Materials Science-Poland, 41(1), 2023, pp. 177-190
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/msp-2023-0015

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PLA filament is not equal to PLA filament: Experimental studies of the influence of the type of pigment on the mechanical and thermal properties of poly(lactic acid) products

Jacek Iwko[1,*], Tomasz Jaruga[2], Oliwia Trzaska[1], Tomasz Stachowiak[2]

[1]Wroclaw University of Science and Technology, Faculty of Mechanical Engineering, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

[2]Czestochowa University of Technology, Faculty of Mechanical Engineering and Computer Science, Aleja Armii Krajowej 21, 42-224 Czestochowa, Poland

The correct manufacture of products using FDM printers is not an easy task, taking into account the value and repeatability of material properties. The properties of elements manufactured in this way depend on many factors, both technological and material. Poly(lactic acid) PLA is one of the most willingly used materials in additive techniques. It is sold in a very wide range of colours. This work was intended to answer the question of how the type of pigment affects the mechanical and thermal properties of products obtained from PLA. The correlation between the material properties and the structure of the material as well as the macroscopic structure of the product has also been investigated. The paper analyses the mechanical and thermal properties of products made of PLA filaments in 12 basic colours obtained from one supplier. Bending, impact strength, HDT and Vicat softening point tests were carried out. The percentage content of residues after calcination the samples was determined. Additional analysis (DSC) was performed to interpret the obtained tests results. They indicate that the mechanical properties differ significantly between different types of PLA with differences of up to 45%. Vicat softening point tests indicate differences of 5°C between the extreme values of these parameters. The DSC interpretive study did not clearly show the reasons for these differences in the properties of the filaments.

Keywords: *PLA, pigments, mechanical properties, DSC, colours, thermal properties*

1. Introduction

Three-dimensional (3D) printing technologies, also known as additive manufacturing (AM), first appeared on the market in the 1980s. However, a rapid growth of interest in AM techniques has taken place in the last decade. Increased interest in 3D printing is observed both from industry and home users. AM is more and more often being used to design and manufacture functional 3D parts and objects. 3D printing involves the production of parts by selectively adding material in successive layers of the cross-section, thus creating an object. AM covers a variety of technologies and is an alternative to traditional subtractive manufacturing (machining, abrasive and erosion treatment). The rise in popularity of AM is due to its many advantages over other traditional manufacturing processes [1–4]. The main reason is the widespread use of inexpensive, stationary 3D printers on the market and quite a large variety of materials. The basic advantages are comprehensiveness and simplicity of design, as well as the ability to produce structures with very complex shapes from technological point of view. Importantly, these structures may also contain moving parts. In addition, the lack of additional tools (extrusion heads, injection moulds, etc.), the high speed of introducing a new product to the market and the lack or minimal amount of waste make AM an environmentally friendly technique. It is also possible to use not only plastics or metal alloys as a material, but also concrete, chocolate or living tissue, which gives a wide range of

* E-mail: jacek.iwko@pwr.edu.pl

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applications of these technologies [5–7].

On the other hand, many aspects of AM processes still need improvement [8, 9]. The high cost of large-scale production, a smaller choice of materials and colours, the limited size of 3D printers and the limited accuracy of printed structures caused by the layer-by-layer structure are the basic elements limiting the wider development of this technique on the market. In addition, printed parts have reduced mechanical strength compared to parts with the same geometry produced from bulk material by traditional manufacturing techniques. It follows that there are many areas in the AM technique that require further research. The development of 3D printing techniques, understood as the study of the impact of its process parameters and material type on product properties, is crucial for the continuous increase in the importance of the AM technique on the market [10].

Many 3D printing technologies have developed with the progress of knowledge. Sometimes the difference between them is small. Often a new technology is referred to a new name, mostly in order to circumvent patent rights or to improve a given technology, after a slight modification. The breakthrough was the expiry of key Stratasys patents for Fused Deposition Modelling (FDM) technology (patent US5121329A, which expired in 2009), which significantly affected the cost of production of 3D printers [5, 11]. It made it possible for the development of small and cheap printers produced mainly in China for individual use, which had a huge impact on the greatest spread of this 3D printing technology. A similar future may await the Selective Laser Sintering technology, whose patent (US5695707A) expired in 2014 [5]; although it is still a relatively expensive technology.

