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6.1 Introduction

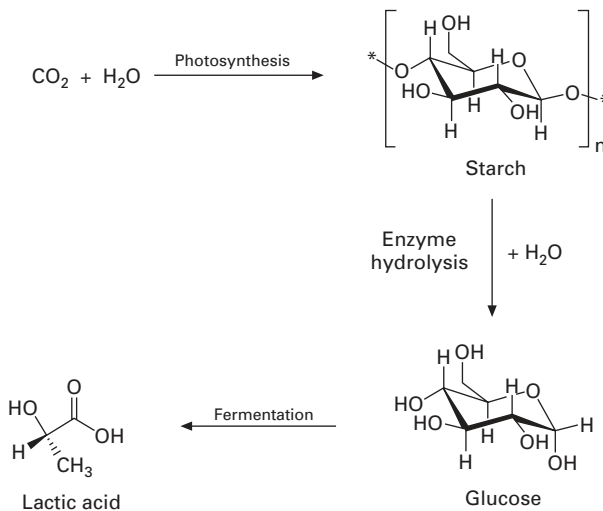
In a world that is becoming increasingly sensitive to the need to protect our environment, the ability to manufacture products from sustainable resources and which are fully compostable at the end of their useful life, is an exciting and attractive proposition. Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic polyester derived from 100% renewable sources such as corn, and the polymer is compostable.^{1,2} However, most initial uses were limited to biomedical applications such as sutures³ and drug delivery systems⁴ due to availability and cost of manufacture. Over the past few years, NatureWorks LLC has developed large-scale operations for the economic production of PLA polymer used for packaging and fiber applications. It is important that PLA is used broadly in textile applications for several reasons. Polyesters currently used for apparel and related fiber applications, mainly poly(ethyleneterephthalate) (PET), account for over 40% of world textile consumption (second only to cotton) and their use is constantly increasing. Production of such polyesters consumes fossil fuel resources and disposal of the polymer adds to landfill sites as they are non-biodegradable and are not easily recycled. In contrast, PLA fiber is derived from annually renewable crops, it is 100% compostable and its life cycle potentially reduces the Earth's carbon dioxide level. The recognition by the FTC in the USA and the EU commission that PLA fibers are a completely new generic class of synthetic fibers further reinforces the validity of this new approach to producing performance melt-spinnable fibers.

This chapter will review the chemistry of PLA and will discuss the commercial manufacturing process that confirms its position as a viable material for many applications in both the fibers and the plastics industries. It will review the various properties of the polymer and consider the fiber properties that make it attractive to the commercial sectors into which it is being developed today. Recognizing that this is very much a new polymer with its own characteristics and processing requirements, the current status

of the downstream technologies in these sectors will be appraised. The environmental benefits of PLA will be discussed and compared with the current petroleum-based polymers. The potential for further improvements in the environmental impact will be considered as the technologies for this new polymer are advanced.

6.2 Chemistry and manufacture of PLA polymer resin

Conventional synthetic polymers rely on reserves of oil and gas for their monomer source and energy to manufacture. These reserves of fossil fuel take millions of years to regenerate and are a declining resource. In contrast, the monomer used to manufacture poly(lactic acid) is obtained from annually renewable crops. Energy from the sun promotes photosynthesis within the plant cells; carbon dioxide and water from the atmosphere are converted into starch. This starch is readily extracted from plant matter and converted to a fermentable sugar (e.g. glucose) by enzymatic hydrolysis. The carbon and other elements in these natural sugars are then converted to lactic acid through fermentation (Fig. 6.1).^{5,6}



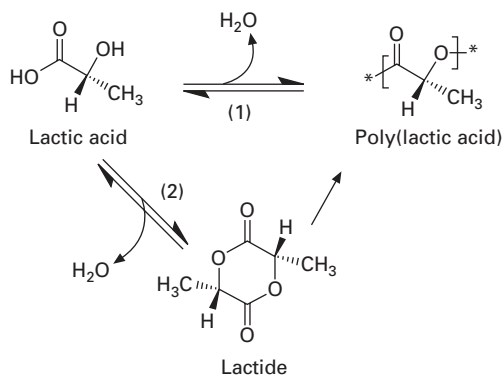
6.1 Production of lactic acid from renewable resources.

Presently, the cheapest and most abundant source of sugar is dextrose (glucose) from corn. The land mass necessary for feedstock production is minimal. Producing 500,000 tonnes of PLA requires less than 0.5% of the

annual US corn crop;⁷ since corn is a cheap dextrose source, the current feedstock supply is more than adequate to meet foreseeable demand. Furthermore, there are many other alternatives for the starch or sugar supply. As fermentation techniques improve, as PLA production improves, and if PLA production extends to other geographies, it is quite likely that other materials such as grass and even biomass could be used; there is no need to be reliant on food crops. PLA takes advantage of a biological system to do chemistry that traditional chemical techniques cannot.

6.2.1 Production of PLA

The polymer is formed either by (1) direct condensation of lactic acid or (2) via the cyclic intermediate dimer (lactide), through a ring opening process (Fig. 6.2).²



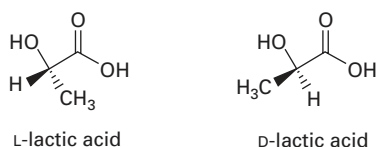
6.2 Polymerization routes to poly(lactic acid).

Polycondensation of lactic acid

This process involves the removal of water by condensation and the use of solvent under high vacuum and temperature; the approach was originally used by Carothers who discovered PLA in 1932. With this route, only low to intermediate molecular weight polymers can be produced, mainly due to the difficulties of removing water and impurities. Other disadvantages of this route are the relatively large reactor required, the need for evaporation, recovery of the solvent and increased color and racemization. Most work has focused on the ring-opening polymerization, although Mitsui Toatsu Chemicals have patented an azeotropic distillation using a high boiling solvent to drive the removal of water in the direct esterification process to obtain high molecular weight PLA.

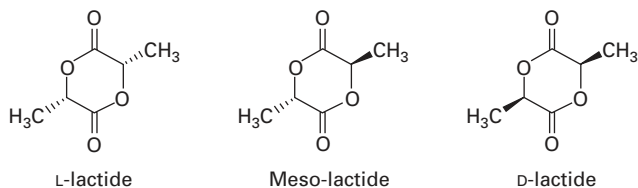
Ring-opening polymerization

This method is a better way to produce a high molecular weight polymer, and has now been adapted commercially due to advances in the fermentation of corn dextrose which have significantly reduced lactic acid production costs. The fermentation of sugar produces chiral lactic acid inexpensively in high yield. Chiral molecules exist as ‘mirror images’ or stereoisomers; lactic acid can exist as the L- or D-stereoisomer (Fig. 6.3). Chemically synthesized lactic acid gives the racemic mixture (50% D and 50% L), however, fermentation is very specific, allowing the production of essentially one major stereoisomer; fermentation derived lactic acid consists of 99.5% of the L-isomer and 0.5% of the D-isomer.



