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Effect of D-Lactide content of annealed Poly(lactic acid) on its thermal, mechanical, heat deflection temperature and creep properties

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ABSTRACT

In our research the effect of D-lactide content of injection moulded and annealed Poly(Lactic Acid) (PLA) was investigated on crystallinity as well as crystalline forms (less ordered α' and the more ordered α crystalline forms) and thus on the mechanical, Heat Deflection Temperature (HDT) and creep properties. Three different PLA grades of 3052D, 3001D and 3100HP were investigated with a D-Lactide content of 4%, 1.4% and 0.5% respectively. The injection moulded PLA specimens were then post-production annealed in a heat chamber at 80-140°C for one hour to develop various crystallinity and various ratio of α' and α crystal forms. It was demonstrated that not only annealing, but also the D-lactide content significantly influences crystallization, crystal structure and accordingly the properties of PLA like notched Charpy impact strength, HDT and also creep characteristics. Higher HDT, impact properties, and creep resistance could be reached by using lower D-lactide content PLA with certain annealing temperature range developing definite crystal structures.

KEYWORDS

Poly(Lactic Acid), D-Lactide content, annealing, crystalline structure, heat deflection temperature, impact strength

INTRODUCTION

Nowadays, the plastic production all over the Globe is still increasing and it recently reached 300 million tons in a year. Most of this produced plastic is still based on crude oil, which is a limited resource and although the crude oil used for plastic production is only a small fraction from total crude oil consumption, but in the very near future alternative resources must be found if plastics are to be further used. Another issue for the 21st century is the huge amount of plastic waste mostly originated from short life cycle packaging products. Even though recycling technologies are available, but the recycling of some of the packaging plastic products are simply not economical, thus they usually end up as waste deposition in landfills.

As an answer to these problems, renewable resource (plant) based and inherently biodegradable polymers (biopolymers in short) could be used as an alternative to crude oil based and not biodegradable plastics [1]. Biopolymers have these two significantly advantageous features that they can be entirely produced by using renewable resources like starch from corn and can also be entirely biodegraded in composting conditions into natural, non-toxic materials like humus, water and carbon-dioxide. In this way, biopolymers can be fit into the life cycle of nature with a theoretically neutral carbon footprint [2-5].

Poly(Lactic Acid) (PLA) is currently one of the most promising biopolymers due to its availability, good mechanical properties and reasonable price. PLA is a thermoplastic, aliphatic, semi-crystalline polyester, that can be produced by the fermentation of glucose obtained from starch containing plants like corn (maize), wheat, potato, rice, pea, etc. in the presence of lactobacillus into lactic acid followed by the polycondensation of lactic acid (or the polymerisation of the dimer of lactic acid named lactide). Since Lactic acid has two stereoisomers named L-, and D-Lactic acid, and two dimers accordingly named L-, and D-Lactide thus different PLA grades can be produced by varying the D-Lactide content of PLA. Typical PLA grades contain around 1-10% of D-Lactide but if a PLA is produced entirely by

using L-Lactic acid (or L-Lactide) or D-Lactic acid (or D-Lactide) than it is referred as Poly(L-Lactic Acid) (PLLA) or Poly(D-Lactic Acid) (PDLA) respectively [6, 7]. In spite of application, the D-Lactide content of PLA is crucial, since it influences crystallisation rate, transparency and crystal melt temperature (T_m). Since PLLA and PDLA grades represent the purest (isotactic) PLA, thus highest T_m as well as the fastest crystallization rate could be achieved compared to other PLA grades [8].

As PLA is a thermoplastic polymer, thus it can be processed by using conventional thermoplastic processing technologies like injection moulding, extrusion, thermoforming, blow moulding, rotational moulding, etc., into cutlery, cups, trays, office utensils, bottles or by certain modifications like flame retarding [9] or biocomposite preparation [10], even engineering products can be made. After processing, the unmodified PLA products exhibit good mechanical properties like high strength (~60-65 MPa tensile strength), high stiffness (~2.5-3.0 GPa tensile modulus), but are considered as brittle (~2-3 kJ/m² notched Charpy impact strength). Besides brittleness, another significant drawback of PLA retarding its wide usage is its low Heat Deflection Temperature (HDT) of around 50-60°C, meaning that above this temperature PLA parts highly warp and distort. The low HDT of PLA is caused by first its low glass transition temperature (T_g) of around 50-60°C and its low crystallinity. Since T_g is a given property of PLA and by producing higher molecular weight PLA grades it could only be increased by a few °C [8], thus the only true and practical modification possibility (not counting cross-linking) to influence properties including HDT or creep is to improve crystallinity and to develop crystal structure.

PLA has several crystal forms including α , β , γ and η [11-17]. The most common type is α (orthorhombic unit cell), which is developed during melt processing when PLA is cooled from melt [12-14]. Besides this more-ordered α , the existence of a less-ordered version was proofed called α' [14-17]. At increased temperature and extensive strain, the α crystal form

could recrystallize into β (trigonal unit cell), which could be performed during PLA fibre extrusion [18, 19]. The rarest crystal form is γ (orthorhombic unit cell), which develops during epitaxial growth on a hexamethylbenzene substrate [20]. Finally, the existence of η crystal form was also proved and named as stereocomplex. This is a special crystal structure that is obtained by melt compounding the optically pure PLLA and PDLA. Its properties were intensively studied by Tsuji et al. [21-27].

In most publications (dealing with single PLA grades thus not stereocomplex), the development conditions of the practically beneficial α and α' was investigated as it is developed during cooling at melt processing. Since in most thermoplastic processing technologies high cooling rate is applied and the crystallisation rate of PLA is slow [28], thus it is rather difficult to generate significant crystallinity in the final PLA product only if nucleating agents are used [29-31]. At the same time, as PLA crystallizes between T_m and T_g , thus if low crystallinity was achieved during cooling from melt, the possibility of post-production annealing (heating the produced part above T_g and letting its crystallization to complete) is still open. However, post-production annealing has low practical benefit due to the fact that injection moulded parts will lose their dimensional accuracy during annealing due to entering rubbery state above T_g , releasing internal stress above T_g and specific gravity change due to crystallization. At the same time, annealing is still a process that can be used to produce various crystal structures in PLA. It was proved by Zhang et al. [32] that according to the annealing temperature various ratios of α and α' develop; if the annealing temperature is below 100°C, only α' crystal form develops, on the contrary, if the annealing temperature is above 120°C entirely α crystal form develops, while between 100 and 120°C both crystal forms appear, where the ratio of α to α' is dependent on the temperature applied. According to the melting process, PLA shows multiple melting behaviour of the Differential Scanning Calorimetry (DSC) scans depending on the crystallization temperature (T_c) and thus on the ratio of α' and α crystal forms.

The crystal structure of the α' and α phases, their development and the effect of T_c , crystallization time (t_c) and molecular weight (M_w) on the melting behaviour of PLA has been investigated by many authors [32-37] by various techniques including DSC, Wide Angle X-Ray Diffraction (WAXD) and Fourier Transformation Infrared Spectroscopy (FTIR). Cocca et al. [38] investigated the effect of T_c on the mechanical properties of annealed PLA films. It was found that by increasing annealing temperature the films became more stiff, but brittle as explained by increasing crystallinity, spherulite size and the ratio of the α/α' crystal forms as well as the decreasing molecular chain packing. In our previous publication [39] the effect of T_c was investigated on injection moulded and annealed samples regarding mechanical, thermo-mechanical, HDT and creep properties and it was found that not only crystallinity, but crystalline structure of α - α' forms significantly influence all these properties.

