Article

# Influence of thermal annealing on sinterability of different grades polylactide microspheres dedicated for laser sintering

Małgorzata Gazińska <sup>1,\*</sup>, Anna Krokos<sup>1</sup>, Bartłomiej Kryszak<sup>1</sup>, Paulina Dzienny<sup>2</sup>, Michał Olejarczyk<sup>3</sup>, Piotr Gruber<sup>3</sup>, Ryszard Kwiatkowski<sup>4</sup>, Arkadiusz Antończak<sup>2</sup>

- <sup>1</sup> Faculty of Chemistry, Department of Engineering and Technology of Polymers, Wroclaw University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland
- <sup>2</sup> Faculty of Electronics, Laser & Fibre Electronics Group, Wroclaw University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland
- <sup>3</sup> Faculty of Mechanical Engineering/Centre of Advanced Manufacturing Technologies, Wroclaw University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland
- <sup>4</sup> Institute of Textile Engineering and Polymer Materials, University of Bielsko-Biała, Willowa 2, 43-309 Bielsko-Biała, Poland
- \* Correspondence: malgorzata.gazinska@pwr.edu.pl

Abstract: Comparison of the influence of conditioning temperature of microspheres made of medical grade poly(L-lactide) (PLLA) and polylactide with 4wt.% of D-lactide content (PLA), on its thermal and structural properties is presented. The microspheres were fabricated by solid-in-oil-in-water method for application in additive manufacturing. The microspheres were annealed below glass transition temperature (Tg), above Tg but below onset of cold crystallization, and at two temperatures selected from the range of cold crystallization corresponding to crystallization of  $\alpha'$  and  $\alpha$  form of poly(L-lactide) respectively, i.e., at 40°C, 70°C, 90°C and 120°C, in order to verify the influence of conditioning temperatures on sinterability of microspheres set as sintering window (SW). Based on differential scanning calorimetry measurements SW of microspheres were evaluated with consideration of existence of cold crystallization and reorganization of crystal polymorph. The results indicate that the conditioning temperature influence on availability and range of SW that depending on the D-lactide presence. We postulate the need for an individual approach for polylactide powders in determining the SW as a temperature range free of any thermal events. Moreover, other core powder characteristic, such as residual solvent content, morphology, particle size distribution, powder flowability and thermal conductivity, as a key property for successful laser sintering, are characterized. The microspheres are close to sphere and the size of microspheres are below 100 µm. Residual solvents content decreases with the increase of annealing temperature. The thermal conductivity is 0.073 W/mK and 0.064 W/mK for PLA and PLLA microspheres, respectively, and it depends on the spherical shape of the microspheres. Furthermore, the WAXD studies prove that an increase in the conditioning temperature causes a slight increase in crystallinity degree for PLLA microspheres and clear increase in crystallization for PLA microspheres.

**Keywords**: polylactide microspheres, thermal conditioning, sintering window, laser sintering, powder morphology and flowability, crystalline structure, additive manufacturing

#### 1. Introduction

(c) (i)

Laser sintering is one of powder bed fusion additive manufacturing technology, in which preheated polymer material in form of powder is fused together using laser radiation. Layer-by-layer process of melting and solidification of subjected to radiation cross-section results in manufacturing three dimensional part. The most commonly materials used in laser sintering (LS) technology are semicrystalline polymers, yet amorphous polymers or even glass and ceramics can be used. The polymer powder applicable in LS must fulfil several conditions such as appropriate particle shape, size distribution, thermal, rheological and optical properties [1]. Only particularly controlled property combination leads to successful LS implementation. In term of thermal properties of semicrystalline polymers crystallization during processing should be avoided. Thus, the processing temperature must be set as in-between melting and crystallization, the temperature range called super cooling window and corresponds to sintering window (SW) [1]. This standard definition of sintering window for LS processing works for polyamide (PA11, PA12), that exhibit sharp melting peak and broad supercooling range [2]. In case of amorphous polymers processing temperature is evaluated differently [3]. Most commonly powder processing temperature is set close to glass transition temperature

 $(T_g)$ , which allows stress relaxation and reduces warpage of produced parts [4–6] is still high, which results with brittle and instable parts due to not proper powders' particles coalescence [7,8].

Another approach concerning SW determination was proposed by Berretta et al. [9] for high-temperature semicrystalline polymers, which do not show super-cooling window, such as poly(ether ether ketone) (PEEK) and poly(aryl ether ketone) (PEAK). The method involves a calculation of the first derivative of the heating curve of a DSC thermogram and then calculating the minimum point and was proven to be corresponding with actual powder processing temperatures for tested high-temperature polymers. Although this technique still needs to be fully validated with a wider range of materials.

Additive manufacturing is increasingly used in the healthcare sector in applications such as anatomical models, medical devices, pharmaceuticals or tissue engineering [10]. Biomaterials processed with LS, which are used or being implemented (being on a different stage of development) in medical industry are PEEK [11,12], PCL [11,13,14], PVA [11,15,16] and PLA [17], PLLA [11,13]. The SW should ensure that the powder lying in the powder bed of a generic LS system does not melt before exposure to the laser and does not crystallize before or during laser exposure. The SW defined as supercooling window for semicrystalline polymer is proper for example for polyamides. But in the group of semicrystalline polymers processed by LS are polymers that crystallize relatively slowly and undergo so-called cold crystallization during heating. They are PET, PLLA, PC and PEEK. Often, in the case of PLLA, the fact of cold crystallization is neglected and printing parameters, i.e., the bed temperature is selected regardless of whether or not cold crystallization will occur [13,18]. If the PLLA powder has a low degree of crystallinity, cold crystallization may occur in the powder bed. Moreover, because a temperature gradient in the powder bed [19,20] as a consequence, the polylactide powder could have spatial crystallinity degree distribution. Therefore, it is important to determine the sintering window taking into account cold crystallization. An alternative solution is additional conditioning before sintering, in order to get completely crystallized powder.

M. Van den Eyden at al. describe the influence of thermal treatment on the laser sinterability of polybutene-1. The author demonstrates two alternative thermal treatments strategy leading to broadening of sintering window of PB-1 and making an unsinterable polymer sinterable [21].

In this scope we focus on determination of thermal and structural properties of microspheres made of two types of polylactides. Medical grade poly(L-lactide) (PLLA) and polylactide (PLA) - stereocopolymer with 4% D-isomer content, were intentionally selected because of its extremely different crystallization behaviour [22].

The principal aim was elucidating the influence of conditioning temperature on thermal and structural properties of the microspheres in order to control the availability and range of SW. Degree of crystallinity and  $\alpha/\alpha'$  crystal form of poly(L-lactide) was determined for PLLA and PLA microspheres annealed at different temperatures. Crystal form of PLLA significantly affect the application–wise properties, such as mechanical and barrier properties [23,24]. In addition, as for degradable polymers, degradability of PLLA is also influenced by the polymorphism. N. Zhang et al. demonstrated different hydrolytic degradation behaviour of  $\alpha'$ - and  $\alpha$ -PLLA [25]. Thus, it is quite important to control the polymorphism for optimizing the properties of PLLA for biomedical applications.