6.3 The stereoisomers of lactic acid.

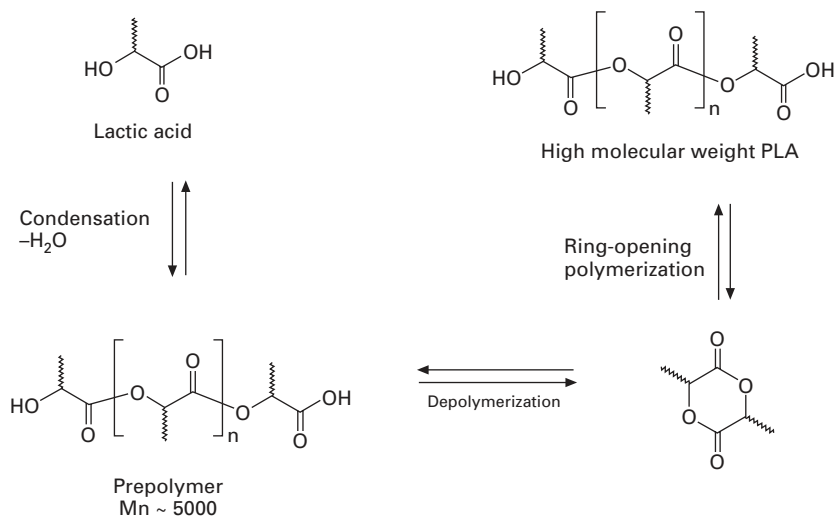
The process is based on removing water under milder conditions, without solvent, to produce a cyclic intermediate dimer, referred to as lactide. This monomer is readily purified under vacuum distillation. Ring-opening polymerization of the dimer is accomplished under heat, again without the need for solvent. By controlling the purity of the dimer, it is possible to produce a wide range of molecular weights. Production of the cyclic lactide dimer results in three potential forms: the D,D-lactide (called D-lactide), L,L-lactide (called L-lactide) and L,D- or D,L-lactide (called meso-lactide) (Fig. 6.4). Meso-lactide has different properties from D- and L-lactide; D- and L-lactide are optically active, meso- is not. Before polymerization, the lactide stream is split into a low D-lactide stream and a high D-/meso-lactide stream. Ring-opening polymerization of the optically active types of lactide can yield a ‘family’ of polymers with a range of molecular weights by varying the amount and the sequence of D-lactide in the polymer backbone. Polymers with high L-lactide levels can be used to produce crystalline polymers



6.4 Dimeric lactide isomers.

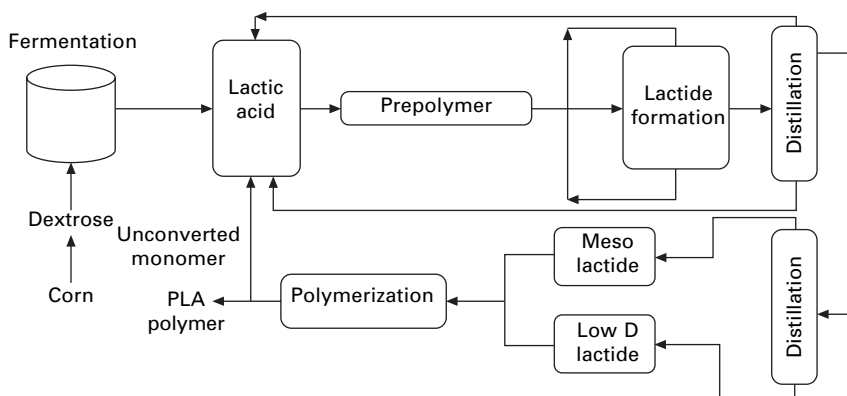
while the higher D-lactide materials (>15%) are more amorphous. By controlling the purity of the lactide it is possible to produce a wide range of molecular weights and by varying the amount and sequence of D-lactic units in the polymer backbone, the product properties can be changed. These changes impact melt behavior, thermal properties, barrier properties, and ductility.⁸

Based on this lactide intermediate method, NatureWorks LLC has developed a patented, low cost continuous process for the production of lactic acid-based polymers.⁹ 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 compostable commodity polymer made from annually renewable resources. The process starts with a continuous condensation reaction of aqueous lactic acid to produce low molecular weight PLA pre-polymer (Fig. 6.5).



6.5 Production of high molecular weight PLA via prepolymer and lactide.

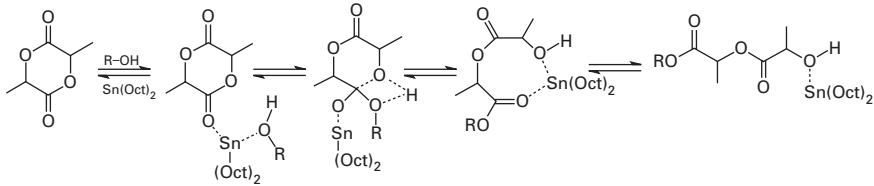
Next, the pre-polymer is converted into a mixture of lactide stereoisomers using tin catalysis to enhance the rate and selectivity of the intramolecular cyclization reaction. The molten lactide mixture is then purified by vacuum distillation. Finally, PLA high polymer is produced using a tin-catalyzed, 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 (Fig. 6.6).



6.6 Non-solvent process to prepare poly(lactic acid).

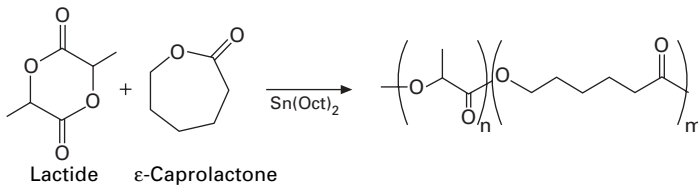
6.2.2 Catalytic polymerization of lactide

Many catalyst systems have been evaluated for the polymerization of lactide including complexes of aluminum, zinc, tin, and lanthanides. Metal alkoxides are the most common metal-containing species for the ring-opening polymerization of cyclic esters. Simple sodium, lithium, and potassium alkoxides are effective, however, the high basicity of these ionic species leads to side reactions such as epimerization of chiral centers in the polymer backbone. Alternatively, covalent metal alkoxides are much more selective and therefore widely used. Initiators such as Al-alkoxides,¹⁰ yttrium and lanthanide alkoxides,¹¹ and recently iron alkoxides¹² have been shown to give a controlled and living polymerization of lactides via a so-called coordination–insertion mechanism with ring opening of the lactide to add two lactic acid molecules to the growing end of the polymer chain. Depending on the catalyst system and reaction conditions, almost all conceivable mechanisms (cationic,¹³ anionic,¹⁴ coordination,^{15,16} 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 ($\text{Sn}(\text{Oct})_2$), 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; the mechanism is also via a coordination–insertion mechanism⁷ (Fig. 6.7). Conversions of >90% and less than 1% racemization can be obtained while providing polymer with high molecular weight. High molecular weight polymer, good reaction rate, and low levels of racemization are observed with $\text{Sn}(\text{Oct})_2$ catalyzed polymerization of lactide. Typical conditions for polymerization are 180–210°C, $\text{Sn}(\text{Oct})_2$ concentrations of 100–1000 ppm, and 2–5 hours to reach *circa* 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.



6.7 Generalized coordination–insertion chain growth mechanism of lactide to PLA; R = growing polymer chain.

Copolymers of lactide with other cyclic monomers such as ϵ -caprolactone¹⁷ can be prepared using similar reaction conditions (Fig. 6.8). These monomers can be used to prepare random copolymers or block polymers because of the end growth polymerization mechanism. Cyclic carbonates, epoxides and morphinediones have also been copolymerized with lactide.



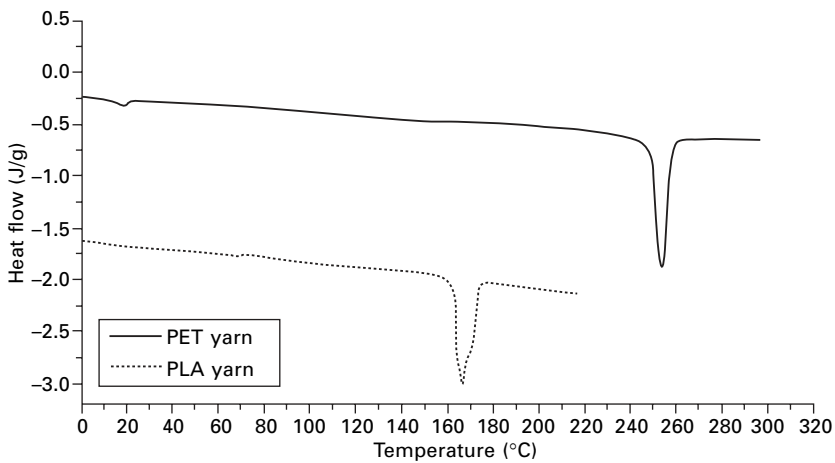
6.8 Copolymerization of lactide and caprolactone.

