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# The Optical and Thermal Properties of PLA Filament in a Context of Material Colour and 3D Printing Temperature

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***Abstract:*** *A detailed analysis of the influence of PLA filament colour on thermal and optical properties of the 3D print was performed. Additionally, the correlation between the temperature of the nozzle of the 3D printer and quality of the printed model was investigated. To add more, a comparison between thermal properties of material exposed to different UV lights and a sample not exposed to such light was performed.*
*The spectrophotometry was used for an analysis of optical properties, such as absorbance, of the samples printed from PLA of different colours. The DSC analysis was used for measuring the thermal properties of the analysed samples.*
*It was determined that the 3D printing process noticeably changes the thermal properties of the PLA filament. These changes were much more significant for higher temperatures of the nozzle of the 3D printer. It was also observed that the thermal properties of the prints and filaments differed between different colours of the material. It is probably a result of different thermal conductivity of dyes used in materials. Although the exposition for UV light caused only negligible changes in thermal properties of the prints, it significantly changed the optical properties of the PLA. To add more, the UV light increased the transparency of the print. The absorbance changed over the exposition time, for some wavelengths it was increased over time, but for the others it was decreasing or constant. The absorbance changesalso differed between different colours of the filament.*
*These findings have significant implications for further research of3D prints made of PLA application in microbiology and for stabilizing the high-energy materials. The modified PLA can be used for foam production that is both biodegradable and has good mechanical properties. The obtained data can be used for optimization of the 3D print settings what, with addition ofadvantages of 3D printing technology, can result in prints with desirable geometry, physical and chemical properties. Such foam can be used as a base for cell cultures and as a stabilizer for unstable substances.*
***Keywords:*** *3D printing, DSC analysis, spectrophotometry, PLA filament*

## I. Introduction

In recent years the availability of 3D printing significantly increased. Thanks to decreasing prices of 3D printers, this technology is commonly used not only for rapid prototyping, but also for academic and domestic purposes. Despite increasing popularity of photo-solidification apparatuses (SLA) and selective laser sintering 3D printing technology (SLS), the most common devices are based on fused deposition modelling (FDM). This type of 3D printers can be fed with a spectrum of thermoplastic filaments like PLA, ABS, PET-G, Nylon, HIPS and rubber. To add more, these filaments can be modified by changing their composition with modifiers like metal, elastomers or even wood [1].

The operation of aFDM 3D printer is also simple as it is based on the movement of the heated nozzle across sectional profile and building up the structure by deposition of molten polymer layer by layer. The final quality of the print is a sum of many factors, such as:

- Material quality – parameters like diameter deviation, uniformity of properties and contamination of the material can cause the inconsistencies, such as cavities and bulges, on the surface of the model. In FDM printing the constant fed ratio of the filament is one of the most important settings, as the all other parameters are dependent on it. In worst case scenario, the bad quality filament can block the nozzle and stop the printing.
- Layer thickness **-** it is dependent on not only software settings, but also on the 3D printer configuration. The minimal achievable layer height is dependent on the diameter of the printing nozzle. Lower layer thickness can increase the print resolution and smoothness at the cost of much slower printing speed.
- Temperature – Each material have different thermal properties, what results in different optimal extrusion temperatures. PLA have the lowest printing temperature among popular printing materials, but it also requires fast cooling, so it is recommended to increase the fan speed for this type of polymer.
- Air circulation – It is highly recommended to reduce the amount of air circulation in a room while printing as much as possible. It is especially important in case of printing with ABS, where cold air can cause cracks

or even separation between printer's table and print. Sometimes special chamber is mounted on the top of the printer in order to eliminate these problems and increase the print quality.

- Calibration of the printer –3-dimensional printing requires very good calibration of the device. As the layer thickness is usually between 50-400 microns, even slight mistakes in levelling the printing table can result in drastic decrease of the print quality. The same thing applies to stepper motors, trapezoidal screws, filament feeder etc.. [2]

Among the thermoplastic polymers, the polyactic acid (PLA) is the most often used in FDM printing, as it is cheap and can be easily adapted for specific applications. Moreover, it is biodegradable and, unlike e.g. ABS, it does not release the toxic fumes during printing process. On the other side, the final properties of the PLA filament is highly dependent on PLA grade and modifiers. Different materials require proper settings and even configuration of the 3D printer. For example, PLA with wood, metal and stone additives requires higher printing temperatures and nozzles with higher diameter [3].

