Alternative Energy Sources, Materials & Technologies (AESMT'20), Volume 2, (pp. 91-92) 2020
ALTERNATIVE MATERIALS, Energy Materials Science

Thermal analysis of 3D printed polylactic acid after accelerated thermal ageing

S. A. Bergaliyeva[1,2*], D. L. Sales[2], S. A. Bolegenova[1], S. I. Molina[3]

[1]*Al-Farabi Kazakh National University, Physics and Technology Dept., 71, al-Farabi ave, 050040 Almaty, Kazakhstan, saltanat.bergaliyevaa@alum.uca.es*
[2]*Universidad de Cádiz, High Polytechnic School of Algeciras, Department of Materials Science and Metallurgical Engineering and Inorganic Chemistry, INNANOMAT, IMEYMAT, Ramón Puyol ave, 11202 Algeciras (Cádiz), Spain*
[3]*Universidad de Cádiz, Campus Río S. Pedro, Department of Materials Science and Metallurgical Engineering and Inorganic Chemistry, INNANOMAT, IMEYMAT, 11510 Puerto Real (Cádiz), Spain*

In this communication we explore the possibility of giving a secondary use to 3D printed polylactic acid. Differential scanning calorimetry test of laboratory accelerated aged 3D printed specimens after 8, 16, 24, 48, 72, 168, 672 and 1334 h were conducted and revealed that (i) after using PLA goods for 16-20 months crystallinity doesn't change and melting temperature of polymer decreased by approximately 2°C, and (ii) further recycling of 3D printed waste is possible but the processing temperature should be reduced.

Keywords: Polylactic acid, thermal ageing, 3D printing, additive manufacturing, differential scanning calorimetry

INTRODUCTION

Polylactic acid (PLA) has become one of the most popular 3D printing materials for Fused Deposition Modeling (FDM). With the 26% annual growth rate of additive manufacturing, especially in the area of 3D polymer printing, the amount of waste from printing is increasing at a rapid rate.

Laboratory accelerated thermal ageing is an effective method to simulate real life conditions that will influence the polymer during its operational time. Differential scanning calorimetry (DSC) analysis of thermal properties helps to predict the future recyclability of PLA polymer used in FDM and the printing parameters that must be used for successful re-manufacturing of recycled PLA.

METHODOLOGY

Specimens were printed by FDM from commercially available PLA filament 1,75 mm using a Witbox2 3D printer from BQ.

Following ISO 188 [1], specimens were stored for 8, 16, 24, 28, 72, 168, 672, 1334 h in a laboratory oven at 50°C. This ageing temperature was chosen to be under the glass transition temperature (T_g) of PLA to prevent the modification of thermal properties during ageing [2]. The Simplified Protocol for Accelerated Ageing states that a service time of about 1 month at room temperature can be simulated by an ageing time of about 72h at 50°C with degradation [3].

For DSC measurements, the specimens were cut from 3D printed aged pieces approximately from 5 mg to 10 mg for the measurements.

The calibration and measurements were carried out using nitrogen purge gas with a flow rate of 10 ml/min and a heating rate of 10 K/min.

The data were taken during the first heating cycle because it was desired to evaluate the properties of especially pre-conditioned specimens without erasing the PLA's previous thermal history.

DISCUSSION AND RESULTS

Fig.1 shows the DSC results. The first relative minimum corresponds to T_g, the maximum around 115°C is due to crystallization process during which the polymer gives off heat and the minimum around 150°C corresponds to melting point. The whole curve suggests that PLA is semicrystalline since it has glass transition and melting temperatures [4].

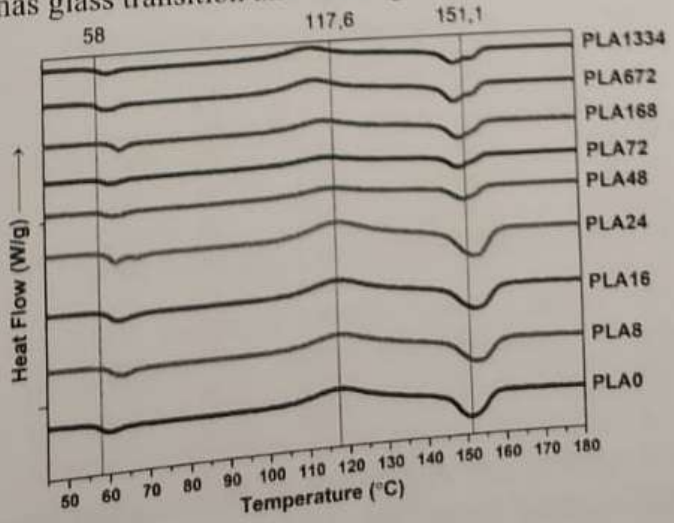

Fig.1. DSC test of PLA specimens

An endothermic peak associated with the glass transition was clearly noticeable in the PLA samples (Fig.1). Its area increased and it was shifted to higher temperatures during time. These thermal events were in agreement with the so-called physical ageing of amorphous and semicrystalline polymers. When a polymer is stored at temperatures lower than its T_g, slow molecular rearrangements occur, which densify the polymer structure. These rearrangements tend to decrease the excess of free energy and free volume of the polymer, and they are accelerated when the storage temperature is close to T_g. As a consequence, when the polymer is stored at $T<T_g$, it becomes more glass-like and less rubber-like during time [5].