6.3 PLA fiber properties

PLA fiber has a number of characteristics that are similar to many other thermoplastic fibers, such as controlled crimp, smooth surface and low moisture regain. One unique property in comparison is that it is the only melt-processable fiber from annually renewable natural resources. The physical properties and structure have been studied by several researchers,¹⁸ and these works confirmed that this polymer has significant commercial potential as a textile fiber. Its mechanical properties are considered to be broadly similar to those of conventional PET,¹⁹ and, probably due to its lower melting and softening temperatures, comparisons to polypropylene are also appropriate²⁰. A résumé of the properties is given, although further detail about specific properties will be covered, as appropriate in Section 6.4, 'PLA Applications':

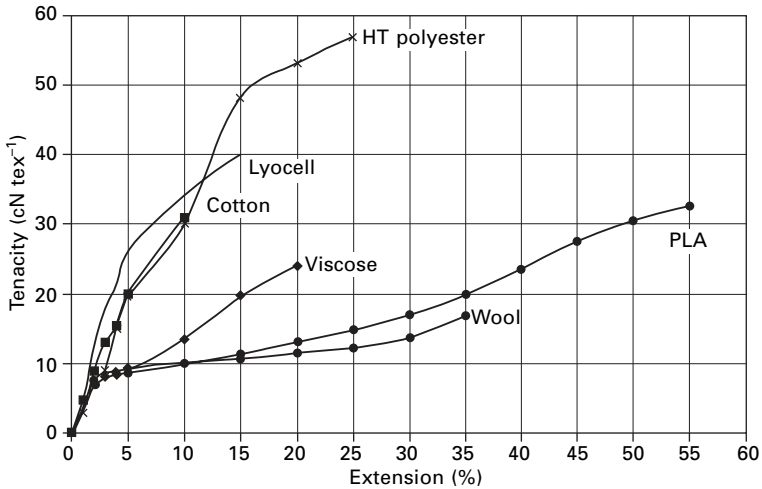
- *Appearance.* Fibers are generally circular in cross-section and have a smooth surface.
- *Density.* The specific gravity is 1.25 g cm^{-3} , lower than natural fibers and PET.
- *Refractive index.* The refractive index of 1.35–1.45 is lower than PET (1.54). Trilobal and other shapes can be made, and give improved antisoiling characteristics.

- *Thermal properties.* PLA is a stiff polymer at room temperature. The glass transition temperature (T_g) is typically between 55–65°C. The melting temperature (T_m) of PLA containing either the L- or D-isomeric form alone, is between 160–170°C. The DSC scans for PLA and PET are shown²¹ (Fig. 6.9). It can be seen that PLA exhibits an endothermic peak (T_m) at approximately 166°C, whereas the T_m of PET is approximately 254°C. This low melting point compared to PET underlines one of the main restrictions for PLA in developing suitable applications. However, as mentioned before, the properties of PLA can be modified by adjusting the ratio and the distribution of the D- and L-isomers in the polymer chain, and melting points as low as 130°C and as high as 220°C have been obtained.



6.9 DSC scans of PET and PLA.

- *Crimp.* PLA can achieve good degree of crimp and good retention level through processing.
- *Fibre types.* Both filament yarns and spun yarns can be made, as with PET.
- *Tenacity.* The tenacity at break ($32\text{--}36\text{ cN tex}^{-1}$) is higher than for natural fibers although, of course, it can be varied according to the degree of drawing that is applied to the undrawn yarn. It is relatively unaffected by changes in humidity at ambient temperature, though as with other manufactured fibers there is a small but measurable increase in elongation. As the temperature is increased the tenacity does reduce quite quickly with a concomitant increase in fiber extension, a feature commonly found in synthetic fibers.
- *Tensile properties.* The tensile properties of PLA fiber as used in staple form for textile processing are shown in Fig. 6.10. Clearly they are very



6.10 Tenacity-extension curves for PLA and other common textile fibers (20°C, 65% RH).

different from those of high tenacity polyester and more akin to wool with a high fiber extension when stressed and relatively low final tenacity. The initial modulus (at 2% extension) is very similar to many other textile fibers, but the yield point is very marked, the fibers (and spun yarns) stretching very easily once past this point. A consequence, however, of the high elongation is that the work of rupture is relatively high giving yarns and fabrics an acceptable performance in commercial use. Elastic recovery is affected by the yield point and is particularly good at low strains. At 2% strain, the recovery is 99.2% \pm 0.75%, and 92.6% \pm 1.60% at 5% strain, higher than for most other fibers. The unusual tensile properties could be expected to have an influence on some of the commercial applications in fiber blend developments. For example, intimate spun yarn blends with cotton (and lyocell) are relatively weak due to the contrast of fiber properties, and this might possibly limit applications to knitted fabrics. However, wool blends well with PLA, and with their load-elongation curves being very similar, this would enable the full properties of both fibers to be exploited.

- *Moisture regain.* At 0.4–0.6%, PLA has extremely low moisture regain, much lower than natural fibers and slightly higher than polyester.
- *Flammability.* Although PLA is not a non-flammable polymer, the fiber has good self-extinguishing characteristics; it burns for two minutes after a flame is removed, and burns with a white and a low smoke generation. PLA also has a higher LOI (limiting oxygen index) compared to most other fibers, meaning that it is more difficult to ignite as it requires a greater oxygen level. Table 6.1 compares PLA with standard PET.

Table 6.1 Comparison of PLA and PET flammability properties

| Fiber property | PLA | PET |
|------------------|---|--|
| Flammability | Continues to burn for two minutes after flame removed | Continues to burn for six minutes after flame is removed |
| Smoke generation | 63 m ² kg ⁻¹ | 394 m ² kg ⁻¹ |
| LOI | 26% | 22% |

- *UV resistance.* Unlike other synthetic fibers, PLA does not absorb light in the visible region of the spectrum; this leads to very low strength loss compared to petroleum-based fibers when exposed to ultraviolet light.
- *Moisture transport.* PLA shows excellent wicking ability. This property and the additional properties of fast water spreading and rapid drying capability give the fiber a very positive inherent moisture management characteristic.
- *Biological resistance.* Although PLA fibers are not inherently ‘antimicrobial’ without suitable after-finish treatment, they do not provide a microbial food source. In addition, testing by Odor Science and Engineering showed that PLA fiber-based fabrics outperformed PET-based fabrics for low odor retention.²²
- *Chemical resistance.* As PLA is a linear aliphatic fiber, its resistance to hydrolysis is therefore relatively poor. This feature means that care must be taken in dyeing and finishing of the fiber.
- *Solubility.* With regard to other chemicals PLA has limited solubility and is unaffected by dry-cleaning solvents for example.

6.4 Applications

The ease of melt processing, coupled with the unique property spectrum and renewable resource origin, has led to PLA fibers finding increasing acceptance across a variety of commercial sectors. It would also seem that with the estimated global increase in fiber demand, there is an opportunity for viable alternative materials. The total fiber business in 2002 was estimated to be some 55 million tonnes, and projections suggest that this could increase to 83 million tonnes by 2015. Particularly relevant within these figures is the growth of man-made fibers from 33 million tonnes in 2002 to 57 million tonnes by 2015, and that the major fibers creating this increase will be synthetic materials, mainly PET.²³

With approximately 50% of the fibers in the market today being synthetic materials from petrochemicals, it is clear that without synthetic fibers there would be insufficient fiber materials to meet the demands, particularly as natural fibers alone (mainly cotton) could not cover this. It is considered that

cotton is already at near peak production, so as the world population and the fiber requirements increase, the opportunity to use such a product as PLA is both logical and in line with our need to address the environmental problems we face.

6.4.1 Apparel

The apparel fiber business in 2002 was estimated at approximately 30 million tonnes (Table 6.2) and projections for 2015 indicate that it will grow to 42 million tonnes. The sector is dominated by two fibers, cotton and PET, and as the total requirement increases, it is PET that is projected to become the majority material. Apparel is by some way the largest sector in the global fiber business, and is a highly technical, fast changing, and demanding industry in terms of design, fashion, color, aesthetic, and performance. However, despite the steady growth in the apparel fiber market size, there has been a reduction in the price points, therefore creating a real pressure on costs through the whole supply chain. In many respects, it would seem that the existing range of fibers could meet all the possible consumer needs, either by virtue of their inherent properties, or with some chemical or physical processing technique within the downstream processing. For a new fiber, the entry into the apparel market could therefore be seen as both a very exciting challenge, but also a very difficult one. Against this backdrop, the real opportunity for PLA lies in the combination of both the fiber's inherent performance properties and the positive environmental advantages of being sourced from annually renewable natural resources, which, at the end of the product life, can be easily composted or recycled.

