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# Degradation of 3D Printed Polymer Composites with Filler of Cellulose-Based Materials

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**Today, the emphasis is on the production of materials that are degradable in nature and on production with modern technologies. For these materials to find a suitable use, they need to be exposed to the conditions that may arise in the application. The effect of degradation was assessed for composite materials with a PLA matrix and a natural-based filler, which were processed by 3D printing technology. The progress of degradation in the climate chamber was monitored over a period of 6 weeks. The results are determined by static tensile test and hardness test and the difference in weights of the test bodies. The test results confirmed. During the degradation process, the test specimens with natural fillers deformed less than the specimens made of pure PLA. The maximum tensile strength values for the material with natural fillers were approximately two thirds lower than for pure PLA. The maximum tensile strength during degradation showed an increasing or stagnant tendency. the maximum elongation decreased during degradation for the material with fillers showed a logarithmic behavior compared to pure PLA with a linear tendency.**

**Keywords:** Additive manufacturing, Biofillers, PLA, mechanical properties

## 1 Introduction

Degradation of polymeric materials with biofillers must be understood as an issue of polymer properties and separately as an issue of biodegradable fillers. At the same time, however, we also have to manage the interaction of the sequential stresses in the function of the production raw material and the product, where specific properties are expected.

Improving the properties of the polymers themselves is defined by the addition of a suitable filler to the polymer matrix. This is doing, for example, by surface modification in the composition organic/inorganic; natural synthetic; based on affinity, i.e. active/passive; using particle size typically nanoparticle/conventional fillers. ¨

Additive technology for creation of polymer products or simplified 3D printing technology is becoming almost an integral part of laboratory equipment of developers, technologists and designers. This unique technology makes it possible to produce almost any model according to specific requirements of the designer and greatly facilitates and speeds up the development of prototypes. Additive components technology can be easily and quickly modified and optimized. Development is more progressive and significantly reduces the cost of creating the final prototype. [1] Like as semi - finished products for FDM printers are use a filament from polymeric material. The 3D model is produced by extruding the material on a printing bed, where the individual layers of polymeric material are layered on top of each other. [2]

### 1.1 Polymer matrices

In general, we require properties from the polymer matrix such as toughness, or the ability to transfer load to the fibres, thermal stability, dimensional stability, chemical resistance, strength, stiffness and resistance to indentation. These should also correlate with the manufacturing processes and their energy intensity. Composite (fibre) polymers are best suited to meet these requirements. As such, the matrices are either thermoplastic or reactoplastic in nature. Thermoplastic: polypropylene (PP), polyamide resins (EP) and (PA), polyimides (PI). Reactoplastic: unsaturated polyester (UP), vinyl ester (VE), phenolic resins (PF). [3]

### 1.2 Biological fillers and matrices

Practice requirements for materials that can be degraded from the product structure at the end of its life are now standard for environmental reasons. The rationale for this requirement is due to the properties of binders such as epoxy, polyester, vinyl ester, polyimide and phenolic binders, which are not subject to biodegradation at the end of their life. The only possible degradation is mechanical or thermal. Other elements are composite fibres and/or films of carbon, aramid and glass.

The use of biopolymers guarantees partial or complete destruction of the product at the end of its life. If a plastic matrix and bio-filler are used, there will be no complete biological decomposition, but only partial, but the mechanically damaged matrix will gradually degrade due to the destruction of the bio-filler, thus guaranteeing long-term decomposition. A similar view can be taken of bio-reinforcement composite materials where glass and other materials replace natural fibres such as wood, bamboo, jute, flax, sisal, coconut or hemp. In comparison, the tensile strength of biological binders and fibres is 60 to 70 MPa for epoxy 60 to 80 MPa, polyester 50 to 75 MPa, vinylester 70 to 80 MPa and phenolic composite 60 to 80 MPa. [4]

