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Large-scale production, properties and commercial applications of polylactic acid polymers

James Lunt*

Cargill Incorporated, EcoPLA Business Unit, 2301 Crosby Road, Wayzata, MN 55391, USA

Polylactic acids (PLA) are not new polymers. However, recent developments in the capability to manufacture the monomer economically from renewable feedstocks have placed these materials at the forefront of the emerging biodegradable plastics industry. Increasing realisation of the intrinsic properties of these polymers, coupled with a knowledge of how such properties can be manipulated to achieve compatibility with thermoplastics processing, manufacturing, and end-use requirements has fuelled technological and commercial interest in PLA products. This paper discusses the various technologies being used to produce polylactic acids. In addition, attention is drawn to how monomer stereochemistry can be controlled to impart targeted utility in the final polymers. Specific applications are described to illustrate further the range of properties that can be developed by utilising both the basic monomer/polymer chemistries in combination with post-modification techniques. Finally, the biodegradation mechanism of polylactic acids will be discussed and contrasted with other biodegradable polymers. © 1998 Elsevier Science Limited. All rights reserved

1 INTRODUCTION

Interest in the manufacture of an aliphatic polyester from lactic acid was pioneered by Carothers in 1932.[1] This product was of a low molecular weight, and possessed poor mechanical properties. Further work by DuPont resulted in a higher-molecular-weight product that was patented in 1954.[2] However, as with all the completely aliphatic polyesters investigated at this time, the susceptibility to hydrolytic degradation led to discontinuation of work in this area. In 1972, Ethicon introduced high-strength, biocompatible fibres for medical resorbable sutures. These products, which are copolymers of lactic and glycollic acids, slowly hydrolyse within the body to the constituent acids. Further applications, also in the medical field, include implants and controlled drug release.

The prohibitive cost of producing such polymers restricted their applicability outside this field until the late 1980s. Advances in the bacterial fermentation of D-glucose obtained from corn introduced the potential to obtain lactic acid considerably cheaper than previously achievable from the petrochemical-derived product. Within 6 years, the technology to produce polylactic acids economically on a commercial scale was developed. Presently, world-wide, at least six companies have announced development activities for polylactic acid polymers. Cargill, Inc., in Minneapolis, presently operates the largest PLA facility. Back integration to the basic corn feedstock guarantees a firm foundation for commercial scale monomer and polymer economics that will enable these polymers to enter the commodity plastics industry. The recent announcement of a Joint Venture between Cargill and Purac Biochem B.V. to build and operate a 34 000 tonne/year lactic acid plant in the US by 1998 will accelerate the growth of biodegradable polymers based on PLA. In addition, uses for optically active lactic acid monomer in non-degradable applications such as esters and other derivatives will continue to drive the monomer cost downwards with subsequent continuing economic improvements in PLA polymer prices.
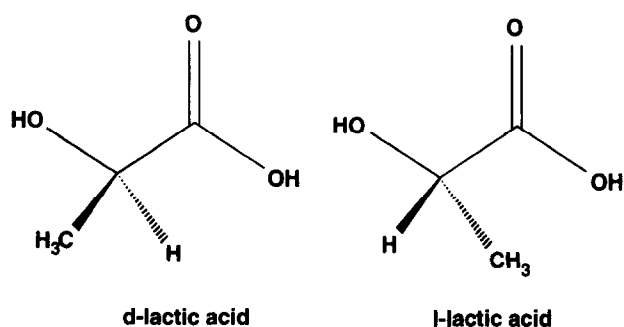
*To whom correspondence should be addressed. Fax: (612) 742-4707; e-mail:Jim_Lunt@Cargill.com

2 MANUFACTURE OF POLYLACTIC ACIDS

Lactic acid is one of the simplest chiral molecule and exists as the two stereo isomers, L- and D-lactic acid. The L form differs from the D form in its effect on polarised light. For L-lactic acid, the plane is rotated in a clockwise (dextro) direction, whereas the D form rotates the plane in a anticlockwise (laevo) direction. Figure 1 illustrates these two forms. Lactic acid produced by the petrochemical route (Fig. 2) exists as a 50/50 optically inactive mixture of the L and D forms. Presently, Musashino in Japan is the sole producer of racemic lactic acid. In contrast, fermentation-derived lactic acid exists almost exclusively as L-lactic acid (Fig. 3). The ability to produce the L isomer in high purity has important ramifications in the chemistry and ultimate process/property relationships achievable in the polymers produced from lactic acid.

