

Super heat deflection resistance stereocomplex crystallisation of PLA system achieved by selective laser sintering

Jinze Wu¹, Runhuai Yang² ✉, Jinjin Zheng¹, Xiang Wang¹

¹Department of Precision Machinery and Precision Instrument, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

²Department of Biomedical Engineering, School of Life Science, Anhui Medical University, 230032, Hefei, People's Republic of China

✉ E-mail: yangrunhuai@ahmu.edu.cn

Published in Micro & Nano Letters; Received on 4th May 2018; Revised on 27th June 2018; Accepted on 16th July 2018

Poly(lactide) (PLA) is a bioresorbable polymer with potential application for bone tissue repair; however, low heat distortion temperature (HDT) limits its biomedical applications. Due to the low-melting point of PLA, only fused deposition modelling (FDM) was used as a rapid prototyping technology to form PLA products. Here, the work presents a PLA stereocomplex formation which was facilitated by melt blending PLA and poly(D-lactide). The melting point was successfully increased to 219.2°C. Besides, the PLA stereocomplex-based three-dimensional scaffold was formed by selective laser sintering (SLS). The parameters of SLS (energy density, scan speed, scan spacing, preheating temperature etc.) were also optimised by comparing the microstructure. Compared with the FDM, the SLS provides many benefits for fabricating tissue engineering scaffolds due to its rough powder surface. Results show that the PLA stereocomplex was successfully obtained and crystallinity of the stereocomplex was 59.7%.

1. Introduction: Polylactide (PLA) has been studied in recent years because of its good performance in biocompatibility, biodegradability, renewability and ideal carbon cycle excluding petroleum resources [1–3]. However, due to the low degree of crystallinity for PLA materials when applied in an injection-moulding process, a low heat distortion temperature (HDT) for PLA products is thorny for applications [4, 5], the lack of HDT limits the specific applications of PLA materials in long-term applications, such as bioengineering products. Therefore, a lot of research has focused on modifying PLA to increase its HDT [6–11].

Fortunately, there are two enantiomers in PLA, namely poly(D-lactide) (PDLA) and poly(L-lactide) (PLLA), which can be incorporated into the unit cell simultaneously and generate stereocomplex crystals (SCs). By forming SCs, the melting point of PLA can be significantly increased to 220°C. Since there are some strong interactions between the two polymers, such as intermolecular hydrogen bonds or van der Waals forces, so they have a denser chain packing structure [12–16]. These denser unit structures give PLA higher heat resistance, better physical properties in biomedical applications such as tissue engineering. Therefore, in recent years, great attention has been focused on promoting the SCs to form [17, 18].

To enhance the thermal and mechanical properties of the PLA, which were applied in the medical and chemical industries, aerospace, construction, and automotive, the stereocomplexation of PDLA and PLLA is one method that has been utilised widely [6]. In 2000, Tusji prepared well-stereo-complex 1:1 blend and non-blend films from PLLA and PDLA by solvent evaporation. This research shows that there were strong interactions between PLLA and PDLA to form a 3D micro network after stereocomplexation [19]. In 2003, Yamane studied the thermal property and crystallisation behaviour of PLLA blended with a small amount of PDLA (1–5 wt%), it reveals that the PDLA molecules added in PLLA formed stereocomplex crystallites in the PLLA matrix, and with increasing PDLA content, stereocomplex crystallites were more easily formed and they acted as nucleation sites [20]. In 2007, Zhang and co-workers succeeded for the first time to observe the phase transition phenomenon when using the highly oriented 1:1 stoichiometric blend of high-molecular-weight PLLA