The T_g value increases about 3°C after 8 h ageing and stay near the same value until 72 h, but then decreases about 1-2°C and stay at approximately 58-59°C after 1334 h. As T_g has an effect on how easily the material will be extruded, how the parts will shrink during the cooling process and the thermostability of the final part [6], it can be predicted that there is a need of additives like plasticizers to prevent such kind of problems.

In Tab.1, it can be noticed that melting temperature (T_m) increases after 8, 16 and 24 h and after 48 h gradually decreases at first from 153.3 to 149.4°C and then to 148.9°C. Actually, both the rising and decreasing tendency in T_m until and after 24 h of thermal treatment could be due to molecular rearrangements with the thermal ageing [7]. So, until 24 h of thermal ageing, shorter polymer chains effectively reorganize themselves into more ordered crystals, hence increasing the relevance of the high temperature melting peak. After 24 h of ageing, shorter polymer chains, due to the higher mobility of macromolecular chains, cause a decrease of T_m.

Table 1. Values of T_g, T_m, ΔH_m and X_c

Ageing time	T_g	T_m	ΔH_m	X_c
h	°C	°C	J/g	%
PLA0	58.	151.1	28	30.1
PLA8	60.8	152.7	28	30.1
PLA16	60.6	153.4	28	30.1
PLA24	60	153.3	28	30.1
PLA48	59	149.4	27	29
PLA72	59.6	149.4	29	31.2
PLA168	62	149.7	28	30.1
PLA672	58.4	148.8	29	31.2
PLA1334	58.7	148.9	28	30.1

PLA672 and PLA1334 DSC thermograms have two melting peaks. This is explained because the annealing occurring during the DSC scans, some regions of the material recrystallize and remelt [8]. When the scan rate is low, i.e., 10°C/min, there is enough time for the thinner crystals to melt and them to recrystallize before a second endotherm at a higher temperature occurs [8].

Degree of crystallinity Xc was quantified according to [7] as

$$Xc=\frac{\Delta Hm}{\Delta H*}\times 100 \quad (1)$$

where ΔH^*=93J/g [7] denotes heat of melting for an infinitely large crystal. The degree of crystallinity stays about 29-31%.

CONCLUSIONS

Lab controlled ageing of PLA has been considered for the prediction of their long-term behaviour and recyclability. T_m values decrease from 151,1°C to 148,9°C and T_g stays approximately in the range 58-61°C. There was not observed severe degradation of PLA after 1334 h of ageing. In this way, secondary PLA can be recycled through FDM using a lower operating temperature. We conclude that accelerated ageing is an effective method to predict the behaviour of recycled PLA used for FDM.

REFERENCES

[1] ISO/TC 45/SC 2 and T. and Analysis, "ISO 188:2011 Rubber, vulcanized or thermoplastic — Accelerated ageing and heat resistance tests," vol. 2013, p. 20, (2013).

[2] S. Solarski *et al.*, "Ageing of polylactide and polylactide nanocomposite filaments," *Polym. Degrad. Stab.*, **93**(3), 707–713, (2008).

[3] A. Boldizar, K. Möller. Degradation of ABS during repeated processing and accelerated ageing. *Polym Degrad Stab*,**81**(2),359–366, 2003.

[4] T. Malmgren *et al.*, "Characterization of poly(lactic acid) by size exclusion chromatography, differential refractometry, light scattering and thermal analysis," *J. Therm. Anal. Calorim.*, **83**, 1, 35–40, (2006).

[5] J. R. Rocca-Smith *et al.* Beyond Biodegradability of Poly(lactic acid): Physical and Chemical Stability in Humid Environments. *ACS Sustain. Chem. Eng.*, **5**(3), 2751–2762, (2017).

[6] A. R. Torrado Perez *et al.*, "Fracture surface analysis of 3D-printed tensile specimens of novel ABS-based materials," *J. Fail. Anal. Prev.*, **14**, 3, 343–353, (2014).

[7] I. Pillin *et al.*, "Effect of thermo-mechanical cycles on the physico-chemical properties of poly(lactic acid)," *Polymer Degradation and Stability*, **93**, 2, 321–328, (2008).

[8] J.-R. Sarasua *et al.*, "Crystallization and Melting Behavior of Polylactides," *Macromolecules*, **31**, 9, 3895–3905, (1998).