

EFFECT OF PRINTING TEMPERATURE ON THE MECHANICAL AND THERMAL PROPERTIES OF PRINTED SPECIMENS MADE FROM PACKAGING PLA

Balázs Ádám, Erika Varga

*Department of Innovative Vehicles and Materials, GAMF Faculty of Engineering and Computer Science, John von Neumann University, H-6000 Kecskemét, Izsáki street 10, Hungary
e-mail: adam.balazs@nje.hu*

Abstract

Traditional plastic packaging ending up in the environment poses a serious problem, one possible solution to which would be the use of biopolymer packaging materials such as PLA. However, it would be even better if we could recycle the used packaging PLA as printing filament. The popularity of 3D printing and the demand for sustainable raw materials would ensure a steady market for recycled PLA filaments. First, we need to know whether the raw material is printable and how it is affected by various printing parameters, such as printing temperature. The properties of the printed test specimens made from the original Ingeo 7032D PLA for packaging can be changed by increasing the printing temperature. The higher the temperature at which they are printed, the higher the degree of crystallinity of the test specimens. Increasing the printing temperature also affects the mechanical properties, but this is not only due to the increase in crystallinity, but as higher printing temperatures also improve the welding of the filaments, thereby improving the mechanical properties.

Introduction

One of the biggest problems of consumer society is the large amount of waste generated and what we do with it, or rather, what we do not do with it. The issue of responsibility goes beyond the average person; we also need to talk about the responsibility of companies, company managers, countries, and country leaders. Just as the average person can decide whether to throw an empty bottle in the trash or just throw it away, companies and country leaders are also responsible for the decisions they make that affect the environment. More studies and publications are coming to light in which the most polluting companies are collected, and it is sad that less than a hundred companies have been causing the greatest destruction to the environment for a little more than a century. These include large oil companies and large food manufacturing companies that package their products in plastic. [1-3]

The sorting and recycling of selectively collected plastic waste could be solved, the main problem is the lack of proper collection, so a lot of otherwise recyclable plastic ends up in landfills. [4-7] Or, even worse, container ships take the garbage of richer countries to for example Africa, labeling the garbage as a second-hand product, and it is dumped right along the coast, then the lightweight plastic pieces can be washed into the sea and oceans, where garbage islands are formed. [8-14]

One of the possible solutions in an engineer way to reduce the amount of waste is to make plastics degradable or to use biodegradable polymers. One of the most intensively researched biopolymers is PLA (Poly-Lactic Acid). PLA can be produced from natural materials and is a biodegradable polymer under industrial conditions, by composting. PLA is a thermoplastic, semi-crystalline polyester, the basis of its production is lactic acid fermentation. Two isomers occur: L-lactide and D-lactide. Commercially available PLA materials are copolymers that contain L-lactide (PLLA, Poly-L-Lactic Acid) and D,L-lactide (PDLLA, Poly-D,L-Lactic

Acid). Due to their different ratios, they have different properties, different glass transition and melting temperatures.

The good mechanical properties of PLA (60 MPa tensile strength, 3 GPa modulus of elasticity) have also contributed to its widespread use in two areas. One of these areas is the packaging industry, where it is a good alternative to traditional materials. The other area is 3D printing, where its ease of use makes it popular not only with companies but also with average consumers. [15-19]

Due to its brittleness, it has not yet become widespread in the engineering field, but many researchers are working to modify this. However, its popularity as a printing material could be exploited, and the production of printer filaments from packaging waste could be an alternative way of recycling it.

Previous research [20] has shown that Natureworks Ingeo 7032D packaging-optimized PLA raw material is suitable for producing printing filaments. The aim of this study is to examine how the different printing temperatures affect the mechanical and thermal properties of the printed test specimen made from the original material.

Experimental

Natureworks Ingeo 7032D is a PLA used for bottle blowing, so it is suitable for replacing traditional PET bottles in case of storing non-carbonated beverages.

The filament from Ingeo PLA was prepared by Collin Teach-Line E20T extruder using a Collin Teach-Line CSG171T extruder line. Before extrusion, PLA was drying at 60°C and 4 hours. The temperatures of the extruder were 190, 200, 210, 220°C (from hopper to die) and the rate of the screw was 40 rpm. The diameter of the filament was 1.75 mm.

