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Evaluating Thermal Ageing of Recycled Bio-based Filament for 3D Printing as Function of Extruder Temperature

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In this work, the effect of thermal ageing on printed parts, produced using Fused Deposition Modelling (FDM) technology, was investigated. The constituting material was made from a common bio-based thermoplastic (polylactide acid, PLA) derived from waste recycling of separate collection bio-bags. The filament was extruded in a 3D printing machine using optimized processing conditions and different extruder temperatures (190°C and 210°C). Specimens were aged for various days (up to 175) in a vacuum oven at 70°C and characterized using dynamic-mechanical analysis (DMA) and infrared spectroscopy in attenuated total reflection (ATR) modality. The findings were presented in terms of storage modulus (E') at 30°C and glass transition temperature (T_g) evaluated at various heat treatment periods (50, 70, 130, 175 days). Although samples printed at 190 and 210 °C had a different initial average storage modulus (about 20%), they came to be almost the same value after 175 days of heat treatment. However, in both cases, the storage modulus (E') at 30°C showed a non-monotonous trend as a function of ageing period, reaching a maximum in correspondence of around 80-90 days. On the contrary, an increasing trend of glass transition temperature from 65 to 70°C was confirmed in two sample series by increasing the ageing time. These outcomes were attributed to changes in physical and chemical arrangements of polymer macromolecules that occurred during the thermal treatment. The remarkable differences in absorbance peaks in ATR spectra of aged specimens were interpreted as confirmation of chemical changes induced in the polymer chain structure by heat at different treatment times.

1. Introduction

Plastics are divided into four groups: i) fossil-based and non-biodegradable plastics; ii) fossil-based and biodegradable plastics; iii) natural-based and non-biodegradable plastics; and iv) natural-based and biodegradable plastics. Poly(lactic acid) (PLA) is one of the most commercially successful bioplastics. The monomer (lactide acid) is produced through the fermentation of renewable sources such as starch or sugar. Corn fiber leaves, stems, and stalks, corn stover, sugarcane bagasse, rice hulls, woody crops, and forest residues are examples of other carbohydrates used in PLA synthesis. However, the poor thermal, mechanical, and rheological properties of PLA polymer limit its practical applicability and recycling technologies.
Environmental conditions (sun, heat, atmospheric agents etc.) can deteriorate the physical-chemical characteristics of materials by inducing a process of natural ageing. Numerous studies have been conducted on the effects of temperature, moisture, or UV-light on the degradation of neat PLA.
For example, PLA plastic films, different in molecular weight, were subjected to temperatures (25, 40, and 55°C) and moisture (10, 50, and 100%)(Ho, Pometto III, and Hinz 1999). Changes in molecular weight, tensile strength, percentage elongation, and strain energy were reported with aging time for each different condition. Experiments revealed that both parameters had a significant impact on increasing the rate of PLA degradation.

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The effect of UV exposure at different combinations of relative humidity (30%, 50% or 100%) and temperature (30, 45 or 60 °C) on the degradation process of PLA was investigated in (Copinet et al. 2004), during a period of 6 weeks, through mechanical and chemical analyses. UV treatment was found to accelerate the reduction of the average molecular weight and mechanical performance.
PLA degradation can be further influenced by impurities, and catalyst, resulting in viscosity and rheological changes, fuming during processing, and poor mechanical properties. At temperatures above 200 °C, PLA decomposes thermally via hydrolysis, lactide reformation, oxidative main chain scission, and inter- or intramolecular transesterification reactions. (Farah, Anderson, and Langer 2016)
Beyond common process technologies of thermoplastics such as extrusion, injection moulding, injection stretch blow moulding, casting, blown film, thermoforming, foaming, blending, fiber spinning, and compounding (Lim, Auras, and Rubino 2008), PLA resins were broadly considered for conventional additive manufacturing (Ilyas et al. 2021). The mechanical degradation of the interface for AM specimens made of PLA polymer was studied in (Moetazedian et al. 2021) by testing specimens immersed at 37 °C to simulate human-body conditions, and at 50 and 65 °C to understand the suitability of accelerated degradation. The interface was damaged similarly to the bulk polymer material, and no deterioration of mechanical and thermal properties was observed after 8 months at room temperature.
In this work, the effect of thermal ageing on 3D printed parts made from recycled PLA was investigated using dynamic mechanical analysis (DMA) and infrared spectroscopy (IR). FDM samples were prepared at two different extruder temperatures (190 and 210°C, respectively) and kept at a constant temperature of 70°C for 175 days. Variations in storage modulus and glass transition temperature, as well as variations in absorbance peaks, were reported as a function of thermal treatment duration.

