



Photo: Purac Biochem

Modification of Polylactide for Technical Applications

PLA Processing. Basic resin properties that have limited the use of unmodified polylactide (or poly(lactic acid)) for technical purposes are its low heat deflection temperature, poor impact strength and relatively low glass transition temperature (T_g). The crystallization behavior, and therefore the heat deflection temperature, can be significantly improved by adding suitable nucleating agents and modifiers.

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In addition to the already established packaging sector, there is also growing interest in biopolymers for technical applications. Drivers for the plastics industry to replace oil-based with bio-based polymers, particularly in compounds for technical durables, are limiting the dependence on petrochemical raw materials and reduction of the carbon footprint. Against this background, this research work is particularly focused on optimizing the injection molding process for poly-

lactides (PLA), and on the associated material properties for technical applications.

In addition, the effect of poly-D-lactide homopolymer as nucleating agent and modifier of material properties like crystallization behavior, heat deflection temperature and mechanical properties, was addressed in more detail.

Identical Properties Required

The requirements for biopolymers used for technical applications are relatively straightforward: after their production and modification, the properties of the obtained biopolymer-based compounds should be almost identical with those of their oil-based counter-parts that they are

to substitute. Preferably, the proportion of renewable raw materials – or so-called “new carbon” – should be as high as possible even after modification. Compared to conventional polymers such as PET, PP and PS, the following processing and service properties of unmodified PLA require improvement:

- Injection moldability (e.g. flow behavior, cooling time and crystallization behavior),
- heat deflection temperature,
- mechanical properties (e.g. impact strength), and
- long-term stability (e.g. relaxation behavior, chemical resistance).

The first efforts to adapt the property profile of PLA to the requirements were, e.g. →

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incorporation of nucleating agents, reinforcing fibers or impact modifiers. Besides the desired service properties, it is also crucial to optimize the processing properties.

Structure and Processing Behavior

The precursor for PLA resin is lactic acid, which occurs in two optical isomers. This results in three different lactic acid dimers, called lactide: L-lactide, meso-lactide and D-lactide [1] (Fig. 1). PLA resins are made by ring-opening polymerization of (mixtures of) these cyclic ester monomers.

The processing and service properties of PLA are critically dependent on the structure and composition of the polyester chain; the L/D ratio has a significant effect on this. The poly-L-lactide homopolymer, which is produced only from L-lactide (PLLA < 0.5 % D-isomer), is an isotactic polymer (cf. iPP). As can be generally seen in polyester copolymers, copolymers of L- and meso-lactide with different D proportions also have significantly lower melting points (-6°C per percent D) than the pure homopolymers PLLA or PDLA, and also crystallize significantly more slowly.

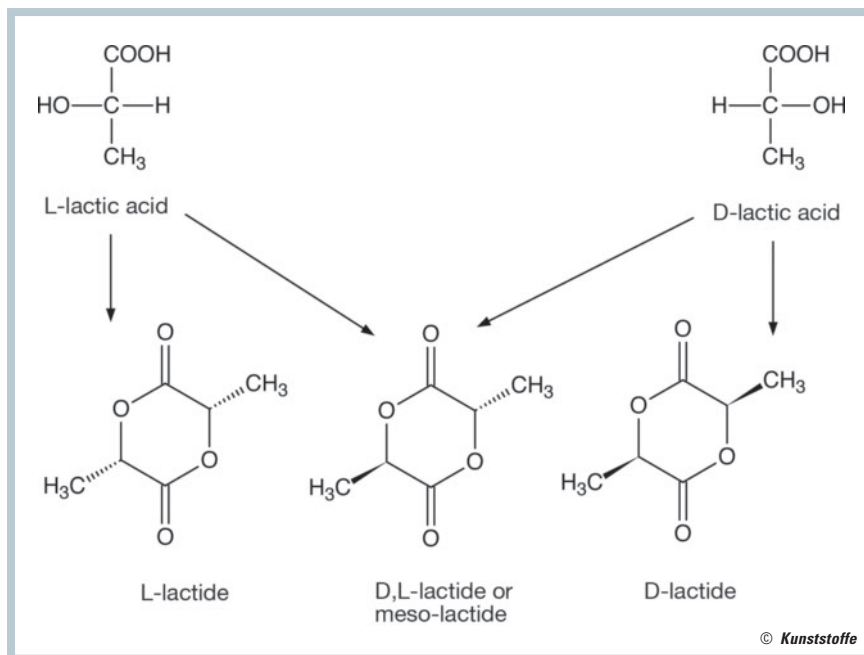


Fig. 1. Lactic acid isomers and the resulting lactide dimers [1, 2]

