Determination of Material Properties for Biodegradable Polylactic Acid Plastic Used in 3D Printers

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Abstract—Within Rapid Prototyping technologies are used many types of materials. Many of them are recyclable but there are still as plastic like, so practically they do not degrade in the landfill. Polylactic acid (PLA) is one of the special plastic materials, which are biodegradable and available for 3D printing within Fused Deposition Modeling (FDM) technology. The question is, if the mechanical properties of produced models are comparable to similar technical plastic materials which are usual for prototype production. Presented paper shows the experiments results for tensile strength measurements for specimens prepared with different 3D printer settings and model orientation. Paper contains also the comparison of tensile strength values with values measured on specimens produced by conventional technologies as injection moulding.

Keywords—3D printing, biodegradable plastic, fused deposition modeling, PLA plastic, rapid prototyping.

I. INTRODUCTION

THE term Rapid Prototyping (RP) refers to group of techniques used for fast production of scaled models, real parts or assemblies based on 3D model, designed by CAD system [1]. The Rapid Prototyping Systems, above all Fused Deposition Modeling systems are very popular today. This technique works on similar principle as fuse-gun [2]. The material is unspool from spool to fuse-head, where is melted and deposited on working table. Support material is after completing of model break away or dissolved in special bath. Also by this technique is the prototype built layer by layer, as was mentioned in the text above (Fig. 1).

For prototype making is used ABS plastic, which is often used in industry, for example in car interior parts. The advantage of ABS plastic is impact resistance, good dimension stability, good stiffness, good resistance against acids and lye [3]. In the present time, there are a lot of polymers materials suitable for Fused Deposition Modeling process. On beginning there was just ABS (Acrylonitrile Butadiene Styrene) plastic, which was used for prototype production for Fused Deposition modeling devices. ABS is durable and strong thermoplastic used across many industrial sectors. This makes this material as ideal for conceptual prototyping, for design and functionality verification. This material has excellent impact resistance, good strength and stiffness (Table I) and relatively low cost.



Fig. 1 FDM technology scheme [4]

TABLE I			
MATERIAL PROPERTIES OF SELECTED POLYMERS			
Material	ABS plus	PLA	
Tensile strength (ultimate)	37 MPa	65,7 MPa	
Elongation at Break	3%	6%	
Flexural Strength	53 MPa	80 MPa	
Heat deflection (455kPa)	96°C	65°C	

Next generations of FDM devices are able to process also others and more types of plastics. For example they can do prototype models or functional parts from Nylon (Polyamide), PC (polycarbonate) or PLA (Polylactic acid), PET (Polyethylene Terephthalate) but also many others composite materials as LayWood, Magnetic Iron PLA, Steel PLA, LavCeramic and others. For example, the LavWood material consists from 60% of polymer as PLA and others 40% are wood particles. The final parts look and smell as wood [5]. There are also more other soluble materials which can be dissolvable in different liquids. These materials can be used as support material for devices with two nozzles for building of structure for overhanging surfaces [6]. But also for building of parts which can be used as pattern for mould preparation, because the will be dissolvable to make space for moulded material.

The PLA material is now probably the most used material for FDM devices, especially for small devices, which can be considered as small desktop devices. There are also many composite materials based on PLA. They are for example

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mixed with wood chips, flexible PLA filament, particles of brass, bronze, copper, ceramics, and other materials (Fig. 2). For this reason, and also because the PLA material is Eco friendly material, we want to know if this material can replace the others conventional plastic materials.



Fig. 2 Samples produced from PLA composite materials, (a) wood composite, (b) flexible material, (c) brass composite, (d) bronze composite, (e) copper composite

II. PLA POLYMERS AS ECO FRIENDLY FILAMENT FOR FDM DEVICE

As we mention before, the PLA material is Environmental friendly. This material has others advantages compared to ABS material and it is produced from renewable sources as cornstarch, tapioca roots, potatoes, starch, or sugarcane. Basic life-cycle of Polylactic Acid material is shown on Fig. 3 [7]. The melting point is much lower (175°C) compare to ABS (205°C). PLA do not require the heated platform in contrast to ABS. ABS models are predisposed for twisting when the model cooling down.

PLA polymers are able to degrade and this makes this polymers environmental friendly. PLA are primary degraded by bacteria. The long chains created in the polymerization are difficult for many bacteria to degrade. They can only attack the molecule at the ends.