and mild-molecular-weight PDLA, the as-drawn sample was found to consist of the two crystalline phases: disordered α form and stereocomplex [21]. In 2010, Anderson and colleagues revealed that the PLLA/PDLA stereocomplex had a much higher hydrolytic stability than plain PLLA because short tie chains are susceptible to hydrolysis and lead to the formation of shorter oligomers compared with hydrolysis of the regular PLLA [22]. In 2012, Tusji and Bouapao investigated the crystallisation of the PLLA and PDLA with different weight-average molecular weights (M_w) [23]. In 2016, Ishii and co-workers investigated that the effect of xylan propionate (XylPr) as a novel biomass-derived nucleating agent on the PLA stereocomplex [24]. Through these studies, we can find that the crystallisation is inhibited significantly when the prepared PLA/PDLA blends had M_w above 6000 g/mol. Therefore, preparing PLA samples with high SC and high M_w content by melt blending is the key to achieving high heat resistance and balanced performance. In the previous work of Bao *et al.*, they found a facile approach to stereocomplexation of high M_w PLA and PDLA [25]. Their results show that the pure stereocomplex can be achieved by a low-temperature approach. The benefit of the low-temperature approach was traditional high-temperature process induced significant degradation of the homopolymer. Also, compared with other low temperature methods, such as solution casting, involving the use of a solvent, which is not friendly to the environment, the method used in this work is a facile and environment friendly method. However, the high-melting temperature of the pure stereocomplex makes it difficult to process conventional thermoplastic products.

Rapid prototyping (RP) technology plays an important role in the manufacturing of complex personalised components. So many experts and scholars have studied processing PLA with fused deposition modelling (FDM) [26, 27], although exhibiting good geometric accuracy and mechanical properties, but relatively poor heat resistance limits its applications. So, we have proposed to process the PLA stereocomplex with a selective laser sintering (SLS) method. SLS is a layer manufacturing process that allows generating complex 3D parts by consolidating successive layers of powder material on top of each other. Consolidation is obtained by processing the selected areas using the thermal energy supplied

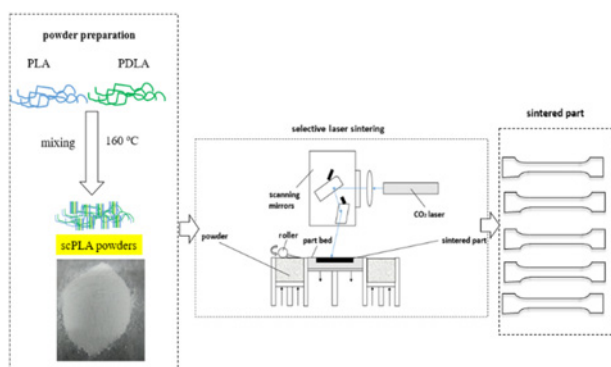


Fig. 1 Schematic of SLS-manufactured PLA stereocomplex powders

by a focused laser beam [28]. Semi-crystalline polymers show a near-full density and mechanical properties comparable with conventionally moulded specimens and enable the direct manufacturing of functional plastic components by SLS. Additionally, compared with other RP techniques, SLS techniques have been suggested to enhance cell adhesion due to the rough powder surface [29], so SLS provides many benefits for fabricating tissue engineering scaffolds.

Therefore, the current work aimed at developing a facile process to shape the pure PLA stereocomplex powders through SLS, as shown in Fig. 1. It promises better heat resistant and cell adhesion ability than normal 3D-print PLA products with FDM due to the high-melting temperature of the PLA stereocomplex. The SLS of this developed material has a potential for biomedical applications.

2. Material and method: We purchased PLA from Natureworks Company (PLA2003D) for this study. The PLA sample had a melt flow index of 6 g/10 min (210°C, 2.16 kg) and a density of 1.24 g/cm³. The PLA sample had a polydispersity of 2.3 and weight-averaged molecular mass of 296 kg/mol by gel permeation chromatography measurement. PDLA synthesised through ring-opening polymerisation of D-lactide at the Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (China) had M_w and M_n of 74 and 46 kg/mol, respectively, and M_w/M_n of 1.6.

Prior to melt blending, PLA and PDLA were vacuum-dried at 80°C for 12 h. Using an XSS-300 torque rheometer (Shanghai Kechuang Co., Ltd.), pure stereocomposite powders were prepared by mixing PLA and PDLA with a mass ratio of 50/50 at 60 r/min for 10 min [30].

Under a nitrogen flow rate of 50 ml/min, the TA Q2000 differential scanning calorimeter (DSC, TA Instruments, New Castle, DE) was used to determine the thermal properties of the sample. By determining the cold crystallisation temperature (T_{cc}), the melting temperature (T_m), the cold crystallised enthalpy, the initial crystallisation state of the PLA matrix phase was examined using a DSC heat flow curve at a rate of 10°C/min during the first heating scan (ΔH_{cc}) and melting enthalpy (ΔH_m). The crystallinity X_c of PLA is determined as follows:

$$X_c = (\Delta H_m - \Delta H_{cc}) / w_f \Delta H^0_m, \quad (1)$$

where w_f is the mass fraction of PLA and ΔH^0_m is the enthalpy of fusion for the 100% crystalline PLA, taken from the literature at a value of 93.7 J/g.