A Craftbot Plus FFF technique 3D printer was used to print test specimens. Two shapes were printed on the measurements, dog bone shaped specimen to tensile test and simple rectangular column shaped specimen for impact test. In both cases 5-5 pieces were measured in every setting, and the investigated cross-section was 4x10 mm.

The printer can create different structures. For the tests, a triangular structure was selected from the standard settings, where a layer of printing is formed from triangular shapes (Figure 1). The infill density was 100%. The printing temperature was set to three different levels: 210, 220, and 230 °C. The tray temperature was 60 °C and the printing speed was 50 mm/s.

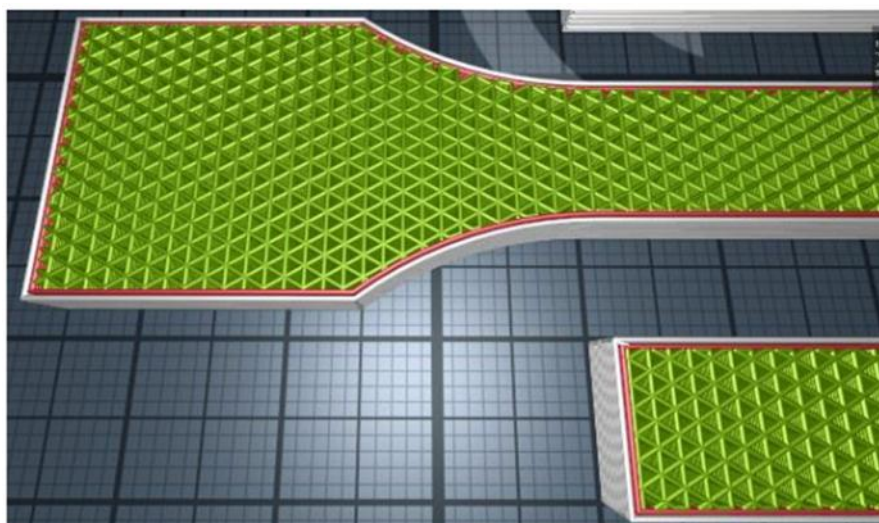


Figure 1. Triangle shape printed structure of the specimens

DSC (Differential Scanning Calorimetry) tests were performed on the specimens by TA Q200 heat-flux DSC instrument. The sample weights were about 5 mg. The applied gas during the DSC scan was nitrogen with 50 mL/min flowing rate. The temperature range was from 30°C to 200°C and the heating rate was 20 °C/min. The DSC measurements were analyzed with the TA Universal Analysis software. Only the first heating was analyzed.

The printing samples were investigated by tensile and Charpy impact tests at room temperature. The tensile test was performed by Instron 3366 universal testing machine with a 10 mm/min measuring rate. Charpy impact test was performed by Ceast Impactor II with 5 J hammer.

Results and discussion

One disadvantage of PLA, similar to PET, is that its crystallization tendency is slow, so with the usual processing technologies and technological settings, it is difficult to achieve the appropriate degree of crystallinity when using pure material and it is more often possible to produce a product with a larger amorphous fraction. [21-26]

The DSC curves of samples printed at different temperatures also confirm this (Figure 2). The cooling conditions of the printing were too intense for PLA, preventing the crystallization process from being completed, resulting in cold crystallization visible at around 120 °C on all three samples. This means that once the glass transition temperature (around 60 °C) is exceeded, the macromolecules begin to move using the heating energy and can create the missing crystalline phases.

