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Improving the shape stability and enhancing the properties of layer dependent material extruded biodegradable polylactic acid for thin implants

1 Introduction

Temporary medical implants manufactured from biodegradable materials are increasingly being used in a wide range of surgeries due to their attractive physical properties, functionalities and as well as their practical preparation (Nair and Laurencin, 2007). Often-preferred material in biomedical applications is polylactic acid (PLA) based materials classified as a polyester since they have good mechanical properties, high levels of biocompatibility, biodegradability, and non-toxicity (Luckachan and Pillai, 2011). Therefore, PLA-based biomedical applications are used extensively when designing and manufacturing medical implants such as orthopaedics, drug carriers, tissue engineering, and ureteral stents (P. Pawar *et al.*, 2014). Depending on the type of application, biomedical implants vary in size and shape (Weisberger and Eppley, 1997; Prowans, El Fray and Slonecki, 2002; Karki *et al.*, 2016).

With the advancement of Additive Manufacturing (AM) technology, customised products have become increasingly commonplace in comparison to using conventional manufacturing technologies (Kumar *et al.*, 2016). Material Extrusion (MEX), is an increasingly accessible process that mostly uses thermal plastic polymers such as PLA (Calignano *et al.*, 2017). In MEX, material is melted and extruded from a nozzle and bonded to either the print bed or previously printed layer (Sun *et al.*, 2008). The thermal history of MEX parts varies throughout the part; therefore, the molecular weight, crystallinity and mechanical properties of non-annealed parts are altered after each layer is deposited (Ekinici *et al.*, 2020). Previous work has identified there was a high dependency in 1-, 3- and 5-layer specimens; however, less

dependency above 5-layers. Preliminary investigations demonstrated that when each layered printed specimens were subjected to *in vitro* degradation in Phosphate Buffered Saline (PBS) had pH of 7.4 at 37°C for 1 month; their shape and structure were distorted, as demonstrated in Figure 1.

Figure 1: (a) Non-annealed specimens, (b) non-annealed specimens degraded at 37°C and (c) annealed specimen degraded at 37°C

Following material deposition, it is likely that residual stress is present within the test specimens (Raasch *et al.*, 2015). Consequently, this results in significant warping, shrinkage, and the twisting of specimens used within degradation studies at 37°C. In order to reduce the residual stress and to keep the shape of test specimens stable, an appropriate annealing treatment can be applied. As well as decreasing the residual stress, annealing increases the degree of crystallinity and enhances mechanical properties depending on the annealing time and applied temperature (Tabi *et al.*, 2010). Therefore, this study aimed to evaluate the distortion of 1-, 3-, and 5-layer non-annealed specimens exposed to degradation and investigate the annealing effect of PLA specimens manufactured by MEX in order to enhance their mechanical and thermal properties and to analyse the molecular weight properties.

2 Materials and methods

2.1 *Materials, printing technology and process parameters*

NatureWorks® 2.85 mm diameter biodegradable PLA filament (3DXTECH® polylactide 4043D, Sigma Aldrich, LOT: 85633) was used within this study. A series of plates measuring 100 x 100 mm in the x- and y-direction was printed. Each layer featured a 0.36 mm line width and was printed longitudinal to the x-direction using the default ‘zigzag’ print path. Each layer measured 0.1 mm in thickness of generating 1-, 3-, and 5-layers in the z-direction to create in total of 0.1, 0.3, and 0.5 mm thickness specimens respectively. Extrusion and bed temperatures were 210°C and 60°C respectively, while the print speed was set at 80 mm/s.

2.2 *Annealing methods*

The printed sheets were placed between two non-preheated aluminium plates and clamped together using bulldog clips. They were then placed in a preheated incubator (Genlab – INC/50/DIG). Following annealing, the clamped aluminium plates were kept at room temperature for 30 minutes for cooling and then the sheets were removed. The annealing methods included two stages: 1) annealing at 70°C, 80°C or 90°C for 2 hours; and 2) at 80°C for 1, 2, 4, 8 or 16 hours, resulting in seven different specimen types for each layer. The specimens were annealed above their glass transition temperature (T_g) until eliminating the cold crystallisation enthalpy.

