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Chemical Degradation of 3D Printed Products

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This template describes the behavior of products created with additive 3D printing technology. The tested material used to produce the samples was polyactide acid (PLA). PLA is one of the most favourite material for 3D printing. This polylactide acid contains a metal additive. The standard dog-bone shaped samples reinforced with internal ribs arranged in a grid with 20% of the internal volume of the rib-filled sample were tested for tensile strength. The samples were subjected to different types of chemical degradation prior to the test. As a degradation agent, there was used an organic solvents. The result of the research is the effect of the degradation factor on the mechanical properties of these samples and possible use in practice, specifically in technology.

Keywords: 3D printig, Tensile testing, Chemical degradation, Polylactide acide, Metal additive

1 Introduction

Nowadays, additive technologies are experiencing a huge boom [5] at a time when computers and their robotized devices are a common part of everyday life. Additive technology for the creation of polymer products or, in a simplified way, 3D printing technology is becoming an almost integral part of the equipment of the laboratory of developers, technologists and designers. This unique technology makes it possible to produce almost any model according to the specific requirements of the designer and greatly facilitates and accelerates the development of prototypes. Additive technology components can be easily and quickly modified and optimized. The development is more progressive and significantly reduces the cost of creating the final prototype. However, the additive technology in comparison with conventional technologies is very different and the mechanical properties of the resulting samples differ [2].

However, the components created by this 3D printing technology come into contact with different environments in common practice. Especially in the case of engineering and the automotive industry, there is a high probability that they will be exposed to considerably adverse effects. One of them is contact with fuels, lubricants and various other agents causing chemical degradation. These can then have a fundamental impact on the properties and durability of these components.

It is therefore absolutely necessary to know at least the basic material properties of the 3D printing components and, eventually, any change in these properties caused by chemical degradation. The aim of the experiments was to compare the effect of chemical degradation on mechanical properties of prints. Liquid substances have been selected as chemical reagents and can be encountered very often in the art. Specifically, diesel, engine oil, and coolant.

2 Material and methods

The experiment was performed on samples in the form of normalized tensile samples. The sample material was polylactide acid-PLA containing bronze particles. See Figure 1. PLA is one of the most commonly used materials for 3D printing [9]. It is a thermoplastic polyester obtained with renewable sources such as corn starch or potato starch. The popularity of this printing material lies in its good printing properties [3]. These are low shrinkage, relatively low print temperatures, and prints can also be done on printers without a temperature-stabilizing box, and easy to remove and clean the print pad [10].

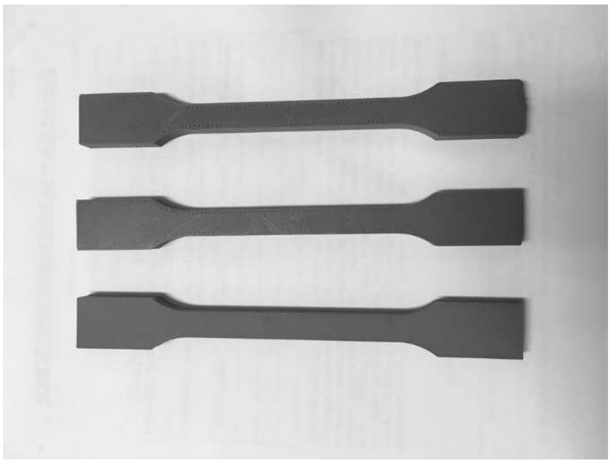

Fig. 1 *Testing speciments according to ČSN EN ISO 527*

The current trend of these materials for tist-filaments is the addition of fillers in their manufacture.

These are, for example, metal, wood or carbon fiber particles. The print is then polished to obtain an authentic appearance, or to change its properties substantially.

As chemically degrading agents, liquids have been chosen which are commonplace in the automotive industry [4]. See Figure 2

Fig 2 *Substances for chemical degradation: diesel, antifreeze and oil*

The first was diesel. This petroleum-derived liquid, along with gasoline, is the most common type of fuel. It is used to drive both automizers and especially heavy machinery such as trucks, land and construction or military vehicles. The tested diesel fuel was not additive and contained up to 7% methyl ester [7].

Another agent was engine oil as a representative of perhaps the most common fluid in the industry. Specifically, mineral oil 15W-40. Oil Viscosity Standard SAE 40 and API CI4 Oil Performance Standard [6]. It is a common engine oil used for lubricating petrol and diesel engines, including turbocharged engines. Not suitable for engines with particle filter.

The last chemical used to degrade is antifreeze. G48 glycol based antifreeze used after mixing with distilled water to cool internal combustion engines. Together with G12 coolant, it is one of the most widely used coolants. It was used in the undiluted concentrated state for the experiment. Freezing point is -72 ° C.

2.1 Sample preparation

The tested samples were printed on the popular 3D printer of the Czech brand Origina Prusa, model MK3. Four sets of samples, each of 15 pieces, were created for testing. Thus, a total of 60 samples. The extruder print temperatures were set at 210 ° C and 60 ° C for the washer [1]. Printhead speed was 40 mm / s. The print was made with a hardened nozzle with a diameter of 0.5mm. PLA bronze fill material. The fill of the samples consisted of a standard grid with orientation of + 45 ° and - 45 °. Fill density was set to optimal 20%. The pattern and density of the sample is shown in Figure 3.

