



Thermoplastic polyurethanes for mining application processing by 3D printing

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ABSTRACT

Purpose: Thermoplastic polyurethanes (TPU) found application in mining. Due to the excellent processing properties, thermoplastic polyurethanes can be also use to make elements that would facilitate miner's work. These elements, however, differ in dimensions depending on the person who is going to use them, that is why they should be personalized. In case of all the above studies, the elements or stuffs were made by means of the injection method. This method limits the possibility of producing mining's stuff only to models that have a mould. The 3D printing technology developing rapidly throughout the recent years allows for high-precision, personalized elements' printing, made of thermoplastic materials.

Design/methodology/approach: The samples from thermoplastic polyurethanes were made using 3D printing and then subjected to the aging process at intervals of 2, 7 and 30 days. The samples were then subjected to a static tensile tests, hardness tests and FT-IR spectroscopy.

Findings: The obtained results of mechanical tests and IR analyses show that the aging process in mine water does not affect the mechanical properties of the samples regardless of the aging time. IR spectral analysis showed no changes in the structure of the main and side polyurethane chains. Both mechanical and spectral tests prove that polyurethanes processed using 3D printing technology can be widely used in mining.

Research limitations/implications: Only one type of TPU was processed in this work. Further work should show that synthetic mine water does not degrade the mechanical properties of other commercially available TPUs.

Practical implications: The additive technology allows getting elements of mining clothing, orthoses, insoles or exoskeleton elements adapted to one miner.

Originality/value: The conducted tests allowed to determine no deterioration of the mechanical properties of samples aged in synthetic mine water. TPU processing using 3D printing technology can be used in mining.

Keywords: Thermoplastic polyurethanes, 3D printing, Mechanical tests, Aging, Processing

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PROPERTIES

1. Introduction

The conditions in the mining industry are extremely tough. Machines and plastic elements are exposed to high stresses from impact, abrasion and aggressive chemicals [1-7]. Linear thermoplastic polyurethanes are classified as elastomers. Most of all, these are characterized by: high tensile and breaking strength, wide range of hardness levels, high value of the maximal strain, high elasticity and resistance to fatigue, low deformation at static and dynamic loads, low abrasibility and low moisture absorptivity [5-13]. That way to these properties, thermoplastic polyurethanes found application in mining. Thermoplastic polyurethanes are used for production for example: high performance hoses, flame retardant mining cables, mining screens or conveyor belts [2,4,12-15]. Due to the excellent processing properties, thermoplastic polyurethanes can be also use to make elements of mining clothing, orthoses, insoles or exoskeleton elements that would facilitate miner's work. These elements, however, differ in dimensions depending on the person who is going to use them, that is why they should be personalized. In case of all the above studies, the elements or stuffs were made by means of the injection method. This method limits the possibility of producing mining's stuff only to models that have a mould. This way, the market offers stuffs in dimensions regulated by the dimensions of the injection moulds [13-18]. The additive technology is to become an answer to these requirements. The 3D printing technology developing rapidly throughout the recent years allows for high-precision, personalized elements' printing, made of thermoplastic materials. In design's terms, however, it is significant to develop and print stuffs exhibiting mechanical properties comparable to the mechanical properties of stuff produced by injection moulds' means [1-3,10,14-19]. The use of 3D printing to produce elements help a miner in his work can be possible only when the products produced will be resistant to the conditions prevailing in a mine [20-21]. The authors aim to conduct commercial thermoplastic polyurethane in the form of a filament, print samples for mechanical tests and test the mine water's impact on the samples' mechanical properties. Authors realize mine waters differ from each other in chemical composition. In the article authors use synthetic mine water described in literature [22].

2. Materials and methods

2.1. Materials

Elastollan 1185A – thermoplastic linear polyurethane was purchased from BASF. Reagents for the preparation of

synthetic mine water: sodium chloride (NaCl), sodium sulphate (Na₂SO₄) and potassium sulphate (K₂SO₄) were purchased from ChemPur. Distilled water was obtained in the laboratory.