Table 6.2 Apparel mill consumption by fiber type 2002

| Fiber type | Million tonnes | % |
|------------|----------------|-----|
| Cotton | 13.0 | 43 |
| Wool | 1.3 | 4 |
| Polyester | 10.2 | 34 |
| Acrylic | 2.0 | 7 |
| Cellulosic | 1.8 | 6 |
| Nylon | 1.2 | 4 |
| Others | 0.5 | 2 |
| Total | 30.0 | 100 |

Kanebo, Inc. introduced a PLA fiber under the trade name Lactron™ fiber at the February 1998 Nagano Winter Olympics, under the theme of 'Fashion for the Earth'. Kanebo exhibited several garments from PLA or PLA/natural fiber blends. More recently, in 2003, Cargill Dow LLC (now NatureWorks LLC) announced their PLA fiber brand Ingeo™ (ingredient from the earth),

and this is now being adopted across a wide range of garment categories globally by leading garment brands.

It is one of the features of PLA that it can be produced as both filament and spun yarns. Fabrics produced from spun yarn have a 'natural' hand and are considered to feel similar to cotton in this respect. Fabrics from filament yarns have a cool and soft hand and exhibit a high fluidity or drape with a degree of elasticity. NatureWorks LLC product development suggests, for example, that a 1.2 dpf PLA achieves the softness of a microdenier PET (e.g. 0.7 dpf).

With the opportunity to create a range of fabrics with attractive aesthetic properties, there are a number of performance properties of PLA that are significant to its positioning and progress in the apparel sector:

- The moisture management properties of good wicking, faster moisture spreading and drying mean that garments are comfortable. This is an important consideration for next-to-skin garments and particularly in the sportswear market. In terms of comfort under normal and active wear conditions, independent laboratory testing by the Hohenstein Research Institute demonstrated that PLA fibers perform better than PET and cotton, either when combined with cotton or as 100% PLA fabric. This testing included a series of different tests, including thermal insulation, breathability, water vapor transport, and buffering capacity to liquid sweat (several tests in this series). The results of the Hohenstein testing concluded that wearers of PLA/cotton fabric would experience improved physiological comfort versus equivalent PET/cotton fabric.²⁴
- The elastic recovery and crimp retention properties provide excellent shape retention and crease resistance.
- Thermosetting capability of the fiber provides for controlled fabric stability, with garments having a low shrinkage through repeated washings.
- The flammability properties described earlier show the potential in specific segments of the apparel market. PLA fabrics with no flame retardant treatments have passed the US tests 16 CFR 1610, and have also achieved the standards specific for children's sleepwear, 16 CFR 1615 and 16 CFR 1616.
- High resiliency and lower specific gravity than natural fibers can give fabrics a light and lofty feel. These properties have been used in garments to provide an effective wadded layer, e.g. ski jackets.
- The after-care properties of garments in washing are very positive. There is no damage in repeated laundering of PLA fabrics: testing has been carried out under simulated conditions in accordance with AATCC standards, with no degradation observed (Table 6.3).⁷ Also, the fabric appearance remains extremely good after washing, without creasing and very clean surface. It would seem that any fiber work-up, which is quite normal under such conditions, is removed during the washing cycles.

Table 6.3 AATCC Test Method 61-1994 (35% PLA/65% cotton blend knitted shirt, simulates five washings)

| Simulated conditions | AATCC Test | Burst strength (psi) | % Dimensional change (width/length) | M _n | M _w |
|--------------------------|------------|----------------------|-------------------------------------|----------------|----------------|
| Control | | 83 | – | 57694 | 117970 |
| Cold hand wash (40°C) | | 79 | 0/–3.82 | 56343 | 107835 |
| Same, no bleach | 1A | 82 | 0/–3.13 | 52123 | 108115 |
| Cold machine wash (40°C) | – | 75 | 0/–4.17 | 56281 | 111206 |
| Same, no bleach | – | 78 | 0/–3.82 | | |
| Warm machine wash (50°C) | 5A | 74 | +6.25/–7.98 | 57190 | 112036 |
| Same, no bleach | 2A | 78 | +7.64/–7.98 | | |
| Hot machine wash (70°C) | 4A | 74 | +2.00/–6.25 | 58005 | 112510 |
| Same, no bleach | 3A | 76 | +2.00/–6.25 | | |

Additional to the above properties that could all be described as positive attributes, there are certain factors in this relatively early stage of technical and commercial development that are somewhat restrictive to the development across a full apparel spectrum:

- The melting point of the yarns that are commercially available today is relatively low at 170°C. This does cause limitations in some of the downstream processing technologies, but the main concern is for the consumer after-care of garments. Garment pressing and ironing temperatures have to be lower than the popular fibers of cotton and PET, and despite the appropriate care labeling instructions being used, it is a fact that consumers often disregard these.
- Hydrolysis degradation of the polymer can occur, particularly under combined aqueous high temperature and alkaline conditions; the degree of hydrolysis is influenced by the time, temperature and pH. This is of particular significance in the dyeing and finishing processes, as it will cause a reduction in the molecular weight of the polymer and therefore the strength of a yarn or fabric, if the appropriate finishing conditions are not observed.

Through all of the manufacturing stages of the supply chain – spinning, fabric formation, dyeing and finishing, and garment making – the existing machinery can be used. There is no need for any specialized capital investment when processing PLA. In many of the downstream processing technologies,

PLA processes and products are compared and are comparable to PET; both are melt spun, both are available in filament and staple form, weaving and knitting set-up conditions are similar, fabrics can be heat treated to give dimensional stability, and they are both dyed with disperse dyes. However, both fibers are unique and they do behave differently. It is therefore important that processors acknowledge this fact, and that the operating details are refined accordingly.

Yarn spinning

There is now a wide selection of commercial yarns being produced. In spun yarns, commercial products currently span the range Ne 5 to Ne 60 while in filament production, typical products such as dtex 70–68, dtex 150–72, are being produced. For both spun and filament yarns spinners have confirmed the processability of the material. An interesting feature of PLA is that processing temperatures are more typical of polyolefins (approximately 240°C), although the properties more typically combine many of the features found in rayon, nylons, acrylics and polyesters. PLA pellets are supplied with a maximum moisture content of 400 ppm. It is important to reduce the moisture content to 100 ppm during processing to prevent hydrolytic degradation, similar to PET and nylon products. For short staple yarns, because the characteristics of PLA are comparable to other thermoplastic fibers, the processing conditions are similar to those for PET. For long staple yarns also, processing can be carried out on conventional long staple equipment as used for thermoplastic fibers in blend with wool.

Fabric formation

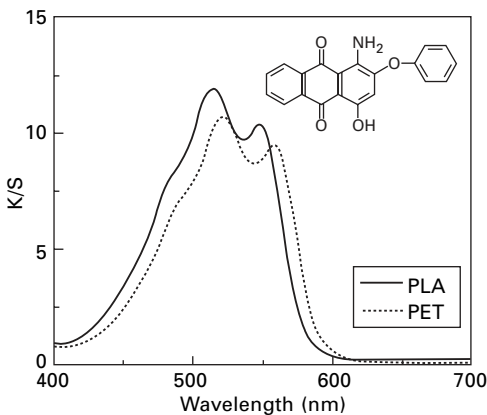
There are no special requirements for knitting, and machine settings are comparable with those for PET. In weaving, the additional points for attention would be: if a size is being applied, to use a PVA or water-soluble size to avoid any need for strong alkali desizing, and to minimize tensions due to the high fiber extension. Woven filament fabrics give a very soft hand, and have a high fluidity/drape compared to PET.

Garment making

The low melting point may mean that precautions are taken at those stages where fiber–metal friction could generate sufficient heat, namely the fabric cutting and the garment panel sewing operations. Care is also needed at the final pressing stage.

