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Mechanical and Hydrolytic Properties of Thin Polylactic Acid Films by Fused Filament Fabrication

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ABSTRACT

Thin polymeric films are widely used as medical applications such as cell culture, stent, drug delivery and mechanical fixation. One of the most commonly used materials is polylactic acid (PLA) - a material, which is non-toxic, biodegradable and biocompatible. In fused filament fabrication (FFF), an additive manufacturing technique, thin films can be manufactured using PLA. FFF is a promising technique for customised biomedical applications due to its relatively low cost and geometrical flexibility where biomedical applications are patient tailored. This study is the first to consider FFF monolayered thin films in terms of mechanical and hydrolytic properties at 37 °C *in vitro* degradation. Throughout degradation, the reduction in mechanical properties was examined by analysing molecular weight and thermal properties. Young's modulus, ultimate tensile strength and molecular weight reduced by approximately 60%, 86%, and 80% after 280 days, respectively, while the degree of crystallinity increased by 143% in comparison to benchmark thin films at day 0. This study provides practical information in terms of mechanical properties to support medical device designers in a range of potential end-use

biomedical applications to achieve safe functional products over the required degradation lifetime.

Keywords: additive manufacturing, fused filament fabrication, polylactic acid, monolayered thin film, hydrolytic degradation, mechanical properties

1. Introduction

Of all aliphatic polymers, polylactic acid (PLA) is a relatively cheap thermoplastic, is easy to process, is non-toxic, and produced from renewable resources (Gonzalez Ausejo et al., 2018). In addition, PLA can be metabolised by biological activities, and therefore, assuming that a PLA-based device is appropriately designed and manufactured, there is no need for surgery to remove such an implant from the body (Ginjupalli et al., 2017). PLA possesses a large range of mechanical and physical properties which when combined with its biodegradability and biocompatibility by hydrolytic or enzymatic degradation, can be utilised for the design and manufacture of temporary biomedical devices (Tyler et al., 2016). Hydrolysis is mostly chosen comparing to enzymatic degradation due to insignificant alteration among patients in terms of the degradation rate in the human body (Gunatillake et al., 2003; Maitz, 2015; Nair and Laurencin, 2007). The degradation is water involved, and cleavage of the ester bonds is primarily presented through the backbone of the PLA (Hayashi, 1994). Carboxylic acid end groups cause hydrolysis. Therefore, hydrolytic degradation of the polymer lead to autocatalysis (Siparsky et al., 1998). Due to autocatalysis, immersing a polymer in a 7.4 pH at 37°C causes bulk hydrolysis where there is no change in size and shape; however, the structure is weakened. (Laycock et al., 2017). Hydrolytic degradation behaviour of PLA and PLA-based compounds in neutral environments have been widely studied (Fukushima et al., 2011; Mainil-Varlet et al., 1997; Proiakakis et al., 2006; Saha and Tsuji, 2006; Vieira et al., 2011; Weir et al., 2004).

It has been examined that the degradation rate of a polymer is dependent on a number of complex features (Karamanlioglu et al., 2017). Molecular weight is the most significant factor where a high molecular weight increases the degradation time and has shown to significantly impact the degradation rate (Mauduit et al., 1996). Additionally, molecular weight is a principal factor affecting mechanical properties. The degree of crystallinity that consists of both amorphous and crystalline regions is another major feature. Amorphous regions are strongly influenced by hydrolysis compared to crystalline regions during the degradation of PLA as water can diffuse into amorphous domains easily in comparison to crystalline domains (Karamanlioglu et al., 2017). The degree of crystallinity also influences the mechanical properties of PLA, much like molecular weight, where higher-level crystalline specimens demonstrate higher mechanical properties.

