EFFECT OF HEAT TREATMENT ON MECHANICAL PROPERTIES OF 3D PRINTED SPECIMENS

Martin Baráth*, Martina Hajková, Martin Kotus

Slovak University of Agriculture in Nitra, Slovakia

Abstract

Currently, there is a need in some areas of metal construction materials for their lighter and cheaper alternative, which will have the same or better properties in terms of value and price. One of the most suitable and used alternatives are composite materials. When choosing a suitable composite material, it is necessary to take into account not only the necessary mechanical properties, but also the thermal load of the machine part. There were no permanent changes in the properties of metal materials, but we can notice changes in properties of composite materials that can positively or negatively affect the strength or life of the part. Due to this fact, presented is focused on the application of the effect of thermal loading of components made of composite materials using 3D printing on their mechanical properties. Laboratory tests were performed on test specimens prescribed for individual tests of mechanical properties. After performing the process of annealing the samples, we performed mechanical tests. Based on the obtained results, it is possible to determine the effect of annealing to the mechanical properties of the selected material and also we can determine the maximum operating temperature at which the properties of the material do not deteriorate.

Keywords: *3D print, annealing, tensile strength, composite, heat treatment*

1. INTRODUCTION

Nowadays AM is used in many areas of production and development. The ASTM society defined AM as “the process of joining materials to produce objects from 3D model data, mostly layer by layer. [1] AM originated in the 1980s. Initially, the use of AM was limited to the production of prototypes, due to the small choice of materials, mostly polymers. But today we can use AM for a wide range of materials from thermoplastics to metals, ceramics, to composite and biocompatible materials. Recently mentioned materials include a composite material reinforced with a continuous fiber. With proper fiber distribution, objects can achieve the strength of aluminum castings. [2, 3]. One of the main advantages of AM is the unlimited freedom of geometric shapes and the complexity of the created objects, which allows AM to match or even surpass conventional production technologies.

Fused deposition modeling (FDM) is the most commonly used AM technology [3]. FDM creates objects by extruding molten plastic layers. The material in the form of a thin fiber is fed to an extruder, where the material is melted and extruded through a nozzle onto the surface of the object [4, 5]. The mechanical properties of composites produced by FDM are worse than the mechanical properties produced by injection molding. The main reason is insufficient bonding between the individual layers, there is also high porosity and residual stress [6]. One alternative to improve the mechanical properties of 3D printed objects is heat treatment [7].

The annealing as a heat treatment is one of the main methods to modify 3D printed polymers, at relatively low cost it directs to adjustable properties on printed objects [8, 9]. Annealing consists to submit the polymer at defined temperature between the glass transition (Tg) and the melting temperature (Tm) for a specified time [10]. The degree of changes depends on the applied temperature and annealing time, generally this procedure purposes to relieve stress concentration, changing crystallite dimensions, accelerating crystallization or developing new crystalline phases [8,11].

To maximize property enhancements with a high degree of crystallinity in objects, the cooling rate has to be slow (leading to a long cycle time) [12]. The amount of crystallinity determines the performance of the material, improving stiffness, strength, heat deflection temperature and chemical resistance.

However, a disadvantage of annealing is that the 3D-printed object might deform, this can affect its function [13].

2. MATERIALS AND METHODS

2.1 Specimens manufacturing

For our research we used Markforged Mark Two 3D printer. This 3D printer offer continuous fiber fabrication (CFF) process. Printer has two nozzles, first for plastic material called Onyx and second for continuous fiber. The printer builds the matrix from Onyx and irons down continuous strands of fibers into the part. The fibers are impregnated with nylon and are fused to the Onyx layer. Printing parameters are shown in Table 1.

Parameter	Value
Print temperature (°C)	275
Layer height (mm)	0.125
Nozzle size (mm)	0.4
Infill	solid
Number of perimeters	2

Table 1. Printing parameters

In our research we used only Onyx material. Onyx is micro carbon fiber filled nylon. It's 1.4 times stronger and stiffer than ABS and can be reinforced with any continuous fiber from Markforged. Mechanical properties of Onyx are shown in Table 2.