Dyeing and finishing

As is usual with any new fiber, the coloration and wet processing technologies demand significant attention. Color is so important, not only because it is the prime driver when purchasing a new garment, but also because the various applications and subsequent finishing treatments have the most chemical and physical effect on any fiber or polymer. Similar to PET, PLA is dyed with disperse dyes. However, dye selection is most important, as the individual dye behavior is quite different from dyeing on PET. In general terms, dyes show their maximum absorption at a shorter wavelength than on PET and tend to look brighter²⁵ (Fig. 6.11). Dyes also show a much greater variation in exhaustion levels; Yang and Huda²⁶ studied the exhaustion of ten disperse dyes on PLA and PET fabrics and found that the percentage dye exhaustion of all the dyes was lower on PLA than on PET. However, the color yield of the dyed PLA was higher than on PET because of the lower reflectance of PLA.



6.11 K/S curves of C.I. Disperse Red 60 on dyed PLA and PET.

Several of the major dye manufacturers have studied their ranges of disperse dyes to provide the most appropriate selection for applying to PLA. DyStar GmbH & Co. have worked closely with NatureWorks LLC to further the commercial dyeing technology for PLA and have recently provided details for dyeing both 100% PLA as well as blends with cotton and wool.²⁷ The optimum dyeing conditions recommended by DyStar for dyeing PLA is 110°C for 30 minutes at pH 5. Practical experience has shown that the use of higher temperatures or longer times of dyeing can cause degradation of the polymer.

One of the observations in the dyeing of PLA is that obtaining dark shades is more problematic, compared to PET. A reason for this is attributable to the

lower exhaustion levels, although, of course, dye selection has to balance many other factors including fastness requirements, reproducibility, and levelness.

There are indications that the color exhaustion and color yields can be increased by modification of the basic PLA polymer, altering the proportions of the D- and L-isomers, and thereby changing the amorphous/crystalline ratios. Higher D-levels have more amorphous and less crystalline regions and allow for increased dye exhaustions.²⁸ Comparison of PLA fabrics with varying D-isomer content revealed differences in the enthalpy of fusion, and, hence, percentage crystallinity; high D-fibers have more amorphous and less crystalline regions in the polymer, with respect to low D-fibers. High D-fabrics display greater dye exhaustion and color strength with respect to low D-fabrics in all dyes and all concentrations as a result of the greater number of amorphous regions in high D-fibers with respect to low D-fibers. In application of a dye mixture for a black shade high D-fibers are able to be dyed to an excellent black shade, whereas low D-fibers appear very brown, due to less exhaustion of the blue component of the mix. In terms of wash fastness, there is very little difference between high D-fibers and low D-fibers; this is because the glass transition temperature for both fibers is very similar.

Color fastness figures tend to be slightly lower than on PET. One reason for lower wet fastness is believed to be due to more movement of dye to the surface by thermomigration, during post-heat treatments. It may also be that the lower thermosetting temperature for PLA (130°C) compared to PET (190°C) means less sublimation of the dye from the surface.²⁹

With the introduction of PLA into apparel, developments and commercial adoptions have included fabrics made from 100% PLA as well as in blend with other fibers. The main blends are either with cellulosic fibers (cotton, lyocell) or wool. Apart from any aesthetic or performance benefits, such blends also have the feature of being biodegradable compared to their PET counterparts.

The wet processing of cellulosic blends need to be adapted to recognize the sensitivity of PLA to alkali treatments. This causes some limitations, as bleaching and dyeing systems for cellulosic fibers generally use alkaline processes. However, the potential significance of this blend has been recognized, and methods are available for all stages of wet processing. These include the use of neutral bleaching systems based on TAED (tetraacetylenediamine), and direct dyes, as well as the more conventional alkaline bleaches and selected reactive dyeing systems. A detailed study into the effect of the various wet processes on the molecular weight and physical strength of PLA was carried out at UMIST, and this confirmed the feasibility for suitable processing.^{30,31} Dyeing of PLA/wool blends does not present such a problem, as both fibers have the same characteristic with regard to alkali. Indeed, with their similar stress-strain profile, there would seem to be some benefits compared to PET/wool.

There is much to be still learnt about the dyeing of PLA but it would seem that processes are available to achieve commercial viability. In real terms, it is not that long ago that fibers such as lyocell and indeed PET were introduced to the textile world, with many technical difficulties in their processing. These are now well accepted fibers and it will be interesting to watch as PLA follows a similar course.

6.4.2 Homeware

Typical products encompassed in this segment range from pillows, duvets, blankets, mattress pads, carpet tiles, office panel fabrics, drapes to bonded fiber products such as mattresses. As in the other sectors, the unique origin of these fibers, being derived from natural sugars obtained from annually renewable resources, coupled with the performance benefits, is proving to have a strong appeal to consumers in various geographies. The resistance to UV and low flammability, low smoke generation and low toxic gas on burning are attractive properties for this market segment, which differentiate PLA fabrics manufactured from conventional petrochemical-based synthetics.

Superior resilience found in crimped staple fiber products such as fiberfill, coupled with the natural wicking performance of the fiber are added features, which further enhance the scope of opportunities for PLA. Since this moisture wicking behavior is inherent to the fiber and achieved without the use of finishes this behavior should not decrease over time. Independent testing indicates the wicking behavior of untreated PLA fibers is superior to either untreated or treated polyester fibers.³² Laboratory UV resistance testing using a Xenon Arc³³ indicates that in comparison with polyester and acrylic fibers, PLA fabrics have superior strength retention than polyester and far superior resistance to discoloration than acrylics.

Independent testing by the Hohenstein Institute³⁴ shows that PLA fibers when used in duvets provide a better microclimate between the body and the duvet. The superior wicking properties of PLA fibers, compared with polyester, results in the dynamic adjustment of the moisture level by dissipating moisture as the humidity level changes. In pillows, testing has shown that PLA fibers offer outstanding filling power and resilience after three years of simulated usage.³⁵

Flammability testing indicates a Limiting Oxygen Index value for PLA fibers of 24–28 when tested according to ASTM D2863. This is superior to untreated PET fibers, cotton, rayon and acrylics and equivalent to natural protein-based fibers such as wool. In addition, flame propagation and time to extinguish are properties of considerable interest in the furnishings segment. Fabrics made from untreated PLA fibers show far shorter burn times than cotton and polyester fibers. Untreated PLA fibers meet the test criteria for UNI 8456(1986), UNI 9174(1987) and UNI 9174/A1 (1996) that measure

the time to self-extinguish (after the fabric is removed from the heat source). This test also measures the rate of flame propagation, char length, and time of flaming of any dripping materials to extinguish. The results enable 100% PLA fabrics to be classified as Category 1 as required by the Italian Drapery Industry.³⁶

Fabrics made from PLA fibers have also passed flammability tests such as NFPA 701, which covers the fire safety requirements for textiles used in interior furnishings for public occupancy buildings.³⁶ Typical products include drapery, cubicle curtains, wall covering and protective outdoor coverings such as tarpaulins and tents.

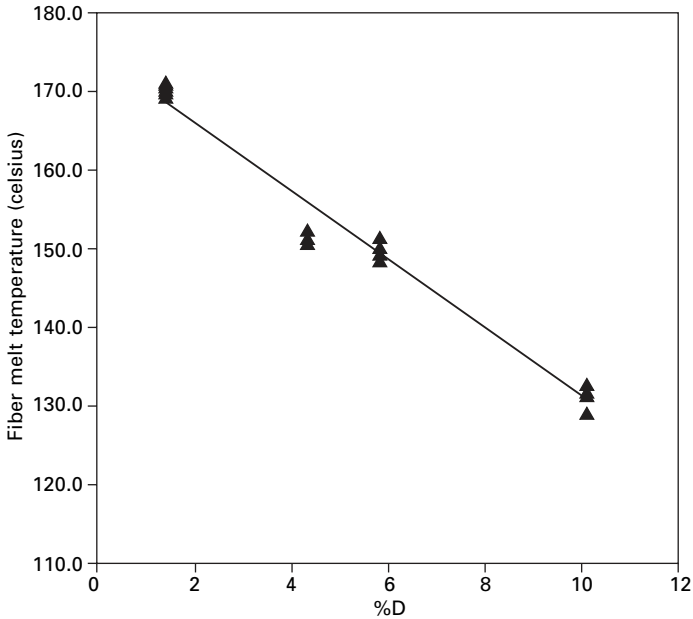
Finally, a prototype mattress made from 100% PLA fibers successfully passed Cal 129 testing for furniture flammability.³⁶ All these tests were conducted on 100% PLA without any flame retardant additives. However, individual results will depend upon fabric construction and the use of finishes or dyestuffs.