There is a range of possible thin biomedical applications of PLA, including, cell carriers, stents, drug delivery, and structural elements to hold tissues or cells together (P. Pawar et al., 2014). Medical applications, being patient-tailored, require precise design, high accuracy and geometrical flexibility. These features are often restricted when traditional manufacturing processes are used. Through the development in Additive Manufacturing (AM) which is used 3-dimensional (3D) digital data, the ability of manufacturing patient based medical applications is materialised (González-Henríquez et al., 2019). One commonly used AM technique is fused filament fabrication (FFF) which is highly suitable for printing PLA. When printing 3D objects with FFF, the raw polymer filament is first melted and then formed through a nozzle to create a layered object in line with user specified process parameters such as infill density, thickness, extrusion temperature, and print bed temperature (Chacón et al., 2017; Dizon et al., 2018; Ekinci et al., 2020; Lanzotti et al., 2015). FFF has high product manufacturing potential and also has the potential to be utilised ahead of some traditional polymer processing methods (Kruth et al., 1998). This technology performs excellent benefits such as high efficiency,

simplicity, reduced manufacturing and design cycle time, eliminated any tooling, and efficiency on material and as well as cost (Guo and Leu, 2013; Zhai et al., 2014). Since biomedical applications manufactured by FFF are layer by layer, the complex behaviour between printed layers within an FFF object presents a significant challenge (Ngo et al., 2018; Sun et al., 2008), which may inhibit fundamental understanding. Therefore, it is important to initially examine the performance and behaviour of monolayered components. Additionally, thin specimens have direct medical applicability as discussed above. There are no comprehensive studies for mechanical and hydrolytic properties degradation of fused filament fabricated PLA at 37 °C; therefore, the first attempt on the mechanical and hydrolytic properties of monolayered thin films that featured a thickness of 100 µm is examined in this study. Additionally, specimens were visually checked, with thermal, molecular weight, mass change, and water uptake were characterised.

2. Materials and methods

2.1 Materials

2.85 mm PLA filament (3DXTECH® branded NatureWorks® polylactide 4043D, Sigma Aldrich, LOT: 85633) was used within this study as a biodegradable polymer. According to the supplier, the PLA filament contains less than 4% d-isomer. Initial number average molecular weight (Mn) and weight average molecular weight (Mw) were not supplied. Density, glass transition temperature, tensile strength and tensile modulus were given at value of 1.24 g cc⁻¹, 60 °C, 56 MPa and 2.865 GPa respectively.

2.2 Specimen preparation and hydrolytic degradation

From the raw material through complete degradation, there were four processes; printing, annealing, cutting and degradation, as presented in Figure 1.

Figure 1. Specimen preparation and degradation method

A monolayer printed thin sheet of PLA with a length and width of 100 x 100 mm was manufactured with a layer thickness of 100 μm . Key manufacturing process parameters such as line width, printing speed, extrusion temperature and bed temperature were set at 0.36 mm, 80 mm s^{-1} , 210 $^{\circ}\text{C}$ and 60 $^{\circ}\text{C}$ respectively. The raster angle was 0° to the x-direction using a zigzag pattern until completion. Following, a printed sheet was placed between two aluminium plates and subjected to annealing at 80 $^{\circ}\text{C}$ for two hours. The monolayered thin films were stamped using ISO-527 2A type 5 to generate seven specimens from each sheet. In total, eight sheets were printed and annealed, and 56 specimens were stamped.

For degradation, test specimens were placed in 28ml screw-top glass bottles. The specimens were submerged in a phosphate-buffered solution (PBS) acquiring a pH of 7.4. Finally, the bottles that contained specimens were stored in an incubator (Genlab - INC/50/DIG, Wolf labs, UK) at 37 $^{\circ}\text{C}$. The temperature was kept constant throughout the degradation investigation. In accordance with ISO 13781:2017, the ratio of PBS in millimetres to the mass of the monolayered thin specimens in grams was maintained to at least 30:1 or higher. The pH of each specimen bottle was regularly measured every 14 days, with the PBS appropriately changed to ensure a pH a range of 7.4 ± 0.2 was maintained. Each degradation time required at least eight monolayered thin tensile specimens where five were used in mechanical testing and three were used for identifying the water intake and mass change. Following measuring mass change, the dried specimens were used to determine molecular weight and thermal properties. The specimens were tested at the same degradation time with 30, 60, 90, 120, 240 and 280 follow up days.