In addition, the goal of the research was precise determination and definition of processing window of different grades polylactide microspheres as an example of semicrystalline polymer that exhibit cold crystallization. The sintering window was determined based on DSC curves recorded at standard rate of 10°C/min. Moreover, due to crystal polymorphism of PLLA, the reorganization of conformationally disordered  $\alpha$ '-crystals into stable  $\alpha$ -crystals occurs on heating. In our previous paper we precisely describe SW determination for PLLA and composite PLLA/HAP microspheres [26]. The research was focused on the influence of HAP particles on SW range.

Among processing window, sinterability of the polylactide microspheres was verified based on morphology, particle size distribution, powder flowability, thermal stability and residual solvent content.

## 2. Materials and Methods

#### 2.1. Materials

The two types of polylactides used in this study were commercial products, polylactide PLA 3051D grade (4% Dlactide content, inherent viscosity 3.0-3.5 dL/g) from Nature Works and medical grade poly(L-lactide) PLLA Resomer L207S (inherent viscosity 1.5-2.0 dL/g) from Evonik. Methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) was supplied from STANLAB and poly(vinyl alcohol) (Mowiol 18-88, Mw~130000, 86.7-88.7 mol% hydrolysis) from Sigma-Aldrich were used in our research.

# 2.2. Preparation of PLA and PLLA microspheres

Microspheres of PLA and PLLA were prepared by conventional emulsion-solvent evaporation technique (O/W). At first 1% aqueous solution of PVA was prepared by stirring with magnetic stirrer and heating up to 70°C. Then both of PLA and PLLA was dissolved in methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) to obtain the 4wt.% transparent solution. The volume ratio of organic phase to aqueous phase is 1:3. Next the organic solution was dropped into PVA solution by using peristaltic pomp while the PVA solution was stirred with magnetic stirred at 800 rpm at room temperature. After emulsification, the methylene chloride was removed by evaporation at room temperature under stirring by 48h. PLA and PLLA microspheres was separated by centrifuging and drying in vacuum at 40°C for 24 h. After preparation microspheres were additionally annealed at 40°C, 70°C, 90°C and 120°C for 5 hours. The series of microspheres were abbreviated PLA\_T and PLLA\_T, were T stands for conditioning temperature.

# 2.3. Scanning Electron Microscopy

Microspheres of PLA and PLLA were characterized by Scanning Electron Microscopy (SEM) using Zeiss EVO MA25 with BSE method and accelerating voltage of 20 kV. Captured images allowed to determine shape and size of investigated powders.

# 2.4. Particle Size Distribution

Particle size distribution of prepared powders was determined by dry laser diffraction spectroscopy using HELOS/BR 4470 C, RODOS/T4, R4 with measurement range of  $0.1 \div 875 \mu m$  according to ISO 13220-1 standard. Dispersing pressure was set at 2 bar along with VIBRI feeder which feed rate was 80% and gap width of 3.5 mm. The particle size, D<sub>50</sub>, was determined that represents powder particle diameter which 50% by volume of the powder are smaller. Additionally, D<sub>10</sub>, D<sub>90</sub> and percentage of particles below 10  $\mu m$  were established. The D<sub>10</sub>, D<sub>90</sub> were used to calculate span, as a following (1):

 $\text{Span} = (D_{90} - D_{10}) / D_{50}$ 

(1)

## 2.5. Powder flowability

Dynamic powder flowability was determined using Revolution Powder Analysis (RPA) method. The drum (GranuDrum, GranuTools) with an inner diameter of 84 mm and 20 mm width is rotating around its axis at an angular velocity ranging from 2 to 60 rpm. The transparent sidewalls allow observing the powder behaviour inside which can be captured by the image vision system [27]. This method allows the measurement of the first avalanche angle (AA), flowing angle ( $\alpha_i$ ) and dynamic cohesive index ( $\sigma_i$ ). The avalanche angle describes the angle at which the powder reaches the highest potential energy (the highest point) in the drum just before the loss of stability visible as an avalanche [8]. The avalanche behaviour of a powder sample can be used as a good predictor of powder flowability for not too cohesive powders [28]. The first avalanche angle is measured by image analysis at low rotational speed, the flowing angle at a variable rotational speed. In general, a low value of these factors corresponds to a good flowability [29], [30]. In this test one rotating speeds (1 rpm) for the first avalanche angle and 9 different rotating speeds between 2 and 60 rpm were used, both at increasing and decreasing an angular velocity, for the flowing angle. 25 images were taken for each rotation speed, separated by 1s. Based on recorded images, the average position of the powder/air interface and the fluctuations around this value was tracked. Regarding the dynamic cohesive index is related only to the cohesive forces acting between the grains [29]. It is assumed that an increase in the cohesiveness of the powder leads to a corresponding increase in the cohesive index. The drum for each batch was half-filled with powder (roughly 55 ml).

## 2.6. Thermogravimetry

TGA/DSC1 Mettler Toledo system is used for the thermogravimetric analysis (TGA) of polylactide and poly(Llactide) microspheres in order to estimation of residual solvent content and thermal stability of microspheres. Samples were heated with rate of 10°C min<sup>-1</sup> from 25°C to 650°C under 60 ml/min of nitrogen flow.

#### 2.7. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed using the Mettler Toledo DSC1 system, coupled with Huber TC 100 intracooler. The instrument was calibrated using indium ( $T_m = 156.6^{\circ}C$ ,  $\Delta H_m = 28.45 \text{ J/g}$ ) and zinc ( $T_m = 419.7^{\circ}C$ ,  $\Delta H_m = 107.0 \text{ J/g}$ ) standards. Samples (~3,5 mg) were measured in the 40 µL aluminium pans

under a constant nitrogen purge (60 mL/min) from 0°C to 200°C. Heating rate was set to 10°C/min. DSC curves for estimation of thermal conductivity of microspheres were recorded from  $150^{\circ}$ C to  $170^{\circ}$ C with the heating rate of 0.5 K/min under 150 ml/min nitrogen flow. The DSC curves presented in Figures 4 were normalized to the sample mass. The evaluation of the thermal properties from DSC and TGA curves has been performed using the STARe software. The initial degree of crystallinity (X<sub>c</sub>) of PLLA was calculated from the first heating DSC curves according to the equation (2):

$$X_c^{DSC} = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^{100\%}},\tag{2}$$

where  $\Delta H_m$  – melting enthalpy [J/g],  $\Delta H_{cc}$  – enthalpy of cold crystallization,  $\Delta H_m^{100\%}$  – melting enthalpy of  $\alpha'$  – form 100% crystalline polylactide (107 J/g) and melting enthalpy of  $\alpha$ -form 100% crystalline polylactide (143 J/g) [31].

