CHEMICAL RESISTANCE OF MATERIALS USED IN ADDITIVE MANUFACTURING

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This article deals with the mechanical testing of polymeric materials processed using 3D printing and exposed to different chemical compounds. Information on this resistance is very important for the user from the point of view of the multi-disciplinary use of prototypes of 3D printers for various applications. Materials used for these purposes are processed using the photopolymer processing technology PolyJet Matrix technology and thermoplastics processed using FDM technology. Testing was conducted in accordance with the international standards ČSN EN ISO 175 and ČSN EN ISO 527. The conclusion of the article describes an evaluation of the mechanical and physical properties of the materials tested before and after chemical loading.

KEYWORDS

fused deposition modelling, polyJet matrix, polymers, tensile test

1 INTRODUCTION

3D printers are able to process various types of polymeric materials, which in turn have different mechanical properties (strength, ductility, impact strength, etc.). Due to this variability, the resulting prototypes can be used in various sectors, either for testing or as a suitable replacement for the existing part. Information on chemical or oil resistance is important for different types of operations. Manufacturers only provide basic information on the mechanical properties of materials (e.g. tensile tests), but little or no information on the chemical resistance of the individual polymers.

Research of the chemical resistance of 3D-printed plastic parts was focused on two technologies. The first technology is Fused Deposition Modelling (FDM), which, in our case, uses acrylonitrile butadiene styrene (ABS) and polylactid acid (PLA), which are the most widely used materials for this technology. The other investigated technology was PolyJet Matrix Technology, which uses photopolymer material. The most frequently used test materials were one- and two-component polymers. ABSlike, VeroBlack, VeroWhite, VeroClear, Durus as well as digital combinations of these basic materials, indicated by the abbreviation DM (digital material) [Stratasys 2016].

1.1 FDM technology

The principle of the FDM technology is shown in Fig. 1. The input material is a polymeric thermoplastic material – a fibre of a given diameter. This fibre is then extruded through a heated outlet nozzle. The model is compiled in layers, where one layer is gradually placed on top of the next (layer by layer). A support material is applied at the same time as the model material, which fixes the model to the build tray and fills in any holes or overhangs. There are various different ways of designing the individual axes of movement, but the most common is the method mentioned in the figure i.e. the print head moves on the XY plane and the table moves along the Z axis.

The support structure is removed either mechanically or chemically (a soluble material in a certain chemical compound). Layers of 3D printing for this technology are usually from 127µm to 330µm. The processed materials are ABS, PLA, PC, Nylon 12, and ULTEM, etc [Stratasys 2016, Sun 2008].

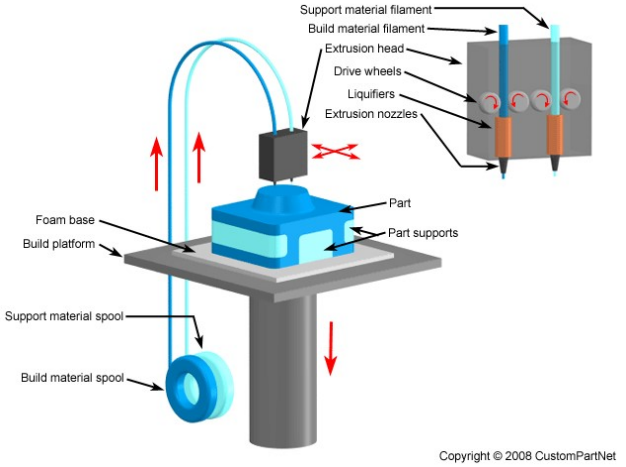


Figure 1. Principle of the FDM technology [Custompartnet.com 2015]

1.2 PolyJet technology

The principle of the PolyJet or PolyJetMatrix technology, which allows two modelled photopolymers to be processed, is shown in Fig. 2. The input material is a photopolymer material sensitive to ultraviolet (UV) radiation. This photosensitive material along with the support material is subsequently applied (laminated) with special small nozzles located on inkjet heads in ultra-thin layers on the printing surface. Ultraviolet radiation is distributed throughout the layer with use of UV lamps which are situated on both sides of the print head. Today's 3D printers are capable of applying layers of 14µm using this technology. The material on the printing surface is subsequently illuminated by the UV lamp along the whole tray and is immediately hardened. This printing method hardens each layer separately, gradually forming the model. This technology is capable of handling different coloured rigid polymers or soft (e.g. rubber - like) materials, as well as their combinations [Bass 2016, Gaynor 2014].