2.2. Filament's extrusion

Prior to the extrusion process, Elastollan 1185A was dried in a convection oven for three hours at 110°C. The filament's extrusion process was carried out on a single-screw extruder built on its own by the author of Noctuo (Gliwice, Poland). The extrusion process' parameters are shown in Table 1. In the extrusion, a filament with a diameter of 1.75 ± 0.1 mm was obtained.

Table 1.

Print parameters' determination from the obtained material

L/D	32
First zone's temperature, °C	151
Second zone's temperature, °C	183
Third zone's temperature, °C	190
Nozzle's temperature, °C	191
Mass' temperature, °C	210
Pressure, bar	36
Screw's rotation, RPM	15
Efficiency, kg/h	20

Experimentally determined print parameters from Elastollan 1185A in fused filament fabrication (FFF) technology. It was determined the optimum temperature for printing is 230°C. The optimal table temperature of the printer is 55°C.

2.3. Samples' preparation for mechanical tests

The samples for mechanical tests were made in accordance with the standard EN ISO 1798 [23]. The samples' geometry is shown in Figure 1. The samples were printed with fused filament fabrication. The samples are shown in Figure 2.

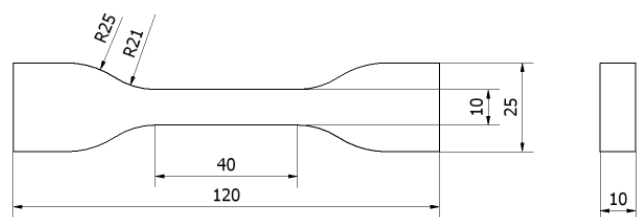


Fig. 1. Sample's geometry

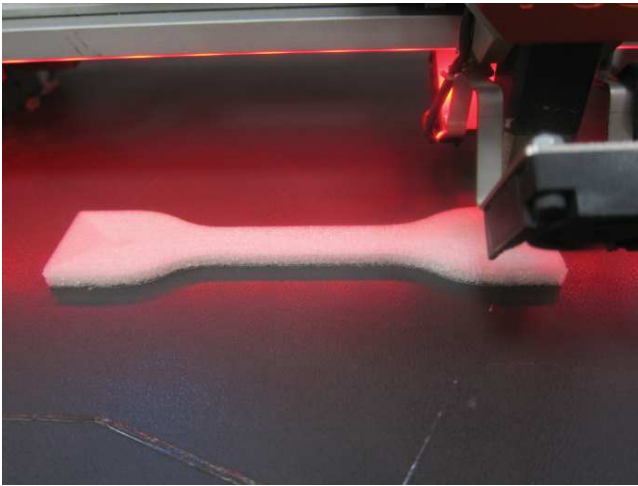


Fig. 2. Sample's printing

2.4. Samples' aging

The samples for tests were placed in an aging chamber with a volume of 10 liters. Synthetic mine water was introduced into the chamber, which was obtained by dissolving 640 g of NaCl, 30 g of Na₂SO₄ and 25 g of K₂SO₄ in 10 liters of distilled water [22]. The aging process was carried out for 2, 7 and 30 days at a temperature of 70°C. The sample population for each aging time was 5.

2.5. Samples' mechanical properties test

The test of samples' mechanical properties was made according to the standard EN ISO 1798 [23]. The test was carried out on the ZWICK Z050 tensile test machine. The test speed was 500 mm/min. The samples aged in synthetic mine water and native samples were stretched. Five measurements were made for each sample population. The results of arithmetic means and standard deviations for all tested samples are presented in Figures 4-7.

2.6. Shore A hardness test

The Shore A hardness test was performed in accordance with the standard EN ISO 7619-1[24]. The measurements were made with a hardness durometer Shore A type (Etopoo). Hardness measurements were made on samples aged in synthetic mine water and on native samples. Five measurements were made for each sample population. The results of arithmetic means and standard deviations for all tested samples are presented in Figure 8.

2.7. Aging's analysis performed using FT-IR

Regardless of the mechanical tests, the degradation's analysis of the tested samples was carried out using Fourier transform infrared spectroscopy (FT-IR). Measurements were made on the FT-IR Nicolet 380 spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) The spectrum was recorded as a transmittance spectrum in the wavelength range from 500 to 4000 cm⁻¹. The spectra for groups of samples are shown in the Figure 9.