2. Materials and methods

2.1 Material

This study employed poly(lactide) acid (PLA)-based filament derived from the waste production of bio bags utilized in the waste and separate collection (cod. PLA EUBIO, Eumakers. Italy). Bio-bags were made of biaxially oriented films, available in pellet form (cod. IngeoTM Biopolymer 4043D, Naturework, USA).

2.2 Samples preparation

Prior to the 3D process, the material was dried in an oven for 10 hours at 70 °C. Then, the filament was extruded into a 3D printer, manufactured by Zortax, (Olsztyn, Poland), to prepare rectangular specimens (2x5x25 mm^3). Platform temperature, layer thickness, top surface layer, retraction speed and distance have been optimized according to previous attempts as reported in (Patti, Acierno, Cicala, Zarrelli, et al. 2022). All adopted conditions for printing process have been summarized in Table 1. Two different temperatures, 190°C and 210°C, have been set up to extrude the filament in the printer.

Table 1: 3D process specifications

Nozzle Diameter	0.4 mm
Layer thickness	0.09 mm
Infill density	100%
Pattern	Linear
Platform temperature	70°C
Retraction speed	27 mm/s
Retraction distance	2.7 mm
Printing speed	Default (100 mm/s)

Thermal ageing of prepared specimens was performed in a vacuum oven (mod. Binder, by Geass SrL, Torino, Italy) at temperature of 70 °C for a period of 50, 70, 130, 175 days, respectively. Aged samples have been characterized through thermal-mechanical properties and infrared spectroscopy.

2.3 Characterization techniques

The dynamic-mechanical analysis was performed on 3D printed samples from room temperature to 80°C by using a Tritec 2000 machine (Triton Technology Ltd., Leicestershire, UK), in single cantilever mode, at 1 Hz frequency, and support distance of 12 mm. For each chosen printing temperature (190 and 210°C) three different specimens were prepared and characterized. Results were reported as average values and standard deviations. The glass transition temperature (T_g) was determined as temperature in correspondence of the peak of damping factor curve (tan delta).

Infrared spectroscopy was conducted in attenuated total reflectance (ATR) mode, using a spectrometer (model Spectrum 65 FT IR), produced by Perkin Elmer (Waltham, MA, USA), endowed with a diamond crystal. A wavenumber range of 400–4000 cm^{-1}, a resolution of 4 cm^{-1} and scans equal to 16 were adopted. The absorbance values were normalized in relation to an internal standard for the PLA polymer (1455 cm^{-1} peak).

3. Experimental Results

3.1 Effect of thermal ageing on thermo-mechanical characteristics of 3D printed parts

The thermo-mechanical characteristics of aged specimens, printed at 190°C and 210°C, respectively, were reported in Figure 1, in terms of storage modulus (E' in Pa), evaluated at temperature of 30°C, as a function of heat treatment period.

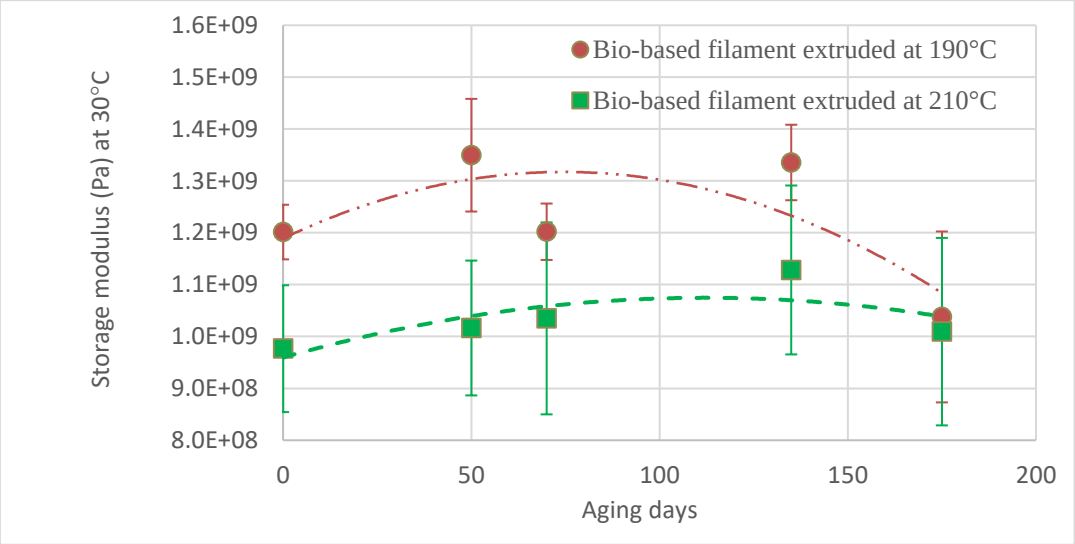

Figure 1: Storage modulus (E', Pa) measured at 30°C for specimens printed at 190°C and 210°C, respectively.