Polyactic acid filament has good mechanical properties, ease of printing process (much lower printing temperatures than other polymers, less prone to warp) and optical transparency (it makes it very easy to dye) [4]. However, it also has some significant drawbacks such as drawability, crystallization in low temperatures and low thermal stability. To add more, manufacturers of the filaments with different colours suggest the same printing settings for each of them, even though pigments have different thermal, chemical and mechanical properties. Additionally, the additives are unknown for the customers, so they cannot take them into account during the calibration of the 3D printer in order to improve the quality of the prints.

Many efforts have been taken in order to address the defects of the final prints. The prints made of PLA are quite vulnerable for high temperatures and direct sunlight, as the surface of the print can breakup and deform. Some experiments with modifications of its crystalline structure, reactive blending and addition of plasticizers were performed [5], but none of them proved to be effective in case of 3D printed models. To add more, all of these methods can be performed only by the manufacturer of the filament, not by the end users. This prevents them from increasing the strength, stiffness or toughness of a print, what limits its range of application.

The aim of this study was to investigate the influence of selected parameters and modifications on the final properties of the 3D printing based on PLA. For this purpose, five types of PLA filament with different dyes were examined. Thermal optical properties of these samples were investigated, as well as the influence of the UV radiation on these properties. To add more, the influence of printing temperature on properties of the print was also examined.

## II. Experimental

### 2.1. Materials

PLA filaments, recommended for extrusion, with different colours were investigated. In order to eliminate influence of PLA quality, all filaments were supplied by the same manufacturer – efilament3D. This company claims that it uses the same PLA pellets brought from USA for production of its filaments. Five different colours of the filament were examined: black, brown, "neon" (colourless fluorescent filament that emits aquamarine light) and colourless. All printing materials had 1.75 mm diameter. The dyes used for these filaments are unknown, as they are a trade secret of their manufacturer. All printing materials were stored in room temperature in boxes with desiccants.

### 2.2. 3D printing

All samples were prepared on a modified FDM 3D printer – Anycubic i3 Mega. The printing model was a 30x30x0.1 mm cuboid. The thickness of the block was set to a minimal layer height for the printer. G-code was prepared with Ultimaker Cura 3.3.0 software with custom settings, which are presented in Table 1.. No adhesives were used for improvement of adhesion between the printing table and a model, although the printing table was cleaned with warm water and isopropyl alcohol before the printing process. It was done in order to remove the contaminations and degrease the surface. When the printing process was finished, the prints were left to cool down to the room temperature, as it allowed to remove the blocks without using the force. Then prints were washed with isopropyl alcohol in order to eliminate all contaminations from surface and put in the container with desiccants.

**Table 1.** Settings of the 3D print

| Parameter | Value | | |
|---|---|---|---|
| Layer height | 0.1 mm | | |
| Wall thickness | 1.2 mm | | |
| Infill density | 100% | | |
| Infill pattern | Zig zag | | |
| Printing temperature (nozzle temperature) | 190°C | 210°C | 280°C |
| Print speed | 45 mm/s | | |

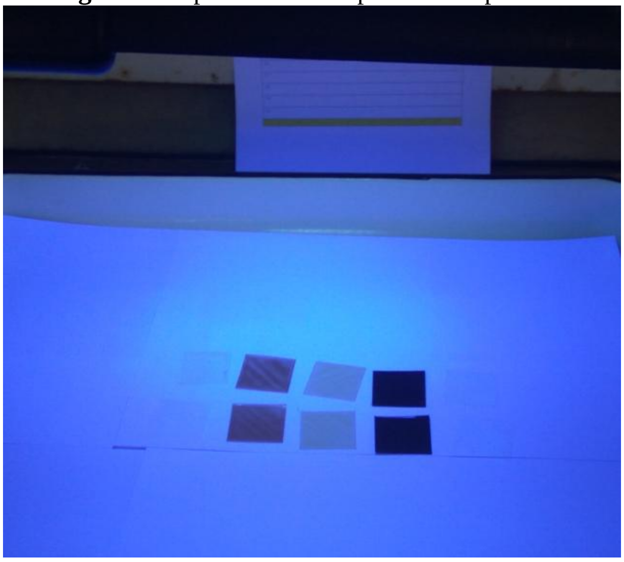
| | |
|---|---|
| Cooling fan speed | 100% |
| Build plate temperature | 60°C |
| Build plate adhesion type | Skirt |

## 2.3. UV treatment

Selected blocks were treated with UV lamps. The installation was set up in fume hood for safety reasons. Samples were punt in a 3 straight lines on a white paper under the lamp (Figure 1.). In order to minimize experimental error, each sample was placed in a way that the side that was touching the printing table was facing the lamp. One type of lamps were used in a test – UV-365.Three exposition times were examined: 15, 60 and 150 minutes. When the time has passed, the samples were collected and stored in a container with desiccants.