2.3 Characterisation

2.3.1 Water intake and mass change

The masses of three specimens were weighted using an electronic balance (PIONEER® ANALYTICAL, OHAUS, SW) before storing the specimens in the incubator. After each degradation time, the specimens were removed from the oven and then wiped with a paper towel to drain any excessive aqueous media. The specimens were then directly weighted in order to measure the water intake, with mean water intake established using equation 1.

$$WI (\%) = ((\mu - m_0) / m_0) * 100 \quad (1)$$

where WI (%), μ and m_0 were, percentage of water intake, the mass of undried specimen, and initial mass respectively.

The specimens were stored in a vacuum oven (Jeio Tech OV-11, Medline scientific, UK) at 30°C for 48 hours at a vacuum of 51 centimetres Hg Torr to calculate the mass change using equation 2 at each degradation time point.

$$MC (\%) = ((m_d - m_0) / m_0) * 100 \quad (2)$$

Where MC (%), m_d and m_0 were, mass change in percentage, dried mass, and initial mass respectively.

2.3.2 Thermal properties

Differential Scanning Calorimetry (DSC) (TQ 200) was used to determine specimen thermal properties such as glass transition (T_g), cold crystallisation (T_c) and melting temperatures (T_m), melting (ΔH_{melt}), and cold crystallisation enthalpy (ΔH_{cc}) using a 50 ml min⁻¹ nitrogen flow rate. Each section for DSC testing weighed approximately 6 mg, was extracted from the

middle of each test specimen, and was tested with 10 °C min⁻¹ increments from 30 °C to 200 °C. The degree of crystallinity (% χ) was calculated using equation 3.

$$\% \chi = (\Delta H_{\text{melt}} - \Delta H_{\text{cc}}) / \Delta H_{\text{ref}} \quad (3)$$

Where ΔH_{ref} was referenced as 93.64 J g⁻¹ for %100 PLLA crystalline.

2.3.3 Molecular weight

Number average and weight average molecular weight, and their distribution, Polydispersity index, (PDI) (Mw/Mn) were determined using Waters® Breeze™ 1515 Gel Permeation Chromatography (GPC) system (2414 differential detector) with a chromatographic column of Agilent PLgel 5 μ m MIXED-C (GB). Thin films cut from the centre of the specimen dissolved in chloroform at a concentration of 2 mg ml⁻¹. Average and standard deviation were obtained using of two measurements. The temperature was kept at 35 °C with a flow rate of 1 ml min⁻¹ and polystyrene used as a standard material.

The hydrolysis mechanism is regarded to be uncatalysed and autocatalyzed (Lyu et al., 2007). Both uncatalysed and autocatalysed degradation model can be used to calculate the hydrolysis rate. In uncatalysed degradation, the water cleaves the ester bonds, and there should be a linear relationship between time and 1/Mn for each degradation time. The equation 4 is used for uncatalysed degradation (Lyu et al., 2007):

$$1/Mn_t = 1/Mn_0 + kt \quad (4)$$

Where, Mn_t, Mn₀, k and t are defined as Mn at time t and initial, degradation constant rate and time respectively.

PLA which is a condensation polymer is an insoluble polymer in aqueous media, and therefore the hydrolysis of ester bonds requires an aqueous media which is an important constituent to

form carboxyl and hydroxyl end groups to facilitate its diffusion into the cleaving ester bonds. Cleaving ester bonds can be achieved by catalysation of the carboxyl end groups of oligomers and monomers and results in autocatalytic degradation. An autocatalysed model was created based on carboxylic acid end groups and followed equation 5 (Pitt and Zhong-wei, 1987):

$$d[E]/dt = -d[COOH]/dt = -k[COOH] [H_2O] [E] \quad (5)$$

where, [COOH] is concentrations of carboxyl end groups, [H₂O] is water and [E] is esters.

