Production, additive printing and mechanical testing of PLA/PHB material with different concentrations of TAC emollient

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Abstract — In order to carry out mechanical testing of samples printed by using additive technology, it is necessary **to** ***specify the parameters of the production of filaments, the parameters of 3D printing and the parameters of mechanical testing. In this article, I will discuss the production of filaments, additive technology for printing samples from PLA/PHB material used for detailed mechanical tests and subsequently for evaluation of these mechanical tests. The real-world application of PLA/PHB products bring great benefits. The aim of this paper is to perform mechanical tests on extruded PLA/PHB samples with three different TAC solvent concentrations. Samples were printed using additive technology. The*** **comparison of the results of the pressure and tensile testing carried out on the apparatus** ***also contributed to the success of the research.***

Keywords — Additive technology, 3D printer, mechanical properties, tensile test, pressure test

I. INTRODUCTION

Environmental interests and green chemistry have played a major role in the development of the next generation of materials, processes, and products in recent years. Efforts to develop new biodegradable polymers from renewable sources have been deepened by concerns about the persistence of plastics in the environment, dwindling oil resources, and concerns about toxic gas emissions during combustion. The demands and direction of the industry in the production of consumer goods led to research into the development of new environmentally friendly green packaging technologies. The design of new structures that must meet the proper functions and sustainability is one of the biggest challenges in researching into new packaging materials. Polylactic acid (PLA) is a linear thermoplastic polyester obtained by fermentation of renewable agricultural crops. It is compostable and degradable over a period of less than one month and is currently the most widely used biodegradable polymer for short-term use. Polyhydroxybutyrate (PHB) as aliphatic polyester synthesized by microorganisms with high crystalline and high melting temperature is often used as an ingredient for mixing with PLA which produces materials that excel in interesting physical, thermal and mechanical properties compared to pure PLA [1] - [6].

Additive or 3D-printing technology is attractive for many areas such as:

- research in prototypes or limited production of prototypes,
- medical field - the objective is to produce 3D biomedical structures, preceded by modeling from the data obtained using medical imaging techniques such as (computed tomography, magnetic resonance imaging, ultrasound),
- manufacturing industry - manufacture of spare parts for cars or aircrafts.

Every year, the development of additive production is accelerating due to reduced production cycles, waste, limited use of cutting fluids [7]. Therefore, it is also often used for the development and manufacturing of flexible medical devices, robotics, dental implants and scaffolds for tissue engineering [8][7]. Methods of additive production are designed for different types of materials, such as thermoplastics (acrylocene-butadiene-styrene (ABS), poly (lactic acid) (PLA), polyamide 6 (PA6), high-strength polystyrene, etc.), resins, metals (Al, steel, Au, Ag, Ti, alloys), gypsum-based powders, ceramics, waxed materials, biomaterials [9]. Polymers are mostly used in the field of 3D printing. Aliphatic polyesters are among the most widely used biopolymers due to their properties such as their non-toxic, biodegradable and biocompatible character.

II. PROCESS OF PRODUCTION AND TESTING OF FILAMENTS

A. PLA/PHB production with different TAC concentrations

In order to perform tensile and pressure tests on objects printed using 3D additive technology from PLA/PHB material with three different types of solvents, it is necessary to produce filaments. The production of filaments is a difficult process because there are few companies in Slovakia and the surrounding countries that specialize in the production of filaments of certain requirements for medical purposes. The required filaments should be made of specific materials such as PLA and PHB with different ratios of solvent added, which further complicates initial scientific research. Table 1 provides an overview of companies

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engaged in custom additive printing and the production of 3D printing filaments.

TABLE I. COMPANY OVERVIEW STUDY

S.n.	Company name	Specialization of the company	Information available at
1.	3Demon	Several years of work in 3D printing and 3D modeling.	https://3d-mon.com/
2.	Fillamentum	Fillamentum specializes in high quality 3D printing. It is located in the southeastern part of the Czech Republic, in the town of Hulin where it was founded in 2011.	https://fillamentum.com/
3.	MATERIALPRO3D	Slovak company that produces and distributes filaments for additive printing.	
4.	MAKERSLAB	Czech company offering custom 3D printing, modeling and workshops.	https://makerslab.cz/.
5.	3D PRINT	A company based in the Czech Republic offering custom-made filaments.	
6.	NEXEO Plastics	A global company providing distribution services, intelligent solutions in the field of additive production.	https://www.nexeoplastics.com/.
7.	Innofil 3D	One of the largest producers in Europe with an exclusive focus on FFF printing threads.	
8.	FILAMENTS.CA	A global company based in Canada providing a wide range of filaments	
9.	Advanced Biomedical Technology Inc.	Established company based in Taiwan engaged in 3D printing for medical purposes.	

