16

Polylactic Acid Technology

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CONTENTS
16.1 Introduction ........................................................................................................528
16.2 Lactic Acid ..............................................................................................................531
16.3 Life Cycle Analysis ..............................................................................................532
16.4 Polymerization of Lactide ................................................................................536
16.5 PLA Physical Properties ....................................................................................538
  16.5.1 Linear Optical Copolymer Structures and Blends ..................................538
  16.5.1.1 Density ..................................................................................................540
  16.5.1.2 Glass Transition and the Amorphous Phase ...................................540
  16.5.2 Rheology ....................................................................................................542
    16.5.2.1 Melt Rheology of Linear PLA .........................................................542
    16.5.2.2 Melt Stability ....................................................................................544
    16.5.2.3 Solution Properties ............................................................................544
    16.5.2.4 Branching ..........................................................................................545
    16.5.2.5 Solid-State Viscoelastic Properties ................................................547
  16.5.3 Crystallinity ..................................................................................................547
    16.5.3.1 Morphology ........................................................................................547
    16.5.3.2 Degree of Crystallinity ....................................................................550
    16.5.3.3 Crystallization Kinetics ....................................................................552
    16.5.3.4 Stereocomplex ...................................................................................553
    16.5.3.5 Stress-Induced Crystallization .........................................................554
  16.5.4 Degradation and Hydrolysis .........................................................................555
    16.5.4.1 Hydrolysis ........................................................................................555
    16.5.4.2 Hydrolysis of Solid Samples Suspended in Aqueous Media ...........558
    16.5.4.3 Solution Hydrolysis ..........................................................................560
    16.5.4.4 Hydrolysis of Samples Exposed to Humidity ...................................561
  16.5.5 Enzymatic Degradation ................................................................................563
  16.6 Applications and Performance ........................................................................563
  16.7 Summary ..........................................................................................................568
ABSTRACT Poly(lactic acid) (PLA) is the first commodity polymer produced from annually renewable resources. Some of the environmental benefits of PLA, such as low energy to produce and reduced green house gas production, are presented and opportunities for the future are given. This chapter on PLA reviews the chemistry and material properties of the polymer and its copolymers. The current technology for the production of lactic acid, lactide, and polymer are presented. Applications for fabricated articles such as films and fibers are also discussed.

16.1 Introduction

Polylactic acid (PLA) is a rigid thermoplastic polymer that can be semicrystalline or totally amorphous, depending on the stereopurity of the polymer backbone. L(-)-lactic acid (2-hydroxy propionic acid) is the natural and most common form of the acid, but D(+)-lactic acid can also be produced by microorganisms or through racemization and this “impurity” acts much like comonomers in other polymers such as polyethylene terephthalate (PET) or polyethylene (PE). In PET, diethylene glycol or isophthalic acid is copolymerized into the backbone at low levels (1–10%) to control the rate of crystallization. In the same way, D-lactic acid units are incorporated into L-PLA to optimize the crystallization kinetics for specific fabrication processes and applications.

PLA is a unique polymer that in many ways behaves like PET, but also performs a lot like polypropylene (PP), a polyolefin. Ultimately it may be the polymer with the broadest range of applications because of its ability to be stress crystallized, thermally crystallized, impact modified, filled, copolymerized, and processed in most polymer processing equipment. It can be formed into transparent films, fibers, or injection molded into blow-moldable preforms for bottles, like PET. PLA also has excellent organoleptic characteristics and is excellent for food contact and related packaging applications.

In spite of this unique combination of characteristics, the commercial viability has historically been limited by high production costs (greater than $2/lb). Until now PLA has enjoyed little success in replacing petroleum-based plastics in commodity applications, with most initial uses limited to biomedical applications such as sutures.1

PLA is not new to the world of polymers. Carothers2 investigated the production of PLA from the cyclic dimer (lactide) of lactic acid as early as 1932. Even before that, low molecular weight dimers and oligomers were detected.
when water was removed from an aqueous solution of lactic acid. The announcement of the formation of a new company, Cargill Dow LLC, in 1997 brought two large companies together to focus on the production and marketing of PLA with the intention of significantly reducing the cost of production and making PLA a large-volume plastic.

In today’s world of green chemistry and concern for the environment, PLA has additional drivers that make it unique in the marketplace. The starting material for the final polymer, lactic acid, is made by a fermentation process using 100% annually renewable resources. The polymer will also rapidly degrade in the environment and the by-products are of very low toxicity, eventually being converted to carbon dioxide and water.

PLA can be prepared by both direct condensation of lactic acid and by the ring-opening polymerization of the cyclic lactide dimer, as shown in Figure 16.1. Because the direct condensation route is an equilibrium reaction, difficulties of removing trace amounts of water in the late stages of polymerization generally limit the ultimate molecular weight achievable by this approach. Most work has focused on the ring-opening polymerization of lactide, although other approaches, such as azeotropic distillation to drive the removal of water in the direct esterification process, have been evaluated.

Cargill Dow LLC has developed a patented, low-cost continuous process for the production of lactic acid-based polymers. The process combines the substantial environmental and economic benefits of synthesizing both lactide and PLA in the melt rather than in solution and, for the first time, provides a commercially viable biodegradable commodity polymer made from renewable resources. The process starts with lactic acid produced by fermentation of dextrose, followed by a continuous condensation reaction of aqueous lactic acid to produce low molecular weight PLA prepolymer (Figure 16.2). Next, the low molecular weight oligomers are converted into a mixture of lactide stereoisomers using a catalyst to enhance the rate and selectivity of the

![Figure 16.1](1741_C16.qxd) 2/11/2005 9:57 AM Page 529

**FIGURE 16.1**
Polymerization routes to polylactic acid.
The intramolecular cyclization reaction. The molten lactide mixture is then purified by vacuum distillation. Finally, PLA high polymer is produced using an organo tin-catalyzed, ring-opening lactide polymerization in the melt, completely eliminating the use of costly and environmentally unfriendly solvents. After the polymerization is complete, any remaining monomer is removed under vacuum and recycled to the beginning of the process (Figure 16.3).
This process is currently in operation in a recently constructed 300 million lb/yr commercial-scale PLA plant in Blair, Nebraska, USA. Cargill Dow LLC has also announced the construction of an additional plant in Europe in the near future.\textsuperscript{7}

PLA has been extensively studied by many researchers and reviewed in detail in several recent publications.\textsuperscript{8} This chapter will not review all of the growing volume of information on PLA, but will focus on the key elements of technology that will change this polymer from a specialty material to a large-volume commodity plastic.

16.2 Lactic Acid

Lactic acid (2-hydroxypropionic acid) is the basic building block for PLA. It is a highly water-soluble, three-carbon chiral acid that is naturally occurring and is most commonly found in the \(L(−)\) form. It is used as an acidulant in foods, as a building block for biodegradable polymers (PLA), and is converted to esters and used as a green solvent for metal cleaning, paints, and coatings. PURAC has been the world’s largest producer of lactic acid, but the recent start-up of the Cargill Dow lactic acid plant, with a capacity of 400,000,000 lb, exceeds that of all producers combined. There are different grades of lactic acid, each varying in purity depending on their end use application. The lowest to highest purity is technical grade, edible grade, pharmaceutical grade, and analytical grade. The lower grades contain sulfates, metals, amino acids, and various carbohydrates. With the need for polymerization-grade lactic acid it has become clear that even the highest purity grade, analytical grade, is not pure enough. The slight traces of carbohydrates and amino acids remaining in analytical grade cause color in the process and even parts per million traces of cations such as Na\(^+\) lead to racemization of the acid, resulting in the less desired \(D(+)\) lactic acid.

A good summary of lactic acid chemistry is found in the book by Holten,\textsuperscript{9} *Lactic Acid, Properties and Chemistry of Lactic Acid and Derivatives*. An older, but still informative review of lactic acid production via fermentation is found in a chapter on lactic acid by H. Schopmeyer.\textsuperscript{10} The major issues of fermentation, purification, and a history of lactic acid growth in the United States are reviewed. It also contains a good literature review up to that time on lactic acid.

A more recent review\textsuperscript{11} (1976) of lactic acid processes by Cox and Macbean looked closely at the details of distillation, liquid extraction, esterification, salt processes, electrodialysis, thermal methods, and ion exchange approaches to providing lactic acid from fermentation of carbohydrates. There have been a large number of proposed routes and patents issued claiming to have improved processes to isolate lactic acid from fermentation broth, but most are combinations or improvements on these basic concepts.
The main stages of lactic acid production consist of (1) fermentation, (2) cell mass and protein removal, (3) recovery and purification of lactic acid, (4) concentration of lactic acid, and (5) color removal.

Research and improvements in lactic acid production have been centered around each of these steps, with continued improvement in the cost and efficiency of each. Better microorganisms for the fermentation that are more robust to temperature, pH, and the organic products they produce have evolved in recent years. Engineering improvements have increased the size and efficiency of the plants, while improved technology for water removal (multiple effect evaporators and membranes) has lowered the cost for production. By far the greatest developments and diversity of approaches have been in the area of separation and purification. Some of the separation and purification processes and their proposed key features are listed in Table 16.1.

Most processes to produce lactic acid rely on bacterial fermentation of dextrose in aqueous slurry with a continual addition of a base, such as calcium hydroxide, to maintain a neutral pH. Bacteria are generally quite sensitive to pH and are only productive in a narrow pH range. This sensitivity to pH is demonstrated in Table 16.2 for the production of acetic acid by *Clostridium thermoaceticum*. Generally, deviation of pH by more than a couple of pH units totally inhibits bacterial fermentation. For the production of neutral species such as ethanol, this is not an issue. However, the production of organic acids such as acetic and lactic acid shifts the pH as the acids are produced. To maintain the optimum pH, bases are continuously added.

At a pH of about 7 (neutral pH), essentially all of the lactic acid is ionized. Isolation of the lactic acid and removal of water requires that a strong mineral acid, such as sulfuric acid, be added to protonate the lactate salt, while at the same time producing a mole of salt for every two moles of acid produced. On a weight basis, about a pound of salt per pound of acid is produced. This significant amount of waste salt contributes to the cost of the lactic acid and is undesirable from a sustainability point of view.

The process of the near future will contain an organism that is tolerant of temperature and acidic conditions and be combined with lactic acid removal technology that does not result in the generation of waste salts. This process will be cost-advantaged and beneficial to the environment.