As it was demonstrated, the development and structure of the α' and α crystal forms was intensively studied on single PLA grades, but according to the best of our knowledge, there is no publication related to the investigation of the effect of D-Lactide content on the development of α' and α crystal forms and thus on the mechanical, HDT and creep properties of the final PLA parts. Accordingly, in our paper, different D-Lactide content PLA specimens were injection moulded, annealed at various temperatures and widely investigated related to practical, application-wise properties including thermal, mechanical, HDT and creep properties.

EXPERIMENTAL

Materials and processing

Injection moulding grade PLA types 3052D, 3001D and 3100HP from NatureWorks (Minnetonka, MN, USA) were used for the research with a D-Lactide content of 4%, 1.4% and 0.5% respectively. The D-Lactide contents were provided by the producer.

All the PLA grades were dried at 80°C for 6 hours prior to processing to remove residual moisture and thus to avoid hydrolytical degradation during processing. ISO standard dumbbell

shape specimens with a cross-section of 4x10 mm as well as 80x80 mm area flat specimens with 1 mm thickness were injection moulded with an Arburg Allrounder 370S 700-290 injection moulding machine (Lossburg, Germany) equipped with a diameter 30 mm, L/D = 25 screw. Injection rate of 50 cm³/s, holding pressure of 600 bars, holding time of 20 sec, residual cooling time of 40 sec, melt and mould temperature of 190°C and 25°C was used respectively. The dumbbell shaped specimens were post-production annealed (crystallized) in a heat chamber type TYFSF WGL 45B (Huanghua, China) at 80-90-100-110-120-130-140°C crystallization temperature (T_c) for one hour to develop various ratios of α' and α crystal forms for each type of PLA. Moreover, for the HDT measurements, not only 1 hour of annealing time was applied, but also time periods of 0 (unannealed), 1, 2, 3, 4, 5, 6, 7, 8, 12, 16, 20, 24, 28, 32, 36, 40, 44, 48, 52, 56 and 60 min to produce not only various crystal forms but also various crystallinity.

Methods

Differential Scanning Calorimetry (DSC) measurements were performed on a TA Instruments Q2000 type calorimeter (New Castle, USA) by using 3-6 mg of samples taken from the middle of the cross-section of the injection moulded specimens. The samples were investigated in non-isothermal mode (heat/cool/heat) from 0 to 200°C at a heating/cooling rate of 5°C/min to determine glass transition temperature (T_g), cold crystallisation temperature (T_{cc}), enthalpy of cold-crystallisation (ΔH_{cc}), melting temperature (T_m), and enthalpy of fusion (ΔH_m). Crystallinity was calculated from the first heating scan by using Equation (1):

$$X = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f} \cdot 100, \quad (1)$$

where X [%] is the calculated crystallinity, ΔH_m [J/g] and ΔH_{cc} [J/g] is the enthalpy of fusion and the enthalpy of cold-crystallisation respectively, ΔH_f [J/g] is the enthalpy of fusion for 100% crystalline PLA (93.0 J/g) [39].

Heat Deflection Temperature (HDT) measurements were performed on a Ceast HV3 6911.000 type HDT(Torino, Italy) measuring equipment according to ISO 75 standard. HDT B type measurements were carried out in flatwise mode with a loading stress of 0.45 MPa, heating rate of 2°C/min (120°C/hour) and with a span length of 64 mm.

The mechanical properties of the annealed and unannealed PLA specimens were analysed by using tensile, flexural and Charpy tests. The tensile and the flexural tests were performed by using a Zwick Z020 universal testing machine (Ulm, Germany) equipped with a Zwick BZ 020/TN2S force measuring cell with a force limit of 20kN and by using a crosshead speed of 5 mm/min. The Charpy impact tests were performed on notched samples (2 mm depth, “V” shaped notch) by using a CeastResil Impactor (Torino, Italy) impact testing machine equipped with a 2J impact energy hammer and a DAS8000 data collector unit. All of the tests were performed at room temperature at a relative humidity of 50 ± 10 %.

The creep tests were performed by using a Zwick Z005 universal testing machine equipped with a 5kN load cell. First, the tensile strength of the PLA specimens was determined by using force controlled tensile testing. A load rate of 20 N/s was used and 20 specimens were tested. Afterwards 20, 25, 30, 35 and 40% of the determined maximum force value was used as static loading force for the creep tests. These are named as load “levels” (for instance 30% load level) since it is a dimensionless quantity. 20 N/s load rate was applied until the force reached the given static loading level and kept it for one hour. Two specimens were used for each loading level if the specimens did not break until the one hour creep test, and 5 specimens were used if they were broken during the creep test. All of the measurements were performed at room temperature ($23 \pm 1^\circ\text{C}$) and at a relative humidity of $50 \pm 10\%$. Finally, by using the load-time equivalence principle, master curves were constructed to estimate long-term behaviour.

Small-angle X-ray scattering (SAXS) measurements were made on the CREDO instrument. 7x7 mm area, 1 mm thick platelets were cut from the middle of the annealed 80x80

mm flat specimens and fixed on the motorized sample holder of the instrument. Scattering patterns were recorded with a Pilatus-300k hybrid pixel CMOS position sensitive detector (Dectris Ltd, Switzerland) placed 530 mm downstream from the sample. The Cu K α radiation (0.154 nm wavelength) has been produced by a GeniX3D Cu ULD integrated beam delivery system (Xenocs SA, France). Corrections for sample self-absorption, detector flatness and instrumental background have been done using the on-line data reduction routine of the instrument control software. The scattering patterns were azimuthally averaged to yield the one-dimensional scattering curves.

Wide-angle X-ray diffraction (WAXD) was performed by using a Philips model PW 3710 based PW 1050 Bragg-Brentano parafocusing goniometer using CuK α radiation ($\lambda = 0.15418$ nm).

Results and discussion

After injection moulding, but prior to annealing, the DSC analysis of the various D-Lactide content specimens was performed (Figure1).