When starch is combined with the PLA, it can be degraded more easily by the bacteria. Plasticisers such as glycerol, sorbitol and triethyl citrate are also added to starch-PLA compounds to prevent brittleness [8]. PLA is fully biodegradable when composted in a large-scale operation with temperatures of 60°C and above. The first stage of degradation of PLA (two weeks) is via hydrolysis to water-soluble compounds and lactic acid" [9]. Microorganisms then break down the lactic acid into CO2, biomass and water.

PLA decomposes into water and carbon dioxide in 47 to 90 days four times faster than a PET-based bag floating in the ocean. However, conditions have to be just right to achieve these kinds of results. PLA breaks down most efficiently in commercial composting facilities at high temperatures.

PLA is very unique material since it is made from corn and not from petroleum. Regular plastics are made from petroleum while PLA is made from corn-based resins, which makes PLA nontoxic and annually renewable resources. PLA is very environmentally friendly material since it is made from renewable resource – Corn. Plastics products may take up to thousand years to degrade while PLA products biodegrade within 3-6 months in a composting system. PLA products will take up to 6 months to degrade in commercial composting facility. In home composting facility, it may take longer time.



Fig. 3 Life-cycle of Polylactic Acid (PLA) material [7]

PLA as the alternative for others conventional plastic as ABS need to be tested, what are its mechanical properties within the context of parts produced by FDM device. For this reason, we have prepared the design of experiment for measurement of mechanical properties. In this article, we will present the measurement of tensile strength.

III. PLA MATERIAL TENSILE STRENGTH MEASUREMENT

First of all, we have selected the appropriate factors of which influence to measured tensile strength we want to monitor and know. In Table II, we can see the three selected factors and their levels. These factors have been selected with regards of previous experiences and producing of different samples. In practice, we know much more factors which are possible to set or change in pre-processing or processing level.

TABLE II Used Factors and Their Levels			
Factors	1	2	3
A – Filler shape	Circuit line	Honeycomb	-
B - Filler volume	100 %	50%	25%
C – Layer Thickness	0,10 mm	0,15 mm	0,20 mm

The first factor (A-Filler shape) obtain two levels. Circuit line is the simply style of placing of fibers inside of produced part. Honeycomb style is much difficult and looks like hexagon. Different possible filler shapes possible used in FDM systems are shown on Fig. 4.

Every of mentioned filler shapes have some advantages and disadvantages and their use is going to produce different results. For example, Honeycomb shape is good for strength. It follows the hexagonal pattern vertically through the produced part. This makes it generally good for mechanical parts. The line shape is faster than others and is god for organic shaped forms. Using of honeycombs cause also increased vibrations by short moves of the print head. In contrast, to concentric shape which cause less vibration in production process [12]. Also generating of G-code program is noticeable shorter when we use just simple lines unlike with using of honeycomb or others difficult filler shapes.



Fig. 4 Overview of different possible filler shape [12]

The second factor (B-Filler volume) means the percentage of material which is inside of model. If the part is fully filled by plastic material fibers, the filler volume is 100%. If there is also some space between fibers, we can also specify this volume. In our case, it is 50% and 25%. Examples of filler volume spacing are shown on Fig. 5.

Basically, the produced model is strong enough with filler volume of 10 to 25 percent. For gear and pulleys, a higher density of up to 50 percent or more may be best for durability. If we are producing the parts with less filler volume, the producing speed will be much higher and also the used filament will be decreased.



Fig. 5 Example of different filler volume [12]

The third factors (C-Layer thickness) specify what is the thickness of produced layer. Our device allow to set this factor in three levels (0,10 mm, 0,15 mm, 0,20 mm). There is also necessary to say on which device are our specimens produced, because from the previous experiment we know that the device type influence the condition of produced parts. In this

experiment and in this specimen production we have used small FDM device DeeGreen from be 3D company (Fig. 7). The basic parameters of device we can see in Table III. Designed specimen suitable for production on available FDM device and suitable for testing on our testing device is shown on Fig. 6.



