The influence of nucleating agents, plasticizers, and molding conditions on the properties of injection molded PLA products

Tamás Tábi [a,b,*], Tatyana Ageyeva [a,c], József Gábor Kovács [a,c]

[a] Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary
[b] MTA–BME Research Group for Composite Science and Technology, Műegyetem rkp. 3., H-1111 Budapest, Hungary
[c] MTA–BME Lendület Lightweight Polymer Composites Research Group, Műegyetem rkp. 3., H-1111 Budapest, Hungary

ARTICLE INFO

ABSTRACT

Poly(lactic acid) (PLA) is a "green" alternative to petroleum-based plastics and a desirable choice for many applications. However, low heat deflection temperature and lack of toughness, together with the slow crystallization kinetic of neat PLA hinder its widespread application. The weak properties of PLA can be improved with the improvement of crystallinity, which depends on molecular weight, D-lactide content, the presence of different modifiers and the processing conditions. We aimed to maximize the crystallinity and crystallization rate of PLA to explore the limitations of PLA when it is processed by injection molding. Therefore, we selected PLA with low D-lactide content, the three effective nucleating agents and the two suitable plasticizers. We found that the heat deflection temperature, tensile strength, and Young's modulus of PLA modified with nucleating agents were considerably better than those of Acrylonitrile Butadiene Styrene (ABS). However, the elongation at break of the annealed and the simultaneously nucleated and plasticized PLA compounds was significantly lower than that of ABS. The addition of nucleating agents and plasticizers and the variation of mold temperature did not improve the brittleness of PLA. The elongation at break of PLA was still very low and stayed in the 1.7–2.5% range.

1. Introduction

Poly(lactic) acid (PLA) is a biodegradable polymer derived from renewable natural resources. PLA belongs to the family of aliphatic polyester thermoplastics with strength and stiffness superior to some petroleum-based commodity plastics, such as Polypropylene (PP) and Acrylonitrile Butadiene Styrene (ABS) [1,2]. This plastic is biocompatible with human tissues [3], moisture resistant, an excellent electrical insulator, and possesses good optical and barrier properties. It is also considered "greener" than petroleum-based plastics due to the less CO_2 emission generated during its lifecycle [4]. Due to its good thermal processability, PLA is suitable for manufacturing products by film extrusion, blow molding, fiber spinning, 3D printing, thermoforming, and injection molding [5–7]. All the merits of PLA make it a desirable choice for the mass production of polymers for different applications. Nowadays, PLA is already widely used in healthcare [8,9] and packaging [10], but due to its low heat deflection temperature (HDT) [11] and

rigidity, PLA is still inadequate for structural usage. Another drawback of PLA is its slow crystallization kinetic. Neat PLA usually demonstrates a half-crystallization time ($t_{1/2}$) in the range of 20–40 min, which is unacceptably long for industrial production, especially for injection molding, where a typical cycle time is 60–90 s [12].

The weak mechanical and thermal properties of PLA can be improved by increasing its crystallinity, which is affected by its molecular weight [13], D-lactide content [14], the presence of different modifiers [15,16], and also by processing conditions, especially mold temperature (T_{mold}) [17]. Increasing T_{mold} above the glass transition temperature (T_g) of PLA is an effective strategy to improve the crystallinity of PLA. Misra et al. [18] investigated the effect of different mold temperatures on the crystallinity of PLA. They found that the crystallinity of PLA increased from 25% to 42% at mold temperatures of 30 °C and 90 °C correspondingly. A similar tendency was reported in many other studies [11,19–21]. The higher the crystallinity of PLA, the lower its molecular weight (M_w) [22]. For PLA with the lowest possible

D-lactide content, $t_{1/2}$ is around 3 min, which is still unacceptably long for injection molding [23]. The crystallization half-time of PLA can decrease dramatically to a minute or even below when an effective nucleating agent is used [11,12,24]. In our recent study [4], we found that the most effective nucleating agents for injection-molded PLA are Zinc PhenylPhosphonate (PPZn), Ecopromote (Eco), and EcopromoteHD (EcoHD). Although the primary role of a plasticizer is to increase the toughness of PLA, plasticizers also enhance molecular chain mobility by diffusing into the polymer chains and thus decrease the glass transition temperature of PLA. By widening the crystallization window between T_g and the melting temperature (T_m), plasticizers enhance the crystallization of PLA [23,25]. Based on the literature analysis [1], one of the most suitable plasticizers for PLA is Oligomeric Lactic Acid (OLA). It has a similar chemical structure to PLA, a relatively high molar mass, and renewable origin, and it also decreases the T_g of PLA effectively [26,27]. Another efficient plasticizer for PLA is Dioctile Adipate (DOA) [28,29].

Although low D-lactide content and the presence of a nucleating agent and a plasticizer improve the crystallinity and thus the thermomechanical properties of PLA, the full potential of this polymer cannot be realized with modifiers only. The crystallinity of PLA highly depends on processing or post-processing conditions, especially the thermal regime. It is worth mentioning that the thermal regime influences the overall crystallinity of PLA and the morphology of crystals [30], which affects the properties of PLA. Like many semi-crystalline polymers, PLA is polymorphic with four possible crystal forms: α, β, γ, ε (also called stereocomplex), and a disordered crystal form α'[31]. The α-form crystals are developed from solution, melt, or cold crystallization at temperatures above 120 °C. The α'-form crystals are formed at temperatures lower than 100 °C, while a mixture of α- and α'-crystals are developed in the temperature range from 100° to 120°C [32]. The other crystal forms develop only under specific processing conditions. For example, the β-form of crystals develops when α-crystals are stretched at around 170 °C [33]. The γ-crystals are formed by epitaxial crystallization of PLA at about 140 °C on a hexa-methyl-benzene substrate [34]. A stereocomplex structure develops when equal amounts of the optically pure PLLA and PDLA are melt-blended [35]. Among all the above-mentioned crystal forms of PLA, the α- and α'- forms are the most significant from a practical point of view. They develop during the melt processing of PLA, such as injection molding, and also during annealing [20]. Both the α- and α'-form have an orthorhombic unit cell, but the α'-form has a less ordered packing manner and lower density compared to the more ordered α-form. Therefore, the α-form crystal of PLA is more thermodynamically stable than the α' form. Ma et al. [32] evaluated the relationship between crystal structure and the thermal and mechanical properties of a melt-processed neat PLA. They found that when crystallization temperature was increased from 100° to 130°C, crystallinity did not change considerably but crystal size increased and the crystal structure became more perfect. This led to an increase in the Young's modulus and heat resistance of PLA. At the same time, the increase in crystallization temperature led to the formation of larger and less regular spherulites, which decreased elongation at break and tensile strength.