The conversion of lactic acid to high-molecular-weight PLA is achieved by two routes. Cargill uses a solvent-free process and a novel distillation process to produce a range of polymers.[3] The essential novelty of the process lies in the ability to go from lactic acid to a low-molecular-weight polylactic acid, followed by controlled depolymerisation to produce the cyclic dimer, commonly referred to as lactide. This lactide is maintained in the liquid form and purified by distillation. Catalytic ring opening of the lactide intermediate results in the production of PLAs with controlled molecular weights. The process is continuous with no necessity to separate the intermediate lactide.

In contrast, Mitsui Toatsu[4] utilises a solvent-based process in which a high-molecular-weight polymer is produced by direct condensation using azeotropic distillation to remove the water of condensation continuously. Figure 4 illustrates the steps involved in these two processes. A more
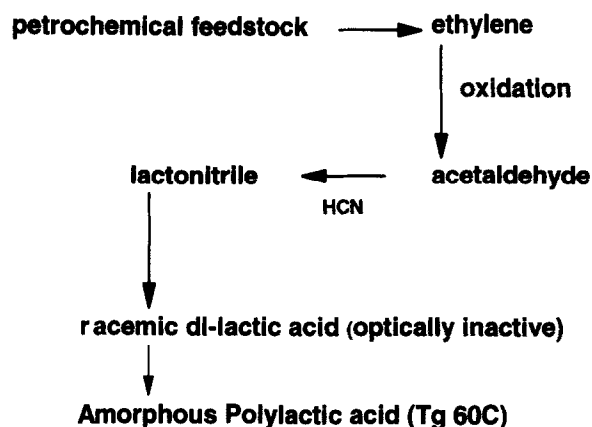

Fig. 2. Petrochemical route to lactic acid.

detailed description of the Cargill process is illustrated schematically in Fig. 5.

Producing the cyclic dimer (lactide) introduces the potential to tailor molecular architecture in the final product. By controlling residence time and temperatures in combination with catalyst type and concentration, it is possible to control the ratio and sequencing of D- and L-lactic acid units in the final polymer. Since L-lactic acid can be controllably racemised to D-lactic acid, then during the depolymerisation stage, three forms of lactide are possible (Fig. 6). Only the L and D forms demonstrate optical activity. The meso form is optically inactive. Compositional control of the lactide stream dictates many properties of the final polymer.

3 INFLUENCE OF OPTICAL COMPOSITION

The optical composition of the polymer significantly affects crystallisation kinetics and the ultimate extent of crystallinity.[5] The level of crystallinity developed is particularly influential in determining the polymer melting point. Poly (L-lactide) has a

d-lactic acid   l-lactic acid

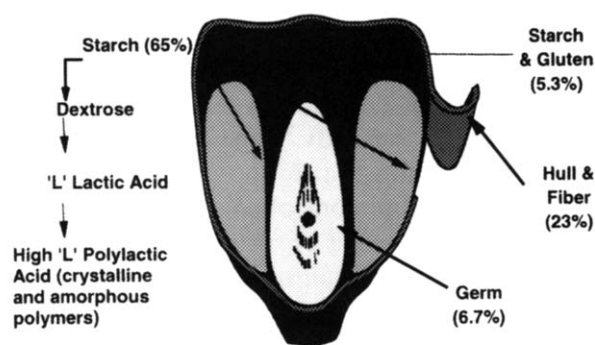Lactic acid stereoisomers

Fig. 1. What is lactic acid?