Property	Testing method (ASTM)	Typical value
Tensile Modulus (GPa)	D638	2.4
Tensile stress at Yield (Mpa)	D638	40
Tensile stress at Break (Mpa)	D638	37
Tensile strain at Break (%)	D638	25
Flexural Strength (Mpa)	D790	71
Flexural Modulus (Gpa)	D790	3.0
Heat Deflection Temp (°C)	D648 B	145
Izod Impact - notched ($J.m^{-1}$)	D256-10 A	330
Density ($g.cm^{-3}$)	—	1.2

Table 2. Mechanical properties of Onyx material

2.2. Annealing

Samples were annealed in LAC LH 30/13 laboratory furnace at 205°C. The temperature was selected in two steps. In the first step we find coarse value of annealing temperature in technical data sheet [14]. In the second step we were inspired by Jain [6] and we performed preliminary research. In this

preliminary research we try three different annealing temperatures. Based on results with looking to maximal increase of tensile strength. Furnace was preheated for desired temperature before placing specimens we determined annealing temperature to 205°C. At the 205°C tensile strength was the highest, at lower temperatures was smaller and at higher temperatures tensile strength start decreasing. After desired temperature was reached we place specimens into furnace and we hold furnace temperature for 1 hour, then we let I cool down to 40°C for 15 hours. In the Fig 1 we can see annealing time and temperature.

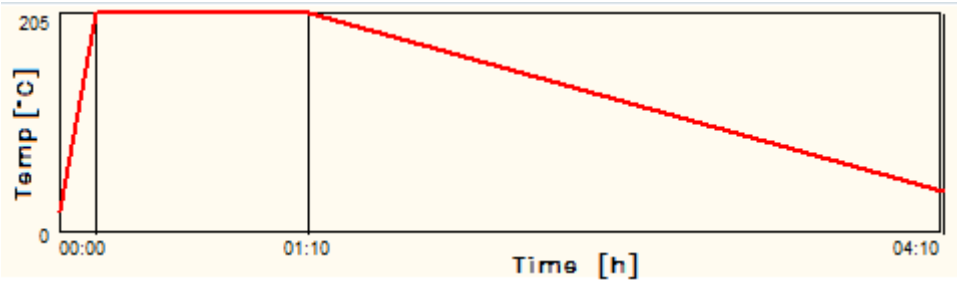


Fig. 1. Annealing time and temperature

2.3. Tensile testing

For tensile tests we used Testometric M500-100 universal tensile testing machine. Tests were performed according to ISO 527-1 and ISO 527-2 standards. Speed rate was set to 10mm.min^{-1}. Shape and dimensions of test specimens are shown in the Fig. 2.

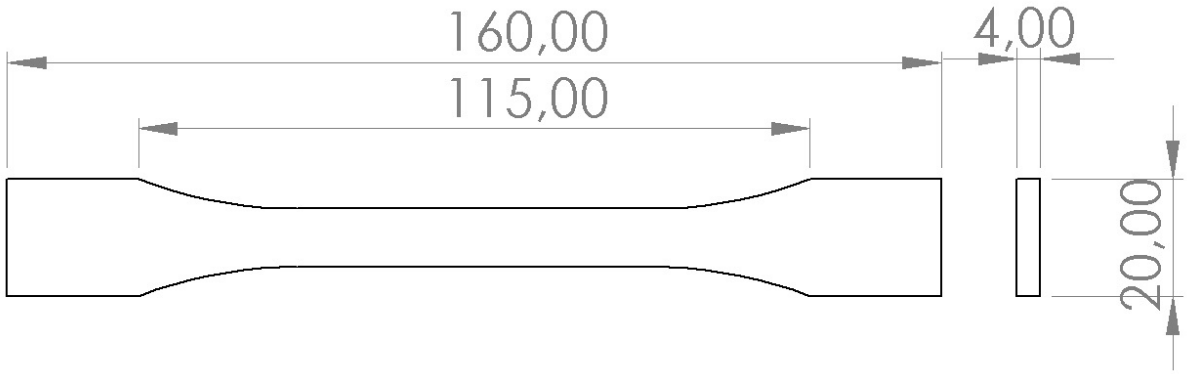


Fig. 2. Test specimen dimensions

3. RESULTS

All specimens were manufacture at same conditions, this means they were manufacture on the same they, at same ambient temperature and ambient humidity. Nylon is hygroscopic and it can absorb moisture from air. Humidity absorbed in nylon can influence mechanical properties of material [16]. Due to this fact tensile tests were performed immediately after manufacturing and annealing process. Tensile tests were performed on unannealed and annealed specimens. Annealing process also affected the shape of fracture surface. In the Fig. 3 we can see a comparison of the shape of the fracture surface of the annealed and unannealed sample. The upper sample is annealed, the lower unannealed. On the annealed sample we can see that the refraction is almost perpendicular to the longitudinal axis, which shows that the material is more brittle and homogeneous. On the unannealed sample, we can see

fracture curvature, which can be caused by greater toughness of the material and also inhomogeneity of the material.