In order to make the most accurate filament from PLA and PHB materials, we contacted foreign companies. Subsequently, after presenting of scientific research and the objective, we received largely negative responses. Fillamentum replied that the material was very specific and they had already heard of it, but they never worked with it in practice. 3Demon wasn't able to produce filament due to the specification of PLA and PHB materials. The other companies made a similar conclusion. We were able to produce filament in cooperation with Bratislava Technical University.

B. Modeling and 3D printing of samples

Dogbone samples are intended for using primarily in tensile tests. The sample has a gap at both ends. The arms are wider than the cross-section, resulting in concentrations of centre tensile strenght at the moment of loading of the sample with tensile force. This concentration increases the probability of the sample bursting from the ends. If the sample breaks in the centre, the material reaches its maximum tensile strength. If the sample breaks at one of its ends, the failure may be attributed to an incorrect load or defect of the material. Therefore, the dogbone sample is designed to ensure the highest probability of the sample bursting due to the maximum tensile load [10]. ASTM D638 is the most common testing standard for determining the tensile properties of reinforced and non-reinforced plastics. The use of plastics in diverse industries is still high and this fact forces manufacturers to measure their mechanical strength. Tests according to ASTM D638 are carried out by applying a tensile force to the sample and then measuring the different characteristics of the sample. The test is carried out on a universal test machine at tensile speeds between 1 and 500 mm/min, until the sample is damaged. There are five types of samples for ASTM D638 with size difference depending on the thickness of the sample and the amount of material available. Type I samples are most widely used with a thickness of 3,2 mm and are usually produced by injection. Type I samples have a total length of 165 mm and a width of 13 mm (Fig. 1) [11][12][13]. The samples were modeled in Solidworks. This sample is intended to be used for tensile tests.

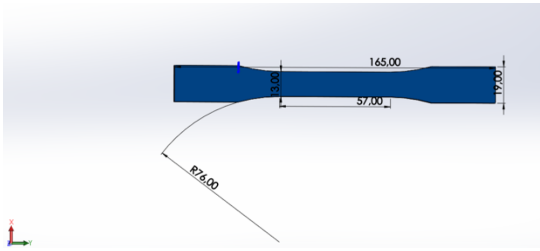

Fig. 1. Dimensions of type I sample for mechanical testing in mm

Figure 2 shows a sample used for pressure tests. It is a simple roller modeled with the help of Solidworks with a diameter of 10 mm and a height of 20 mm.

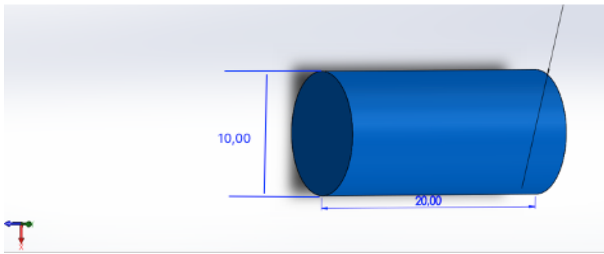

Fig. 2. Dimensions of sample for pressure tests in mm

A TRILAB printer was used to print objects for subsequent tensile and pressure tests. TRILAB DeltiQ is a very reliable 3D printer, even in a more demanding professional environment. The objects were relatively simpler in shape, but the problem was the newly tested material, which tended to jam and then clogged the print nozzle. This printer stands out for its simplicity and very well-mastered design. TRILAB DeltiQ is usable in many areas due to its reliability and quality outputs, as has been shown in our case. According to experts, printing with this device is also described as very precise and fast, allowing you to significantly save time, which is important for 3D printing. There are no errors caused by the movement of the model when printing. The printer is also able to print more complicated departments and angles without support. Print progress is predictable from the beginning of the first layer to the end of the last layer. The architecture of this printer uses ultralight moving parts for high print head acceleration and high print speed [14][15].

C. *Printing parameters and preparation of samples for tensile and pressure testing*

To perform tensile and pressure tests, it was necessary to print 90 rollers and 30 bones. The total estimated printing time was 36 hours. All rollers made of all three materials were printed in 13.5 hours. 22.5 hours were needed to print the bones. The individual parameters are listed in the Tab. 2.

TABLE II. PRINT PARAMETERS.

