Article

Effects of Heating PLA for Controlling Accelerate Ageing after FFF

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Abstract: The effects of post-treatment temperature-based methods on 1D single PLA filaments after FFF have been studied. This lets to decouple the variables related to the 3D structure (layer height, raster angle, infill density, and others) from the variables solely related to the material (molecular weight, molecular orientation, crystallinity, and others). PLA 1D filaments have been aged at 20, 39, 42, 51, 65, 75 and 80 ºC in a water-bath-inspired process in which the hydrolytic degradation of the PLA has been minimised for the ageing temperatures of interest. The evolution of the thermal and mechanical properties of the PLA filaments at different temperatures was recorded. Differential scanning calorimetry (DSC) was used to evaluate thermal and physical properties, in which the glass transition, enthalpic relaxation, crystallisation and melting reactions were analysed. Tensile tests were performed to evaluate the tensile strength and elastic modulus. The flow-induced molecular orientation, the degradation, the logistic fitting and the so-called summer effect –stabilisation of properties at higher temperatures– are discussed for assessing the safeness of accelerating ageing.

Keywords 1D PLA filaments; mechanical properties; thermal properties; temperature; ageing

1. Introduction

Polylactic Acid (PLA) is a biomaterial commonly studied for biomedical applications. It is also being researched as a matrix on PLA composites which can be printed as 3D structures and used for scaffolds that will help to regenerate tissues [1]–[4]. All of this is of great interest. However, before testing any PLA or PLA-based composite materials, it should be mandatory to age the PLA fully –and prove it– to make possible the comparison of results between the research community. This said, in our first work on PLA filaments, we did a comprehensive study on how the neat PLA naturally aged. It was obtained that a high molecular weight PLA (PLA 2003D from Nature Works with 182.000 g/mol) required up to 90 days –inside ZIP bags with desiccant– to stabilise its mechanical and thermal properties. That result never published before brought our attention to controlling and accelerating the ageing of the PLA filaments at our desire.

It is not new that the ageing rate of a polymer can be controlled with temperature. It is well known that the ageing rate can be accelerated by increasing the temperature. In our previous work dealing with the ageing rate of the PLA, it was demonstrated that its ageing could be safely stopped by freezing the PLA at -24 ºC. However, no research was done on accelerating its ageing. For effective ageing in which the properties increase until they stabilise, it is necessary to use temperatures as close as possible but below the glass transition (T_g). Tg is a second-order transition in which the polymer chains highly increase their mobility, and this is observed in a DSC scan as an endothermal drop. This drop is not instantaneous, but it is defined at some point between a changing line in the DSC graph, meaning that there is an onset and an offset temperature. There are different methods for defining Tg, but they provide higher temperature values than the onset temperature. Thus, slightly lower values than T_g should be used, more precisely, smaller than the onset temperature. Even more, the value of T_g depends on the DSC or DMA's heating rate,

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which is the measured Tg lower at lower heating rates. This means that even it a T_g value is measured at 10ºC, ageing at 1 degree that measured T_g might not age the polymer. If this is not complicated enough, the Tg value increases with the ageing of the PLA. Thus, the T_g values measured on aged samples are unsuitable for ageing a right-after-printed material.

Regarding PLA and the literature, plenty of works study the effect of heating the PLA after it was processed via FFF. Some researchers have studied thermal treatments at temperatures above Tg to improve the mechanical properties of PLA by increasing the crystallinity [5] weaver. We know that none of them considered the isolated printed filament (1D) after FFF; only the whole 3D printed structure. This is a crucial handicap, as the number of variables influencing the final properties of any 3D-printed structure is enormous. Most of the studies were related to 3D-printed PLA structures. Even though they try to simplify the problem to fewer variables, the same problems arise: 1) the number of variables affecting the final properties of the PLA is considerably considerable (infill density, nozzle temperature, printing speed, layer thickness, raster angle, bed temperature) [6] and, 2) the effects of the structure and material on the properties of the product are mixed by essence, the mechanical properties of the material – analysed here – are always based on the geometry of the product [6]–[8].

From a scientific perspective, it is helpful to understand how the thermal treatments affect the material decoupled from the structure as much as possible. Studying the most fundamental building block of any 3D printed structure, a 1D filament will help unveil which phenomenology is underlying the changes observed in a 3D printed product after a thermal treatment. This way, it can be decoupled the changes related to the structure – for example, the improvement of the filament-filament adhesion – from the changes related to the material itself – for example, degradation of the PLA or ageing, simplifying the multivariable problem of 3D printed parts from a novel perspective not found on the literature.

This paper will analyse and discuss the effects solely affecting the material (filaments) when its ageing is accelerated by increasing the ageing temperature. Decoupling the structure effects from the material ones will be possible by studying 1D filaments, following the methodology developed in previous works of the group [1], [9], [10]

This paper complements our previous study on controlling the ageing of the PLA [10]. The effects of freezing the PLA to stop its ageing are understood in that study. Now we are looking to understand the opposite, how accelerating the ageing rate by increasing the ageing temperature impacts the mechanical and thermal properties of the filaments after FFF, the building block of any 3D printed structure. Furthermore, an economical method is also proposed for the safe age of PLA materials.

Accelerating the ageing is essential to shorten the research schedule, and here it is understood the effect on the material decoupled from the 3D printed structure by studying 1D printed filament. Together with the freezing of the PLA, this work enlightens these aspects:

1. The effects on the material decoupled from the 3D structure will help to understand how thermal treatments affect the 3D structure, where more variables are included, like height layer, printing direction, infill percentage, bed temperature, printing speed, nozzle size, and many more, among others.