We designed samples using SolidWorks modelling software, the designs were then exported to an HK P500 SLS machine (Huazhong University, China) in the STL file format, SLS experiments were carried out using CO₂ laser operating at 10,600 nm wavelength, and 55 W maximum power. An infrared heater placed inside the working chamber was used for preheating.

Appropriate parameters (laser power P , scan speed V , scan spacing H) were taken using the energy density equation, and compared samples' forming quality by experiments.

Polarising light microscopy (POM) was used to observe the crystallisation morphology for pure stereocomplex powders. Also, to evaluate the quality of sintered parts, scanning electron microscopy (SEM) analysis was performed to analyse the microstructure of the different energy density samples.

3. Results and discussion: Commonly, solution casting and melting blending methods were used to generate stereocomplex crystallites. Unfortunately, the volatile organic solvents were used to facilitate processing and requires high temperature (220–250°C) to melt blending, which induces degradation of the homopolymer significantly. Bao *et al.* presented a simple but novel method for enhancing a sample stereocomplexation of high-molecular-weight PLA and PDLA by a low-temperature approach. The process took the advantage of the temperature window at which only the stereocomplex can grow and homopolymers can no longer crystallise. Interestingly, the appearance of PLA/PDLA 50/50 blends prepared by this low-temperature approach can be in powder form. Fig. 1a shows the appearance of the stereocomplex powder prepared at 160°C. Compared with melt blending at a high-processing temperature and solution casting, from which the products are very difficult to be powdered for further application. In contrast, the low-temperature approach can obtain the powder of stereocomplex directly.

POM was used to elucidate the size of complex powder from the low-temperature approach. Figs. 2b and c show the morphology of the complex powder in POM with different magnification. As shown in Fig. 2b, the complex powders present on bright spots in POM and all the spots show similar sizes. From Fig. 2c, in a much larger magnification view, the size of the complex powder can be measured, which is near 2–5 μ m.

To further investigate the crystal form and crystallinity, the result of the DSC for the PLA complex powder is presented in Fig. 3. As shown in Fig. 2, there are two thermodynamic transitions, the lower one in 62.0°C is corresponding to the glass transition of the PLA, while the higher transition in 219.2°C is the melting peak of the PLA complex crystal because the melting peak of homocrystalline is at 168°C. There is only one melt peak at high temperature, indicating that only complex crystals were formed during the blending process at low temperature. According to the heat fusion of a 100% PLA stereocomplex of 102 J/g, crystallinity of the stereocomplex can be calculated, which is 59.7% (the heat fusion in stereocomplex fusion is 60.85 J/g). Thus, fine powders from the stereocomplex are successful obtained.

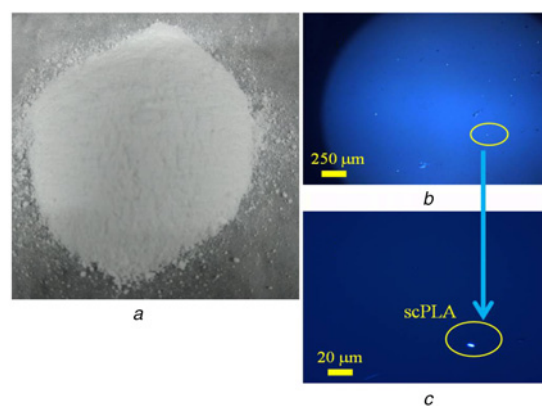


Fig. 2 Appearance of equimolar PLA/PDLA blend powders prepared at 160°C

a PLA/PDLA blend powders prepared for SLS
b Micrograph of scPLA, scale bars indicate 300 μ m
c Zoom-in view of scPLA, scale bars indicate 20 μ m