If blends are produced from PDLA and PLLA, the different polymers form racemic crystals with melting points in the range from 190 to 240°C, which are also known as stereocomplex-PLA. [2–4] These scPLA crystallites (circled red in Fig. 2), which are formed in situ by admixing low-molecular poly-D-lac-

tide, act as nucleating agents for PLA crystallization and thereby increase the crystallization rate in the PLA. [2] To generate good results in the injection molding process, i.e. to produce semi-crystalline polylactides with a high heat deflection temperature, it is necessary, with the addition of the PDLA nucleating agent, to have a higher L-content, or lower D-content, in the corresponding starting PLA (Fig. 2).

Materials and Test Methods Used

The investigation concentrated on four commercially available PLA grades (copolymers of L- and meso-lactide) from the U.S. company NatureWorks

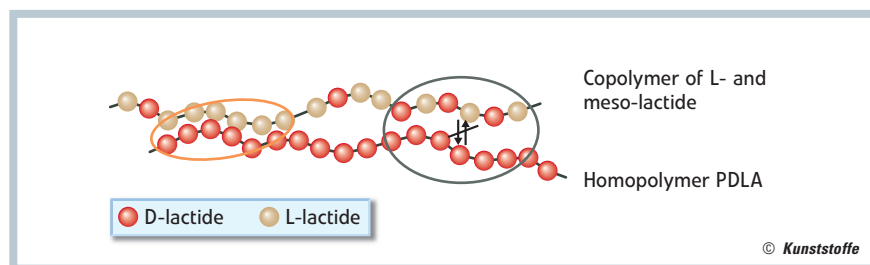


Fig. 2. Initial conditions for stereocomplex PLA formation [3]

Abbreviation		3251D	3001D	6201D	4042D	PLLA	PDLA
Glass transition temperature	[°C]	55–65	55–60	55–60	55–60	58	45
Melting temperature	[°C]	160–170	160–170	160–170	145–155	175–185	160–170
L/D isomer ratio	[%]	98.8/1.2	98.6/1.4	98.6/1.4	97.7/4.3	99.5/0.5	1/99
Molecular mass	[kg/mol]	86.8	112.2	110.2	170	140	<50
MFI	[g/10 min], 190 °C, 2.16 kg	37	10	11	2.7	20	>100
HDT B	[°C]	57	60	55	55	55	-
Tensile modulus	[MPa], 23 °C	3,610	3,620	3,450	3,500	3,650	-
Tensile strength	[MPa], 23 °C	70.1	71.8	70.8	68.3	63.5	-
Charpy-notched impact strength	[KJ/m²], 23 °C	1.57	1.66	1.0	2.1	1.4	-
Application		Injection molding	Injection molding	Fibers	Film	Injection molding	Nucleation agent
Nomenclature		Amorphous copolymers of L and meso-lactide, PLA copolymer				Semicrystalline homopolymer poly-L-lactide	Semicrystalline homopolymer poly-D-lactide

Table 1. Overview of the properties of the polylactides used

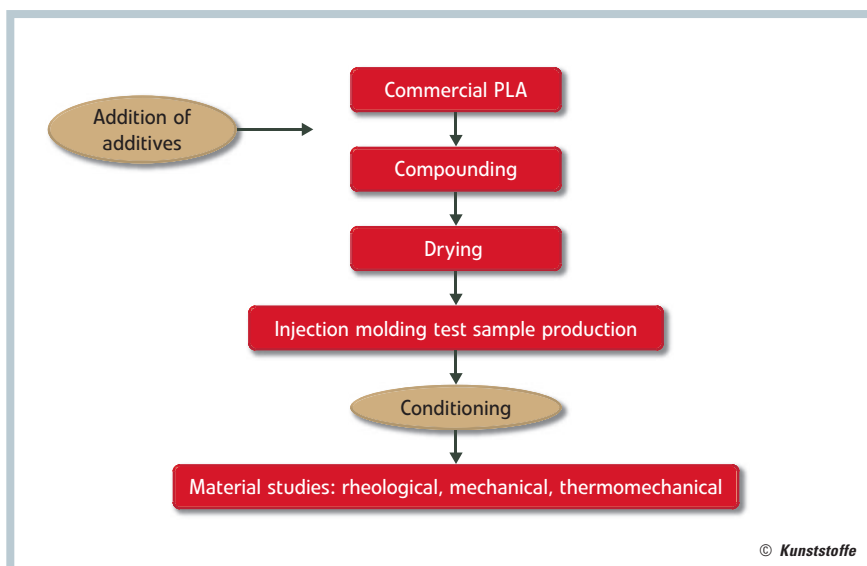


Fig. 3. Modification of PLA (sources of graphs 3, 5 to 9: University of Applied Sciences and Arts in Hanover)

LLC, Blair, NE, and two semi-crystalline homopolymers (poly-L-lactide [PLLA] and poly-D-lactide [PDLA]) from Purac Biochem, Gorinchem, Netherlands, which are currently at the R&D stage. Table 1 presents an overview of the different PLA grades that were used in this work [5].