Fig. 3. Annealed and unannealed specimens after tensile tests

In the Fig.4 we can see force-elongation curves of unannealed specimens. On this curves we can see plastic deformation region which means the material is ductile. Curves have almost identical shape and maximum load force. This means we can use FFF technology for creating objects with very good repeatability of mechanical properties.

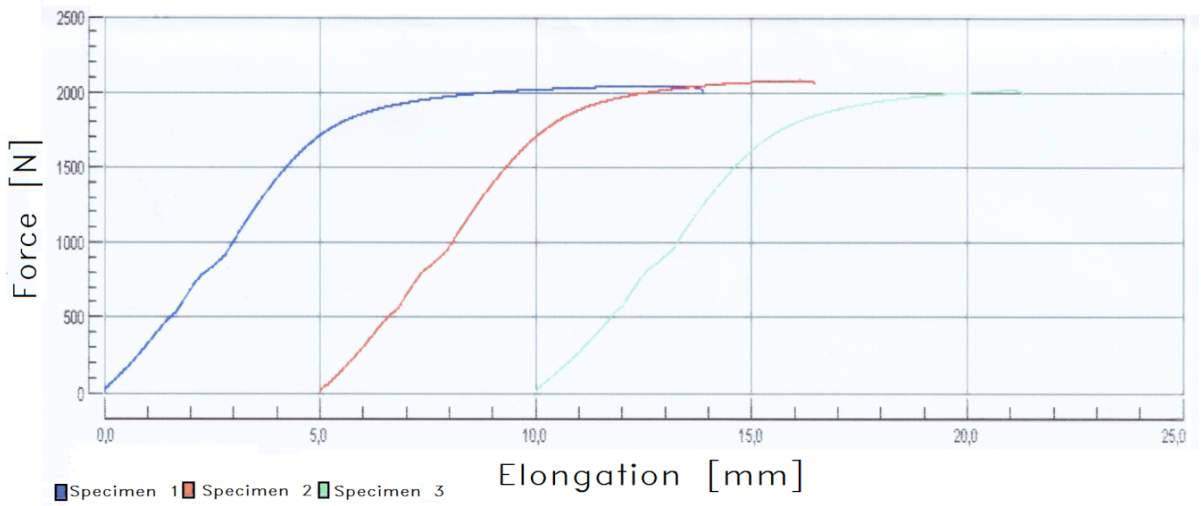


Fig. 4. Tensile test diagram of unannealed specimens

In the Fig.5 we can see force-elongation curves of annealed specimens. We can see annealed specimens had higher maximal force but they had smaller elongation and almost any region of plastic deformation which means material is more brittle. This means annealing improved tensile strength of specimens but material became more brittle.