### 16.3 Life Cycle Analysis

In recent years, products, processes, and technology have been judged for their overall sustainability. Those that use large quantities of energy, deplete natural resources, pollute the environment, or emit greenhouse gases are viewed as less sustainable. Green chemistry is the use of chemistry for pollution prevention or the production of materials that fulfill the definition of sustainability. More specifically, green chemistry is the design of chemical products and processes
<table>
<thead>
<tr>
<th>Feature</th>
<th>Advantage/Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrodialysis</td>
<td>1. Does not require acidification of fermentation.</td>
</tr>
<tr>
<td></td>
<td>2. Energy cost and capital.</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>1. Higher productivity because one can maintain low acid level in fermenter.</td>
</tr>
<tr>
<td></td>
<td>2. Fouling of the membrane.</td>
</tr>
<tr>
<td>Liquid extraction</td>
<td>1. Suitable for continuous process and provides efficient removal from many non-acidic impurities.</td>
</tr>
<tr>
<td></td>
<td>2. High cost of capital.</td>
</tr>
<tr>
<td></td>
<td>3. Solvent loss costs.</td>
</tr>
<tr>
<td>Ion exchange (acidification)</td>
<td>1. Eliminates the need to add a strong acid to the fermentation.</td>
</tr>
<tr>
<td></td>
<td>2. Cost of resin and issues of resin regeneration.</td>
</tr>
<tr>
<td>Ion exchange (purification)</td>
<td>1. This is the solid equivalent of t-amine extraction technology without the solvent loss issues.</td>
</tr>
<tr>
<td></td>
<td>2. Regeneration of the resin.</td>
</tr>
<tr>
<td></td>
<td>3. Cost and availability of the resin.</td>
</tr>
<tr>
<td>Distillation</td>
<td>1. Lactic acid can be steam distilled.</td>
</tr>
<tr>
<td></td>
<td>2. Significant purification must be done prior to distillation.</td>
</tr>
<tr>
<td></td>
<td>3. Depending on conditions, some degradation and oligomerization can occur.</td>
</tr>
<tr>
<td>Insoluble salt processes</td>
<td>1. Simple process that utilizes low-cost capital.</td>
</tr>
<tr>
<td></td>
<td>2. The crystallization of CaSO₄ occludes impurities and results in relatively impure acid.</td>
</tr>
<tr>
<td>Esterification</td>
<td>1. Distillation and separation of esters gives high-quality product.</td>
</tr>
<tr>
<td></td>
<td>2. Requires reconversion to acid.</td>
</tr>
</tbody>
</table>
that reduce or eliminate the use and generation of hazardous substances. In a production supply chain, green products and processes integrate engineering, chemistry, and environmental issues. The supply chain evaluation incorporates the energy, wastes, and emissions for operations during the production and transportation of all raw materials throughout the entire process, from production of all raw materials to disposal of the final articles.

An excellent method to quantify the sustainability of a product or process is to do a life cycle analysis (LCA). LCA looks at all factors from raw materials, transportation, product manufacture, end use, to disposal. The energy, air and water pollution, as well as the hazards of the chemicals are assessed and judged against alternate products or solutions. Each step from cradle to grave is quantified and the total impact on the environment in each of the areas is thus known.

Cargill Dow’s process embodies the well-known Principles of Green Chemistry by (1) preventing pollution at the source through the use of a natural fermentation process to produce lactic acid, (2) substituting annually renewable materials for petroleum-based feedstock, (3) eliminating the use of solvents or other hazardous materials, (4) completely recycling product and by-product streams, and (5) efficiently using catalysts to reduce energy consumption and improve yield. In addition, NatureWorks™ PLA products can be either recycled or composted after use.

PLA, as produced by Cargill Dow LLC, uses from 20 to 50% less fossil fuel than conventional plastic resins (Figure 16.4), meaning that up to 2 to 5 times more PLA can be produced with a given amount of fossil fuel than petrochemical-derived plastics. The ability to produce the polymer on a favorable cost/performance basis is critical to realizing these human health and environmental benefits. This has been achieved through efficient use of raw materials, reduced energy utilization, and elimination of solvents.

PLA is also a low-impact, greenhouse gas polymer because the CO₂ generated during PLA biodegradation is balanced by an equal amount taken from the atmosphere during the growth of plant feedstocks. In contrast, petrochemical-based polymers contribute to volatile organic compound (VOC) emissions and CO₂ generation when incinerated. LCA calculations indicate that PLA has a greenhouse gas emission rate of about 1600 kg CO₂/metric ton, while polypropylene, polystyrene, PET, and nylon have greenhouse gas values of 1850, 2740, 4140, and 7150 kg CO₂/metric ton, respectively.₁³ Figure 16.5 shows the relative comparison of greenhouse gas

| TABLE 16.2 |
| Fermentation Performance of *Clostridium Thermoaceticum* vs. pH in Acetic Acid Production |
| pH | 6.8 | 5.5 |
| Productivity (g/hr) | 0.8 | 0.6 |
| Acetate –g/l (as acid) | 45 | 16 |
| Yield (%) | 85–90 | 77 |
**FIGURE 16.4**
MJ/kg of energy required to produce various polymers (From Gruber, P., Keynote address, Massachusetts Green Chemistry Symposium, Amherst, MA, 2001. With permission.)

**FIGURE 16.5**
Greenhouse gas emissions (kg/ton) for production of various polymers. Long-term emissions for PLA are based on utilization of biomass for the production of lactic acid.
contribution to the environment for common plastic products. Longer term, as PLA is produced from field wastes or other biomass, PLA can become a CO₂ sink and actually contribute to a net reduction in greenhouse gases.

Although problematic in the past, recycling can offer an environmentally attractive disposal option for plastics. However, recycled plastics are typically contaminated with other incompatible materials and thus have reduced properties. Consequently, recycled plastics are often relegated to low-performance/low-value applications. In contrast, PLA articles can be readily hydrolyzed with water to form lactic acid, which is then purified and polymerized to remake prime polymer. PLA can also be naturally composted into humus, carbon dioxide, and water, with complete degradation occurring within only a few weeks under typical compost conditions. However, polymer hydrolysis and monomer recovery offer the preferred method for PLA recycling.

16.4 Polymerization of Lactide

Many catalyst systems have been evaluated for the polymerization of lactide including complexes of aluminum, zinc, tin, and lanthanides. Even strong bases such as metal alkoxides have been used with some success. Depending on the catalyst system and reaction conditions, almost all conceivable mechanisms (cationic, anionic, coordination, etc.) have been proposed to explain the kinetics, side reactions, and nature of the end groups observed in lactide polymerization. Tin compounds, especially tin(II) bis-2-ethylhexanoic acid (tin octoate), are preferred for the bulk polymerization of lactide due to their solubility in molten lactide, high catalytic activity, and low rate of racemization of the polymer. Conversions of > 90% and less than 1% racemization can be obtained while providing polymer with high molecular weight.

The polymerization of lactide using tin octoate is generally thought to occur via a coordination-insertion mechanism with ring opening of the lactide to add two lactyl units (a single lactide unit) to the growing end of the polymer chain shown schematically in Figure 16.6. The tin catalyst facilitates the

![Generalized coordination-insertion chain growth mechanism of lactide to PLA: R, growing polymer chain.](image)
polymerization, but hydroxyl or other nucleophilic species are the actual initiators. There is generally several hundred parts per million of hydroxyl impurities in the lactide from water, lactic acid, and linear dimers and trimers.

High molecular weight polymer, good reaction rate, and low levels of racemization are obtained with tin octoate-catalyzed polymerization of lactide. Typical conditions for polymerization are 180°–210°C, tin octoate concentrations of 100–1000 ppm, and 2–5 h to reach 95% conversion. The polymerization is first order in both catalyst and lactide. Frequently hydroxyl-containing initiators such as 1-octanol are used to both control molecular weight and accelerate the reaction.

Copolymers of lactide with other cyclic monomers such as caprolactone can be prepared using similar reaction conditions (Figure 16.7). These monomers can be used to prepare random copolymers or block polymers because of the end growth polymerization mechanism. Cyclic carbonates, epoxides, and morpoline diones have also been copolymerized with lactide.

In addition to the work done on catalysts and comonomers, a significant amount of work has been done designing the optimum polymerization process from a cost and versatility perspective. Most of this work has used lactide dimer as the starting point. Batch polymerization as well as continuous processes can be used. Continuous processes (Figure 16.3) have a cost and productivity advantage and thus are the focus of most work. Stirred tank or pipe reactors have been evaluated alone as well as in combination. Because of the low energy of the ring-opening polymerization and the potential to obtain high rates of polymerization, melt extruders have been extensively evaluated as reactors to produce PLA. A number of groups have reported or patented specific aspects of the use of extruders or combinations of several reactor concepts to produce PLA.

DuPont recognized the importance of high rates of lactide polymerization and the economic viability of using extruders. They investigated the issues surrounding hydroxyl initiators, catalysts, and acidic impurities. DuPont’s patent (US 5,310,599) provides examples showing the dramatic (negative) effect of acidic impurities, such as the linear dimer (DP2) on the rate of lactide polymerization. The acid impurities coordinate with the tin catalyst and render it ineffective as a ring-opening polymerization site. As an example, 389,000 MW PLA can be made with a 5-min residence time (6000:1
monomer: Sn octoate) at 180°C in the absence of acidic impurities, and 98% conversion is obtained. The conversion in 5 min drops to 50% at an impurity:catalyst ratio of 2:1 and to 12% in 5 min at a 6:1 ratio.

The rate of polymerization of lactide can be accelerated by the use of hydroxyl initiators such as butanol or by higher catalyst loading. However, increased initiator levels will reduce the molecular weight while more catalyst will reduce the thermal stability and increase the color of the PLA.

16.5 PLA Physical Properties

Several excellent reviews have been written which include details on the properties and characteristics of PLA. A discussion of the variety of structures and their thermal and mechanical behavior follows.

The physical characteristics of high molecular weight PLA are to a great extent dependent on its transition temperatures for common qualities such as density, heat capacity, and mechanical and rheological properties. In the solid state, PLA can be either amorphous or semicrystalline, depending on the stereochemistry and thermal history. For amorphous PLAs, the glass transition ($T_g$) determines the upper use temperature for most commercial applications. For semicrystalline PLAs, both the $T_g$ (~58°C) and melting point ($T_m$), 130°–230°C (depending on structure) are important for determining the use temperatures across various applications. Both of these transitions, $T_g$ and $T_m$, are strongly affected by overall optical composition, primary structure, thermal history, and molecular weight.

Above $T_g$, amorphous PLAs transition from glassy to rubbery and will behave as a viscous fluid upon further heating. Below $T_g$, PLA behaves as a glass with the ability to creep until cooled to its $\beta$ transition temperature of approximately ~45°C. Below this temperature PLA will only behave as a brittle polymer.

16.5.1 Linear Optical Copolymer Structures and Blends

Having two optical arrangements for lactic acid (L-lactic acid, D-lactic acid), and three optical arrangements for lactide (L-lactide, D-lactide, meso-lactide), the variety of primary structures available for PLA is substantial. In addition, many other monomers have been copolymerized with lactic acid and/or lactide, the subject of which will not be covered in this chapter. Techniques for measuring PLA stereosequences by NMR have been published by Thakur et al.

Containing the discussion to strictly PLA linear optical copolymers, there are several notable primary structures which lead to a variety of highly ordered crystalline structures. The simplest is that of the isotactic homopolymer
poly(l-lactide) (PLLA) or its opposite enantiomer poly(d-lactide) (PDLA) where all of the monomers in the chain are of the same optical composition. A greater amount of research has been done on PLLA due to the fact that the commercial production of lactic acid has been predominantly l-lactic acid. The crystal structure of PLLA homopolymer exists in $\alpha$ and $\beta$ forms. A more detailed description of the crystal structures and unit cell parameters follows.