3. Results

3.1. The results of mechanical tests

Mechanical tests were to show how the aging process in synthetic mine water affects the mechanical properties of polyurethane samples made with the 3D printing. For this purpose, the samples belonging to all tested groups were stretched on a universal testing machine. In order to fully characterize the test materials from the stress-strain diagram, four values were read out for each sample: stress at the yield strength (σ_1), stress at break (σ_2), elongation at the yield strength (ϵ_1) and elongation at break (ϵ_2). Points from which the characteristic values were read are shown in Figure 3. Such characteristics are related to the preparation of samples. The samples were printed using the contours and the mechanical characteristics presented in this way best reflect their properties.

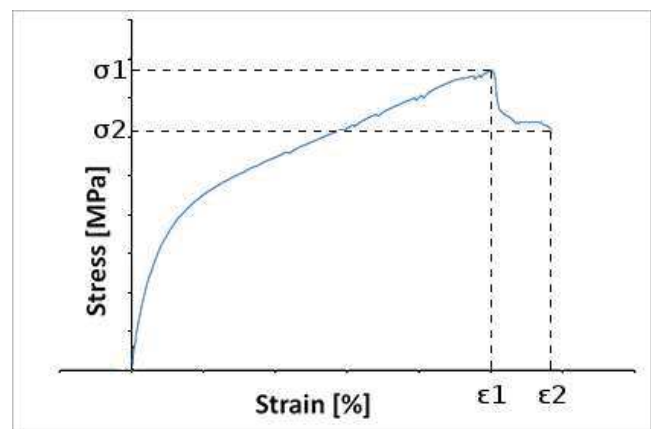


Fig. 3. The method of reading values from the stress-strain diagram

Averaged values along with the standard deviation read from the stress-strain diagram are shown in Figures 4-7.

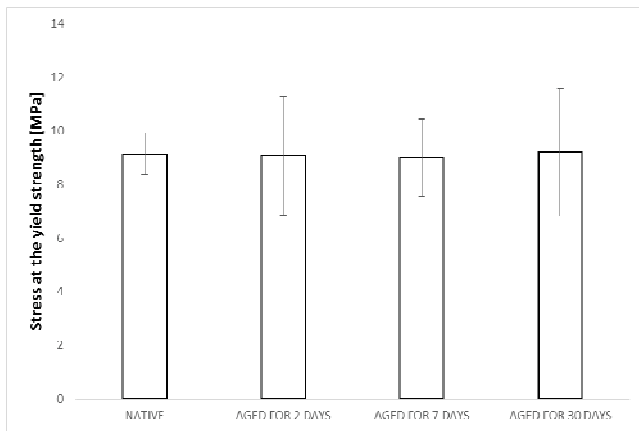


Fig. 4. Stress at the yield strength, MPa

The stress at the yield strength values of all groups of samples tested are similar to those of native samples: 9.15 ± 0.78 MPa, for samples aged in mine water for two days: 9.07 ± 2.23 MPa, for samples aged for 7 days: 9.01 ± 1.43 MPa, while for samples aged for 30 days: 9.21 ± 2.38 MPa. Similar average results for all tested groups prove the absence of the effect of aging in synthetic mine water on stress at the yield strength values for polyurethane samples printed using the 3D printing.

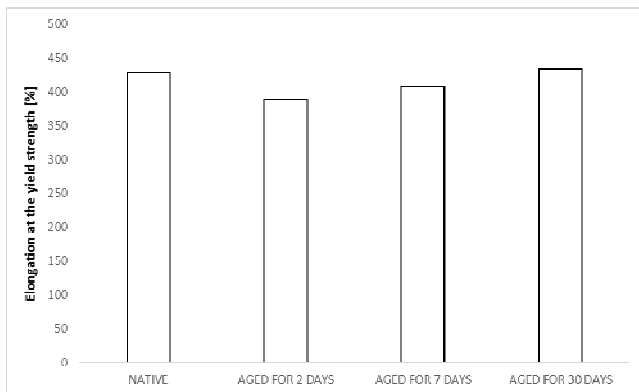


Fig. 5. Elongation at the yield strength, %

Figure 5 shows the average results of elongation at the yield strength. The obtained results, similarly as in the case of stress at the yield strength, were similar for all the tested groups. The elongation at the yield strength value for native samples was 428%, for samples aged for 2 days 389%, for samples aged for 7 days 407%, and for samples aged for 30 days: 433%. All obtained mean values do not differ from each other and prove that regardless of the samples' aging time in synthetic mine water the value of elongation at the yield strength does not change significantly.