The slow crystallization rate of PLA can also be improved with the optimization of molding conditions. Santis et al. [17] assessed the crystallization kinetics of PLA injected into a cold and a hot mold (25 °C and 105 °C, respectively) with subsequent annealing at 105 °C. The authors found that annealing at 105 °C was faster than in-mold crystallization at the same temperature. However, the samples injected into a hot mold demonstrated higher HDT than those from the cold mold even though crystallinity was the same. Tabi et al. [11] found that nucleated PLA can fully crystallize (crystallinity ~50%) in a hot mold (90 °C) within an injection molding cycle. In contrast, in a cold mold (25 °C), even nucleated PLA did not crystallize completely. Although the crystallinity of injection-molded PLA can be further increased by annealing, the inherent warpage and distortion of the annealed parts restrict the usability of this post-production method.

Although a lot of studies investigate the possibility of increasing the crystallinity of PLA by using various approaches (increasing the mold temperature, adding nucleating agent, adding plasticizer), to the best of our knowledge, none of them investigate the combined effect of the three mentioned approaches. Moreover, no attempt was made previously to maximize the crystallinity of PLA using the most effective crystallization enhancer additives (nucleating agents and plasticizers) in a single injection molding cycle and thus to improve the heat deflection temperature of the molded product this way. In the current study, we research the effect of molding conditions, especially mold temperature, on the crystallinity and the thermal and mechanical properties of simultaneously nucleated and plasticized injection-molded PLA specimens. We aimed to maximize the crystallinity and crystallization rate of PLA to explore the limitations of PLA when it is processed by injection molding. Therefore, we selected a PLA grade with the lowest D-lactide content (referred to as PLLA), the three most effective nucleated agents found in our previous wide range of literature review (PPZn, Ecopromote, and EcopromoteHD [11]), and the two most suitable PLA plasticizers (OLA [36] and DOA [29,37]).

2. Materials and equipment

2.1. Materials

We used 3100HP grade PLLA from NatureWorks (Minnetonka, MN, USA), with a D-lactide content of 0.5%. The density of PLA was 1.24 g/cm^3, its T_g was in the range of 55–60 °C, its melting temperature in the range of 170–190 °C, and its melt flow index was in the range of 22–24 g/10 min (at 210 °C, with a 2.16 kg load). To minimize hydrolytic degradation, we dried the PLA pellets at 80 °C for 6 h before compounding. The nucleating agents we used were Zinc PhenylPhosphonate (PPZn) synthesized in our laboratory [11], and commercially available Ecopromote and Ecopromote HD (both purchased from Nissan Chemical Industries Ltd., Tokyo, Japan). The plasticizers we used were Dioctyl Adipate (DOA), trade name Plastomoll® (BASF, Germany, Ludwigshafen), and Oligomeric lactic acid (OLA) under the trade name OLA2 (Mw= 1200, viscosity = 90 mPas at 40 °C) and OLA8 (Mw= 1100, viscosity = 22.5 mPas at 100 °C) (representing two different molar masses) (Condensia Química S.A., Spain, Barcelona). 80 °C 1 h drying was applied to decrease the viscosity of OLA8 to a processable level and also for OLA2 to have the same thermal history as OLA8.

2.2. Equipment for the production of specimens

For compounding, we used a twin-screw extruder LabTech LTE 26-44 Scientific (Labtech Engineering Co., Ltd., Samutpreken, Thailand) with a screw of 26 mm in diameter, and L/D = 40. The temperature profile was 175–180–185–190 °C (from the hopper to the die), and the screw rotational speed was 10 rpm. We added 2 wt% of each nucleating agent to PLA and 5 wt% of each plasticizer. The exact recipes of the compounds produced are presented in Table 1. The compound was

Table 1
The recipes of compounds.

Specimens	Nucleating agent			Plasticizer		
	PPZn	Ecopromote	EcopromoteHD	DOA	OLA2	OLA8
I	2 wt %	–	–	–	–	–
II	–	2 wt%		–	–	–
III	–	–	2 wt%	–	–	–
IV	–	–	2 wt%	5 wt %	–	–
V	–	–	2 wt%	–	5 wt %	–
VI	–	–	2 wt%	–	–	5 wt %

cooled with ventilated air and pelletized for a length of 3 mm. The second drying sequence was used at 80 °C for 6 h to crystallize the pellets before injection molding.

We produced standard specimens (ISO 527-2/1 A) with a cross-section of 4 × 10 mm with an injection molding machine Arburg Allrounder 370 S 700-290 (Arburg GmbH., Lossburg, Germany) with a screw of 30 mm in diameter, and L/D= 25. To produce ISO 527 1 A specimens we used the following injection molding parameters: an injection rate of 50 cm^3/s, a holding pressure of 600 bars, a holding time of 20 s, and a melt temperature of 190 °C. We used in-mold crystallization of specimens in a cold mold (at 25, 30, 40, and 50 ºC) and in a hot mold (at 90, 100, 110, and 120 ºC). When a cold mold was used, the cooling rate was high, and the part was cooled below T_g. Therefore, the part was adequately demolded, and the overall cycle time was relatively short. The residual cooling time in the case of a cold mold was 60 s. With a hot mold, demolding was essentially different. PLA can crystallize above T_g inside the mold; therefore, instead of a cooling time, the term "in-mold crystallization time" was used. In-mold crystallization time was 90 s. The forming crystalline structure ensured enough stiffness to demold a PLA part adequately, even though mold temperature was higher than the HDT of the just ejected (demolded) PLA part. We also produced specimens from neat PLA, which were annealed at 80, 90, 100, 110, and 120 ºC for 4 h. We used the annealed samples from neat PLA as references. In-mold crystallization of neat PLA was not possible due to the inevitable appearance of large sink marks causing low dimensional accuracy, and this way, the specimens became unsuitable for measurements.

2.3. Equipment for the testing of specimens

To determine the crystallization and crystallinity of PLA with different nucleating agents and plasticizers we used a Differential Scanning Calorimetry (DSC) TA Instruments Q2000 (TA Instruments, New Castle, USA). For this we cut 2–4 mg samples from the middle of the injection-molded specimens. We used a non-isothermal mode (heat/cool/heat) from 0° to 200°C at a heating and cooling rate of 5 °C/min to determine the T_g, crystallization temperature (T_c), enthalpy of crystallization (ΔH_c), enthalpy of fusion (ΔH_m), and melting temperature (T_m). From the first heating scan we calculated crystallinity with the following equation:

$$X = \frac{\Delta H_m - \Delta H_c}{\Delta H_f \bullet (1 - \alpha)} \bullet 100\%,$$

where X is crystallinity, %; ΔH_c and ΔH_m are the enthalpy of crystallization and the enthalpy of fusion, respectively, J/g; ΔH_f – the enthalpy of fusion for 100% crystalline PLA (93.0 J/g) [38], and α is the mass fraction of the modifiers. The standard deviation (human evaluation and equipment repeatability) was determined previously as a general maximum 3% (crystallinity %).