2. A method to adapt the research schedule to the circumstance.

3. The importance of studying aged materials is essential for comparing with confidence the research community's work.

2. Materials and methods

This study analysed the first three months of natural ageing as it was known from our previous study that a high-molecular PLA required three months of natural ageing at 20 ºC for stabilising its properties. As the primordial objective was to compare the room

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temperature (20 ºC) with the samples aged at higher temperatures (39, 51 and 65 ºC), no other times were considered.

A summary of the methods is provided in figure 1.

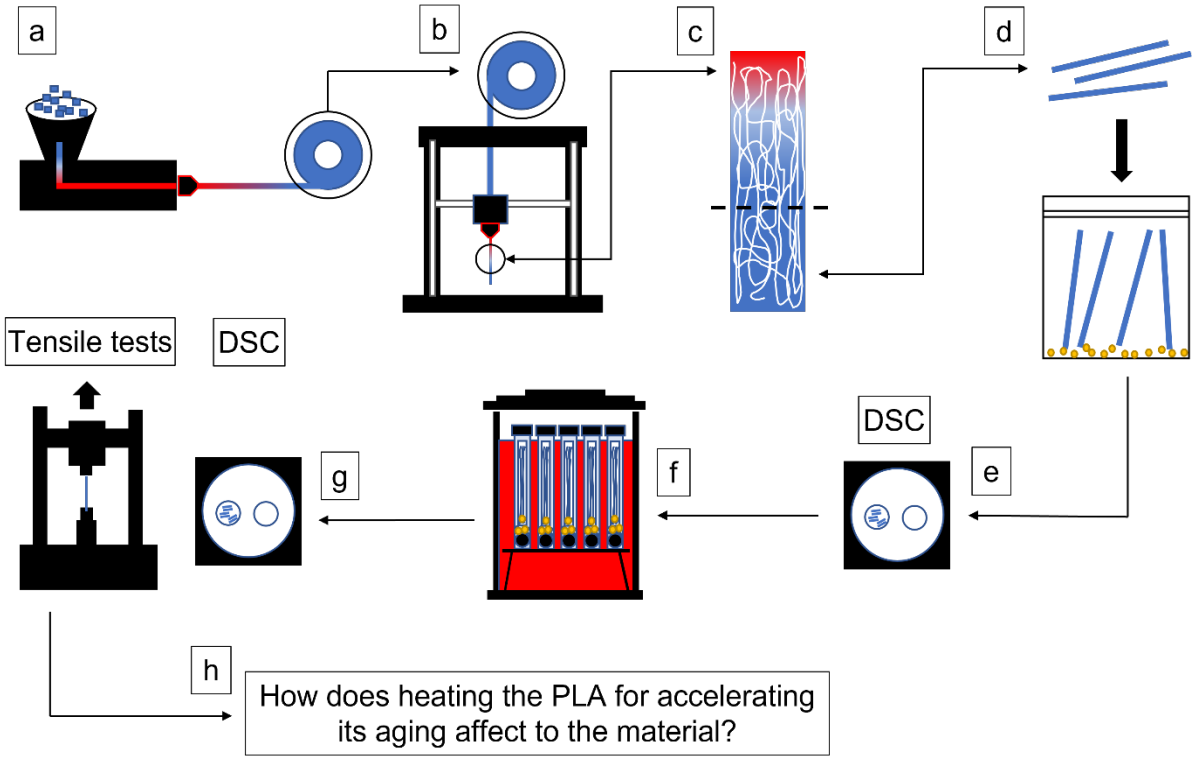

Figure 1. – Scheme of the experiments performed.

2.1. Materials and FFF

The material studied was the 4043D from Nature Works and supplied by Presa. The material was printed in a Prusa i3MK3S+ with a 0.4mm nozzle at 215 ºC and an extrusion rate of 20 mm/s. Filaments with diameters between 350 and 450 micrometres were obtained. Printed filaments were stored inside zip bags with a desiccant inside to ensure a low-humidity-controlled atmosphere, essential to avoid any degradation by hydrolysis of the PLA. The PLA was printed in a room at 23 ºC and ambient humidity and frozen at -24 ºC right-after-printed (2 hours of natural ageing at 20 ºC).

This material was compared with the 2003D from Nature Works, a high molecular weight PLA (182.000 g/mol) used in our previous studies [1], [9], [10].

2.2. Ageing procedure

Ageing at room temperature was performed inside PET zip bags with desiccant. The bags were later placed in a dark room, with no UV light sources and at a controlled temperature of 20 ± 1 ºC. The ageing temperatures were 39, 42, 51, 65, 75 and 80 ºC. The reason for these temperatures is explained through the discussion. The ageing at temperatures higher than room temperature was done inside a water bath device. Instead of water, Premium Mineral Oil 10W-40 (Repsol) was used as a liquid-bath in the device, as shown in figure 2. Then, the PLA filaments were introduced inside PET zip bags with a desiccant inside. After this, the zip bags with the filaments were introduced inside PP test tubes with more desiccant. The PP tubes were sealed with vacuum grease applied to the caps-tube joints. A steel ball was placed at the bottom to ensure the tubes were sunk in the oil. Finally, the tubes were immersed inside the oil, with the oil previously stabilised at the required temperature. The temperature was monitored with a precision of ±0.1 ºC with the help of a thermocouple (FLUKE 50D K/J Thermometer) introduced in a reference test

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tube –and not directly into the oil –ensuring that the measured temperatures were the actual ageing temperatures. The oil level in the oil bath was slightly below the cap-tube joint, as schematised in figure 2.a.

