OVERVIEW OF POLY(LACTIC ACID) (PLA) FIBRE

Part I: Production, Properties, Performance, Environmental Impact, and End-use Applications of Poly(lactic acid) Fibres

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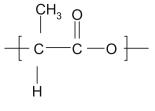
Poly(lactic acid) (PLA), the first melt-processable synthetic fibre produced from annually renewable resources, combines ecological advantages with excellent performance in textiles. PLA successfully bridges the gap between synthetic and natural fibres and finds a wide range of uses, from medical and pharmaceutical applications to environmentally benign film and fibres for packaging, houseware, and clothing. Ease of melt processing, unique property spectrum, renewable source origin, and ease of composting and recycling at the end of its useful life has led to PLA fibres finding growing interest and acceptance over a range of commercial textile sectors. Our review of poly(lactic acid) (PLA) fibre is divided into two parts. Part I of this review gives information about production, properties, performance, environmental impact, and end-use applications of PLA fibres. The aim of Part II is to review the wet processing (pretreatment, dyeing, clearing, subsequent finishing treatments, washing, etc.) of PLA fibre and its effects on the fibre. These were accomplished through a broad literature survey, including recent research and development in the area.

Poly(lactic acid) (PLA) is an aliphatic polyester that can be derived from 100% renewable resources [1]. PLA $[(C_3H_4O_2)_n]$ is the first melt-processable natural-based fibre [2,3] (Fig. 1). PLA molecule chains have a helical structure [4]. It is a synthetic polymer based on lactic acid $(C_3H_6O_3)$ and produced from the fermentation of agricultural resources, such as corn. PLA polymer is compostable, as it easily degrades by simple hydrolysis under the appropriate conditions [1,5,6]. PLA is of increasing commercial interest in packaging and textiles applications as a result of its interesting properties, potentially "green" credentials, and capability of being processed as a standard thermoplastic on existing industrial equipment [7,8]. It was discovered in 1932 by Carothers (DuPont) who produced a low molecular weight product by heating lactic acid under vacuum. However, the initial uses were limited to medical and pharmaceutical applications such as resorbable implants, sutures, and controlled drug-release applications due to its availability, high cost of manufacture, and low molecular weight [9-12]. PLA is preferred in biomedical applications due to its biodegradability, biocompatibility, and non-toxicity. The recent advancement in the fermentation of dextrose obtained from corn has dramatically reduced the cost to make the lactic acid monomer, which is the precursor to PLA production [13].

NatureWorks LLC currently operates the world's largest PLA manufacturing plant. This company has developed a patented, low-cost continuous process for the economic production of PLA polymer for packaging and fibre applications [14,15]. Some of the companies who produce commercial PLA are NatureWorks LLC (trademarks of the polymer and fibre; NatureWorks® and Ingeo®, respectively), Kanebo Gohsen Ltd. (polymer and fibre trademark Lactron®), Shimadzu Corp. (polymer trademark Lacty®), Toray Industries (trademark of Ecodear® as both fibre and resin products), Unitika (fibre trademark Terramac®), Kuraray (fibre trademark Plastarch®), and Mitsui Chemicals (resin trademark Lacea®) [13,16-25].

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Poly(lactic acid)

Fig. 1. Structure of PLA.

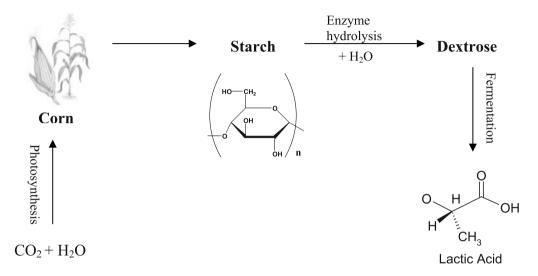


Fig. 2. Production of lactic acid from renewable resources such as corn [13].

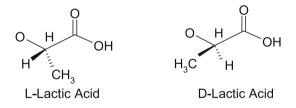


Fig. 3. Two stereoisomers of lactic acid

The processability of PLA is equivalent to that of petroleum-based synthetic materials, where PLA polymer uses conventional polyester type fibre melt spinning processes. PLA fibres use conventional spinning machinery. Finally, PLA fabrics use conventional dyeing and finishing machinery.