The most common commercial polymers of PLA are optical copolymers of predominantly l-lactide, with small amounts of d- and meso-lactides, made through bulk polymerization with tin octoate catalyst via ring-opening polymerization (ROP). While these copolymers are generally described as random, there is evidence of some degree of stereoselectivity. Selectivity of tin octoate is discussed by Thakur et al.\textsuperscript{38} Condensation polymerization of mostly l-lactic acid with small amounts of d-lactic acid, polymerized in solution, has also been used. The optical comonomers introduce “kinks” in PLA’s natural helical conformation and “defects” in the crystal arrangement, which results in depression of the melting point, reduction in the level of attainable crystallinity, and reduction in the rate of crystallization. Optical purity (OP) is a common nomenclature to describe polymers of this variety. As OP decreases, crystallization eventually becomes impossible and the polymer is amorphous (occurring about when OP $< 0.78$). For the purposes of this chapter, the designation a-PLA will be used for PLAs made with insufficient optical purity to crystallize, and c-PLA will be used to designate PLAs that are crystallizable. Stereoselective catalysis has been used to develop optical copolymers having a highly tapered concentration of optical purity (OP) along the chain.\textsuperscript{39}

Random copolymers made from meso-lactide result in an atactic primary structure referred to as poly(meso-lactide) and are amorphous. Random optical copolymers made from equimolar amounts of d-lactide and l-lactide are commonly referred to as PDLLA or poly(rac-lactide). PDLLA is also essentially atactic, but the primary structure is segregated into optical doublets of the lactyl group, and it is also amorphous.

Ovitt and Coates\textsuperscript{40} have made two novel stereoregular primary structures using chiral catalysts. The first was syndiotactic PLA, made by ROP of meso-lactide with a chiral aluminum alkoxide catalyst, which selectively opened the l-lactyl side of the meso-lactide molecule and resulted in alternating stereocenters along the growing chain. This can be visualized as an optical head-to-tail addition and results in an –LDLDLD- arrangement of lactyl stereocenters along the chain. In this case, optical purity (OP) will refer to the fraction of stereoregular syndiotactic sequences. The material was shown to crystallize with a melting point of about 152°C with an OP of 0.96. The second structure, referred to as di-syndiotactic PLA or heterotactic PLA, was made by ROP of meso-lactide with a racemic catalyst that would add meso-lactide. However, the reacted lactide stereocenter would add in an alternating fashion, in what can be visualized as an optical head-to-head addition resulting in sequences of –LLDDLLDD- along the chain. The heterotactic PLAs produced did not crystallize, and had a $T_g$ of about 40°C. Ovitt also showed that
racemic catalysts can be used to polymerize rac-lactide into stereoblock copolymers that have long sequences of poly(l-lactide) and poly(d-lactide) blocks, referred to as isotactic stereoblock PLA. \(^4\) Similar work had been performed earlier by Yui et al.\(^4\) With sufficiently long isotactic run lengths, these polymers are able to crystallize into the stereocomplex crystal arrangement.

Blends of PLA optical copolymers have also offered a variety of new properties. The most notable is that of the stereocomplex PLA, which is made by solvent or melt blending PLLA and PDLA where the polymers undergo stereocomplexation or racemic crystallization. This phenomenon has been an area of intense study since first described by Ikada et al.\(^4\) A more detailed description of stereocomplex will follow. A second blend receiving attention is the blend of crystallizable PLA (c-PLA) with noncrystallizable PLA (a-PLA).

Key melting point and glass transition data for PLA structures and blends are listed in Table 16.3.

### 16.5.1.1 Density
Volumetric measurements show that PLA and lactide isomers in the liquid state have approximately the same density as a function of temperature, with a thermal coefficient of expansion \(\alpha = 7.4 \times 10^{-4} \, ^\circ C^{-1}\). The melt density can be approximated using Equation (16.1) by Witzke:\(^3\)

\[
\rho (g/cm^3) = \frac{\rho_{150}^\circ C}{1 + \alpha(T(\circ C) - 150)}
\]

where \(\rho_{150} = 1.1452\).

The solid amorphous PLA density is \(-1.25 \, g/cm^3\). The purely crystalline PLLA density\(^3\) is estimated to be \(1.37-1.49 \, g/cm^3\).

### 16.5.1.2 Glass Transition and the Amorphous Phase
The PLA glass transition \((T_g)\) increases with \(M_n\) and OP. Orientation and physical aging also affect the \(T_g\). The infinite molecular weight \(T_g\) for PLLA, poly(meso-lactide) and PDLLA were estimated to be 61°, 46°, and 53°, respectively, by Witzke,\(^3\) who developed an equation describing the \(T_g\) of unoriented poly(l-lactide-co-meso-lactide), Equation (16.2)

\[
T_g = 45 - \frac{180,000}{M_n} + 16 w_{L-mer} - 7 w_{meso}
\]

where \(w_{L-mer}\) and \(w_{meso}\) are the starting mole fractions of l-lactide and meso-lactide, respectively.

Physical aging affects the glass transition of PLA. It can occur between \(-45°C\) and \(T_g\).\(^3\) The free volume reduction, characteristic of physical aging, is observed by DSC as an endothermic volume expansion immediately after \(T_g\) and is often referred to as the enthalpy of relaxation. Crystallization and orientation reduce the rate and extent of PLA aging. The rate of aging increases with temperature up to the \(T_g\).
TABLE 16.3
Melting Point and Glass Transition Data for PLA Structures and Blends

<table>
<thead>
<tr>
<th>PLA Structure Description</th>
<th>PLA Structure</th>
<th>Description</th>
<th>$T_m$ (°C)</th>
<th>$T_m^*$ (°C)</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotactic poly(L-lactide) or poly(D-lactide)</td>
<td>LLLLLLLLLL or DDDDDDDDDDD</td>
<td>170–190</td>
<td>205 Tsuji and Ikada (1995)</td>
<td>55–65 Tsuji and Ikada (1999)</td>
<td></td>
</tr>
<tr>
<td>Random optical copolymers</td>
<td>Random level of meso or $\alpha$-lactide in $\alpha$-lactide or $\gamma$-lactic acid in $\gamma$-lactic acid</td>
<td>130–170</td>
<td>165–210 Runt (2001)</td>
<td>45–65 Runt (2001)</td>
<td></td>
</tr>
</tbody>
</table>
A significant reduction in the \(T_g\) is found for PLLA crystallized under partially constrained conditions, where the polymer is prevented from shrinking.\(^{44}\) It was proposed that the constrained crystallization process increases the net free volume in the amorphous phase. \(T_g\) depression increased with increasing crystallinity. In contrast, when samples are allowed to shrink or crystallize quiescently, \(T_g\) increases with crystallinity. It was shown that the \(T_g\) could vary by as much as 30°C between the two methods, while the melting point (\(T_m\)), heat of fusion (\(\Delta H_m\)), and overall degree of crystallinity (\(x_c\)) were not influenced. It is possible that the reduction in \(T_g\) under partially strained conditions may be related to suppressing physical aging.

Blends of PLAs of different optical compositions have been studied for miscibility and compatibility. The most notable blend is that of the PLA stereo-complex, which occurs when PLLA is mixed with PDLA and the homopolymers cocrystallize into a new arrangement with a markedly higher melting point. The interesting features of the stereocomplex crystal will be discussed later. Tsuji and Ikada\(^ {45}\) reported that the \(T_g\) of stereocomplex PLA is 5°C higher than that of the nonblended components. This was attributed to the strong interaction between the \(L\)-lactyl and \(D\)-lactyl unit sequences in the amorphous region of the blends, resulting in a more dense chain packing. A second very interesting blend is to blend a crystallizable polymer (c-PLA) of high optical purity (OP) with a polymer of low OP (a-PLA). Urayama et al.\(^ {46}\) investigated blends of PLLA with PDLLA by dynamic mechanical analysis (DMA). \(T_g\) behavior supported compatibility of both polymers. The modulus remained constant regardless of blend ratio. Modulus changes were consistent with homopolymers, where the \(E'\) of the blends dropped from 2–3 \(\times\) \(10^9\) Pa to a rubbery plateau of 1–3 \(\times\) \(10^6\) Pa across the \(T_g\) for amorphous specimens. The rubbery plateau increased to a different level depending on the crystallinity of the blend. Blends of this type provide a route to modify flexibility of the polymer above the glass transition by controlling the overall level of crystallinity (\(x_c\)).

### 16.5.2 Rheology

Rheological properties are useful in evaluating thermoplastics for their performance during processing operations. The literature reports a wide variety of processes and products using PLA, spanning from high orientation processes such as fiber spinning and oriented films to lower orientation processes such as thermoforming and foams. The time scales of these processes are very different. Considerations for material flow characteristics, orientation, and crystallization must be made to gauge and predict the resulting properties of the products made from these processes. Intrinsic factors affecting the flow characteristics of PLA are molecular weight distribution, degree and type of branching, optical composition, optical block length distributions, and melt stability.

#### 16.5.2.1 Melt Rheology of Linear PLA

PLA, like many thermoplastics, is a pseudoplastic, non-Newtonian fluid. Above the melting point, PLA behaves as a classic flexible-chain polymer
across all optical compositions. PLA’s zero shear viscosity and shear thinning behavior have been measured by a variety of groups. However, complicated by the array of optical copolymers studied, the difficulty associated with measuring the absolute molecular weight of PLA, and the issues of melt stability, the interpretation of PLA’s rheology has not always been consistent.

The most comprehensive studies of linear PLAs in the melt were performed by Janzen and Dorgan who showed that zero shear viscosity \((\eta_0)\) scales very close to the usual 3.4 power with \(M_w\), and that PLA obeys the Cox-Merz rule well into the shear thinning region when in the linear viscoelastic range. The plateau modulus for PLLA is \(~1\) MPa, which corresponds to a critical molecular weight of about 9000 g/mol. Previous reports by Cooper-White and MacKay measured the rheological properties of PLLA with molecular weights ranging from 2,000 to 360,000 and reported a dependence of zero shear viscosity \((\eta_0)\) on chain length to the 4.0 power \((M_w^{4.0})\). However, only a very small number of samples were used to build the 4.0 power relationship. Dorgan also showed that PLA exhibits strain hardening during extension in the melt, a characteristic necessary for fiber spinning.

The complex viscosity for PLA with 213,000 \(M_w\) (relative to polystyrene) and 13.0% D was measured at many temperatures and shear rates. The shifted data shown in Figure 16.8 depict rheological behavior across six orders of magnitude in shear for 180°C.

FIGURE 16.8
Melt rheology of 213,000 \(M_w\) (relative to polystyrene) 13.0% D PLA shifted to 180°C.
*Measurements by Jay Janzen, Colorado School of Mines.
16.5.2.2 Melt Stability

Issues with PLA melt stability during processing and rheological testing have been cited by Witzke,\textsuperscript{32} Dorgan et al.,\textsuperscript{48} Ramkumar and Bhattacharya,\textsuperscript{52} and Feng and Hanna.\textsuperscript{53} Reactions leading to poor melt stability include chain scission due to hydrolysis, chain scission due to thermal instability, and lactide formation by the well-documented “back-biting” mechanism. Hydrolysis can be reduced or essentially eliminated with conventional drying operations where water is removed prior to melting. Recommended drying conditions are available for commercial PLAs. When PLA is exposed to a humid environment following drying, moisture is quickly absorbed into the polymer up to its equilibrium level of swelling. Kinetics for melt hydrolysis depend on water concentration, acid or base catalysis, and polymerization catalyst concentration.

The proton in the CH group of the main chain of PLA is labile. It has been suggested that the proximity of this labile proton to the ester group affects the thermal sensitivity of the polymer.\textsuperscript{52} The proton may be abstracted resulting in the breakdown of the molecular chain. In practical extrusion processes, thermal stability becomes important at temperatures greater than 250°C.

Using PLA polymerized with tin octoate catalyst, Cicero et al.\textsuperscript{54} showed that the melt stability of PLA can be improved by the addition of small amounts of tris(nonylphenyl)phosphite (TNPP), likely due to balancing chain extension with degradation reactions. Adding TNPP during rheological testing greatly stabilized the polymer and lengthened the time available for testing.