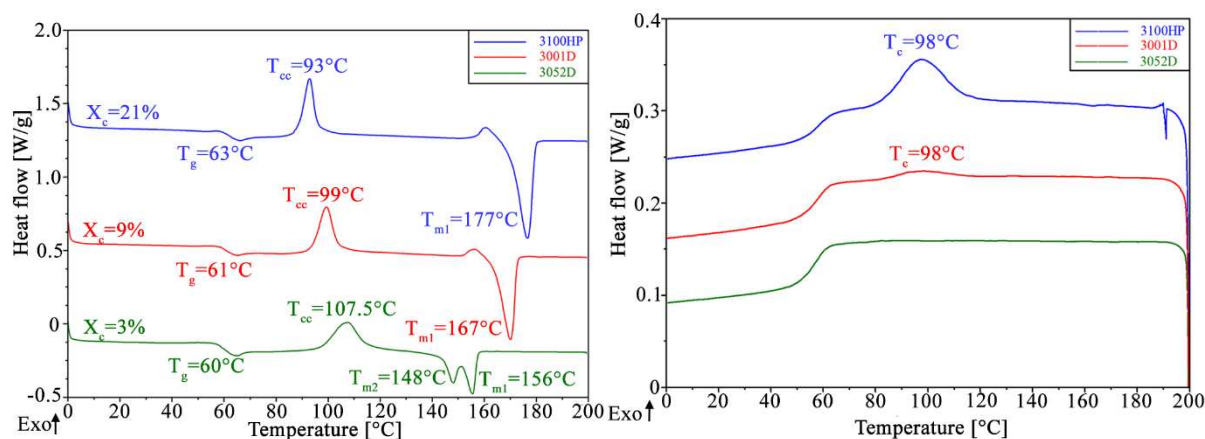


Figure1. DSC heating (a) and cooling (b) curve of various D-Lactide content PLA prior to annealing

Since the crystallization of the specimens was not completed due to high cooling rate applied during injection moulding, thus above glass transition temperature (T_g) a cold crystallization exothermic peak was visible, where the crystallization could complete (3%, 9%

and 21% regarding 4%, 1.4% and 0.5% D-Lactide content PLA respectively). Accordingly, despite of the low initial crystallinity of the specimens, the samples fully crystallized during the DSC scan and thus melting peaks were also visible. As it can also be observed, the D-Lactide content had significant effect on the calorimetric properties. Unlike molecular weight [8], D-Lactide content was found to have only minor effect on the T_g . At the same time, cold-crystallization temperature (T_{cc}), half-time of cold-crystallization ($t_{1/2}$) as well as crystal melt temperature (T_m) are highly influenced by the D-Lactide content (Figure2). Note that crystallization half time was not possible to determine for the 4% D-Lactide content PLA due to its too slow crystallization even at $5^\circ\text{C}/\text{min}$ cooling.

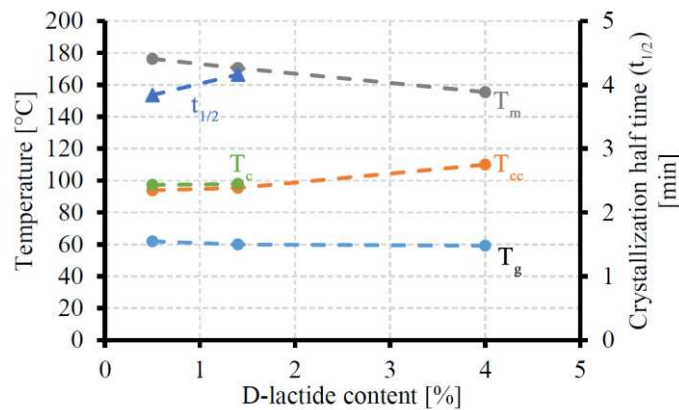


Figure2. Crystal melting temperature, cold-crystallization temperature and glass transition temperature as a function of D-Lactide content

The lower the D-Lactide content, the faster the crystallization rate of the given PLA grade, thus the cold-crystallization temperature shifted to lower temperatures from 108°C to 93°C and also the cold-crystallization half-time decreased (the exothermic peak became narrower). The shift in crystal melt temperature to higher temperatures was not caused by the increased crystallization rate, but the more isotactic molecular structure, which could be directly related to the lower D-Lactide content, as it was already proved by Saeidlouet. al [8]. An important observation could also be made that since the cold-crystallization temperature shifted

due to altered crystallization caused by the D-Lactide content, thus the developed crystal structure, which developed during cold-crystallization has changed.

According to the results of Zhang et. al [32] related to annealed (crystallized) PLA, when the crystallization temperature (T_c) applied was below 100°C, just prior to melting a small exothermic peak was visible representing the solid phase transition of α' to α followed by the melting of the developed α . When T_c was between 100 and 120°C, a bimodal endothermic melting peak could be found both related to the melting of α crystal form. The lower temperature peak refers to the synchronous melting of the original α form crystals developed during annealing and to the α' to α crystalline phase transition in a melt-recrystallization process while the higher temperature endotherm refers to the melting of the α crystals formed during the α' to α crystalline phase transition. Finally, when T_c was above 120°C, only one melting endothermic peak appeared referring to the melting of the α phase.

Accordingly, in our case, for 3100HP (0.5% D-Lactide) and 3001D (1.4% D-Lactide) grade PLA, the rather fast crystallization represented by the low cold-crystallization temperature (93°C and 99°C for 3100HP and 3001D PLA grades respectively) caused to develop the less-ordered α' crystal form. This can be stated since the α' to α solid state recrystallization exotherm was visible on the heating scans just prior to melting. At the same time, in the case of 3052D (4% D-Lactide), the higher cold-crystallization temperature (108°C) caused to develop bimodal melting peak proving the presence of both the less-ordered α' and the more ordered α crystal forms. Accordingly, the likeliness of developing α' crystal form increased by decreasing D-Lactide content. By investigating the cooling curves, the effect of D-Lactide content was also very significant. For 3052D and 3001D grade PLA, no or very minor crystallisation exotherms could be found respectively, while for 3100HP grade PLA, a definite crystallization peak was found at 98°C. According to the different crystallization rates, the injection moulded specimens (produced by using 25°C temperature mould) represented 3%,

9% and 21% crystallinity for 3052D, 3001D and 3100HP PLA grades respectively in decreasing order of D-Lactide content as calculated from the first heating scan.

After the injection moulding and annealing the specimens at 80-140°C for 1 hour, DSC measurements were again carried out to analyse crystallinity, crystal structure and the differences caused by the various D-Lactide content (Figure3).

