THE RESEARCH OF THE THERMAL AND MECHANICAL PROPERTIES OF MATERIALS PRODUCED BY 3D PRINTING METHOD

by

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A comparative analysis of thermal properties of semi-crystalline and amorphous polymeric materials was carried out. Samples were produced using 3D printing technology on the SIGNAL-ATMAT printer. The following polymeric materials were used to make the samples: thermoplastic polyurethane elastomer, acrylonitrile-butadiene-styrene copolymer, Laywood, ethylene terephthalate, poly (lactic acid). The materials were tested for their thermal and mechanical properties. The research included the analysis of thermal properties by differential scanning calorimetry of manufactured materials. The tensile strength also was determined.

Keywords: *thermal properties, mechanical properties, polymer materials, 3D printing*

Introduction

Nowadays more and more industry sectors are beginning to use 3D printing instead of injection moulding for their polymer parts. Comparing to injected elements 3D printing in less expensive to launch production, we do not need to create mould and adjust injection moulding machine to get first parts [1-4]. Parts from 3D printing could be made after the 3-D model of desired model is created without any additional costs [5]. Printed elements are more precise comparing to parts made by injection moulding due to less thermal shrinkage, also printing allows us to add fast changes to printed elements when we have some mistakes in early production, if we need to add some changes to product obtained by injection moulding it is necessary to redo mould [6, 7]. One of tested materials is thermoplastic polyurethane elastomer (TPU), this polymer is characterized by high flexibility, good values of deflection, high abrasion resist and high resistance to oils, fats and some solvents. Next from tested materials is acrylonitrile-butadiene-styrene (ABS) this material is widely used in automotive industry due to its properties: light weight, good chemical resistance, easily thermoformable and machining, highly resistance to cracks, and impact. When ABS is printed we should remember to ventilate room or print in insolated room, because this polymer creates highly unhealthy va-

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pours that can pose risk to people or animals, but this material is perfect for internal parts of cars and it can be used to produce rotary parts. An interesting material is Laywood, because after 3D printing it could be subjected the same treatment as plywood such as polishing, turning or drilling. Laywood after 3D printing and further treatment is characterized by smell of wood. Another tested material was ethylene terephthalate (PET), this polymer is grate for package thanks to its transparency similar to glass, light weight which combined with flexibility and mechanical resistance, makes package of this material resistant to breakage. The PET is also known from such properties: good mechanical properties ensures adequate flexibility, well slip and sliding properties, good resistance for weak acids oils, and fats and thought and strong surface. Last testes material is poly (lactic acid) (PLA), this material is fully biodegradable, it is created from renewable natural resources. This polymer is used for dental implants, resorbable surgical threads, also it is one of most used material in 3-D printing such as mock-ups, prototype elements or steady parts of machines or electrical devices. The PLA is not the best choice for printing moving parts due to its low flexibility and low temperature resist [8]. The most important in 3D printing is to choice ideal material for specific use, when incorrect material is chosen and process parameters are wrong for material and type of element being made, it may cause: difficulties in obtaining ideal part shape, early wear of element, incomplete filling. Next difficulties in 3D printing are based on process adjust such as: table and printing temperature, nozzle and filament dimension and right adhesive on table [9, 10]. When some of discussed factors will be incorrect it could cause nozzle clogging, incomplete plastination of applied polymer, delamination of subsequent layers, polymer contractions could be bigger than it was accepted [11]. The purpose of research is to analyse changes in thermal properties and differences in tensile strength of tested 3D printed samples with 96% polymer fulfilment.

In this paper investigations of thermal properties by differential scanning calorimetry (DSC) were made. Samples for testing using the DSC method were cut out from 3D printouts.

So far, in your scientific work, the authors of the paper have also conducted thermal analysis (TG, DTG, DTA, DSC) on the combustion and pyrolysis of fuels. They enabled a comparative analysis of thermal effects accompanying these processes on fuels with different composition and properties [12, 13].

Thermal analysis provides a range of measurement possibilities, for example:

- study of chemical and physical changes of substances, under the influence of temperature,
- determination of phase and chemical composition and substance purity,
- determining the properties of substances or materials sensitived to temperature,
- study of process kinetics, and
- essential help in identifying transformation products under the influence of temperature.

Based on the TG-DTG and DTA/DSC curves it is possible to obtain the following information:

a) for TG-DTG curves:

- whether are there changes in the tested substance, related to the change in its mass,
- in which temperature ranges does take place change of the mass of the tested substance,
- what is the change in the mass of the heated substance,

b) for DTA-DSC curves:

- whether any substance is present in the tested substance transformations associated with absorption or excretion of heat,
- how much heat was separated or absorbed during process,

– what kind of changes are there,
– at what temperatures (temperature ranges) have a place these changes [14].