## 2.8. Wide Angle X-ray Diffraction

WAXD (wide angle X-ray diffraction) experiments were done at room temperature on Rigaku Ultima IV diffractometer (Bragg–Brentano geometry) with Ni filtered CuK $\alpha$  ( $\lambda$  = 1.54178 Å) radiation generated by sealed X-ray tube. The radiation source was powered by a generator operated at 40 kV and 30 mA. Data were collected within the range of 20 from 1.5° to 65.0° in a continuous scan mode with step width 0.005° and scanning rate 5°C/min. The background corrected WAXD patterns were resolved into Lorenzian shape diffraction peaks and diffusion maxima by using the Levenber-Marquardt non-linear fitting procedure implemented on OriginPro 9.0 software. The degree of crystallinity was calculated according to the following relation (3):

$$X_c^{WAXD} = \frac{\sum A_c}{\sum A_c + \sum A_a} \cdot 100\%,$$
(3)

where  $A_c$  and  $A_a$  represent the integrated intensities under the crystalline reflections and the integrated intensities under diffuse maxima.

## 3. Results and discussion

The analysis of morphology, particle size distribution, powder flowability and thermal conductivity was performed for PLA and PLLA microspheres conditioned at 40°C, whereas in order to optimise crystallinity degree, processing window and residual solvent content XRD, DSC and TGA analysis were extended to microspheres annealed at higher temperatures (70°C, 90°C and 120°C).

# 3.1. Scanning Electron Microscopy

The morphology of prepared powders is presented in Figure 1. Both PLA and PLLA have a spherical shape with the more homogeneous surface which is considered as a most favourable powder's particle shape due to its high flowability and high powder packing density [8]. Besides spherical particles in each powder a small amount of residues in form of flakes from the preparation process can be observed. SEM images confirms that powders are suitable for LS process.



Figure 1. Microscopic images of powder particles of PLA (A) and PLLA (B).

# 3.2. Particle Size Distribution

Measured by dry laser diffraction spectroscopy powder's properties are shown in Table 1. Reported Particle Size Distribution (PSD) used in commercial LS systems should be up to 200  $\mu$ m, which in practice is commonly in rage of 20  $\mu$ m to 80  $\mu$ m [32]. The lower limit of particle size is commonly presented as 10  $\mu$ m due to its negative influence in bulk flow at high temperatures [33]. Cumulative particle size distribution is shown in Figure 2, both material distribution can be characterized as narrow and symmetrical and unimodal.



Figure 2. Cumulative distribution and distribution density of PLA and PLLA.

**Table 1**. First avalanche angle (AA), flowing angle ( $\alpha_{f}$ ,) cohesive index ( $\sigma_{f}$ ) and particle size distribution of prepared PLA and PLLA powders.

Sample	AA [°]	<b>α</b> f [°]	σf[a.u.]	d₅0 [µm]	(d90-d10)/d50	<10 µm [%]
		at 30 rpm (†)	)	-	[u.u.]	
PLA_40	33.9	55.9	24.8	36.45	1.37	3.78
PLLA_40	30.0	51.0	28.0	36.01	1.37	3.03

# 3.3. Powder flowability

The basic flowability parameters are shown in Table 1, additionally dynamic flowability represented by cohesion index curves as a function of rotating speed are presented in Figure 3. The avalanche angle, which is the first angle that triggers the pouring of powder, provides information that in the quasi-static conditions PLLA has a slightly better flowability. However, when looking at the cohesive index, especially for lower velocities (up to 20 rpm) one can see that the dynamic flowability properties of PLLA are better which is confirmed by the smaller cohesive index. These differences may be caused by the lower percentage of particles below 10 µm.



**Figure 3.** Cohesive index curves recorded as a function of the increasing (†) and decreasing (↓) rotation speed for PLA and PLLA powders.

#### 3.4. Residual solvent content and thermal stability of microspheres

Based on TGA curves of PLA and PLLA microspheres presented in Figure S1 (in the Supplementary Materials) residual solvents content as a mass loss in the range up to 200°C and thermal stability corresponding to 5wt.% of mass loss (T-5%) were determined. The data collected in Table 2 demonstrates that with increasing annealing temperature of microspheres the content of residual solvents (water and methylene chloride) in microspheres of PLA and PLLA decreases. Annealing at higher temperatures leads to faster rates of solvent removal from the microspheres. Residual solvents content decreases from 0.49wt.% to 0.02wt.% for PLA and from 0.25wt.% to 0.02wt.% for PLA microspheres with the increase of annealing temperature. The residual solvent content in the microspheres of PLA is significantly lower after drying process at 70°C than at 40°C, whereas the microspheres of PLA require a higher drying temperature. Residual solvent and adsorbed/absorbed water content must be removed to minimize agglomeration of microspheres and emission of toxic substances during laser sintering process [8]. Moreover dichloromethane belong to class 1 of residual solvents in pharmaceuticals according to classification of residual solvents by risk assessment. If their use in order to produce a medicinal product is unavoidable, their levels should be restricted because of unacceptable toxicities [34]. Due to these two aspects, such as safety of LS processing and biomedical applications of "printed" details, the content of residual CH<sub>2</sub>Cl<sub>2</sub> should be qualified as a standard control parameter and must be kept to the lowest possible level.

In both of type microspheres thermal stability rise slightly with increasing conditioning temperature reaching T-5% higher about 3°C for PLA and 4°C for PLLA microspheres annealed at 120oC.

Commlo	Mass loss at 30÷200°C	T-5%		
Sample	[wt.%]	[°C]		
PLA_40	0.49	332		
PLA_70	0.06	335		
PLA_90	0.05	337		
PLA_120	0.02	338		
PLLA_40	0.25	329		
PLLA_70	0.24	329		
PLLA_90	0.04	329		
PLLA_120	0.02	333		

Table 2. Mass loss at 200°C and temperature corresponding to 5wt% mass loss of PLA and PLLA microspheres.

# 3.5. Thermal properties of microspheres

DSC analysis was performed in order to characterize thermal properties of microspheres as prepared and to determine the influence of conditioning temperature. The main purpose was to determine temperature range of processing window and verification of possibility of tuning SW by conditioning of the microspheres.

The first heating and cooling DSC curves of PLA microspheres are presented in Figure 4A and the evaluated thermal properties are collected in Table 3. Based on comparison of the first heating DSC curves of PLA microspheres can be stated that curing temperature influence on thermal properties of PLA, the strongest differences concern cold crystallization behaviour and crystallinity degree. Microspheres annealed at 40°C and 70°C during heating crystallize above glass transition temperature. The enthalpy of cold crystallization ( $\Delta$ H<sub>cc</sub>) of PLA\_40 is higher than PLA\_70, indicating on higher content of crystalline phase of PLA\_70 microspheres than PLA\_40. Microspheres PLA annealed at 90°C and 120°C reached maximum degree of crystallinity during conditioning, as it is confirmed by lack of exotherm of cold crystallization during heating with the rate of 10°C/min. At higher temperatures endotherm of melting is visible on the DSC curves of PLA microspheres. The melting endotherms of PLA\_40, PLA\_70, PLA\_90 exhibit two maxima, denoted as Tm<sup>1</sup> for lower temperature maximum and Tm<sup>2</sup> for main melting maximum. Presence of small entodermic maximum on the leading edge of maim melting peak indicates on presence of mixture of  $\alpha'$  and  $\alpha$  crystals. Moreover, there is a clearly visible trend of Tm<sup>1</sup> decrease with decreasing of conditioning temperature due to lower stability of crystals that were formed at higher supercooling [35].