2.3 *Specimen preparation*

Following printing and annealing, the sheets were stamped in-line with the material deposition direction to form ISO 527-2 type 5A specimens. From each sheet, seven tensile specimens were generated; five of which to obtain mechanical properties and two to ascertain thermal and molecular weight properties.

2.4 Characterisation of 3D printed and annealed specimens

2.4.1 Distortion calculation

The distorted tensile specimens was calculated in both x- and y-direction for seven samples to ascertain mean and standard deviation based on the reference specimen's length, as shown in Figure 2.

Figure 2: x- and y-distortion calculation of distorted specimen

The length of all of the tensile specimens was 75 mm referred in the x-direction while the reference point for y-direction was 0 mm. The distortion in x-direction was found by measuring the specimens from end points and subtracting that value from the reference's length. In the y-direction, the distortion was measured from the both sides and the average was taken.

2.4.2 Thermal properties

A TQ (200) Differential Scanning Calorimetry (DSC) testing machine was used to determine the thermal properties. Cross-section of materials weighing between 5.5 – 6.0 mg were cut from the middle of the specimen and tested. The DSC heating cycle ranged from 20°C to 200°C, increasing at a rate of 10°C/min. The DSC thermogram was used to obtain the T_g , cold crystallisation (T_c) and melting temperature (T_m) (in °C), the cold crystallisation enthalpy (ΔH_{cc} in J/g) and melting enthalpy (ΔH_{melt} in J/g). The reference enthalpy of fusion (ΔH_{ref} in J/g) of 100% crystallinity of PLLA is reported to be 93.64 J/g (Fischer,

Sterzel and Wegner, 1973).

$$\% \chi = \frac{\Delta H_{\text{melt}} - \Delta H_{\text{cc}}}{\Delta H_{\text{ref}}} \quad (1)$$

Degree of crystallinity (% χ) calculated using equation 1 where ΔH_{melt} and ΔH_{cc} are melting enthalpy and cold crystallization enthalpy respectively.

2.4.3 *The molecular weight properties*

A Waters Breeze2 Gel Permeation Chromatography (GPC) system was used to determine molecular weight properties. A cross-section removed from the centre weighing between 8-12 mg were dissolved into 1 ml of High-Performance Liquid Chromatography (HPLC) grade Dimethylformamide (DMF). Two measurements were used to calculate the molecular weight and the unit for number average molecular weight (M_n) and weight average molecular weight (M_w) was kilodalton (kDa).

2.4.4 *Mechanical properties*

An Instron 3345 Universal Testing System equipped with a 5 kN load cell was used to test the annealed PLA tensile specimens. The strain rate was constant at 1 mm/min. Load – extension curves were used to calculate the mechanical properties. Five replicates for each thickness were tested to establish mean and standard deviations.

3 Result and discussion

In this section, the distortion of each layered non-annealed specimen subjected to 37°C degradation was calculated in the x- and y- direction. Thermal, molecular and mechanical properties were investigated for annealed specimens.

3.1 Distortion calculation of tensile test specimens

The distortion in x- and y-direction for each layered non-annealed specimen degraded at 37°C are presented in Figure 3.

Figure 3: Distortion of each layered non-annealed specimens

Distortion in the 1-layer non-annealed specimens was measured at 16.08 ± 3.27 mm on x-direction and 6.50 ± 1.79 mm in y-direction. 3-layer non-annealed specimens showed a decrease by 73% at 9.30 ± 2.71 mm in x-direction whilst y-direction distortion increased by 30% at 9.35 ± 1.22 mm in comparison to 1-layer. Following, the 5-layer non-annealed specimens had the lowest distortion in both x- and y-directions with values of 2.72 ± 0.64 mm and 3.32 ± 0.44 mm respectively. Thin printed specimens tended to be more distorted than thick specimens due to their low resistance. Additionally, the shape instability may have occurred due to having larger amorphous region, where shape distortion is higher (Wong and Venkatraman, 2010). The degree of crystallinity of the non-annealed specimen was 4.81%, 2.13%, and 0.72% for 1-, 3-, and 5-layer respectively (Ekinici *et al.*, 2020).