The ester bond cleavage rate is proportional to time according to the basic hydrolysis kinetics model. Presuming the water and ester are constant, the final autocatalysed model related to molecular weight can be given as shown in equation 6:

$$Mn_t = Mn_0 e^{kt} \quad (6)$$

This equation can be then interpreted to find equation 7:

$$\ln Mn = -kt + \ln Mn_0 \quad (7)$$

2.3.4 Mechanical properties

Mechanical properties were measured using a universal testing system (Instron 3345 with a 5000 N load cell) under a speed of 1 mm min⁻¹. Following removal from the aqueous media in accordance with ISO 13781:2017 standard, five monolayer tensile specimens were wet during testing. From these five specimens, an average and standard deviation of Young's modulus (E) and ultimate tensile strength (UTS) were determined.

3. Results and discussion

The degraded thin film specimens were visually inspected, and molecular weight and thermal properties determined. Following, the mechanical properties were calculated to understand how the properties decreased through degradation.

3.1 Visual examination

Degraded monolayered thin specimens at each degradation time are presented in Figure 2. The non-degraded specimens were opaque, and the colour changed from opaque to white during degradation, as shown in Figure 2.

Figure 2. Visual examination of monolayered thin specimens at each degradation time point

The specimens slowly turned to white colour until day 90. It was observed that the complete monolayer specimen shifted to white colour at 120 days. The colour change can be explained due to forming crystal during degradation (Pantani and Sorrentino, 2013). However, the size and shape did not change at each degradation time point. This outcome can give an insight to understand the degradation mechanism of bulk degradation (Tsuji, 2010).

3.2 Molecular weight

Molecular weight is known to be the most significant property that affects degradation, as well as properties such as glass transition temperature, Young's modulus, and UTS. Molecular weight decreased over time during degradation, where at day 0, Mn and Mw were recorded at 53.95 kDa and 137.80 kDa respectively. Following, obtained values of Mn and Mw at each degradation time point are shown in Figure 3.

Figure 3. Changes in Mn and Mw of monolayered thin specimen through degradation (gray line inside the markers demonstrates the error bars)

After 30 days, the Mn and Mw of the monolayer specimens decreased by 10% and 25% respectively. At 120 days the Mn of specimens were half that originally recorded at day zero, while Mw was halved by day 90. After 280 days, the reduction for Mn and Mw was around 81% and 83% respectively, with recorded values of 10.33 kDa and 22.84 kDa. Therefore, the PDI demonstrated no obvious pattern and ranged between 2.11 and 2.46. In Figure 3, the Mn and Mw decreased exponentially with time with a high R^2 correlation with the values of 0.97 and 0.99 respectively.

Analysing the molecular weight data demonstrated in Figure 4a and Figure 4b with equation 4 and equation 7, the degradation rate constant was ascertained using linear regression. Considering the linear equations demonstrated in Figure 4a and Figure 4b, the degradation rate constant and correlation coefficient were calculated as presented in Table 1 for monolayered thin specimens for uncatalysed and autocatalysed models. The degradation rate constant was found at a value 0.00029 day^{-1} with high correlation coefficient at 0.97 for uncatalysed model and 0.00617 day^{-1} with high correlation coefficient at 0.98 for the autocatalysed model.

Figure 4. Degradation models a) uncatalysed degradation model ($1/M_n$ vs degradation time)
b) autocatalysed degradation model ($\ln M_n$ vs degradation time)

Model	Uncatalysed		Autocatalysed	
Temperature	k (day^{-1})	R^2	k (day^{-1})	R^2
37 °C	0.00029	0.9678	0.00617	0.9826

Table 1. Degradation rate and linear coefficient of monolayer specimen at 37 °C degradation
for uncatalysed and autocatalysed model

Both the uncatalysed and autocatalysed model showed almost a similar behaviour with a high linear correlation. The uncatalysed hydrolysis theory is validated with the experiments done by Schliecker et al. due to finding no acceleration on degradation with adding oligomers (Schliecker et al., 2003). The autocatalytic hydrolysis theory is supported by other experimental studies (Schliecker et al., 2003; Siparsky et al., 1998; Tsuji, 2002). The autocatalytic model has been widely used on publications because this model is well-matched with the experimental data in aqueous media (Lyu et al., 2007; Schliecker et al., 2003; Tsuji, 2002). Additionally, not taking into account the possibility of autocatalysis accelerated the rate of degradation of the polymer is a disadvantage of uncatalysed approach (Weir et al., 2004).