The thermodynamic equilibrium between polylactide and lactide monomer varies with temperature and is about 4.3% lactide at 210°C.\textsuperscript{32} Since lactide imparts undesirable characteristics during processing, such as fuming, it is desirable to depress the lactide formation kinetics and stabilize the polymer. Gruber et al.\textsuperscript{55} showed that lactide formation could be substantially reduced under normal processing by complexing the catalyst with additives, resulting in a melt-stable PLA polymer.

16.5.2.3 Solution Properties

The dilute-solution properties of PLA are critical for characterizing molecular weight, chain flexibility, and defining solvent quality. Factors reported to affect PLA’s intrinsic viscosity ([η]) are molecular weight and distribution, optical composition, and branching. A recent publication submission by Janzen et al.\textsuperscript{47} systematically measured the dilute-solution properties of PLAs of wide OP in three solvent systems. Mark-Houwink parameters were determined by comparing [η] to a broad range of molecular weights determined by light scattering in a mixed solvent system first used on PLA by Kang et al.\textsuperscript{56} Tables 16.4 and 16.5 are taken from Janzen’s publication submission. Surprisingly, no effect of optical composition was found to affect [η], within the error of the experiments. Earlier work by Schindler and Harper\textsuperscript{57} had shown a significant difference between the Mark-Houwink parameters of PLLA and PDLLA.
Polylactic Acid Technology

545

Calculated values for some key PLA parameters, including entanglement molecular weight, critical molecular weight, and reptation parameters (Reference 47) are shown in Table 16.5. The characteristic ratio ($C_\infty$) for PLA is $6.74 \pm 0.67$. In sharp contrast to this value for $C_\infty$, Kang et al.\textsuperscript{56} characterized PLA of varying OP by static and dynamic laser light scattering in conjunction with Raman spectroscopy, and calculated a $C_\infty$ of 12.4 for PLLA. Some debate still remains as to the flexibility of PLAs of varying optical composition.

16.5.2.4 Branching

With the introduction of branching, the rheological properties of PLA can be significantly modified. Since the linear polymer exhibits low melt strength,

**TABLE 16.4**

Dilute-Solution Constants for PLAs at 30°C

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CHCl$_3$</th>
<th>Solvent</th>
<th>CH$_3$CN &amp; CH$_2$Cl$_2$ Mix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schulz-Blaschke concentration factor $k_{SB}$</td>
<td>0.302 ± 0.005</td>
<td>0.289 ± 0.005</td>
<td>0.373 ± 0.016</td>
</tr>
<tr>
<td>Mark-Houwink fit $K$, mL/g</td>
<td>0.0131 ± 0.0048</td>
<td>0.0174 ± 0.0046</td>
<td>0.0187 ± 0.0075</td>
</tr>
<tr>
<td>a</td>
<td>0.777 ± 0.031</td>
<td>0.736 ± 0.023</td>
<td>0.697 ± 0.034</td>
</tr>
<tr>
<td>Stockmayer-Fixman fit $K_a$, mL/g</td>
<td>0.112 ± 0.017</td>
<td>0.101 ± 0.014</td>
<td>0.096 ± 0.011</td>
</tr>
<tr>
<td>$10^6$b</td>
<td>5.82 ± 0.69</td>
<td>4.76 ± 0.65</td>
<td>2.30 ± 0.36</td>
</tr>
<tr>
<td>Characteristic ratios $C_\infty$</td>
<td>6.74 ± 0.67</td>
<td>6.29 ± 0.57</td>
<td>6.08 ± 0.46</td>
</tr>
</tbody>
</table>


**TABLE 16.5**

Flexible Linear Polymer Melt Chain Dimension Comparisons

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_p$, relative molecular mass per backbone bond</td>
<td>24.02</td>
</tr>
<tr>
<td>$L_2^2$, Å$^2$</td>
<td>2.05</td>
</tr>
<tr>
<td>$p$, g/cm$^3$</td>
<td>1.152</td>
</tr>
<tr>
<td>$G_0$, MPa</td>
<td>1.0</td>
</tr>
<tr>
<td>$M_e$, entanglement molecular mass</td>
<td>3,959</td>
</tr>
<tr>
<td>$M_e/M_p$, backbone bonds</td>
<td>165</td>
</tr>
<tr>
<td>$M_c$, critical molecular mass</td>
<td>9,211</td>
</tr>
<tr>
<td>$M_c/M_p$, backbone bonds</td>
<td>383</td>
</tr>
<tr>
<td>$&lt;r^2&gt;0/M_e$, Å$^2$</td>
<td>0.574</td>
</tr>
<tr>
<td>$C_\infty$</td>
<td>6.7</td>
</tr>
<tr>
<td>$p$, packing length, Å</td>
<td>2.51</td>
</tr>
<tr>
<td>$d_t$, tube diameter, Å</td>
<td>47.7</td>
</tr>
<tr>
<td>$d_t/p$ (Ronca-Lin ratio)</td>
<td>19</td>
</tr>
</tbody>
</table>


Calculated values for some key PLA parameters, including entanglement molecular weight, critical molecular weight, and reptation parameters (Reference 47) are shown in Table 16.5. The characteristic ratio ($C_\infty$) for PLA is $6.74 \pm 0.67$. In sharp contrast to this value for $C_\infty$, Kang et al.\textsuperscript{56} characterized PLA of varying OP by static and dynamic laser light scattering in conjunction with Raman spectroscopy, and calculated a $C_\infty$ of 12.4 for PLLA. Some debate still remains as to the flexibility of PLAs of varying optical composition.
for certain applications it is desirable to increase the melt strength by introducing long-chain branching. Several routes have been used to obtain long-chain branching. Figure 16.9 shows the effect of branching on the complex viscosity of PLA.

1. Multifunctional polymerization initiators have been used to make star- and comb-shaped molecules. A number of studies have examined reacting lactides with branched polyols since first proposed by Schindler et al. Dorgan et al. published rheological characterization of linear and star PLAs. Relaxation spectra show that the transition zones for the linear and branched materials are nearly indistinguishable, while the star polymers have greater contributions to the terminal regime and a much steeper dependence of $\eta_0$ as a function of $M_w$.

Zhao et al. made starburst structures by polymerizing lactide onto dendrimer macroinitiators. From 16 to 21 polylactide arms were attached to the surface of the initiator. Molecular weight is controlled by the ratio of monomer to initiator.

2. Hydroxycyclic ester and/or carbonate polymerization initiators are comprised of an initiation group (e.g., hydroxyl) and a ring capable of copolymerizing with a growing PLA chain. Drumright et al. reported polymerizing PLA with hydroxycarbonate initiators, resulting in long-chain branching and enhanced melt elasticity. Tasaka et al. made branched PLA with mevalonic lactone initiator.

![Complex viscosity of branched PLA made by peroxide treatment.](image-url)
3. Multicyclic ester, multicyclic carbonate and/or multicyclic epoxy comonomers are comprised of multiple rings (most commonly two) capable of copolymerizing with a growing PLA chain. Drumright et al.\textsuperscript{63} also reported on polymerizing PLA with bicyclic diesters and/or dicarbonates to control rheological properties. The bicyclic diesters and dicarbonates copolymerize easily with lactide to form copolymers that can have tailored levels of branching. The copolymers showed excellent rheological properties, including increased melt tensions and improved shear thinning, compared to the analogous linear polymers. A typical polymer was manufactured by polymerization of L-lactide at 130°–185°C with 0.1% \(\alpha,\alpha\)-2,5-dioxabicyclo[2.2.2]octane-3,6-dione. Since multicyclic lactones do not contain an initiator, the chemistry can theoretically be used to cross-link PLA to infinite molecular weight. A patent by Gruber et al.\textsuperscript{64} describes rheological modification of PLA by copolymerizing with multifunctional expoxidized oil.

4. Cross-linking via free radical has been accomplished in the melt by treating PLA with peroxides.\textsuperscript{65} Small amounts of peroxide result in long-chain branches. The polymer remains melt processable and is stable. Large improvements in melt elasticity have been measured using die swell, melt tension, and parallel plate rheometry. Blends of linear and branched PLAs showed good compatibility and predictable melt rheology by the mixing rule.\textsuperscript{66}

\subsection*{16.5.2.5 Solid-State Viscoelastic Properties}

Solid-state rheological properties of amorphous PLA typically show a storage modulus (\(E^\prime\)) of about 2–3 \(\times 10^7\) Pa below the glass transition temperature. As the sample is heated, a sharp drop in modulus occurs between 55° and 80°C, and \(E^\prime\) decreases to \(~1–3 \times 10^6\) Pa as the glass transition (\(T_g\)) is exceeded.\textsuperscript{67} Semicrystalline samples show less of a drop in \(E^\prime\) across the \(T_g\), and also a higher \(T_g\) with increasing crystallinity. Peak height of the tan \(\delta\) curve will decrease, but the width of the tan \(\delta\) will increase as the percentage of crystallinity increases. Highly crystalline samples will typically show a tan \(\delta\) peak at 70°–80°C. Optical composition and crystallization conditions will strongly influence the onset of melting, and the corresponding drop in \(E^\prime\). The \(\beta\) transition of PLA is very small and is scarcely detectable by DMA.

\subsection*{16.5.3 Crystallinity}

\subsubsection*{16.5.3.1 Morphology}

The morphology of PLA crystals is influenced by composition and thermal history. Abe et al.\textsuperscript{68} showed that PLLA crystals grown at different temperatures go through three regime changes associated with nucleation and crystal growth rates. A morphology change was observed between regimes I and II. For PLLA crystallized isothermally from the melt, spherulitic morphology
is observed at crystallization temperatures below 145°C (regime II). During isothermal growth, the radius of the spherulites increases linearly with time, and the slope of the curve is the linear crystal growth rate (LCR). At higher temperatures, a smaller number of spherulites are formed due to a decrease in the nucleation density. This leads to larger spherulites with increasing crystallization temperature. Crystallizing PLLA at temperatures greater than 150°C (regime I) results in hexagonal lamellar stacking crystal morphology.

Spherulites have been shown to contain stacked lamellar morphology, with the long axis of the lamellar crystal running parallel to the spherulite radius. Within the crystal, PLA exists as a polymeric helix, with an orthorhombic unit cell with dimensions $a = 1.070$ nm and $b = 0.614$ nm. Amorphous polymer resides between the lamellae. The lamellar thickness of PLA varies with the temperature of crystallization ($T_c$), crystallization time ($t_c$), optical purity (OP), and molecular weight. PLLA grown at 120°, 140°, and 160°C had lamellar periodicities measured at 14–16, 16–18, and 18–22 nm, respectively, measured by AFM.\textsuperscript{68}

For L-rich polymers with small amounts of D- and meso-lactides, there is an observed decrease in the equilibrium melting point with decreasing OP. At least two possible explanations for this have been considered. In one extreme case it is assumed that the optically impure units are incorporated into the crystal structure as defects. This results in a decreasing melting point ($T_m$) due to the decrease in the enthalpy of fusion. In the other extreme case, it is assumed that the optically impure units are rejected from the crystal structure, causing a reduction in $T_m$ due to entropy effects. Baratian et al.\textsuperscript{69} studied the degree of crystallinity, spherulitic growth rate, lamellar thickness, and melting temperature of a series of optical copolymers of this variety, comparing the effects of D-lactide and meso-lactide optical impurities. Small-angle x-ray scattering (SAXS) results showed that lamellar thickness decreases with decreasing OP at a given degree of supercooling. It was proposed that a critical sequence length that is free of stereo defects is necessary for crystallization and that the stereo defects are excluded from the crystalline regions. In a different study by Zell et al.,\textsuperscript{70} it was shown that, at least under long crystallization times, a certain fraction of optical impurity (in this case, a small percentage of labeled L-lactide copolymerized into a polymer of predominantly D-lactide) is incorporated into the crystal lamellae. Zell et al.\textsuperscript{70} went on to develop a model for determining the fraction of crystallizable PLA based upon a critical chain length necessary for crystallization that allows stereo defects to be included in the crystalline region if they are surrounded by a sufficient isotactic run length.