3.2 Thermal properties

Each layered specimen at 70°C, 80°C, and 90°C for 2 hours showed similar behaviours for each T_g , T_c , and T_m as shown in Figure 4 where data points from different layered specimens directly overlap.

Figure 4: T_g , T_c and T_m of each layered annealed specimen at 70°C, 80°C, and 90°C for 2 hours

The glass transition (T_g) and melting temperature (T_m) were around 58°C and 150°C for 2 hours annealed specimens at 70°C, 80°C, and 90°C respectively. The cold crystallisation temperature (T_c) appeared only at 70°C and 80°C with values of 117°C and 111°C respectively.

When annealing at 80°C for 1, 2, 4, 8, and 16 hours as shown in Figure 5, the glass transition and melting temperature were constant at approximately 60°C and 150°C respectively. The cold crystallisation temperature was 115°C for 1-hour annealing, however, it was not recorded for following 4, 8, and 16 hours annealing.

Figure 5: Tg, Tc and Tm of each layered annealed specimen at 80°C for 1, 2, 4, 8 and 16 hours

Figure 6 presents the degree of crystallinity of each layered annealed specimen at 70°C, 80°C, and 90°C for 2 hours.

Figure 6: %χ of each layered specimen at 70°C, 80°C, and 90°C for 2 hours

Annealing at 70°C for 2 hours increased the degree of crystallinity to approximately 6% for each layered specimen. Annealing for 2 hours at 80°C increased the degree of crystallinity by

19% - 21%. Here, the difference was only 9% between each layered specimen. At 90°C annealing for 2 hours, the degree of crystallinity was approximately 34% and increased almost 70% in comparison to 80°C annealing for 2 hours.

In Figure 7, increasing annealing time at 80°C increased the degree of crystallinity.

Figure 7: % χ of each layered annealed specimen at 80°C for 1, 2, 4, 8 and 16 hours

The degree of crystallinity of 1-hour annealing was recorded at 7.42%, 5.92%, and 4.12% for 1-, 3-, and 5-layer respectively. 4 hours annealed specimens showed an increase of approximately 16%, 26%, and 28% in comparison to 2 hours annealing, reaching a degree of crystallinity of 24%, 27%, and 28% for 1-, 3-, and 5-layer respectively. Furthermore, the outcome of each layered specimen almost plateaued having the same degree of crystallinity when annealed for greater than 4 hours. The degree of crystallinity increased by approximately 15%, 27%, and 28% for 1-, 3-, and 5-layer annealed specimens respectively.

Understanding the glass transition temperature is crucial for annealing. Annealing above the glass transition temperature helps to decrease or eliminate the cold crystallisation temperature

due to molecular mobility (Pretula, Slomkowski and Penczek, 2016). Annealing has a significant impact on degree of crystallinity as it is a function of temperature and time depending on its glass transition temperature (Wolszczak *et al.*, 2018). The annealing treatment resulted in crystallisation as the crystalline region does not allow for the mobility of amorphous chains; therefore, the degree of crystallinity increased with increasing temperature until cold crystallisation disappeared. The cold crystallisation was completely disappeared for specimens annealed at 80°C for 4, 8 and 16 hours and at 90°C for 2 hours; therefore, it featured a higher degree of crystallinity.

3.3 Molecular weight properties

Mn and Mw of each layered annealed specimen at 70°C, 80°C, and 90°C for 2 hours are given in detail in Figure 8 and the outcomes were compared with the previous study (Ekinici *et al.*, 2020).