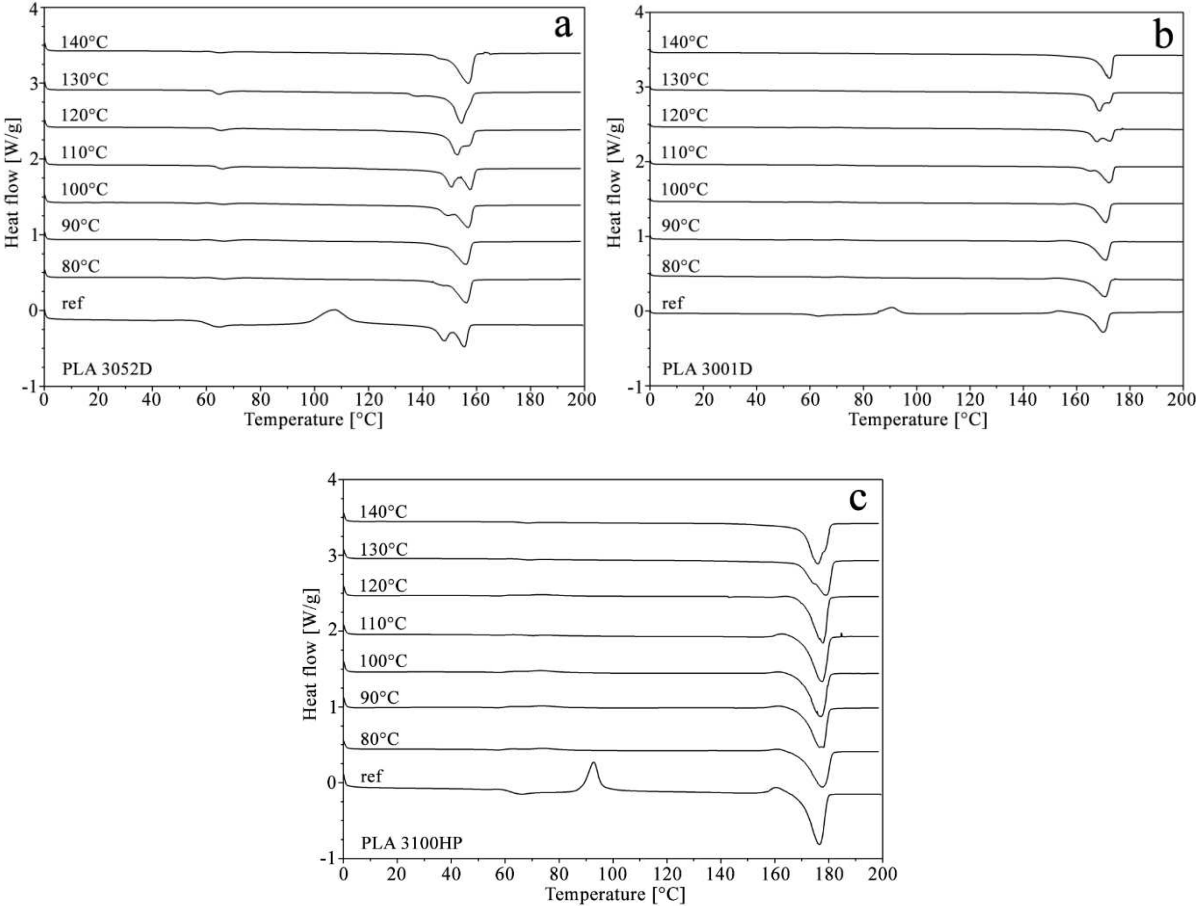


Figure3. The first DSC heating scans of 3052D (a), 3001D (b) and 3100HP (c) grade PLA annealed at 80°C-140°C for 1 hour

For each sample the first heating scan was analysed to determine the crystalline ratio and to characterise the crystalline forms of α' and α . In every grade the unannealed samples showed a cold-crystallization peak, which meant that the crystallization has not completed perfectly due to the slow crystallization rate of PLA and the high cooling rates generally applied during injection moulding. This cold crystallization exothermic peak was absent for all of the

annealed samples meaning that crystallization was completed during the annealing. The crystallinity calculated from the first heating curves was found to increase with the decreasing D-lactide content and differences could also be seen in the melting peaks and thus in the α' and α crystal structure (Table 1).

Table 1. Crystallinity and crystal structure 3052D, 3001D and 3100HP grade PLA annealed at 80°C-140°C for 1 hour

Crystallinity [%] and crystal structure (α , α')			
	3052D	3001D	3100HP
reference	3 (α' , α)	9 (α')	21 (α')
80°C	26 (α')	42 (α')	51 (α')
90°C	30 (α')	43 (α')	54 (α')
100°C	30 (α' , α)	43 (α')	52 (α')
110°C	36 (α' , α)	42 (α' , α)	54 (α')
120°C	38 (α' , α)	44 (α' , α)	54 (α')
130°C	39 (α)	50 (α' , α)	55 (α' , α)
140°C	39 (α)	52 (α)	55 (α' , α)

As it can be observed, for the same annealing temperature the ratio of the α' and α crystal forms was found to be different for the various D-Lactide content PLA grades. By decreasing D-Lactide content the development of the α' crystal form during annealing was found more and more favourable. In other words, a shift was found in the temperature regions where the α' and α crystal forms develop. Moreover, by decreasing the D-Lactide content, the maximum achievable crystallinity increased. For instance, at 100°C annealing temperature, crystallinity increased from 30% to 43% and 52% by decreasing the D-Lactide content from 4% to 1.4% and 0.5% respectively. Moreover, by increasing the annealing temperature, crystallinity was also found to increase. The crystalline structure of the PLA grades with various D-Lactide content has also been studied with SAXS (Figure4) and WAXD measurements (Figure5).

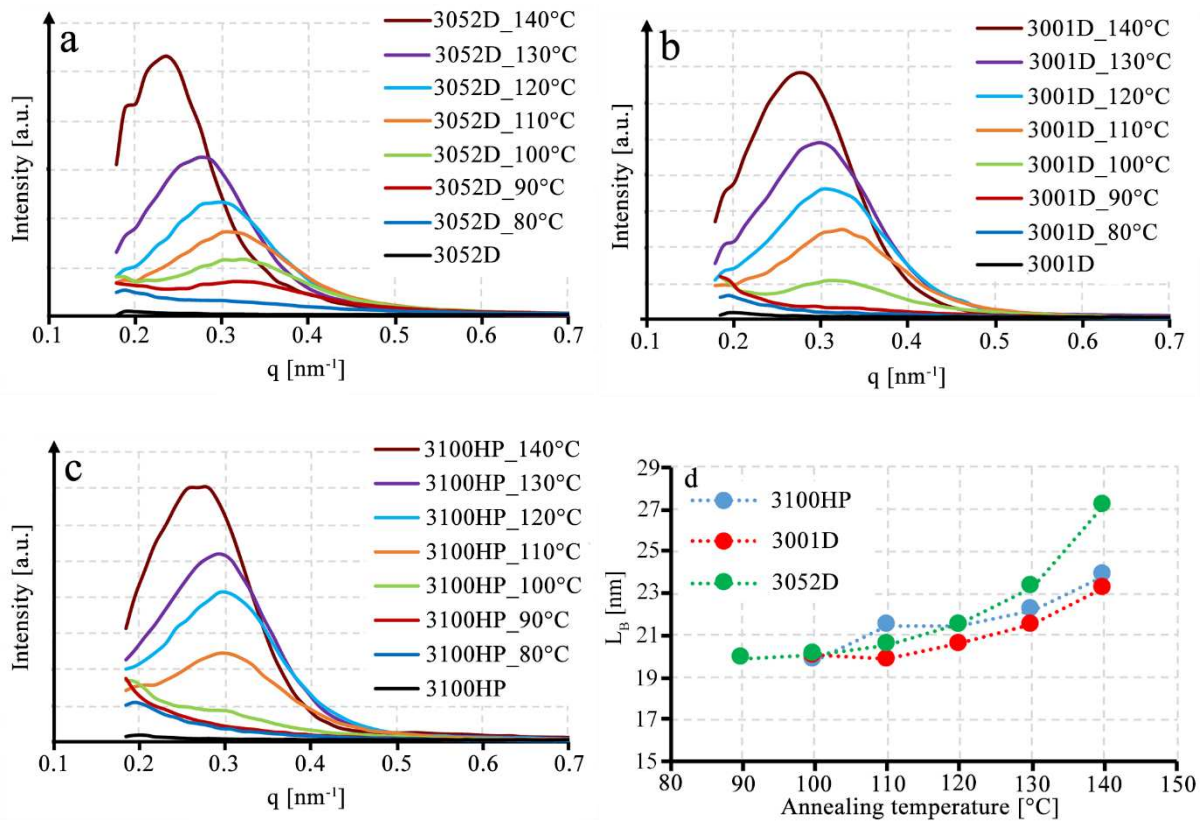


Figure4. SAXS curves of 3052D (a), 3001D (b) and 3100HP (c) grade PLA annealed at 80°C-140°C for 1 hour as well as the lamellae thickness (L_B) (d) as a function of annealing temperature

In case of SAXS measurements, it was found that due to annealing, a peak appeared on the SAXS curves representing the lamellae thickness (L_B) of the developed crystal structure. It was also found that this peak became more and more intense and shifter to lower regions, thus it can be stated that due to the increasing annealing temperature, and thus due to increased molecular chain mobility, the L_B increases from 20 nm to 27 nm. As it can be seen, there was no significant difference between the L_B values of the 0.5% and 1.4% D-Lactide content PLA, however, in the case of 4% D-Lactide content PLA, the thickness of the lamellae started to significantly differ above 130°C of annealing temperature compared to the other two D-Lactide content PLA grades. The crystalline structure of the PLA grades with various D-Lactide content has also been studied with WAXD measurements (Figure5).