Different methods were tested for the ageing at elevated temperatures, involving water as the hot liquid in the water bath; however, any method involving water instead of oil failed as the desiccant changed its colour in just a few minutes.

The cost of the ageing device with the oil and desiccant was 150 €, making it an economical and practical method for the rest of the researchers.

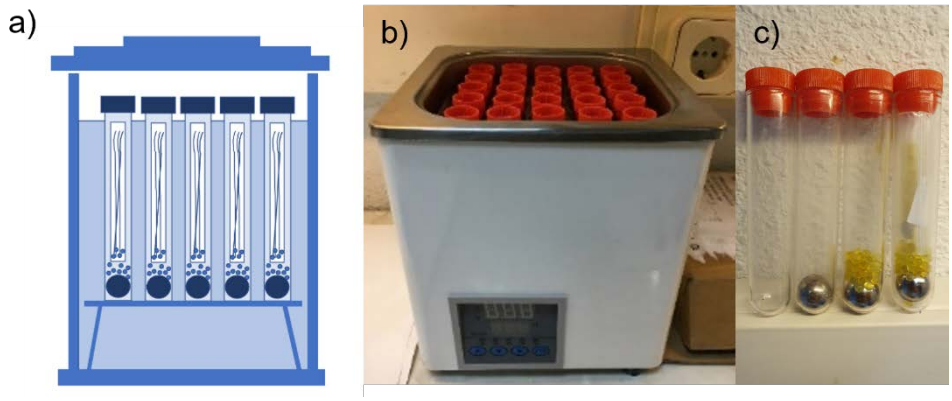

Figure 2. – Ageing device. a) Scheme, b) real ageing device, c) left to right: PP tube, with a ball of steel, with desiccant, with the samples inside zip-bag with more desiccant inside.

2.3. Differential Scanning Calorimetry

The differential scanning calorimetry (DSC) was performed on a Mettler Toledo 822e device at a heating rate of 10 ºC/min from 30 to 180 ºC. The device was calibrated following the Indium standard. Aluminium crucibles of 40 microlitres, in which 4.5 to 5.5 mg of PLA filaments were cut into 2-3 mm pieces, were placed, ensuring that all the pieces were in contact with the bottom, as indicated in figure 2. This was important to minimise measurement errors, as it was found that differences of up to 1 ºC were obtained if not all the PLA was in direct contact with the crucible. So, it increases the mass of PLA over the contact surface with the crucible. To ensure that all the PLA studied were under the same conditions, a large batch of printed PLA filaments was frozen, proven as a safe and effective way to store PLA and stop the ageing PLA [10].

2.4. Tensile Test

Mechanical tests were performed on an Instron 5866 universal tensile test machine with a load cell of 1 kN. Before the mechanical testing, samples were attempered at room temperature inside zip bags with desiccant for 2 hours. Then, it followed the same procedure described in our previous study []. The strain rate of 1 mm/min on filaments of 20 mm length, plus 7.5 mm extra on each side that were glued with a cyanoacrylate-based adhesive to cardboard. Then, the cardboard was fitted with mechanical clamps, as shown in figure 3. The clamps were joined to the load cell will rotulas to avoid non-tensile stresses on the filaments during the tests.

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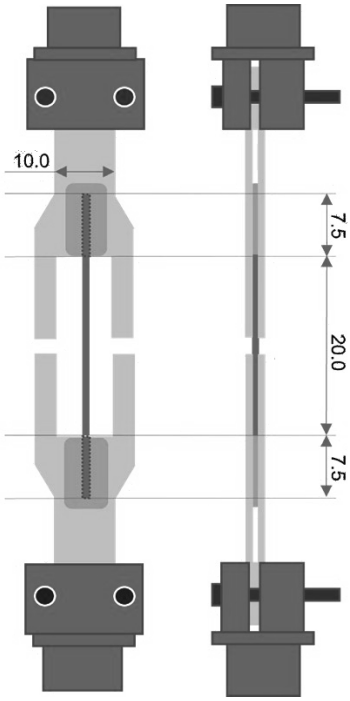

Figure 3. – Mechanical testing of PLA filaments.

For the modelling of the mechanical properties, it was used the logistic model proposed in our previous study [1].

3. Results

3.1. Thermal properties

All the results for the thermal properties measured on the DSC are summarised in table 1.

Table 1. Thermal properties of the extruded 1D PLA. All samples have been printed at 215 °C.