FDM is currently still the most popular technology on the 3D printing market [12, 13]. This AM technique creates products by melting a thermoplastic polymer and applying it layer by layer on a heated bed. This process takes place in a closed chamber maintaining a higher temperature (for most materials) or without the presence of a chamber (mainly PLA printing). The raw material for the process is a polymer fiber (filament) with a standard diameter of 1.75 or 2.85 mm. The fiber is fed into a heated extrusion die, where the polymer is plasticized. The molten polymer is laid down in layers on a heated bed. As the polymer leaves the extruder nozzle, it begins to solidify. The printer applies the polymer layer by layer until the entire product is obtained.

Many researchers have focused on methods to improve the effects of interlayer adhesion in printed objects. Interlayer adhesion is a key factor related to the mechanical properties of components produced with material extrusion (ME) processes. Research aimed at improving layer adhesion mainly included optimisation of printing process parameters [14–17], thermal post-processing to increase strength [18, 19], physical and chemical cross-linking of the material polymer [20, 21] and chemical post-treatment of manufactured parts [22].

Polymers such as PLA, PS, PET, PP or TPU and various copolymers and blends such as ABS, ASA and PC/ABS can be used for 3D FDM printing. Polylactic acid (PLA) is most commonly used in the FDM process. This polymer can exist in various polymorphs. Depending on the lactic acid monomers used during the synthesis (L-lactic acid and D-lactic acid), the following can be obtained: poly(L-lactic acid) (PLLA), poly(D-lactic acid) (PDLA) and poly(DL-lactic acid) (PDLLA). Both L and D forms of lactic acid can be cyclized to form dimers: homochiral lactides (L,L- and D,D) or heterochiral lactide (meso-lactides), from which PLA can be obtained. Lactic acid from agricultural crops is a source of L or D stereoisomers. Racemic mixtures are obtained during synthesis [23]. Depending on the crystallisation conditions, different types of PLA crystallites can be obtained [24].

PLA has a semi-crystalline structure and is a glossy, rigid and colourless polymer with some, though limited, light transmission. Additives (pigments) are added to the material to colour PLA. They can change its various properties, mainly rheological [25], but also mechanical and thermal [4, 13, 26]. This is also confirmed by the results of tests performed for the ABS filament [27, 28].

Considering the latter issue, recent studies have shown that some seemingly insignificant differences in filaments, such as the type of pigment and

the degree of crystallinity, can significantly affect the mechanical, thermal and dimensional properties of printed products [13, 26, 29]. Given the continuous development of AM, it now seems that one of the main goals of the development in this field is the standardisation of raw materials and processing conditions [30]. On the other hand, in order to fully exploit AM by engineers, still more research is required. These studies could link significant relationships between the material construction and the properties of the ME. This paper is devoted to such type of analysis.

Experimental studies were carried out on 12 types of PLA filaments obtained from one manufacturer in order to determine how differences in the type of pigment affect the material properties of the products. In this study, a series of standard mechanical and thermal tests were performed on a set of 12 commercially available PLA filaments. Similar studies have been conducted before [4, 13, 26, 29]. However, they included a smaller amount of materials and a smaller scope of material testing. This work had two main research goals. The main goal of this work was to quantify how the choice of filament colour can lead to differences in the mechanical and thermal properties of the resulting products. The second goal was an attempt to create the correlation between the measured material properties and the structure and characteristics of the material (degree of crystallinity, glass transition temperature), as well as the macroscopic structure of the products.

2. Experimental methods

2.1. Materials and sample preparation

PLA filament was purchased from 3D Printers Company (Poland). Eleven filaments with different pigments and one filament without pigment were tested, which was a reference to the other samples. PLA samples were printed in the following colours: *natural* (without pigment), *white, silver, iron gray, black, green leaf, yellow, orange, red, sky blue, dark blue* and *magenta*. Detailed information on the chemical composition of the pigments, their concentration and the type of polylactide is not available. Figure 1 shows all printed sample types (in all colours) used in testing.

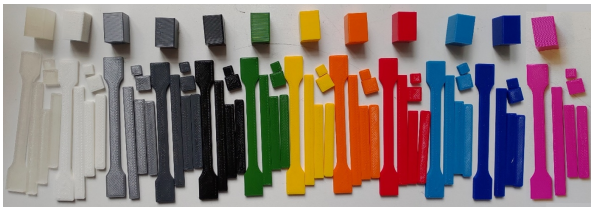


Fig. 1. PLA test samples printed in different colours

Test samples were printed using the HBOT 3D F300 printer. The accuracy of its printing (provided by the manufacturer) is +/− 0.1 mm. The working area of the printer is 300x300x300 [mm]. The working platform is made of borosilicate glass. The diameter of the PLA filament was 2.85 mm. All samples were printed with the same printing parameters as shown in Table 1. After the printing process, the samples were not subjected to any finishing treatment. They were left for 72 hours in order to season.