We identified the mechanical properties of the specimens with tensile and Charpy tests. For the tensile tests, which were conducted according to ISO 527, we used a Zwick Z020 universal testing machine (UTM) (Zwick, Ulm, Germany). The UTM was equipped with a force-measuring cell Zwick BZ 020/TN2S with a force limit of 20 kN. The speed of a crosshead during the tensile tests was 5 mm/min. For the Charpy impact test (ISO 179) we used notched samples and an impact testing machine Ceast Resil Impactor (Ceast, Torino, Italy), which was equipped with a 15 J impact energy hammer and a DAS8000 data collector unit. All the tensile and impact tests were performed at room temperature (between 20 ºC and 25 ºC) and at a relative humidity of 50 ± 10%. In each test we used six specimens.

We measured the storage modulus of the specimens with a Dynamic Mechanical Analyzer (DMA) Q800 (TA Instruments, New Castle, USA). We investigated the storage modulus in the temperature range of 0–170 °C at a heating rate of 2 °C/min. For the DMA test, we cut samples from the middle of the injection-molded specimens. From each compound we tested two specimens to determine their thermomechanical properties. During the testing we used the dual cantilever mode with a frequency of 1 Hz and a 20-micron amplitude.

Finally, we measured the HDT (ISO 75) of the samples with a Ceast HV3 HDT (Ceast, Torino, Italy) device. We conducted the HDT B type tests in a flatwise mode with a loading stress of 0.45 MPa, and at a heating rate of 2 °C/min (120 °C/hour). A span length was 64 mm. The HDT test stopped at deflection of 0.34 mm. We tested three specimens and calculated an average value of the HDT.

3. Results and discussion

3.1. The effect of mold temperature on crystallinity

First, we determined the crystallinity of the nucleated and plasticized compound (injection molded into a mold with various mold temperatures), as well as the annealed PLA, which was the reference (Fig. 1). Please note, that ISO standard 1 A specimen has a thickness of 4 mm, thus a certain thermal gradient develops during molding. In every case the small samples for the crystallinity determination were cut from the middle of the injection molded specimens representing the highest crystallinity the given specimen had since the cooling rate is typically the lowest in the center line of an injection molded product.

We found that even with the use of the lowest D-lactide content PLA and a highly effective nucleating agent as well as plasticizers, we still did not reach the maximum achievable crystallinity of PLA using a cold mold. When we gradually increased the mold temperature from 25 °C to 90 °C, the crystallinity of the final PLA part practically linearly increased for all the investigated compounds. Note that with a mold temperature between 50 °C and 80 °C it was not possible to injection mold specimens, due to the slow crystallization rate and the proximity of the T_g of PLA. A further increase of mold temperature from 90 °C to 120 °C did not significantly affect the amount of crystal phase formed. This result has two main consequences. First, all the IMC temperatures applied were adequate to fully crystallize PLA during the injection molding cycle, and the maximum crystallinity values were determined. Secondly, increasing mold temperature from 90 °C to 120 °C most likely only caused crystal ordering but no further increase in crystallinity. All the examined nucleating agents increased crystallinity, and the applied IMC method caused an increase in crystallinity of around 10% compared to the annealed neat PLA samples. Among all the studied nucleating agents, Ecopromote produced a slightly higher crystallinity than Eco-promoteHD and PPZn (Fig. 1/a). The addition of a plasticizer further increased the crystallinity of nucleated PLA by almost 8% (especially at low mold temperatures, 25 °C and 40 °C), and by 4–5% at high mold temperatures, but only for the PLA compounds with the less effective nucleating agents; thus overall crystallinity could not be increased further (Fig. 1/b). The maximum possible crystallinity was between 53.9% and 60.0% for all the nucleated and plasticized PLA compounds. In every case, this crystallinity was higher than the crystallinity of the annealed neat PLA specimens.

3.2. The effect of mold temperature on the HDT

Within a mold temperature range of 25 °C to 50 °C, the HDT of a nucleated and plasticized PLA was found practically constant (~55 °C). This was mainly due to the moderate level of crystallinity that developed at these low mold temperatures, as low mold temperature hinders crystallization (Fig. 2).

At the same time, the high level of crystallinity that developed at high mold temperatures (from 90–120 °C) led to a significant increase in HDT. The HDT of the nucleated PLA specimens processed with the IMC method was in most cases 5–10 °C lower compared to the HDT of the annealed (processed with the PPC method) specimens, even though annealed specimens had 10–15% lower crystallinity. This difference
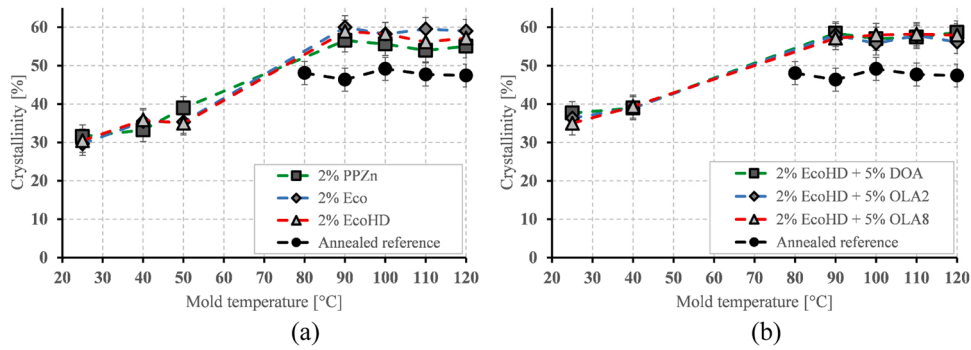
Fig. 1. The crystallinity of 3100HP grade PLA nucleated with 2 wt% PPZn, Ecopromote, and EcopromoteHD (a) as well as nucleated with 2 wt% EcopromoteHD and plasticized with 5 wt% DOA, OLA2, and OLA8 (b) as a function of mold temperature.
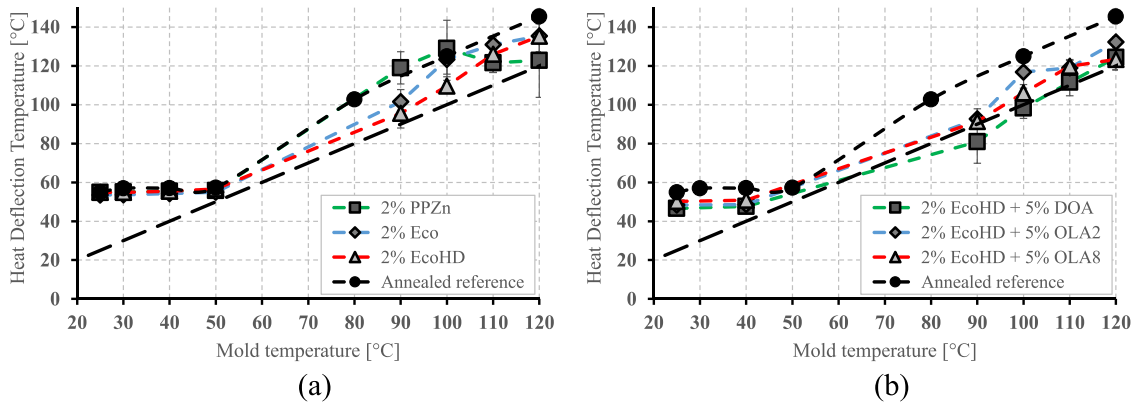