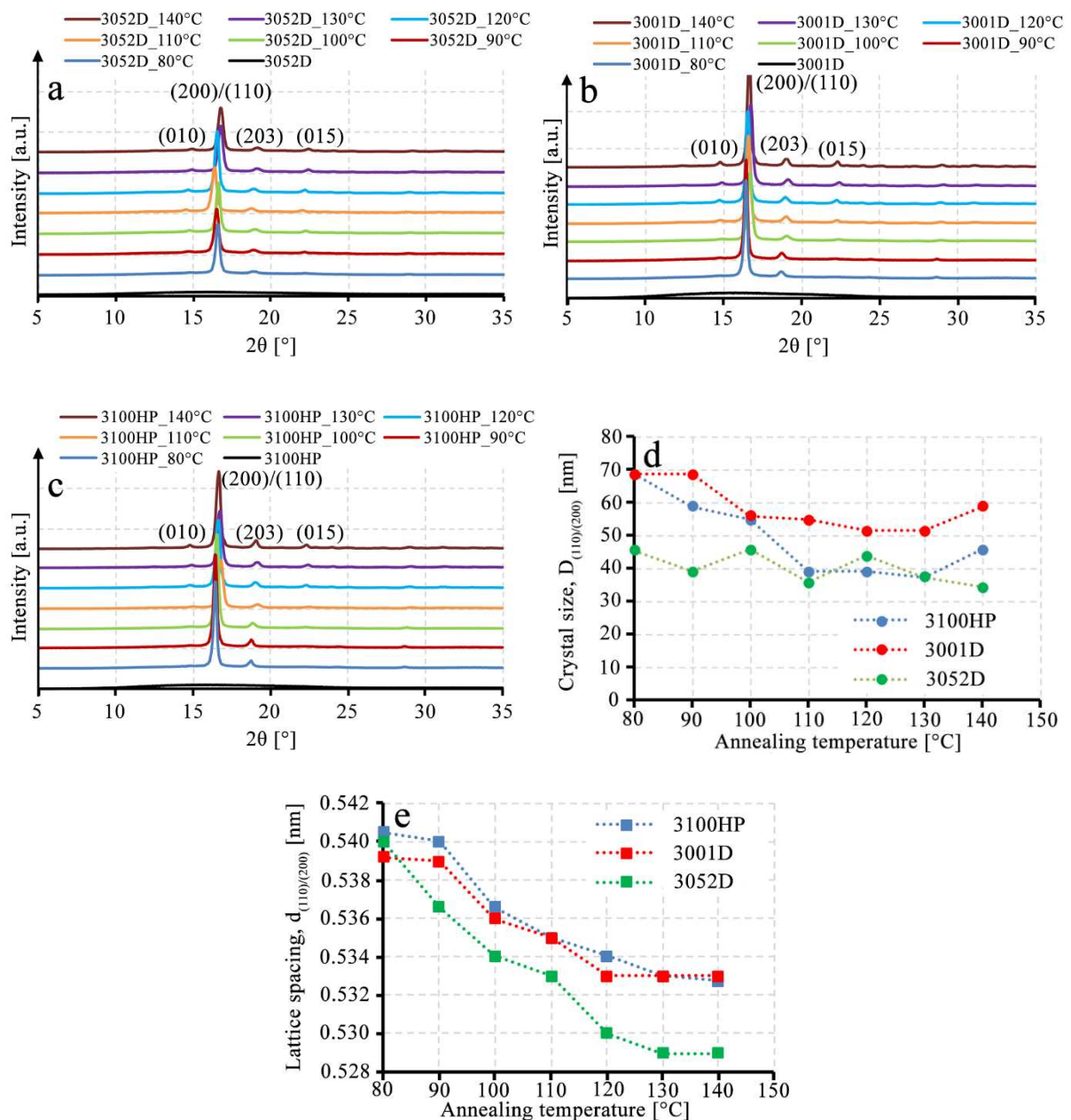


Figure 5. WAXD curves of 3052D (a), 3001D (b) and 3100HP (c) grade PLA annealed at 80°C-140°C for 1 hour as well as the crystal size (d) and the lattice spacing (e) as a function of annealing temperature

Based on the WAXD results, the crystal size decreased for the 0.5% and 1.4% D-Lactide content PLA grades by increasing annealing temperature, while for the 4% D-Lactide content PLA grade, it was practically constant. Also, the lattice spacing decreased for all of the various D-Lactide content PLA grades, however, above 130°C, the decrease levelled off. By summarizing the WAXD and SAXS results, it was found that by increasing annealing temperature, the molecular chain mobility increases, thus the interplanar distance decreases and

the lamellae thickness increases. Accordingly, as a resultant of these two, the crystal size slightly decreased depending on the D-Lactide content.

To continue the research, the effect of these morphological differences were investigated on the properties of injection moulded PLA specimens. First, the HDT of the various D-Lactide content PLA specimens were investigated (Figure. 6). In this case not only 1 hour of annealing time was applied, but also time periods of 0 (unannealed), 1, 2, 3, 4, 5, 6, 7, 8, 12, 16, 20, 24, 28, 32, 36, 40, 44, 48, 52, 56 and 60 minutes to produce not only various crystal forms but also various crystallinity.