Ageing	Ageing temperature	$T_{g.1}$	$T_{ER.1}$	$\Delta H_{ER.1}$	$T_{g.2}$	T_{CC}	ΔH_{CC}	T_m	ΔH_m	$\chi_{\%}$
0.5 h	20 ± 0.1	-	-	-	54.4	123	-15.2	152	15.2	<3
2 h[1]		45.5	-	-	57.5	123	-15.2	152	15.2	<3
3 h		46.4	-	-	57.6	123	-14.7	151	16.4	<3
1 d		51.5	-	-	59.9	124	-17.0	154	17.2	<3
4 d		54.8	-	-	61.1	121	-16.8	152	16.4	<3
7 d		56.1	58.6	0.15	62.6	122	-15.6	152	15.9	<3
14 d		56.6	58.9	0.79	-	121	-15.8	152	16.3	<3
24 d		56.9	60.0	1.61	-	122	-16.2	152	16.5	<3
49 d		57.2	60.6	2.5	-	122	-15.9	152	16.3	<3
91 d		57.5	61.0	3.7	-	123	-15.7	153	16.5	<3
1 d	**39 ± 0.1**	58.4	61.4	2.0	-	125	-14.4	153	15.2	<3
2 d		59.0	61.7	3.3	-	124	-17.8	152	18.6	<3
4 d		59.4	62.2	4.0	-	125	-14.5	152	15.7	<3
7 d		60.7	63.2	4.4	-	125	-14.7	152	15.5	<3
14 d		61.0	63.5	4.7	-	124	-15.0	152	15.7	<3
24 d		61.2	63.5	5.0	-	124	-15.9	152	17.2	<3
1 d	42 ± 0.1	59.5	62.1	3.2	-	124	-14.0	152	15.4	<3
4 d		63.3	65.6	5.7	-	124	-15.2	152	16.9	<3

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1 d	51 ± 0.1	57.5	61.5	0.6	-	122	-21	152	22	<3
4 d		58.2	62.5	0.9	-	122	-22	152	23	<3
7 d		57.7	62.0	0.8	-	121	-25	151	24	<3
14 d		57.1	63.0	0.7	-	121	-23	152	23	<3
24 d		57.5	62.3	0.8	-	121	-24	152	24	<3
42 d		57.2	62.0	0.8	-	121	-24	152	24	<3
1 d	65 ± 0.1	57.7	61.9	0.6	-	118	-27	150	27	<3
1d	75 ± 0.1	60.8	-	-	-	-[2]	-[2]	154	28	20
1d	80 ± 0.1	61.9	-	-	-	-	0	153	27	28

Temperature measured in ºC with a ± 0.5 error (except indicated), enthalpies in J/g with a 3.4% error of total value, time in hours (h) or days (d) with an error of ± 0.1, all aged samples at temperatures above 20 ºC have been aged after 2 hours of natural ageing (for example, one day at 39 ºC means that the material has been 2 hours at 20 ºC and one day at 39 ºC), crystallinity in percentage (%) with an error of ± 1. Positive enthalpy changes indicate that the material absorbs the energy, following IUPAC's convention. $T_{g.1}$: first glass transition on the DSC during heating; T_{ER}: enthalpic relaxation temperature; ΔH_{ER}: enthalpy of enthalpic relaxation; T_{CC}: cold crystallisation temperature; ΔH_{CC}; enthalpy of cold crystallisation; T_m: melting temperature; ΔH_m: enthalpy of melting; $\chi_{\%}$: Crystallinity percentage. The symbol "-" is used for not detected values.

1. Accelerated ageing materials start from this reference at 2 hours of natural ageing at 20 ºC.

2. A precise calculation is not possible. Values detected, but highly mixed values between alpha' and alpha-related reactions.

To accelerate the PLA's ageing, it is generally said that it must be done at temperatures below T_g. For this reason, T_g was measured on samples right after printing (0.5 and 2 hours) to set a maximum ageing temperature. However, how this maximum ageing temperature should be obtained is not further explained. Our goal was to use the highest temperature possible. Two DSC tests were performed to obtain a picture of the T_g reaction on the PLA right-after-printed. An exciting phenomenology was not described yet in the literature, as far as we know, in which two glass transition reactions appeared. This was later sought and found on other PLAs. Figure 4 are shown the DSC scans at 10 ºC/min of the PLA aged at 20 ºC at different times.

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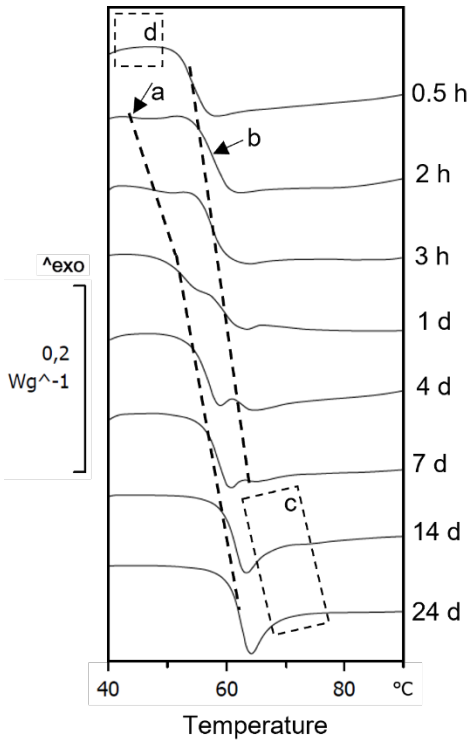

Figure 4. – Detail of DSC scans at 10 ºC/min of 4043D PLA samples aged at 20 ºC, for illustrating the double T_g observed: a) hidden T_{g1} on right-after-printed PLA, which was used to determine the maximum temperature at which the material could be aged; b) second glass transition, T_{g2}; c) missing T_{g1}; d) missing T_{g2}.