Fig. 2. Heat deflection temperature of 3100HP grade PLA nucleated with 2 wt% PPZn, Ecopromote, and EcopromoteHD (a) and nucleated with 2 wt% EcopromoteHD and plasticized with 5 wt% DOA, OLA2, and OLA8 (b) as a function of mold temperature. Note that the long dashed line represents the same mold temperature and HDT values.

could be related to a more ordered crystal structure that developed during annealing (cold crystallization) compared to the less ordered structure that developed during cooling from the melt, and also to increased spherulite size. Additionally, although crystallinity was the same for the nucleated samples when mold temperature was between 90 °C and 120 °C (Fig. 1), the HDT continued to grow with increasing mold temperature. This could also be explained by the increased spherulite size and the more ordered crystal structure developing at higher temperatures [39], even though only the less ordered α' crystal form was found in the compounds. In Fig. 2, a straight dashed linear line represents the same values of mold temperature and heat deflection

temperature connected, which is practically the border between acceptable (above the dashed line) or unacceptable (below the dashed line) from the point of view of demolding, since the values above this dashed line represent specimens with higher HDT than the actual mold temperature that was used for the IMC method. As can be seen, the HDT of the final injection molded parts is only slightly higher (by 10–30 °C) than the mold temperature itself, therefore some injection-molded parts were still soft during demolding. Naturally, after demolding and cooling outside the mold, the parts became stiff, but the small difference between HDT and demolding temperature can cause problems with demolding and/or the accuracy of the parts produced.
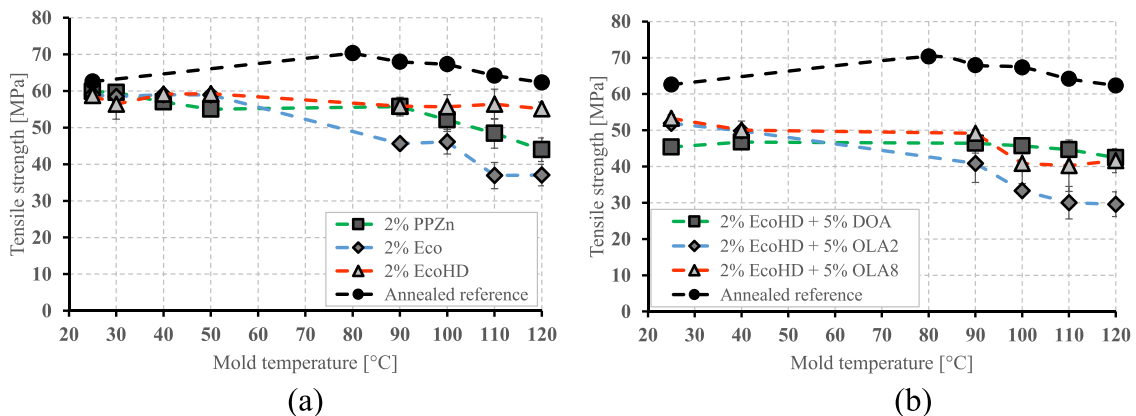

Fig. 3. Tensile strength of 3100HP grade PLA nucleated with 2 wt% PPZn, Ecopromote, and EcopromoteHD (a) and nucleated with 2 wt% EcopromoteHD and plasticized with 5 wt% DOA, OLA2, and OLA8 (b) as a function of molding temperature.

3.3. The effect of mold temperature on mechanical and thermomechanical properties

We observed that the tensile strength of nucleated and plasticized PLA decreased as mold temperature was increased (Fig. 3).

On the contrary, the annealed specimens in all cases demonstrated higher tensile strength than the samples with nucleating agents with or without plasticizers. Moreover, the annealed specimens showed the highest increase in tensile strength when an annealing temperature of 80 °C was applied. A further increase of the annealing temperature led to a gradual decrease in tensile strength. This phenomenon can be explained by spherulite size, where the low annealing temperature produces smaller spherulites, causing higher tensile and impact strength, while a higher annealing temperature leads to larger spherulites, which results in increased modulus and heat deflection temperature [32]. These results are in accordance with our previous research results performed on neat PLA [39]. The tensile modulus of annealed and nucleated PLA increased with increasing mold temperature (Fig. 4/a).

This phenomenon is due to the increased crystalline order of the α' crystal form and the larger spherulite size. At the same time, with the addition of a plasticizer, this increase in modulus became insignificant due to the plasticizer effect, thus the modulus of the nucleated and plasticized PLA compounds became practically independent of mold temperature (Fig. 4/b). We also found that mold temperature significantly decreased the strain at break of PLA samples Fig. 5.

The lowest drop in strain was observed when we used the EcopromoteHD nucleating agent alone or together with the DOA plasticizer. Moreover, the annealed reference specimens also suffered a decrease in strain at break with the increase of crystallization temperature. This could again be explained by the large spherulites that developed at higher annealing temperatures. Finally, mold temperature had practically no effect on the impact strength of nucleated as well as simultaneously nucleated and plasticized PLA (Fig. 6).

Their impact strength was in the range of 2.1–3.6 kJ/m^2, depending on the composition and mold temperature used for the IMC method. Surprisingly, when neat PLA samples were annealed at 100 °C, impact strength increased to 12.8 ± 0.7 kJ/m^2. This level of impact strength even approaches the impact strength of ABS (19 kJ/m^2), which is often used due to its toughness. At the same time, only the annealed samples had this high increase in impact properties—in-mold crystallized samples did not. Moreover, this was observed only for neat PLA and only for PLLA grades (e.g. 3100HP) but not for PLA grades with higher D-Lactide content [40]. This is probably because it requires pure PLA (isotactic), and also, crystallization needs to be performed within an annealing process (solid-phase crystallization) and not from melt to induce high impact strength. Finally, we also investigated the storage modulus of the injection-molded parts in the temperature range from 0° to 170°C. Note that due to the similarities of the obtained curves, only the compound nucleated with EcopromoteHD (Fig. 7/a) as well as the compound nucleated with EcopromoteHD and plasticized with 5 wt% DOA are discussed (Fig. 7/b).