Fig. 6 Design of specimen suitable for tensile strength testing

TABLE III				
FDM DEVICE PARAMETERS				
Rapid Prototyping Technology	FDM			
Printing area	150x150x150 mm			
Precision	0,1 mm			
Layer thickness	0,15 / 0,1, / 0,2 mm			
Nozzle diameter	0,4 mm			
Printing speed	90 mm/s			
Material	PLA, PVA			
External dimensions	495x395x390 mm			
Weight	20 kg			

When is clear what we want to measure and what are the selected factors and their levels, we can make design of experiment (Table IV). Depending on selected factors and their levels, we prepared full factors experiment (complete experiment plan). This plan consists from all possible combinations of all factor levels. It is the simplest and the most comprehensive plan of experiment. Allows to estimate all parameters of regression model and easy find out influence and weight of most important factors and their interactions to measured parameters [10].

If we have in our case k = 3 factors and measurement will be realized on $h_1 = 2$ levels for one factor and on $h_2 = 3$ levels for 2 factors. With accepted q = 3 repetitions, the total number of measurement will be $N_c = q \cdot h_1^k \cdot q \cdot h_2^k = 3 \cdot 2^1 \cdot 3^2 = 54$ repetitions. The design of experiment is shown in Table IV.



Fig. 7 DeeGreen device for prototype production

Measurement of tensile strength has been realized o Universal measurement device Inspekt Desk 5 kN (Fig. 8). The maximum possible loading of specimens is 5kN. Depending on this maximum loading force, we had to design the specimen dimensions. This measurement device automatically records all data and evaluates them. All data can be after exported to MS Excel software with possibility to prepare graphical illustration of testing progress. We can independently analyze the tensile force progress or tensile strength progress in dependence to elongation or other measured data.



Fig. 8 Tensile strength testing device –Inspekt Desk 5 kN

IV. RESULTS AND DISCUSSION

Measured data are presented in Table IV, where we can also see the design of experiment. This measured data are also graphically illustrated on Fig. 9.

As we can see from Fig. 9, there is some specific regularity in measured data. Measurements number 1, 2 and 7, 8 and 13, 14 are much higher than others are and are almost the same, in the frame of measurement uncertainty. When we see the design of experiment (Table IV) the reason of this, that when the filling of model interior is 100%, no matter what is the shape of filler, if it is circuit or honeycomb. The Factor C was evaluated as not significant so the best results are reached with combination of significant factors A and B. The best combination is for A-B factors with levels 1-1 or 2-1.

The lowest values of tensile strength have been measured in case of lowest filling volume (25%). This is understandable, because these samples (5, 11, 17) have the minimum content of plastic fibers.

The mass of plastic material can be easy illustrated by measurement of specimens weight (Fig. 10). Comparing of tensile strength (Fig. 9) and weight (Fig. 10) measured data we can see that the development of these two values is similar. The number of experiment with high value of specimen weight is identical with experiment number with high value of tensile strength.



Fig. 9 Tensile Strength values

TABLE IV
PLAN OF EXPERIMENT AND MEASURED VALUES OF TENSILE STRENGTH

No.	А	В	С	<i>R</i> _m (MPa)
1	1	1	1	52,90
2	2	1	1	52,43
3	1	2	1	29,93
4	2	2	1	40,07
5	1	3	1	27,03
6	2	3	1	41,87
7	1	1	2	49,97
8	2	1	2	51,57
9	1	2	2	31,57
10	2	2	2	41,50
11	1	3	2	23,60
12	2	3	2	40,07
13	1	1	3	51,50
14	2	1	3	51,57
15	1	2	3	30,70
16	2	2	3	41,63
17	1	3	3	26,80
18	2	3	3	39,20

The total average of measured tensile strength values:

$$R_{m} = \frac{\sum_{i=1}^{k} R_{m_{ji}}}{k} = 40,22MPa$$
(1)

where i = 1, 2, 3...k (k = 18) is number of experiments.



Fig. 10 Measured specimens weight values

This average value is similar or close to values measured in case of experiments 4, 6, 10, 12, 16 and 18. All of this experiment has the A-B factors combination 2-2 or 2-3. The factor C is not significant, so it have no influence in our realized experiments.

We also prepared the exact statistical evaluation by Analysis of Variances (ANOVA) and the final results data are published in Table V.