In this figure 4, a clear endothermal transition coherent with T_g, called T_{g2}, was quickly identified even after 0.5 hours of the printed material. However, a slight endothermal process was noticed before the T_{g2} on the samples aged for 2 hours. It was studied the PLA at heating rates of 10 ºC/min during the following days, figure 4, and it was observed: 1) that the T_{g2} was disappearing, and 2) the slight endothermal reaction was getting bigger and bigger and forming the typical shape of the glass transition, calling it T_{g1} as it was the first glass transition to appear on the DSC heating scan. For the T_{g1} to show up consistently, it required at least 2 hours of natural ageing at 20 ºC after the FFF process, figure 4, making this double T_g a potential problem if any study on the literature made a DSC on right-after-printed samples at ageing times lower than 2 hours. Notice that the PLA 4043D-based materials are commonly studied in the literature [11]–[18]. Samples studied at 0.5 hours after being printed did not show T_{g1}, figure 4. Also, this T_{g1} phenomenon is so subtle that having a large mass of PLA-to-surface contact between the PLA, and the aluminium crucible made it even more challenging to detect it, indicating the importance of carefully placing the material inside the DSC crucible in the most controlled and reproducible manner, as not only up to +1 ºC shifts were found on the temperature peaks and glass transitions, but also a widening of the peaks. The evolution of T_{g1} was found to be extremely fast (compare its value at 2 and 3 hours on samples aged at 20 ºC in table 1), making it hard to define a proper maximum temperature limit for accelerated ageing.

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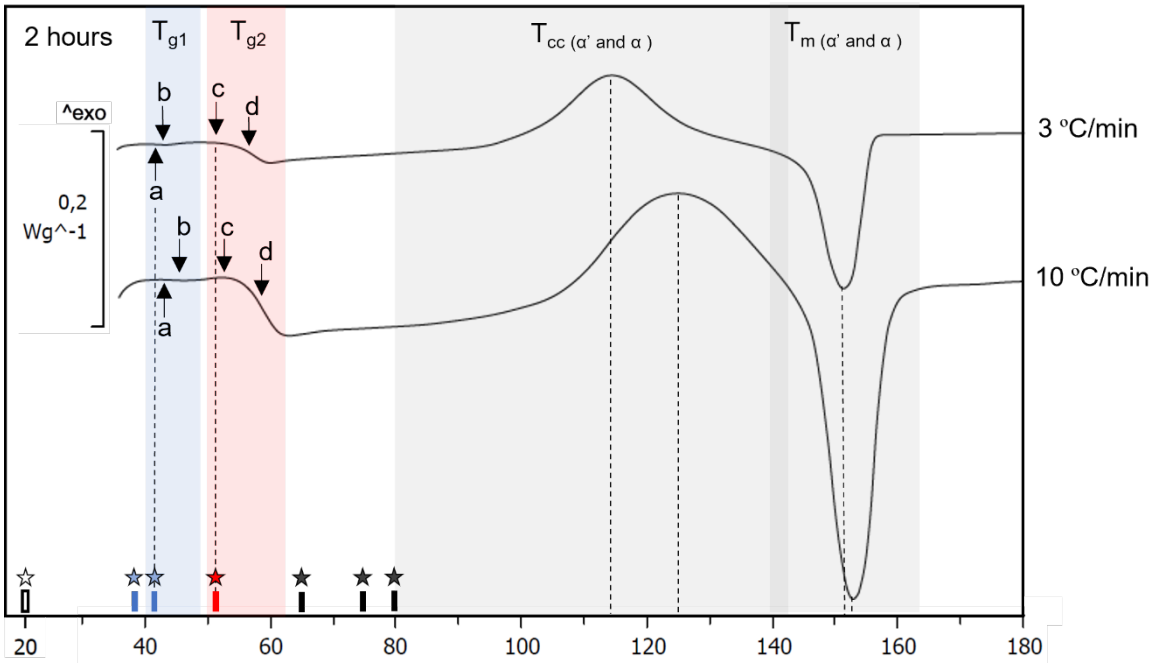

Figure 5. – DSC of neat PLA right after printed via FFF at heating rates of 3 and 10 ºC/min. Stars indicate the ageing temperatures used: 20, 39, 42, 51, 65, 75 and 80 ºC. a) T.onset of the first glass transition; b) T_g of the first glass transition; c) T.onset of the second glass transition; d) T_g of the second glass transition. Crystallisation and melting reactions are also indicated. Crystallisation and melting temperatures are indicated too. Dashed lines are included for reference.

After this discussion on the double glass transitions and considering that the T_g is defined approximately as the half point of the glass transition –depending on the standardised method used–it was used, not the glass transition, but the onset temperature of the glass transition as the maximum temperature at which the ageing could be effectively done. The onset temperature of the first glass transition (T_{g1}) was 42.9 ºC, figure 5.a. This temperature was measured from a DSC at 10 ºC/min after 2 hours of natural ageing at 20 ºC, and it is known that for obtaining precise values, slower DSC scans should be used. The heating rate of 10 ºC/min is the most commonly found in the literature; thus, it was the one used for this study. However, notice the difference between the scan at 10 ºC and 3 ºC in figure 5. The onset temperature of T_{g1} on the DSC scan at 3 ºC/min was 41.7 ºC, decreasing by 1.2 degrees the measured onset temperature.