On the one hand, when a cold mold was used (25–50 °C), the final injection molded part lost most of its modulus above T_g (~55 °C), namely, it dropped from around 3000 MPa to below 100 MPa, resulting in a part that had a rubber-like state with no possible practical application at or above this temperature. This temperature correlates well with the previous HDT results (Fig. 2). As mold temperature was increased from 25–50 °C, the lowest modulus in the rubbery state increased from 19.9 to 55.8 MPa due to increased crystallinity. When these specimens were heated above 75 °C, cold crystallization started, which caused the storage modulus to increase until the specimens reached maximum possible crystallinity around 90 °C. Above this temperature, the storage modulus monotonously decreased, and finally, this decrease became more and more significant as the crystal melt temperature approached. However, when a hot mold was used (90–120 °C), and the examined compounds were fully crystallized in the mold, the storage modulus of the final injection-molded part suffered a much smaller drop above T_g, since the crystalline ratio prevented micro-Brownian movement of the polymer chains, and it finally resulted in an increased HDT and dimensional stability. As mold temperature was increased from 90 °C to 120 °C, modulus further increased, which confirms the increase in HDT (Fig. 2). As discussed before, this was the effect of a more ordered crystal structure as well as increased spherulite size. Based on the storage modulus of nucleated and, at the same time plasticized PLA compounds, when a cold mold was used for production, we found that the curves shifted to a lower temperature region as a consequence of the plasticizer effect (decreasing T_g). On the contrary, cold crystallization temperature also shifted to a lower temperature region. These were our two findings regarding the curves of PLA compounds containing a nucleating agent and plasticizer, but at the same time, the shape of the curves was similar to the curve of the PLA compound containing only the nucleating agent. Finally, the results indicate that the optimal crystallization temperature (both mold temperature and annealing temperature) for PLA compounds is 90–100 °C, because at this temperature, the balance between heat deflection temperature, impact and thermomechanical properties is optimal.

3.4. Comparison of the thermal and mechanical properties of nucleated and plasticized PLA with those of ABS

Since ABS is a generally used plastic for applications where improved HDT and impact properties are needed, in most cases, the material developers of PLA aim for these properties and use them as a benchmark.
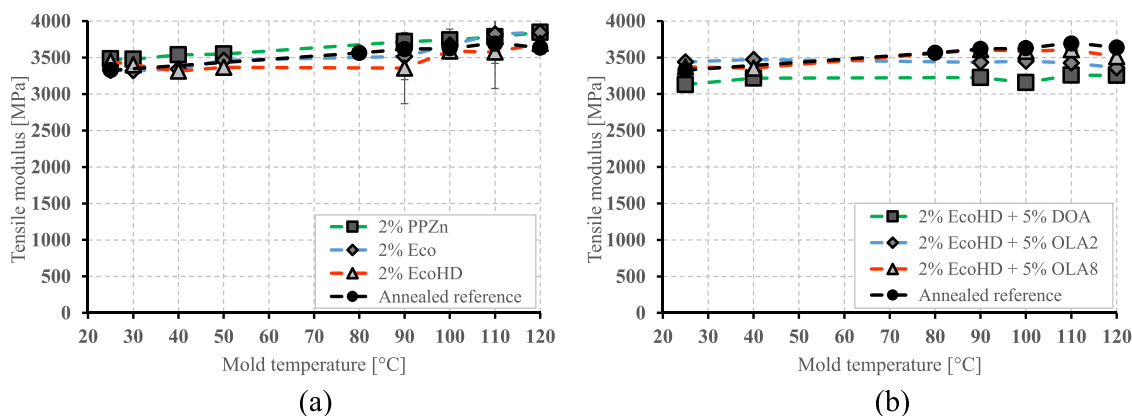

(a)   (b)

Fig. 4. The tensile modulus of 3100HP grade PLA nucleated with 2 wt% PPZn, Ecopromote, and EcopromoteHD (a) and nucleated with 2 wt% EcopromoteHD and plasticized with 5 wt% DOA, OLA2, and OLA8 (b) as a function of mold temperature.
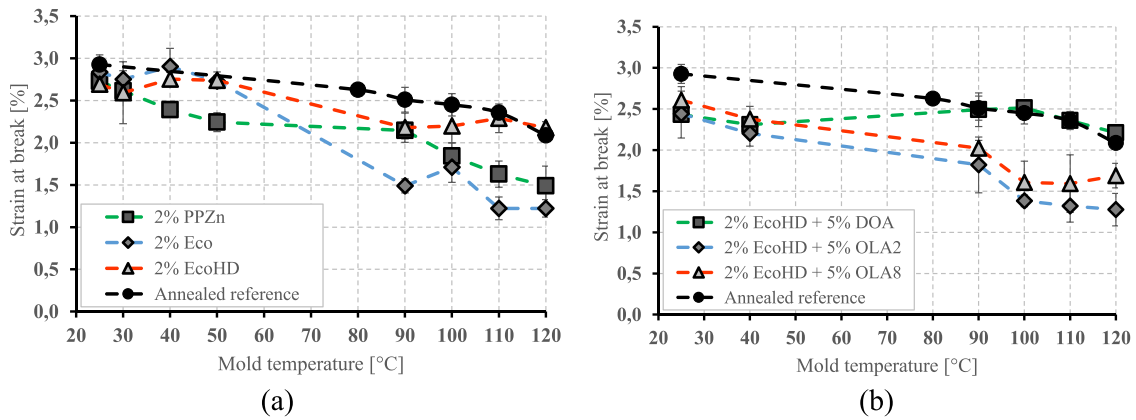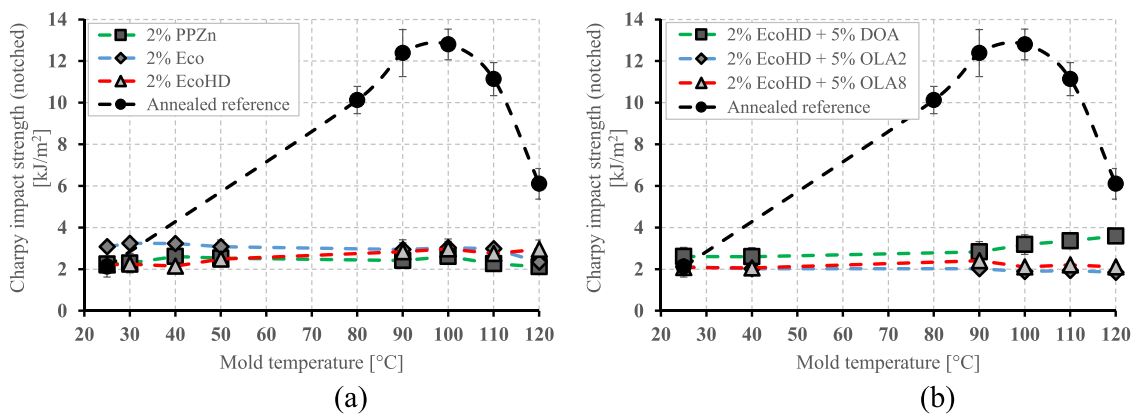
Fig. 5. The strain at break of 3100HP grade PLA nucleated with 2 wt% PPZn, Ecopromote, and EcopromoteHD (a) and nucleated with 2 wt% EcopromoteHD and plasticized with 5 wt% DOA, OLA2, and OLA8 (b) as a function of mold temperature.
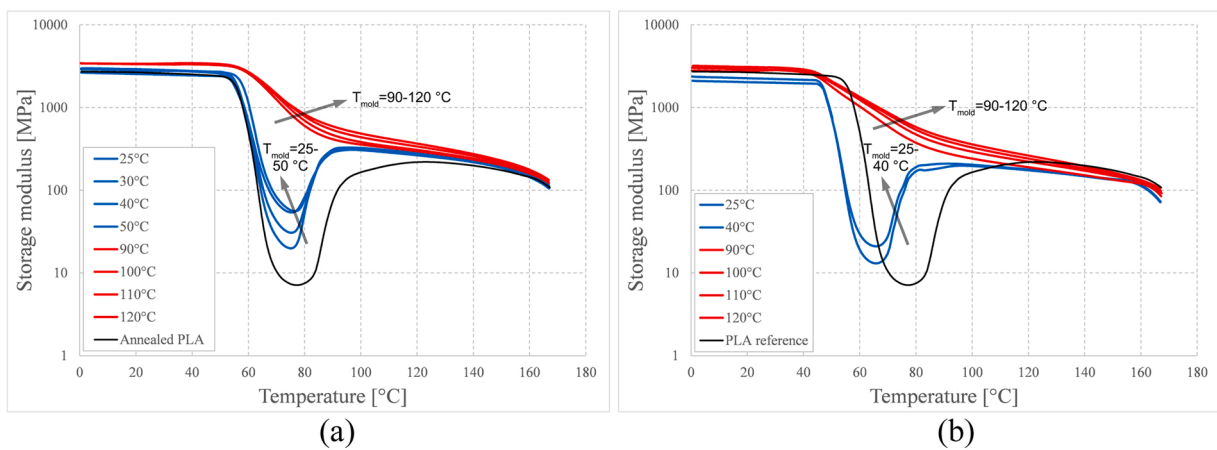