Besides PDLA as nucleating agent, modifiers were additionally used, e.g. to improve the flow properties and increase the impact strength.

Material properties that have limited the use of unmodified PLA for technical purposes are its low heat deflection temperature, poor impact strength and slow crystallization rate that prohibits injection molding of semi-crystalline products with economical cycle times.

The primary goals of this work as regards the industrial applications of PLA were to reduce the cooling time for injection molding and increase the crystallization rate and heat deflection temperature.

As shown in Figure 3, all PLA grades were modified with different additives

(nucleating agents and modifiers, e.g. flow improvers). Because of the moisture sensitivity of PLA as polyester, it is important to dry the PLA pellets before injection molding (at least 4 hours at 80°C). Moist material is very susceptible to hydrolysis during the process, particularly at high temperatures.

The test samples (tensile bars, type 1A, DIN EN ISO 527) were produced using a type 160-750CX injection molding machine (manufacturer: KraussMaffei). Some key technical data of the machine are given in Table 2.

Clamping force	1,600 kN
Injection pressure	2,500 bar
Screw diameter	40 mm
L/D ratio	25.2
Screw speed	265 rpm
Heating zones, incl. nozzle	6

Table 2. Technical information on injection molding machine KM 160-750CX

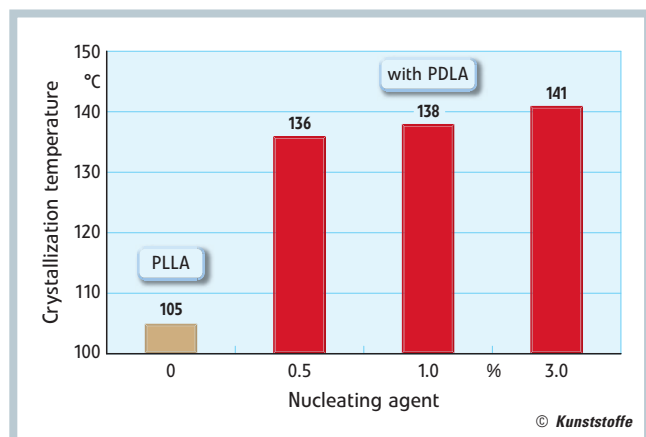


Fig. 4. Improvement of the the crystallization temperature of PLLA by PDLA addition [4]

Table 3 shows selected injection molding parameters, which are used to produce the tensile bars (two cavities).

The tensile bars were produced to optimize the injection molding process on standardized test samples (cooling times) as well as for the following further investigations:

- Thermomechanical studies, e.g. HDT and Vicat for determining the heat deflection temperature;
- mechanical studies, e.g. tensile test or notch impact bending test for determining the impact strength;
- thermal analysis methods, e.g. dynamic scanning calorimetry (DSC), for determining the crystallization temperature.

Accelerating PLA Crystallization

Earlier research results, such as those of Anderson and Hillmyer (Fig. 4), have shown that the addition of various weight proportions of low-molecular PDLA to poly-L-lactide homopolymer significantly increases its crystallization temperature. Comparing the pure unmodified PLLA with the PLLA + PDLA homopolymer blend clearly shows that when 3 % PDLA is added, crystallization from the melt starts at 141°C as opposed to only 105°C for the PLLA homopolymer. The crystallization rate is increased by addition of PDLA, which forms the nucleating stereocomplex crystallites. [4]

Increasing PLA Heat Deflection Temperature

It has also been shown that the heat deflection temperature of PLA could be significantly increased by the addition of PDLA as nucleating agent. Figure 5 shows the results of the first HDT/B tests on PLA/PDLA(95/5) blends and indicates clear dependencies. The mold tempera-

Clamping force	1,000 kN
Injection pressure	1,000 bar
Back pressure	500 bar
Time back pressure	15 s
Screw speed	28 mm/s
Heating zones	40°C, 120°C, 155°C, 195°C, 200°C
Nozzle	200°C
Mold temperature	100°C