Table 1. Parameters for printing test samples set on the HBOT 3D F300 printer

parameter	**size**
Working table temperature [°C]	60
Nozzle temperature [°C]	235
Nozzle diameter [mm]	0,60
Layer height [mm]	0,30
Sample filling degree [%]	100
Filling type	rectangular
Printing direction	horizontal
Print speed [mm/s]	50

2.2. Tests

2.2.1. Flexural strength

Bending tests are used primarily to determine the properties of rigid polymers (such as PLA), which are characterised by a relatively large modulus of elasticity E. The use of bending loads is particularly useful when testing brittle materials, whose characteristic feature is low value of relative elongation at break, usually ε_r = 1-5%. Eight rectangular samples of each colour with dimensions of 120x10x4 [mm] were used for the test. The tests

were carried out using the Tinus Olsen H25KT testing machine with a 10 kN measuring head.

2.2.2. Compressive strength

The compressive strength σ_M is the maximum stress that can be carried by a sample during a compression test. Compressive strength measurements were carried out in accordance with PN-EN ISO 604:2006 on a Tinus Olsen H25KT testing machine. Eight samples of each colour with dimensions of 10 x 10 x 20 mm were used for the study.

2.2.3. Impact strength

Impact strength determines the brittleness of the material, that is, its resistance to impact fracture. It can be defined as the work necessary to dynamically break the sample related to its cross-section at the fracture site. Impact tests can be performed using notched or unnotched specimens. PLA is a brittle material, and there was no need to make a notch before testing (unless the test itself is intended to determine the sensitivity of the material to notch action). A Charpy hammer manufactured by Werkstoffpruefmachinen Leipzig was used to measure the impact strength according to the PN-EN ISO 179-2 standard. Eight rectangular beams of each colour with dimensions of 80 x 10 x 4 [mm] were used for the test.

2.2.4. Vicat softening point

The softening point of polymeric materials can be determined and thus also their static heat resistance can be determined using the Vicat apparatus. Six samples from each series were tested. The Monagraph Studio Vicat/HDT Automatic apparatus was used for the tests. Its main part is a bath filled with silicone oil, connected to a heater that heats the entire system at a preset speed. During one measurement, three identical samples are placed in the apparatus. The load acting on the needle is 10 N. The rate of temperature increase in this test was 50°C/h.

2.2.5. DSC research

The tests of the thermal properties of the samples were carried out using differential scanning calorimetry using DSC Polyma 214 from NETZSCH. PLA samples weighing approximately 10 mg were placed in aluminum vessels, using an empty vessel as a reference sample. They were subjected to dynamic analysis in a nitrogen atmosphere at a constant heating or cooling rate of 10 K/min.

Thermal analysis was carried out using three temperature programs:

- I - heating from 20°C to 200°C; then the samples were kept at 200°C for 2 minutes;
- II - cooling from 200°C to 50°C; then the samples were held at 50°C for 2 minutes;
- III - second heating from 50°C to 200°C.

In order to determine the degree of crystallinity (X) of the samples, the known formula (1) was used, taking into account the presence of modifying additives included in the PLA filaments used to print the samples [4]:

$$X = 100\left(\frac{\Delta H_m - \Delta H_c}{(100 - p_a)\Delta H_0}\right) \tag{1}$$

X – degree of crystallinity of the sample [%]
ΔH_m – endothermic heating enthalpy of the sample, determining the amount of heat needed to melt the sample [J/g]
ΔH_c – exothermic enthalpy of cold crystallisation, determining the amount of heat absorbed by the sample during cold crystallisation [J/g]
ΔH_0 – endothermic heating enthalpy of the sample, determining the amount of heat needed to melt the sample with 100% crystallinity [J/g]
p_a – percentage content of additives present in the PLA filament [%]

The content of additives was determined by calcination of PLA samples weighing about 1g in porcelain crucibles in an oven at 400°C for 6 hours.

3. Results and Discussion

Below are the results of material tests with a brief analysis. Error bars in the graphs indicate the standard deviation of the mean value taking into account the critical coefficient of the t-Student's distribution.