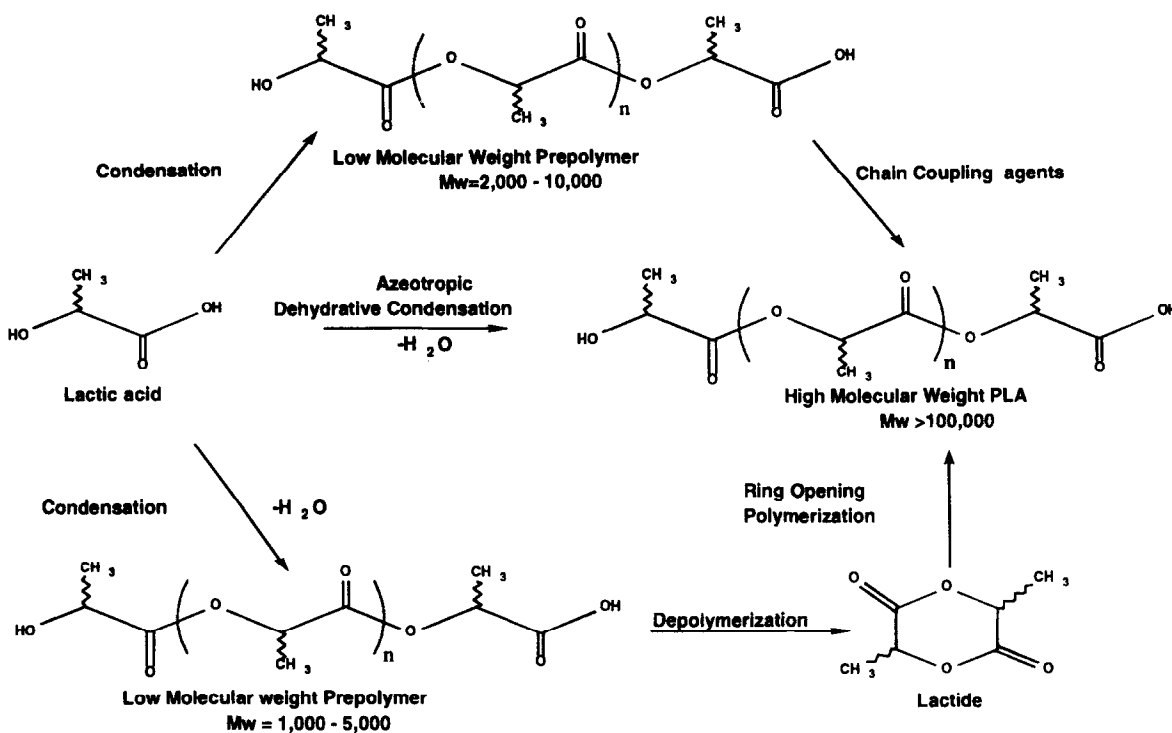Fig. 3. Fermentation route to lactic acid (using corn as the feedstock).
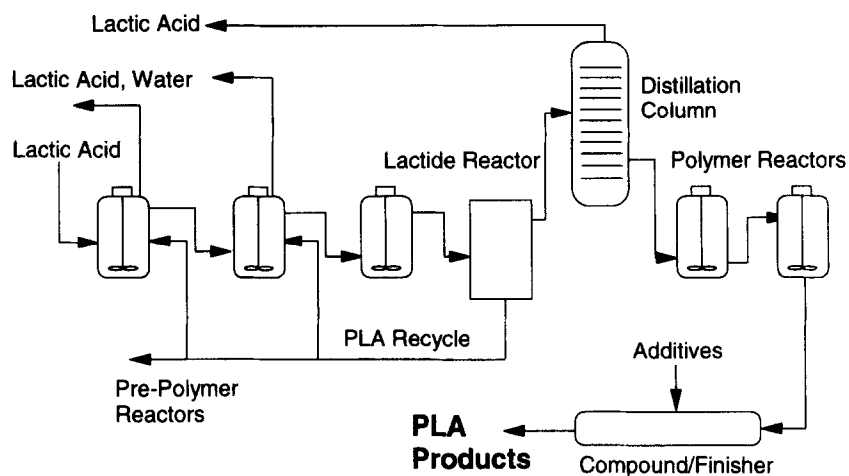
Fig. 4. Manufacturing routes to polylactic acids.

Fig. 5. Cargill commercial manufacturing process.

practical melting point of 180°C. Introduction of meso lactide depresses the crystalline melting point to as low as 130°C. For many products, crystallinity is a desirable attribute as indicated in Table 1.