TABLE V ANOVA Analysis Results				
]	Factor / Interaction	F (calculated)	<i>p</i> (signification)	$F_{\mathrm{tab}0,95}$
	А	F(1,36) = 590	p<0,000001	5,424
	В	F(2,36) = 1107	p<0,000001	4,051
	С	F(2,36) = 2,74	p<0,078249	4,051
	A*B	F(2,36) = 146	p<0,000001	4,051
	A*C	F(2,36) = 1,78	p<0,183737	4,051
	B*C	F(4,36) = 4,67	p<0,003883	3,126
	A*B*C	F(4,36) = 1,71	p<0,170109	3,126

When we see the results from Analysis of Variances (ANOVA), the most significant is factor B (Filling volume). It makes sense, because the more materials contain the produced part, the stronger should be the structure of such model. The second most significant in the row is factor A (Filling shape). We can clearly see that the hexagonal honeycombs are stronger than just simple circuit lines. This goes from the shape of filling, because the load is better distributed to honeycomb structure.

From this experiments looks that the factor C (layer thickness) is not significant, but on different experiments, where the specimens are produced on different devices, also this factor is marked as significant. From the Analysis of Variance is as third most significant also interaction between factor A and B.

V. CONCLUSION

There are many experiments, which deal with tensile strength of different materials [11]. When we want to use the PLA material instead of other conventional plastic materials, for example ABS, we can say that the PLA material can fully replace the ABS material. The PLA material has even higher tensile strength value as with ABS plastic. Only in few cases this value is lower as tensile strength value of ABS material mentioned in Table I. Values in Table I are measured with injected specimens, not with FDM produced specimens. So we suppose that also ABS tensile strength values of specimens produced on FDM devices will be lower, as we can see in case of PLA material.

As we mentioned before, the PLA material have also more advantages compare to ABS material, so we can really say, that PLA can be used instead of ABS plastic in Fused Deposition Modeling device for prototypes or parts for final use production.

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REFERENCES

- [1] Rapid Prototyping & Manufacturing Technologies, IC Learning Series, The Hong Kong Polytechnic University, Industrial Centre
- [2] D. T. Pham, S. Dimov, Rapid Prototyping, A time compression tool, Manufacturing engineering centre, Cardiff University
- [3] J. Beniak, J.; Rapid prototyping and accuracy of created models, In: ERIN, - ISSN 1337-9089. roč. 5, č. 6 (2012), s. 2-9
- [4] M. Stanek, D. Manas, M. Manas, J. Navratil, K. Kyas, V. Senkerik, A. Skrobak, "Rapid Prototyping Methods Comparison"; *Recent Researches in Circuits and Systems*, 2012, ISBN: 978-1-61804-108-1
- [5] J. Beniak, Systémy Rapid Prototyping. 1. vyd. Bratislava: Nakladateľstvo STU, 2014. 133 s., 82 obr., 31 tab. ISBN 978-80-227-4287-0
- [6] C. K.Chua, K. F.Leong, C. S.Lim, *Rapid Prototyping*, Principles and Applications, Nanyang Technological University, Singapore, World Scientific Co. Pte. Ltd, 2003, ISBN 981-238-117-1

- [7] R. A. Gross, B. Kalra, "Biodegradable Polymers for the Environment", in Science 2 August 2002: Vol. 297 no. 5582 pp. 803-807, DOI: 10.1126/science.297.5582.803
- [8] W. Harris, "How long does it take for plastics to biodegrade?" 15 December 2010. HowStuffWorks.com, Available: 21 June 2015, http://science.howstuffWorks.com/science-vs-myth/everydaymyths/how-long-does-it-take-for-plastics-to-biodegrade.htm.
- [9] A. Shah, F. Hasan, S. Hameed, *Biological Degradation of Plastics*: A Comprehensive Review. Biotechnol. Adv. 2008, 26, 246-265
- [10] E. Jarošová, Navrhování experimentů. Česká společnost pro jakost, 1997
- [11] J. Lipina, P. Kopec, V.Krys, *Tensile tests on samples manufactured by the rapid prototyping technology in comparison with the commercially manufactured material*. In SAMI 2015 IEEE 13th International Symposium on Applied Machine Intelligence and Informatics, Proceedings, 2015-01-01, pp. 325-328.
- [12] R. Salinas, 3D Printing with RepRap Cookbook, Quick answers to common problems, PACKT Publishing, June 2014, ISBN 978-1-78216-988-8.

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