During the experiment small containers with Fricke dosimeter were present in order to measure the dose of UV radiation for different exposition times. The dosimeter was prepared accordingly to the formula prepared by Weiss, Allen and Schwarz [6].

**Figure 1.** Experimental setup for UV exposition



## 2.4. Spectrophotometry

Samples treated with UV light were investigated with spectrophotometer in order to measure the absorbance of the material. The JASCO V-530 with custom settings (Table 2.) was used for this purpose. All samples were arranged in a same way before the test – the side that was touching the table during 3D printing was facing the lamp. Thanks to it the results were much more repeatable as the surface was more smooth than on the other side. The obtained results were then processed with dedicated software (adjusting base line, smoothing the curves etc.).

**Table 2.** Settings of the spectrophotometer

| Parameter | Value |
|---|---|
| Photometric mode | Abs |
| Responce | Medium |
| Band width | 2.0 nm |
| Scanning speed | 1000 nm/min |
| Start length | 1000 |
| End lenght | 190 |
| Data pitch | 1.0 nm |

## 2.5. DSC analysis

The DSC analysis was performed in order to investigate the thermal properties of all samples. The NETZSCH DSC 200 with NETZSCH ASC controller was used for that purpose (Table 3.). Each time small a 2-5 mg sample was cut from the blockand put into calorimetric crucible. Due to the construction of the calorimeter whole sample had to maintain contact with the bottom of the crucible. When the measurement was finished the obtained data was processed with the dedicated software. The combustion chamber was cleaned from the reaction remnants and other contaminations between each measurement.

**Table 3.** Settings of the DSC

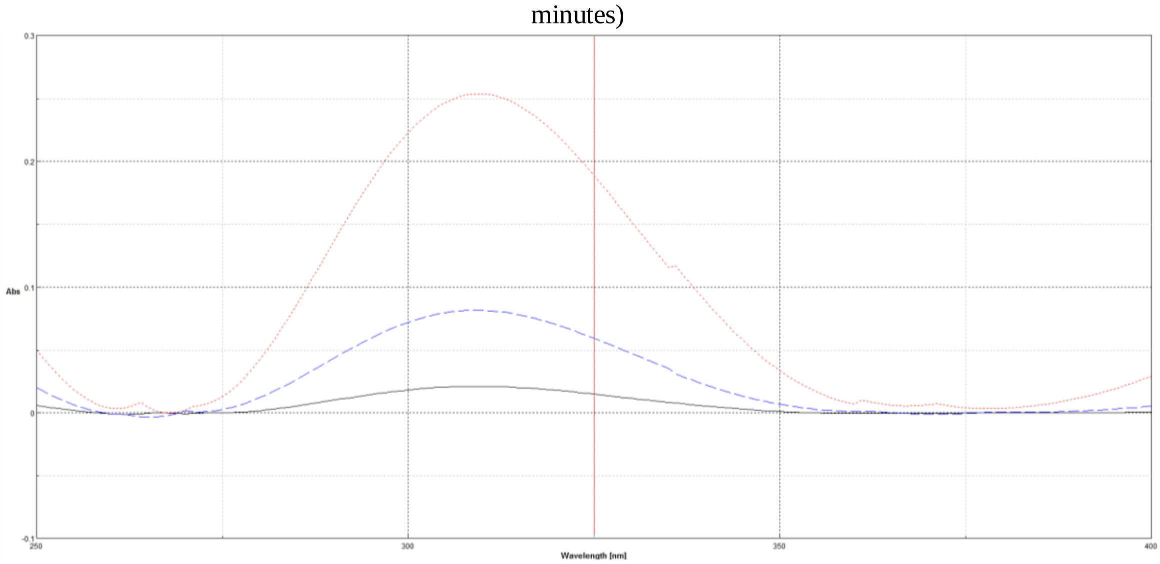
| Parameter | Value |
|---|---|
| Temperature range | 40-450°C |
| Temperature rise rate | 10°C/min |
| Stove fan | Enabled |
| Purge gas | Enabled |
| Protective gas | Disabled |

## III. Results

### 3.1. Spectrophotometry

In order to properly illustrate the connection between the UV exposition and properties of the samples, the dose of UV radiation had to be measured. For this purpose the Fricke dosimeter was used. The samples were investigated in spectrophotometer for 200-400 nm ranges, as the highest absorbance for this dosimeter can be observed for 224 and 305 nm [7]. For the calculations, the values obtained for 305 nm peak were used. At first, the extinction coefficient was calculated as shown in Beer-Lamert Law. The value of absorbance was obtained during spectrophotometric analysis, the other parameters were known and constant.