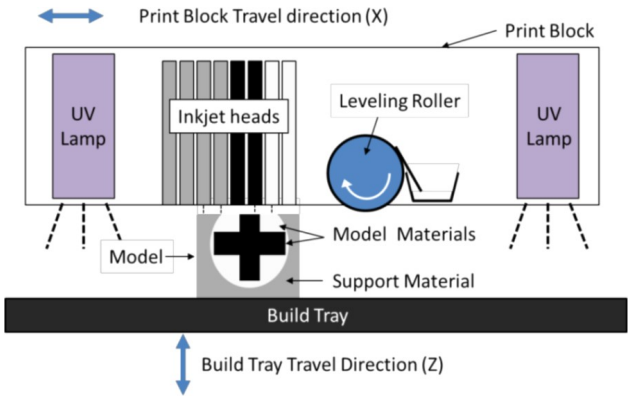


Figure 2. Principle of the PolyJet technology [Gaynor 2014]

The support material is a gel, which can be subsequently removed mechanically or by water pressure. The results of this process of 3D printing are very accurate and detailed models.

2 MATERIALS AND METHODS

The first step in the testing was to select the test materials and chemical compounds. This was based on long-term experience of different materials, but also the frequency of use of these different materials and chemical compounds. In total, nine test materials, nine chemical compounds and one sterilization process were selected, see Tab. 1.

	Tested materials	Chemicals	Sterilization process
1.	ABS	Acetone	Autoclave
2.	ABS-like	Ethanol	
3.	DM 8530	H_2O	
4.	DM 9895	HCl	
5.	DurusWhite	Chloroform	
6.	PLA	Motor oil	
7.	TangoBlack	NaOH	
8.	VeroBlack	U6002 solvent	
9.	VeroWhite	Benzine	

Table 1. Tested materials and chemical compounds

In order to ensure compliance with the due process and correct determination of the results of the performed tests, it was necessary to proceed according to the relevant standards. The chemical resistance of the materials was tested pursuant to the international standard CSN EN ISO 175; Plastics - Methods of test for the determination of the effects of immersion in liquid chemicals. The subsequent static tensile tests were performed pursuant to the international standard CSN EN ISO 527; Plastics - Determination of tensile properties [CSN EN ISO 175 2016, CSN EN ISO 527 2016].

2.1 Description of the standard CSN EN ISO 175

The international standard CSN EN ISO 175 is used to determine the properties of plastic test specimens before and after immersion in a test liquid for a prescribed time period at a given temperature. Because of their varied use, plastics are often exposed to contact with liquids such as chemicals, diesel fuel, oil, etc. The action of these compounds, particularly their absorption, may lead to a chemical reaction in the plastics, followed by significant changes in their initial physical properties. Behaviour of plastic materials in the presence of such chemicals can be determined by tests with clearly defined rules. These rules, for example the type of chemicals, immersion time, ambient temperature, method of evaluation of the results, depend mainly on the final application of the test material. However, it is not possible to make a direct comparison of the test results and the behaviour of the material in operation.

The actual test involves first placing the sample into a suitable container e.g. a beaker and completely immersing it in the test liquid (use of a weight is allowed). There must be at least 8 ml per cm^2 of the total surface area. If there is more than one test sample of the same composition, it is possible to put these samples into the same container. It is equally important to ensure that contact between the samples and the walls of the container, between the samples themselves as well as between the samples and the weights is kept to a minimum. After the immersion time, in our case 24hrs, the test specimen is removed from the container and one of the following possible rinse methods is selected:

a) For samples immersed in acids, alkalis or other aqueous solutions - rinse thoroughly with clean water

b) For samples taken from non-volatile, water insoluble organic liquids – rinse with a mild but volatile solvent such as petrol.

The samples are then wiped dry using filter paper or a clean cloth. In the event that the test sample is immersed in alcohol or acetone at room temperature, no rinsing or wiping is necessary [CSN EN ISO 175 2016].