In 3d printing, biodegradable polylactic acid (PLA) filament is used in large quantities as an input material, and this is produced by polymerisation in the presence of a catalyst. The biological and physical properties of PLA depend on the enantiomeric purity of the lactic acid stereopolymers. This material is characterised by compostability, low or no toxicity and satisfactory mechanical properties. Unlike the reported polymers, PLA has a very low heat resistance and associated low dimensional stability, i.e. an HDT (Heat Deflection Temperature) of 50 to 60 °C. [5]

### 1.3 Biofillers

By this we mean cellulose, which is the basic building material of vascular plants, but also of animals, marine plants and bacteria. This polysaccharide is the most common and abundant organic compound found on earth. The primary building unit of cellulose is formed by a hydroxyl functional group, which is the skeleton of the H bond within the macromolecule – influencing considerable hydrophilia. In terms of filler function, the gradual degradation due to moisture and complete decomposition on contact with liquid water must be taken into account.

Biological (fibre) fillers are not homogeneous and contain pectin, lignin, fats and waxes in addition to cellulose. In terms of purity, the best filler is cotton, which contains 99 % cellulose. The other commonly used fillers sisal, flax, coconut, ramie and hemp contain cellulose ranging from 81 % (flax) to 43 % (coconut). Different physical and chemical characteristics also mean different properties and uses. Typically, bast fibres will be a suitable composite for matrices and leaf fibres more likely to be used as filler in matrices. Their mechanical properties give a little more clue: the density of these materials ranges from 1.25 to 1.51 g/cm3 (most cotton, least coconut); the Young's modulus E (GPa, a model of tensile elasticity) has a fairly wide range from 6 to 80 MPa (most flax and least coconut); the tensile strength is given in the range 5 to 47 GPa (most hemp, least coir); elongation at break from 1,2 to 25 % (most coir, least flax); moisture acceptance 7 to 25 % (least flax, most cotton). By comparison, glass fibre has a density of 2,55 g/cm3, a model tensile modulus E of 73 GPa, a tensile strength of 29 MPa, an elongation at break of 3 % and is non-absorbent.[6]

To this overview belongs also a material called PLA, which is produced, among other things, as a composite PLA with wood filler, with a tensile strength of 29.5 MPa, a flexural strength of 40.4 MPa, a flexural modulus of 1.7 GPa and a flexural modulus of 0.65 GPa, elongation at break of 5%. [7]

The aim of the research was to determine the basic mechanical properties of commercially available 3D printing materials and whether the presence of a climate chamber affects these properties.

## 2 Materials and methods

Four types of commercially available filament were used. All filaments were produced by PLASTIKA TRČEK proizvodnja in trgovina d.o.o. The filaments used were PLA-transparent (further marked PLA), PLA-wood (further marked Pine), PLA-cork (further marked Cork), PLA-bamboo (further marked Bambus) according to the manufacturer of the filaments with filler (wood, cork, bamboo) according to the information from the filament manufacturer the materials contain approximately 40% filler.

The test specimens were created by a Prusa i3 MK3S+ 3D printer. According to the ČSN EN ISO 527-2 standard, test solid 1B was modelled using Autodesk Inventor 2021.The shape of this solid was used for printing. 50 specimens were printed from each material. After unpacking, all filaments were placed in a modified Sencor SFD 815GR fruit dryer in which the filaments were dried for six hours at a set temperature of 55°C.

Print preparation was performed using PrusaSlicer 2.1. A nozzle with a diameter of 0.6 mm was used to reduce the probability of nozzle clogging. The printing parameters were as follows. Layer height 0.2 mm. 100% straight fill at 45° and -45° to the x-axis, with three perimeters around the perimeter of the body. Print speed was set at 45 mm/s with a deceleration to 35 mm x $s^{-1}$ at the outer perimeter. A printing speed of 20 mm x $s^{-1}$ was used for the first and last layer. Printing was carried out at a temperature setting of 200 °C on the nozzle and 50 °C on the heated pads. The cooling fan speed was set to 80 % for printing the first two layers and the cooling fan was turned off. The retraction distance was 5 mm, the retraction speed was 70 mm x $s^{-1}$ and the deretraction speed was 30 mm x $s^{-1}$. During One Print, 7 specimens were printed. The specimens were on the print pad horizontally with the print x-axis.