The evolution of T_{g1} was found to evolve extremely fast, making it even harder to define a proper maximum temperature limit for accelerated ageing. Thus, it was chosen the lowest temperature measured. It was found that 42 ºC worked great for accelerating the ageing of the PLA 4043D naturally aged 2 hours after FFF (results in table 1), temperature above the measured 41.7 ºC, which could be explained due to the fast evolution of T_{g1}, (+1 degree if compared 2 hours of ageing at 20 ºC with 3 hours) and that it could be significantly increased during the heating process, shifting it towards higher temperatures.

For setting a safe temperature for accelerating the ageing that indeed would work, it was defined and used a maximum temperature, approximately 3 degrees below the onset temperature, 39 ºC. This temperature was 6 degrees lower than the first glass transition measured (T_{g1} at 10 ºC/min on samples aged 2 hours at 20 ºC after FFF) and 15 degrees lower than the T_{g2} measured at 0.5 hours after printing.

The 51 ºC ageing temperature was chosen as it was close but below the second glass transition (T_{g2}) found on the right-after-printed PLA, to demonstrate that it cannot be directly used the T_g measured as an indicator of the maximum temperature for accelerating the ageing of the PLA, especially if it was measured right-after-printed.

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The 65, 75 and 80 ºC were used to provide further information on how ageing at higher temperatures could affect the PLA on the ageing device and show any potential degradation evidence together with the mechanical tests to confirm the safeness of accelerating the ageing of the PLA.

DSC results are discussed together with the mechanical properties.

3.2. Mechanical properties

All the results from the tensile tests on the 4043D PLA are summarised in figures 6 and figures 7. Tests at 0.5 hours were not viable, as the adhesive clamp does need time to harden, and the minimum possible ageing time at room temperature was 2 hours from printing to a reliable tensile test.

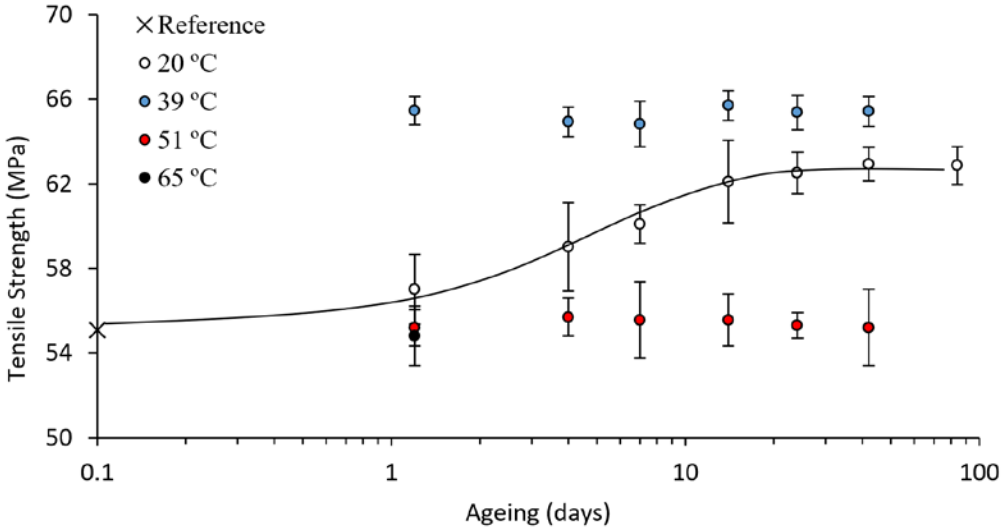

Figure 6. – Tensile strength evolution with ageing time at different ageing temperatures.

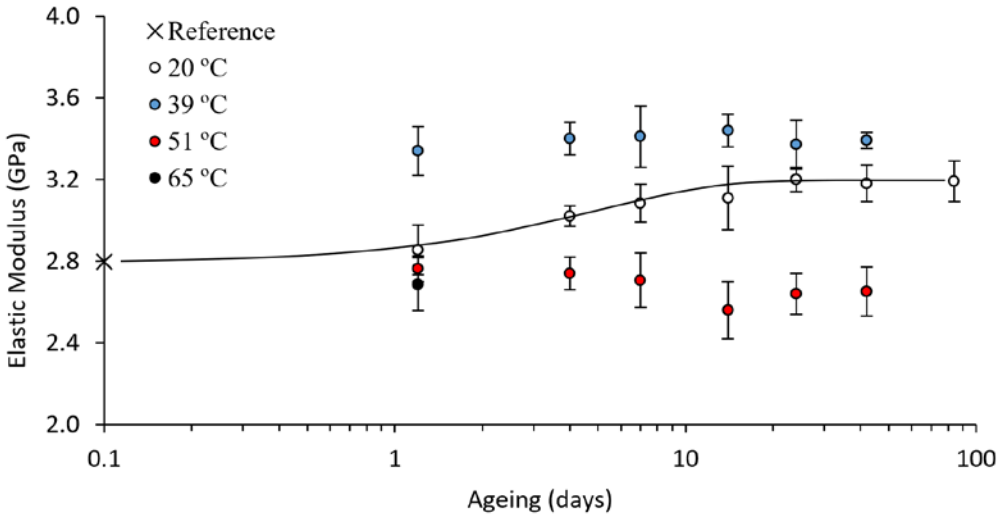

Figure 7. – Elastic modulus evolution with ageing time at different ageing temperatures.

Thermal and mechanical properties were measured, and they are highly interrelated. For an appropriate discussion, all the results must be considered together.