Utilising GPC enabled the collection of key molecular weight information, therefore obtaining more data about the complex nature of biodegradable polymer degradation, and also providing information about the molecular weight distribution of samples by narrowing the entire GPC chromatogram. GPC chromatograms of the monolayer degraded specimens are presented in Figure 5 at 0, 60, 120, and 240 days.

Figure 5. GPC chromatogram of degraded specimen at 0, 60, 120 and 240 days

With hydrolytic degradation, GPC chromatograms shifted to low molecular weight with similar monomodal distribution.

3.3 Water Intake and mass change

The water intake is an amount of absorbed water due to ingress of the aqueous media into the test specimens, and mass loss resulted from oligomers and monomers solved in the aqueous media. In monolayered thin specimens, mass loss and gain were observed therefore, the mass change was calculated. The water intake and mass change of monolayer degraded specimen is presented in Table 2.

Days	30	60	90	120	180	240	280
Water Intake (%)	0.22	0.30	0.59	0.85	2.99	3.93	18.19
Mass Change (%)	-0.35	-0.25	-0.18	-0.09	0.09	0.17	0.23

Table 2. Water intake and mass change in percentage for each degradation time period

There was a slight increase in terms of water intake in specimens between 0 to 120 days degradation, ranging from 0.2% to 0.85%. At 240 days, the water intake increased to approximately 4%; however, the most notable result from Table 2 is that the water intake increased to 18% at 280 days. This extreme growth could be ascribed to extensive pores and cracks (Lehtonen et al., 2013). Additionally, water intake can have an effect on the degradation rate where low water intake slows the degradation and can be dependent on molecular weight. The water intake steadily increased until it reached the critical M_n and then it increased substantially. Generally, mass loss of a polymer-based specimen begins when the specimen is immersed in the water and continues until a critical point. However, both mass loss and mass gain has been observed in this study. It can be seen in Table 2 that; the mass loss was 0.35% at day 30 while the mass gain was 0.23% at day 280. The mass gain could be due to aqueous

media being trapped in the specimens in spite of drying (Ndazi and Karlsson, 2011). This could be interpreted that there was no evidence of mass loss while molecular weight decreased (Shi et al., 2018). Therefore, it can be stated that the monolayer thin specimens demonstrated bulk degradation.

3.4 Thermal properties

Table 3 presents thermal properties, including glass transition temperature, melting temperature, and degree of crystallinity of monolayer test specimen at each degradation time point.

Days	0	30	60	90	120	180	240	280
T_g (°C)	60.52	61.06	63.45	62.62	59.84	55.84	54.33	49.80
T_m (°C)	150.60	150.36	150.91	150.89	153.63	152.93	152.05	149.68
%	20.15	23.64	25.29	27.32	32.00	36.75	42.63	48.97

Table 3. Glass transition temperature, melting temperature and degree of crystallinity at each degradation time point

Thermal properties such as glass transition and melting temperatures and the degree of crystallinity are other important factors that affect degradation. As demonstrated in Table 3, the change in melting temperatures was not significant during degradation. The melting temperature remained similar until 90 days and slightly increased until 240 days and then decreased with increasing degradation time point. Following, the diffusion of aqueous media, at a molecular grade, improves the free volume resulted in increased chain mobility. Therefore, the increase could be related to the development of perfect crystals, while the reduction at 280 days could be associated with surface erosion of the crystalline region (Pantani and Sorrentino,

2013). However, this is not yet clear, and understanding the decrease in melting temperature requires further investigation.