The spherulite structure for L-lactide-rich PLA was studied by Pyda et al.\textsuperscript{71} Figure 16.10 shows the crystal imaging using AFM and polarized light microscopy.

A graph showing the observed melting point by DSC after isothermal treatments at crystallization temperature $T_c$ is shown in Figure 16.11 for a series of poly(L-lactide-co-D-lactide)s that are rich in L-lactide content.\textsuperscript{69} Polymers were made by ROP using tin octoate catalyst.
Using the Hoffman-Weeks\textsuperscript{72} method for determining equilibrium melting temperature ($T_{m0}$) of a polymer [linear extrapolation of experimentally observed melting points ($T_m$) vs. crystallization temperature ($T_c$)]
intersecting with the line $T_m = T_c$, the equilibrium melting point for PLLA has been observed to be 211°–212°C. However, some have questioned the appropriateness of the Hoffman-Weeks approach for copolymers. Baratian et al. elected to use a Gibbs-Thompson approach for estimating $T_m^0$ that requires direct measure of the lamellar thickness and uses the following relationship:

$$T_m^0 = T_m^0 \left[ \frac{1-2\sigma_e}{\Delta H^0_m(l_c)} \right]$$

(16.3)

where $T_m$ is the observed melting point for lamella of thickness $l_c$, $\sigma_e$ is the end (fold) surface free energy, and $H^0_m$ is the enthalpy of fusion for 100% crystalline PLA. $T_m^0$ is estimated by extrapolation of $T_m$ vs. $1/l_c$ data to $1/l_c = 0$. The lamellar thickness for PLLA measured by Baratian et al. agrees reasonably well with that of Abe et al. Their combined data are shown in Figure 16.12. Experimental equilibrium melting points for a series of L-lactide-rich polymers are shown in Figure 16.13.

During normal processing and crystallization procedures, polymers do not reach their equilibrium melting temperature. A practical equation describing melting point for PLAs of predominantly L-lactide with meso-lactide is simply $T_m(°C) = 175°C-300 w_{meso}$ where $w_{meso}$ is less than 0.18. The melting point is depressed about 3°C for every 1% initial meso-lactide.

### 16.5.3.2 Degree of Crystallinity

Most commonly, an enthalpy of fusion of 93.1 J/g is used for a 100% crystalline PLLA or PDLA homopolymers (i.e. $\Delta H^0_m = 93.1 \text{ J/g}$) having infinite
crystal thickness, and Equation (16.4) is used to calculate percent crystallinity from DSC scans:

$$\text{Crystallinity (\%)} = \frac{\Delta H_m - \Delta H_c}{93.1} \times 100$$  \hspace{1cm} (16.4)
where $\Delta H_m$ is the measured heat of fusion and $\Delta H_c$ is the heat of crystallization. This value of 93.1 J/g is used throughout the PLA literature. However, since $T_m^0$ decreases with decreasing OP, it is expected that using a constant value for $\Delta H_m^0$ across all optical compositions will introduce error. No reference was found that systematically calculated $\Delta H_m^0$ for homopolymers of reduced OP. It is well known that for PLAs of essentially random optical copolymers of predominantly L-lactide, with small amounts of D- and meso-lactides, the attainable percentage of crystallinity ($x_c$) decreases with decreasing optical purity (OP), and crystallization is essentially nonexistent about when $OP < 0.78$.

### 16.5.3.3 Crystallization Kinetics

The crystallization kinetics of PLA are strongly dependent on the optical copolymer composition. The degree of crystallinity, nucleation rate, and spherulite growth rate decrease substantially with decreasing optical purity (OP). Under quiescent crystallization conditions, Kolstad showed that the bulk crystallization half time increases by roughly 40\% for every 1 wt\% increase in the meso-lactide.\(^{75}\) PLA has the highest rate of crystallization between 100° and 130°C.

Two phenomena contribute to the bulk crystallization rate, nucleation and crystal growth. For instantaneous nucleation and spherulitic growth (Avrami $n = 3$), the crystallization rate constant is given by

$$ k = \frac{4}{3} \pi N G^3 $$

For the rate equation,

$$ x = 1 - e^{-kr^t} $$

where $x = \Delta H_m(t)/\Delta H_m(\infty)$, $N =$ the density of primary nucleation sites to initiate spherulitic growth, and $G$ is the lineal growth rate of a spherulite.

The rate of PLA lineal crystal growth ($G$) of a spherulite is dependent on $T_c$, OP, and molecular weight. Nucleation density ($N$) depends on $T_c$, polymer characteristics, thermal history, and impurities.

When PLA is isothermally crystallized from the melt or from a quenched state, the size of the spherulites changes dramatically. Pluta and Galeski\(^{76}\) showed that spherulites were larger in samples crystallized via cooling from the melt than those in samples crystallized via heating from the glassy amorphous state. On the lamellar level, the structures were similar for samples prepared by the two methods under similar time and temperature conditions. The thermal properties, $T_m$ and $H_m$, were similar.

Technology to increase the rate of crystallization of PLA has been investigated because even the fastest crystallizing PLAs are considered to be slow when compared to many conventional thermoplastics. Kolstad\(^{75}\) showed that talc is an extremely effective nucleating agent for PLA homopolymers.
Schmidt and Hillmyer showed that a small level of stereocomplex crystal is effective for seeding the crystallization of PLA homopolymers. Liao et al. studied the crystallization characteristics of blends of PLLA and PDLLA. Crystallization behavior of PLLA in the blends was similar to that of the homopolymer when PDLLA < 30%.

16.5.3.4 Stereocomplex

Stereocomplexation has been reported in the literature for a number of polymers including polylactide. The PLA racemic crystal structure consists of alternating L- and D-PLA chains packed side by side with a 1:1 ratio of L:D monomer units. The chain conformation in the stereocrystal is a 3\textsubscript{1} helix vs. the 10\textsubscript{3} for the unstrained homopolymer crystal. The 3\textsubscript{1} helix winds a little tighter, going from 108° to 120° rotation per residue, resulting in a significant change in the molecular shape. The 3\textsubscript{1} configuration allows a chain-to-chain separation difference of 0.4 Å smaller. This tighter packing results in more favorable nonbonding interactions that contribute to the higher crystalline melting point. The equilibrium melting temperature of PLA stereocomplex has been reported by Tsuji and Ikada to be 279°C, a very marked improvement over homocrystals, with the minimum tacticity sequencing needed to produce stereocomplex for the L-rich and D-rich PLAs to be 15 lactyl (or 7.5 lactide) units. The heat of fusion for pure stereocomplex has been determined to be 142 J/g by Loomis and Murdoch.

Melting points for stereocomplex are dictated by the optical purity (OP) of both the L-lactide-rich and D-lactide-rich polymers (in terms of optically pure run lengths) as well as molecular weight and blend ratio. Maximum regularity is attained with a blend of PLLA and PDLA. The greater the deviation in OP of the L-rich and/or D-rich chains, the greater the decrease in stereocomplex melting peak. This follows the equivalent behaviors of PLA homocrystals, but is shifted to a higher temperature. A practical upper attainable melting temperature that would be achievable for commercial resins approaches 230°C.

Melting point \( T_m \) and enthalpy of melting \( \Delta H_m \) of the stereocomplex is dependent on the ratio of L-lactide-rich polymer and D-lactide-rich polymer. For a constant optical purity of racemic polymers, the \( T_m \) varies only by a few degrees across the possible blend ratios, whereas the stereocomplex \( \Delta H_m \) varies directly with the blend ratio with maximum at 1:1. Tsuji et al. published an excellent series of papers on the crystallization, mechanical behavior, and hydrolysis properties of PLA stereocomplexes.

Kang et al. have examined the PLA stereocomplex by Raman spectra and determined that C=O stretching bands are related to the packing formation of the polymer chain. By combining Raman spectroscopy and DSC techniques, they deduced the enthalpy of fusion for stereocomplex to be 126 J/g. During crystallization, packing order led the conformation order during early stages. The C=O dipole interaction is believed to be the driving force for crystallization.
16.5.3.5 Stress-Induced Crystallization

While the slow quiescent crystallization kinetics of PLA may limit its speed of processing for some applications, opportunities utilizing stress-induced crystallization (SIC) with PLA have been enjoying success commercially because of the naturally wide processing window. It is possible to highly orient PLA in the rubbery or molten state during operations such as film stretching or fiber spinning. Fabrication processes such as this take full advantage of the semicrystalline nature of PLA to develop different properties. Kokturk et al.\textsuperscript{96} showed that PLA exhibited almost ideal stress-strain behavior in the temperature range 65°–80°C. As films are stretched, crystallization and strain hardening leads to uniform thickness at high deformation. This effect is referred to as self-leveling, and it is a highly desirable property for orientation processes. Crystallization of homopolymers, during orientation processes, results in β crystals in a 3\textsubscript{1} helix conformation.

Puiggali et al.\textsuperscript{97} characterized PLA crystals made through SIC, using electron diffraction and conformational energy analysis. Chains were shown to be arranged as a frustrated packing of 3\textsubscript{1} helixes in a trigonal unit-cell of parameters $a = b = 1.052$ nm, $c = 0.88$ nm. The frustrated packing is of the type described as North-South-South (NSS).

The effects of uniaxial drawing conditions on the orientation of various poly(L-lactide) (PLLA) samples have been investigated using Fourier transform IR dichroism and thermal analysis.\textsuperscript{98} Orientation in uniaxially stretched PLLA was influenced by the drawing rate, drawing temperature, and draw ratio. It was shown that spherulites could be deformed at high temperature under drawing conditions into new crystal morphologies.

Kister et al.\textsuperscript{99} first examined the Raman and IR spectra of poly(L-lactic acid) in the amorphous and semicrystalline states from 3600 to 100 cm\textsuperscript{-1}. Vibrational assignments were proposed, and Kister et al. indicated that Raman data supported the 10\textsuperscript{3} helical conformation for PLA. Raman spectroscopy has been further developed for PLA more recently. Smith et al. and Kang et al. have reported on a technique for characterizing orientation in both the amorphous and crystalline phases for films in multiple axes.\textsuperscript{100–102} Correlations to level of crystallinity were also developed. Film shrinkage was correlated to crystallinity level and orientation of the amorphous phase.

Randall et al.\textsuperscript{103} studied the melting points of PLAs made by SIC fabrication processes of very different time scales using DSC. At a given OP, PLA homopolymers tended to develop the same melting point during film orientation, bottle inflation, and fiber spinning.