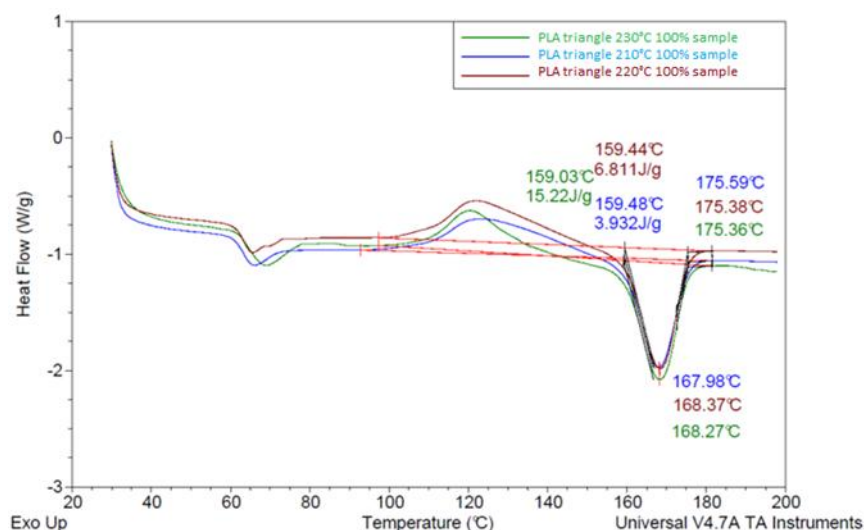


Figure 2. DSC curves of printed specimens

However, Figure 2 also shows that, with increasing printing temperatures, with almost the same melting curves, the shapes of the cold crystallizations differ, appearing smaller as the temperature increases, and the heat of melting values read in J/g also increase. In Figure 2 corrected values are represented that no longer include the J/g values measured during cold crystallization. The enthalpy change of cold crystallization has been subtracted from the enthalpy change of melting. It means that higher printing temperatures result in the formation of more crystalline phases. This is presumably due to the fact that, under the same cooling conditions, the higher printing temperature allows more time for the material to cool, thus allowing more time to create a hierarchically built-up polymer crystal structure.

Since the degree of crystallinity of the printed test specimen increases with rising printing temperature, this predicts a change in strength values.

Table 1 shows the mechanical properties of the examined test specimens. The results prove that increasing the printing temperature causes a slight increase in impact strength and tensile strength, while the tensile modulus decreases slightly accordingly. Due to the brittle behavior of PLA, increasing the printing temperature has practically no effect on tensile strain.

However, the change in mechanical properties cannot be entirely attributed to the increase in crystallinity, as higher printing temperatures also improve filaments welding, which leads to an increase in strength values, too.

At higher temperatures, the viscosity of the material decreases, its flowability improves, allowing the macromolecules of the contacting surfaces to diffuse into each other more easily.

Table 1. Mechanical properties of the printed specimens

Mechanical properties	Printing temperature [°C]		
	210	220	230
Impact strenght, average [kJ/m ²]	9,08	9,95	12,5
Impact strenght, st. dev. [kJ/m ²]	0,82	0,58	0,96
Tensile modulus, average [MPa]	2161	2109	1881
Tensile modulus, st. dev. [MPa]	129	90	130
Tensile strenght, average [MPa]	28,7	30,2	33,9
Tensile strenght, st. dev. [MPa]	2,89	1,94	3,82
Tensile strain, average [%]	2,15	2,17	2,33
Tensile strain, st. dev. [%]	0,2	0,07	0,33

Conclusion

The properties of printed test specimens from Ingeo 7032D packaging PLA can be changed by increasing the printing temperature. The higher the temperature at which they are printed, the higher the degree of crystallinity of the test specimens, because the material has more time to cool down, allowing it to form more crystalline phases.

Increasing the printing temperature also affects the mechanical properties, with an increase in impact strength and tensile strength values. However, these are not only due to the increase in crystallinity; the higher printing temperature also improves the welding of the filaments, thereby improving the mechanical properties.

References

- [1] Ekwurzel, B. (2017), The rise in global atmospheric CO₂, surface temperature, and sea level from emissions traced to major carbon producers, *Climatic Change*, 144:579–590., DOI: 10.1007/s10584-017-1978-0
- [2] <https://www.theguardian.com/environment/2020/dec/07/coca-cola-pepsi-and-nestle-named-top-plastic-polluters-for-third-year-in-a-row>
- [3] <https://www.theatlantic.com/science/archive/2018/08/nyt-mag-nathaniel-rich-climate-change/566525/>
- [4] Ronkay, F., Dobrovshky, K., Toldy, A. (2014) *Műanyagok újrahasznosítása, egyetemi tankönyv*, Printer kiadó, Budapest.
- [5] Nagy, B. (2011), *Újrahasznosítási ismeretek, egyetemi tankönyv*, Szent István Egyetem, Győr.
- [6] Farkas, F. (2000), *Műanyagok és a környezet: Környezetterhelés, környezetszennyezés-elhárítás, hulladékhasznosítás*, Akadémia kiadó, Budapest.