The glass transition temperature, as presented in Table 3, ranged from 63.45 °C to 49.80 °C during degradation. The glass transition temperature remained almost plateau with a slight increase until 60 days. However, the glass transition temperature started to decrease until day 280. It is formulated that glass transition temperature is related to molecular weight and aligns with the Flory-Fox equation as expressed by equation 8 (Fox and Flory, 1954, 1950).

$$T_g = T_{g\infty} - (K/M_n) \quad (8)$$

Where $T_{g\infty}$ is the glass transition temperature at infinite molecular weight, and K is the constant of the free volume end groups. The relationship between glass transition temperature and molecular weight of the degraded specimens is illustrated in Figure 6a.

Figure 6. a) Changes in glass transition temperature over molecular weight, b) relationship between glass transition temperature over $1/M_n$ according to Flory-Fox equation

The glass transition temperature increases with an increased molecular weight until a critical point was reached and then remained constant. By using equation 8, the $T_{g\infty}$ and K were found and shown in Figure 6b. The linear coefficient determination, R^2 , was recorded at 0.89. The

glass transition temperature at infinity molecular weight was found to be 65.5 °C and constant K calculated at 151 °C kDa⁻¹ for degraded monolayered thin specimens respectively.

The degree of crystallinity showed an increase during degradation, as presented in Figure 7. Thin specimens increased exponentially with a high R² at 0.99. At 280 days, the degree of crystallinity increased by approximately 143% from 20.15% to 48.97%.

Figure 7. Increase in glass transition temperature through degradation

The chain cleavage during the degradation progress, especially in the amorphous region results in a higher degree of crystallinity. This increase is associated with crystallisation during degradation due to higher chain mobility as a result of the existence of water and a decreased molecular weight (Tsuji and Muramatsu, 2001). Therefore, a relationship between a normalised degree of crystallinity and normalised molecular weight as a function of time is demonstrated in Figure 8.

Figure 8. Correlation between normalised degree of crystallinity and molecular weight over normalised time

3.5 Mechanical properties

The mechanical properties including Young's modulus and UTS at each degradation time period were calculated from five stress-strain curve, as presented in Figure 9.

Figure 9. Typical stress-strain behaviour of specimen at 0, 60, 120, 180 and 280 days

Overall, the stress-strain curve for each tested time period shifted from ductile to brittle behaviour with an increasing degradation time. Figure 10 presents a linear reduction in Young's modulus, with a high confidence interval for R^2 above 95%, with increasing degradation time.

Figure 10. The reduction in Young's modulus over degradation time

The mean Young's modulus was recorded at 1.91 ± 0.09 GPa at day 0. At the start of the degradation process, for example, at 30 days and 60 days, the Young's modulus of specimens decreased sharply - decreasing by 13% at 30 days and by 21% at 60 days in comparison to benchmarked specimens. Between 60 and 180 days, the decrease in Young's modulus was slower. Monolayer degraded specimens demonstrated a reduction in Young's modulus by approximately 50% at 240 days in comparison to their initial Young's modulus, while the Young's modulus at 280 days had decreased by approximately 60%.

During degradation, a reduction in Young's modulus was expected. Since biodegradable materials are used for the creation of temporary body implants, understating the reduction rate of Young's modulus was crucial. Young's modulus is also associated with molecular weight.

The degradation is initiated by chain scission resulting in a decrease in molecular weight and Young's modulus (Ding et al., 2012). Additionally, the chain scission in the lamella of amorphous regions led to a reduction in the Young's modulus (Tsuji et al., 2000). In some previous studies, the Young's modulus initially increased, and there was a delay between a decrease in Young's modulus and decrease in molecular weight. However, this study contradicts those results. In polymers, the lamella is expected to have a robust connection called "tie-chains" (Chu, 1981). Here, the Young's modulus is dependent on the density of the tie-chains; therefore, the decrease in Young's modulus would be based on the amount of tie-chain scission where there should be no delay between a decrease in molecular weight and Young's modulus.