The unique resistance to staining and soiling of PLA Bulk Continuous Filament (BCF) has led to significant interest in PLA fibers for use in carpets. Presently, PLA fibers are used in carpet mats for the hybrid Toyota Prius in Japan as well as in carpet tiles for domestic and institutional markets.

In the technology development area PLA/PLA binder fibers are finding application in mattresses, and other bonded batting areas.

As described earlier, PLA bicomponent technology utilizes the unique polymer properties induced by the two optically active forms of the lactic acid monomer. By controlling the ratio and distribution of the D- and L-isomers in the polymer chain, it is possible to induce different crystalline melting points during melt processing; this feature offers distinct benefits particularly in the binder fiber area. Bicomponent fibers with a sheath softening point of 60°C (amorphous) up to a crystalline melting point of 175°C can be produced (Fig. 6.12). As well as bonding to other PLA fibers or petroleum-based synthetics, PLA bicomponent binder fibers are increasingly being used to bond natural fibers such as jute and hemp in automotive applications for spare wheel covers and door panels. Bicomponent PLA technology is also finding applications in self-crimping and micro denier technologies. Technology growth areas are in sheath/core, side by side, segmented pie and islands in the sea structures.

Overall, PLA binder fibers can replace existing synthetic polymers where renewable resource is a benefit or where additional performance such as controlled temperature bonding, controlled shrinkage or lower temperature processing is required. In addition, improved or reduced adhesion and alternative approaches to soluble/non-soluble island/sea combinations are all possible and under development.



6.12 PLA fiber melt temperature as a function of % D-isomer.

6.4.3 Nonwovens

Nonwoven products are a major application segment offering great potential for the unique benefits of PLA fibers. Outside of the fiberfill products the major markets are in spun bond, industrial and household wipes, hygiene and filtration areas. Spun bond PLA products can be produced on typical polyester spun bond lines in a variety of fabric weights. Filament velocities of 3500 m min^{-1} and above are needed to produce fabrics with the required low shrinkage performance. Key applications are in carpet backing, hygiene, and compostable geotextiles for soil erosion control and plant as well as crop protection. Under the correct conditions of temperature and humidity PLA fabrics are completely compostable and return naturally to the soil releasing carbon dioxide and water. Under normal storage conditions and use, however, the fabrics are durable enough to meet the various market and supply chain requirements.

Industrial/household wipes

In recent years there has been a significant growth in the wipes market, and in particular the wet wipes segment across a variety of applications. Most wet wipes comprise a blend of cellulose, viscose or rayon with a synthetic fiber such as polyester or polypropylene. Up to 50% of the wipe comprises

these synthetic fibers. Recent surveys indicate a 6.5% annual growth in personal care wipes versus 2.5% in baby wipes in the US.³⁷ Similar trends are being seen in Europe and Japan. New product introductions in personal care and household cleaning markets are occurring rapidly. Typical new trends and applications for wet wipes include:

- Feminine hygiene, facial cleansing, hemorrhoid treatment, etc.
- Functional treatments (antimicrobial, cleaners, abrasives, etc.).
- Decorative patterns.
- Continued push toward cloth-like aesthetics.
- Environmentally friendly materials and processes.

Spun laced investments have recently been announced by Jacob Holm, Spuntech, Orlandi, & Green Bay Nonwovens. In addition, Japan has large spun lace capacity with markets that are seeking environmental solutions. Wipes converters globally are expanding capabilities and expediting line extensions. PLA fibers show superior wicking performance when compared with the petroleum-based synthetics used in these applications. This inherent property leads to increased rates of liquid absorption,³² in addition the appeal of an all-natural-based wipe has demonstrated strong consumer pull. The wipes market is, however, extremely price sensitive; recent price fluctuations in the price of oil coupled with the advances made in PLA fiber and resin production means that pricing differences between the petrochemical-based and PLA fibers continues to narrow.

Hygiene

PLA fibers, because of their natural wicking properties, are finding utility in the diaper and feminine hygiene markets, both in spun bond top sheets and acquisition/distribution layers. Again the ability to replace petroleum-based fibers with enhanced performance with a natural-based fiber has strong consumer appeal. An additional benefit is that since PLA fibers are fully compostable the products can be disposed of by composting if the infrastructure for disposal is in place.

Filtration and separation

Two areas of potential applicability of PLA polymers have appeared in the industry in recent years.

- Triboelectric media to improve filtration efficiency.
- Filters, for example in the automotive and chemical industries, as well as single use applications.

The unique combination of properties displayed by PLA fibers offers promise

in these areas. Untreated PLA fibers are repelled by glass surfaces and are attracted to polypropylene, indicating that they are somewhat electropositive. Disposable filters are also an area of interest for PLA fibers.

6.4.4 Medical applications

Textile fibers can be used to cultivate different human organs. The process involves culturing and growing living cells, taken from human organs, on a textile scaffold, to the desired 2-dimensional and/or 3-dimensional shapes. The scaffold is made from biodegradable and resorbable fibers which are in turn produced from biocompatible and degradable polymers. The major bioresorbable fibers used in implants are PLA and PGA (polyglycolic acid – see Chapter 7). They can either be used as a single polymer or by blending a copolymer of PLA and PGA. Varying the proportions of PLA and PGA alters the degradation rate and strength retention time of the fiber. These properties can therefore be varied in this way according to the requirements of specific medical applications. During the process of degradation, fibrous connective tissues replace the degrading implant. The key advantage is that no further surgery is required to remove the products since they slowly degrade in the body without any side effects. The US Food and Drug Administration (FDA) has approved the use of PLA for certain human clinical applications. Also, PLA-based materials have been used for bone support splints.

6.4.5 PLA as a plastic

Although it is outside the scope of this chapter, it is important to recognize the tremendous scope for PLA as a plastic in several applications. The material has significant potential use in fresh food rigid packaging, bottles for beverages like milk, juice and non-carbonated water. PLA can also be made into an ideal film for use as labels, wrappers and windows.

6.5 Environmental sustainability

The previous sections of this chapter have examined the manufacturing of PLA, its various properties as a polymer and a fiber, and considered the potential for its use in a range of commercial applications. Additionally, the environmental aspects for producing and using PLA products must be appraised in any discussion about its significance as a sustainable commercial polymer material.

Environmental sustainability is about making products that serve useful market and social functions with lower detrimental environmental impact than the currently available alternatives. The case for PLA in this respect

would seem to be very strong and needs to be appraised in any discussion about its potential as a significant polymer material. The ideal environmentally sustainable product provides equivalent function as the product it replaces and is available at competitive costs. It is made from renewable resources, can itself be constantly renewed without degradation in quality or performance, and has a minimum environmental impact. Such a product is made using only substances known to be safe for both humans and the environment. Ideally the life cycle of the sustainable product is in balance with the surrounding ecosystem.

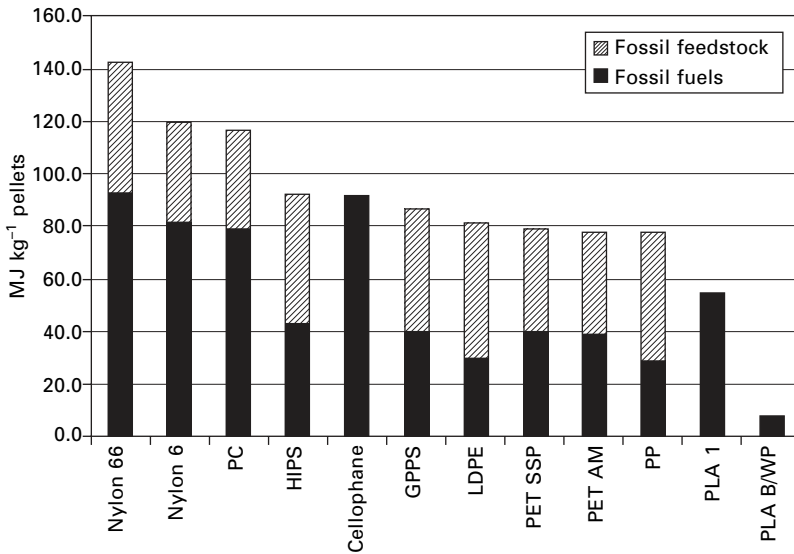
6.5.1 Polymer processing and environmental measures

According to Vink *et al.*³⁸ there are probably three items that are generally considered to have an increasing global importance with regard to environmental concerns: fossil energy use; greenhouse gas emissions; and water use.