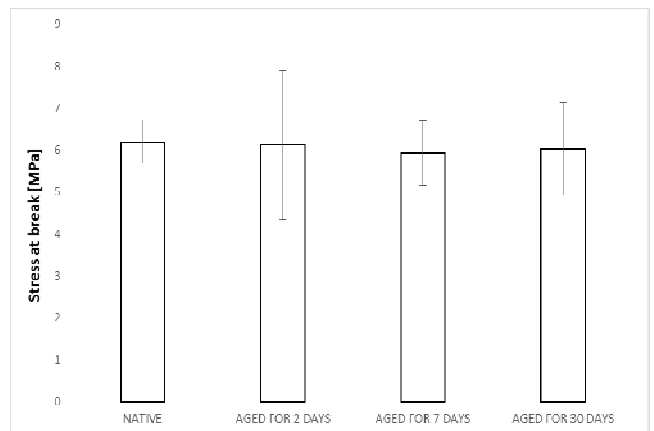


Fig. 6. Stress at break, MPa

The stress at break figure presents similar trends as the stress at the yield strength diagram. Stress at break values do not differ significantly for all tested samples. For native samples stress at break is 6.19 ± 0.51 MPa, samples aged for 2 days: 6.12 ± 1.78 MPa, samples aged for 7 days 5.92 ± 0.77 MPa, and samples aged 30 days were characterized by stress at break 6.03 ± 1.1 MPa. These results are similar, hence the conclusion that aging in synthetic mine water does not affect the stress at break.

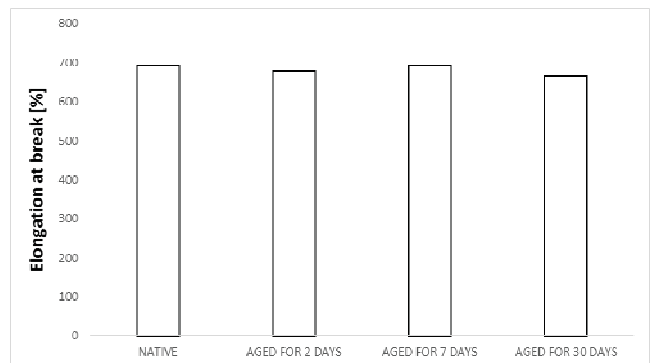


Fig. 7. Elongation at break, %

The elongation at break values presented in Figure 7 are characterized by similar values. For native samples, the average elongation at break is 692%, for 679% aged for 2 days, 693% for aged 7 days and 665% for aged 30 days. All average elongation at break values are similar and prove the insignificant impact of aging in synthetic mine water on elongation at break.

3.2. Result of hardness test

The influence of aging in synthetic mine water on the mechanical properties of samples printed with 3D printing

technology was determined by testing the hardness of aged samples. The Shore A test is designed to test the hardness of elastic materials including gums. Native and aged samples were subjected to the Shore A hardness test by collecting 5 measurements. The average values for each sample group together with the standard deviation are presented in Figure 8.