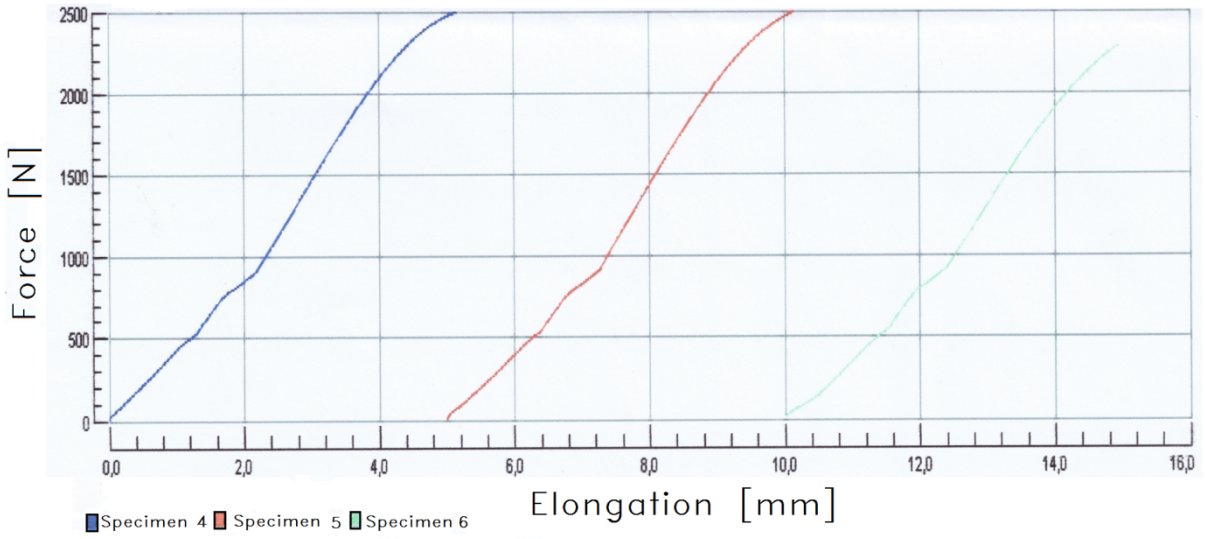


Fig. 5. Tensile test diagram of annealed specimens

In the Fig. 6 we can see tensile strength before and after annealing. Tensile strength was increased by 18.4% related to unannealed specimens. Standard deviation of unannealed specimens was 0.69 and standard deviation of annealed specimens was 2.45. This behavior can be explained by increased degree of crystallinity. The increase of degree of crystallinity in nylon has been shown to cause more brittle behavior, especially at degree of crystallinity above 40% [15]. Additionally, recrystallization induced by annealing was shown to cause additional crystallization shrinkage in material, which in case of the composite will be constrained due to the presence of microscopic short fibers.

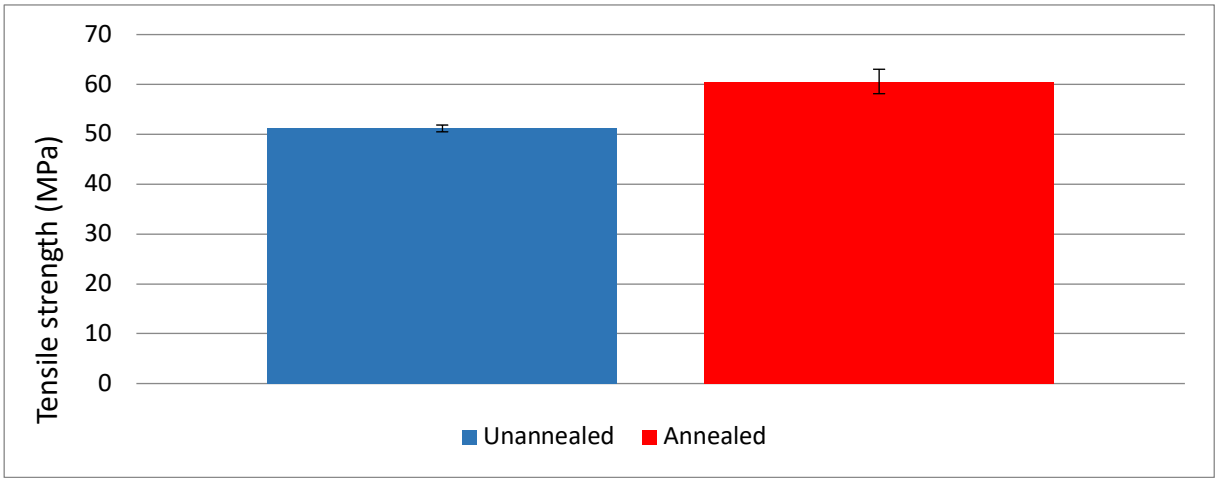


Fig. 6. Tensile strength of unannealed and annealed specimens

4. DISCUSSION

In this paper, we investigated the effect of annealing on the tensile strength of Onyx material. We found that the tensile strength increased from 51.2 MPa to 60.6 MPa. Jain [6] investigated the effect of annealing nylon composites on their mechanical properties. Despite the fact that he used nylon filled with glass fiber and we used nylon filled with carbon fiber we achieved similar results. Based on the results of our research and the results published by Jain [6], we can state that the process of improving the mechanical properties of the material takes place in a certain temperature range of approximately

170 ° C to 210 ° C. However, when the temperature exceeds about 210 ° C to 220 ° C, the mechanical properties of the material deteriorate and degrade. This statement is confirmed by the results of research published by Carlos [8].

ACKNOWLEDGMENTS

This paper was created within the project KEGA no. 003SPU-4/2021 "An Innovation of Study Programs using New Education Methods and Advanced Manufacturing Technologies."