Usually, the higher the processing temperature, the lower the viscosity of melted polymer, the weaker the bonding between layers of 3D printed parts, and consequently, the poorer the mechanical properties (Patti, Acierno, Cicala, Tuccitto, et al. 2022). Contrary to expectation, in this case, specimens extruded at lower temperature (190°C) always possessed a storage modulus at 30°C superior compared to specimens extruded at higher temperature (210°C). The average E' at 30°C for bio-based filament processed at 190°C began from 1.2 $x10^9$ Pa while for biobased specimens processed at 210°C the starting average E' value was slightly lower than $1x10^9$ Pa. As the printing temperature was increased, the reduction in E' was ascribed to the occurrence of thermal degradation phenomena of polymer chains during the extrusion (Patti, Cicala, and Acierno 2021). Previous rheological characterization on the same material confirmed that the complex viscosity remained nearly constant over time at 170°C. Then, the rheological signal underwent to a slight reduction at 190°C that became more evident by increasing testing temperature at 210°C. This was regarded as a proof of the reduction of polymer molecular weight caused by thermo-mechanical decomposition and increasing the processing temperature (Patti, Acierno, Cicala, and Acierno 2022). Thermal degradation can cause chemical reactions like random chain scission, crosslinking, and branching, all of which have opposing effects on polymer molecular structure. While the chain scission leads to decrease the polymer molecular weight, the crosslinking and branching lead to increment the chains length and mass. The extrusion process involves high temperatures and higher shear rates, and structural changes in macromolecules are primarily attributed to thermal-oxidation mechanisms that begin with mechanical destruction and oxidation (El'darov et al. 1996). According also to Taubner and Shishoo (Taubner and Shishoo 2001), PLA should be handled at low extruder temperatures to minimize the loss of polymer molecular weight during the process and cause minimal damage of the mechanical properties. Indeed, the stress and strain at break of samples extruded at 240°C were lower than those extruded at 210°C. The trend of storage modulus as function of ageing time (in days), for specimens printed at 190°C, seemed to slightly increase, to achieve a maximum around $1.3x10^9$ Pa after about 80 days of thermal treatment, and then to decrease up to $1x10^9$ Pa. The same increasing trend of the

storage modulus vs the ageing, but with less pronounced effect, appeared also in the case of specimens extruded at 210°C. The glass transition temperature (T_g) of samples printed at 210°C remained however slightly lower that achieved for a printing temperature of 190°C, but in all cases, the value increased with ageing days. The increment of E' and T_g was attributed to potential physical movements of macromolecular chains, occurred during the theating process. In general, PLA resins were mainly characterized by an amorphous structure that, being unstable, could undergo some physical reorganizations. During ageing, this structure could evolve towards more stable state through molecular rearrangements (Pluta et al. 2008).
These results found agreement with several literature works. For example, accelerated thermal ageing of 3D printed specimens from PLA filament was studied at temperature below the glass transition (50°C) for 1344 h (56 days) by Bergaliyeva et al. (2022). Through a simplified protocol, an ageing time of 1344 h at 50 °C was correlated to about 1.5–2.5 years of real service time. The tensile test results showed a fluctuating trend of the Young' s modulus from 150 MPa at 0 h (for unaged specimens) to 186 MPa at 1344 h. The authors concluded that PLA could be reused before 1.5 years of age without significant loss of properties.
Barrasa et al.(2021) investigated the effects of printing temperature (180 and 190 °C) and natural weathering on the properties of PLA-based filaments up to one year. Even though the material extruded at 190 °C performed better than the material extruded at 180 °C, both systems behaved similarly after one hundred days of natural ageing. Significant changes in the elastic modulus from 2.4 GPa in one-day-aged samples, up to 4 GPa once entirely, were verified. Increasing values of glass transition temperature from 51 °C after one day to nearly 60 °C after 84 days have been also observed.