Although essentially structure-dependent, crystallinity can be developed in two ways. During injection-moulding, the use of nucleating agents coupled with control of D-lactic units in the polymer allows quiescent crystallisation during cooling from the melt. Presently, however, the practical rate of crystallisation achieved is too slow to allow

injection-moulding cycle times typical of those achieved for polystyrene in applications such as cutlery. An alternative method of achieving crystallinity is by stress-inducing the polymer during processing. Stress induced crystallisation is most effective in those processes that allow orientation during processing and in which the stress is applied at approximately 10°C above the glass transition temperature followed by a heat-setting period. This mechanism lends itself readily to processes such as fiber-spinning or biaxial orientation of film (tenter frame and double bubble processes).
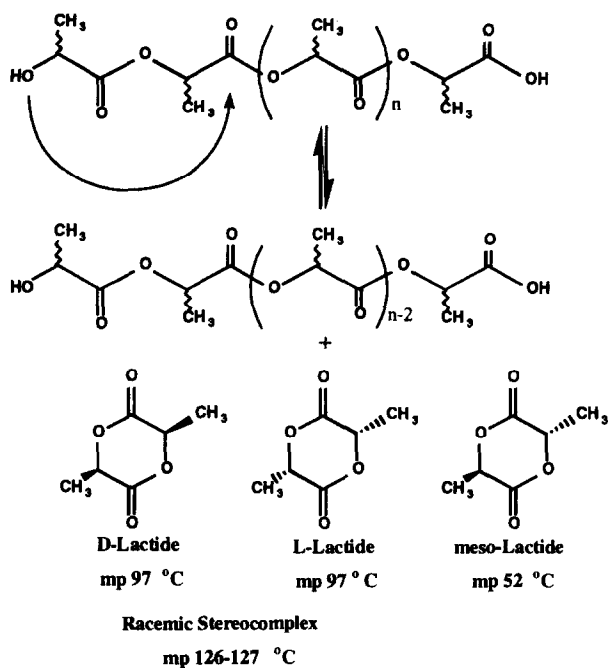
Fig. 6. Lactide formation mechanism.

Lower crystalline melting points achieved by introducing meso lactide into the polymerisation also allow lower melt-processing temperatures of the final polymer. Reduction in the processing temperature reduces hydrolytic and oxidative degradation as well as minimising lactide reformation. Lactide reformation can be predicted from knowledge of residence time, temperature, catalyst concentration and initial monomer concentration. Figure 7 outlines the equation used to allow prediction of residual lactide. Actual curves generated are given in Fig. 8. Control of melt temperature and catalyst level allow minimisation of lactide reformation. It is also possible to reduce lactide formation considerably by the use of stabilisers. Residual lactide in the polymer, while not deleterious from a health perspective, is undesirable in that the volatile nature of this monomer can lead

Table 1. Crystallinity benefits

Product	Benefits
Fibres/non wovens	Improved heat set Chemical resistance Higher strength
Cutlery	Heat resistance Stiffness
Deli trays/cups	Heat resistance e.s.c.r
Films	Blocking resistance Permeability Chemical resistance

to 'plating out' on processing equipment as well as reduced storage stability of the polymer.

4 BASIC PLA PROPERTIES

4.1 Rheological properties

PLA produced either via the lactide process or by direct condensation is normally a linear polymer. In comparison with polyolefins, the polymer has poor melt elasticity as evidenced by low die swell. This feature can lead to problems during extrusion processes typically used for cast film, paper-coating and blown-film manufacture. Typical issues are high 'neck in' or poor bubble stability. This poor elasticity results from the low degree of molecular chain entanglement. The most promising method of increasing the level of entanglement is to introduce branching into the polymer. Cargill utilises low levels of an epoxidised natural oil to introduce branching into the polymer chain during polymerisation.[6] This technique is preferred to post-modification approaches that are also used for certain applications. Branching achieved during polymerisation has the additional benefit of reducing melt viscosity, which further assists in processing. For certain applications where higher melt elasticity is required beyond that presently achieved by the *in-situ* polymerisation approach, additional techniques can be utilised. Practical modifications involve the use of cross-linking agents such as peroxides, which, when used at very low levels, can lead to significant further increases in melt elasticity, but at the cost of a slight increase in melt viscosity. Table 2 and Fig. 9 indicate the various approaches utilised to control melt elasticity and their subsequent effects. Essentially, as the polydispersity (PDI) of the polymer increases, the