Additionally, an entropy-based study for amorphous polymer modelled by Wang et al. demonstrated the relationship between the molecular weight and Young's modulus (Wang et al., 2010). In spite of modelling for amorphous polymer, this theory can be used for semi-crystalline polymers with a low degree of crystallinity. Similar behaviour to that presented in Figure 11 has been observed in previous studies. The slow reduction in both Young's modulus and Mn continued until a critical point, in this study this point being approximately 70% of the initial molecular weight, then a sharp decrease occurred.

Figure 11: Normalised Young's modulus over normalised molecular weight

As well as Young's modulus and molecular weight, there was also a reduction in UTS through degradation, as shown in Figure 12. The mean UTS at day 0 was 49.28 ± 1.64 MPa.

Figure 12: Demonstration of UTS at each degradation time

Monolayered thin specimens lost their UTS by almost 22% at day 30 in comparison to benchmark specimens at day 0. At 120 days, the remained UTS was measured at 58%, while 50% reduction was projected at day 145 using the linear equation demonstrated in Figure 12.

Following, the UTS decreased by 75% at 240 days, and finally, the value of UTS decreased to 14% at 280 days.

There is still remains some uncertainty about the change of tensile strength of specimens following hydrolytic degradation. Tensile strength is influenced by molecular weight and degree of crystallinity. The low molecular weight decreases the strength of the material while increasing the degree of crystallinity enhances stiffness and strength (Zhang et al., 2019). However, the increase in the degree of crystallinity through degradation was moderate. The positive effect of crystallinity on the mechanical tensile strength is less significant than the negative effect of molecular weight on tensile strength (Pan, 2015). Therefore, the witnessed reduction in the mechanical properties of specimens is nearly identical to the decrease in molecular weight, thus the reduction in strength could be directly associated with a decrease in molecular weight. The change in UTS using molecular weight data is presented in Figure 13a.

Figure 13: a) Changes in UTS over molecular weight b) linear relationship between UTS and $1/Mn$ based on Flory's theory

The monolayer specimens followed Flory's theory where the UTS steadily decreased at high molecular weight, with a significant linear decrease occurring with a decrease in Mn. Equation

9 was used to calculate the tensile strength at infinite molecular weight using Flory's theory (Farrar and Gillson, 2002):

$$\sigma = \sigma_{\infty} - (A / M_n) \text{ Equation} \quad (9)$$

Where; σ , σ_{∞} , A and M_n are strength, strength at infinite molecular weight, constant and molecular weight respectively. The σ_{∞} and A were calculated using the linear trendline of UTS versus $1/M_n$ as shown in Figure 13b. The linear coefficient correlation was 0.90 while the UTS at infinite molecular weight was calculated to be 48.56 MPa.

4. Conclusion

The results and understanding from this study can be potentially applied to enhance the operational performance of bespoke thin biomedical devices for a range of functions. Understanding the degradation effects of the monolayered thin films of a PLA using FFF component is crucial. FFF printed thin films can be manufactured patient based with relatively low cost, reliability and geometrical flexibility. The current study examined the *in vitro* degradation of monolayered thin films manufactured via FFF at 37 °C for up to 280 days across seven distinct time points. Molecular weight, mass, thermal, and mechanical properties alongside supporting theories have been presented in order to understand the degradation behaviour of monolayer specimens. The following notable outcomes are obtained from this investigation, including:

- The relationship between the Young's modulus and molecular weight was observed when both Young's modulus and molecular weight were normalised. The Young's modulus steadily decreased by 20% while the molecular weight decreased by approximately 70% until day 180; whereas, it was followed by a sharp linear

reduction in Young's modulus, while there was only an additional 10% reduction in molecular weight.

- The UTS decreased by approximately 22%, 50% and 86% at day 30, 145 and 280 respectively. Monolayered thin films followed Flory's equation in terms of UTS where UTS at infinite molecular weight was recorded at 48.6 MPa.
- There was no significant mass change during degradation as monolayer specimens demonstrated autocatalysis bulk degradation with a high linear coefficient at 98%.

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