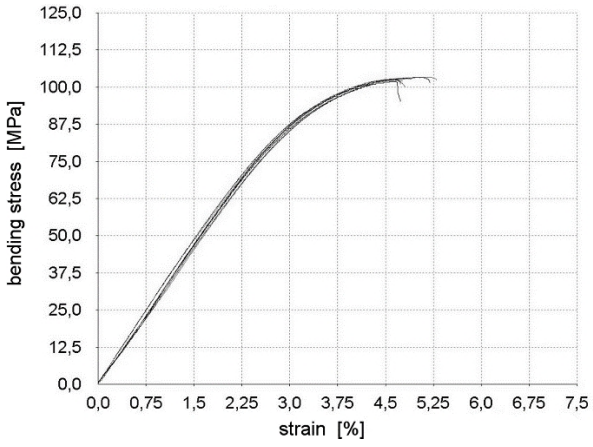


Fig. 2. Bending curves for natural samples

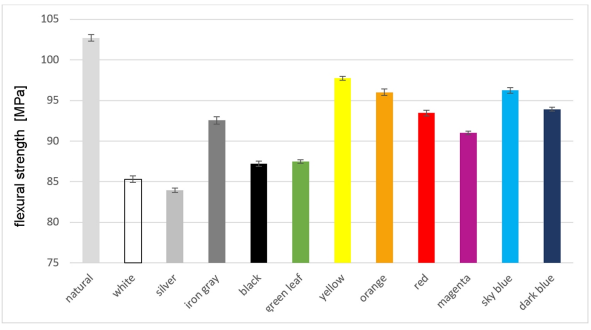


Fig. 3. Flexural strength of the tested materials

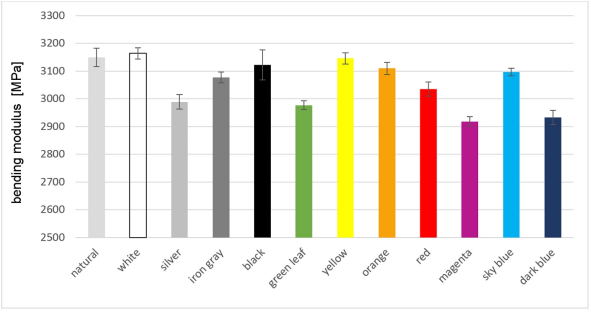


Fig. 4. Flexural modulus of the tested materials

3.1. Flexural strength

Figure 2 shows the bending curves of *natural* samples. The maximum flexural stress was reached at the moment of sample fracture. Figures 3 and 4 show the relationship between bending strength and bending modulus as a function of the type of pigment. The manufacturer's specification does not include parameters measured in the bend test. The highest flexural strength is found for *natural* samples (103 MPa), and the lowest for *silver* (84 MPa) and *white* samples (85 MPa). Generally, it can be seen that the addition of any pigment more or less significantly reduces the strength of the material (pure PLA), the change in strength is in the range of 5–18%.

Analysing the flexural modulus, the highest values have the *white* (3.17 GPa) and *natural* (3.15 GPa) samples, and the lowest have *magenta* and *dark blue* samples (slightly over 2.90 GPa). The differences in properties are less visible here. The addition of pigment does not affect the module value so much, which in a few cases remains at a similar level within the margin of error (*white, black, yellow*), and the maximum decrease in the module value is about 7%. Apart from the modulus value for *white* and *black* samples, the differences in its values for individual materials are qualitatively similar to the differences in flexural strength.

The obtained differences in the results of flexural strength and flexural modulus for individual materials are similar to the values of tensile strength and Young's modulus. The results of tensile strength tests were not presented in detail due to their very similar nature and analogous differences for individual materials. The modulus values for tensile and bending are very similar (for tensile they are higher by approximately 10%), while the tensile strength values are approximately 40% lower than the flexural strength for individual materials.

3.2. Compressive strength

Figure 5 shows the obtained compression curves for *natural* samples, while Figures 6 and 7 show the results of compressive strength and compression modulus measurements. There are no properties of the compression test in the manufacturer's specification. Analysing the measured values, it can be seen that the *white* (90 MPa) samples are by far the most resistant to compression, in contrast to the *iron gray* (73 MPa) samples. We can see that the addition of any pigment not only does not reduce the value of compressive strength, but in some cases even improves it, unlike in the