### 2.1 Degradation

First, six specimens (of each material) were tested to see if they could withstand degradation according to CSN EN ISO 9142 with a selected cycle consisting of three parts, see. Tab. 1. Changing the required parameters between parts of the cycle was performed within 15 min.
After the first week of checking the specimens, it was already obvious that the specimens had degraded too much and that the mere handling of the specimens had caused the disintegration of the specimens. The assumption was that the chosen moisture was to blame. Therefore, a second test was conducted where moisture was eliminated during the cycle in the climate chamber in Part 1 and Part 3. For this reason, it was decided to perform only thermal degradation without the presence of the selected moisture in the climate chamber.

42 specimens from each material were placed in the climate chamber The degradation of the test bodies was carried out in the climate chamber. One cycle (24 h) consisted of three parts, see Tab. 1, a total of 42 cycles were performed, corresponding to 6 weeks. After every 7 cycles (1 week) 7 samples were taken.

***Tab. 1*** *Degradation cycle*

| Parts | Part1 | Part2 | Part 3 |
|---|---|---|---|
| Temperature [°C] | 70 | -40 | 70 |
| Moisture [%] | 90 (-) | - | 50 (-) |
| Time [h] | 16 | 3 | 5 |

### 2.2 Weight

All printed specimens were weighed 3 times on the Electronic balance (ABS 120-4, KERN & GmbH) scale after production and then after removal from the climatic chamber (after 2 h - for the reason that the specimens have an identical ambient steady-state temperature). Subsequently, the average weight of the test specimens before and after degradation was calculated. It was investigated whether the degradation had an effect on the weight of the test specimens.

### 2.3 Tensile strength

The tensile test was carried out 40 days after removal from the climate chamber. Between the tensile test and the removal of the specimens from the climate chamber, the specimens were stored in airtight bags without access to UV radiation at laboratory temperature. The tensile strength test was carried out on a LabTest 5.50ST type (LaborTech, Opava, Czech Republic) universal testing machine. The destructive test speed used was 10 mm/min. Before placing the test specimen, each specimen was measured with a caliper, the thickness width of the specimen was measured at 3 points of the test section and the diameter was calculated. From these diameters, the cross section of the specimen was then calculated to determine the max strength. The maximum material strength and elongation of the 7 pieces test specimen at break were investigated.

### 2.4 Hardness

The hardness of the material was measured on the same day as the tensile strength, i.e. 40 days after removal from the climatic chamber. The hardness was measured on a machine (DuraJet G5 Rockwell) according to the ČSN EN ISO 2039-2 standard. The injector used was a ball with a diameter of 5 mm and the loading force was 961 N.

### 2.5 Scanning electron microscope

Electron microscopy (Tescan Mira 3 GXM) was used to describe the interfacial interaction of the filler with the matrix, the morphology and the size of the filler part. The evaluation was carried out in the area after destructive tensile testing. The examined parts of the specimens were plated with gold

## 3 Results

This chapter will describe the results of the individual parameters investigated.

### 3.1 Dimensions

In the climate chamber, the test specimens were deformed due to temperature. The deformation took place in the first week of degradation and in the following weeks the deformation did not develop further. The specimens shrunk. The cross-section of the test bar also changed. The PLA material underwent the greatest shrinkage, shrinking by 5.2 %. The Bamboo material experienced the least shrinkage, with a shrinkage of 1.5 %. Tab. 2 describes the shrinkage of the specimens.

***Tab. 2*** *Shrunk of test specimens*

| Material | Original dimension [mm] | shrunk dimension [mm] | standart deviation [%] |
|---|---|---|---|
| PLA | 150 | 142.08 | 0.27 |
| Pine | 150 | 147.30 | 0.10 |
| Bambus | 150 | 147.65 | 0.11 |
| Cork | 150 | 146.32 | 0.17 |

### 3.2 Weight

The Fig. 1 describes the percentage weight loss for the test specimens before and after degradation. The graph shows that after the first week of degradation there was a significant weight loss. For the Pine material, it was 0.5 % in the first week. This weight loss may be due to the absence of the moisture in the climatic chamber, the moisture contained in the material was dried by the high temperature in the climatic chamber. In the following weeks the weight loss is not statistically significant.