2.2 Description of the standard CSN EN ISO 527

The subsequent static tensile test was performed pursuant to the international standard CSN EN ISO 527; Plastics - Determination of tensile properties. This standard specifies the procedure for tensile testing of plastic materials. A basic description of this process is as follows: the test piece is elongated in the direction of its main longitudinal axis at a constant test speed until it breaks or until the tension (load) or deformation (elongation) reaches a preselected value. During the test, measurements are taken of the load acting on the test specimen and the elongation. Test specimens can be moulded, machined, carved or punched to the selected final dimensions. The standard specifies the preferred dimensions for each method. These dimensions are essential for determining the correct results, if any of the dimensions or production processes are not followed this may lead to results that cannot be compared with each other. It is also essential to ensure a constant test speed and correctly prepare all of the samples. The specimen selected to test the influence of the orientation of the part on its mechanical properties is shown in Fig. 3. Specifically, the part is a tensile test specimen, which is commonly used for determining the mechanical properties of plastic materials. The shape and dimensions were selected pursuant to CSN EN ISO 527-2 [CSN EN ISO 527 2016].

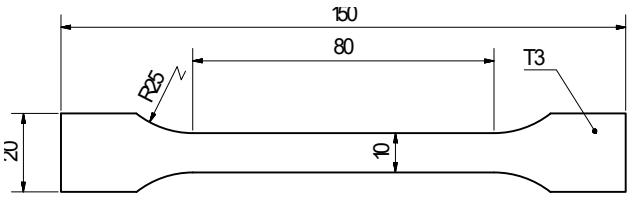


Figure 3. Tensile test specimen

2.3 3D print of the specimens

The parts made from ABS material were printed on a Dimension SST 768 machine (Stratasys Ltd.). The thickness of the layer was set to 254µm. Physical models were supported with SR-30 material during the building process (Fig. 4) [Stratasys 2016].

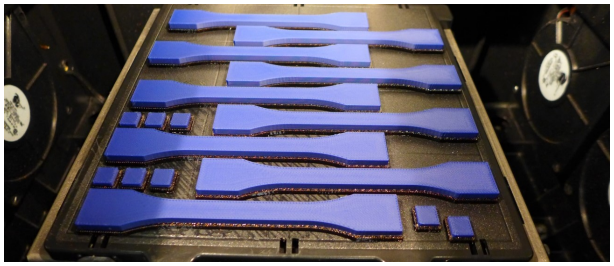


Figure 4. Specimens from ABS material after printing.

The parts made from PLA material were printed on an Easy3DMaker machine from 3Dfactories company. The

thickness of the layer was set to 254µm [3Dfactories 2016, PLA 2016].
The parts made from photo-polymeric materials were printed on a Connex 500 machine (Stratasys Ltd.). The thickness of the layer was set to 30 µm. Physical models were supported with FullCure705 material during the building process in Fig. 5.

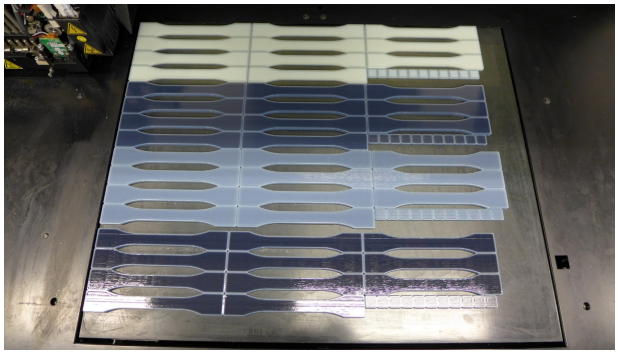


Figure 5. Specimens of photo-polymer materials after printing

2.4 Chemical and oil resistance

An initial test of the samples was performed in the first part of the determination of the chemical and oil resistance of the prototype parts from the 3D printers. This test was performed in order to obtain a basic overview of the chemical resistance of the materials and also for economic purposes. This information was used to determine the suitability of the given materials and chemical compounds for further testing, i.e. to determine the exact number of subsequently produced specimens, see Tab. 1.
The test method was applied in accordance with the above-mentioned standards, the refined samples are first weighed, and then they are placed in petri dishes, with each chemical having one set of samples (i.e. one piece of each material, nine pieces in total). Finally, the chemical is added and the dishes are closed and sealed (Fig 6).