Fig. 6. Charpy impact strength (notched) of 3100HP grade PLA nucleated with 2 wt% PPZn, Ecopromote, and EcopromoteHD (a) and nucleated with 2 wt% EcopromoteHD and plasticized with 5 wt% DOA, OLA2, and OLA8 (b) as a function of mold temperature.

Fig. 7. Storage modulus (stiffness) of 3100HP grade PLA nucleated with 2 wt% EcopromoteHD (a) and nucleated with 2 wt% EcopromoteHD and plasticized with 5 wt% DOA (b) as a function of temperature.

Therefore, we summarized the values of thermal and mechanical properties of the developed PLA compounds that were crystallized (either by annealing (PPC) or crystallization in a mold (IMC)) at a temperature of 90 °C and compared them to the properties of ABS (Table 2).

The results show that the HDT, tensile strength, and Young's modulus of an annealed PLA and PLA compounded with PPZn or EcopromoteHD are considerably better than the same properties of ABS. At the same time, the strain at break and impact strength of the nucleated

and plasticized PLA compounds is still significantly lower than those of ABS, thus the PLA compounds are still not tough enough. On the other hand, the impact strength of pure PLA and PLA annealed at 90 °C was close to that of ABS, which suggests some advantage of annealing (PPC) over in-mold crystallization (IMC) regarding impact strength. However, there are drawbacks of annealing as well. First, it is an additional processing step, and second, the dimensional accuracy of injection molded PLA is typically lost during annealing. Accordingly, the use of IMC

Table 2
Comparison of the mechanical and thermal properties of the developed injection molded PLA compounds in-mold crystallized (IMC) at 90 °C with those of injection molded ABS (grade Terluran GP-35) and unannealed PLA as well as PLA annealed at 90 °C – post-production crystallization (PPC).

Property	PLA								ABS
	Unannealed	Annealed (PPC 90 °C)	PPZn (IMC 90 °C)	Eco (IMC 90 °C)	EcoHD (IMC 90 °C)	EcoHD + DOA (IMC 90 °C)	EcoHD + OLA2 (IMC 90 °C)	EcoHD + OLA8 (IMC 90 °C)	
Crystallinity X,%	28 ± 3	48 ± 3	57 ± 3	59 ± 3	58 ± 3	59 ± 3	58 ± 3	58 ± 3	–
Tensile strength σ_T, MPa	62.6 ± 0.3	68.0 ± 1.2	55.7 ± 2.6	45.6 ± 0.9	55.9 ± 2.2	46.4 ± 2.8	40.8 ± 5.2	49.2 ± 1.1	44
Young's modulus, GPa	3226 ± 16	3616 ± 17	3718 ± 83	3515 ± 316	3356 ± 486	3225 ± 82	3434 ± 23	3607 ± 43	2300
Strain at break, %	2.93 ± 0.12	2.51 ± 0.15	2.15 ± 0.10	1.49 ± 0.08	2.18 ± 0.18	2.49 ± 0.20	1.82 ± 0.34	2.02 ± 0.10	12
Notched impact strength, kJ/m^2	2.5 ± 0.4	12.4 ± 1.1	2.4 ± 0.4	2.9 ± 0.5	2.8 ± 0.4	2.8 ± 0.5	2.0 ± 0.1	2.4 ± 0.4	19
HDT, °C	54.4 ± 0.5	113.8 ± 2.1	119.0 ± 8.3	101.5 ± 6.3	95.6 ± 7.6	81.0 ± 11.1	92.7 ± 5.2	91.4 ± 2.0	95

should be preferred despite the better properties that could be achieved with PPC, and the use of impact modifiers seems necessary.