**Figure 4**. The first heating and cooling DSC curves of PLA (A) and PLLA (B) microspheres annealed at 40°C, 70°C, 90°C and 120°C. For simplicity only one cooling curves recorded after complete melting and isotropisation of PLA and PLLA microspheres are presented on the A and B graphs respectively. The cooling curves of series of PLA as well as PLLA microspheres are similar within series independently on annealing temperature (Figure S2 in the Supplementary Materials).

One of the key purposes of DSC measurements was determination of temperature range of processing window. Typically, sintering window for semicrystalline polymers is defined as temperature band between onset of melting ( $T_m^{onset}$ ) and onset of melt crystallization ( $T_c^{onset}$ ). Presence of cold crystallization has a significant impact on the temperature range of the processing window. In case of PLA\_40 broad range of cold crystallization, starting above enthalpy relaxation effect overlapping on glass transition and continuing up to melting, indicate on lack of processing window and should exclude these microspheres from any thermal processing. Similarly, microspheres PLA\_70, although the cold crystallization starts at higher temperature, they are also not suitable for laser sintering. Based on the DSC curves of PLA\_90 and PLA\_ 120 can be concluded that due to crystallization that occurred during conditioning at 90°C and 120°C PLA microspheres poses processing window. The PLA microspheres under cooling do not crystallize from melt, as it stems from the cooling DSC curve (Figure 4A), thus the lower limit of sintering window can be defined as the onset of glass transition ( $T_g^{onset}$ ). The  $T_g^{onset}$  designated form cooling DSC curve is lower than endset of glass transition ( $T_g^{endet}$ )

from heating scan (65°C and 67°C for PLA\_90 and PLA\_120, respectively). The  $T_g^{endset}$  is defined as the extrapolated endset temperature of glass transition and indicates the end temperature of the glass transition, where the heat capacity dependence becomes linear. Because of processing temperature should start above glass transition, we emphasize the necessity to use  $T_g^{enset}$  from heating DSC curve as lower limit of SW as more correct than  $T_g^{onset}$  from cooling. Therefore, sintering window set as temperature range between  $T_g^{enset}$  and onset of melting ( $T_m^{onset}$ ) for PLA\_90 and PLA\_120 is within the range of 65°C÷146°C and 67°C÷144°C respectively.

The first heating DSC curves of PLLA microspheres conditioned at different temperatures are presented in Figure 4B. Comparing to PLA microspheres, they have about 26°C higher melting temperature, higher melting enthalpy and degree of crystallinity, due to differences in enantiomeric isomers, L-lactide and D-lactide, content. PLLA microspheres crystallize from the melt in contrast to PLA microspheres as it is visible on the cooling DSC curve.

In contradiction to PLA microspheres, conditioning temperature doesn't influence significantly on PLLA microspheres thermal properties (Fig. 2B). Weak exothermic effect of cold crystallization is visible only on the DSC curves of PLLA\_40 and PLLA\_70 ( $\Delta H_{cc} = 0.7$  J/g and 1.8 J/g for PLLA\_40 and PLLA\_70, respectively). The temperature range of cold crystallization is narrower than for PLA\_40 and PLA\_70, and thus for PLLA microspheres annealed at 40 and 70°C SW is available in contradiction to respective PLA microspheres.

Processing window according to typically used definitions (SW<sup>onset</sup>), set as between onset of melt crystallization ( $T_c^{onset}$ ) and onset of melting, is within the range 116°C÷174°C for PLLA\_40 and differ maximally about 1°C due to  $T_m^{onset}$  being in range of 174÷175°C in PLLA microsphere series.

High temperature limit of sintering window is typically defined as onset of melting. Onset of melting in differential scanning calorimetry is evaluated as the intersection point of the extrapolated baseline prior to the melting transition and the inflectional tangent [36,37]. The additional transition point is sometimes identified, such as temperature of first detectable deviation from the interpolated baseline, as we further denoted as  $T_m^{beginning}$  for melting. We had proposed to use  $T_m^{beginning}$ , as temperature of beginning of melting endotherm, in place of onset [26]. The melting of semicrystalline polymers is a very broad process and onset temperature doesn't take into account the shape of leading edge of polymer melting peak. Thus, we had proposed to designate beginning of melting endotherm ( $T_m^{beginning}$ ) as a high temperature limit of sintering window (SW<sup>beginning</sup>). The high temperature limit of sintering window set as  $T_m^{beginning}$ allow for consideration existence of broad leading edge of melting peak such in case of PLLA and PLA microspheres and cuts off any thermal events taking place above  $T_m^{beginning}$  from sintering window. In case of polylactide, at the broad temperature range of melting, reorganization of  $\alpha'$  to  $\alpha$  crystal forms [38] can occur, such in case of PLA\_90 microspheres. Determination of the processing window as band between  $T_m^{beginning}$  and  $T_c^{onset}$  ensure elimination of the changes in the degree of crystallinity and in the crystalline form of presintered polylactide powder.

SWbeginning is narrower than SWonset and ends at 140°C, 143°C, 144°C and 146.0°C for PLLA\_40, PLLA\_70, PLLA\_90 and PLLA\_120, respectively. For PLA\_90 and PLA\_120 high temperature limit of SW<sup>beginning</sup> is at 118°C and 117°C, respectively.

We also verified the first and second derivatives of the heat flow signal for identifying the correct onset of melting transition, as suggested by S. Beretta et al. [9]. The first and second derivatives was automatically evaluated using "2nd Derivative" tool in the STARe software, and are presented in Figure 5 and Figure S3 (in the Supplementary Materials). Onset of melting taken as maximum of the first and second derivatives, 176°C and 175°C, respectively, does not exclude broad leading edge of endothermic peak of PLLA\_90 from sintering window (Figure 4). The importance of the correct determination of the upper limit of the sintering window as the beginning of endotherm can be seen on the example of PLA\_90 microspheres, as there are two overlapping effects,  $\alpha'$ - $\alpha$  reorganization with maximum at T<sub>m</sub><sup>1</sup> and melting with a maximum T<sub>m</sub><sup>2</sup> (Figure 4A, Figure S3 in the Supplementary Materials).

The thermal properties of polylactide microspheres, i.e. SW, were evaluated from DSC curves recorded at 10°C/min heating and cooling rates, that never exist in LS process. Moreover, the polymer structure depends on heating and cooling conditioning, thus from practical perspective the estimated SW should serve as the powder bed temperature. We plan to verify the estimated SW experimentally using a new two-beam laser sintering method. This research will be presented in our next publication.



Figure 5. The first heating DSC curve of PLLA\_90 combined with the 1<sup>st</sup> and 2<sup>nd</sup> derivative of the heat flow.