**Figure 2.** Absorbance of Fricke dosimeters (black line – 15 minutes exposition, blue – 60 minutes, red – 150 minutes)




Then, the calculated value was used to calculate the dose of the radiation. The equation that is generally used in case of direct spectrophotometric method is presented in Equation 1. However, this equation can be simplified, as shown in the Equation 2. and the Equation 3. [7]. The results of the calculations are presented in Table 4.

$$D = \frac{(E_D - E_W) * N * 100}{(\varepsilon_{Fe^{3+}} - \varepsilon_{Fe^{2+}}) * G(Fe^{3+}) * f * d * l * 1000} \text{ [rad]} \qquad \text{(Equation 1.)}$$

$$D = \frac{9{,}42 * 10^8 * A}{\varepsilon_{Fe^{3+}} * [1 + 0{,}0069(t - t_W)] G(Fe^{3+}) * l} \text{ [rad]} \qquad \text{(Equation 2.)}$$

$$D = \frac{6{,}023 * 10^{22} * A}{\varepsilon_{Fe^{3+}} * [1 + 0{,}0069(t - t_W)] G(Fe^{3+}) * l} \text{ [eV/ml]} \qquad \text{(Equation 3.)}$$

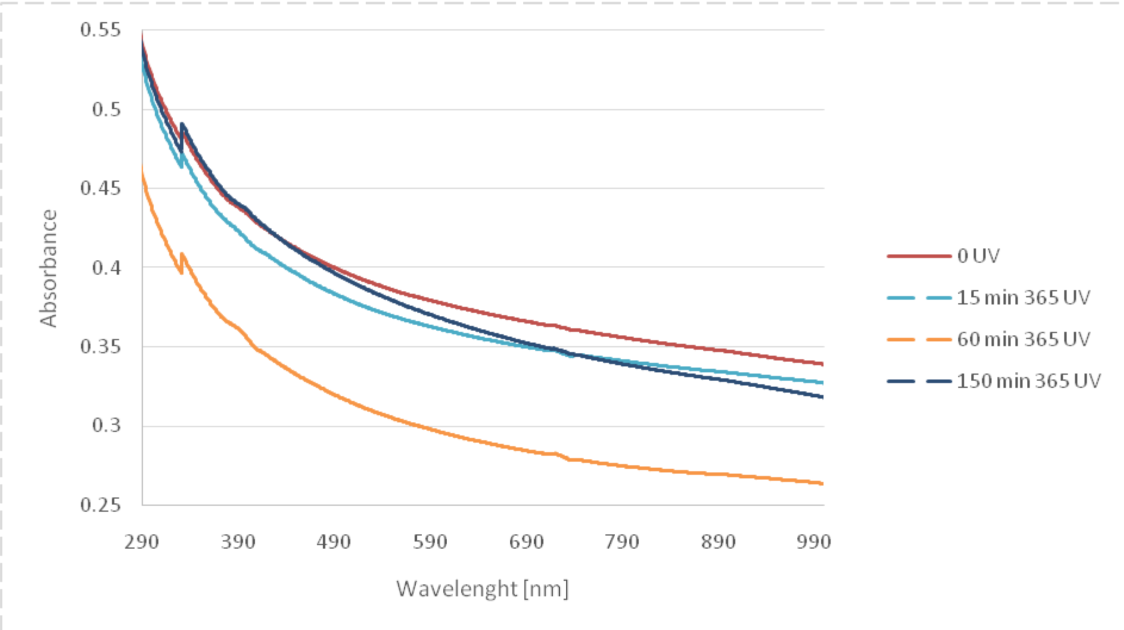
Where:
D – dose of radiation
A- absorbance [-]
$E_D$ – Extinction of investigated sample [-]
$E_W$ - Extinction of reference sample [-]
N – Avogadro number ($6{,}023*10^{23}$) [1/mol]
ε – molar extinction coefficients [1/mol*cm]
$G(Fe^{3+})$ – efficiency of $Fe^{3+}$ ions oxidation [1/eV*$10^{-2}$]
f – conversion factor – $6{,}242*10^{13}$ eV/rad
d – density of the solution [g/cm$^3$]
t – measurement temperature (20°C)
$t_W$ – temperature of molar extinction coefficient measurement (25°C)

**Table 4.** Radiation doses calculations

| Exposition time [minutes] | A [-] | Absorbance coefficient ε [1/mol*cm] | D [rad] | D [eV/cm$^3$] |
|---|---|---|---|---|
| 15 | 0,0212 | 0,0679 | 1,954*10$^7$ | 1,249*10$^{21}$ |
| 60 | 0,0812 | 0,0177 | 2,866*10$^8$ | 1,832*10$^{22}$ |
| 150 | 0,2544 | 0,0056 | 2,813*10$^9$ | 1,799*10$^{23}$ |

The spectrophotometry was then used for investigation of the absorbance of the light and optical properties of the samples. As shown on Figure 3. an exposition to UV light noticeably increases the transparency of the prints. It is represented by a decrease of light absorbance of the samples when compared to the sample that was not exposed to the UV light. The best results were obtained plates that were irradiated for 60 minutes. Longer exposition resulted in decreasing the transparency of the samples, as the values of plates absorbance exposed for 15 and 150 minutes are similar.