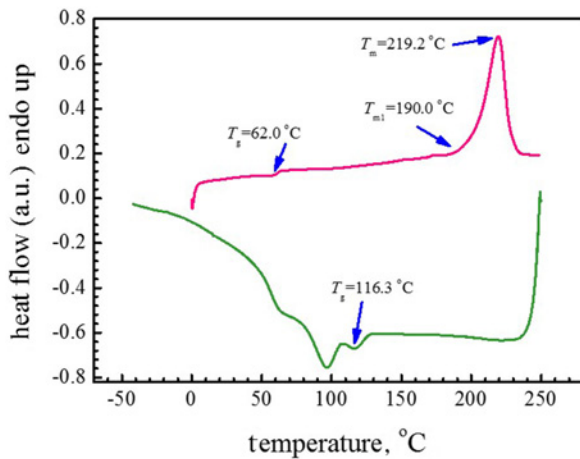


Fig. 3 DSC curve of PLA/PDLA blend powder

Applicable process parameters are one of the most important research points when applied to SLS. To ensure that the PLA/PDLA nanocomposites can be formed successfully by SLS, we conducted a single-layer SLS experiment firstly, and use the energy density (ω) to choose suitable parameters, the energy density was defined as the laser energy applied on per unit area, which can be calculated by (2) [31], ω ranged from 0.02 to 0.04 J/mm². Therefore, the laser sintering process of the PLA/PDLA nanocomposite powders was chosen with a layer thickness (D) of 0.1 mm, scan spacing (H) of 0.2 mm, preheating temperature of 120°C and laser power (P) ranged from 10 to 14 W, scan speed (V) ranged from 1500 to 3000 mm/s, as shown in Table 1. After the scanning process, the specimen was held at the temperature for 10 min. Pictures of partially sintered single-layer specimens are shown in Fig. 4.

As we can see, when $\omega = 0.02$ J/mm² ($P = 12$ W, $V = 3000$ mm/s, $H = 0.2$ mm), due to the energy density was too low, the sample failed to form. As energy density increased to 0.025 J/mm² ($P = 10$ W, $V = 2000$ mm/s, $H = 0.2$ mm), the particles can be sintered relatively denser and we can get a complete part, but the porosity was very high and forming quality was awfully poor. When $\omega = 0.03$ J/mm² ($P = 12$ W, $V = 2000$ mm/s, $H = 0.2$ mm), the sintered sample became denser, porosity reduced obviously, and we can get a more perfect part. When energy density increased to 0.035 J/mm² ($P = 14$ W, $V = 2000$ mm/s, $H = 0.2$ mm), the particles were sintered excessively and the sample's density became worse. When energy density finally increased up to 0.04 J/mm² ($P = 12$ W, $V = 1500$ mm/s, $H = 0.2$ mm), the particles were excessive sintered so seriously that cannot form a normal part.

Based on the above results, we conducted the multi-layer sintering experiment with energy density $\omega = 0.03$ J/mm², but at the preheating temperature $T = 120^\circ\text{C}$, the double layers were formed hardly because of warping due to the residual stress. Therefore, we increased the preheating temperature to prevent warping. For a crystalline polymer, the working temperature range ($T_m - T_c$)

Table 1 Parameters of SLS

Parameters	Value
energy density: ω , J/mm ²	0.020, 0.025, 0.030, 0.035, 0.040
scan spacing: H , mm	0.20
thickness: D , mm	0.10
preheating temperature: T , °C	120
laser power: P , W	3.5, 5.0, 6.5, 8.0
laser speed: V , mm/s	180, 360
scan direction	X-Y crossover

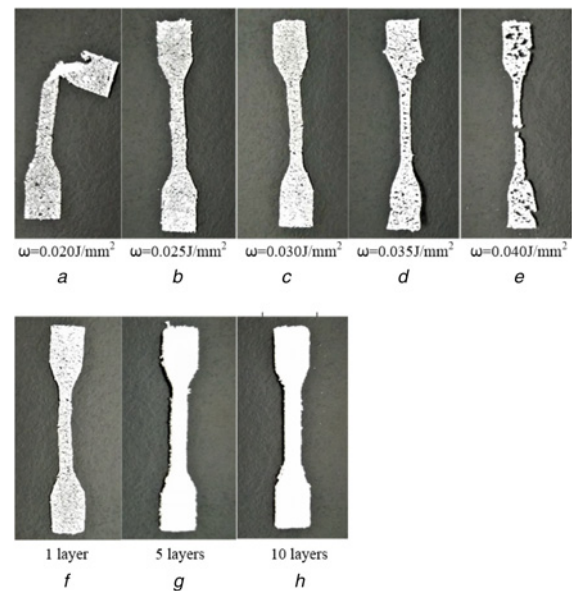


Fig. 4 PLA/PDLA samples with different process parameters
a–e Five samples' photos of a single-layer SLS with the energy density of 0.020–0.040 J/mm²
f–h Different layers samples' pictures of an SLS experiment with the preheating temperature of 120–170°C