<b>Table 3.</b> Thermal parameters of PLA and PLLA microspheres annealed at 40°C, 70°C, 90	)°C and 120°C.
--	----------------

Sample	Tg	Tcc <sup>onset</sup>	Tcc	$\Delta H_{cc}$	Tm <sup>beginning</sup>	Tm <sup>onset</sup>	Tm	$\Delta H_{\text{m}}$	$X_c (\Delta H_m - \Delta H_{cc}) / \Delta H_m^{100\%}$
	[°C]	[°C]	[°C]	[J/g]	[°C]	[°C]	[°C]	[J/g]	[%]
PLA_40	63	104	115	16.9	133	144	152	41.7	23.2
PLA_70	61	106	110	10.5	131	143	152	42.3	29.7
PLA_90	64	-	-	-	118	146	152	44.4	41.1
PLA_120	63	-	-	-	117	144	150	44.8	31.3
PLLA_40	61	88	94	0.7	140	174	178	65.5	45.3
PLLA_70	68	85	92	1.8	143	174	178	63.9	43.5
PLLA_90	64	-	-	-	144	174	178	53.6	37.5
PLLA_120	73	-	-	-	146	175	179	54.4	38.0

The influence of conditioning temperature on processing window steam from differences in crystallinity level. Unfortunately, estimation of crystallinity degree (X<sub>c</sub>) from DSC results is sometimes not entirely correct. During recording of the first heating DSC curve starting material is changing, cold crystallization takes place followed by reorganization of  $\alpha'$  into the order  $\alpha$  phase. Moreover, the melting enthalpy of 100% crystalline  $\alpha$ -crystals PLLA and  $\alpha'$ -crystals PLLA are different. This different values of  $\Delta H_m^{100\%}$  for the  $\alpha$ - and  $\alpha'$ -crystals should be taken into account for the determination of the crystalline content from the experimental melting enthalpies. The estimated X<sub>c</sub> values depends on the  $\Delta H_m^{100\%}$ (107 J/g and 143 J/g) assumed for the calculation. We have made an estimation of X<sub>c</sub> from DSC results, more correct X<sub>c</sub> values, independent on heat of fusion, are determined based on WAXD results and are presented further.

Crystallinity degree (X<sub>c</sub>) for PLA\_40, PLA\_70 and PLA\_90 was estimated with taking to account the enthalpy of melting of  $\alpha$ -form 100% crystalline polylactide (107 J/g) and the enthalpy of melting of  $\alpha$ -form 100% crystalline polylactide (143 J/g) for the others microspheres [31]. Presence of  $\alpha$ -form crystals in case of all PLLA microspheres and PLA\_120 is indicated by lack of exothermic effect of  $\alpha'$ - $\alpha$  transition on the first heating DSC curves [38]. For PLA\_40, PLA\_70, based on broad range of cold crystallization and presence of Tm<sup>1</sup> peak, was assumed that  $\alpha'$ -form is dominant. The PLA\_90 microspheres were intentionally annealed at 90°C in order to crystallize in  $\alpha'$ -form [39]. Since the  $\alpha'$  and  $\alpha$  phases precise contents in PLA\_40, PLA\_70 and PLA\_90 are unknown, for simplification of X<sub>c</sub> calculations, the enthalpy of  $\alpha'$ -form 100% crystalline was employed (Table 3). In the series of PLA microspheres with increasing annealing temperature X<sub>c</sub> increases from 23.1% to 33.5%. Whereas in PLLA microspheres crystallinity level is higher but not as strong dependent on conditioning temperature.

# 3.6. Thermal conductivity of microspheres

Due to layer-by-layer manner of LS process it is crucial not only how the polymer absorbs the laser radiation yet how to applied heat is transmitted in all spatial directions [8]. Schmid et al. report that stable layer connection is achievable only if the thermal conductivity of processed polymer is sufficient to transmit the heat in depth of at least one previous layer. Jiaming Bai et al. suggest that polyamide 12 with addition of carbon nanotubes (PA12-CNT) allowed to produce wider and deeper laser penetration then powder without additives [40]. Better laser penetration is connected with greater thermal conductivity of PA12-CNT.

Thermal conductivity ( $\kappa$ ) of microsphere powders was determined based on DSC measurements according to Camirand's method [41]. The measurement of  $\kappa$  is made at discrete temperatures that correspond to the melting points of selected pure metal references. As a metal reference indium was used and thermal conductivity of microspheres was obtained from the slope of the low temperature side of the melting peak of indium bead placed on top of microspheres filling the 40 µL aluminium pan. The slope of the low temperature side of indium melting peak depends on thermal resistance (R) of measured powder. R is given by reciprocal of the slope (S).  $\kappa$  was determined from R using equation (4):

$$\kappa = \frac{\varepsilon}{\pi R} \left( \frac{1}{D_m} - \frac{1}{D_p} \right),\tag{4}$$

where  $D_m$  is the diameter of the reference metal bead (1.00 mm) and  $D_P$  is the diameter of the pan. The value of the constant  $\epsilon$ , for a cylindrical aluminium pan with 5.80 mm of diameter and 1.44 mm of height, is 1 [42]. For the thermal conductivity of PLA and PLLA microspheres estimation, the DSC curves were measured with nitrogen flow, because the commercially available SLS printers enable processing in inert atmosphere. Measured DSC curves of indium beades on top of PLA\_40 and PLLA\_40 microspheres are presented in Figure 6 and the estimated thermal conductivity and resistivity values are collected in Table 4.



Figure 6. Melting endotherms of indium beads placed on PLA\_40 and PLLA\_40 microspheres.

Table 4. Thermal resistivity and conductivity of microspheres.						
Sample	S [W/K]	R [K/W]	к [W/mK]			
PLA_40	4.54.10-4	2.20.103	0.073			
PLLA_40	4.00.10-4	2.50.103	0.064			

The thermal conductivity is 0.073 W/mK for PLA microspheres and 0.064 W/mK for PLLA microspheres. It is worth noting that, in contrast with their bulk counterparts, microspheres/powders have very similar conductivities and that these are lower than in bulk (0.084 for PLA and 0.104 for PLLA – Figure S4 in the Supplementary Materials). According to S.M.Lebedev et al. [43] the thermal conductivity of neat PLA is 0.193 W/mK. Lu Bai et al. [44] described impact of the

crystallinity of semicrystalline polymers on the thermal conductivity of polymer material and claimed that thermal conductivity of PLLA increases with increasing crystallinity but not significantly. Thermal conductivity for PLLA with the crystallinity of 56% is 0.196 W/mK and 0.171 W/mK for amorphous PLLA.

The thermal conductivity of microspheres differs significantly from the solid materials. The lower thermal conductivity of microspheres depends on the spherical shape of the microspheres. Between particles there are only small contact areas and air in the pores acts as thermal isolator. So far, the semicrystalline thermoplastics, such as polyamide 12 (PA12) was commonly used in manufacturing technology related with laser sintering [45]. Alessandro Franco et al. [46] characterized the thermal conductivity of industrial powder of polyamide 12, which is equal 0.13 W/mK. Mengqi Yuan et al. [47] also investigated that the range of thermal conductivity was 0.09 to 0.12 W/mK for polyamide 12 powder depending of the test temperature, whereas their counterpart in bulk laser sintered polyamide 12 has a thermal conductivity of 0.22 to 0.33 W/mK from 40°C to 170°C, so approximately three times more than the loose powder. The thermal conductivity is a key parameter in the LS of polymer powders. Due to thermal properties of PA12 and our polylactide microspheres, which are appropriate for thermoplastics used for rapid prototyping the polyamide 12 powders or polylactide microspheres are suitable materials for laser sintering processes.