**Figure 3.** Absorbance of the light of colourless PLA




As shown on the Figures 4., 5. and 6., the optical properties of materials with different colours differ significantly. On these figures red curve represents sample after 15 minutes of UV exposition, blue – 60 minutes exposition and purple one – 150 minutes exposition.Figure 4. shows changes in absorbance of colourless prints. As presented on the figure, an increase in irradiation time results in an rise of ultraviolet and red and infrared light absorbance. The samples also absorbed purple and blue light, although no correlation between absorbance of these wavelengths and exposition time can be created. Minor absorbance of yellow and green light can also be observed.

**Figure 4.** Absorbance of the light of colourless PLA with adjusted baseline (UV-365)

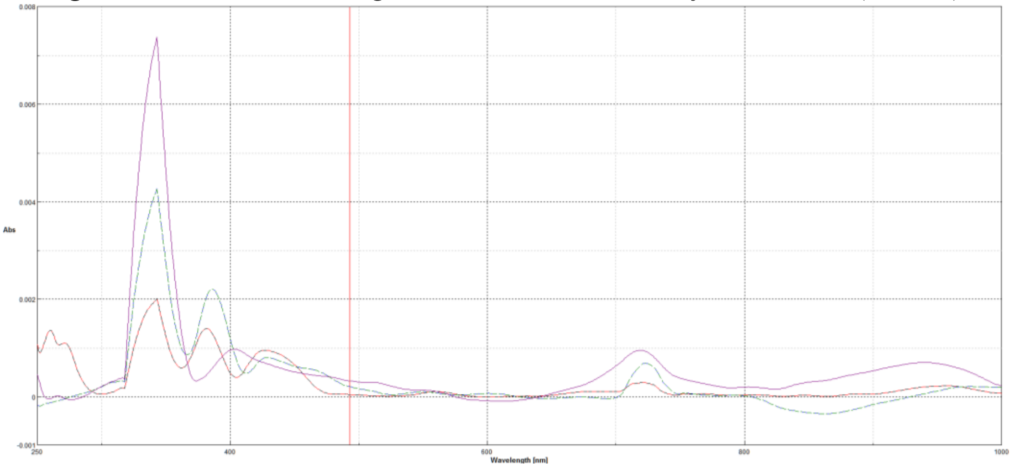
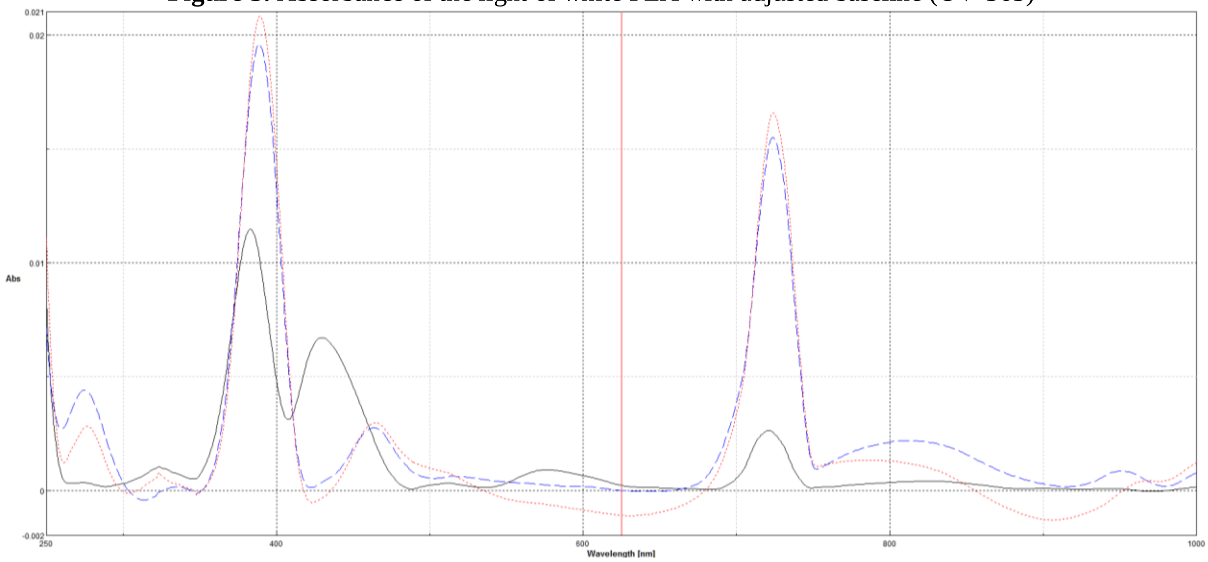