Production of PLA

The production of PLA starts with the extraction of starch from plants such as corn or the extraction of sugar from plants such as sugar beet. Starches can also be extracted from rice or wheat, rye, and sweet potato, and sugar can be obtained from sugar beet, whey, or molasses [3,26-31]. Grass or even biomass and other low value by-product wastes could be used for PLA production in the near future [14]. If the production starts with starch, the starches are then converted to fermentable sugars (e.g., glucose and dextrose) by enzymatic hydrolysis. Micro-organisms break the sugar into a smaller species known as lactic acid, through fermentation [14,32,33] (Fig. 2). Lactic acid production costs have considerably decreased in the last decade because of advances in the fermentation of corn dextrose [14].

Lactic acid has two optically active stereoisomers: dextro- (D-) and levo- (L-) (Fig. 3). Natural fermentation will generally yield a mixture of the two in the approximate proportions 99.5% (L) form lactic acid and 0.5% (D) [34].

The two isomers have identical physical properties, with the exception that of the L-form rotates the plane of polarized right in a clockwise sense while the D-form rotates it anti-clockwise [12].

Lactic acid is the starting material for the PLA production process. There are two major routes to produce PLA from the lactic acid monomer (Fig. 4). The conventional process for making PLA is by the polycondensation of lactic acid. This process is carried out under high vacuum and high temperature. Solvent is used to extract the water produced by the condensation reaction [23,29]. Carothers used this route to produce PLA polymer [13]. The product obtained tends to have low to intermediate molecular weight (Mw 10,000-20,000) due to difficulties of removing water and impurities [4,14,35-38].

The second method is ring-opening polymerization of a cyclic dimer of lactic acid (viz. the lactide) (Fig. 4). This method results in a higher molecular weight polymer and uses milder conditions [39]. Production of lactide from lactic acid potentially creates three different stereoisomeric forms, namely: L-lactide, D-lactide, and meso-lactide (Fig. 5).

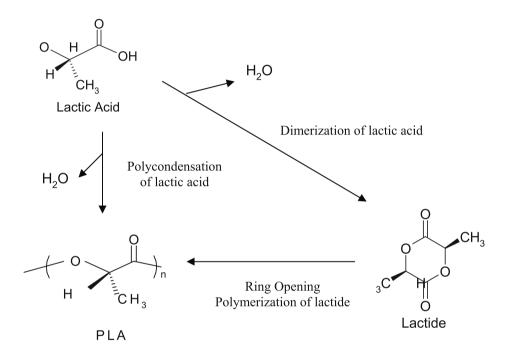


Fig. 4. Polymerization routes to PLA [7, 12].

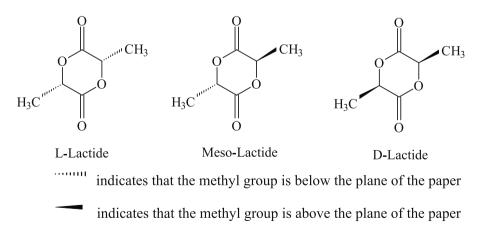


Fig. 5. Different forms of lactide isomers [7].

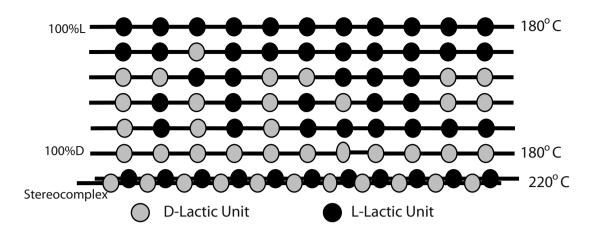


Fig. 6. Examples of molecular configurations of PLA obtained through combining the two lactic acid isomers in varying proportions [34, 45].

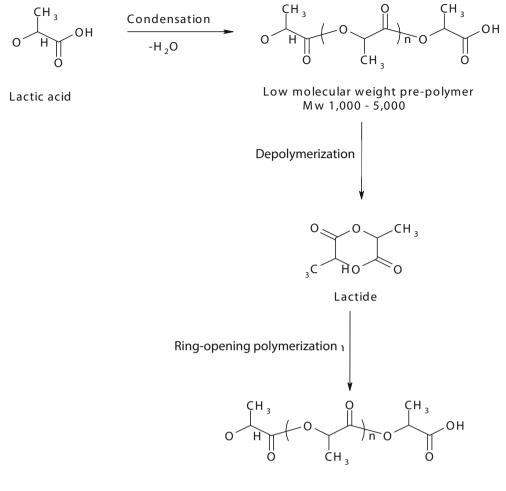
L-lactide and D-lactide are optically active. Meso-lactide is dimerized from D- and L-lactic acids. It is optically inactive and exhibits a lower melting point than optically active lactides [13] (Fig. 5). Lactide is purified and ring-opening polymerization is carried out under heat without a solvent (Fig. 4). Ring opening polymerization of lactide provides different stereopolymers depending on the isomeric type of the starting dimers [7,19,40]. Poly(DL-lactic acid) is generated from L-lactide, D-lactide, and either meso-lactide or an equimolar mixture of D-and L-lactides.