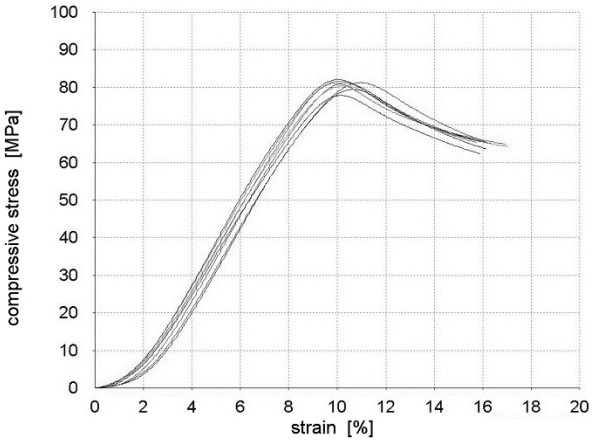


Fig. 5. Compression curves for natural samples

case of bending. The improvement is significant for the *white* material and minimal for the *red* material. This is due to the different characteristics of the test – in bending the sample is subjected to simultaneous stretching and compression, unlike the compression process itself. Another reason may be probably the highest pigment content in the *white* material, which is confirmed by the results of density tests of individual materials. Although these results were not presented graphically, it is worth adding that the measured density values were approx. 1.22±0.01 g/cm^3 for all types of materials except for *white*, whose density was determined to be 1.30 g/cm^3, and thus significantly differs from the values for PLA in other colours. Compressive strength for individual materials varies (except for *white*) in the range of 73–82 MPa. However, taking into account the *white* material, the difference between the material with the highest and the lowest strength is about 19%.

Analysing the compression modulus of tested materials, the *white* material again exhibits the highest stiffness in compression, probably due to the previously described higher density of this material compared to the other filaments, which is important in the compression test. The biggest difference is between *white* and *black* material and amounts to almost 18%. "Coloured" materials (from *green leaf* to *dark blue*) have similar modules (within the error limits), amounting to less than 800 MPa.

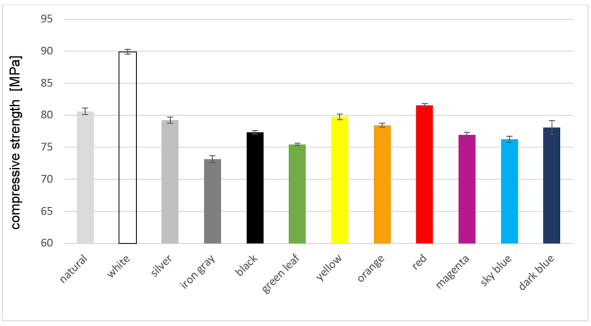


Fig. 6. Compressive strength of the tested materials

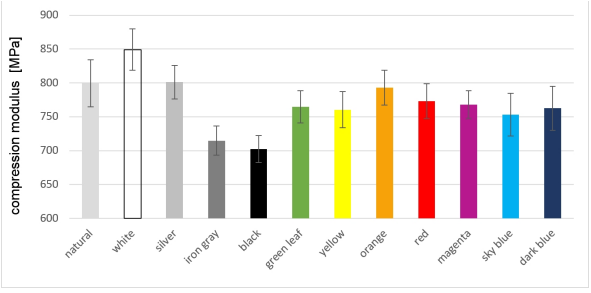


Fig. 7. Compression modulus of the tested materials

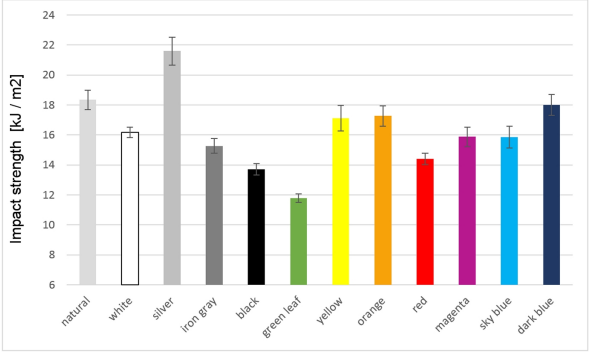


Fig. 8. Impact strength of the tested materials

3.3. Impact strength

Figure 8 shows the dependence of the unnotched Charpy impact strength as a function of the type of pigment. The impact strength value for pure PLA is approx. 18 kJ/m^2. Different effects of particular pigments can be observed in the case of impact strength, although the addition of pigment reduces impact strength in general. The *silver* material (21.6 kJ/m^2) has the highest impact strength – the improvement in impact strength compared to pure PLA is 18%. *Silver* is the only

material whose impact strength is higher than that of pure PLA (*natural*). The least resistant is *green leaf* (11.8 kJ/m^2), and for this material, the deterioration of impact strength is approximately 35% compared to *natural* material. When analysing the impact strength of all materials, the difference between *silver* and *green leaf* is in the order of 45%.

3.4. Softening temperature

Figure 9 shows the dependence of the softening temperature as a function of the type of pigment. The highest value was obtained by *natural* material (59.7°C) and *iron gray* (59.8°C) materials. The addition of any other pigment lowers the PLA's softening point. The effect of the pigment on the deterioration of heat resistance is very small, what means the order of 1°C. The exception is the *white* material, which has the lowest softening point of 56.5°C. Here, the reduction of the Vicat's temperature in relation to the *natural* material is 3.2°C (5.4%).