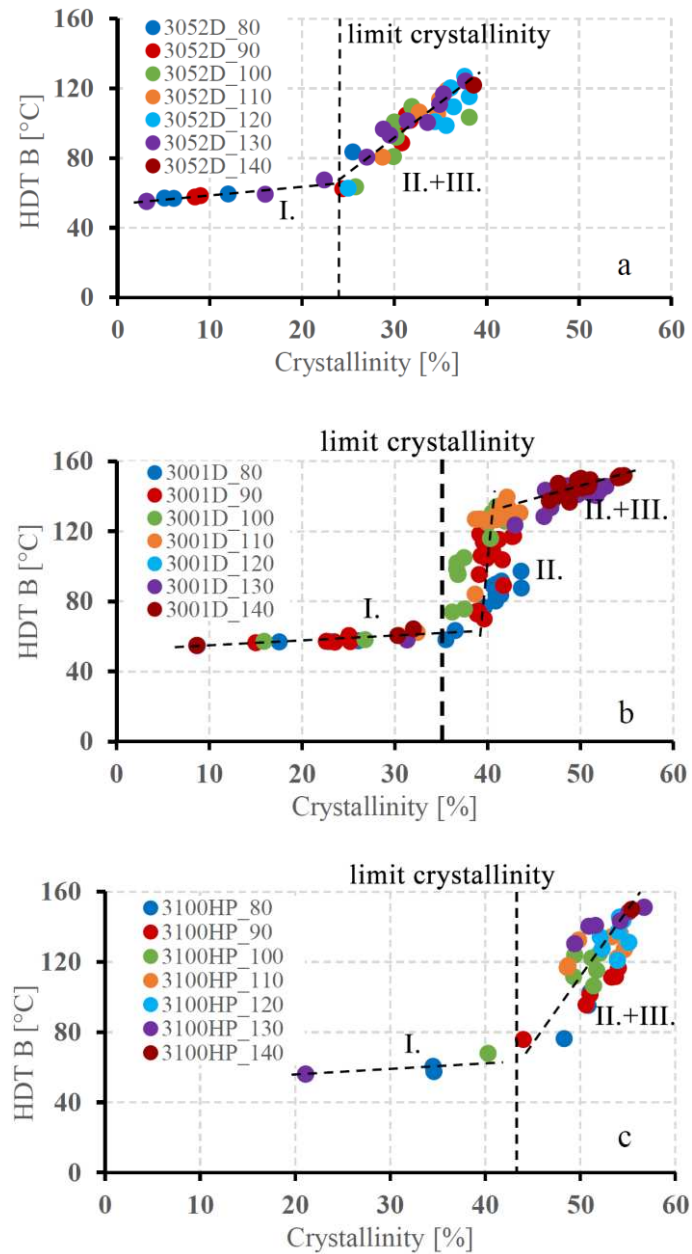


Figure 6. The HDT of the 3052D (a), 3001D (b) and 3100HP (c) grade PLA annealed at 80°C-140°C for various times. Trend lines I, II and III were plotted on the results to highlight the various ranges of the improvement in HDT

It was found that the maximum possible achievable HDT is practically the same for the 0.5% and 1.4% D-Lactide content PLA grades, while it is significantly, 15-20°C lower for the 4% D-Lactide content PLA grade. This could be the effect of the significantly lower crystallinity of this grade (39%) even in fully crystallized state (Table 1). When further investigating the connection between crystallinity and HDT, it can be observed easily that the

connection is not linear and a limit value of crystallinity could be determined. Below this limit value of crystallinity, the HDT of the annealed specimens is practically determined by the glass transition temperature with only a few °C of improvement. For the investigated PLA grades, the limit value of crystallinity was found to be between 25-45% depending on the D-Lactide content, thus at least this crystallinity should be developed if significant HDT improvement is to be achieved. At the same time, above the limit value of crystallinity, the HDT of the annealed specimens significantly increase and it is not only influenced by the crystallinity but also by crystal forms (α' and α) and lamellae thickness. For instance, in case of 3001D grade PLA with 1.4% D-Lactide content (Figure. 6/b), the annealing at 80°C and 120°C resulted in a practically same crystallinity of 42% and 44%, but a highly different HDT of 99°C and 140°C respectively. This resulted an almost vertical region in the diagrams in case of 3001D (1.4% D-Lactide content) and 3100HP (0.5% D-Lactide content) PLA grades. For the 3052D grade (4% D-Lactide content), above the limit value of crystallinity the HDT values were both influenced by increasing crystallinity and ordering crystal structure. Accordingly, trend lines were applied on the diagrams to highlight the two or three regions of the improvement in HDT, namely: I. Below the limit value of crystallinity, where T_g and thus entering into rubbery state of the amorphous phase limits significant HDT improvement, and only minor improvement could be achieved, II. Above the limit value of crystallinity, where the effect of crystal forms and their ordering is dominant in case of practically same crystallinity, III. Above the limit value of crystallinity, where further increasing crystallinity causes additional improvement in HDT.

The investigation continued by analysing the mechanical properties.

On the tensile and flexural strength values, it was found that both properties could be improved by 9-14% and 14-23% respectively, by annealing the PLA specimens. At the same time, by increasing annealing temperature, first the strength of the specimens increased up to around 80-90°C annealing temperature, where the maximum values were found, while above

this temperature, the strength started to drop and in most cases, especially in case of flexural strength, these values dropped below the values of the unannealed specimens. In contrast, the modulus values monotonously increased by increasing annealing temperature and thus an average improvement of 39% and 29% could be achieved in tensile and flexural modulus respectively. Regarding the effect of D-Lactide content no obvious tendencies were found between the three different PLA grades. Parallel to the monotonous increase in modulus values, the strain at break values monotonously decreased. The main difference between the three different investigated PLA grades was that the unannealed specimens had higher initial elongation (2.99%, 3.62% and 4.01%) with decreasing D-Lactide content. The investigation of the properties continued by the analysis of Charpy impact strength (Figure7).

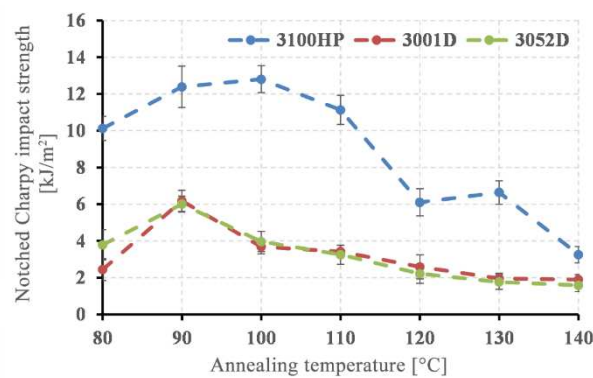


Figure7. Charpy impact strength (notched) of the 3052D, 3001D and 3100HP grade PLA specimens annealed at 80°C-140°C for 1 hour

It could be observed, that both the D-Lactide content and the annealing temperature had very significant influence on the impact properties. Simply by annealing, the impact strength could be improved for all of the investigated PLA grades. At the same time, the highest impact strength values were reached by annealing the lowest D-Lactide content PLA. In this case, by annealing the 0.5% D-Lactide content PLA grade (3100HP), its impact strength could be improved from 2.1 kJ/m² (unannealed) even up to 12.8 kJ/m². Additionally, independently from the D-Lactide content, the maximum impact strength values were reached by applying 90-100°C annealing temperature range. By further improving the annealing temperature, the

impact properties drop, which could be the effect of change in multiple morphological parameters including increased lamellae thickness as well as increased α to α' crystal form ratio. Accordingly, the most significant improvement in impact strength was reached for the 0.5% D-Lactide content PLA annealed at 90-100°C as the effect of high crystallinity (~52-54%) and the presence of α' crystal form.

Finally, the creep properties of the various D-Lactide content PLA specimens were investigated (Figure8).