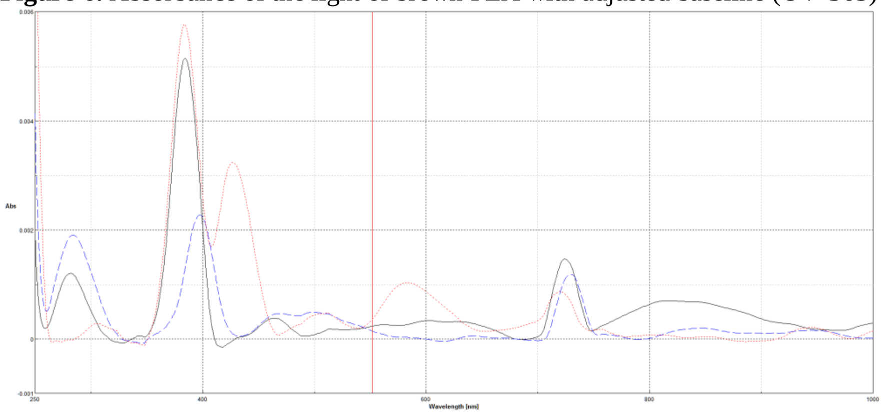

Figure 5. shows the absorbance of a white PLA. The obtained results are similar for those gathered during the investigation of colourless material, although it is worth noting, that absorbance of samples exposed to UV light for 60 and 150 minutes are almost identical. It is possible that the material achieved its final properties between after 60 and 150 minutes irradiation. It shows that exposition longer than one hour is not beneficial in any way. White PLA absorbs light much better than colourless material (e.g. at least 3 times better for purple light and 16 times more for red light), especially the red light. Small amounts of green and yellow light are also being absorbed. It is also worth noting that with longer exposition samples' ability to absorb blue light is much worse.

**Figure 5.** Absorbance of the light of white PLA with adjusted baseline (UV-365)




As shown on the Figure 6., the absorbance of brown PLA is much worse than in case of the previous colours. Like colourless and white material, the brown PLA absorbs the ultraviolet and red and infrared light. Unlike previous samples, the absorbance of red light is decreasing for longer duration of UV irradiation. Too add more, UV exposition changes absorbance of almost every wavelength. For example, long exposition improves absorbance of blue and yellow light, but it drastically reduces the absorbance of ultraviolet and infrared light.

**Figure 6.** Absorbance of the light of brown PLA with adjusted baseline (UV-365)



Two other colours of the filament were also investigated. The results of a neon PLA were almost identical to those obtained during measurements of colourless material. It can be explained by the fact that these samples were almost undistinguishable between each other for the naked eye. It also proves that fluorescent dye does not change optical properties of the filament significantly. The black PLA could not be investigated, as it was not transparent enough to let the light pass through it. For this reason, the measurements of optical properties of this material were not possible.

### 3.2. Differential Scanning Calorimetry (DSC)

DSC analysis was used for investigation of thermal transitions and properties of different coloured PLA filament. It is worth noting that placement of the curves on the Y axis (where Y means a heat flow) on the graphs representing the obtained data is not important, as it just serves a way to put all the curves on one figure [8]. Figure 7. shows the DSC curves for colourless filament, where three types of samples were compared: raw filament and two plates printed in 190°C, one that was not exposed for UV light and one irradiated with UV-365 lamp for 150 minutes. Two types of thermal transitions can be spotted in 50°C to 300 for each sample °.First one appears for approximately 60-65°C (depending on the sample) and a second oneis represented by a peak that can be seen at around 150-155°C. First transition can be interpreted as a glass transition, as a change in a slope of a DSC curve without any troughs or peaks can be observed [9].It is worth noting that glass transition in not present in a print that was not exposed to UV light. The temperature of the glass transition is higher for the filament than in case of the 3D prints. The second transition can be interpreted as the melting process. According to the obtained data the process of 3D printing increases the melting temperature (from 151 to 155°C) and UV exposition decreases it. UV-365 exposition also has a noticeable effect on the melting temperature decrease. The decomposition temperature for each sample is approximately 350°C and it does not differ significantly between them.