Research methodology

Samples were made of 1.75 mm polymer filament thread from Devil Design company. Atmat Signal was used for printing samples from, Laywood, PET, ABS, PLA, TPU polymer materials. This printer could be equipped with round nozzles from 0.1 mm to 1.0 mm dimension. Nozzle used for printing samples was 0.8 mm, this nozzle allows to reach melting temperature of 270 °C. Printers table could be cooled by fan or be heated to 100 °C, in order to improve detaching samples from table adhesive Dimafix was imposed. Filament could be feed with speed of 0.1 to 1 cm^3 per minute, that velocity allows printer to reach accuracy of 0.1 mm of shape and position inaccuracy. According to producer information about filaments following process parameters were set, tab. 1. Investigations of thermal properties by DSC were carried out using the NETZSCH PC 200 device. Samples for testing using the DSC method were cut out from 3D printouts. Samples were weighed using a SARTORIUS balance with 0.01 mg precision, an internal calibration option and a closed weighing space.

Table 1. Printing parameters composition

Sample	LAYWOOD	PLA	TPU	PET	ABS
Nozzle temperature	220 °C	230 °C	250 °C	242 °C	230 °C
Table temperature	55 °C	55 °C	60 °C	60 °C	100 °C
Printing speed	60 mm/s	60 mm/s	25 mm/s	50 mm/s	60 mm/s
Filament application speed	Compliant with the manufacturer’s recommendations				
Layer height	0.21 mm	0.21 mm	0.21 mm	0.21 mm	0.21 mm
Print cooling	YES	YES	YES	YES	YES
Fulfilling	96 %	96 %	96 %	97 %	96 %

Table 2. Temperatures of DSC

Sample	DSC
LAYWOOD	120-300 °C
PLA	120-300 °C
TPU	120-300 °C
ABS	40-200 °C
PET	20-300 °C

The weight of the test samples ranged from 7 to 12 mg. The DSC curves were recorded when heating the samples at a rate of 10 °C per minute in the temperature range given in tab. 2. The thermal parameters of the test samples were analyzed using the Netzsch Proteus software. This software allows you to examine the sample melting profile in a given temperature range and determine the area between the thermographic curve and the baseline in the endothermic effect. Standard PN-EN ISO 527-2:2012 was foundation for static tensile study. Electromechanical machine Zwick 100 was used to measure strength of investigated materials, this machine allows to test samples in the range of 0 to 100 kN.

Results and discussion of research

The results of semicrystalline material tests using the DSC method are summarized in tab. 3. Figures 1-5 presents thermograms of the materials tested. For semicrystalline polymers, the highest crystalline melting point temperature was recorded for TPU of 202.4 °C, with the lowest melting point characterized by PLA of 141.4 °C. The widest range of crystalline phase melting was recorded for PLA, the narrowest for LAYWOOD. The highest melting enthalpy value 41.86 J/g was recorded for PLA, and for TPU 12.9 J/g. In the case of amorphous ABS, the glass transition temperature of 113.9 °C was recorded in the tested temperature range, and for the PET 79.4 °C.

Table 3. The results of tests using DSC method

Samples	Melting enthalpy [Jg^{-1}]	Melting range [°C]	Maximum melt temperature [°C]
LAYWOOD	16.04 J/g	146.2-155.1 °C	152.4 °C
PLA	41.68 J/g	141.4-153.9 °C	141.4 °C
TPU	12.9 J/g	194.9-207.5 °C	202.4 °C