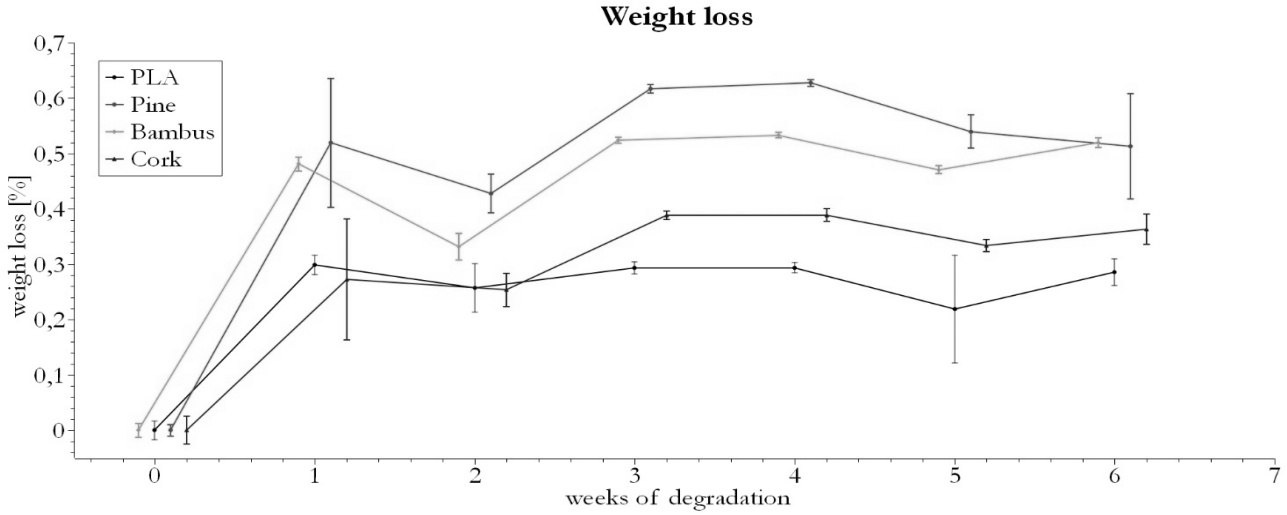


***Fig. 1*** *Weight loss*

### 3.3 Maximum strength

Fig. 2 describes the maximum strength of the materials as a function of the number of weeks of degradation. From the figure it can be seen that the materials with natural fillers show approximately half the strength of PLA. The materials do not show any significant change during the degradation process. The PLA-transparent materials showed an increase in maximum tensile strength from 59.51 MPa with 1.6 % of CV for the non-degraded material to 65.95 MPa with 0.6 % of CV at the sixth week of degradation, the increase was 10.8 %. The increase in tensile strength may be due to the relatively high temperature during the degradation process, which resulted in better bonding of the individual lines and layers of the 3D printed specimen.