Fig. 3 *20% infill of samples*

Printed groups of samples were sorted into four groups prior to testing. First group without chemical exposure, second for diesel, third for engine oil and fourth for antifreeze. The samples were exposed to these fluids for 4 hours, ie for 1/6 of the day. After this time, the samples were removed, dried and prepared for tensile testing.

2.2 Testing of samples

The individual sets of prepared specimens were gradually inserted between the jaws of the ZDM-50 universal tearing machine [8]. The static tensile test was then run. The test was stopped after sample failure. This stressing process was monitored and the load force values [F] were recorded. Tensile force values depended to displacement [s] was recorded by the computer.

Fig. 4 *Sample clamped between jaws of testing device*

The computer is connected to all sensors mounted on a universal tear device. An integral part of the computer is a special evaluation software. It can graphically represent the real-time loading of the material in real time and allows further processing of the obtained data.

The results of the measurements were plotted as graphs of dependence of loading force on sample elongation. In the conclusion, statistical processing of maximum load force data [F] was performed for the individual groups of degraded samples in the form of box graphs [11].

3 Result and discussion

All loading force and elongation data were plotted in graphs. The groups shown are selected by representative samples that relate to the mechanical properties of the degraded material in the tensile test. From graphs that relate to individual groups. See Figure 5

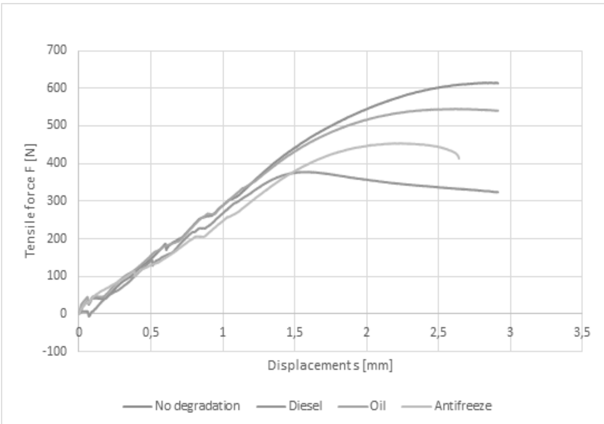

Fig. 5 *Comparison of force curves of degradated samples*

The graph shows the effect of degradation factors on the mechanical properties of the material. The curves of the individual groups are shown. Blue shows samples that have not been exposed. The gray color shows the material degraded by engine oil. Yellow describes the behavior of a sample degraded by coolant and an orange group of samples subjected to chemical degradation in diesel.

The set of samples that were not degraded reached an average maximum force of 617.8N. The graph shows that samples degraded in engine oil had the best results. After a four hour exposure, they still achieved relatively high tensile strength.

The average maximum force achieved after degradation by the engine oil is 546 N. It follows from the box graph that the dispersion of the maximum load force values is very similar to the non-degraded samples.

Worse results were achieved by the coolant group. Here, the average maximum load force of 455 N was reached. The load graph shows greater plasticity than the previous two groups. Also, greater variability of measured data was found.

The worst mechanical properties were achieved by a group of samples degraded in diesel. The samples were already considerably more plastic and lightly etched after removal from the bath. In the tensile test, there were often cracks in several places, or deformation, or a significant reduction in loading force, without breaking the specimen in the entire fabric. Therefore, further weighting did not make sense. A detail of the damage to the sample degraded in diesel is shown in Figure 6. This group of samples reached an average loading force of only 353 N. This is almost half the breaking strength compared to the undegraded samples.