Production of PLA via the lactide route allows the possibility of modifying for superior control of the polymer properties by controlling the optical sequence of the polymer backbone [33]. Different characteristics of the polymer could be obtained through the controlled production of the optical isomers of the lactic acid via combining the two forms of lactic acid through the three lactide intermediates [12]. A wide range of molecular weights of PLA could be produced by controlling the purity of the lactide [13,14]. The ratio of D- and L-isomers and their distribution along the polymer backbone influence the molecular weight, crystallinity, and melting point of the end product PLA [12,14,41]. A high proportion of L-lactide can be used to produce crystalline polymers. Highly crystalline polymers can be achieved when the D-lactide content in the materials is less than 2% [42]. The crystallinity of PLA decreases with increased D isomer level [13]. Amorphous polymers can be produced using a relatively high D-lactide content (greater than 15%) [12,14]. The crystallinity and melting point of pure poly-L-lactide are about 37% and 175-178 °C, respectively [43,44]. For example, PLA produced from meso-lactide is an amorphous polymer [37]. On the other hand, Poly (L-lactic acid) (PLLA) is a part crystalline, relatively hard material with a regular molecular structure [15]. The right balance of stiffness, toughness, melting temperature, and degree of crystallinity of PLLA can be controlled without disturbing the crystallinity with the insertion of D-lactide units. [43]. The D-form is normally thought of as an impurity in fermented lactic acid [44].

Representations of PLA polymer chains having different ratios and distributions of the D- and L- isomers are shown in Fig. 6. Different melting points of PLA, varying from 130°C to 220°C, can be obtained [14]. P(L)LA having only L-lactic units has a melting temperature of 180°C and is shown in the upper row of Fig. 6. A blend of poly(L-lactic acid) and poly(Dlactic acid) can lead to a polymeric stereocomplex with higher melting point than either L- or D-polymers alone and with improved mechanical properties (See the last row of Fig. 6).

However, the mixing ratio and the molecular weight of both polymers influence the stereocomplex formation [46-48]. The melting temperature of the stereo-complex can be as high as 220°C [12,14]. Nevertheless, the spinnability of the stereo-complex polymer still needs further research [12]. NatureWorks LLC has developed a patented, low-cost continuous process for the manufacture of PLA polymer [1,14]. (Fig. 7)

Synthesis of lactide and PLA from melt rather than in solution with this process possesses environmental and economic benefits [14]. The continuous condensation of lactic acid is the first step in the production of low molecular weight PLA pre-polymer. Then, the pre-polymer is converted into a mixture of lactide stereoisomers. Finally, high molecular weight PLA is obtained via ring-opening polymerization. This process completely eliminates the use of costly and environmentally



High molecular weight PLA Mw > 100,000

Fig. 7. NatureWorks LLC's continuous production process of high molecular weight PLA [44, 49].

unfriendly solvents. The remaining monomer is eliminated under vacuum and recycled back to the beginning of the process after the completion of the polymerization [1,14].

Environmental Impact of PLA

PLA is acknowledged to be a more environmentally-friendly polymer than PET (Table 1). The typical life cycle of PLA is shown in Fig. 8. The monomer of PLA is sustainable. PLA, whose raw material (such as corn) is both renewable and non-polluting, eliminates the use of a finite supply of oil as a raw material [2].

Production of PLA fibres from corn will not result in a food crisis, since the amount of corn consumed in the production of PLA fibres is less than 0.02% of the total amount of world production [50].

PLA is produced from plants and polymerized and processed into the desired products. Production of PLA requires 25-55% less fossil energy and 20-50% less fossil fuel resources than the production of petroleum-based polymers [14,51].

The net result is lower greenhouse gas emission and significant energy savings. Even though PLA uses fossil fuels in processing the raw material and in producing polymer, like all synthetic polymers, it is obvious that PLA will play a part in reducing society's dependence on fossil fuels. PLA avoids the problems related to plastic waste accumulation, thereby giving it a significant advantage over PET [53].