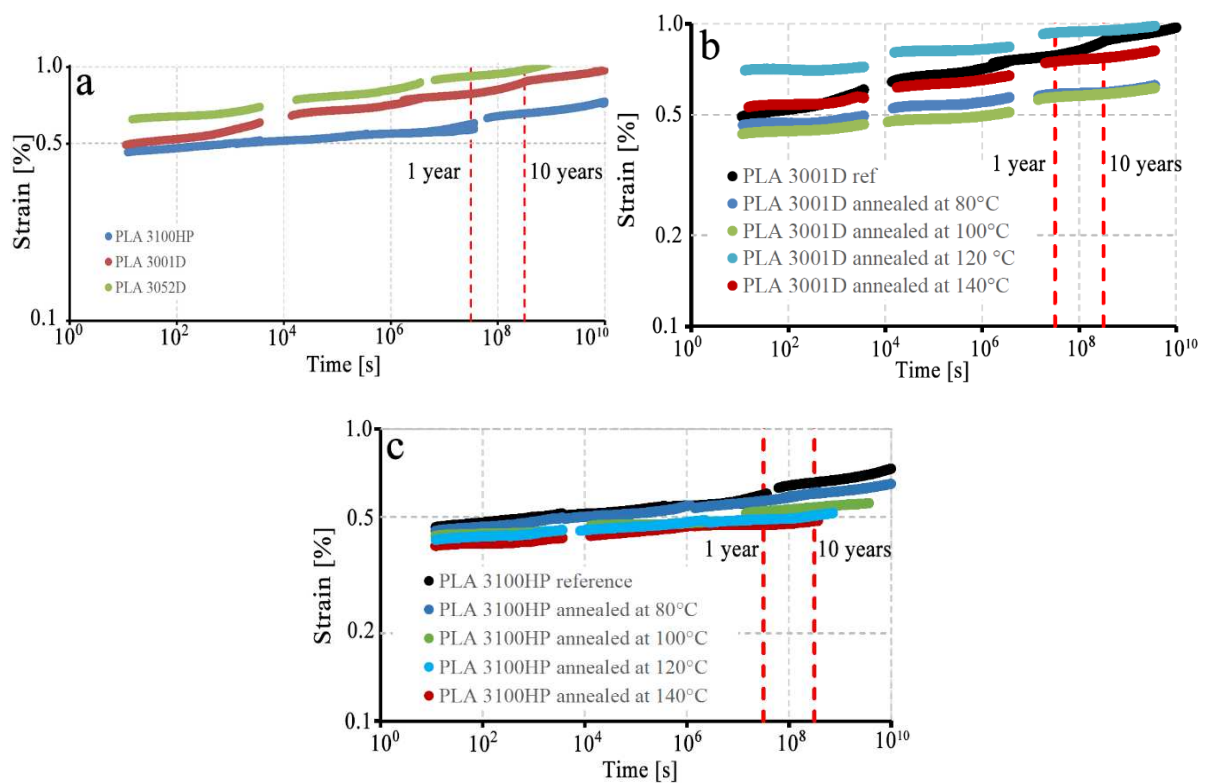


Figure8. The strain as a function of time for the injection moulded, unannealed 3052D, 3001D and 3100HP grade PLA specimens as well as for the 3001D (b) and 3100HP (c) grade PLA specimens annealed at 80°C-140°C for 1 hour (mastercurve constructed in case of 30% loading level)

In case of the unannealed PLA specimens, lower strain in time (higher creep resistance) was found with decreasing D-Lactide content. At the same time, this could not only be the effect of D-Lactide content itself, since with decreasing D-Lactide content, the crystallinity of the specimens increased from 3% to 21% as demonstrated previously (Table 1). By annealing the specimens and developing various crystal structures, the creep resistance could be further

improved and thus the initial strain as well as the strain in time (slope of curve) decreased. Interestingly, in case of 3001D PLA grade, only the 80°C and 100°C annealing caused to decrease the initial strain in time, but by further increasing the annealing temperature, this initial strain value increased, despite of slope of the whole strain in time curve still being lower compared to the reference. A possible explanation should be looked in the change in modulus values. In our recent paper [39], the storage modulus of annealed 3001D PLA grade was investigated and found that by increasing annealing temperature, first the modulus measured 23°C increases, while above 100°C annealing temperature it decreases. At the same time, this is not fully supported by the tensile modulus results, thus further measurements will be needed to explore this behaviour and find the exact explanations.

Nevertheless, as it was demonstrated, the change in morphological parameters due to annealing including lamellae thickness as well as α to α' crystal form ratio highly influenced the various properties (mechanical, HDT and creep). Accordingly, annealing in the 80-90°C temperature range was found to be an effective tool to significantly improve HDT, strength, modulus, impact properties and creep resistance, but unfortunately strain at break decreased. Additionally, by further increasing the annealing temperature from 90°C to 140°C, the HDT, modulus and creep resistance could be further improved as well, but it was disadvantageous regarding strength, impact and strain at break values. In case of a real, PLA based part, a compromise should be made between the necessary mechanical (including impact), HDT and creep properties to select the appropriate annealing temperature.

CONCLUSION

In our research the effect of D-lactide content of injection moulded and annealed Poly(Lactic Acid) (PLA) was investigated on crystallinity as well as crystalline forms (less ordered α' and the more ordered α crystalline forms) and thus on the mechanical, Heat Deflection Temperature (HDT) and creep properties. Three different PLA grades of 3052D,

3001D and 3100HP were investigated with a D-Lactide content of 4%, 1.4% and 0.5% respectively. By decreasing D-Lactide content the cold-crystallization temperature (T_{cc}) shifted to lower temperatures, and thus the development of the α' crystal form during annealing was found more and more favourable. Accordingly, a shift was found in the temperature regions where the α' and α crystal forms develop. When investigating the connection between crystallinity and HDT, a limit value of crystallinity could be determined (25-45% depending on the D-Lactide content). Below this limit value of crystallinity, the HDT of the annealed specimens is practically determined by the glass transition temperature with only a few °C of improvement, while above the limit value of crystallinity, the HDT of the annealed specimens significantly increase and it is not only influenced by the crystallinity but also by crystal forms and lamellae thickness. Enormous improvement was found in the impact strength by using annealing between 80-90°C, moreover, the highest impact strength values were reached by annealing the lowest D-Lactide content PLA (from 2.1 kJ/m² (unannealed) up to 12.8 kJ/m²), as the effect of high crystallinity (~52-54%) and the presence of α' crystal form. Finally, the creep properties were investigated, where lower strain in time (higher creep resistance) was found with decreasing D-Lactide content even for unannealed specimens. Additionally, by annealing various crystal structures were developed in the specimens ensuring higher creep resistance manifested in lower initial strain as well as strain in time (slope of curve). Finally, annealing in the 80-90°C temperature range was found to be an effective tool to significantly improve HDT, strength, modulus, impact properties and creep resistance, but unfortunately strain at break decreased, while by further increasing the annealing temperature from 90°C to 140°C, the HDT, modulus and creep resistance could be further improved as well, but it was disadvantageous regarding strength, impact and strain at break values.