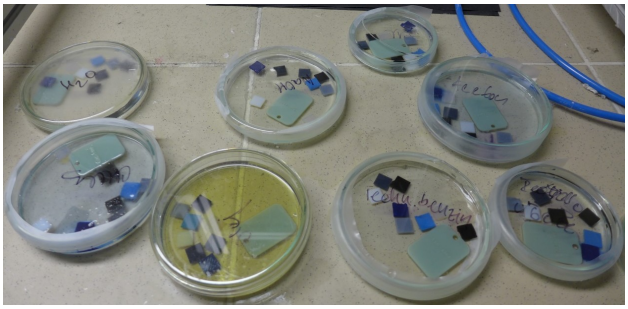


Figure 6. Specimens from different materials on the testing base

After the immersion time (24 h) the samples were removed, wiped and dried in a plastic dryer and then weighed again. The testing was first evaluated by determining the changes in weight of the samples and then by visual assessment of the conditions of samples e.g. changes in the surface structure, size and shape. Based on the analysis of the initial test, it was possible to exclude materials from further testing that did not pass this test. This led to a 11% saving on the cost of the production of the test specimens.

The test procedure is clearly visible in Fig. 6. This figure shows two images of the samples tested in acetone taken before and after loading. The left image shows incipient blue coloration caused by the dissolution of the sample of ABS. On the right image the sample of ABS has completely dissolved, the blue colour is noticeable. The distorted structure of most of the materials, especially PLA and VeroWhite, can be clearly seen. TangoBlack and DM 9895 showed visible swelling and the material was heavily creased after drying.

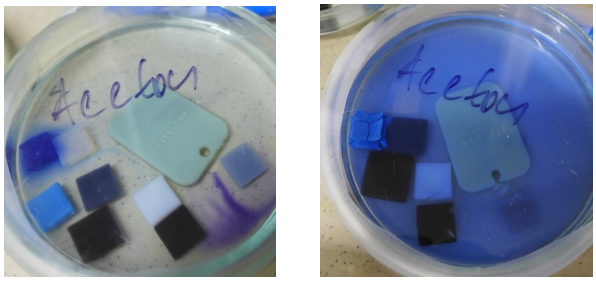


Figure 7. Samples tested in acetone, before and after loading

The chemical resistance of the test specimens was also tested in the laboratory pursuant to the international standard CSN EN ISO 175. This method was used to determine the properties of the plastic specimens before and after immersion in the test liquid. The main criterion for this test was to determine the changes in the tensile properties of specimens. For this reason, the size and shape of these specimens was selected pursuant to the relevant international standard CSN EN ISO 527. In addition, changes in the weight of the specimens were determined. All of the above-mentioned changes were evaluated based on the rules contained in the cited standards.
The following temperature of the test environment, immersion time and amount of test fluid were selected for this type of test pursuant to CSN EN ISO 175.

- Temperature 23 °C ± 2 °C
- Immersion time (test) 24 h
- Amount of fluid ± 440 ml

The test specimens were placed into measuring cylinders of the appropriate size, with each chemical compound having three specimens of the same material. Subsequently, a given volume of chemical compound was added and the cylinder was sealed (Fig 8). At the end of the immersion time the specimens were removed from the bath, rinsed, wiped and dried in a plastic dryer. The test specimens were then weighed.

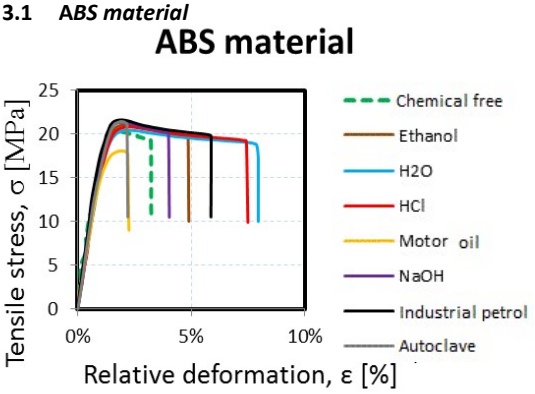
Figure 8. Test specimens immersed in ethanol

Changes in the properties of the test specimens (weight, tensile load) were determined for untreated and then treated specimens. Most of the specimens showed an increase in weight due to the significant water absorption of the plastics. The absorption of liquid may induce changes in the physical and chemical properties and, therefore, changes in tensile strength, ductility and hardness. Therefore, the measurement of these properties after exposure to the liquids is important. The table shows three samples of each test material with the highest increase in weight. It is clear that the highest observed absorption across the test materials was for acetone, U6002 solvent and ethanol.