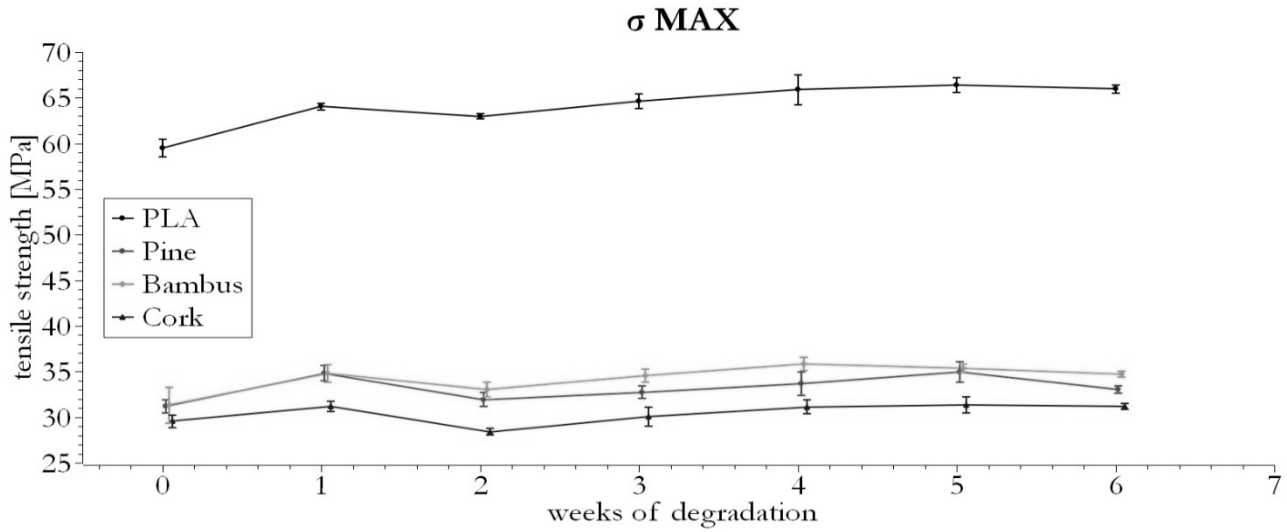


***Fig. 2*** *Max strength*

### 3.4 Elongation

Extension at break describes Fig. 3. The PLA-Cork material with no degradation effect achieved the highest average elongation (7.71 mm). The presence of the material in the climatic chamber had a high influence on the maximum elongation already after the first week, at 5.34 mm. With longer presence in the climatic chamber, the values still decreased to 4.29 mm after six weeks the total decrease in elongation was 44.3 %. The PLA-transparent material dropped from a maximum elongation value of 4.99 mm to 4.07 mm after six weeks and the decrease was therefore 18.4 %. The PLA-transparent material shows a linear decrease when the values are interleaved with a linear line compared to the filler materials which show a more logarithmic decrease.

The PLA-Pine material dropped to a value of 2.82 mm after six weeks from a value of 5.69 mm before degradation, for a total drop of 50.4 %. The PLA-Bamboo material had an elongation without degradation of 4.76 mm after six weeks the elongation was 2.96 mm, the decrease was 38.8 %.