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CAPTIONS

Figure 1. DSC heating (a) and cooling (b) curve of various D-Lactide content PLA prior to annealing

Figure 2. Crystal melting temperature, cold-crystallization temperature and glass transition temperature as a function of D-Lactide content

Figure 3. The first DSC heating scans of 3052D (a), 3001D (b) and 3100HP (c) grade PLA annealed at 80°C-140°C for 1 hour

Figure 4. SAXS curves of 3052D (a), 3001D (b) and 3100HP (c) grade PLA annealed at 80°C-140°C for 1 hour as well as the lamellae thickness (L_B) (d) as a function of annealing temperature

Figure 5. WAXD curves of 3052D (a), 3001D (b) and 3100HP (c) grade PLA annealed at 80°C-140°C for 1 hour as well as the crystal size (d) and the lattice spacing (e) as a function of annealing temperature

Figure 6. The HDT of the 3052D (a), 3001D (b) and 3100HP (c) grade PLA annealed at 80°C-140°C for various times. Trend lines I, II and III were plotted on the results to highlight the various ranges of the improvement in HDT

Figure 7. Charpy impact strength (notched) of the 3052D, 3001D and 3100HP grade PLA specimens annealed at 80°C-140°C for 1 hour

Figure 8. The strain as a function of time for the injection moulded, unannealed 3052D, 3001D and 3100HP grade PLA specimens as well as for the 3001D (b) and 3100HP (c) grade PLA specimens annealed at 80°C-140°C for 1 hour (mastercurve constructed in case of 30% loading level)

Table 1. Crystallinity and crystal structure 3052D, 3001D and 3100HP grade PLA annealed at 80°C-140°C for 1 hour

REFERENCES

1. Luyt, A. S. *Express Polym. Lett.* **2017**, 11, 764.
2. Srikanth, P. In *Handbook of bioplastics and biocomposites engineering applications*, John Wiley and Sons Inc.: New Jersey, **2011**.
3. Ren, X. *J. Clean. Prod.* **2003**, 11, 27-40.
4. Long Y. In *Biodegradable polymer blends and composites from renewable resources*, John Wiley and Sons Inc.: New Jersey, **2009**.
5. Flieger, M.; Kantorová, M.; Prell A.; Rezanka, T.; Votruba, J. *Folia Microbiol.* **2003**, 48, 27-44.
6. Lim, L. T.; Auras, R.; Rubino, M. *Prog. Polym. Sci.* **2008**, 33, 820–852.
7. Auras, R.; Lim, L. T.; Selke, S.E.M. Tsuji, H. In *Poly(Lactic Acid) Synthesis, Structures, Properties, Processing and Applications*, first ed., John Wiley & Sons Inc.: New Jersey, **2010**.
8. Saeidlou, S.; Huneault, M. A.; Li, H.; Park, C. B. *Prog. Polym. Sci.* **2012**, 37, 1657–1677.
9. Chow, W. S.; Teoh, El L.; Karger-Kocsis, J. *Express Polym. Lett.* **2018**, 12, 396-417.
10. Tábi, T.; Bakonyi, P.; Hajba, S.; Herrera-Franco, P. J.; Czigány, T.; Kovács, J. G. *J. Reinf. Plast. Comp.* **2016**, 35, 1600-1610.
11. Pan, P.; Inoue, Y. *Prog. Polym. Sci.* **2009**, 34, 605–640.

12. Hoogsteen, W.; Postema, A. R.; Pennings, A. J.; ten Brinke, G. *Macromolecules* **1990**, *23*, 634–642.
13. Sasaki, S.; Asakura, T. *Macromolecules* **2003**, *36*, 8385–8390.
14. Righetti, M. C.; Gazzano, M.; Di Lorenzo, M. L.; Androsch, R. *Eur. Polym. J.* **2015**, *70*, 215–220.
15. Zhang, J.; Duan, Y.; Sato, H.; Tsuji, H.; Noda, I.; Yan, S.; Ozaki, Y. *Macromolecules* **2005**, *38*, 8012–8021.
16. Zhang, J.; Tashiro, K.; Domb, A. J.; Tsuji, H. *Macromol. Symp.* **2006**, *242*, 274–278.
17. Cho, T.-Y.; Strobl, G. *Polymer* **2006**, *47*, 1036–1043.
18. Puiggali, J.; Ikada, Y.; Tsuji, H.; Cartier, L.; Okihara, T.; Lotz, B. *Polymer* **2000**, *41*, 8921–8930.
19. Sawai, D.; Takahashi, K.; Sasashige, A.; Kanamoto, T. *Macromolecules* **2003**, *36*, 3601–3605.
20. Cartier, L.; Okihara, T.; Ikada, Y.; Tsuji, T.; Puiggali, J.; Lotz, B. *Polymer* **2000**, *41*, 8909–8919.
21. Tsuji, H. *Macromol. Biosci.* **2005**, *5*, 569–597.
22. Bouapao, L.; Tsuji, H. *Macromol. Chem. Phys.* **2009**, *210*, 993–1002.
23. Tsuji, H.; Ikada, Y. *Macromolecules* **1993**, *26*, 6918–6926.
24. He, Y.; Xu, Y.; Wei, J.; Fan, Z.; Li, S. *Polymer* **2008**, *49*, 5670–5675.
25. Narita, J.; Katagiri, M.; Tsuji, H. *Macromol. Mater. Eng.* **2011**, *296*, 887–893.
26. Yamane, H.; Sasai, K. *Polymer* **2003**, *44*, 2569–2575.
27. Rahman, N.; Kawai, T.; Matsuba, G.; Nishida, K.; Kanaya, T.; Watanabe, H.; Okamoto, H.; Kato, M.; Usuki, A.; Matsuda, M.; Nakajima, K.; Honma, N. *Macromolecules* **2009**, *42*, 4739–4745.

28. Barrau, S.; Vanmansart, C.; Moreau, M.; Addad, A.; Stoclet, G.; Lefebvre, J.-M.; Seguela, R. *Macromolecules* **2011**, *44*, 6496–6502.
29. Harris, A. M.; Lee, E. C. *J. Appl. Polym. Sci.* **2008**, *107*, 2246–2255.
30. Chow, W. S.; Leu, Y. Y.; Ishak, Z. A. M. *Period. Polytech. Mech.* **2016**, *60*, 15–20.
31. Scaffaro, R.; Sutura, F.; Mistretta, M. C.; Botta, L.; La Manita, F. P. *Express Polym. Lett.* **2017**, *11*, 555–564.
32. Zhang, J.; Tashiro, K.; Tsuji, H.; Domb, A. J. *Macromolecules* **2008**, *41*, 1352–1357.
33. Kawai, T.; Rahman, N.; Matsuba, G.; Nishida, K.; Kanaya, T.; Nakano, M.; Okamoto, H.; Kawada, J.; Usuki, A.; Honma, N.; Nakajima, K.; Matsuda, M. *Macromolecules* **2007**, *40*, 9463–9469.
34. Pan, P.; Kai, W.; Zhu, B.; Dong, T.; Inoue, Y. *Macromolecules* **2007**, *40*, 6898–6905.
35. Zhang, J.; Tsuji, H.; Noda, I.; Ozaki, Y. *Macromolecules* **2004**, *37*, 6433–6439.
36. Zhang, J.; Tsuji, H.; Noda, I.; Ozaki, Y. *J. Phys. Chem. B* **2004**, *108*, 11514–11520.
37. Pan, P.; Zhu, B.; Kai, W.; Dong, T.; Inoue, Y. *Macromolecules* **2008**, *41*, 4296–4304.
38. Cocca, M.; Di Lorenzo, M. L.; Malinconico, M.; Frezza, V. *Eur. Polym. J.* **2011**, *47*, 1073–1080.
39. Tábi, T.; Hajba, S.; Kovács, J. G. *Eur. Polym. J.* **2016**, *82*, 232–243.
40. Wacha, A.; Varga, Z.; Bóta, A. *J. Appl. Crystallogr.* **2014**, *47*, 1749.
41. Wacha, A. *J. Appl. Cryst.* **2015**, *48*, 1843.