was depended on the material's onset melting temperature and onset recrystallisation temperature, so the preheating temperature was [116.3 and 190°C]. As shown in Fig. 4, we firstly increased the temperature to 150°C, the warping phenomenon was improved obviously, and we can sinter up to five layers. When the temperature reached 170°C, the warping phenomenon was overcome further so that the sintered parts can up to ten layers, and it can meet the requirement of our design samples

$$\omega = P/v * H. \quad (2)$$

As shown in Fig. 5, SEM analysis was performed to analyse the microstructure of the different energy density samples. At the

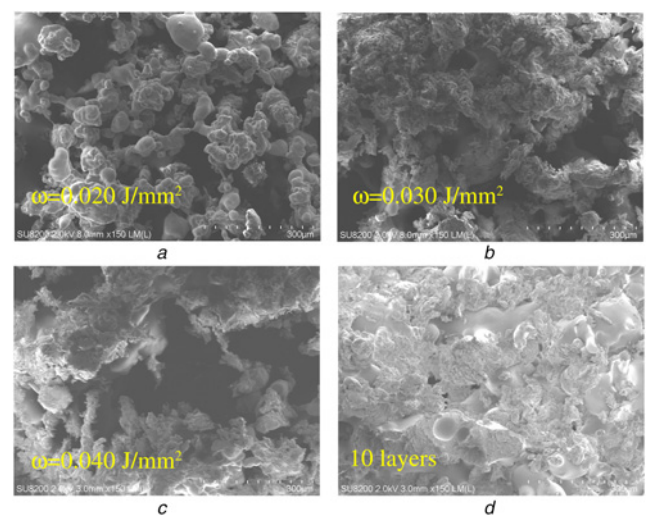


Fig. 5 SEM micrograph of PLA/PDLA SLS manufactured samples, Scale bars indicate 300 μm
a $\omega = 0.020$ J/mm²
b $\omega = 0.030$ J/mm²
c $\omega = 0.040$ J/mm²
d Ten layers

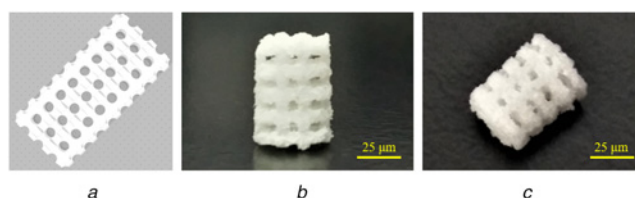


Fig. 6 The design and fabrication of PLA/PDLA scaffold
a STL design file for the porous cylindrical scaffold
b, c PLA/PDLA nanocomposite powders scaffold fabricated by SLS

energy density of 0.02 J/mm^2 , the adjacent particles only bonded together at the contact regions slightly, and the powder basically retained its virgin shape (Fig. 5a). When energy density increased to 0.03 J/mm^2 , increasing energy density increased the temperature of the powder, the polymer macromolecular chains became more active and thus the polymer microstructure became denser, but small holes still existed (Fig. 5b). When energy density finally lifted up to 0.04 J/mm^2 , the sintering necks continued to grow, some small particles fused together to form big particles, and thus the relative density was increased but due to the over-sintered in partial areas, some large holes appeared (Fig. 5c).

The SEM image of ten-layer specimen's cross-section is shown in Fig. 5d, we can notice that there was no obvious layers' stratification occurred, the connection between layers was quite dense. These results indicated that we can get better quality sintered parts when using $\omega = 0.03 \text{ J/mm}^2$ ($P = 12 \text{ W}$, $V = 2000 \text{ mm/s}$, $H = 0.2 \text{ mm}$).