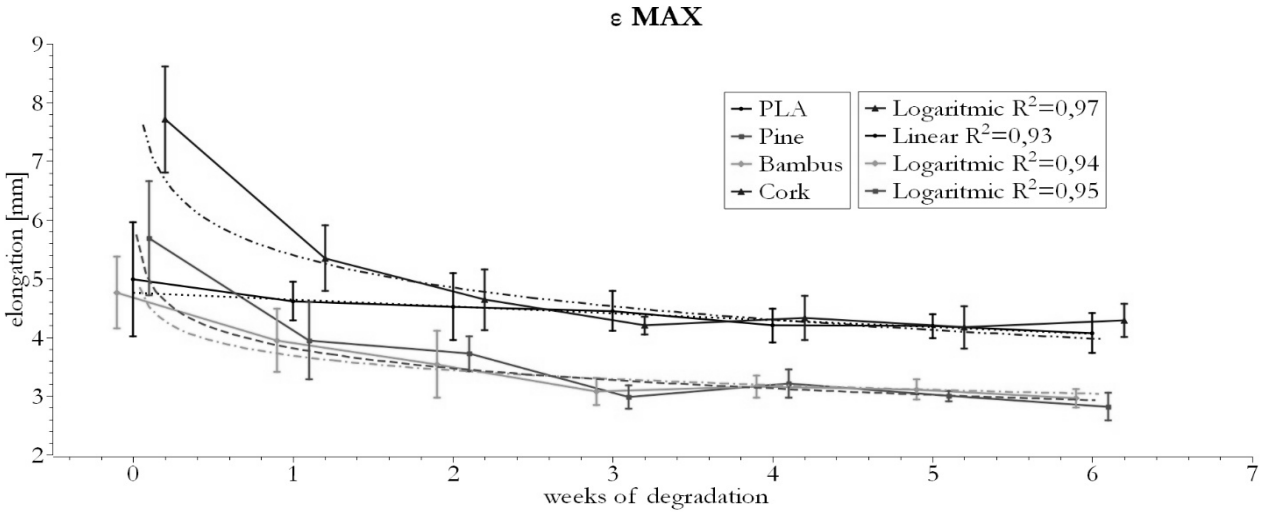


***Fig. 3*** *Elongation*

### 3.5 Hardness

The greatest influence on the hardness of the material was the first week of degradation (Fig. 4), in which the hardness increased by 18.7 % for PLA-transparent. In the following weeks the material did not show significant variations. The materials with fillers showed a similar trend with only lower hardness values. The hardness increased after the first week of presence in the climate chamber and in the following weeks the values show a slight decrease. The hardness values of the PLA-Pine material show an increase of 18.5 % after the first week of degradation and an increase of 9.7 % after six weeks of degradation compared to the pre-degradation value.

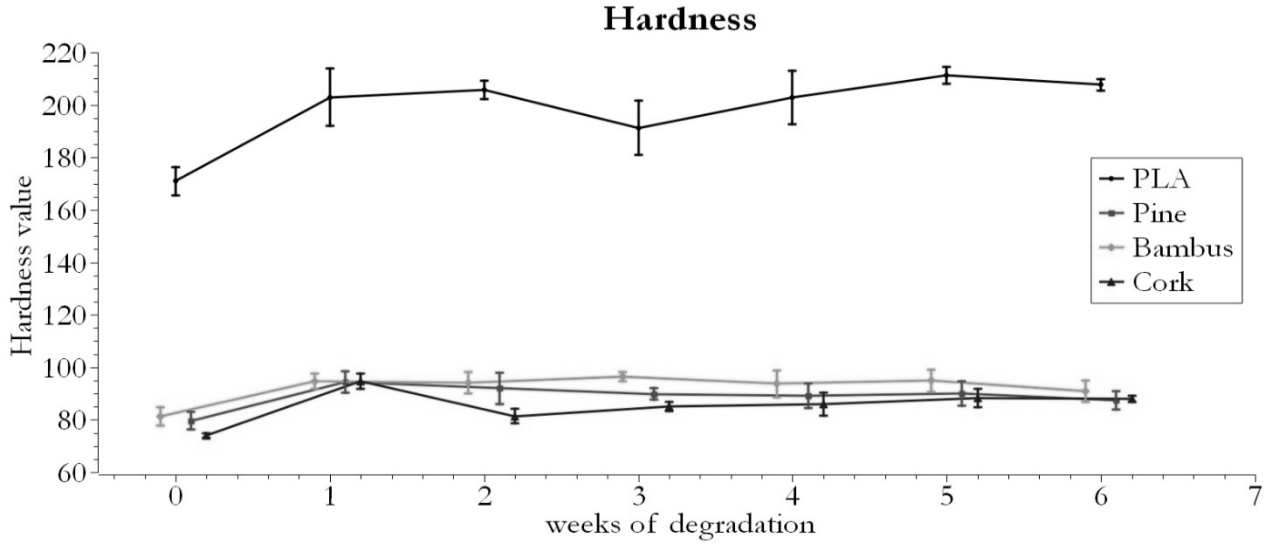


***Fig. 4*** *Hardness*

### 3.6 Scanning electron microscope

PLA without filler after six weeks of degradation (Fig. 5) is uniform in texture without pores. The material is uniform. Comparing with PLA without degradation is shown. In the image, the texture is not uniform like the material after degradation. In the part of without of degradation (B) the individual layers are noticeably observed in the material, which were formed by the deposition of the material during the printing of the specimen. It is possible that the relatively high temperature in the climate chamber caused the material to undergo a glass transition and the individual layers to interlock (in the part of A after 6 weeks of degradation), resulting in an increase in the strength of the material.

For the PLA-Bambus material, the material is compact and uniform in the Fig. 6 in the part of without of degradation (B). The interfacial interaction is better than that after 6 week of degradation (A), the texture of PLA with bamboo fiber is disturbed. The interfacial interaction is worse than that of the samples without degradation. In some fibers, there is an air capsule between the matrix and the fiber.