4. Conclusions

In our paper, we aimed to maximize the crystallinity of injection molded Poly(Lactic Acid) (PLA) within an injection molding cycle. To increase crystallinity, we used PLA with the lowest D-lactide content available (PLLA grade) and compounded it with three highly effective nucleating agents—Zinc PhenylPhosphonate (PPZn), Ecopromote, and EcopromoteHD, as well as two suitable plasticizers—Oligomeric Lactic Acid (OLA) and Dioctile Adipate (DOA). These additives were all selected from the literature review in one of our earlier studies. We examined the influence of mold temperature (25–120 °C) on the crystallinity of nucleated as well as nucleated and plasticized PLA compounds. Two sets of mold temperatures were used: the so-called "cold mold" (25–50 °C), where mold temperature was kept below the glass transition temperature (T_g) of PLA, and the so-called "hot mold" (90–120 °C), where the mold temperature of PLA was kept above the T_g of PLA. Applying a cold mold could be regarded as an ordinary injection molding cycle, where the goal is to cool the product to the desired stiffness for demolding (below T_g), while the latter was referred to as in-mold crystallization (IMC), where the required stiffness is achieved by crystallization and not by cooling. The results were compared to pure and annealed (or so-called post-production crystallized (PPC)) PLA. We found that even with the lowest D-lactide content PLA and one of the most effective nucleating agents, as well as plasticizers, it was still not possible to produce the maximum achievable crystallinity of PLA during a single injection molding cycle when a cold mold was used. On the contrary, IMC was a practical method of increasing the crystallinity of PLA to its maximum possible level, and it also resulted in a significant increase in the heat deflection temperature (HDT) of the injection molded parts—from 55 °C to even above 120 °C. We found that a further increase in mold temperature from 90 °C to 120 °C caused the HDT to monotonously increase. This was caused by the increased storage modulus in the critical temperature region above T_g, most probably due to the increased crystal order and increased spherulite size. Although using IMC highly increased HDT and the tensile modulus, it decreased tensile strength as well as strain at break. Therefore it made PLA more brittle, which could not be overcome with effective plasticizers. Finally, we compared our results to the properties of Acrylonitrile butadiene styrene (ABS), and found that the HDT, tensile strength, and Young's modulus of annealed PLA and PLA modified with nucleating agents PPZn or EcopromoteHD are high—PLA even outperforms ABS regarding these properties. However, the strain at break of the annealed and simultaneously nucleated and plasticized PLA compounds is still significantly lower than those of ABS. Accordingly, it is essential to use impact modifiers along with nucleating agents and the IMC method for injection molded PLA parts with suitably high HDT and good impact properties for widespread applications.

CRediT authorship contribution statement

Tamás Tábi: Conceptualization, Data curation, Investigation, Methodology, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Tatyana Ageyeva**: Conceptualization, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. **József Gábor Kovács**: Conceptualization, Funding acquisition, Methodology, Project administration, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

References

[1] T. Tábi, T. Ageyeva, J.G. Kovács, Improving the ductility and heat deflection temperature of injection molded poly(lactic acid) products: a comprehensive review, Polym. Test. 101 (2021) 107282, https://doi.org/10.1016/j.polymertesting.2021.107282.

[2] A. Antunes, A.S. Luyt, P. Kasak, O. Aljarod, M.K. Hassan, A. Popelka, Effect of plasma treatment on accelerated pla degradation, Express Polym. Lett. 15 (2021) 725–743, https://doi.org/10.3144/expresspolymlett.2021.60.

[3] Y. Ramot, M. Haim-Zada, A.J. Domb, A. Nyska, Biocompatibility and safety of pla and its copolymers, Adv. Drug Deliv. Rev. 107 (2016) 153–162, https://doi.org/10.1016/j.addr.2016.03.012.

[4] E.R. Ghomi, F. Khosravi, A.S. Ardahaei, Y. Dai, R.E. Neisiany, F. Foroughi, M. Wu, O. Das, S. Ramakrishna, The life cycle assessment for polylactic acid (pla) to make it a low-carbon material, Polymers 13 (2021) 1854, https://doi.org/10.3390/polym13111854.

[5] S. Milovanovic, J. Pajnik, I. Lukic, Tailoring of advanced poly(lactic acid)-based materials: a review, J. Appl. Polym. Sci. 139 (2021), e51839, https://doi.org/10.1002/app.51839.

[6] A. Jalali, S. Romeo-Diez, M. Nofar, C.B. Park, Entirely environment-friendly polylactide composites with outstanding heat resistance and superior mechanical performance fabricated by spunbond technology: exploring the role of nanofibrillated stereocomplex polylactide crystals, Int. J. Biol. Macromol. 193 (2021) 2210–2220, https://doi.org/10.1016/j.ijbiomac.2021.11.052.

[7] T. Tábi, K. Pölöskei, The effect of processing parameters and calcium-stearate on the ejection process of injection molded poly(lactic acid) products, Period. Polytech. Mech. Eng. 66 (2022) 17–25, https://doi.org/10.3311/PPme.18246.

[8] V. DeStefano, S. Khan, A. Tabada, Applications of pla in modern medicine, Eng. Regen. 1 (2020) 76–87, https://doi.org/10.1016/j.engreg.2020.08.002.

[9] S.T. Sikhosana, T.P. Gumede, N.J. Malebo, A.O. Ogundeji, Poly(lactic acid) and its composites as functional materials for 3-d scaffolds in biomedical applications: a mini-review of recent trends, Express Polym. Lett. 15 (2021) 568–580, 10.3144.expresspolymlett.2021.48.

[10] M. Gerometta, J.R. Rocca-Smith, S. Domenek, T. Karbowiak, Physical and chemical stability of pla in food packaging, in: Reference Module in Food Science, vol. 2019, Elsevier Inc, 2019, p. 11.

[11] T. Ageyeva, K.G. Kovacs, T. Tabi, Comparison of the efficiency of the most effective heterogeneous nucleating agents for poly(lactic acid), J. Therm. Anal. Calorim. (2021), https://doi.org/10.1007/s10973-021-11145-y. 10.1007/s10973-021-11145-y.

[12] A.M. Harris, E.C. Lee, Improving mechanical performance of injection molded pla by controlling crystallinity, Appl. Polym. Sci. 107 (2008) 2246–2255, https://doi.org/10.1002/app.27261.

[13] N. Zirak, M. Shirinbayan, S. Farzaneh, A. Tcharkhtchi, Effect of molecular weight on crystallization behavior of poly (lactic acid) under isotherm and non-isotherm conditions, Polym. Adv. Technol. (2021) 1–10, https://doi.org/10.1002/pat.5603.

[14] H. Urayama, T. Kanamori, K. Fukushima, Y. Kimura, Controlled crystal nucleation in the melt-crystallization of poly(l-lactide) and poly(l-lactide)/poly(d-lactide) stereocomplex, Polym 44 (2011) 5635–5641, https://doi.org/10.1016/S0032-3861(03)00583-4.

[15] LauraAliotta, P. Cinelli, M.B. Coltelli, M.C. Righetti, M. Gazzano, A. Lazzeri, Effect of nucleating agents on crystallinity and properties of poly (lactic acid) (pla), Eur. Polym. J. 93 (2017) 822–832, https://doi.org/10.1016/j.eurpolymj.2017.04.041.

[16] D. Notta-Cuvier, J. Odent, R. Delille, M. Murariu, F. Lauro, J.M. Raquez, B. Bennani, P. Dubois, Tailoring polylactide (pla) properties for automotive applications: effect of addition of designed additives on main mechanical properties, Polym. Test. 36 (2014) 1–9, https://doi.org/10.1016/j.polymertesting.2014.03.007.

[17] F. De Santis, V. Volpe, R. Pantani, Effect of molding conditions on crystallization kineticsand mechanical properties of poly(lactic acid), Polym. Eng. Sci. 57 (2017) 306–311, https://doi.org/10.1002/pen.24414.