## 3.7. WAXD analysis



**Figure 7.** Diffraction curves of the PLA (A) and PLLA (B) microspheres conditioned at temp. of 40, 70, 90 and 120°C. A'), B') exemplary deconvolution of curves, respectively of the PLA\_90 and PLLA\_40. The diffraction peaks marked with asterisks in the graphs A 'and B' are characteristic only for the  $\alpha$  phase. The others can be connected with both  $\alpha$  and  $\alpha$  '.

WAXD measurements were performed to assess the crystallinity of PLLA microspheres annealed at different temperatures and PLA microspheres that exhibit SW (PLA\_90 and PLA\_120). Figure 7 shows a summary of the WAXD diffractograms of the PLA (A) and PLLA (B) microspheres. The course of the curves is characteristic of polylactide [26,31].

A detailed deconvolution of the curves into diffraction peaks and diffusion maxima was made. When carrying out this procedure, the literature reports were followed [26,48,49]. Figure 7 A', B' shows two examples for PLLA and PLA powders annealed at 40°C (a complete breakdown of deconvolution is provided in the Supplementary Materials in

Figure S5). The diffraction maxima on the graph denoted with asterisks (\*) correspond selectively to the crystalline pseudo-orthorhombic, helical  $\alpha$  phase of this polymer, while the others are characteristic of both the  $\alpha$  and the disordered  $\alpha$ ' phase. The expressiveness of these  $\alpha$  -phase characteristic peaks indicates a significant share of the  $\alpha$  phase in the crystal structure of polymers (for both PLLA and PLA) in relation to the disordered  $\alpha$ ' phase [31].

The X-ray diffraction study also allowed to determine the degrees of crystallinity (X<sub>c</sub>) of individual samples. The results of the calculations made are placed above the individual curves and they are consistent with DSC results. The conducted research shows that an increase in the conditioning temperature causes a slight increase in the polymer crystallinity degree in the case of PLLA. The situation is different for PLA, where the microspheres are initially almost amorphous and clearly crystallize with increasing annealing temperature.

WAXD studies also confirm the results obtained on DSC, indicating the presence of the  $\alpha'$  phase in the PLLA\_70 microspheres. It manifests itself in the shift of the maxima of the main crystalline reflexes towards lower angular positions (by about 0.1°) in relation to the PLA\_120 sample.

From comparison of the values of X<sub>c</sub> calculated from DSC and WAXD results some differences can be noticed. The estimation of crystallinity based on DSC curve does not correctly reflect the initial crystallinity of the polylactide microspheres, and depends on the assumed heat of fusion as it has already been emphasized. The X<sub>c</sub> values from WAXD values are in the range of X<sub>c</sub> limit values from DSC calculated for  $\Delta$ H<sub>m</sub><sup>100%</sup> taken as 107 J/g and 143 J/g. Despite the differences in the X<sub>c</sub> values from DSC and WAXS, both techniques show the same trend of the dependence of the crystalline phase content in PLA microspheres on the conditioning temperature, higher crystallinity of PLLA microspheres, and a slight influence of conditioning temperature in the PLLA microspheres.

#### 4. Conclusion

The aim of the presented research was determination of the influence of annealing temperature on thermal properties and crystalline structure of microspheres made of polylactides of different grades. Microspheres were obtained by conventional emulsion-solvent evaporation technique from medical grade poly(L-lactide) and polylactide with 4wt.% of D-lactide content, chosen because of different crystallization behaviour. The microspheres were annealed at four temperatures, below glass transition (at 40°C), above  $T_g$  but below onset of cold crystallization (at 70°C), and at two temperatures from the range of cold crystallization corresponding to crystallization of a' and a form of poly(L-lactide) (at 90°C and 120°C). The microspheres are dedicated for LS processing, thus their sinterability was verified based on sintering window, residual solvent content, morphology, particle size distribution and powder flowability.

In term of powder's morphology along with its particle size distribution both powders meet the requirements of LS process. Worth noticing is a particle shape of PLA and PLLA which is close to a sphere, which is considered to be most desirable for LS technology. The main distributions are narrow and symmetrical, and in case of PLA which has a bimodal one it can be corrected by sieving to eliminate particles above 100 µm. Dynamic flowability of both powders show small hysteresis. Good flowability properties can be archived for higher rotating speeds which translates to higher recoating speeds. DSC analysis reveals that conditioning temperature influence on degree of crystallinity and crystal structure of polylactide microspheres in different extent depending on polylactide grade. In case of microspheres made of PLA (stereocopolymer with 4wt.% of D-lactide) degree of crystallinity can be precisely controlled due to lower crystallization ability of PLA comparing to PLLA. These results were also confirmed by wide angle X-ray diffraction analysis. Presence of sintering window of PLA microspheres depends on crystallinity level. The PLA microspheres annealed at 40°C and 70°C exhibit cold crystallization under heating and thus they do not have sintering window available. But thermal treatments at higher temperatures makes unsinterable PLA microspheres sinterable due to presence of sintering window.

Annealing step after manufacturing of the microspheres turned out to be an essential stage also due to necessity of removing of residual solvents, as it was confirmed by thermogravimetry. Due to safety of LS processing and future biomedical applications of "printed" details, the content of residual CH<sub>2</sub>Cl<sub>2</sub> should be kept to the lowest possible level.

In term of sintering window of polylactides we propose precise determination of processing window as a temperature range free of any thermal events. Polylactide is a semicrystalline polymer that exhibit cold crystallization and polymorphism. Any PLLA transformations such as cold crystallization and reorganization of crystal structure should be excluded from the processing window, because  $\alpha$  and  $\alpha'$  crystal forms of PLLA have different degradation kinetics and mechanical properties. Moreover, the powder in the printer bed should not change its properties prior to the sintering process. This is important because the temperature gradient is already present in the standard SLS printing system.

Therefore, we postulate the need for an individual approach in determining the processing window for polylactide powders. As the upper limit of the processing window, we propose the beginning of melting as the temperature of first detectable deviation from the interpolated baseline of melting peak. Such upper limit allows to exclude any thermal and structural changes of polylactide from the process window and designated temperature range ensure stable sintering window. The estimated SW ranges according to proposed rules are experimentally verified and will be presented in our next publication.

#### Acknowledgments

The research was supported by project Opus "Laser modification of bioresorbable polymeric materials in thermic processes of additive manufacturing" financed by National Science Centre (UMO-2017/27/B/ST8/01780).