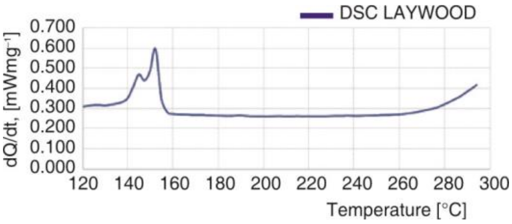

Figure 1. Thermogram of LAYWOOD

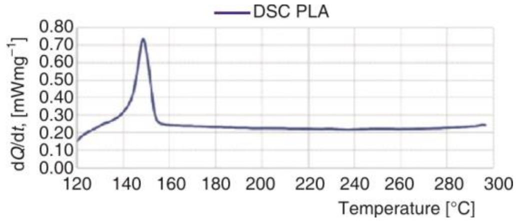

Figure 2. Thermogram of PLA

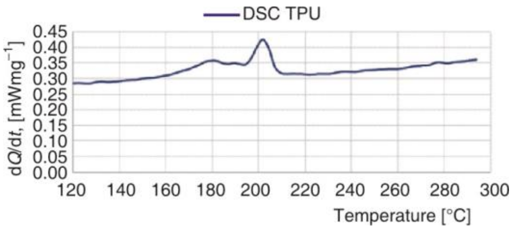

Figure 3. Thermogram of TPU

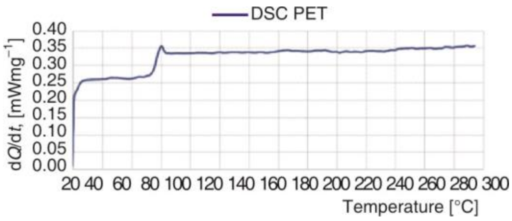

Figure 4. Thermogram of PET

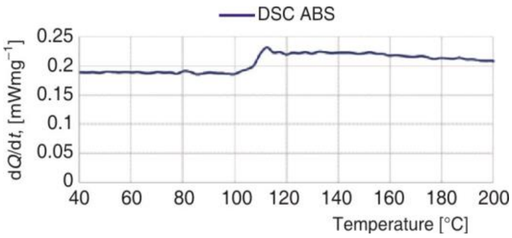

Figure 5. Thermogram of ABS

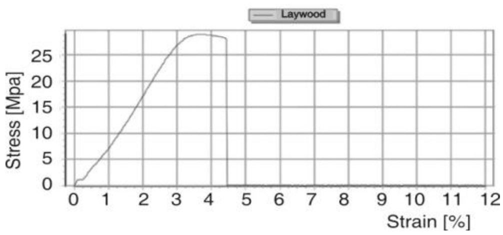

Figure 6. Relations between stress and strain for LAYWOOD

On figs. 6-10 stretching curves of examined samples are shown, and in tab. 4 the results of tested materials obtained during the uniaxial stretching test are presented.

According to all test and results presented on graphs and table, the lowest force stand elastomer TPU about 622 N. On the other way PLA show the highest resistance to tearing force. Chart where is presented stress and strain curve for LAYWOOD display ending moment of tearing when wood specks are detaching from binder which is TPU. This moment is presented at chart when stress is slowly decreasing before tearing of material, and in the same time strain is growing. The TPU have also quaint chart, ending of curve is decreasing three times, it is presented in chart by three drops before tearing of material. Couse of this quaint is cracking of filament threads from sample.

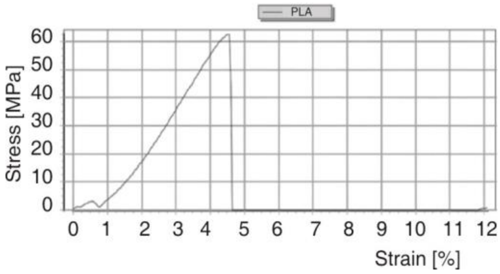

Figure 7. Relations between stress and strain for PLA

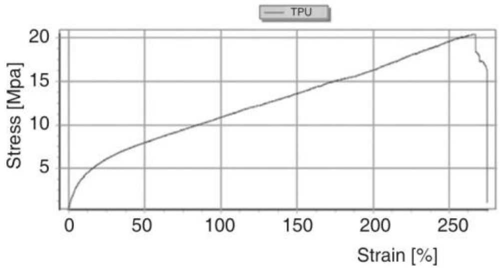

Figure 8. Relations between stress and strain for TPU

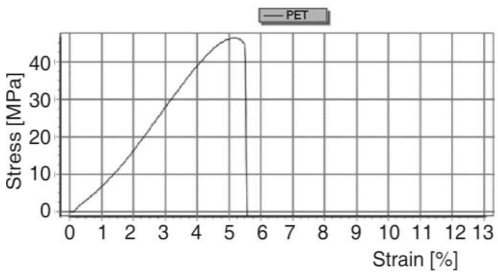

Figure 9. Relations between stress and strain for PET

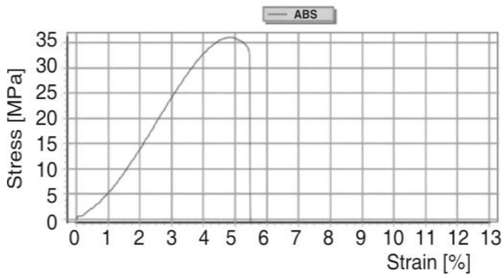

Figure 10. Relations between stress and strain strain for ABS

Table 4. Results of tensile strength testing

Material	F_{max} [N]	R_m [MPa]
LAYWOOD	1157	28
PLA	2499	63
TPU	622	14
ABS	1440	35
PET	1858	45

Summary

Summarizing the analysis of the conducted tests, it was found that for this type of 3D printing there are melting enthalpy values and glass transition temperatures suitable for given plastics. Visible is also dependence between semi-crystalline material melting enthalpy, and its tensile strength, because when melting enthalpy in decreasing, the distance between the critical axial loads is reached and total cracking happens. It is visible at PLA when it cracks after reaches maximal axial load, but TPU is cracking slowly what is shown by peaks on chart.

Nomenclature

ABS – acrylonitrile-butadiene-styrene copolymer
DSC – differential scanning calorimetry
DTA – differential thermal analysis
DTG – differential thermogravimetry
TG – thermogravimetry
TPU – thermoplastic polyurethane elastomer
PET – ethylene terephthalate
PLA – poly (lactic acid)

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