M(t)= Meq + (M0 - Meq) exp (-keff*t)

and

Xm = [M0 - Meq + (Meq - M0) exp (-keff*t)]/M0

Where

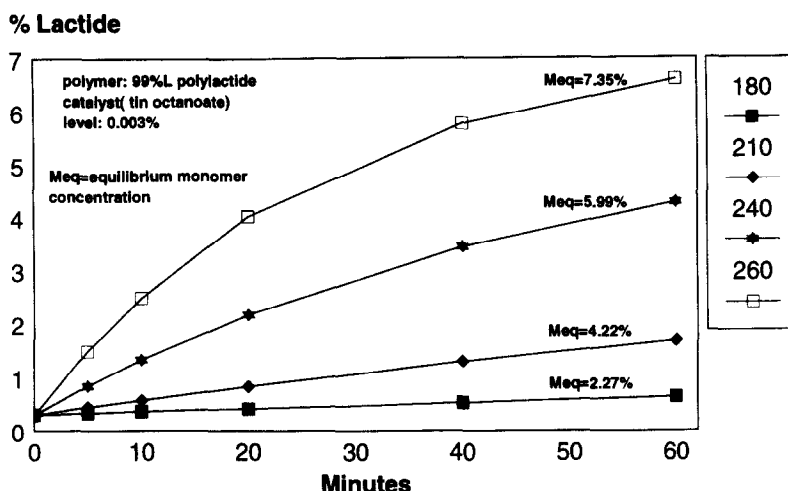|	
M(t)-	Monomer Concentration at Time of Interest
Meq-	Equilibrium Monomer Concentration
M0-	Monomer Concentration at Time Zero
Xm-	Fractional Monomer Conversion to Polymer
t-	Time of Interest
keff-	Rate Constant at a Specified Catalyst and Temperature

Fig. 7. Kinetic model for lactide reformation.

Fig. 8. Predited Lactide reformtion versus time and temperature.

melt elasticity increases. Here, we have used M_z/M_n as a measure of PDI where:

$$M_z = \frac{\Sigma n_i M_i^3}{\Sigma n_i M_i^2},$$

where n_i is the number of molecules of size i, and M_i is the molecular weight of molecules of size i.

5 MECHANICAL PROPERTIES

PLA polymers range from amorphous glassy polymers with a glass transition of 60°C to semi-crystalline/highly crystalline products with crystalline melting points ranging from 130 to 180°C. Quiescent nucleated crystalline products are essentially opaque, whereas stress-induced crystalline materials are transparent. In many aspects, the basic properties lie between those of crystal polystyrene and PET. In particular, properties noteworthy of mention include:

- flexural modulus > polystyrene;
- resistance to fatty foods and dairy products equivalent to PET;
- excellent flavour and aroma barrier;
- good heat sealability;

Table 2. Methods of polydispersity control

Process	Mz/Mn
Base PLA	3.8
Comonomer	4.6
Reactor configuration	6.1
Initiator	6.1
Cross-linker	7.6

- for amorphous and biaxial films, clarity and gloss exceeds PET, OPP and OPET;
- high surface energy allowing easy printability.

In addition to these inherent polymer properties, technologies have been developed to flexibilise PLA using renewable resource-based plasticisers. Figure 10 illustrates the influence of a citrate ester plasticiser (tri-acetyl *n*-butyl citrate), on the glass transition temperature of PLA. Careful selection of PLA stereochemistry, coupled with judicious plasticiser selection, allows flexible blown and cast film products to be successfully manufactured.

These properties, coupled with the renewable resource-based monomeric building block and inherent compostability/biodegradability of the various polymers, has led to specific focus being directed into single-use disposable product markets. Presently, a flexible film product suitable for kitchen waste biobags, bin liners and lawn and leaf applications (US) is available in the marketplace. Many other products are in the various stages of development, including thermoformed containers, non-wovens, paper-coated and injection-moulded articles.