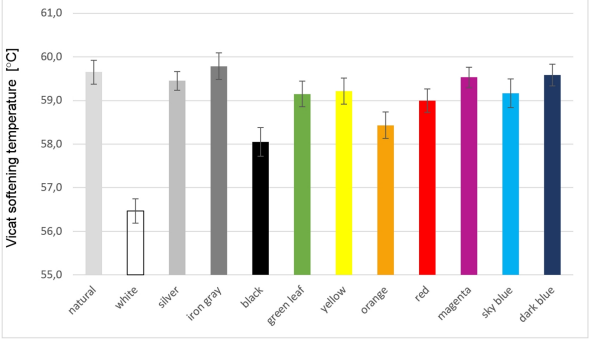


Fig. 9. Vicat softening point of the tested materials

3.5. DSC

The melting temperatures (T_m) of the samples ranged from 151.8 to 162.8°C (during the first heating) and from 149.2 to 161.3°C (during the second heating) in DSC tests carried out in this work. The glass transition temperatures (T_g) (read from the first heating) ranged from 61.8 to 66.2°C. In the case of pure PLA (*natural*), T_m during the first and second heating and T_g were, respectively: 162.5°C, 158.6°C and 63.4°C. Other PLA samples contain pigments as additives. Analysing the literature data, it can be assumed that the tested polymer samples may have a semi-crystalline structure, in which the share of D enantiomers does not exceed 12%. Melting points, not exceeding 162.8°C, exclude the possibility of the tested samples in the form of blends. They may, therefore, be PLA copolymers. However, referring to the data from Table 1, in the case of PLLA/PDLA copolymers, the glass transition temperature does not exceed 60°C, and the melting point ranges from 125 to 164°C, depending on the contents of D enantiomers. In the case of PLLA homopolymer, the glass transition temperature is 63°C, but the melting point is much higher than the T_m of the tested samples, and it reaches 178°C [31], while the range of glass transition temperatures for semi-crystalline PLLA is from 60 to 70°C, according to [32]. On the other hand, for semi-crystalline PLA, the range of glass transition temperatures is from 55 to 60°C (with a melting point range from 160 to 180°C) [33]. Taking into account the fact that most of commercial PLA are copolymers of the L and D enantiomers of lactic acid (meso-lactide) with the L-lactide content above 95% [34] and taking into account the values of the melting points of the samples tested in this work, it can be concluded that that the analysed PLA samples are semi-crystalline PDLLA copolymers with the content of D enantiomers not exceeding 10%. The shift of the glass transition temperature above 60°C can be explained by the presence of modifying additives and pigments. In the case of the α and α' polymorphs, the melting points are approximately 180 and 150°C, respectively [32], which suggests that the α' polymorphic structure prevails in the tested PLA samples.

Tables 2 and 3 summarise the basic thermal parameters obtained from the first and second heating of the samples, respectively, and the degree of crystallinity (X) calculated according to the formula (1). When one temperature peak was observed during melting, it was marked as $Tm1$. When two temperature peaks were observed during melting, they were marked as $Tm1$ and $Tm2$.

All samples had similar curves (Figure 10) during the first heating from 20°C to 200°C, in which the glass transition temperature (Tg) was distinguished, then the exothermic process of cold

Table 2. Summary of the data produced from DSC testing of first heating scan for the PLA filaments considered including heat capacity (C_p) at temperature of glass transition, glass transition temperature (T_g), cold crystallisation temperature (T_c), enthalpy of cold crystallisation (ΔH_c), melting temperature (T_m), enthalpy of melting (ΔH_m) and degree of crystallinity (X)

	I heating							
	J/(g*K) ΔCp	°C Tg	°C Tc	J/g ΔHc	°C Tm1	°C Tm2	J/g ΔHm	% X
natural	1,463	63,4	106,4	29,24	162,5	153,9	43,34	13,2
white	0,884	61,8	98,2	24,55	160,6	149,6	40,98	15,4
silver	0,930	65,2	103,1	25,91	152,8		35,95	9,5
iron gray	0,555	64,0	101,8	24,33	153,0		38,10	13,0
black	0,752	64,6	101,4	18,31	155,0	148,0	36,20	16,8
green leaf	1,622	64,6	106,0	28,63	152,5		35,25	6,2
yellow	1,461	65,5	103,4	19,98	151,8		39,67	18,5
orange	1,425	65,7	100,2	21,74	153,7		34,39	11,9
red	1,327	64,8	101,3	27,88	155,2	148,3	32,67	4,5
magenta	1,149	66,2	95,0	21,60	161,9		38,88	16,2
sky blue	0,933	66,1	96,0	28,05	162,8		38,99	10,3
dark blue	0,995	64,3	97,1	30,12	162,8		40,17	9,4