As shown in Fig. 6a, a cylindrical porous scaffold (6.3 mm diameter, 8.0 mm height, 0.5 mm pore diameter), with three-dimensional orthogonal periodic porous architectures, was designed by Solidworks software. Fig. 6b shows the scaffolds fabricated by SLS. This structure was designed and fabricated to provide a three-dimensional space for cells to survive, ensure cells to penetrate the pores, the pore size should be large enough and the pores must be interconnected to each other so that waste and nutrient exchange between cells.

4. Conclusion: PLA/PDLA scaffolds fabricated through the SLS show great potential for replacement of bone tissues. It promises better heat resistant due to the high-melting temperature of the PLA stereocomplex. Our results demonstrated that the appropriate SLS process parameters for this new applied material by comparing the microstructure with different energy densities. Further efforts are required to improve the mechanical strength of the SLS manufactured PLA/PDLA scaffolds as well as to assess their effects on cell differentiation.

5. Acknowledgments: This work was supported by the National Natural Science Foundation of China (project no. 61603002), the 973 Project (grant no. 2014CB931804), 111 the Projects (grant no. B07033), the NSFC-CAS Joint Fund (grant no. U1332130), and the Key Research and Development Program of Anhui (grant no. 1704a0902051) for their financial support.

6 References

- [1] Yu L., Dean K., Li L.: 'Polymer blends and composites from renewable resources', *Prog. Polym. Sci.*, 2006, **31**, (6), pp. 576–602
- [2] Gupta B., Revagade N., Hilborn J.: 'Poly (lactic acid) fiber: an overview', *Prog. Polym. Sci.*, 2007, **32**, (4), pp. 455–482
- [3] Raquez J.M., Habibi Y., Murariu M., *ET AL.*: 'Polylactide (PLA)-based nanocomposites', *Prog. Polym. Sci.*, 2013, **38**, (10–11), pp. 1504–1542
- [4] Sodergard A.S.M.: 'Properties of lactic acid based polymers and their correlation with composition', *Prog. Polym. Sci.*, 2002, **27**, pp. 1123–1163
- [5] Zhang Z.C., Gao X.R., Hu Z.J., *ET AL.*: 'Inducing stereocomplex crystals by template effect of residual stereocomplex crystals during thermal annealing of injection-molded polylactide', *Ind. Eng. Chem. Res.*, 2016, **55**, (41), pp. 10896–10905
- [6] Tan B.H., Muiruri J.K., Li Z., *ET AL.*: 'Recent progress in using stereocomplexation for enhancement of thermal and mechanical property of polylactide', *ACS Sustain. Chem. Eng.*, 2016, **4**, (10), pp. 5370–5391
- [7] Zhang Z.C., Sang Z.H., Huang Y.F., *ET AL.*: 'Enhanced heat deflection resistance via shear flow-induced stereocomplex crystallization of polylactide systems', *ACS Sustain. Chem. Eng.*, 2017, **5**, (2), pp. 1692–1703
- [8] Wang Y., Wei Z., Leng X., *ET AL.*: 'Highly toughened polylactide with epoxidized polybutadiene by in-situ reactive compatibilization', *Polymer*, 2016, **92**, pp. 74–83
- [9] Fang H., Jiang F., Wu Q., *ET AL.*: 'Supertough polylactide materials prepared through in situ reactive blending with PEG-based diacrylate monomer', *ACS Appl. Mater. Interfaces*, 2014, **6**, (16), pp. 13552–13563
- [10] Nagarajan V., Mohanty A.K., Misra M.: 'Perspective on polylactic acid (PLA) based sustainable materials for durable applications: focus on toughness and heat resistance', *ACS Sustain. Chem. Eng.*, 2016, **4**, pp. 2899–2916
- [11] Oyama H.T., Abe S.: 'Stereocomplex poly (lactic acid) alloys with superb heat resistance and toughness', *ACS Sustain. Chem. Eng.*, 2015, **3**, (12), pp. 3245–3252
- [12] Tsuji H., Fukui I.: 'Enhanced thermal stability of poly(lactide)s in the melt by enantiomeric polymer blending', *Polymer*, 2003, **44**, pp. 2891–2896