Printing temperature	210 °C
Plate temperature	55 °C
Printing time for 1 bone	45 min
Printing time for 1 roller	9 min
Total printing time	4:36 p.m.
Materials used	PLA/PHB with 0 % TAC, PLA/PHB with 6 % TAC, PLA/PHB with 8 % TAC

KISSlicer was required to edit and transform the *.stl* file created in solidworks. KISSlicer is a very simple and powerful software, also suitable for the general public. It is an effective software for different platforms, which splits *.stl files* into printer-ready G-code files. Printing itself led to various problems, stuttering the printer filament. Some modifications had to be made that helped to make the filament more passable. The resulting products had good quality without pores. The shortcomings on the test objects are due to the actual printing and selection of the 3D printer. In Figure 3, there are objects which were printed for mechanical testing.

Fig. 3. Rollers and dogbone.

After the samples had been printed, preparation for the testing itself began. Two types of objects were printed: a simple pressure test roller and a dogbone for the tensile test. The resulting object was measured using measuring devices. Calliper was used the most. Samples had to be marked for data accuracy. Tensile and pressure tests were carried out according to ASTM D638 on a machine from Hegewald & Peschke. Hegewald & Peschke develops and manufactures machines for testing destructive materials, components and finished products cameras and programs. Labmaster PROFESSIONAL is a software that provides 4-channel data collection and signal adjustment. Sofware also has a wide application in mechanical tensile and pressure tests. The RTSS Videoextensometer measures longitudinal and transverse stress during material tests such as tensile tests. The system can be used for both flat and round samples in the field of vision (FOV) from 10 mm to 1000 mm [16][17][18].

III. ANALYSIS OF THE PRACTICAL PART OUTPUTS

A. *Evaluation of the pressure test*

On the basis of the pressure test in which 90 rollers from three different materials were tested, the data recorded in the graphs and tables were obtained. Sets 1, 2 and 3 were tested. There were 30 rollers in each set. The graphs record the force data in N and the displacement in mm, where the graph shows the tension curve at which the roller has deformed.

$$\sigma = \frac{F}{A} \text{ [MPa]} \qquad (2)$$

The compressive strength is defined as the force *F,* applied to area *A* at the moment of crushing.

The curves of 30 samples of set 1 are in Figure 4, where parts of the 16 samples are not pushed into each other, leaving a brittle fracture with no more visible changes to the sample. The material with no signs of the use of a plastic softener also has an impact. On the x-axis, the position is in mm and on the y-axis the force in N.

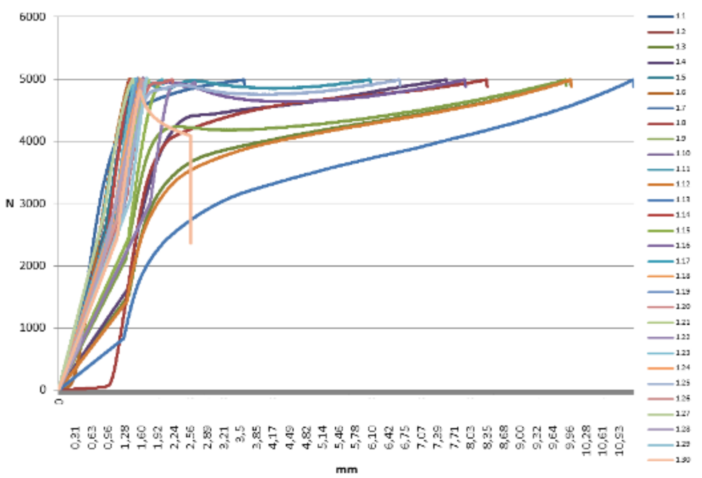

Fig. 4. Graphical representation of the values of test set 1.

Curves of 30 samples of set 2 (Fig. 5) which are made of PLA/PHB material with a 6 % TAC show worse strength characteristics compared to set 1, for the reason that parts of 18 samples began to be pushed together.

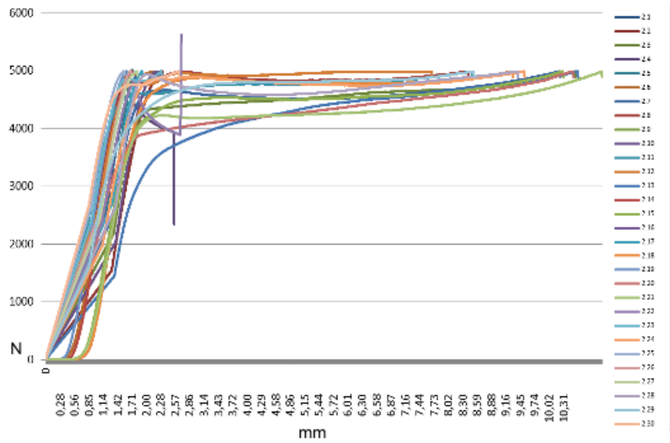

Fig. 5. Graphical representation of the values of test set 2.