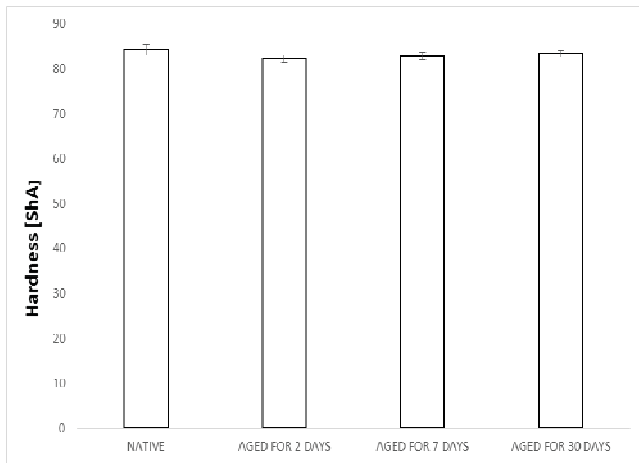


Fig. 8. Hardness, ShA

The Shore A hardness values do not differ from each other for all studied groups. For native samples, the hardness is 84.2 ± 1.14 ShA, for samples aged for 2 days: 82.2 ± 0.84 ShA, for samples aged for 7 days: 82.9 ± 0.84 ShA, while for samples aged 30 days: 83.4 ± 0.74 ShA. The hardness test results show that aging in synthetic mine water for 30 days does not affect the hardness of the materials tested.

3.3. Results of FT-IR spectroscopy

Samples from all tested groups were examined on an infrared spectrometer to evaluate the degradation of the polyurethane structure. The research was to show whether aging in synthetic mine water affects degradation of the main chain and polyurethane side chains used to print test samples. Overlapping spectra of native and aged samples are shown in Figure 9.

The spectra of all test samples presented in Figure 9 overlap over the entire spectrum length. In no place has the appearance of new peaks responsible for the emergence of new chemical groups or bonds. This proves that aging in synthetic mine water does not affect degradation of the main and side polyurethane's chains.

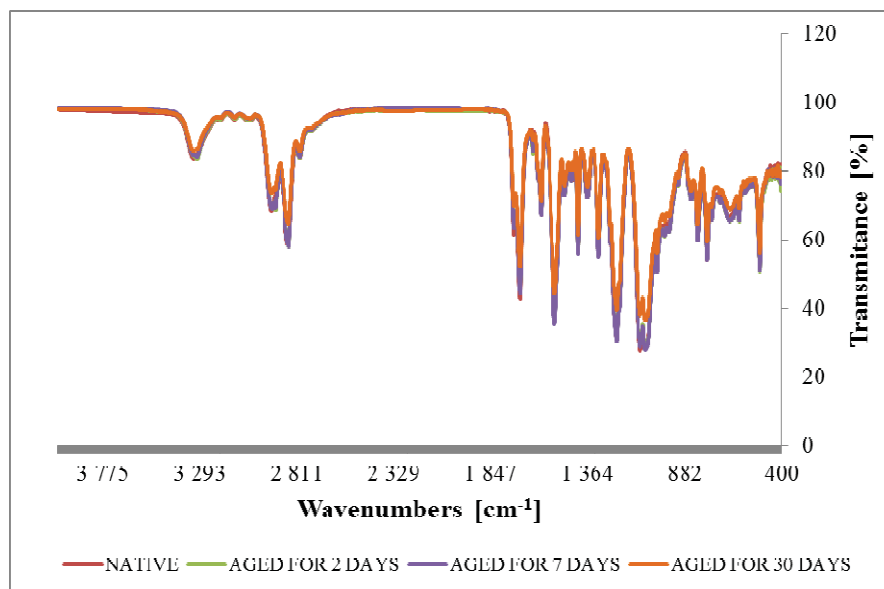


Figure 9. IR spectrum of the tested samples

4. Conclusions

The conducted research proved there is no harmful effect of aging in mine water on the mechanical properties

of polyurethane samples prepared on a 3D printer. The values of stress at the yield strength, stress at break, elongation at the yield strength and elongation at break did not change significantly regardless of the aging time, which

was 2, 7 and 30 days respectively. Shore A hardness tests also showed no changes in the hardness of the aged samples with respect to the native samples. The FT-IR spectroscopy tests of native and aged samples additionally confirmed that during the aging process the polyurethane chain was not degraded. To sum up, it can be concluded that polyurethane samples obtained by 3D printing are resistant to the action of synthetic mine water and as such can be widely used in many branches of mining.

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Additional information

Authors state that there is not any conflict of interest. Authors state that the research was conducted according to ethical standards.

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