- [13] Lin T.T., Liu X.Y., He C.B.: 'A DFT study on poly (lactic acid) polymorphs', *Polymer*, 2010, **51**, pp. 2779–2785
- [14] Na B., Zhu J., Lv R.H., *ET AL.*: 'Stereo complex formation in enantiomeric polylactides by melting recrystallization of homocrystals: crystallization kinetics and crystal morphology', *Macromolecules*, 2014, **47**, pp. 347–352
- [15] Shao J., Sun J.R., Bian X.C., *ET AL.*: 'Modified PLA homochiral crystallites facilitated by the confinement of PLA stereocomplexes', *Macromolecules*, 2013, **46**, pp. 6963–6971
- [16] Hemmi K., Matsuba G., Tsuji H., *ET AL.*: 'Precursors in stereo-complex crystals of poly(L-lactic acid)/poly(D-lactic acid) blends under shear flow', *J. Appl. Crystallogr.*, 2014, **47**, pp. 14–21
- [17] Brochu S., Prudhomme R.E., Barakat I., *ET AL.*: 'Stereocomplexation and morphology of polylactides', *Macromolecules*, 1995, **28**, pp. 5230–5239
- [18] Tsuji H., Takai H., Saha S.K.: 'Isothermal and non-isothermal crystallization behavior of poly (L-lactic acid): effects of stereocomplex as nucleating agent', *Polymer*, 2006, **47**, pp. 5430–5430
- [19] Tsuji H.: 'In vitro hydrolysis of blends from enantiomeric poly (lactide)s part 1. Well-stereo-complexed blend and non-blended films', *Polymer*, 2000, **41**, (10), pp. 3621–3630
- [20] Yamane H., Sasai K.: 'Effect of the addition of poly(D-lactic acid) on the thermal property of poly(L-lactic acid)', *Polymer*, 2003, **44**, (8), pp. 2569–2575
- [21] Zhang J., Tashiro K., Tsuji H., *ET AL.*: 'Investigation of phase transitional behavior of poly(L-lactide)/poly(D-lactide) blend used to prepare the highly-oriented stereocomplex', *Macromolecules*, 2007, **40**, (4), pp. 1049–1054
- [22] Anderson S.R., Hakkarainen M., Inkinen S., *ET AL.*: 'Polylactide stereocomplexation leads to higher hydrolytic stability but more acidic hydrolysis product pattern', *Biomacromolecules*, 2010, **11**, (4), pp. 1067–1073
- [23] Tsuji H., Bouapao L.: 'Stereocomplex formation between poly (L-lactic acid) and poly(D-lactic acid) with disproportionately low and high molecular weights from the melt', *Polym. Int.*, 2012, **61**, (3), pp. 442–450
- [24] Ishii D., Kimishima M., Otake K., *ET AL.*: 'Enhanced crystallization of poly(lactide) stereocomplex by xylan propionate', *Polym. Int.*, 2016, **65**, (3), pp. 339–345
- [25] Bao R.Y., Yang W., Jiang W.R., *ET AL.*: 'Stereocomplex formation of high-molecular-weight polylactide: a low temperature approach', *Polymer*, 2012, **53**, (24), pp. 5449–5454
- [26] Torres J., Cotel J., Karl J., *ET AL.*: 'Mechanical property optimization of FDM PLA in shear with multiple objectives', *JOM*, 2015, **67**, (5), pp. 1183–1193
- [27] Afrose M.F., Masood S.H., Iovenitti P., *ET AL.*: 'Effects of part build orientations on fatigue behaviour of FDM-processed PLA material', *Prog. Addit. Manuf.*, 2016, **1**, pp. 21–28

- [28] Kruth J-P., Mercelis P., Van Vaerenbergh J.: 'Binding mechanisms in selective laser sintering and selective laser melting', *Rapid Prototyping J.*, 2005, **11**, (1), pp. 26–36
- [29] Williams J.M., Adewunmi A., Schek R.M., *ET AL.*: 'Bone tissue engineering using polycaprolactone scaffolds fabricate via selective laser sintering', *Biomaterials*, 2005, **26**, pp. 4817–4827
- [30] Tsuji H., Ikada Y.: 'Stereocomplex formation between enantiomeric poly(lactic acid)s. XI. Mechanical properties and morphology of solution-cast films', *Polymer*, 1999, **40**, (24), pp. 6699–6708
- [31] Hopkinson N., Majewski C.E., Zarringhalam H.: 'Quantifying the degree of particle melt in selective laser sintering®', *CIRP Annu. Manuf. Technol.*, 2009, **58**, pp. 197–200