30 samples of set 3 (Fig. 6) made of PLA/PHB material with 8 % TAC, show lower compressive strength and greater plasticity compared to other materials, as parts of all 30 samples were pushed together. The use of the TAC emollient with the highest concentration of up to 8 % has an impact on this course.

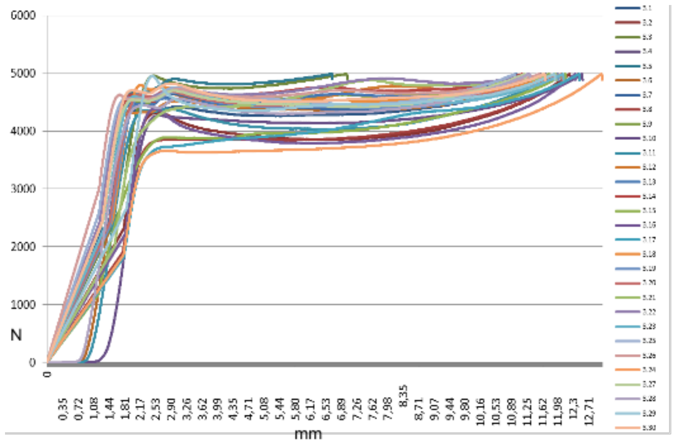

Fig. 6. Graphical representation of the values of test set 3.

B. *Evaluation of the tensile test*

The evaluation of carried out tensile test consists of the evaluation of the *modulus of elasticity* E [MPa] and the tension σ_{MAX} [MPa].

During the tensile test, the tensile machine software recorded the cross-sectional *value* S_O, the value of the module elasticity in tensile *E*, the maximum $\sigma_{tension\ MAX}$ value, or the tension value between the $\sigma_{slip\ Y}$. The auxiliary extensometer device recorded the initial measured length *Lo*, proportional elongation, and percentage elongation. In total, 30 samples were tested in three sets of 10 samples. Colored graphical evaluation with appropriate tables serves as the best interpretation of obtained results.

C. *Evaluation of the modulus of elasticity*

The values of the modulus of elasticity are shown in the Tab. 3.

TABLE III. THE VALUE OF THE MODULUS OF ELASTICITY .

	Modulus of elasticity [MPa]		
Test sample	***Set 1***	***Set 2***	***Set 3***
1	1065,523	1025,238	1066,986
2	677,3	569,497	963,873
3	1144,988	472,724	1103,005
4	975,5	1058,407	823,571
5	1319,02	1321,501	711,621
6	911,393	1433,128	1283,201
7	988,572	954,864	938,795
8	871,41	830,077	1360,67
9	378,99	1040,054	1058,021
10	1303,15	904,446	1169,553
Average	963,5846	960,9936	1047,9296

The above values are shown graphically in the graph (Fig. 7). It follows that sample 6 from the second set made of PLA/PHB material with a 6 % TAC shows the largest value - 1433,128 MPa. By contrast, the smallest value - 378,99 MPa was obtained by a sample 9 from the first set, made of PLA/PHB material with a 0 % TAC.

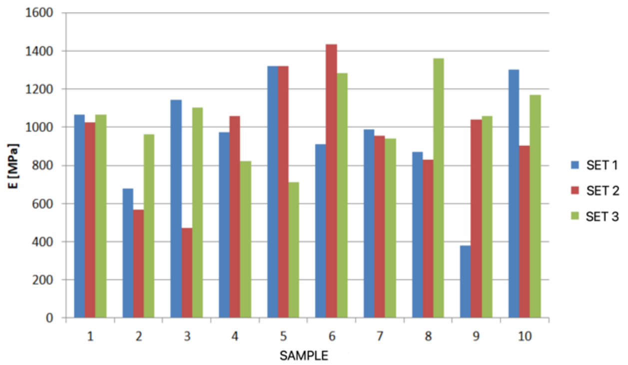

Fig. 7. Graphical representation of the tensile modulus of elasticity.

When comparing all data (Fig. 8), set 3 reached the highest value - 1047.9296 MPa.