Table 3. Summary of the data produced from DSC testing of second heating scan for the PLA filaments considered including cold crystallisation temperature (T_c), enthalpy of cold crystallisation (ΔH_c), melting temperature (T_m) and enthalpy of melting (ΔH_m)

	II heating				
	°C Tc	J/g ΔHc	°C Tm1*	°C Tm2**	J/g ΔHm
natural	131,4	3,575	158,6		3,564
white	124,3	44,900	155,7	159,2	42,360
silver	126,3	15,340	152,9		16,430
iron gray	124,3	25,780	152,2		25,130
black	102,7	17,240	150,4	153,9	42,500
green leaf	126,6	14,210	152,6		13,570
yellow	105,9	20,850	149,2		38,360
orange	122,2	33,090	152,1		28,490
red	127,7	13,560	153,8		13,140
magenta	116,5	12,110	159,4		7,293
sky blue	113,1	47,870	155,2	161,3	46,310
dark blue	118,4	52,560	155,5	160,9	45,020

crystallisation and the endothermic melting process were observed (Figure 11). Two temperature peaks were observed during melting for the *natural*, *white*, *black* and *red* samples (Table 2).

The first heating process reveals thermal effects related to the thermal history of the sample, such as sample preparation (thermal and mechanical impacts related to the production of the sample – the production of filaments and the 3D printing process in this case), aging or annealing the sample. In the case of samples that are 3D-printed products, their properties may be affected by the temperature of the nozzle (235°C in this case) as well as the storage conditions of the samples. It should also be noted that during the printing process, the temperature of the platform was 60°C, and the printing process itself is time-consuming. Therefore, 3D printed PLA products can be treated as partially aged/annealed, because during their production they are subjected to ambient temperature,

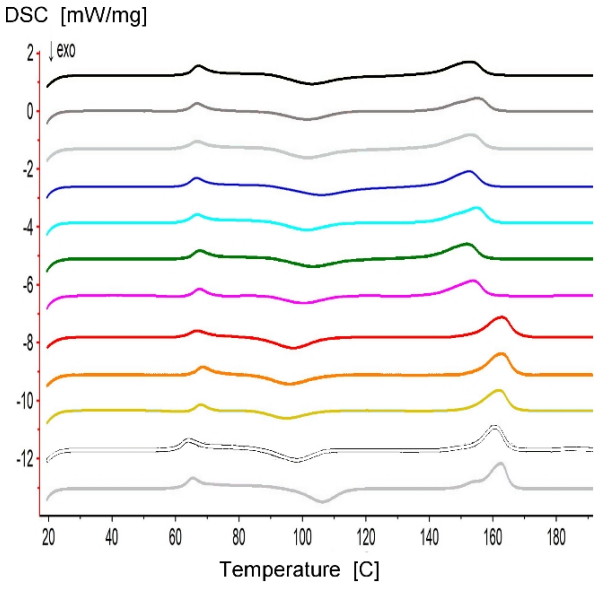


Fig. 10. The course of the DSC curves for the tested materials for the first heating (respectively from the bottom: *natural, white, yellow, orange, red, magenta, green leaf, sky blue, dark blue, silver, iron gray, black*)

close to the range of glass transition temperatures of the tested samples. During this time, further spatial ordering of polymer chains may occur (system with lower energy, more thermodynamically stable), and thus an increase in the proportion of crystal structures. The presence of double temperature peaks during PLA melting was explained in the work [35], where the following theories were presented:

I. the lamellar thickness model – the double thermal peak in the endothermic transformation is associated with the presence of two types of lamellae of different thickness. Thinner lamellae have a lower melting point, and thicker ones – a higher one;

II. melting recrystallisation model – during lamella melting, part of the melted crystalline fraction is recrystallised to a more ordered structure with a higher melting point than the melting point of the crystalline fraction that melted earlier; and

III. a new model proposed by [35] suggesting the simultaneous occurrence of two processes of melting and crystallisation – this model assumes the existence of three crystal structures, where during the melting of the crystal part, recrystallisation occurs to a new, more ordered form, which also melts and recrystallises.