Fossil energy use

The existing range of petrochemical-based plastics is diverse, specialized and mature, so that precise and exact comparisons with PLA, a single product performing multiple functions, are difficult, especially considering the great number of impact categories compared. Figure 6.13 plots the fossil energy requirement for these products. Data for the petroleum-based polymers was supplied by the Association of Plastics Manufacturers in Europe (APME). The data is valid for the polymers as produced in Europe. A key finding of the analysis is that the first generation polylactide production system (PLA1) uses 25 to 55% less fossil energy than the petroleum-based polymers.^{38,39} Process improvements are targeted by NatureWorks LLC for the near future involving the use of biomass (B) and wind power (WP) as energy sources in the PLA production process (PLA B/WP), and with these improvements the use of fossil energy can be reduced by more than 90% compared to any of the petroleum-based polymers being replaced. This also will give a significant reduction in fossil energy related air and water emissions. This comparison represents the outstanding potential for environmental benefits for polymers made from renewable resources.

It needs to be recognized that the data for PLA1 and PLA B/WP represent engineering estimates. In addition, there is good reason to expect improvements in the actual performance versus the estimates.³⁸ Despite years of development work, the commercial manufacturing process for PLA is in its infancy. If the experience from petrochemical-based polymers offers any instruction, it is that process improvements implemented in the early years of a technology typically lead to substantial cost improvements. This is because the pursuit



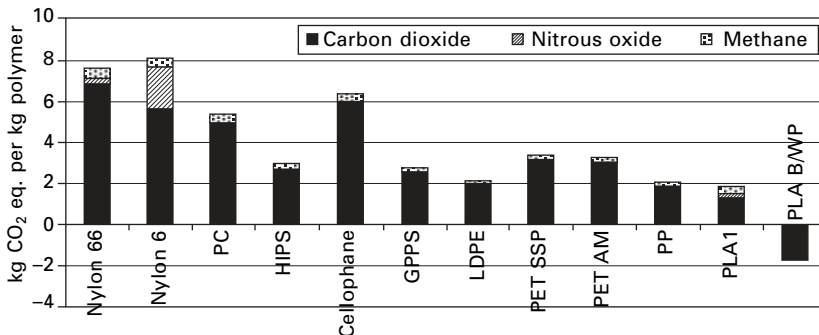
6.13 Fossil energy requirement for some petroleum-based polymers and polylactide. The cross-hashed part of the bars represent the fossil energy used as chemical feedstock (the fossil resource to build the polymer chain). The solid part of each bar represents the gross fossil energy use for the fuels and operations supplies used to drive the production processes. PC = Polycarbonate; HIPS = High impact polystyrene; GPPS = General purpose polystyrene; LDPE = Low density polyethylene; PET SSP = Polyethylene terephthalate solid state polymerization (bottle grade); PET AM = Polyethylene terephthalate Amorphous (fibers and film grade); PP = Polypropylene; PLA1 = Polylactide (first generation); PLA B/WP (Polylactide, biomass/windpower scenario).

of cost improvements for competitive reasons often targets energy use due to its relatively high contribution to overall material costs. For example, through work on biocatalyst and lactic acid manufacturing process, NatureWorks LLC expects to achieve improvements that should further improve the performance of their production plant and simultaneously reduce energy demand. There is therefore good reason to expect a performance improvement trajectory for PLA1 that mirrors the experience from the current incumbent materials.

Global climate change

Global climate change has been identified as perhaps the most important environmental issue of this century.⁴⁰ Greenhouse gas emissions are not exactly the same as combusted fossil fuel emissions, because several non-combustion gases can contribute to global climate change as well. For example,

methane (CH_4) is a potent greenhouse gas that can emanate from natural gas system leaks, decomposition of biological materials, and chemical/industrial processes. However, greenhouse gas emissions are closely correlated to fossil fuel emissions because combustion of fossil fuels is the source of most anthropogenic greenhouse gases. NatureWorks LLC has undertaken a comparison of the contributions to global climate change from a range of petrochemical-based polymers as well as the two PLA cases described above.³⁸ This comparison is depicted in Fig. 6.14. In conducting this analysis, Vink *et al.*³⁸ relied upon the 100-year time horizon Global Warming Potentials for greenhouse gases, a time period generally accepted as the mean atmospheric residence time for the most volumetrically significant greenhouse gas, carbon dioxide. A check of the data revealed that use of the 20- and 500-year time horizons generates the same ranking among the products studied. According to the Intergovernmental Panel on Climate Change (IPCC) the relative global warming potentials of the three largest (volumetric) greenhouse gases are: CO_2 -1, CH_4 -21, and N_2O -310.⁴¹ These factors were used in NatureWorks LLC's analysis. As in the comparison of fossil energy use, the analysis compares conventional polymers with PLA from cradle to pellet (from raw materials to the point where the product is ready for shipment to a converter or fabricator). All emissions values were converted to CO_2 equivalents in order to facilitate comparison.



6.14 Contributions to global climate change for some petrochemical polymers and the two polylactide polymers (for key to polymers see Figure 6.13)

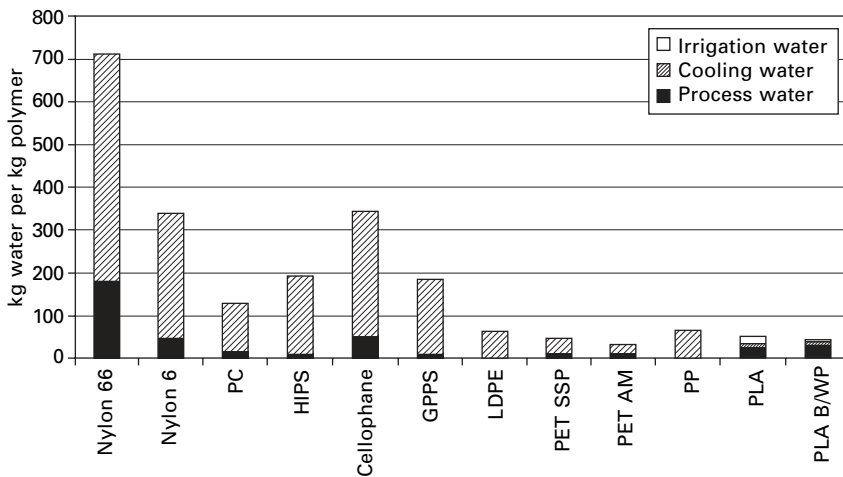
The analysis demonstrates that the PLA1 production process enjoys a substantial advantage over most polymers, and is comparable to several others. Even more exciting are the greenhouse benefits that derive from the transition to biomass feedstocks and reliance on wind energy for the balance of plant energy requirements. The utilization of the lignin fraction of lignocellulosic feedstocks for process heat generation 'closes the loop' on carbon related to energy generation, and in combination with other factors

yields a negative greenhouse gas impact for PLA pellets. A most appealing result of the use of agricultural feedstocks for the PLA polymer production and most of the process energy requirement means that customers using PLA cannot only use PLA as a product, but as a component of their greenhouse gas reduction strategies.

Life cycle assessment reveals that no petroleum-derived polymer can rival the greenhouse gas sink effect of the improved PLA process. Although disposal of PLA products – whether by combustion, composting or other conventional means – results in a return of carbon dioxide to the atmosphere, this advantage survives.