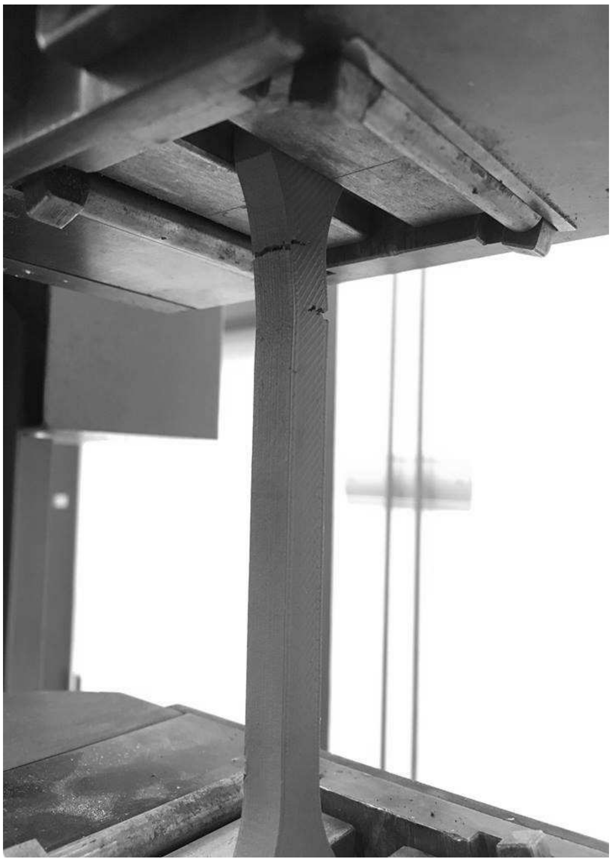

Fig. 6 *Cracked sample degradated in diesel*

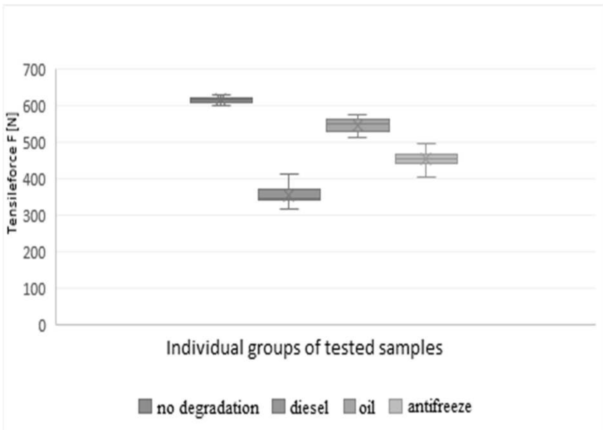

Fig. 7 *Maximum tensile strengths in box graph*

Results from all measurements were statistically processed and a common box graph was created. It visualizes the basic statistical indicators of value sets and the variability of measured values in individual sample groups. The graph shows a comparison of variability of maximum tensile strength values for individual groups. The greatest variability was found in samples degraded in diesel fuel. On the other hand, in the non-degraded samples, the range of values was very small. See Figure 7.

4 Conclusion

The experiment was focused on testing the mechanical properties of materials used by additive 3D printing technology subjected to chemical degradation. Bronze-doped PLA specimens were subjected to chemical degradation in diesel, engine oil, and coolant for 4 hours. Tensile strength tests were then performed. After comparing the load curves of the individual sample groups, a conclusion describing the effect of chemical degradation on the mechanical properties of this material was made.

Diesel fuel had the greatest impact on the tensile strength. The strength decreased compared to non-degraded samples by almost half. The degradation factor also had an effect on the plasticity of the material. The second most aggressive agent is the coolant, which has also substantially reduced the strength of the material. Engine oil had the smallest effect on mechanical properties. The tensile curve is very similar to that of undegraded material, only the strength limit has changed.

Thus, these chemicals commonly used in the automotive industry greatly alter the mechanical properties of the prints. The use of PLA-produced bronze 3D printing products is therefore very limited in practice. Experimental degradation was for only 4 hours. In practice, long-term contact with these substances is therefore unsuitable. However, it can be assumed that short-term exposure, such as accidental liquid splashes, will not have a significant effect on the mechanical properties of the printout.

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References

[1] BEHALEK, L. (2016). Polymery. Verze knihy 17. [Online]. Available at: https://publi.cz/books/180/Cover.html. [2018-04-08].

[2] BELLINI, A., GUCERI, S. (2003). Mechanical characterization of parts fabricated using fused deposition modeling. *Rapid Prototyping Journal*, 9(4), 252–264

[3] MULLER, B. (2012). Additive Manufacturing Technologies – Rapid Prototyping to Direct Digital Manufacturing. *Assembly Automation*, 32(2).

[4] NICHOLSON, J.W. (2006). *The chemistry of polymers*. 3rd ed., UK: RSC Pub, Cambridge

[5] PRUSA, J., PRUSA, M. (2014). Základy 3D tisku [Online]. Available at: https://www.prusa3d.cz/kniha-zaklady-3d-tisku-josefa-prusi/. [2018-02-09].

[6] ROBERTSON, W.(1984) *Lubrication in Practice*. Macmillan Press Ltd., Houndmills, Basingstoke.

[7] SIMACEK P., KUBICKA D., POSPISIL M., SEBOR G. (2012) *Paliva 4*, 28. VSCHT, Praha

[8] ÚNVMZ. (2012). Plasty - Stanovení tahových vlastností - Část 1: Obecné principy. ČSN EN ISO 527-1. Úřad pro technickou normalizaci, metrologii a státní zkušebnictví, Praha

[9] STANEK M., MANAS M., OVSIK M. (2019). Polymer Flow Influenced by Mold Cavity Surface Roughness, *Manufacturing technology*, Volume 19, Issue 2, p. 327-331.

[10] DVORAK K., ZARYBNICKA L., DVORAKOVA J., (2019). Quality Parameters of 3D Print Products by the DMLS Method, *Manufacturing technology*, Volume 19, Issue 2, p. 209-219.

[11] HANZL P., ZETKOVA I., DAŇA M., (2019) Uniaxial Tensile Load of Lattice Structures Produced by Metal Additive Manufacturing, *Manufacturing technology*. Volume 19, Issue 2, p. 228-231