Figure 8: Mn and Mw of each layered annealed specimen at 70°C, 80°C, and 90°C for 2 hours

The Mn and Mw of 1-layer specimens were 225 and 346 kDa for 70°C, 244 and 325 kDa for 80°C, and 218 and 336 kDa for 90°C respectively. 3-layer specimens showed no significant difference for 70°C and 80°C at 197 and 310 kDa for Mn and Mw; however, the Mn and Mw of 90°C annealed specimens were 245 and 338 kDa respectively. The Mn of the 3-layer annealed specimen showed a decrease by approximately 8% at 70°C and 80°C annealing respectively in comparison to non-annealed specimens; however, it increased by approximately 15% when annealed at 90°C. The Mn of the 5-layer specimens decreased by approximately 12%, 20%, and 8%, while Mw decreased by approximately 9%, 20%, and 13% for 70°C, 80°C, and 90°C annealed specimens respectively when compared to the 5-layer benchmark printed specimens.

Figure 9 presents the Mn and Mw of each layered annealed specimen annealed at 80°C for 1, 2, 4, 8 and 16 hours.

Figure 9: Mn and Mw of each layered specimen annealed at 80°C for 1, 2, 4, 8 and 16 hours

The Mn and Mw of all specimens showed almost no significant difference. The Mn and Mw ranged from 218 to 225 kDa and from 325 to 335 kDa respectively for 1-layer. Similar to 2

hours annealed specimens at 70°C and 90°C, the Mn and Mw of 80°C annealed specimens increased by approximately 17% and 12% in comparison to 1-layer non-annealed specimens. The 3-layer specimen showed a decrease trend in terms of their Mn and Mw up to 4 hours annealing from 13% to 5%; however, the Mn and Mw increased by 7% and 2% respectively for 8 and 16 hours annealing in comparison to non-annealed specimens. The Mn and Mw of the 5-layer specimens decreased by approximately 10% for 1 hour and 20% for 2 and 4 hours. 8 and 16 hours annealing increased the Mn and Mw by 16% and 13% respectively compared to 2 and 4 hours annealing.

It is known that the initial molecular weight of a biodegradable polymer has an impact on degradation time, where a higher molecular weight decreases the degradation rate. Increasing of the molecular weight is not common for PLA-based material following annealing; however, this increase could have been related to the variation in molecular weight of the raw material as the molecular weight was not constant throughout the filament. Specifically, the Mn and Mw of the 1-layer non-annealed specimens increased by approximately 17% and 18% following 70°C annealing, 17% and 10% following 80°C annealing, and 14% and 14% following 90°C annealing respectively. This increase after annealing was only specified for all 1-layer annealed specimens. At 80°C annealing with different annealing times, the Mn and Mw also increased in comparison to non-annealed specimens outlined in literature. This is rarely observed (Perego, Cella and Bastioli, 1996); therefore there is currently no explanation and further investigation is needed to understand the mechanism facilitating such an increase in molecular weight for 1-layer.

3.4 Mechanical properties

Previous research has showed that 1-, 3-, and 5-layer printed tensile specimens showed different mechanical properties (Ekinici *et al.*, 2020). The Young's modulus (E) was 1.44, 1.32, and 1.23

GPa, while the ultimate tensile strength (UTS) of 1-, 3-, and 5-layer printed specimens was recorded at 43.32, 47.73, and 48.71 MPa respectively.

The mechanical properties are presented in detail in Figure 10 (a) for Young's modulus and Figure 10 (b) for UTS.

Figure 10: (a) E and (b) UTS of each layer annealed at 70°C, 80°C and 90°C for 2 hours

The Young's Modulus of the 1-layer specimens was 1.41 GPa following annealing at 70°C; however, annealing at 80°C increased the Young's modulus by approximately 30% and was recorded at 1.91 GPa. Annealing at 90°C caused a slight decrease and the Young's Modulus to 1.69 GPa. The UTS of the 1-layer specimens were 46.11 MPa, 49.28 MPa, and 49.16 MPa for annealed specimens at 70°C, 80°C, and 90°C respectively.