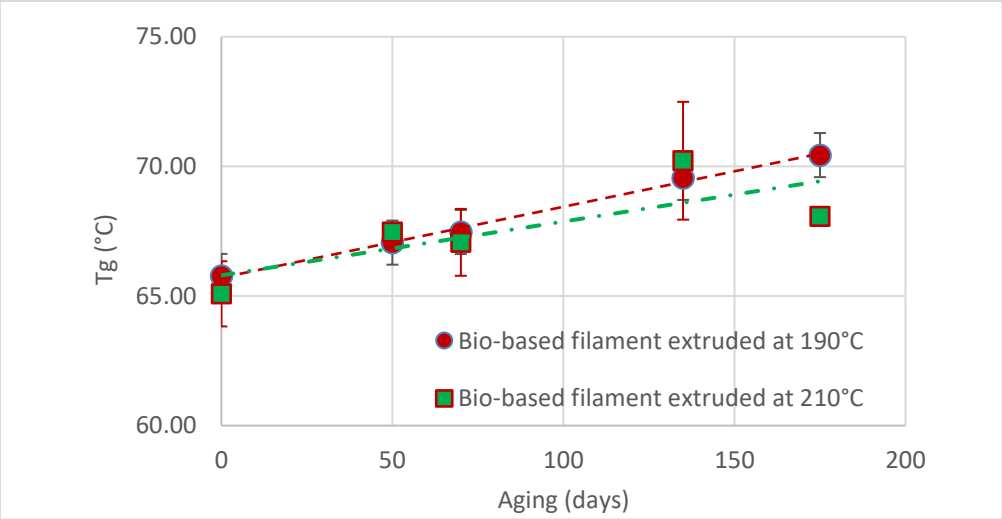

Figure 2: Glass transition temperature (°C) against ageing days for both specimens extruded at 190°C and 210°C, respectively.

3.2 Infrared spectroscopy on the aged specimens

Figure 3 depicts a comparison of ATR spectra for aged and unaged samples. The absorbance intensity is plotted against the wavelength number (cm^{-1}) for each aged specimen.
ATR spectrum of the basic material (dashed black curve) displayed the characteristic peaks of PLA polymer: the stretching vibrations of hydroxyl groups hydroxyl (OH) in the wavelength range of 3000-3700 cm^{-1}; C-H alkane stretching vibration in the range of 2800-3000 cm^{-1}, carboxyl group (C=O) stretching at 1750 cm^{-1}; C-O vibration of ester group (symmetric stretching) and C-O-C vibration of ester group (asymmetric stretching) at 1183 cm^{-1} and at 1085 cm^{-1}, respectively. (Patti, Acierno, Cicala, Zarrelli, et al. 2022)
After 50 days of thermal treatment (light red curve), the absorbance of the hydroxyl band (OH) increased significantly, while the carboxyl group vibration completely disappeared. After 70 days of thermal ageing (dashed red curve), the absorbance of the aforesaid typical bands began to decrease while the carboxyl group (C=O) peak returned to appear at 1750 cm^{-1}. After 130 days of thermal ageing (dark-red solid curve) the ATR spectra of aged specimen and starting material were almost similar. Finally, after 175 days (green solid curve) of thermal ageing the carboxyl vibration and ester groups signals seemed to slightly increase, while the alkane and hydroxyl groups absorbance decreased.
Therefore, it seemed that the degradation occurred primarily through hydrolysis and random chain scission. According to the mechanism proposed in (Al-Itry, Lamnawar, and Maazouz 2014), moisture could attack the

double bonds of carboxyl groups. Then, a hydrogen transfer reaction occurred, which led to the formation of ester end groups by dividing the macromolecule into smaller portions.
In table 2, normalized absorbance values for specific wavelength have been summarized both for 3D printed parts processed at 190°C and 210°C, respectively. Same considerations verified in the case of specimens at 190°C have been displayed for specimens extruded at 210°C. A sharp increase in absorbance intensity was recorded after 50 days of heat treatment, after which the absorbance settled around the zero-time values.