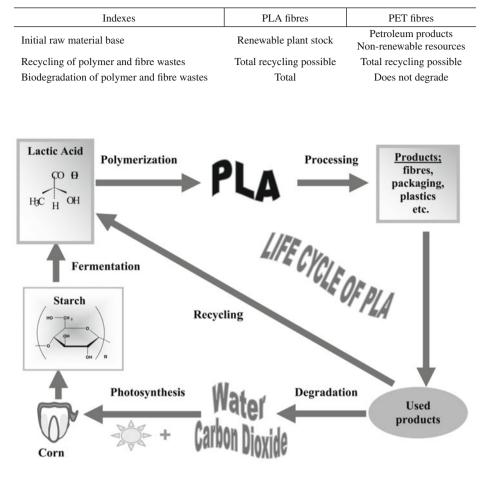


 Table 1. Comparison of raw material type and possibility of recycling and biodegradation of PLA and PET polymer and fibres

Fig. 8. Life cycle of PLA [drawn from Refs. 13, 33, 52].

PLA must be subjected to a hydrolytic process to obtain biodegradable lactic acid [54]. PLA products can be easily composted or recycled under appropriate conditions at the end of the product life [55]. Although PLA fibres are stable enough under normal use as natural fibres [13,14,34], they are completely compostable under specific composting conditions, typically around 60°C, with 90-95% relative humidity [14,28,33]. PLA material degrades first by hydrolysis, then by microbial action (consumed by microbes), eventually degrading simply to carbon dioxide and water, the basic necessities for new growth [33]. The ability to recycle back to lactic acid by hydrolysis will lead to a reduction in landfill volumes [56,57]. The recycling of PLA can be performed with water at a wide range of temperatures from 100 to 250°C, leading to lactic acid [14]. This lactic acid can be re-used as a monomer in the production of new PLA [12,58].

Applications of PLA

PLA finds a wide range of uses from medical [26,28,38,59-82] and pharmaceutical applications [26,83-87] to environmentally benign film and fibres for packaging [3,26,80,88-91], houseware [26,28,58], and clothing [28,31,52,58,92-96]. PLA is also used in composite materials [26,28,35,58,93,97]. Primary applications are in fibres, fibrefill (pillows, comforters, mattresses, duvets), apparel (sport, active, underwear and fashion wear), and nonwoven applications (agricultural and geo textiles, hygiene products, wipes). A wide spectrum of forms from staple fibre to composite materials can be produced from PLA (Table 2) [85].

Staple fibre
Monofilament
Multifilament
Trilobal BCF
Bicomponent fibre
Knitted structure
Woven structure
Spun bonded nonwoven
Needle punched nonwoven
Composite materials

Table 2. Different forms of PLA

PLA fabrics are well suited for producing sportswear articles since they exhibit very good moisture management. PLA can be used in blends with cotton, lyocell, and wool, or alone. For example, NatureWorks LLC promotes the IngeoTM fibre for use in apparel, fibre-fill, carpets, furnishings, nonwoven, and industrial applications. Pillows and apparel made from IngeoTM fibre are already being sold in three continents. However, the low melting temperature of IngeoTM fibre is a limitation. Therefore the research of NatureWorks LLC continues to produce second-generation PLA fibre with a higher-melting point (210-220°C), based on stereocomplex PLA. Nevertheless, the spinnability of the stereo-complex polymer still needs further research [36]. It is possible that it may become commercially available in the near future.

Performance and Properties of PLA

PLA combines ecological advantages with very good technical performance in textiles. PLA has high mechanical strength, compostability, and biocompatibility [33]. As a melt-processable fibre from a vegetable source, PLA has many characteristics similar to many other synthetic fibres [2]. The properties of PLA fibres are between those of Polyamide 6 and PET [98,99]. On the other hand, the mechanical properties of PLA are considered to be broadly similar to those of conventional PET [1].

Poly(lactic acid) is a relatively stiff polymer at room temperature [7,14], but its glass transition temperature (Tg) is rather low, being in the range of 55-65°C [14]. PLA polymer from meso-lactide can exhibit a glass transition temperature as low as 34°C [100]. The melting temperature (T_m) of PLA, having either the L- or D- isomeric form alone, is between 160-180°C, whereas the melting temperature of stereocomplex PLA is 220°C [14,41]. Introduction of meso-lactide can decrease the melting point of PLLA by as much as 50°C [101]. The PLA polymer demonstrates a clear decrease in molecular weight on heat treatment above 190°C, at which the thermal degradation of PLA starts to take place [102]. Different mechanical properties of PLA, ranging from soft and elastic materials to stiff and high strength materials, can be achieved to a large extent. If higher mechanical properties of PLA are needed, semi-crystalline PLA is preferred to the amorphous polymer. The degree of crystallinity and molecular weight of the polymer extensively influence its mechanical properties [103,104]. If the molecular weight of PLA polymer increases, the tensile strength and modulus increase.