The Young's Modulus of the 3-layer annealed specimens at 70°C decreased by 5% to 1.26 GPa while the UTS increased by 4%. Furthermore, annealing at 80°C increased the Young's Modulus and UTS by approximately 19% to 1.58 GPa and 57.39 MPa in comparison to 3-

layer printed specimens. Increasing the annealing temperature to 90°C reduced the Young's Modulus to 1.41 GPa and UTS to 55.35 MPa.

5-layer specimens that were annealed at 70°C remained unchanged in terms of their Young's Modulus in comparison to printed specimens. However, the UTS was higher than the printed specimens by approximately 9%. Annealing at 80°C increased the Young's Modulus and UTS by 16% and 15% respectively when compared to printed specimen. Additionally, the Young's Modulus of 90°C annealed specimens substantially reduced to 1.29 GPa.

The mechanical properties gathered from stress-strain curves are displayed in detail in Figure 11 (a) for Young's modulus and Figure 11 (b) for UTS.

Figure 11: (a) E and (b) UTS of each layer annealed at 80°C for 1, 2, 4, 8 and 16 hours

The Young's Modulus of the 1-layer annealed specimens ranged from 1.56 GPa to 1.91 GPa. The highest Young's Modulus were recorded at an annealing time of 2 hours and then decreased with further increases annealing duration. The UTS showed no significant difference ranging from 48.78 MPa to 49.60 MPa.

The Young's Modulus of the 3- and 5-layer annealed specimens showed similar results as the 1-layered specimens which featured the highest Young's Modulus at 1.58 GPa and 1.41 GPa for 2 hours respectively. The UTS demonstrated in Figure 11 (b) was highest at 57.39 MPa and lowest at 52.08 MPa for 3-layer annealed specimens for 2 hours and 1-hour respectively. However, 5-layer annealed specimens showed almost no differentiation in terms of their UTS, ranging between 55 -56 MPa.

The degree of crystallinity and molecular weight have impacted the mechanical properties of a polymer (Wang *et al.*, 2010). In this study the Young's Modulus and tensile strength increased by 30% and 20% respectively following annealing due to a higher degree of crystallinity. The decrease in Young's Modulus at 90°C and UTS could have occurred due to molecular deterioration or delamination of adjacent layers caused by thermal annealing (Seo *et al.*, 2014). However, there was no evidence of thermal degradation within this study. At 4, 8, and 16 hours annealing there was no significant difference in terms of the observed Young's Modulus, and the UTS was also reflective of the value of degree of crystallinity and molecular weight.

4 Conclusion

Non-annealed each layered thin specimen were not suitable for degradation studies due to the distortion at 37°C. This distortion was eliminated via the annealing process. The followings are the main outcomes for distortion calculation of each layered non-annealed specimen subjected to degradation and for properties of annealed specimens:

- The distortion of non-annealed specimens in x-direction reduced by increasing the number of layers while distortion in the y-direction increased with increasing the number of layers for 3-layer specimens but decreased for 5-layer specimens.

- Each layered annealed specimen at 90°C for 2 hours possessed the highest degree of crystallinity with a value of 34%; however, 70°C annealed specimens obtained the lowest at 6%. Following, degree of crystallinity of each layered specimen annealed at 80°C linearly increased up to 4 hours, and then plateaued for each layered specimen.
- The highest Young's modulus was recorded for each layered annealed specimen at 80°C for 2 hours while the lowest was at 70°C for 2 hours. The uppermost increase was 35% for 1-layer annealed specimens at 80°C for 2 hours in comparison to 2 hours annealing at 70°C.
- The maximum UTS was also high for each layered annealed specimen at 80°C for 2 hours and the minimum UTS was documented for annealed at 70°C. The UTS of each layer overlapped for annealed specimens at 80°C for 2, 4, 8 and 16 hours.

The insights and outcomes from this research will directly inform future research activities focused on the utilisation of material extruded thin films for the design, development, and optimisation of degradable biomedical implants.

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