3 TENSILE TESTS

The 3D printed specimens were subjected to standard tensile tests, which were performed on an Instron 5967 universal testing machine. Given testing machine has a two-column construction with a load capacity of 30 kN. The test was driven under strain control with constant load rate of 10 mm/min. A contactless optical strain gage with a sampling frequency of 2.5 kHz was used to measure the strain of the specimens. This device is compliant with international standards ISO 7500-1, ISO 9513, and also CSN EN ISO 527, according to which the tensile test was performed.

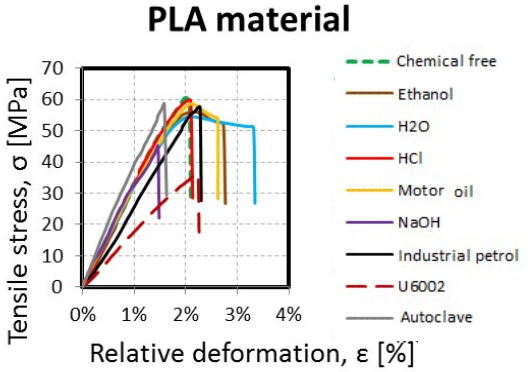
3.1 *ABS material*



Graph 1. Dependence of the relative deformation on tensile stress for ABS material

The results of the testing of ABS test specimens confirmed a generally known fact about this material, i.e. its significant moisture absorption. It showed an increase in ductility in the majority of the test specimens, and the most for water with an approx. 150% increase (Graph 1). Another observed property of this material is its low resistance to solvents. The solids completely dissolved when immersed in acetone and U6002 solvent. The measured tensile strength values were significantly lower for all of the test specimens than the data provided by the manufacturer, which could be due to poor quality raw materials used in the manufacturing or a difference caused by a different specimen production process.

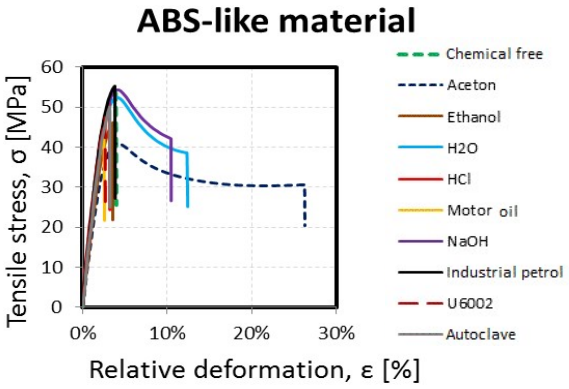
3.2 *PLA material*



Graph 2. Dependence of the relative deformation on tensile stress for PLA material

Polylactic acid is a hygroscopic material whose properties led to a significant increase in elongation for several of the chemical compounds (Graph 2). The most significant was exposure to H_2O, which increased the moisture content of the material and consequently decreased intermolecular forces, resulting in a decrease in strength of 10% and an increase in elongation of 60%. Chemical corrosion is significantly reflected in the specimens tested in the U6002 solvent and NaOH. Acetone caused a total dissolution of the material.

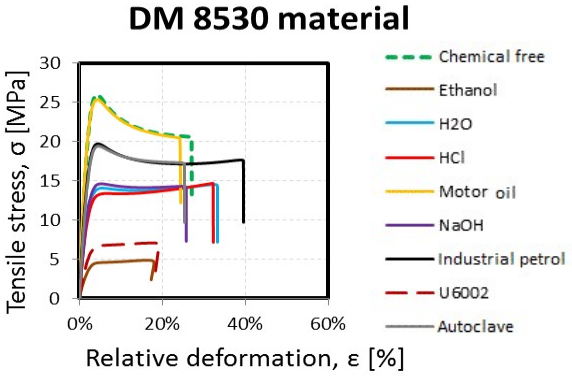
3.3 *ABS-like material*



Graph 3. Dependence of the relative deformation on tensile stress for ABS-like material

The curves shown on graph 3 have the usual characteristics for a brittle and rigid polymer, which ABS-like definitely is. The tensile strength values in this case correspond to the values specified by the manufacturer of the photopolymer. The hardness of the test material increased for specimens with a significant plastic area (acetone, H_2O, NaOH). As with the ABS material, the ductility increased due to absorption caused by the delaying of the macromolecules in the internal structure of the material, which leads to a decrease in macromolecular forces. The most notable change in mechanical properties can be seen in the case of Aceton. Specifically, a 24 % decrease in tensile strength was evaluated for ABS-like material influenced by the solution.

