargilldow.com/corporate/release.asp>. Access date 10/6/2003.
- [297] Compostable Yard Bag, *BioCycle*, October 1996.
- [298] "Kanebo Corn Fiber", available at: http://www.kanebo.co.jp/english/jigyo/E_seni.htm. Access date 10/06/2003.
- [299] J. Cicero, J. R. Dorgan, *J. Polym. Environ.* **2001**, 9, 1.
- [300] J. Lunt, A. Shafer, "Polylactic Acid Polymers from Corn: Potential Applications in the Textiles Industry", available at: <http://www.cdply.com/pdf/lunttech.pdf>. Access date 10/06/2003.
- [301] A. G. Mikos, A. J. Thorsen, L. A. Czerwonka, Y. Bao, R. Langer, D. N. Winslow, J. P. Vacanti, *Polymer* **1994**, 35, 1068.
- [302] K. Arai, S. Ohya, "Biodegradable Lactide and Polyester Copolymers for use in Packaging and Their Film Properties", 2001, Dainippon Ink and Chemicals, Inc. Available at: <http://www.dic.co.jp/eng/rd/tech/rev02/rep0210.html>. Access date: 8/25/2003.
- [303] E. T. H. Vink, K. R. Rábago, D. A. Glassner, B. Springs, R. P. O'Connor, J. J. Kolstad, P. Gruber, *Macromol. Biosci.* **2004**, 4, 551.
- [304] E. T. H. Vink, K. R. Rábago, D. A. Glassner, P. Gruber, *Polym. Degrad. Stab.* **2003**, 80, 403.
- [305] A. M. Mohan, *Packag. Digest* **2002**, 30–32, 34.
- [306] J. Nageroni, *Flexible Packag.* **2001**, 25–26.
- [307] O. B. Michael, "Ilip Launches New Fresh Food Packaging Solution", available at: <http://www.cargilldow.com/corporate/release.asp?id=110>. Access date 2/27/2003.