- [7] Balázs, G., Belina, K. (1998), *Műanyagok és környezetvédelem, előadási jegyzet*, Budapesti Műszaki egyetem, Vegyészmérnöki Kar, Budapest.
- [8] Lavender Law, K., Starr, N., Siegler, T.R., Jambeck, J.R., Mallos, N.J., Leonard, G.H. (2020), The United States' contribution of plastic waste to land and ocean, *Science Advances*, Vol. 6., No. 44., DOI: 10.1126/sciadv.abd0288
- [9] <https://www.theguardian.com/us-news/2019/jun/17/recycled-plastic-america-global-crisis>
- [10] <https://www.bloomberg.com/news/articles/2019-05-29/the-rich-world-s-electronic-waste-dumped-in-ghana>
- [11] <https://edition.cnn.com/2019/07/29/opinions/by-exporting-trash-rich-countries-put-their-waste-out-of-sight-and-out-of-mind-varkey/index.html>
- [12] <https://www.greenpeace.org/international/story/52154/africa-waste-colonialism-plastic-treaty/>
- [13] <https://www.dw.com/en/activists-slam-europe-for-dumping-on-africa/a-61315412>
- [14] <https://theoceancleanup.com/great-pacific-garbage-patch/>
- [15] Pál Károlyné (2012), *Komposztálható és az élő szervezetben lebomló politejsav alkalmazása*, <http://www.muanyagipariszemle.hu/2012/01/komposztalható-es-az-élszervezetben-lebomló-politejsav-alkalmazása-17.pdf>
- [16] Dr. Tábi Tamás (2015), *Biopolimerek, biopolimer kompozitok*, Budapesti Műszaki Egyetem előadás, www.pt.bme.hu/futotargyak/57_BMEGEPTMG12.../Biopolimerek_előadás_2015.pdf
- [17] Dr. Bodnár Ildikó (2014), *Lebomló polimerek*, Debreceni Egyetem előadás, www.eng.unideb.hu/userdir/bodnari/lebonthato%20muanyagok/lbm-ea-2014.pdf
- [18] Lim, L.-T., Auras, R., Rubino, M. (2008), Processing technologies for poly(lactic-acid), *Progress in Polymer Science* 33, 820-852., DOI: 10.1016/j.progpolymsci.2008.05.004
- [19] Södegard, A., Stolt, M. (2002), Properties of lactic acid based polymers and their correlation with composition, *Progress in Polymer Science* 27, 1123-1163., DOI: 10.1016/S0079-6700(02)00012-6
- [20] Ádám, B., Weltsch, Z. (2021) Thermal and Mechanical Assessment of PLA-SEBS and PLA-SEBS-CNT Biopolymer Blends for 3D Printing, *Applied Science*, 11(13), 6218. DOI: 10.3390/app11136218
- [21] Gao, Y., Wang, Y., Shi, J., Bai, H.W., Song, B. (2008), Functionalized multi-walled carbon nanotubes improve nonisothermal crystallization of poly(ethylene terephthalate), *Polymer Testing*, 27, 179-188., DOI: 10.1016/j.polymertesting.2007.09.012
- [22] Si, M.M., Feng, J., Hao, J.W., Xu, L.S., Du, J.X. (2014), Synergistic flame retardant effects and mechanisms of nano-Sb₂O₃ in combination with aluminum phosphinate in poly(ethylene terephthalate), *Polymer Degradation and Stability*, 100, 70-78., DOI: 10.1016/j.polymdegradstab.2013.12.023
- [23] Wang, Y.M., Gao, J.P., Ma, Y.Q., Agarwal, U.S. (2006), Study on mechanical properties, thermal stability and crystallization behavior of PET/MMT nanocomposites, *Composites Part B-Engineering*, 37, 399-407., DOI: 10.1016/j.compositesb.2006.02.014
- [24] Nagy, D., Ádám, B., Czél, Gy. (2016) Thermal Investigation of flame retardant containing PET, *Gradus*, Vol. 3, No. 2.
- [25] Ke, Y.C., Wu, T.B., Xia, Y.F. (2007) The nucleation, crystallization and dispersion behavior of PET-monomer-disperse SiO₂ composites, *Polymer*, 48, 3324-3336., DOI: 10.1016/j.polymer.2007.03.059
- [26] Belina, G., Menyhárd, A., Juhász, P., Belina, K. (2001) Heterogén gócképzők hatékonysága PET hulladékban, *Műanyag és Gumi*, 38(12), 441-446.