3.4 *Digital material DM8530*

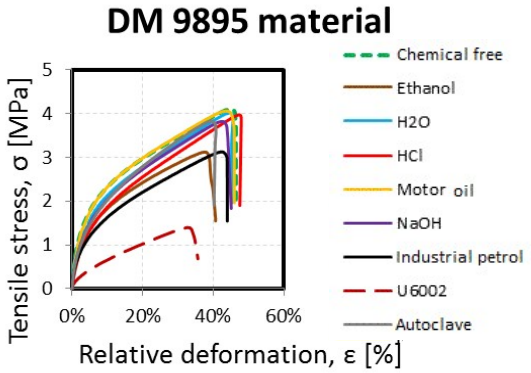


Graph 4. Dependence of the relative deformation on tensile stress for DM 8530 material

The strength of the composite material DM 8530 corresponds to a soft plastic material e.g. polypropylene. The increased ductility and lower strength of specimens loaded in gasoline, H_2O and HCl can again be explained by the delaying of the macromolecules and the reduced macromolecular forces of the plastic (Graph 4). Unlike specimens for which there is a significant reduction in strength and ductility (ethanol, U6002), here the chemical compound attacks the material leading to chemical corrosion. Generally, this process occurs in plastic materials that have a similar chemical composition as the chemical compound acting on the specimen. Acetone caused complete degradation of the material.

3.5 *Digital material DM9895*

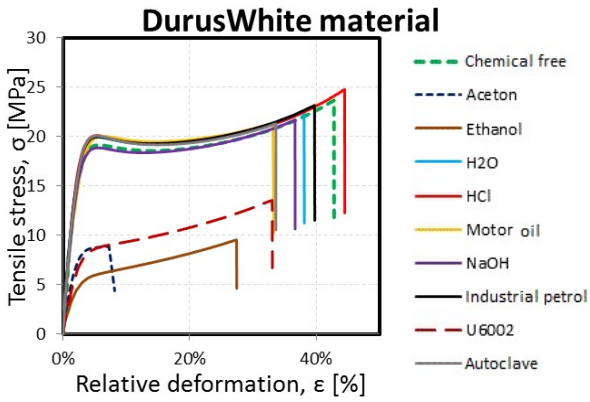
Graph 5 shows the results of loading with various chemicals for DM 9895 material, which has strength compatible to hard rubber. This material is not rubber, but only rubber-like material from photopolymer. In this case, specimens showed no chemical corrosion after loading with motor oil, H_2O and HCl. The measured data reach statistically identical values to the untreated specimens.



Graph 5. Dependence of the relative deformation on tensile stress for DM 9895 material

This material resists the least to loading with U6002 solvent, the tensile strength is decreased by approx. 65%. The tensile strength of the untreated specimen is about 2 times lower than the data given by the manufacturer. An explanation of this may be due to the different thickness of the printed layer or the lower intensity/degradation of the UV lamp. Acetone caused complete degradation of the material.

3.6 D*urusWhite material*

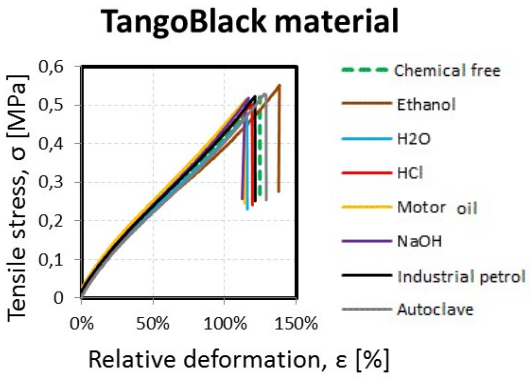


Graph 6. Dependence of the relative deformation on tensile stress for DurusWhite material

There was no significant change of the mechanical properties of most of the tested specimens of DurusWhite from the initial state (Graph 6). Specimens immersed in acetone and ethanol showed the most chemical corrosion, with a decrease in the tensile strength by approx. 60% in both cases. The tested specimens of DurusWhite underwent a single chemical load of chloroform, but even in this case it was not possible to carry out a tensile test due to the strong degradation of the material.