**Figure 7.** DSC curves of colourless PLA

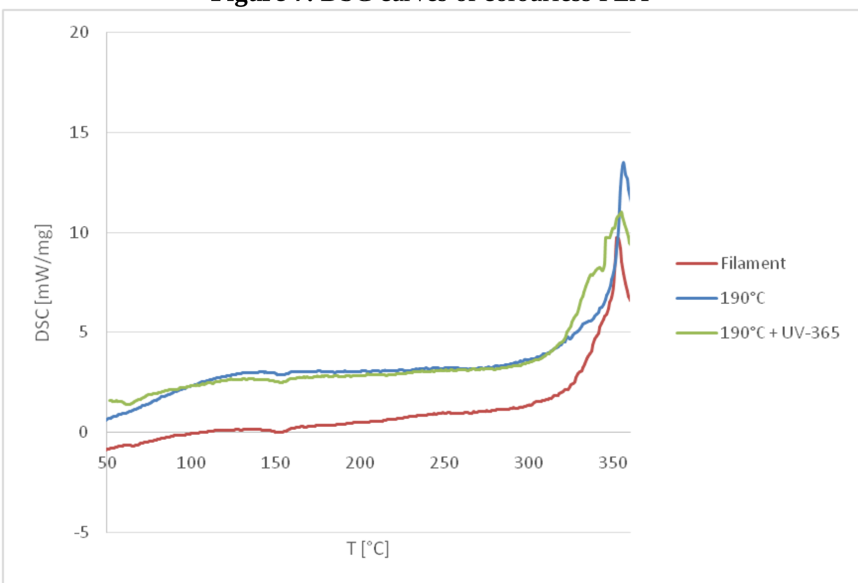
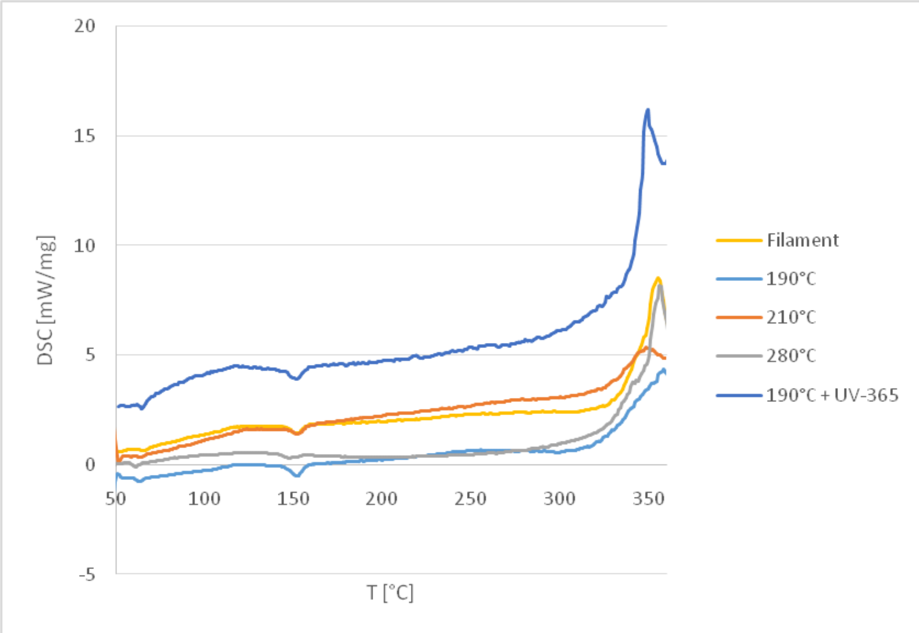


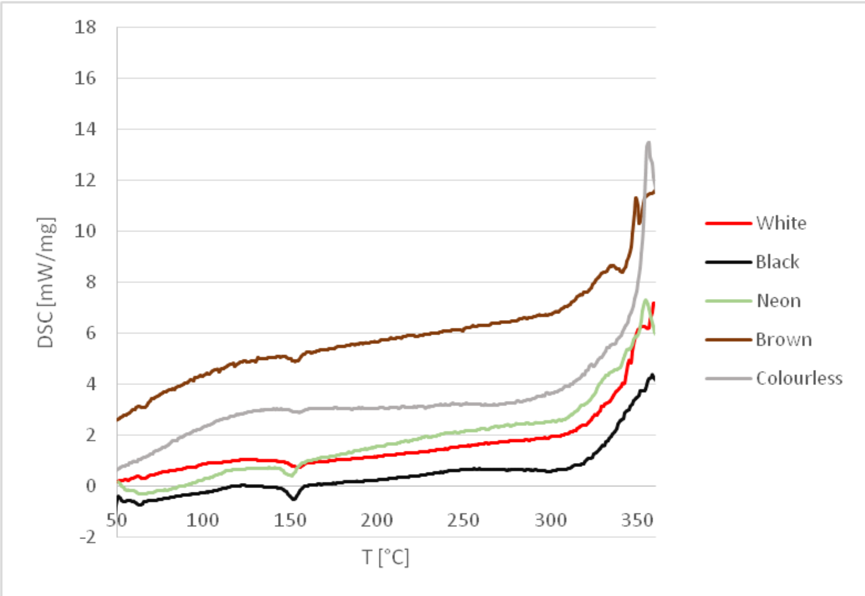
Figure 8. summarizes the DSC curves of black PLA, where the impact of the temperature of the3D printer nozzle on thermal properties of the prints was investigated. As shown on the graph, thehighest glass transition temperature can be observed for the raw filament (65,4°C) and the lowest for 280°C print (60,8°C). The melting temperature is also affected by the change of printing temperature. The highest can be observed for raw filament, for optimal printing temperatures range its value does not change and its lowest value can be observed for sample printed in 280°C. It is also worth noting that UV exposition didn't affect the melting temperature value.