Table 3. Injection molding parameters for producing tensile bars type 1A, two cavities

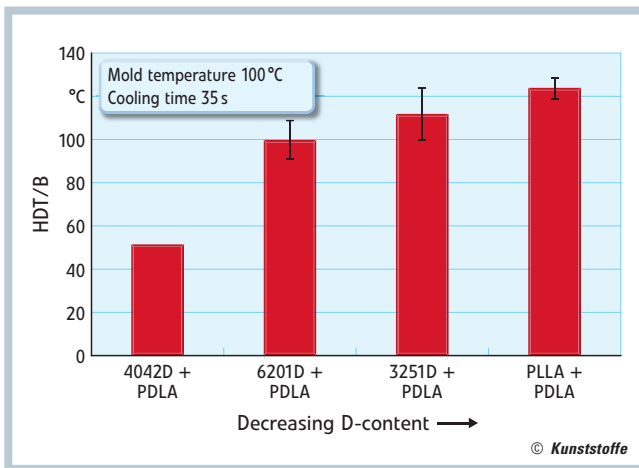


Fig. 5. Heat resistance of various PLA/PDLA(95/5) blends depending on the D-isomer content in the initial PLA resin

composition of the starting PLA affect the cooling times during injection molding.

This study was based on the PLA copolymer type 6201 from NatureWorks (D-content 1.4 %) compared to the homopolymer PLLA from Purac (D-content < 0.5 %). In order to improve melt flowability, which promotes crystallization from the melt, during injection molding, 5 wt.-% of di-(2-ethylhexyl) adipate (DOA) was added to the formulations.

The PDLA-modified samples (addition 5 %) that were processed at a mold temperature of 100°C exhibited the best HDT/B values and the shortest cooling times. Both processability in injection

ture is crucial to these results. If a cold injection mold is used (25°C, cooling time 35 s), a transparent, amorphous PLA is obtained. The heat deflection temperature (independent of the content of PLA or D), remains unchanged at a low level (55°C) (cf. Fig. 6). Upon decreasing the D-isomer content in the starting PLA resin in binary blends with PDLA, the heat deflection temperature increases if a mold temperature of 100°C is used. For example, injection molding a 5/95 (w/w) blend of PDLA and PLA with a D-content of 1.2 % resulted in HDT/B values of over 110°C. The highest HDT value (125°C) for these 5/95 PDLA/PLA blends was

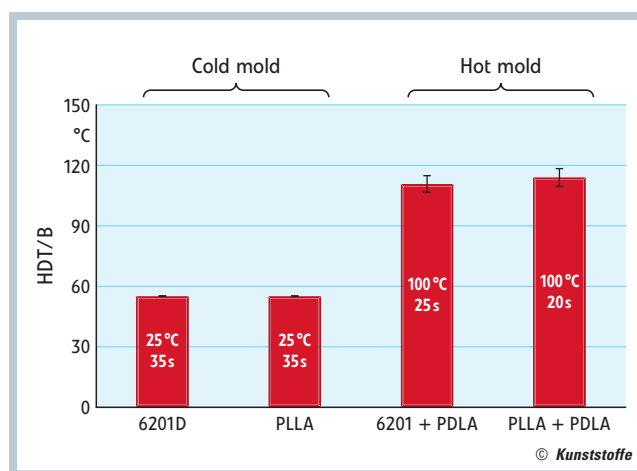


Fig. 6. Influence of mold temperature (25°C and 100°C) on the HDT-B values at various cooling times

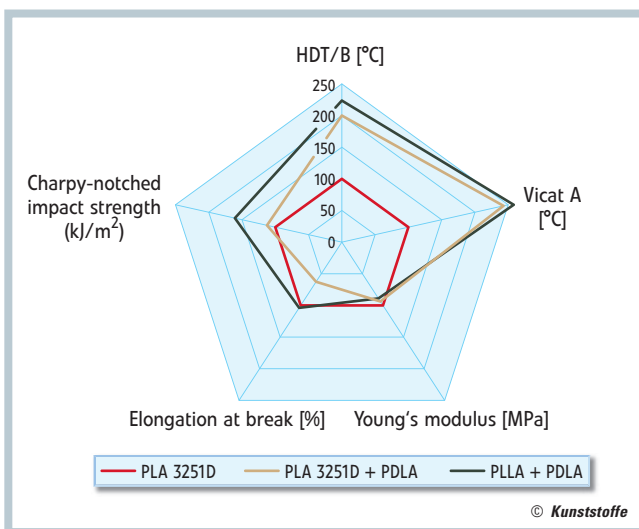


Fig. 7. PLA copolymer and PLLA, each blended with 5 % PDLA compared to pure PLA copolymer

molding and heat resistance benefit from having the lowest possible D-isomer content in the initial PLA resin.