6 BIODEGRADATION OF PLA POLYMERS

PLA polymers are aliphatic polyesters. The susceptibility to moisture observed by Carothers *et al.* in 1932 provides the primary driving force in the degradation pathway. As illustrated in Fig. 11, cleavage of the ester linkages by absorbed water produces a successive reduction in molecular weight. The rate of this hydrolytic degradation is

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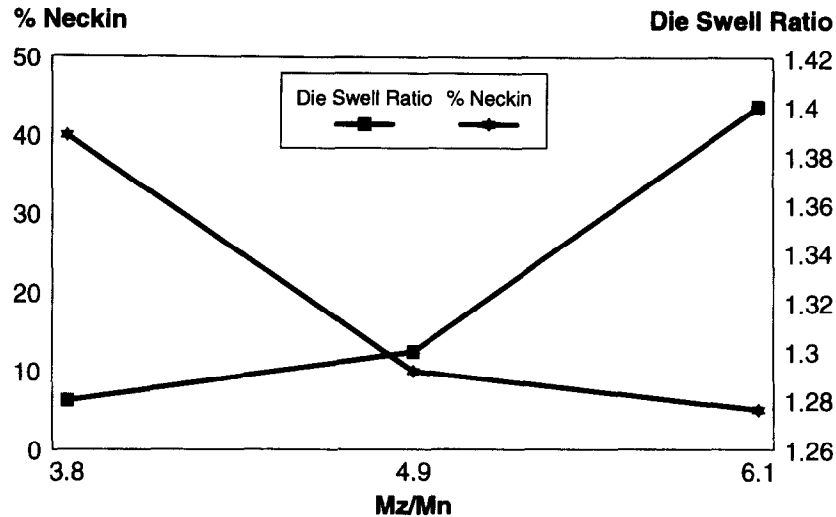

Fig. 9. Melt strength versus polydispersity.

primarily temperature- and humidity-dependent. Table 3 illustrates the rate of hydrolytic degradation as a function of temperature. In the primary degradation phase, no micro-organisms are involved. This is a useful attribute, particularly for product storage and in applications requiring food contact.

As the average molecular weight reaches approximately 10 000 (as determined by GPC in reference to polystyrene standards), micro-organisms present in the soil begin to digest the lower-molecular-weight lactic acid oligomers, producing carbon dioxide and water (Fig. 12).

This two-stage mechanism is distinctly different to many other biodegradable products presently on the market. Typically, biodegradable polymers degrade by a single-step process, involving bacterial attack on the polymer itself. For biodegradable applications, the preferred disposal route is by

composting. In this environment of high humidities and temperature (55–70°C), PLA polymers will degrade rapidly. However, at lower temperatures and/or lower humidities, the storage stability of PLA products is considered to be acceptable.

7 CONCLUSIONS

Extensive research and development activities are clearly indicating the benefits offered by PLA polymers. Continuing fundamental studies coupled with large scale application development and commercial product introductions will guarantee a viable future for these materials.

This paper has attempted to provide a brief insight into the versatility of this technology. However, significant challenges still remain to utilise fully the benefits discussed and overcome
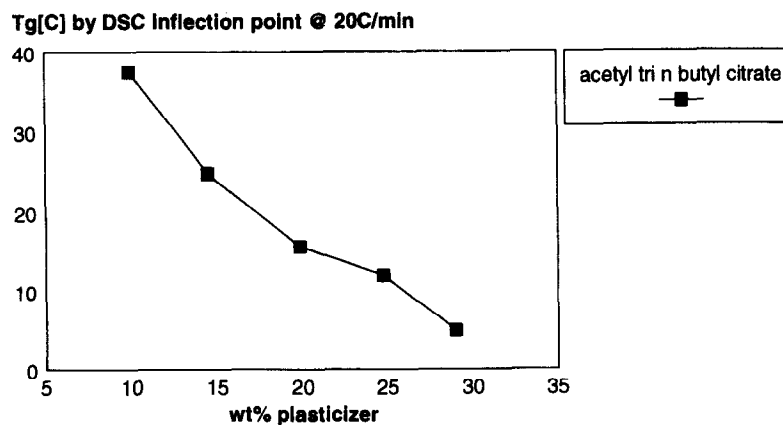
Tg[C] by DSC Inflection point @ 20C/min