Some typical properties of PLA are compared with those of conventional polyester (PET) in Table 3. The specific gravity of PLA is lower than that of PET. Varying the optical composition of PLA allows control of the melting point in the range from 130°C to 175°C [13], and typical melting point of PLA is around 170°C [54], whereas that of PET is around 254-260°C [105]. However, its low melting point results in a low domestic ironing temperature, leading to limitations for end users. Temperatures for ironing and garment processing should be lower than these of cotton and PET [14]. Elastic recovery is superior to PET compared at 5% strain. The elastic recovery and crimp retention properties lead to good shape retention and crease resistance.

PLA also has advantages with respect to smoke generation and flammability, having both higher limiting oxygen index (LOI) and lower smoke generation than PET. The deeper shades can be achieved because of the lower refractive index of PLA compared to PET using a given concentration of disperse dye on fibres of similar dimensions. PLA is highly resistant to degradation by ultraviolet radiation, with no loss in elongation after 100 hours in Xenon arc testing [33]. PLA fibres do not provide a microbial food source and they do not support bacterial growth [14]. PLA fibre based fabrics exhibit lower odor retention than PET fibre based fabric [106]. It is unaffected by dry-cleaning solvents [14].

Table 3. Fibre properties of PLA and PET

Fibre properties	PLA	PET
Specific gravity	1.25	1.39
T _m (°C)	130-175	254-260
Tenacity (g/d)	6.0	6.0
Elastic recovery (5% strain)	93	65
Moisture regain (%)	0.4-0.6	0.2-0.4
Flammability	Continues to burn for 2 mins after flame removed	Continues to burn for 6 mins after flame removed
Smoke generation	63 m²/kg	394 m²/kg
Limiting oxygen index (%)	26	20-22
Refractive index	1.35-1.45	1.54

PLA exhibits good moisture management and comfort properties. This is particularly important in respect of applications such as sportswear, underwear, and bed linen. Moisture management is the ability to transmit moisture away from the body with good wicking, faster moisture spreading, and drying [14]. Breathability of fabrics is closely related to the transmittance water vapor through the fabric and by wicking of water. Hydrophilic fibres such as cotton and wool are usually considered to be comfortable and breathable whereas hydrophobic fibres such as polyester and polypropylene tend to be less so [107]. The moisture regain and wicking property of PLA are superior to PET [13,108]. PLA fibres wick moisture well without absorbing large amounts of water, which benefits sports and performance apparel. Its lower contact angle compared to PET leads to improved wicking with water [108]. PLA exhibits a quick removal of moisture from the body [12]. It is stated that PLA fibres performed better than PET and cotton, either as 100% PLA fabric (alone) or when combined with cotton according to series of tests including breathability, water vapor transport, and thermal insulation measurements [14]. Improved physiological comfort was experienced with PLA/cotton blend fabric compared to equivalent PET/cotton blend fabric [14].

PLA exhibits higher sensitivity to alkali [2] than does PET. Some loss of fibre strength during subsequent wet processing is observed if care is not taken in dyeing and finishing of the fibre because of this sensitivity. PLA has a surface cohesion that gives the fibres a property known as scroop [2]. Scroop of fibres causes a sound or 'crunchiness' to be felt when the fibres are rubbed against one another, most likely caused by a stick-slip action as fibres slide past each other. This feature of PLA fabrics may influence the resilience and thus cause problems in some applications by resisting the recovery after deformation. Scroopiness might be overcome by applying a suitable fabric finish [2].

Conclusion

Poly(lactic acid) fibre combines ecological advantages with excellent performance in textiles. Ease of melt processing, renewable source origin, unique property spectrum and ease of composting and recycling at the end of its useful life has led to PLA fibres finding increasing interest and acceptance over a range of commercial textile sectors. PLA finds a wide range of uses from medical and pharmaceutical applications to environmentally benign film and fibres for packaging, houseware and clothing. Although the use of PLA fibre is in its early stage compared with conventional synthetic fibres such as PET, the potential applications of PLA in textile industry are promising. The use of PLA fibre is expected to increase in the future due to its ecological advantages with very good technical performance as a textile fibre. However, a variety of wet processing applications (pre-treatment, dyeing, clearing, and subsequent finishing treatments) that imparts the most chemical and physical effect on the PLA fibres necessitate major attention. Part II of this review will deal with the wet processing (pre-treatment, dyeing, clearing, subsequent finishing, etc.) of PLA fibre and its effects on the fibre.

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