Cicero et al.\textsuperscript{104,105} characterized the crystal morphology of fibers made with linear and branched architectures. The level of crystallinity increased with draw ratio. The morphology was fibrillar, with microfibril diameters ranging from 20 to 30 nm for both architectures. Cicero et al. noted that the orientation of the crystal blocks was similar to nylon. Two-step drawn fibers undergo a morphology transition from class 2 to class 1 within the classification proposed by Keller et al.\textsuperscript{106} at higher draw conditions.
16.5.4 Degradation and Hydrolysis

Under conditions of high temperature and high humidity, as in active compost, for example, PLA will degrade quickly and disintegrate within weeks to months. The primary mechanism of degradation is hydrolysis, followed by bacterial attack on the fragmented residues. The environmental degradation of PLA occurs by a two-step process. During the initial phases of degradation, the high molecular weight polyester chains hydrolyze to lower molecular weight oligomers. The rate of hydrolysis is accelerated by acids or bases and is dependent on moisture content and temperature. Article dimensions, crystallinity, and blends will affect the rate of degradation. PLA products rapidly degrade in both aerobic and anaerobic composting conditions:

<table>
<thead>
<tr>
<th>Stage</th>
<th>Molecular Weight</th>
<th>Rate of MW Decrease</th>
<th>Weight Loss</th>
<th>Hydrolysis Reaction</th>
<th>Degradation Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>First stage</td>
<td>High</td>
<td>Slow (rate determined)</td>
<td>None</td>
<td>Nonenzymatic</td>
<td>Bulk</td>
</tr>
<tr>
<td>Critical (Mn: 10,000 – 20,000)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second stage</td>
<td>Low</td>
<td>Rapid</td>
<td>Onset Rapid</td>
<td>Nonenzymatic and enzymatic</td>
<td>Bulk and surface</td>
</tr>
</tbody>
</table>

Under typical use conditions, PLA is very stable and will retain its molecular weight and physical properties for years. This is typified by its growing use in clothing and durable applications. High molecular weight PLA is also naturally resistant to supporting bacterial and fungal growth, which allows it to be safely used for applications such as food packaging and sanitation.

A recent review by Tsuji gives an excellent account of PLA degradation studies.

16.5.4.1 Hydrolysis

Degradation of PLA is primarily due to hydrolysis of the ester linkages, which occurs more or less randomly along the backbone of the polymer. It requires the presence of water according to the following reaction:

\[
\text{PLA} + \text{H}_2\text{O} \rightarrow \text{PLA} + \text{CH}_3 + \text{CH}_3 + \text{OH} + \text{HO} + \text{OPLA}
\]
The rate of hydrolysis is determined by its intrinsic rate constant, water concentration, acid or base catalyst, temperature, and morphology. Two major challenges to the stabilization of PLA with regard to hydrolysis are the fact that it is quite permeable to water and that the hydrolysis reaction is autocatalytic. Polyethylene terephthalate, for example, is also a polyester that hydrolyzes, but the inherent rate of hydrolysis is slower than PLA and it is not autocatalytic.

The autocatalytic hydrolysis reaction is the following:

$$R-COOH \xrightarrow{k_a} R-COO^- + H^+$$

An equation describing decrease in ester concentration \([E]\) over time is the following:

$$\frac{d[E]}{dt} = k[-COOH][H_2O] = \frac{d(1/M_n)}{dt}$$

(16.7)

for random chain scission where \([-COOH] \propto 1/M_n\) and the product \([H_2O][E]\) is constant. Rearranging to

$$M_n d(1/M_n) = k dt$$

(16.8)

the integrated form becomes

$$\ln M_{n,t} = \ln M_{n,0} - kt$$

(16.9)

where \(M_{n,t}\) = number average molecular weight at time \(t\), \(M_{n,0}\) = number average molecular weight at time zero, and \(k\) is the hydrolysis rate constant. These kinetics were derived by Pitt et al.\textsuperscript{109} and were again supported by Tsuji.\textsuperscript{108}

Siparsky et al.\textsuperscript{110} proposed a slightly different equation using an autocatalytic model:

$$\frac{d[-COOH]}{dt} = k_b[-COOH][H_2O][E]$$

(16.10)

They found that this equation did not fit their solution kinetics so they derived a second equation using quadratic autocatalysis kinetics. This model
fit the data much better. It is of the following form:

\[
\frac{dx}{dt} = k_h[E][\text{H}_2\text{O}][x]
\]

where \(x = K_a[-\text{COOH}]^{1/2}\), and \(K_a\) is the acid dissociation constant. This form accounts for the dissociation of the acid.

Stated differently,

\[
\frac{d[E]}{dt} = k_h[\text{H}_2\text{O}][E][-\text{COOH}]^{1/2}
\]

(16.11)

The expression makes it possible to take into account all the acid species in the polymer. It also removes the water dependence of the rate constant expression. A comprehensive predictive hydrolysis model for PLA autocatalysis also requires temperature dependence for \(k_h\) above and below \(T_g\), and accurate prediction of water concentration. Combining this expression with mass transfer terms for \([\text{H}_2\text{O}]\) and \([-\text{COOH}]\) as a function of position in an article may be useful for some applications.

Strategies for stabilizing PLA to hydrolysis include reducing the level of residual monomer to as low a level as possible and lowering the water concentration in PLA and preventing autocatalysis. The equilibrium moisture content can be decreased by controlling morphology (highly crystalline, oriented, fibrular structure). Reduction in the rate of autocatalysis has been accomplished by incorporation of basic, buffering salts such as CaCO\(_3\). Certain impurities and classes of additives increase the rate of PLA hydrolysis, including lactide and oligomers and some acidic and basic additives. A second approach to preventing autocatalysis was reported by Lee et al.\(^{111}\) by functionalizing the PLA end group chemistry. End groups studied included \(\text{OH}^-, \text{COOH}^-, \text{Cl}^-, \text{and NH}_2^-\) of \(\text{NH}_2^-\) and \(\text{Cl}-\) terminated PLAs were more resistant to thermal and hydrolytic degradation. The thermal stability of the \(\text{OH}\)-terminated PLA was poor (likely due to lactide formation), and the hydrolytic stability of the \(\text{COOH}\)-terminated PLA was also poor.

The hydrolysis of PLA has been studied using at least four experimental designs: melt hydrolysis (discussed in rheology section above) to simulate extrusion conditions, solution hydrolysis of PLA dissolved in various solvents, and two types of solid-state hydrolysis methods. The first type of solid-state hydrolysis experiment utilizes solid samples suspended in aqueous media. The second type utilizes exposure of solid samples to humidity. Since the product of the hydrolysis reaction is also a catalyst for further reaction, the hydrolysis of PLA is autocatalytic. Melt hydrolysis, solution hydrolysis, and solid exposure to humidity experimental designs generally give rise to homogeneous hydrolysis. In contrast, exposure of solid samples suspended in water or aqueous buffers gives rise to very inhomogeneous hydrolysis. This is due to differences in hydrolysis rate as a function of depth within the sample and it is caused by extraction of PLA oligomers from the surface of the sample into the aqueous medium. It is the chain end groups of the PLA oligomers that catalyze the rate of hydrolysis, and therefore the
inside of the sample actually hydrolyzes faster than the surface for thick samples submersed in water.

It is important that the data used for the determination of any type of stability analysis be consistent with the type of hydrolysis conditions of the intended application. In vivo degradation of PLA is outside the scope of this chapter.

Four key features mark the hydrolytic degradation of PLA:

1. The pKₐ of PLA's carboxylic acid end group and its oligomers is unusually low (~3) compared to most carboxylic acid groups (4.5 to 5). PLA's carboxylic acid end groups catalyze the ester hydrolysis, which generally leads to a faster rate of degradation as the polymer degrades (autocatalysis).
2. Two reaction mechanisms apparently occur. The first is a random chain scission and the second a chain-end hydrolysis. The chain-end scission is about 10 times faster than the random scission reaction at low pH values but is negligible at neutral and basic pH values. The number of ester groups along the chain is much greater than that of the chain ends and is statistically much more important.
3. The crystalline regions hydrolyze much more slowly than the amorphous regions.
4. The rate of hydrolysis (slope) is much greater above the glass transition temperature \((T_g)\) than below.

In the following, we summarize each of the four hydrolysis experimental design conditions independently. Melt hydrolysis is covered in the rheology section pertaining to melt stability.

16.5.4.2 Hydrolysis of Solid Samples Suspended in Aqueous Media

Hydrolytic degradation of PLA is autocatalytic due to the production of carboxylic acid end groups that catalyze further hydrolysis. An effect of this is that for a thick sample immersed in a 7.4 pH buffer at 37°C, bulk hydrolysis occurs faster than surface hydrolysis. The pH of the surface remains that of the 7.4 pH buffer whereas the pH of the interior of the sample is reduced due to the accumulation of PLA acid end groups and the inability of the oligomers to quickly diffuse into the buffer medium.

Vert et al. summarized the literature on the hydrolytic stability of solid, suspended PLA in 1997 and captured several key points including autocatalysis and leaching effects. In addition, morphology and structure were addressed. The rate of degradation is strongly influenced by the number average molecular weight. Lower \(M_n\), PLA degraded faster as did PLA with higher levels of oligomers. The presence of lactide also increased the rate of hydrolytic degradation. Effects of \(M_n\) oligomers, and lactide can all be attributed to autocatalysis. PLA’s amorphous domains are more susceptible to hydrolysis than the crystalline domains. This is due to the ability of
water to permeate within the amorphous phase but not the crystalline phase, 
and leads to differences in water concentration throughout the article on the 
microscale. Hydrolysis of the crystalline domain occurs mainly by a surface 
erosion mechanism.

Grizzi et al. used the fact that surface hydrolysis is slow compared to bulk 
hydrolysis to stabilize PLA to hydrolysis simply by using small dimen-
sions.\textsuperscript{113} By suspending PLA samples of varying size in water and determin-
ing the rates of hydrolysis, they showed that leaching could be used to slow 
down the rate of solid-state hydrolysis. They estimated that the skin, which 
was formed due to the leaching of catalytic oligomers, was about 200 to 
300 $\mu$m in thickness. Samples smaller than this size were found to degrade 
much more slowly than large samples.

The heterogeneity of the process makes it difficult to determine hydrolysis 
kinetics constants for solids suspended in aqueous media. Translation of data 
from these kinds of studies to other environments is suspect for this reason.

In alkaline media, Iwata and Doi\textsuperscript{118} studied the change in morphology 
and crystalline state of solution-grown single crystals of PLLA. Samples were 
characterized by transmission electron microscopy (TEM), atomic force 
microscopy (AFM), and gel permeation chromatography (GPC). As hydrol-
ysis proceeded, the molecular weight of the degraded crystals corresponded 
to the value calculated from lamellar thickness measured by AFM. The 
explanation for this is that the PLA first degrades in the more loosely packed 
chain folding regions. In the later stages of hydrolysis, the more persistent 
crystalline region’s molecular weight approaches that of the lamellar thick-
ness, and the degradation mechanism will change to that of surface erosion.

Tsuji and Nakahara\textsuperscript{119} tested PLLA films at pH 2.0 (1. HCl solution, 
2. D,L-lactic acid solution), 7.4 (phosphate buffered), and 12 (NaOH soln). 
While the alkaline media degraded faster than the neutral pH control, the 
samples in acid media degraded at about the same rate as the neutral pH con-
trol. Using microcapsules suspended in buffer solutions, Makino et al.\textsuperscript{120} 
showed that PLA degrades slowest at pH 5.0 and increases in acidic and alka-
line solutions. The activation energy of hydrolysis at pH 7.4 and ionic strength 
0.15 was 19.9 kcal/mol for PDLLA microcapsules and 20.0 kcal/mol for PLLA 
microcapsules when the initial $M_w$ was about 100,000 for both polymers.