Starting with the samples aged at 20 ºC, these samples were used for setting a reference. This way, it was possible to compare the evolution of the samples aged at higher

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temperatures with these controls. As expected, the evolution of these PLA samples aged at room temperature was coherent with our previous study. The difference with that study is that it studied the 2003D instead of 4043D. However, the trends on the evolution of the properties remained similar: 1) the enthalpic relaxation (both temperature and enthalpy) increased until stabilisation, 2) the enthalpic relaxation enthalpy keeps increasing even after the stabilisation of the glass transition, 3) the crystallisation and melting reactions remained unaltered, 4) the elastic modulus and yield strength evolved until they stabilised, requiring times similar to the stabilisation of the glass transition.

This similar evolution trend was further proven by applying the logistic fitting to the mechanical properties –elastic modulus and yield strength– and the fitting provides an excellent description of the evolution of these two properties.

The logistic fittings in figures x and x, for both the tensile strength and the elastic modulus, correspond with the following equations:

$$\sigma_y(\text{MPa}) = \frac{62.7}{1 + 0.13e^{-0.20t}} \quad (1)$$

$$E\ (GPa) = \frac{3.18}{1 + 0.13e^{-0.24t}} \quad (2)$$

Where σ_Y is the yield strength in MPa, E is the elastic modulus in GPa and t is the ageing time in days. This confirms that our proposed logistic fittings correctly described the evolution of the mechanical properties with the ageing at room temperature. The logistic fitting on the samples aged 39 and 51 ºC was not possible, as there was only the initial value, and the rest were stabilised values. Intermediate points are required for making the fitting.

Samples aged at **39 ºC** showed excellent accelerated ageing, reaching almost stable properties after just one day of ageing. This result was again coherent with the literature as it was on the limit of the maximum temperature that can be used for accelerating ageing, as explained before. Nonetheless, as it is known and previously measured, the T_g increases with ageing. Thus, the maximum ageing temperature could be increased proportionally to the increase of T_g but fully optimising the accelerated ageing process was not the objective of this work. It was exciting to achieve properties close to the stable ones after just one day of ageing.

Moreover, the values at which the material stabilised at 39 ºC were higher than the stable values of the samples aged at 20 ºC. This effect was referred to as the summer effect, as samples which might be stable at ambient conditions, if not stored properly, could evolve to higher values due to summer temperatures. The higher energy barriers explain this summer effect that the macromolecules with higher kinetic energy –higher temperature– can jump. This allows the 39 ºC macromolecules on the PLA to find even more favourable positions to fit in the polymer and provide a stronger and more rigid material.

This last reasoning –summer effect– applies too for explaining the outstanding results obtained on the samples aged at 42 ºC, in which even higher values were obtained on the DSC scans after just 1 and 4 days for the T_{g1} and its enthalpic relaxation without any signal of degradation.

Samples aged at 51 ºC did not evolve, as the temperature was over the T_{g1}. The samples, however, had a relatively high T_g, as if they were aged. However, the enthalpic relaxation value was as if the material was right-after-printed, raising a contradiction for any direct relation between the glass transition and the enthalpic relaxation: samples which are not aged regarding the enthalpic relaxation might show values like an aged material. This shows that it is difficult, if not impossible, to correlate some of the thermal properties measured on the PLA. For example, a T_{g1} of 60 ºC, an average value of T_g found on aged materials, is not necessarily a sign of a high enthalpic relaxation enthalpy, which is the type used to figure in the literature to indicate how aged the PLA is. However, some trends can be found and modelled [9]. No significant signs of hydrolytic degradation were found on the PLA aged at 51 ºC on the DSC scans, except for a slight decrease in the crystallisation temperature and an increase in the crystallisation enthalpy.

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Regarding the desiccant, it remained stable during the first days of ageing. However, after 42 days, the desiccant turned into a blueish colour indicative of adsorbed humidity and highlighted a potential hydrolytic degradation of the PLA. Concerning the mechanical tests, the material behaved mainly as the 2 hours right-after-printed at 20 ºC. It was noticed that the elastic modulus had a slightly decreasing trend. This could be associated with the loss of the flow-induced molecular orientation, which is a known phenomenon that occurs when a polymer is extruded [19]–[21], especially important for small extrusion shapes, like our filaments which were in the range of 350 to 450 micrometres, and of which there is almost no literature on its effect on printed polymers via FFF.

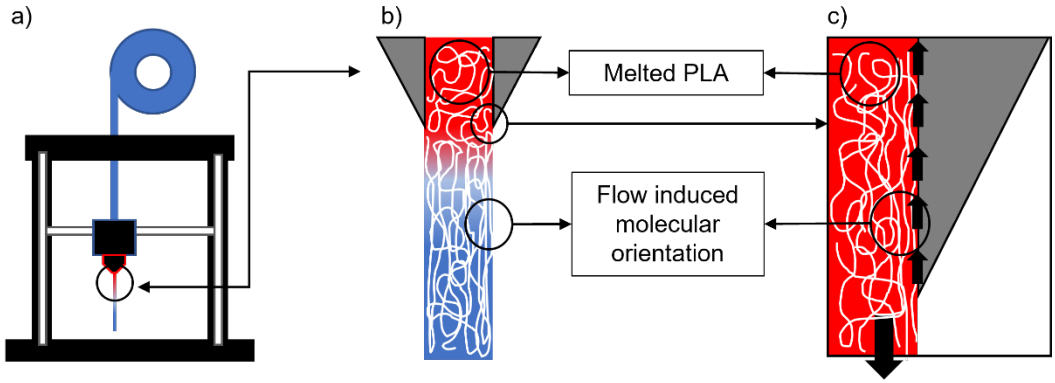

Figure 8. – Flow induced molecular orientation.