REFERENCES

1. Kumar, SA & Prasad, RV 2021, "Basic principles of additive manufacturing: different additive manufacturing technologies", *Additive Manufacturing: A Tool for Industrial Revolution 4.0*, pp. 17 – 35, viewed 11 April 2022, <https://doi.org/10.1016/B978-0-12-822056-6.00012-6>.
2. Morgan, P 2005, *Carbon fibers and their composites*, Boca Raton, Florida, CRC Press, 199pp
3. Kuncius, T, Rimašauskas, M & Rimašauskiene, R 2021, "Interlayer Adhesion Analysis of 3D-Printed Continuous Carbon Fibre-Reinforced Composites", *Polymers*, no. 10: 1653, viewed 18 April 2022, <https://doi.org/10.3390/ polym13101653>.
4. Madaj, R & Kohár, R 2020. *Aditívne technológie*, Žilinská univerzita, Žilina.
5. Wächter, J, Fuhrmann, C & Moritzer, E 2021, "Investigation of the processability of different high-performance materials in the fdm process with regard to the shrinkage behavior", *Materials, Methods & Technologies*, vol. 15, pp. 58- 67,

   <https://www.scientific-publications.net/get/1000048/1632392253682605.pdf>.
6. Jain, PK, Sattar, S, Mulqueen, D, Pedrazzoli, D, Kravchenko & SG, Kravchenko, OG 2022, "Role of annealing and isostatic compaction on mechanical properties of 3D printed short glass fiber nylon composites", *Additive Manufacturing*, vol. 51, viewed 24 March 2022, <https://doi.org/10.1016/j.addma.2022.102599>.
7. Eduardo, F, Carlos, B, Danilo, S, Edcleide, A, Danyelle, F & Renate, W 2021, "Annealing Effect on Pla/Eva Blends Performance*", Journal of Polymers and the Environment,* no. 30*,* pp.541-554, viewed 10 April 2022 < https://doi.org/10.1007/s10924-021-02220-4 >.
8. Carlos, B, Luna, B, Danilo, D, Edcleide M & Renate, W 2021, "Annealing efficacy on PLA. Insights on Mechanical, thermomechanical and crystallinity characters" *Momento*, no 62, pp 1-17, viewed 22 April 2022 < doi: 10.15446/mo.n62.89099 >.
9. Tábi, T, Sajó, I, E, Szabó, F, Luyt, A, S & Kovács, J, G 2010, "Crystalline structure of annealed polylactic acid and its relation to processing", *Polymer Letters*, vol.4, no. 10, pp 659 – 668, viewed 25 March 2022 < doi: 10.3144/expresspolymlett.2010.80 >.
10. Malchev, PG, Vos, G, Norder,B, Picken, SJ & Gotsis, AD 2007, "Evolution of the morphology and the mechanical properties of ternary PE/PA6/GF composites during annealing", *Polymer*, vol. 48, no. 21, pp. 6294 – 6303, viewed 21 April 2022 , <https://doi.org/10.1016/j.polymer.2007.08.037.>.
11. Chen, J, V, Tanaka, K, S, Dang, B, C & Dang, A 2020, "Identifying a commercially-available

    3D printing process that minimizes model distortion after annealing and autoclaving and the effect of steam sterilization on mechanical strength", *3D Printing in Medicine,* no. 6, pp 1-10, viewed 15 April 2022 <https://doi.org/10.1186/s41205-020-00062-9 >.
12. Srithep, Y, Nealey, P & Turng, L 2013, "Effects of Annealing Time and Temperature on the Crystallinity and Heat Resistance Behavior of Injection-Molded Poly(lactic acid) ", *Polymer Engineering & Scienc*e, no. 53, pp 580 – 588, viewed 3 April 2022

< https://doi.org/10.1002/pen.23304 >

13. Wijnbergen, D,C, Stelt, M & Verhamme, L, M 2021, "The effect of annealing on deformation and mechanical strength of tough PLA and its application in 3D printed prosthetic sockets", *Rapid Prototyping Journal*, vol. 27, no. 11, viewed 28 March 2022, <https://www.emerald.com/insight/content/doi/10.1108/RPJ-04-2021-0090/full/html>.
14. Plastics International, *Annealing of nylon & reinforced nylons*, viewed 12 March 2022, <https://www.plasticsintl.com/media/wysiwyg/Nylon___Reinforced_Nylon_Annealing.pdf>.
15. Bessell, TJ, Hull, D & Shortall, JB 1975, "The effect of polymerization conditions and crystallinity on the mechanical properties and fracture of spherulitic nylon 6", *Journal of Materials Science,* no.10, pp. 1127-1136, viewed 19 March 2022, <https://doi.org/10.1007/BF00541393>.
16. Zhou, SM, Tashiro, K & Tadaoki, I 2001, "Moisture Effect on Structure and Mechanical Property of Nylon 6 as Studied by the Time-Resolved and Simultaneous Measurements of FT-IR and Dynamic Viscoelasticity under the Controlled Humidity at Constant Scanning Rate", *Polymer Journal*, vol. 33, no. 4, pp. 344-355, viewed 18 April 2022.