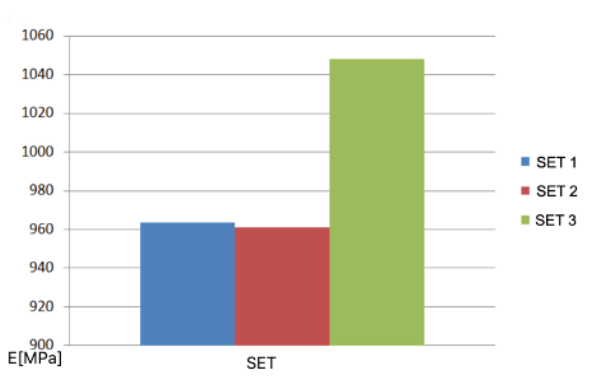

Fig. 8. Average values of tensile flexibility set.

D. *Tension evaluation*

The tension evaluation procedure is identical to the modulus of elasticity. Table 4 shows the tension values.

TABLE IV. TENSION VALUES.

	Tension [MPa]		
Test sample	***Set 1***	***Set 2***	***Set 3***
1	40,786	32,511	37,908
2	36,327	21,969	21,566
3	29,485	39,924	35,885
4	38,961	33,745	18,689
5	45,204	38,62	15,109
6	20,498	37,115	33,494
7	40,741	36,489	17,431
8	18,173	16,175	27,8
9	31,235	23,946	37,894
10	46,591	27,348	23,107
Average	34,8001	30,7842	26,8883

The above values are graphically shown in the graph (Fig. 9). It follows that sample 10 from the first set made of PLA/PHB material with a 0 % TAC shows the largest values of 46,591 MPa. By contrast, the smallest values of 15,109 MPa were obtained by sample 5 from set 3, made of PLA/PHB material with an 8 % TAC.

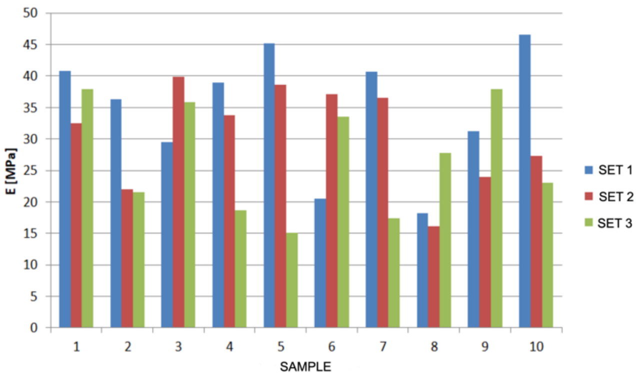

Fig. 9. Graphical representation of tension.

When comparing all data (Fig. 10), set 1 reached the highest value of 34.8001 MPa.

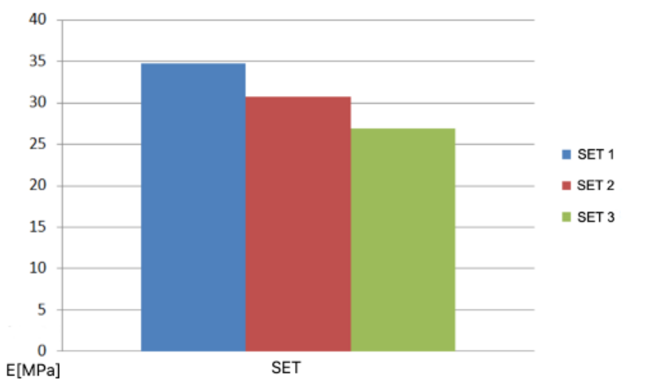

Fig. 10. Average tension set values.

IV. CONCLUSION

Prepared theoretical part and its possible application in practice represent a benefit for the area of mechanical testing of materials. The study aims to provide new knowledge and bring it to the practical sphere. The individual benefits can be summarised in the points below.

A. *Thesis contribution to science, research and practice*

- Formulation of methodological procedure for the tensile and pressure test.
- Presentation of the Thesis results in the publication activity.
- Theoretical basis for further research in this field.

B. *The benefits of work for practice*

From the results of mechanical tests obtained, PLA/PHB-based materials could be used in different areas:

- food industry – production of health-free products,
- environmental ecology – materials are more biodegradable than other plastics.

During tensile tests, the smallest amount of solvent was used for set 1, and largest for set 3. The results show that set 1 achieves the highest tension values and set 3 highest values of the modulus of elasticity.

In the pressure tests, samples with the highest addition of the TAC solvent showed lower compressive strength and greater plasticity. The Less solvent added, the better the tensile strength.

The overall evaluation of the flexibility and tension module is in Tab. 5.

TABLE V. OVERALL RESULTS.

	Modulus of elasticity [MPa]	**Tension [MPa]**
Set 1	963,5846	34,8001
Set 2	960,9936	30,7842
Set 3	1047,9296	26,883

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