#### **Supplementary Materials**

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- Schmid, M.; Amado, A.; Wegener, K. Polymer powders for selective laser sintering (SLS). AIP Conf. Proc. 2015, 1664, doi:10.1063/1.4918516.
- Schmid, M.; Wegener, K. Additive Manufacturing: Polymers applicable for laser sintering (LS). *Procedia Eng.* 2016, 149, 457–464, doi:10.1016/j.proeng.2016.06.692.
- 3. Sagar, M.B.; Elangovan, K. Consolidation & factors influencing sintering process in polymer powder based additive manufacturing. *IOP Conf. Ser. Mater. Sci. Eng.* 2017, 225, doi:10.1088/1757-899X/225/1/012075.
- 4. Yan, C.; Shi, Y.; Yang, J.; Liu, J. Investigation into the selective laser sintering of styrene-acrylonitrile copolymer and postprocessing. *Int. J. Adv. Manuf. Technol.* **2010**, *51*, 973–982, doi:10.1007/s00170-010-2681-8.
- 5. Wang, C.Y.; Dong, Q.; Shen, X.X. Research on warpage of polystyrene in selective laser sintering. *Appl. Mech. Mater.* **2011**, *43*, 578–582, doi:10.4028/www.scientific.net/AMM.43.578.
- XiaoHui, S.; Wei, L.; PingHui, S.; QingYong, S.; QingSong, W.; YuSheng, S.; Kai, L.; WenGuang, L. Selective laser sintering of aliphatic-polycarbonate/hydroxyapatite composite scaffolds for medical applications. *Int. J. Adv. Manuf. Technol.* 2015, *81*, 15–25, doi:10.1007/s00170-015-7135-x.
- Schmid, M.; Amado, A.; Wegener, K. Materials perspective of polymers for additive manufacturing with selective laser sintering. J. Mater. Res. 2014, 29, 1824–1832, doi:10.1557/jmr.2014.138.
- 8. Schmid, M. Laser Sintering with Plastics; Carl Hanser Verlag GmbH & Co. KG, 2018; ISBN 9781569906835.
- 9. Berretta, S.; Evans, K.E.; Ghita, O.R. Predicting processing parameters in high temperature laser sintering (HT-LS) from powder properties. *Mater. Des.* **2016**, *105*, 301–314, doi:10.1016/j.matdes.2016.04.097.
- 10. Szymczyk-Ziółkowska, P.; Łabowska, M.B.; Detyna, J.; Michalak, I.; Gruber, P. A review of fabrication polymer scaffolds for biomedical applications using additive manufacturing techniques. *Biocybern. Biomed. Eng.* **2020**, *40*, doi:10.1016/j.bbe.2020.01.015.
- 11. Tan, K.H.; Chua, C.K.; Leong, K.F.; Cheah, C.M.; Gui, W.S.; Tan, W.S.; Wiria, F.E. Selective laser sintering of biocompatible polymers for applications in tissue engineering. *Biomed. Mater. Eng.* **2005**, *15*, 113–124.
- Tan, K.H.; Chua, C.K.; Leong, K.F.; Naing, M.W.; Cheah, C.M. Fabrication and characterization of three-dimensional poly(ether-ether-ketone)/-hydroxyapatite biocomposite scaffolds using laser sintering. *Proc. Inst. Mech. Eng. Part H J. Eng. Med.* 2005, 219, 183–194, doi:10.1243/095441105X9345.
- 13. Leong, K.F.; Chua, C.K.; Gui, W.S.; Verani Building porous biopolymeric microstructures for controlled drug delivery devices using selective laser sintering. *Int. J. Adv. Manuf. Technol.* **2006**, *31*, 483–489, doi:10.1007/s00170-005-0217-4.
- Yeong, W.Y.; Sudarmadji, N.; Yu, H.Y.; Chua, C.K.; Leong, K.F.; Venkatraman, S.S.; Boey, Y.C.F.; Tan, L.P. Porous polycaprolactone scaffold for cardiac tissue engineering fabricated by selective laser sintering. *Acta Biomater.* 2010, *6*, 2028–2034, doi:10.1016/j.actbio.2009.12.033.

- 15. Chua, C.K.; Leong, K.F.; Tan, K.H.; Wiria, F.E.; Cheah, C.M. Development of tissue scaffolds using selective laser sintering of polyvinyl alcohol/hydroxyapatite biocomposite for craniofacial and joint defects. *J. Mater. Sci. Mater. Med.* **2004**, *15*, 1113–1121, doi:10.1023/B:JMSM.0000046393.81449.a5.
- 16. Williams, J.M.; Adewunmi, A.; Schek, R.; Flanagan, C.; Krebsbach, P.H.; Feinberg, S.E. Bone tissue engineering using polycaprolactone scaffolds fabricated via selective laser sintering. *Biomaterials* **2007**, *2*, 4817–4827.
- 17. Bai, J.; Goodridge, R.D.; Hague, R.J.M.; Okamoto, M. Processing and characterization of a polylactic acid/nanoclay composite for laser sintering. *Polym. Compos.* **2017**, *38*, 2570–2576, doi:10.1002/pc.23848.
- Zhou, W.Y.; Lee, S.H.; Wang, M.; Cheung, W.L.; Ip, W.Y. Selective laser sintering of porous tissue engineering scaffolds from poly(L-lactide)/carbonated hydroxyapatite nanocomposite microspheres. J. Mater. Sci. Mater. Med. 2008, 19, 2535– 2540, doi:10.1007/s10856-007-3089-3.
- Tian, X.; Peng, G.; Yan, M.; He, S.; Yao, R. Process prediction of selective laser sintering based on heat transfer analysis for polyamide composite powders. *Int. J. Heat Mass Transf.* 2018, *120*, 379–386, doi:10.1016/j.ijheatmasstransfer.2017.12.045.
- Nelson, J.A.; Rennie, A.E.W.; Abram, T.N.; Bennett, G.R.; Adiele, A.C.; Tripp, M.; Wood, M.; Galloway, G. Effect of process conditions on temperature distribution in the powder bed during laser sintering of Polyamide-12. *J. Therm. Eng.* 2015, *1*, 159–165, doi:10.18186/jte.13739.
- Van den Eynde, M.; Strobbe, D.; Verkinderen, O.; Verbelen, L.; Goderis, B.; Kruth, J.P.; Van Puyvelde, P. Effect of thermal treatments on the laser sinterability of cryogenically milled polybutene-1. *Mater. Des.* 2018, 153, 15–23, doi:10.1016/j.matdes.2018.04.072.
- 22. Opaprakasit, P.; Opaprakasit, M. Thermal properties and crystallization behaviors of polylactide and its enantiomeric blends. *Macromol. Symp.* **2008**, *264*, 113–120, doi:10.1002/masy.200850418.
- Tábi, T.; Hajba, S.; Kovács, J.G. Effect of crystalline forms (α' and α) of poly(lactic acid) on its mechanical, thermomechanical, heat deflection temperature and creep properties. *Eur. Polym. J.* 2016, *82*, 232–243, doi:10.1016/j.eurpolymj.2016.07.024.
- 24. Cocca, M.; Lorenzo, M.L. Di; Malinconico, M.; Frezza, V. Influence of crystal polymorphism on mechanical and barrier properties of poly(l-lactic acid). *Eur. Polym. J.* **2011**, *47*, 1073–1080, doi:10.1016/j.eurpolymj.2011.02.009.
- Zhang, N.; Yu, X.; Duan, J.; Yang, J. hui; Huang, T.; Qi, X. dong; Wang, Y. Comparison study of hydrolytic degradation behaviors between α'- and α-poly(L-lactide). *Polym. Degrad. Stab.* 2018, 148, 1–9, doi:10.1016/j.polymdegradstab.2017.12.014.
- 26. Krokos, A.; Gazińska, M.; Kryszak, B.; Dzienny, P.; Stępak, B.; Olejarczyk, M.; Gruber, P.; Kwiatkowski, R.; Bondyra, A.; Antończak, A. Comparison of thermal, structural and morphological properties of poly (L-lactide) and poly (L-lactide)/ hydroxyapatite microspheres for laser sintering processes. *Polimery* 2020, 65, 505–512.
- 27. Amado, A.; Schmid, M.; Levy, G.; Wegener, K. Advances in SLS Powder Characterization. In Proceedings of the International Conference on Solid Freeform Fabrication 2011 (SFF '11); Austin, TX, USA, 2011; Vol. 1, pp. 438–452.
- 28. Tay, J.Y.S.; Liew, C.V.; Heng, P.W.S. Powder Flow Testing: Judicious Choice of Test Methods. *AAPS PharmSciTech* 2017, *18*, 1843–1854, doi:10.1208/s12249-016-0655-3.
- 29. Lumay, G.; Boschini, F.; Traina, K.; Bontempi, S.; Remy, J.C.; Cloots, R.; Vandewalle, N. Measuring the flowing properties of powders and grains. *Powder Technol.* **2012**, *224*, 19–27, doi:10.1016/j.powtec.2012.02.015.
- 30. Lumay, G.; Tripathi, N.M.; Francqui, F. How to gain a full understanding of powder flow properties, and the benefits of doing so. *ONdrugDelivery* **2019**, *2019*, 42–47.
- 31. Righetti, M.C.; Gazzano, M.; Di Lorenzo, M.L.; Androsch, R. Enthalpy of melting of α'- and α-crystals of poly(L-lactic acid). *Eur. Polym. J.* **2015**, *70*, 215–220, doi:10.1016/j.eurpolymj.2015.07.024.
- 32. Mielicki, C.; Gronhoff, B.; Wortberg, J. Effects of laser sintering processing time and temperature on changes in polyamide 12 powder particle size, shape and distribution. **2014**, *728*, 728–731, doi:10.1063/1.4873880.
- Gregor, A.; Filová, E.; Novák, M.; Kronek, J.; Chlup, H.; Buzgo, M.; Blahnová, V.; Lukášová, V.; Bartoš, M.; Nečas, A.; et al. Designing of PLA scaffolds for bone tissue replacement fabricated by ordinary commercial 3D printer. *J. Biol. Eng.* 2017, *11*, 1–22, doi:10.1186/s13036-017-0074-3.
- 34. Witschi, C.; Doelker, E. Residual solvents in pharmaceutical products: Acceptable limits, influences on physicochemical