Water use

Vink *et al.* also studied the water use.³⁸ Figure 6.15 gives the gross water use of the traditional polymers and the two PLA cases (PLA1 and PLA B/WP) as described above. The gross water use is the sum of public supply, river, canal, sea and well water and used as cooling water, process water and irrigation water. Despite the use of irrigation water during corn growing and the two water-based processes (dextrose and lactic acid production) the total amount of water required is competitive with the best performing petrochemical polymers.



6.15 Gross water use by petrochemical polymers and the two PLA cases (for key to polymers see Figure 6.13).

6.5.2 Disposal options

The most common waste management options for the fossil fuel-based polymers are incineration, landfill and mechanical recycling. In addition to these

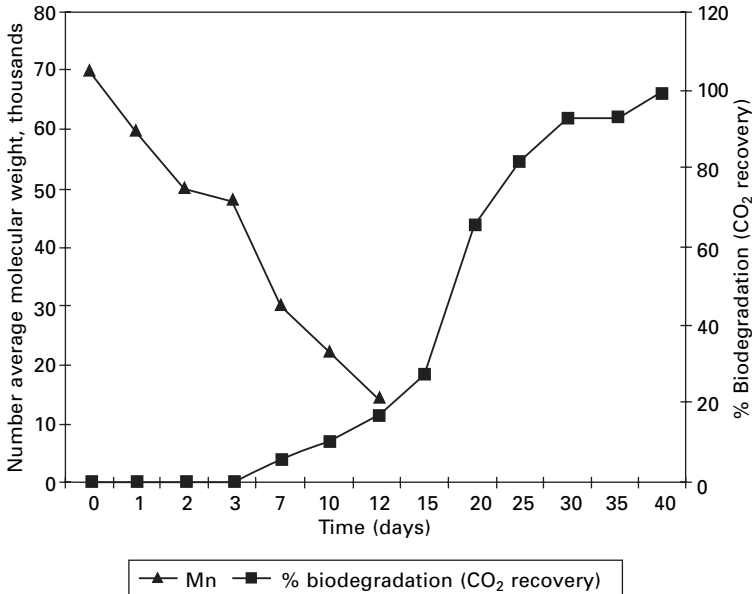
traditional processing routes, the PLA waste streams can also be processed using composting, chemical recycling and anaerobic digestion (see Chapter 1).

Composting

Composting is a beneficial waste management system, particularly where landfill sites are limited, and in more densely populated locations. It does require an appropriate infrastructure to be set up, but progress is being made, particularly in parts of Western Europe.⁴² Composting is a method of waste disposal that allows organic materials to be recycled into a product that can be used as a valuable soil amendment. The primary mechanism of degradation of PLA is hydrolysis, catalyzed by temperature, followed by bacterial attack on the fragmented residues. In composting, the moisture and the heat in the compost pile attacks the PLA polymer chains and splits them apart, creating smaller polymer fragments, and finally, lactic acid. Microorganisms, found in active compost piles, consume the smaller polymer fragments and lactic acid as energy source. Since lactic acid is widely found in nature, a large number of naturally occurring organisms metabolize lactic acid. At a minimum, bacteria and fungi are involved in PLA degradation. The end result of the process is carbon dioxide, water and some humus.⁷ In summary, via composting, the carbon dioxide which has been harnessed during corn growing flows back into the atmosphere and the short cycle carbon dioxide loop has been closed. The degradation process is temperature and humidity dependent. PLA is compostable at industrial composting facilities, but will not degrade sufficiently fast in domestic composting piles since the minimum required conditions are typically not present.⁴³ A typical degradation curve of PLA under composting conditions is shown in Fig. 6.16.

Chemical recycling

Vink *et al.* describe⁴³ the possibilities of chemical recycling as a promising future alternative waste disposal route. The PLA polyester polymer is formed from reversible polycondensation reactions and can be depolymerized by hydrolysis. This equilibrium results in recycling advantages for polyesters such as PLA. Manufacturing waste, converter waste, or post-consumer PLA materials can be recycled by chemical means to produce lactic acid monomers and oligomers. These materials can then be fed to the front end of a manufacturing process for making PLA lactide, ethyl lactate, or other lactide derivatives. The recycling can be carried out with water at a wide range of temperatures (100–250°C). The reaction rate is enhanced by a catalyst such as nitric acid as is common in the PET recycling industry. The reactor residence times for PLA hydrolysis are in the order of hours, and depend on reactor temperature and catalyst level.



6.16 Biodegradation of PLA in compost at 60°C + 95% humidity.

Chemical recycling should be considered in any waste management system for PLA, since from a life-cycle perspective, it represents a relatively small amount of net chemistry compared to the CO₂-to-PLA cycles for incineration or composting. Simple hydrolysis can turn waste PLA back into fully functional lactic acid, at potentially low economic and environmental cost, contributing to the total sustainability of PLA production.

The inferences from the studies of Vink *et al.*⁴³ confirm the positive impact that PLA has in addressing the key environmental concerns of today when compared to petrochemical-based polymers. They also show the additional benefits that can be gained by making environmentally responsible modifications to the existing manufacturing process. The commercial producer of PLA, NatureWorks LLC, states that its commitment and ethos is based on 'making plastics from annually renewable resources which meet the needs of today without compromising the earth's ability to meet the needs of tomorrow'. Its philosophy is based on 'reducing the environmental footprint' and on 'designing products with end-use disposal in mind'.⁴⁴ The company is committed to environmental responsibility and therefore it would seem that the polymer market as we know it today will experience some very significant changes in the near future.

6.6 Future trends

The vision for PLA fibers is more than just developing new performance products; it encompasses the additional goal of reducing total environmental impact. The result is a product that is more sustainable than comparable polymers on the market today. PLA fibers have made significant steps towards creating more sustainable products with unique performance attributes.

This technology allows one of the world's most commonly used materials, plastics, to be made from simple plant sugars, which are then turned into fibers using conventional melt spinning equipment and processes. Made from annually renewable resources, PLA plastics and fibers use 20 to 50% less fossil fuel resources than is required by conventional petroleum-based resins. Fossil resource use in the manufacture of these materials will continue to decrease as plans are put into place to switch feed stocks to biomass (corn stalks, leaves, etc.) and possibly integrate alternative energy sources, such as windpower. With PLA, carbon dioxide is removed from the atmosphere when growing the feedstock crop and is returned to the earth when PLA is composted. Since this process recycles the earth's carbon, PLA emits less CO₂ compared to other petroleum-based fibers. Disposal of PLA fits within the existing disposal systems but also includes the additional option of composting.

PLA fibers are increasingly penetrating markets traditionally occupied by petroleum-based synthetics. The rationale for this trend is the increasing public concern over the depletion of natural resources and the accompanying atmospheric pollution. Various studies indicate that reserves of oil and gas will eventually be depleted, although the actual time scale is a topic of considerable debate. It is evident, however, that the use of annually renewable crops as a means of producing the materials we need to sustain our everyday lives will continue to accelerate.

PLA fibers offer the promise of ultimately reversing the damage we have imposed upon the earth while extending the usable life of the diminishing oil and natural gas reserves. Ultimately the technology of using natural crops to produce fibers and packaging will become widespread across the globe. The use of waste products, referred to as biomass, will also provide the fuel to drive the factories used to convert these polymers to the variety of products needed to sustain the ever-increasing demands for an improved quality of life. The key to this transformation lies in the economical manufacture of these renewable resource-based products coupled with meeting the performance demands of the targeted applications.

PLA fibers and packaging products are well on the way to realizing this goal. Presently these fibers are produced from natural corn sugar. However, as the technology develops, any starch-based crop will be used. Advances in farming practices will enable higher crop yields with subsequent improved

economics. Additional improvements in the fermentation and polymerization processes along with economies of scale will also contribute to the improved cost basis for these products.

PLA products have come a long way from the early work of Carothers in 1932. The ability to economically manufacture packaging and fibers products has led to rapid growth. This growth will continue. We are at the beginning of a new industrial revolution in which PLA fibers are playing a leading role. In addition, PLA fibers are still in their infancy: improvements in chemistry and downstream process development will lead to new applications and a bright future for these renewable resource-based melt-spinnable fibers.

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