A decrease in the molecular weight could also explain the slight decrease of the elastic modulus due to the degradation of the material, degradation which is especially important when the temperature increases over 50 degrees in a humid ambient [22]. Although a low humidity atmosphere was obtained with the different barriers used during the ageing –the oil bath, the PP tube with desiccant, the vacuum grease used in the joint, and the PET zip-bag with even more desiccant inside– the desiccant ended up turning blueish after 42 days at 51 ºC. As a reference, the desiccant only remained yellow for a few minutes if it was placed at ambient conditions, and if it was placed inside our ageing device, it required some weeks, figure 8.

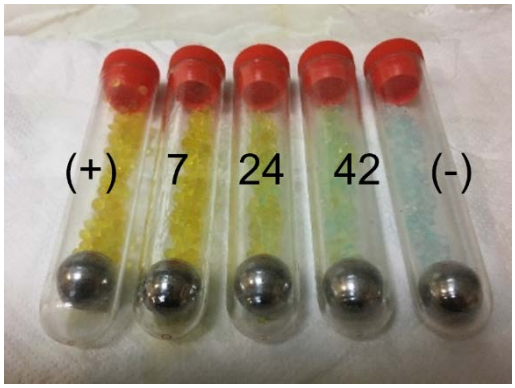

Figure 8. - Desiccant control samples after 7, 24, 42 days of ageing at 51 ºC. (+) stands for the positive reference with desiccant at 0 days, and (-) stands for a negative reference with the desiccant in direct contact with the air for some minutes.

Considering both the loss of flow-induced molecular orientation and the degradation as the two possibilities for explaining the decreases of the elastic modulus, it was tested PLA aged at even higher temperatures for one day, forcing the mechanisms of both the degradation and the loss of flow-induced molecular orientation. Note that the influence of the crystallinity was discarded entirely, as the measured values were around 2% for all

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the samples. There were three higher temperatures analysed: 65, 75 and 80 ºC. Both the 75 and 80 ºC were discarded from the mechanical test as it was observed on the DSC that they crystallised after 1oneday of ageing (up to 28 % of crystallinity content compared with the 2-3% crystallinity contents on the samples aged at lower temperatures), introducing new variables to consider in the system which are out of the scope of this study. Nonetheless, the desiccant remained bright yellow after one day of ageing at those 75 and 80 ºC. After discarding the 75 and 80 ºC, the chosen temperature was 65 ºC, which did not crystallise during the ageing.

The test on the PLA aged at 65 ºC was not enough to provide information to support any of the mechanisms: it had similar mechanical values to the long-period aged PLA at 51 ºC, and the error bars of the measurements are within the error bars of the reference samples. The DSC results showed that the material was slightly degraded as both a decrease in the crystallisation temperature and an increase in the crystallisation enthalpies, related to higher mobility of the polymeric chains, and a degradation of the polymer.

After all, the same analysis considering the error bars applies to the samples aged at 51 ºC. The elastic modulus indeed decreased a 5-6 % considering the average values, but it is also true that the error bars fall within the error bars of the reference sample. This makes it impossible to conclude why the elastic modulus of the PLA aged at 51 ºC decreases. However, it provides handy information: the degradation of the PLA and the loss of flow-induced mechanical orientation are almost neglectable for a sample aged for 42 days at 51 ºC, thus making those phenomena completely neglectable for ageing the PLA for one or some days at 39 ºC –potentially at 42 ºC– until it reaches stable properties.

4. Conclusions

It has been used at an elevated temperature to accelerate the ageing of the PLA as single (1D) PLA filaments (not scaffolds) after FFF; the essential building block of any printed structure. This allows an understanding of the material's effects and a better understanding of the accelerated ageing effects on 3D printed structures.

Summarising the results obtained from the samples studied, the detailed results are:

1. It is safe to accelerate the ageing rate of the PLA at 39 ºC, which aged the material properties close to the stable ones after just one day.

2. A double glass transition was found and characterised, which for being noticed that the printed material needed at least 2 hours of ageing at 20 ºC. Possible mistakes that this phenomenon can induce during the thermal characterisation of the PLA were discussed to raise awareness of its existence.

3. The summer effect stabilisation characterises it at higher tensile strength values, elastic modulus, glass transition and enthalpic relaxation peak.

4. If any loss of flow-induced molecular orientation or degradation occurs, it will occur at a rate slow enough not to be even suitable to conclude anything after 42 days of ageing at 51 ºC, without suffering degradation. Direct mechanical tests used here, were not suitable for decoupling the degradation from the loss of flow-induced molecular orientation.

This covers the objective of this research, understanding the effects of accelerating the ageing rate on the PLA, and it is concluded that it can be safely done and opens the door to future work for a deeper understanding of the flow-induced molecular orientation and decoupling the effects of the degradation. Also, it would be interesting to see how much the summer could be forced and increase the PLA properties as much as possible.

Combined with our previous research in which it is understood the effects of freezing the PLA for stopping its ageing [10], it provides a complete view of how the thermal treatments affect the PLA and demonstrate that it is safe to accelerate the ageing of the PLA, freeze it, and test it whenever the researcher is available for it. It will help to improve the research schedule of PLA and to obtain more repeatable results.

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