[18] R. Vadori, A.K. Mohanty, M. Misra, The effect of mold temperature on the performance of injection molded poly(lactic acid)-based bioplastic, Macromol. Mater. Eng. 298 (2013) 981–990, https://doi.org/10.1002/mame.201200274.

[19] V. Nagarajan, K. Zhang, M. Misra, A.K. Mohanty, Overcoming the fundamental challenges in improving the impact strength and crystallinity of pla biocomposites: Influence of nucleating agent and mold temperature, ACS Appl. Mater. Interfaces 7 (2015) 11203–11214, https://doi.org/10.1021/acsami.5b01145.

[20] T. Tabi, The application of the synergistic effect between the crystal structure of poly(lactic acid) (pla) and the presence of ethylene vinyl acetate copolymer (eva) to produce highly ductile pla/eva blends, J. Therm. Anal. Calorim. 138 (2019) 1287–1297, https://doi.org/10.1007/s10973-019-08184-x.

[21] H. Schäfer, C. Pretschuh, O. Brüggemann, Reduction of cycle times in injection molding of pla through bio-based nucleating agents, Eur. Polym. J. 115 (2019) 6–11, https://doi.org/10.1016/j.eurpolymj.2019.03.011.

[22] R. Auras, L.T. Lim, S.E.M. Selke, H. Tsuji, Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications, John Wiley & Sons, Inc, Hoboken, New Jersey, USA, 2010, https://doi.org/10.1002/9780470649848.

[23] S. Saeidlou, M.A. Huneault, H. Li, C.B. Park, Poly(lactic acid) crystallization, Prog. Polym. Sci. 37 (2012) 1657–1677, https://doi.org/10.1016/j.progpolymsci.2012.07.005.

[24] N. Petchwattana, P. Naknaen, B. Narupai, Combination effects of reinforcing filler and impact modifier on the crystallization and toughening performances of poly (lactic acid), Express Polym. Lett. 14 (2020) 848–859, https://doi.org/10.3144/expresspolymlett.2020.70.

[25] M. Maiza, M.T. Benaniba, G. Quintard, V. Massardier-Nageotte, Biobased additive plasticizing polylactic acid (pla), Polimeros 25 (2015) 581–590, https://doi.org/10.1519/0104-1428.1986.

[26] O. Martin, L. Avérous, Poly(lactic acid): plasticization and properties of biodegradable multiphase systems, Polym 42 (2001) 6209–6219, https://doi.org/10.1016/S0032-3861(01)00086-6.

[27] I. Armentano, E. Fortunati, N. Burgos, F. Dominici, F. Luzi, S. Fiori, A. Jimenez, K. Yoon, J. Ahn, S. Kang, et al., Bio-based pla_phb plasticized blend films: processing and structural characterization, LWT Food Sci. Technol. (2015) 980–988, https://doi.org/10.1016/j.lwt.2015.06.032, 10.1016/j.lwt.2015.06.032.

[28] M. Murariu, A. Da Silva Ferreira, M. Pluta, L. Bonnaud, M. Alexandre, P. Dbois, Polylactide (pla)-caso4 composites toughened with low molecular weight and polymeric ester-like plasticizers and related performances, Eur. Polym. J. 44 (2008) 3842–3852, https://doi.org/10.1016/j.eurpolymj.2008.07.055.

[29] V.P. Martino, A. Jimenez, R.A. Ruseckaite, Processing and characterization of poly (lactic acid) films plasticized with commercial adipates, J. Appl. Polym. Sci. 112 (2009) 2010–2018, https://doi.org/10.1002/app.29784.

[30] H. Tsuji, Y. Ikada, Properties and morphologies of poly(l-lactide): annealing condition effects on properties and morphologies of poly(l-lactide), Polymer 36 (1995) 2709–2716.

[31] T.T. Lin, X.Y. Liu, C. He, A dft study on poly(lactic acid) polymorphs, Polymer 51 (2010) 2779–2785, https://doi.org/10.1016/j.polymer.2010.03.062.

[32] B. Ma, X. Wang, Y. He, Z. Dong, X. Zhang, X. Chen, T. Liu, Effect of poly(lactic acid) crystallization on its mechanical and heat resistance performances, Polymer 212 (2021), 123280, https://doi.org/10.1016/j.polymer.2020.123280.

[33] D. Sawai, T. Yokoyama, T. Kanamoto, M. Sungil, S.-H. Hyon, L.P. Myasnikova, Crystal transformation and development of tensile properties upon drawing of poly (l-lactic acid) by solid-state coextrusion: effects of molecular weight, Macromol. Symp. 242 (2006) 93–103, https://doi.org/10.1002/masy.200651015.

[34] L. Cartier, T. Okihara, Y. Ikada, H. Tsuji, J. Puiggali, B. Lotz, Epitaxial crystallization and crystalline polymorphism of polylactides, Polym (2000) 41, https://doi.org/10.1016/S0032-3861(00)00234-2.

[35] N. Naga, Y. Yoshida, K. Noguchi, Crystallization of poly(l-lactic acid)/poly(d-lactic acid) blend induced by organic solvents, Polym. Bull. 76 (2019) 3677–3691, https://doi.org/10.1007/s00289-018-2563-z.

[36] F. Cicogna, S. Coiai, C.D. Monte, R. Spiniello, S. Fiori, M. Franceschi, F. Braca, P. Cinelli, S.M.K. Fehri, A. Lazzeri, et al., Poly(lactic acid) plasticized with low-molecular-weight polyesters: structural, thermal and biodegradability features, Polym. Int. 66 (2017) 761–769, https://doi.org/10.1002/pi.5356.

[37] M. Murariu, A. Da Silva Ferreira, M. Pluta, L. Bonnaud, M. Alexandre, P. Dubois, Polylactide (pla)–caso4 composites toughened with low molecular weight and polymeric ester-like plasticizers and related performances, Eur. Polym. J. 44 (2008) 3842–3852, https://doi.org/10.1016/j.eurpolymj.2008.07.055.

[38] D. Battegazzore, S. Bocchini, A. Frache, Crystallization kinetics of poly(lactic acid)-talc composites, Express Polym. Lett. 5 (2011) 849–858, https://doi.org/10.3144/expresspolymlett.2011.84.

[39] T. Tábi, S. Hajba, J.G. Kovács, Effect of crystalline forms (α′ and α) of poly(lactic acid) on its mechanical, thermo-mechanical, heat deflection temperature and creep properties, Eur. Polym. J. 82 (2016) 232–243, https://doi.org/10.1016/j.eurpolymj.2016.07.024.

[40] T. Tábi, A.F. Wacha, S. Hajba, Effect of d-lactide content of annealed poly(lactic acid) on its thermal, mechanical, heat deflection temperature, and creep properties, J. Appl. Polym. Sci. 136 (2019) 47103, https://doi.org/10.1002/app.47103.