properties, analytical methods and documented values. Eur. J. Pharm. Biopharm. 1997, 43, 215-242.

- Androsch, R.; Di Lorenzo, M.L. Effect of molar mass on the α'/α-transition in poly (L-lactic acid). *Polymer (Guildf)*. 2017, 114, 144–148, doi:10.1016/j.polymer.2017.02.063.
- 36. ASTM International Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning. *ASTM Stand.* **2012**, *D4318-08*, 1–7, doi:10.1520/D3418-15.2.
- 37. Schawe J., Evaluation and interpretation of peak temperatures of DSC curves. Part 1: Basic principles, Mettler Toledo Therm. Anal. *UserCom.* 23 (2006) 6–9.
- Androsch, R.; Schick, C.; Laura, M.; Lorenzo, D. Melting of Conformationally Disordered Crystals (α'-Phase) of Poly (L-lactic acid). *Macromol. Chem. Phys.* 2014, 215, 1134–1139.
- Zhang, J.; Tashiro, K.; Tsuji, H.; Domb, A.J. Disorder-to-order phase transition and multiple melting behavior of poly(Llactide) investigated by simultaneous measurements of WAXD and DSC. *Macromolecules* 2008, 41, 1352–1357, doi:10.1021/ma0706071.
- 40. Bai, J.; Goodridge, R.D.; Yuan, S.; Zhou, K.; Chua, C.K.; Wei, J. Thermal influence of CNT on the polyamide 12 nanocomposite for selective laser sintering. *Molecules* **2015**, *20*, 19041–19050, doi:10.3390/molecules201019041.
- 41. Camirand, C.P. Measurement of thermal conductivity by differential scanning calorimetry. *Thermochim. Acta* **2004**, *417*, 1–4, doi:https://doi.org/10.1016/j.tca.2003.12.023.
- 42. Pujula, M.; Sánchez-Rodríguez, D.; Lopez-Olmedo, J.P.; Farjas, J.; Roura, P. Measuring thermal conductivity of powders with differential scanning calorimetry: A simplified method. *J. Therm. Anal. Calorim.* **2016**, *125*, 571–577, doi:10.1007/s10973-016-5274-4.
- 43. Lebedev, S.M.; Gefle, O.S.; Amitov, E.T.; Berchuk, D.Y.; Zhuravlev, D. V. Poly(lactic acid)-based polymer composites with high electric and thermal conductivity and their characterization. *Polym. Test.* **2017**, *58*, 241–248, doi:10.1016/j.polymertesting.2016.12.033.
- 44. Bai, L.; Zhao, X.; Bao, R.Y.; Liu, Z.Y.; Yang, M.B.; Yang, W. Effect of temperature, crystallinity and molecular chain orientation on the thermal conductivity of polymers: a case study of PLLA. *J. Mater. Sci.* **2018**, *53*, 10543–10553, doi:10.1007/s10853-018-2306-4.
- 45. Laumer, T.; Wudy, K.; Drexler, M.; Amend, P.; Roth, S.; Drummer, D.; Schmidt, M. Fundamental investigation of laser beam melting of polymers for additive manufacture. *J. Laser Appl.* **2014**, *26*, 042003, doi:10.2351/1.4892848.
- Franco, A.; Lanzetta, M.; Romoli, L. Experimental analysis of selective laser sintering of polyamide powders: An energy perspective. J. Clean. Prod. 2010, 18, 1722–1730, doi:10.1016/j.jclepro.2010.07.018.
- 47. Yuan, M.; Diller, T.T.; Bourell, D.; Beaman, J. Thermal conductivity of polyamide 12 powder for use in laser sintering. *Rapid Prototyp. J.* **2013**, *19*, 437–445, doi:10.1108/RPJ-11-2011-0123.
- Kryszak, B.; Szustakiewicz, K.; Stępak, B.; Gazińska, M.; Antończak, A.J. Structural, thermal and mechanical changes in poly(l-lactide)/hydroxyapatite composite extruded foils modified by CO2 laser irradiation. *Eur. Polym. J.* 2019, *114*, 57– 65, doi:10.1016/j.eurpolymj.2019.02.030.
- Monnier, X.; Delpouve, N.; Basson, N.; Guinault, A.; Domenek, S.; Saiter, A.; Mallon, P.E.; Dargent, E. Molecular dynamics in electrospun amorphous plasticized polylactide fibers. *Polymer (Guildf)*. 2015, 73, 68–78, doi:10.1016/j.polymer.2015.07.047.