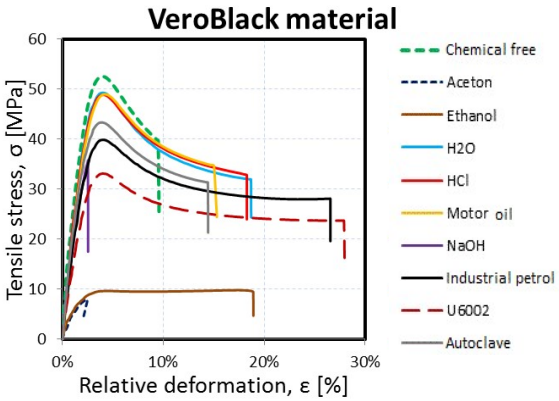
3.7 *TangoBlack+ material*

TangoBlack + is a very specific material, it is a soft and ductile like rubber. Mechanical properties are of course different from standard rubbers. The test results are more or less the same, with only the specimen immersed in ethanol exhibiting slightly higher strength as well as ductility. Statistically, these are the same values; therefore, for a qualified conclusion it would be better to test more samples. The tensile strength threshold given by the manufacturer of the filament is approx. 60% higher. An explanation for this may again be poor quality material or a different manufacturing process. Complete dissolution was Specimens immersed in acetone and U6002 completely dissolved.



Graph 7. Dependence of the relative deformation on tensile stress for TangoBlack+ material

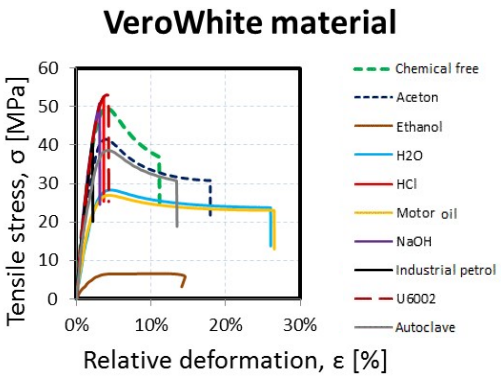
3.8 *VeroBlack material*



Graph 8. Dependence of the relative deformation on tensile stress for VeroBlack material

The initial assumption for VeroBlack and VeroWhite from the information given by the manufacturer of the filament was that both materials share the same mechanical properties. The test results, however, partly disproved this assumption (Graphs 8 and 9).

3.9 *VeroWhite*



Graph 9. Dependence of the relative deformation on tensile stress for VeroWhite material

The untreated specimens had statistically identical values. In terms of chemical resistance, various different reactions were observed. In general, VeroBlack is more hygroscopic because of the higher number of specimens with an increase in ductility and at the same time decrease strength (HCl, U6002, technical petrol).
This physical phenomenon can also be attributed to the delaying of macromolecules with the associated decrease in macromolecular forces. This theory can also be applied to specimens of both of the tested materials loaded in motor oil, autoclave and H_2O. The test results for specimens immersed in ethanol showed significant chemical corrosion, and also NaOH, where the specimen lost its initial plasticity. Conversely, the curves for testing in acetone are very different; in this case, further analysis would help to determine the precise characteristics.

DISCUSSION

The results can be summarized into a few basic observations. Primarily, one of the basic properties of most polymers - water absorption was verified. This physical phenomenon was exhibited to a varying extent by most of the tested materials, leading to individual chemical compounds entering the structure of the test material, subsequent delaying of the macromolecules of plastic and decreasing macromolecular forces. The resulting effect is a reduction in tensile strength and an increase in ductility. Another crucial process observed in chemically loaded solids is chemical corrosion. This process has a major impact on the structure of the material, leading to violations in the structural (macromolecular) chain of the test specimens, i.e. irreversible degradation of the material.

CONCLUSION

This article describes the effect of chemical compounds on print materials for 3D printing. It was confirmed that the chemical compounds that caused the highest increase in the weight (acetone, U6002 solvent, ethanol) of the tested samples were also those that caused the most prominent degradation of the test specimens. We clearly demonstrated that ABS-like has a greater overall chemical resistance than ABS. According to the manufacture ABS-like material is a substitute for the standard ABS material in terms of its mechanical properties. Furthermore, a direct link was found between certain chemical loads (acetone) and material composition (DM 8530, DM 9895). These materials consist of certain amounts of TangoBlack and VeroWhite. From the above-mentioned materials TangoBlack showed a zero chemical resistance to acetone. ABS-like material had the best results of all of the samples tested. Even after the 24-hour chemical load, this material proportionally retained the best mechanical properties of all of the chemicals.

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