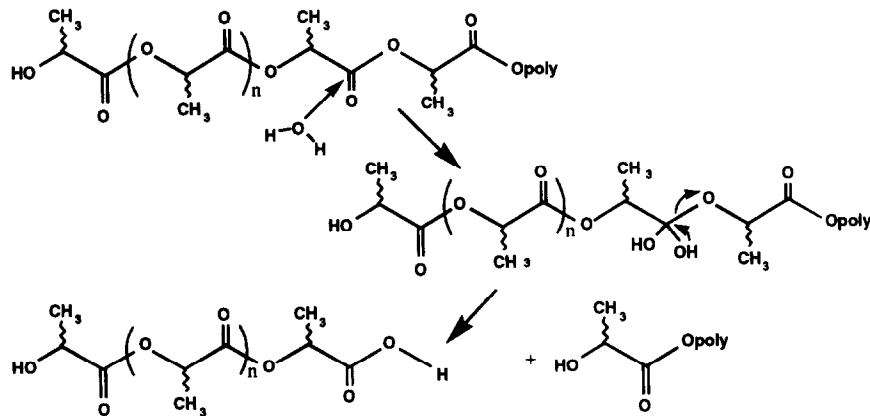Fig. 10. Tg depression of PLA with the addition of plasticiser.
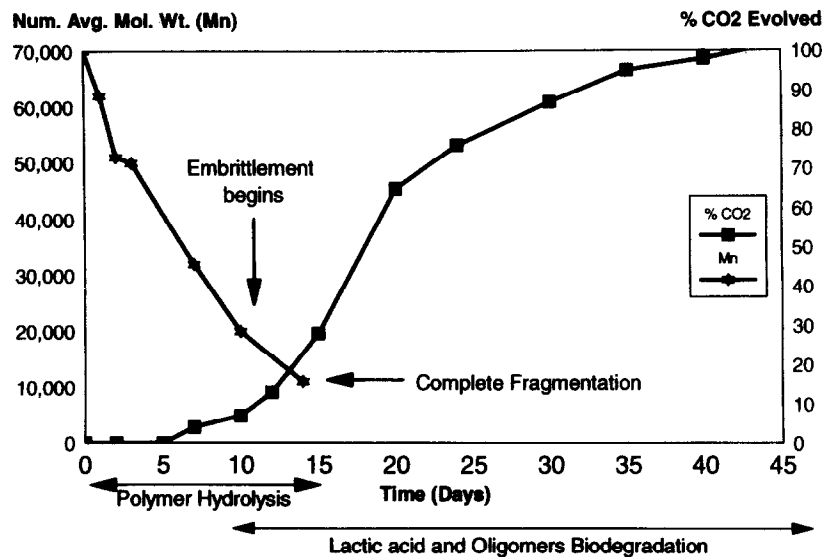
Fig. 11. Hydrolysis of PLA.

Fig. 12. Biodegration of polylactioc acid in 60°C compost.

Table 3. Length of time taken to degrade to PLA?*

Temperature	Onset of fragmentation	Onset of biodegradation
4°C 40°F	64 months	123 months
13°C 55°F	25 months	48 months
25°C 77°F	6 months	11.4 months
30°C 86°F	4.4 months	8.5 months
50°C 122°F	1.5 months	2.9 months
60°C 140°F	8.5 days	16 days
70°C 158°F	1.8 days	3.5 days

*In water.

deficiencies, particularly in the areas of crystallinity and extending applicability to the wider range of thermoplastic technologies.

Although the focus of this paper has been directed towards biodegradable applications, it should be noted that the availability of fermentation-derived lactic acid also offers a new optically active monomer. This monomer is presently being studied to produce polymers that can utilise some of the unique attributes of PLA polymer in combination with other monomers or polymer systems in applications where biodegradability is not required.

ACKNOWLEDGEMENTS

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