The degradation characteristics of PLA in seawater are important for cer-
tain applications and potential disposal routes. Yuan et al.\textsuperscript{121} tested PLLA 
fibers in saline buffer at 37°C for molecular weight loss and mechanical 
properties. The results suggested that the tensile properties of the PLLA 
fibers were stable for 35 weeks, even though their molecular weights 
decreased remarkably and obvious spotty defects appeared on their sur-
faces. Tsuji and Suzuyoshi\textsuperscript{122} showed that PLA degraded faster in natural 
seawater than controlled static seawater, although the rate of molecular 
weight loss is slow. Makino et al.\textsuperscript{120} showed that AlCl$_3$, CaCl$_2$, and KCl had 
no or little effect on the degradation rate.

At temperatures above the glass transition, PLA’s degradation rate increases 
substantially. Tsuji et al.\textsuperscript{123} tested PLLA films in buffers at 97°C and showed
that the hydrolysis takes place predominantly and randomly at the chains in the amorphous region. Amorphous samples crystallized while degrading and higher initial crystallinity slightly slowed the rate of hydrolysis.

In a very extreme case showing the effect of morphology, fibers (drawn to a draw ratio of about $8 \times$ using a solution spinning approach) were examined. These fibers possessed few defects (chain folds, microvoids) together with high crystallinity, low fractional free volume, and small cross-sectional dimension. The PLLA fiber was very stable over a 5-year period immersed in water at room temperature under a static load and lost 10% of its diameter and less than 25% of its tensile strength. The perfection of morphology was thought to reduce the penetration and diffusion of water into the fiber.

Effects of processing conditions were also examined by Iannace et al. Samples of PLLA crystallized under isothermal and nonisothermal conditions were prepared. Initial morphology developed during the isothermal crystallization affected the rate of hydrolysis in buffer solutions. Larger crystals developed at higher $T_c$ were more resistant to erosion compared to less perfect and smaller crystals developed at higher degrees of supercooling.

Tsuji and Suzuki also studied stereocomplex degradation over the course of 30 months, in 7.4 pH buffer solution using 1:1 blends and nonblended films prepared from PLLA and PDLA. Properties and molecular weight were monitored with GPC, tensile tests, DSC, SEM, optical polarizing microscopy, x-ray diffractometry, and gravimetry. The rate of molecular weight loss, tensile strength, Young’s modulus, melting temperature, and mass remaining of the films in the course of hydrolysis was more stable for the stereocomplex film than for the nonblended films.

16.5.4.3 Solution Hydrolysis

Solution hydrolysis is generally thought to occur by random scission of the ester linkages in PLA. It has been reported, however, that base and neutral hydrolysis occur by random chain scission but acid hydrolysis occurs by a mixture of two mechanisms, random and chain-end scission, with chain-end scission being the faster. This was determined in dioxane/water solution with $^1$H NMR and GPC using a statistical method where the level of lactic acid produced by hydrolysis is compared to the degree of degradation across the entire molecular weight distribution. The chain-end scission is sometimes referred to as “unzipping.”

PLA solution hydrolysis was also studied in acetone/water by Zhang et al. and acetonitrile/water by Siparsky et al. The latter solvent had a much higher dielectric constant ($\varepsilon = 36$) than acetone ($\varepsilon = 21$) or dioxane ($\varepsilon = 2$) so that the carboxylic acid groups were more ionized, as in water ($\varepsilon = 79$). Autocatalysis was observed in acetonitrile whereas it was not in the lower dielectric solvents due to a lower extent of ionization of the carboxylic acid.

The solution hydrolysis rate constant (in dioxane solution) did not depend on the optical purity (OP) of the polymer whereas it does in solid-state degradation (probably due to crystallinity differences). CaCO$_3$ was
observed to slow the rate of hydrolysis due to its buffering capacity and water insolubility.

16.5.4.4 Hydrolysis of Samples Exposed to Humidity

Samples exposed to temperature and humidity best simulate the shelf-life environment for many PLA applications. The equilibrium moisture level as a function of humidity is known for PLA at room temperature. It has not been as thoroughly studied for elevated temperatures. Hydrophilic impurities such as lactide and carboxylic acid end groups, whose concentration increase as degradation proceeds, increase the level of moisture.

Sharp et al. measured the water uptake of PDLLA using a quartz crystal microbalance in humid environments at various temperatures. Kinetics of water adsorption and equilibrium concentrations were measured, and the Flory Huggins interaction parameter $X$ was found to be 3.5 at 20°C using binary mixing theory. The equilibrium swell level of water in PLA increases with decreasing molecular weight due to the strong affinity of acid and hydroxyl end groups for water. It was also shown that the $T_g$ of high molecular weight PLA was depressed by 11°C at 7000 ppm water (the highest level of swelling studied) compared to zero ppm water.

Witzke measured the swelling concentrations of water in PLA using Karl-Fisher coulometric titration and arrived at an empirical model fit for estimating swell concentration:

\[
\text{Water (ppm)} = 40.8\text{RH(\%)} + 6.6 \times 10^{-7}\text{RH(\%)}^5
\]

where water is in parts per million by weight and RH is the relative humidity. A plot of this equation is shown in Figure 16.14.

![Figure 16.14](image-url)

Equilibrium swelling concentration of water in high molecular weight PLA in humid environments.
Crystalline pellets reach an equilibrium level of moisture much more slowly (by a factor of 2.4) than amorphous pellets, and crystalline pellets dry 1.5 times slower than amorphous pellets due to differences in water diffusion. However, Siparsky et al. found that once PLA was equilibrated with moisture, crystallinity had little effect on the solubility or diffusion constant of water. They also showed that the diffusion of water in PLA is much faster than the rate of hydrolysis in the temperature range between 20° and 50°C.

Li and McCarthy found that the water absorption of PLA increased markedly as the hydrolysis proceeded, presumably due to the production of the more hydrophilic acid and alcohol end groups. Others substantiated this point. Two distinct populations of absorbed water were observed for poly(D,L-lactide-co-glycolide), one bound and one mobile. The rate of hydrolysis of the copolymer correlated with the level of bound water.

The rate of hydrolysis increases markedly above T_g. Compost studies on PLA articles show that at temperatures above the T_g, the rate of hydrolysis is fast enough to completely consume articles in a matter of months. Results of a Cargill Dow LLC internal study showing M_w loss over time at various aggressive storage conditions are shown in Figure 16.15.

Lactide has a large effect on hydrolytic degradation in humid environments because it rapidly hydrolyzes to a relatively strong acid, which promotes hydrolysis. At high levels (>2%) the presence of lactide has a dramatic effect on PLA molecular weight loss. Acidic or basic additives catalyze the rate of PLA hydrolysis. MgSO_4 and SiO_2 promoted degradation whereas CaCO_3 inhibited hydrolytic degradation. Li and Vert showed that the presence of porous coral in a blend with PLA (60% coral) dramatically reduced the rate of PLA degradation by neutralizing the effect of autocatalysis.

![FIGURE 16.15](image)

Cargill Dow LLC internal study showing molecular weight loss for amorphous PLA stored at various aggressive temperatures and humidity.
The crystalline regions of PLA were found to hydrolyze very slowly.\textsuperscript{112,125} The rate of molecular weight loss follows a two-step process, the first occurring very fast (interpreted as loss of the amorphous phase) and the second occurring much slowly (interpreted as loss of the crystalline phase). The apparent percentage of crystallinity increases during the amorphous phase hydrolysis, consistent with the interpretation. The molecular weight of the remaining PLA after the amorphous phase was degraded was about 5000 to 9000 (DP = 70 to 125), roughly that of the fold length of the lamella.\textsuperscript{74,137} Crystalline injection-molded samples lost physical properties faster than amorphous samples, although the rate of $M_w$ loss was similar between them.\textsuperscript{125} This was interpreted as the loss of amorphous tie chains between the crystals causing catastrophic failure of the system. Also, chain folds and tie chains connecting crystallites are thought to hydrolyze preferentially because they are stressed due to a "reeling in" force.\textsuperscript{138} These observations may be the result of chain end groups and catalysts concentrating in the amorphous regions.

Morphology also affects water permeation in another way. Microvoids or porosity allow water to migrate more freely into the material and thereby enhance the rate of hydrolysis. This is probably a small effect for samples exposed to humidity because the rate of hydrolysis is slow compared to the water diffusion rate, as discussed above. Localized regions of high water absorption may cause mechanical stresses due to increased osmotic pressure.

### 16.5.5 Enzymatic Degradation

Several enzymes have been shown to catalyze PLA hydrolysis. Enzymatic hydrolysis of PLLA with varied crystal morphologies was studied using proteinase K by Tsuji and Miyauchi.\textsuperscript{139,140} It was concluded that the enzymatic degradation proceeded via mainly a surface erosion mechanism. Amorphous regions hydrolyzed more readily than crystalline regions. The enzymatic hydrolysis rate ($R_{EH}$) was modeled using the following equation:

$$R_{EH}(\mu g/(mm^2\cdot h)) = 0.36(1 - x_c)$$  \hspace{1cm} (16.13)

where $x_c$ = the fraction of crystalline PLLA. Tie chains degraded more readily than folds or restricted amorphous chains.

### 16.6 Applications and Performance

Since PLA is an environmentally friendly polymer that can be designed to controllably biodegrade, it is ideally suited for many applications in the environment where recovery of the product is not practical, such as agricultural
mulch films and bags. Composting of post-consumer PLA items is also a viable solution for many PLA products. However, the large growth seen for PLA in many applications does not depend upon the biodegradability of the material.

PLA resins can be tailor-made for different fabrication processes, including injection molding, sheet extrusion, blow molding, thermoforming, film forming, or fiber spinning. The key is controlling certain molecular parameters in the process such as branching, D-isomer content, and molecular weight distribution. The ability to selectively incorporate L-, D-, or meso-lactide stereoisomers into the polymer backbone allows PLA to be tailored for specific applications. The ease of incorporation of various defects into PLA allows for control of both crystallization rate and ultimate crystallinity.

Typical properties of NatureWorks PLA from Cargill Dow LLC for injection molding and extrusion applications are given in Table 16.6. The various grades of NatureWorks PLA differ in stereochemical purity, molecular weight, and additive packages. Each grade is optimized for both processing and end use performance in its intended application.

**TABLE 16.6**

Properties of Extrusion/Thermoforming and Injection Molding Grades of NatureWorks PLA

<table>
<thead>
<tr>
<th>PLA Polymer 2000D&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ASTM Method</th>
<th>PLA Polymer 3010D&lt;sup&gt;b&lt;/sup&gt;</th>
<th>ASTM Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity (g/cc)</td>
<td>1.25</td>
<td>1.21</td>
<td>D792</td>
</tr>
<tr>
<td>Melt index, g/10 min (190°C/2.16 kg)</td>
<td>4–8</td>
<td>10–30</td>
<td>D1238</td>
</tr>
<tr>
<td>Clarity</td>
<td>Transparent</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>Tensile strength at break, 7,700 (53) D882</td>
<td>7,000 (48) D638</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile yield strength, 8,700 (60) D882</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile modulus, 500 (3.5) D882</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile elongation (%)</td>
<td>6.0</td>
<td>2.5</td>
<td>D638</td>
</tr>
<tr>
<td>Notched izod impact, 0.24 (0.33) D256</td>
<td>0.3 (0.16) D256</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexural strength, 12,000 (83) D790</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexural modulus, 555 (3.8) D790</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> 2000D is a product of Cargill Dow LLC designed as an extrusion/thermoforming grade; properties typical of extruded sheet.