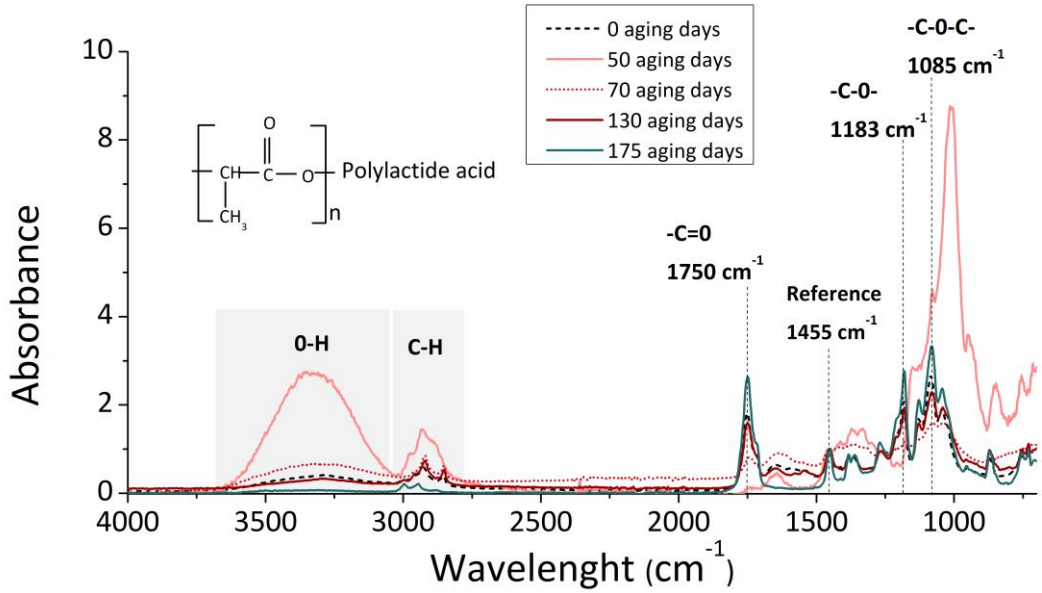

Figure 3: ATR spectra of aged specimens compared with unaged ones for extruded samples at 190°C.

Table 2: Normalized absorbance (Norm. Abs) and enhancement (Enh., %) with respect to zero-time value, at specific wavelengths, for samples printed at 190°C and 210°C.

	Printing temperature of 190°C							
	2920 cm^{-1}		1750 cm^{-1}		1183 cm^{-1}		1085 cm^{-1}	
	Norm. Abs.	Ehn. (%)	Norm. Abs.	Ehn. (%)	Norm. Abs.	Ehn. (%)	Norm. Abs.	Ehn. (%)
0 days	0.301	/	1.808	/	2.082	/	2.659	/
50 days	0.653	117%	0.079	-96%	0.848	-59%	4.230	59%
70 days	0.372	24%	0.787	-56%	1.149	-45%	1.555	-42%
130 days	0.290	-4%	1.586	-12%	1.880	-10%	2.252	-15%
175 days	0.179	-41%	2.632	46%	2.715	30%	3.270	23%
	Printing temperature of 210°C							
	2920 cm^{-1}		1750 cm^{-1}		1183 cm^{-1}		1085 cm^{-1}	
Ageing	Norm. Abs.	Ehn. (%)	Norm. Abs.	Ehn. (%)	Norm. Abs.	Ehn. (%)	Norm. Abs.	Ehn. (%)
0 days	0.652	/	1.845	/	2.405	/	2.472	/
50 days	1.595	145%	0	-100%	0.718	-70%	5.217	111%
70 days	0.658	1%	1.131	-39%	1.475	-39%	2.037	-18%
130 days	0.767	18%	1.668	-10%	1.921	-20%	2.280	-8%
175 days	0.263	-60%	2.305	25%	2.007	-17%	2.910	18%

4. Conclusions

3D printed parts, made from a recycled bio-based polymer, were prepared at two different extruder temperatures. Specimens were thermally aged and characterized by DMA and IR spectroscopy. Thermo-mechanical characteristics of aged samples were found to be higher by decreasing the extruder temperature. This outcome was ascribed to possible thermal degradation of macromolecular chains, occurred at higher

processing temperatures (above 190°C). The average E' at 30°C of parts produced at 190°C underwent to a reduction of about 20% after 175 ageing days, whereas in the case of printed parts at 210°C, the value remained almost constant around the initial point. The glass transition temperature always showed an almost increasing trend with ageing time, reaching about 5°C higher after 175 days of heat treatment than the initial value. The weak non-monotonous trend of E' at 30°C and the increased glass transition temperature with the ageing periods were attributed to the different structural arrangements of polymer macromolecules induced by thermal treatment. Chemical changes in aged specimens, as evidenced by differences in absorbance intensity, were interpreted as a sign of polymer degradation, which primarily could occur via hydrolysis and chain scission mechanisms.

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