**Figure 8.** DSC curves of black PLA




On the Figure 9. the DSC curves comparison between 190°C prints made of different colour filaments is presented. The glass transition temperature differs slightly between them. The lowest can be observed for black filament (62,4°C). It can be explained by a presence of a dye, that could increase the thermal conductivity of the filament. The other filaments have glass transition temperature of approximately 65°C. The melting temperatures of the plates are also very similar. The neon and black filaments have the lowest melting points: 150,7 and 151,6°C. A brown filament's melting temperatures is slightly higher – 153,1°C. The highest temperatures were observed for colourless and white filaments – 155,1 and 155,3°C.

**Figure 9.** Comparison of DCS curves for 190°C prints of different colours



## IV. Discussion and conclusions

The differences in thermal and optical properties of the filaments of different colours were noticeable but not significant. This confirms that for general use, the decision of manufacturers to not change recommended settings for different colours of the PLA filament is not without foundation for the majority of the 3D printer users. On the other side, these deviations between them are present and they should be taken into consideration during specific use of the material. Some of the most important conclusions from theseinvestigations are:

- The UV radiation slightly changes the thermal properties of the material. It increases the glass transition temperatures for examined samples, although this change is not significant (up to 3°C). The melting temperature of the PLA can also be affected by exposition to UV light, however, this change is much more prominent for filament without dyes. For colourless and neon filaments it could change up to 5°C, although this value varied depending on the sample. For the other samples the change was either unnoticeable or insignificant (below 1°C). The decomposition temperature does not change noticeably among the samples.
- The UV lightsignificantly changes the optical properties of the samples. The absorbance of the light is highly impacted but not only the colour of the sample, but also by type of UV lamp and time of exposition. The relation between light absorbance and UV exposition time varied depending on the wavelength and have to be investigated further for other filament colours and manufacturers. It is also worth noting that the UV light increased the transparency of the prints. The effect was noticeable for not only the spectrophotometry, but in some cases even for naked eye.
- The printing process and the printing temperature have a significant impact on the thermal properties of the polymer. Printing reduces the glass transition temperatures and the melting temperatures for all of the investigated filaments. The higher printing temperature can also result in a larger decrease of these temperatures. They also reduce the energy of the thermal transitions.
- The modification of the samples with UV light also affect the thermal properties of the PLA filament. It increased the glass transition temperatures and affected the melting temperatures. It also changed the energy effects of these transitions.
- The decomposition temperature have not changed significantly among tested samples.
- The glass transition did not appear for colourless PLA in low temperature prints. To add more, it was present for the samples modified with UV light and for higher temperature prints.
- The colour of the filament has an slight effect on the thermal properties of the print. However, the differences among the investigated materials are not high. The quality of the prints of the materials of different colours can be spotted, but they are not significant.
- The series of test was performed for samples irradiated with UV-350 lamp. The obtained results differed significantly from those observed for UV-365 lamp. Therefore, it was decided that different UV lamps will be examined in future investigations.

For future work, more samples would be tested in order to give the data more confidence. More colours of the filaments are planned to be put into the tests as well as the printing materials from other manufacturers. Also, different analysis methods like FTIR analysis or mechanical analysis would allow to study the other properties of the material. To add more, other modification methods, like treating the material with low temperatures or with microwaves can be tested. The results of this study will also contribute to the other planned studies as using the 3D printed elements in microbiology or in experiments with high energy substances. The PLA after proper modifications can expand its interface surface and, with right knowledge about printing settings and material modification, be used as e.g. basis for growing a cell colonies or in a green chemistry.

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