For technical purposes, PLA requires not only optimized processing properties but also specific service properties. Figure 7 shows the first results for this. The graph shows a comparison of two 5/95 PDLA/PLA blends, based on commercial PLA 3251D and on PLLA homopolymer, respectively. Unmodified PLA resin, type 3251D, was used as a reference. All the samples were processed at 100°C mold temperature and a cooling time of 35 s.

Besides the heat deflection temperature, in the case of both PDLA-modified blends the Charpy-notched impact strength was also remarkably improved with minimal loss in Young's modulus.

Another important point is the resulting (ideally improved) long-term resistance of PLA under varying climate conditions. Initial studies of this were also performed. Figure 8 shows the profile used of the climate cycle test, which was used by analogy with automotive industry test methods.

achieved with PLLA homopolymer as the starting PLA. The injection molding parameters were identical in all cases and the cooling time was 35 s.

Reduction of the Injection Molding Cycle Times

A principal aim of this research work is practical injection molding. Rapid cycle

times and short cooling times are the main prerequisites for industrial plastics processing. Therefore, only samples that were produced in fully automatic operation were used for material characterization.

Figure 6 clearly shows that the mold temperature is crucial both for injection molding and for the service properties. In addition, the mold temperature and the

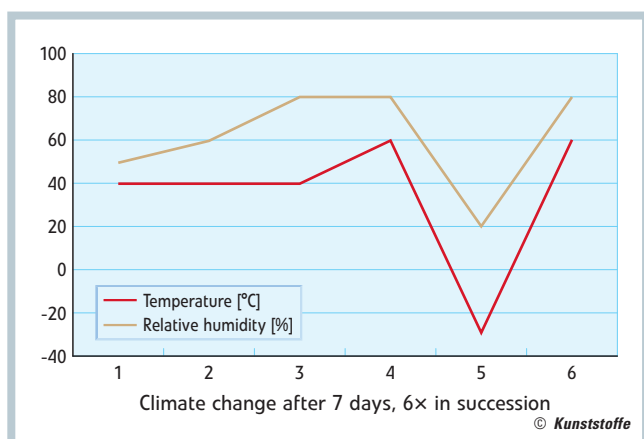


Fig. 8. Profile of the climate cycle test

The first results (in this case Vicat A) can be taken from Figure 9. As already explained, these values increase with increasing crystallinity as well. It is crucial, in particular, that the heat deflection temperature is hardly decreased in the 42-day climate cycle test. Further climate testing is currently in progress.

Summary

In this first study on injection molding of semi-crystalline PLA under industrial conditions, it was confirmed that the addition of low-molecular homopolymer PDLA indeed has a significant influence on the injection molding process and the resulting material properties. Blending PLA homopolymers or copolymers (>98 % L-content), with only 5 % PDLA results in in situ formation of stereocomplex crystallites that prove to be efficient nucleating agents for PLA homocrystallization.

Moreover, the use of further additives is important for the injection molding capability of PLA-PDLA blends. With high mold temperatures (100°C), HDT/B values of over 120°C could be achieved in

fully automatic injection molding. Due to the high crystallization rates, the cycle times could also be reduced so that practically useful cycle times could be achieved for PLA processing. Not only the processing and thermal properties, but also the mechanical properties could be improved.

If homopolymer PLLA is used as the starting PLA, the improvement of properties resulting from the addition of PDLA is even more significant. ■

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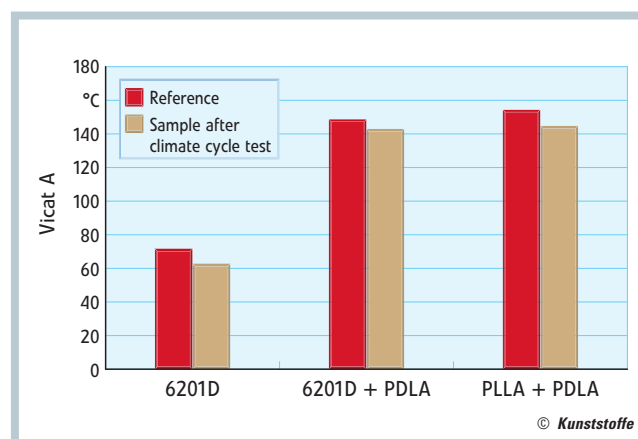


Fig. 9. Results before and after the climate cycle test

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