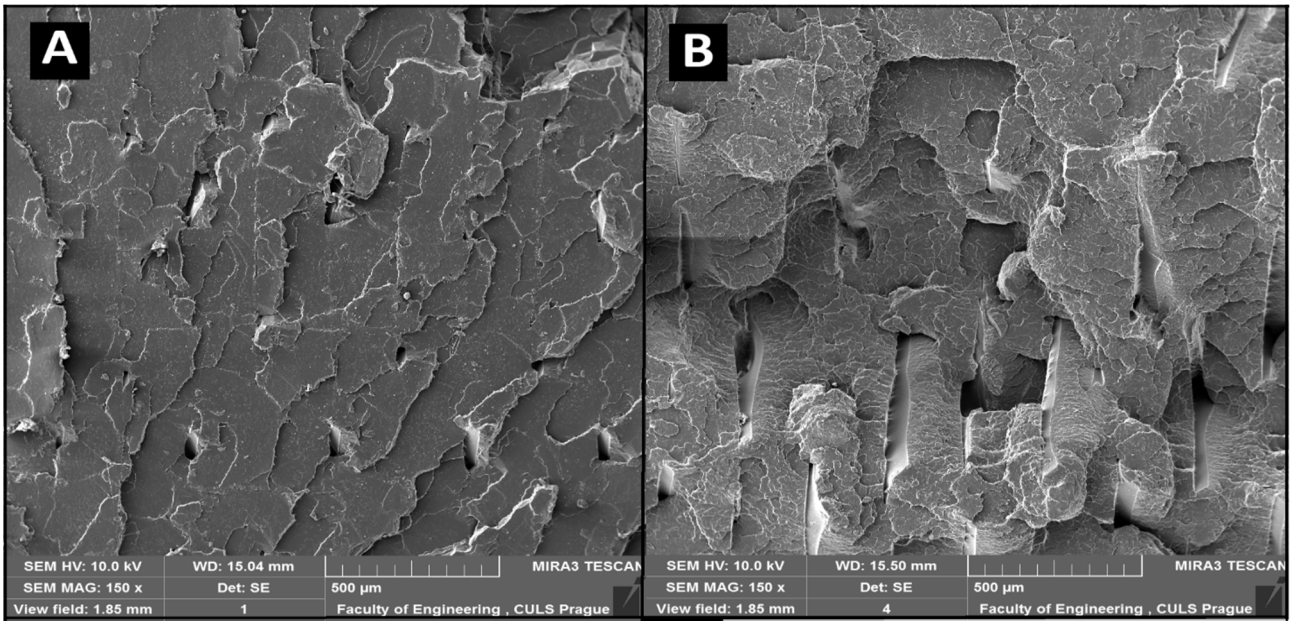


***Fig. 5*** *PLA after 6 weeks of degradation (A) and without of degradation (B)*

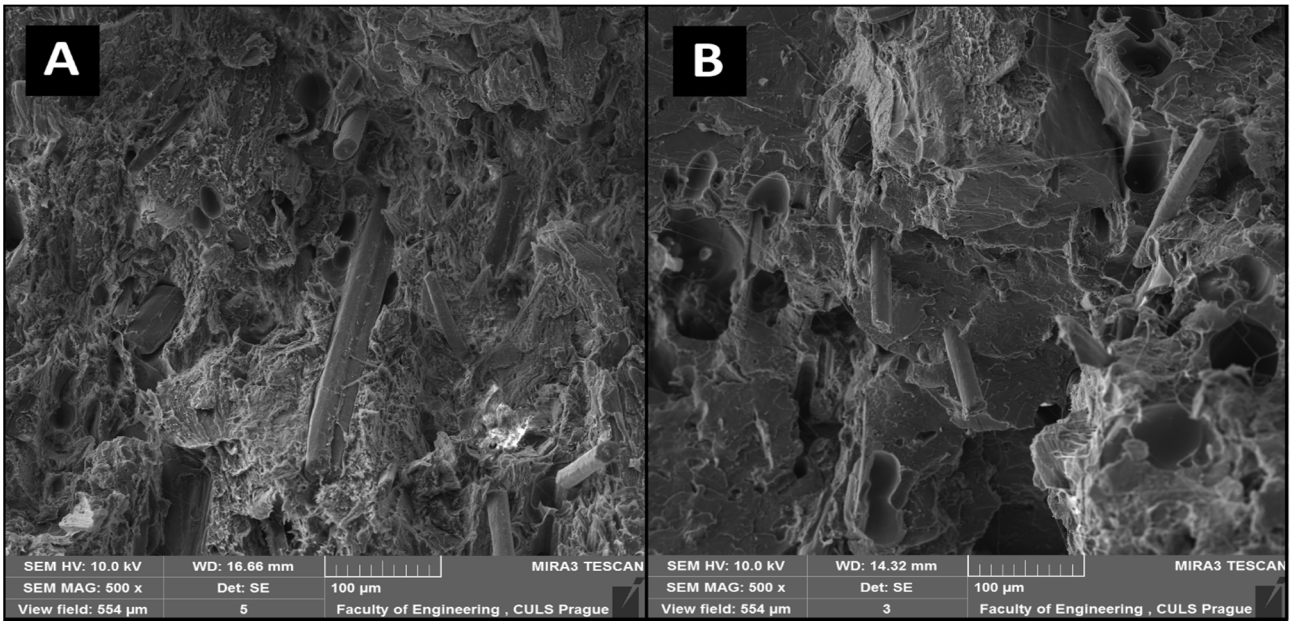


**Fig. 6** *PLA-Bambus after 6 weeks of degradation (A) and without of degradation (B)*

## 4 Conclusion

The presence of specimens in the climate chamber caused the specimens to shrink. Surprisingly, the PLA-Transparent specimens shrunk more (5.2 %) compared to the bio base filler materials, which shrunk by 1.5-2.5 %. Weight loss of the specimens was observed after the first week of degradation for the PLA-Pine material the weight loss was 0.5 %. It is possible that the weight loss was caused by the temperature in the climate chamber

and evaporation of moisture present in the polymer occurred. In the following weeks the weight loss is not statistically significant. The tensile strength had an increasing tendency during degradation. The PLA-Transparent material increased in tensile strength by 10.8 % after six weeks of degradation. The increase in material strength could have been due to the relatively high temperature in the climate chamber where the glass transition temperature may have been exceeded and the bonding of the individual layers of the 3d printed specimens. Materials with natural fillers had approximately one-third the tensile strength. A value in the vicinity of 30 MPa confirms LIU, Zhaobing et al. (2019) claim. The values of tensile strengths agree with Mazur, Karolína et. Al. who investigated the effect of ambient temperature on the material properties of PLA and PLA with natural fillers for 3D printing. They measured the tensile strength of PLA without degradation 58.5Mpa with comparison to our measured values of 59.5Mpa, also the tensile strengths of PLA+ filler material (bamboo, cork, wood) where the values ranged from 24.1Mpa to 26.3Mpa with comparison to our measured values of 29.5Mpa - 31.3Mpa for material with fillers [8]. However, it is likely that the input material has a large effect on the tensile strengths. For example, Pernica, Jakub et. Al. measured a PLA strength for 3D printed solids of 42.28Mpa [9] and a value of 41.89Mpa [10] these values are approximately one third lower when compared to our measured values.

The maximum elongation values showed that degradation on materials with bio base fillers had a greater effect than on mate-rial without bio base fillers. For the PLA-Cork material, the decrease in maximum elongation was already 31 % after the first week. The overall decrease after six weeks was 44.1 %. The hardness results showed an increase in hardness units after the first week in further weeks the hardness changes do not have statistical significance.

SEM analysis shows indications of interconnection of the 3d layers of the printed specimens after degradation. It also shows a decrease in interfacial interaction at the interface of PLA and bio base filler after material degradation.

## Acknowledgement

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