<sup>b</sup> 3010D is a product of Cargill Dow LLC designed as an injection molding grade; properties typical of injection molded tensile bars.
Injection molding of heat-resistant products requires rapid crystallization rates that can be achieved by PLA, typically containing less than 1% D-isomer and often with the addition of nucleating agents. These compositions allow high levels of crystallinity to develop during the fast cooling cycle in the mold. Extrusion-thermoforming is optimized at a D-isomer content that does not allow crystallization to occur during the melt processing steps, with 4–8% D-content being the effective range. Branching can be introduced by a variety of methods, thus enhancing melt strength during fabrication and opening up new application opportunities in the areas of foams and extrusion coating. Examples of a number of articles fabricated from PLA are shown in Figure 16.16. In short, the rheological characteristics and physical properties of PLA can be tailored for use in a variety of processes and applications.

Fiber is one of the largest potential application areas for PLA. PLA is readily melt spinnable, stress crystallizes upon drawing, and can be designed for

FIGURE 16.16
Articles produced from PLA. (a) Injection stretch-blow molded bottles. (b) Films. (c) Extrusion-thermoformed containers. (d) Fiberfill products. (e) Carpet and coverings.
TABLE 16.7
Properties of NatureWorks PLA Fabricated into Fibers

<table>
<thead>
<tr>
<th>Material Properties</th>
<th>PLA Polymer 6700D&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PLA Polymer 6200D&lt;sup&gt;b&lt;/sup&gt;</th>
<th>ASTM Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.25–1.28</td>
<td>1.25–1.28</td>
<td>D792</td>
</tr>
<tr>
<td>Melt density, 230°C (445°F)</td>
<td>1.08–1.12</td>
<td>1.08–1.12</td>
<td>D1238</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt; °C (°F)</td>
<td>55–60 (130–140)</td>
<td>60–65 (140–150)</td>
<td>D3417</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt; °C (°F)</td>
<td>145–155 (295–310)</td>
<td>160–170 (320–340)</td>
<td>D3418</td>
</tr>
<tr>
<td>Melt flow rate, 210°C (410°F)</td>
<td>5–15</td>
<td>15–30</td>
<td>D1238 A &amp; B</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fiber Properties</th>
<th>Monofilament</th>
<th>Cotton-Type</th>
<th>POY&lt;sup&gt;c&lt;/sup&gt;</th>
<th>FDY&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Denier (dpf)</td>
<td>512</td>
<td>1.5</td>
<td>475</td>
<td>3.04</td>
</tr>
<tr>
<td>Total denier/filament count</td>
<td>staple/ N.A.</td>
<td>114/24</td>
<td>73/24</td>
<td>D1907</td>
</tr>
<tr>
<td>Strength (kg)</td>
<td>2.9</td>
<td>5.7</td>
<td>2.8</td>
<td>57</td>
</tr>
<tr>
<td>Tenacity (g/den)</td>
<td>5.75</td>
<td>5.7</td>
<td>2.8</td>
<td>57</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>26.2</td>
<td>35</td>
<td>61</td>
<td>29</td>
</tr>
<tr>
<td>Boiling water shrinkage (%)</td>
<td>0</td>
<td>21</td>
<td>&lt;10</td>
<td>D2102</td>
</tr>
</tbody>
</table>

<sup>a</sup> 6700D is a product of Cargill Dow LLC designed for extrusion into mechanically drawn monofilament.

<sup>b</sup> 6200D is a product of Cargill Dow LLC designed for extrusion into mechanically drawn staple fibers or continuous filaments.

<sup>c</sup> Partially Oriented Yarn (POY).

<sup>d</sup> Fully Drawn Yarn (FDY).
many fiber applications. Some of the current fiber uses include hollow fiber-fill for pillows and comforters, bulk continuous filament (BCF) for carpet, filament yarns, and spun yarns for apparel, spunbond, and other nonwovens and bicomponent fibers for binders and self-crimping fibers. Most fiber applications require polymer with high optical purity (OP) to allow high levels of crystallinity to develop and to have adequate heat resistance in the application. Binder fibers are unique in that low crystallinity in the sheath layer is desired to allow ease of melting and adhesion to other fibers; thus, high (8–20%) D- or meso-lactide content is incorporated. PLA can be processed on standard thermoplastic fiber spinning equipment with the appropriate temperature profiles relative to its crystal melting point. Melt temperatures of 200°–240°C are typically used. As with all melt processing of PLA, care must be taken to ensure that the material is dry and does not pick up moisture, otherwise unacceptable molecular weight loss will occur. Typical drying conditions are 2–4 h in a hopper dryer with –40°C dew point air with a resulting moisture content of less than 50 ppm. Some of the properties of PLA fibers are shown in Table 16.7 and compared to other natural and synthetic fibers in Table 16.8.

PLA fiber can be combined with natural or regenerated fibers including cotton, wool, silk, viscose, lyocell, and others along with synthetic fibers made from PET, nylon, and other petroleum-based synthetics. PLA can be included as a minor component (5–15%) or as the major fiber, depending on the balance of properties and appearance desired. One of the fastest growing application areas is in nonwoven wipes containing 35% PLA and 65% viscose. PLA is replacing PET in these applications because of its superior performance and the fact that the disposable products can be produced from fibers that are from 100% renewable resources and are also 100% biodegradable.

Some of the beneficial characteristics of PLA fiber products include its natural soft feel, ease of processing, and unique stain and soil resistance. PLA excels at resistance to stain in standard tests with coffee, cola, tea, catsup, lipstick, and mustard. PLA also burns with low smoke generation, has good ultraviolet resistance, is easily dyeable, and brings good wickability of moisture to applications.

**TABLE 16.8**

Properties of Synthetic and Natural Fibers

<table>
<thead>
<tr>
<th>Fiber Property</th>
<th>Nylon 6</th>
<th>PET</th>
<th>Acrylics</th>
<th>PLA</th>
<th>Rayon</th>
<th>Cotton</th>
<th>Silk</th>
<th>Wool</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>1.14</td>
<td>1.39</td>
<td>1.18</td>
<td>1.25</td>
<td>1.52</td>
<td>1.52</td>
<td>1.34</td>
<td>1.31</td>
</tr>
<tr>
<td>Tenacity (g/d)</td>
<td>5.5</td>
<td>6.0</td>
<td>4.0</td>
<td>6.0</td>
<td>6.0</td>
<td>4.0</td>
<td>4.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Moisture regain (%)</td>
<td>4.1</td>
<td>0.2–0.4</td>
<td>1.0–2.0</td>
<td>0.4–0.6</td>
<td>11</td>
<td>7.5</td>
<td>10</td>
<td>14–18</td>
</tr>
<tr>
<td>Elastic recovery (5% strain)</td>
<td>89</td>
<td>65</td>
<td>50</td>
<td>93</td>
<td>32</td>
<td>52</td>
<td>52</td>
<td>69</td>
</tr>
<tr>
<td>Flammability</td>
<td>Medium high smoke</td>
<td>Medium low smoke</td>
<td>Burns</td>
<td>Burns</td>
<td>Burns</td>
<td>Burns slowly</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV resistance</td>
<td>Poor</td>
<td>Fair</td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
<td>Fair</td>
<td>Fair</td>
<td>Fair</td>
</tr>
</tbody>
</table>
Films are the second largest application area for PLA. Again, the ability to modify the crystallization kinetics and physical properties for a broad range of applications by D- or meso-comonomer incorporation, branching, and molecular weight change makes PLA extremely versatile. Films are transparent when stress crystallized and have acceptance by customers for food contact. PLA films can be prepared by the blown double bubble technology or preferably, cast-tentering. Cast-tentered films have very low haze, excellent gloss, and gas (O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O) transmission rates desirable for consumer food packaging. PLA films also have superior dead fold or twist retention for twist wrap packaging. Some of the properties of PLA films are shown in Table 16.9.

### TABLE 16.9
Properties of Biaxially Oriented NatureWorks PLA

<table>
<thead>
<tr>
<th>Film Properties</th>
<th>PLA Polymer 4040D&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ASTM Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity (g/cc)</td>
<td>1.25</td>
<td>D1505</td>
</tr>
<tr>
<td>Tensile strength (kpsi)</td>
<td>16</td>
<td>D882</td>
</tr>
<tr>
<td>Tensile modulus (kpsi)</td>
<td>480</td>
<td>D882</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>160</td>
<td>D882</td>
</tr>
<tr>
<td>Elendorf tear (g/mil)</td>
<td>15</td>
<td>D1922</td>
</tr>
<tr>
<td>Spencer impact (J)</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Transmission rates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;, cc-mil/m²/24 h atm</td>
<td>550</td>
<td>D1434</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;, cc-mil/m²/24 h atm</td>
<td>3000</td>
<td>D1434</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O, g-mil/m²/24 h atm</td>
<td>325</td>
<td>E96</td>
</tr>
<tr>
<td>Optical characteristics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haze (%)</td>
<td>2.1</td>
<td>D1003</td>
</tr>
<tr>
<td>Gloss, 20°</td>
<td>90</td>
<td>D1003</td>
</tr>
<tr>
<td>Thermal characteristics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T&lt;sub&gt;(0)&lt;/sub&gt;, °C (°F)</td>
<td>52 (126)</td>
<td>D3418</td>
</tr>
<tr>
<td>T&lt;sub&gt;(m)&lt;/sub&gt;, °C (°F)</td>
<td>135 (275)</td>
<td>D1003</td>
</tr>
</tbody>
</table>

<sup>a</sup> 4040D is a product of Cargill Dow LLC suitable for preparation of biaxially oriented film. Properties on 1 mil film oriented 3.5× in MD and 5× in TD.

<sup>b</sup> MD refers to machine direction and TD refers to transverse direction.

Films are the second largest application area for PLA. Again, the ability to modify the crystallization kinetics and physical properties for a broad range of applications by D- or meso-comonomer incorporation, branching, and molecular weight change makes PLA extremely versatile. Films are transparent when stress crystallized and have acceptance by customers for food contact. PLA films can be prepared by the blown double bubble technology or preferably, cast-tentering. Cast-tentered films have very low haze, excellent gloss, and gas (O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O) transmission rates desirable for consumer food packaging. PLA films also have superior dead fold or twist retention for twist wrap packaging. Some of the properties of PLA films are shown in Table 16.9.

### 16.7 Summary
Polymers of polylactic acid have finally become a commercial reality with the construction of a world-scale plant. The cost-performance balance of PLA has
resulted in its use in many applications, including packaging, paper coating, fibers, films, and a host of molded articles. PLA is not being used in these applications solely because of its degradability nor because it is made from renewable resources. PLA is in both durable and short-term applications. The use of PLA as a cost-effective alternative to commodity petrochemical-based plastics will increase demand for agricultural products such as corn and sugar beets, and is an advanced example of sustainable technology.

One of the additional benefits of large commercial production of lactic acid for PLA is the increased availability and reduced cost of lactic acid or lactide for the production of lactic acid esters. These esters, especially ethyl lactate, are finding increased use as environmentally friendly solvents, cleaning agents, and diluents. They are replacing more hazardous solvents such as chlorinated organic and aromatic compounds.

As we move into the 21st century, increased utilization of renewable resources will be one of the strong drivers for sustainable products. Reduced energy consumption, waste generation, and emission of greenhouse gases will take on greater emphasis. Polylactic acid is the first commodity plastic to incorporate these principles and Cargill Dow LLC was awarded the 2002 Presidential Green Chemistry Award for their process to produce NatureWorks PLA. Future developments will include blends of PLA, copolymers, and impact-modified products, which will further expand the applications where this unique polymer can be used.

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