The difference between the total enthalpy of endothermic melting and exothermic cold crystallisation processes is the confirmation of the last model assuming the existence of three crystal structures. The presence of the β form (with a melting point lower by 10°C compared to the α form, that is, approximately 170°C) can be expected, in addition to the α and α' forms. α' crystal structures nucleate at temperatures below 100°C. Both α and α' polymorphic forms nucleate in the range between 100 and 120°C. Only the α form crystallises above 120°C. Polymorphic transition from the α' to α structure takes place at a temperature of approximately 115°C [36].

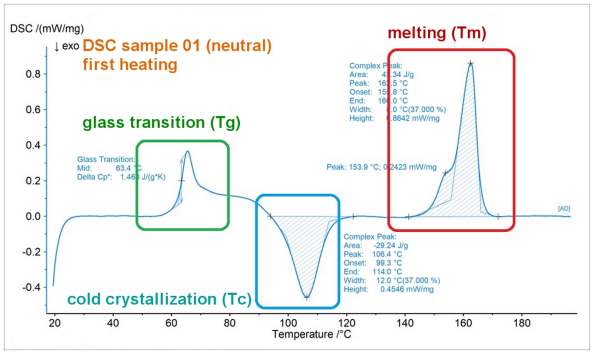


Fig. 11. DSC curve of the first heating at a constant rate of 10 K/min for the natural sample – two temperature peaks can be observed appearing in the melting area

3.6. Correlations

In order to analyse the obtained results in terms of possible correlations between the results obtained from DSC measurements and the mechanical and thermal properties of the tested materials, the linear correlation coefficients R were determined. The coefficients of determination R^2 are

Table 4. Table of R^2 coefficients between the parameters determined in the DSC study

	X [%]	*Tg*	*Tc (I)*	*Tc (II)*	*Tm1 (I)*	*Tm1 (II)*	*Cp*	*Hc (I)*	*Hm (I)*	*Hc (II)*	*Hm (II)*
X [%]	1,00										
Tg	0,00	1,00									
Tc (I)	0,03	0,06	1,00								
Tc (II)	**0,36**	0,16	0,11	1,00							
Tm1 (I)	0,01	0,03	**0,33**	0,00	1,00						
Tm1 (II)	0,00	0,02	0,14	0,19	**0,71**	1,00					
Cp	0,06	0,04	0,19	0,06	0,02	0,00	1,00				
Hc (I)	**0,57**	0,06	0,01	**0,45**	0,16	0,21	0,03	1,00			
Hm (I)	0,28	0,17	0,01	0,00	**0,41**	0,25	0,01	0,02	1,00		
Hc (II)	0,00	0,02	**0,41**	0,04	0,14	0,00	0,15	0,03	0,04	1,00	
Hm (II)	0,08	0,01	0,19	**0,41**	0,01	0,16	0,20	0,05	0,02	**0,66**	1,00

Table 5. Table of R^2 coefficients between the parameters determined in the DSC test and the mechanical properties of the tested materials

	bending modulus [MPa]	*flexural strength [MPa]*	*compress. modulus [MPa]*	*compress. strength [MPa]*	*impact strength [kJ/m2]*	*Vicat softening temp. [C]*
X [%]	**0,20**	0,01	0,01	0,02	0,02	0,07
Tg	0,15	0,04	0,16	**0,38**	0,00	**0,27**
Tc (I)	0,08	0,01	0,00	0,00	0,00	0,04
Tc (II)	0,03	0,00	0,30	0,04	0,03	0,02
Tm1 (I)	0,01	0,08	0,07	0,06	0,02	0,00
Tm1 (II)	0,09	0,04	0,17	0,04	0,03	0,02
Cp	0,00	0,17	0,11	0,01	0,01	0,02
Hc (I)	0,10	0,03	0,08	0,00	0,01	0,11
Hm (I)	0,07	0,14	0,06	0,07	0,11	0,00
Hc (II)	0,00	0,00	0,01	0,03	0,01	0,11
Hm (II)	0,11	0,01	0,03	0,02	0,00	0,20

presented in Tables 4 and 5. Coefficients (I) and (II) indicate the heating number.

Observation of the results presented in Table 4 does not generally indicate any correlation between the degree of crystallinity X and other thermal parameters, with the exception of two negative correlations related to crystallisation parameters: the correlation R between X and Tc (II) is -0.60, and between X and Hc(I) is -0.75.

The analysis of the correlation of mechanical test results with the degree of crystallinity of the material also did not bring any effects, except for a small positive correlation between X and the bending modulus (R = 0.45). It seems that none of the determined parameters (strength, impact strength and softening point) is in any way positively correlated with the degree of crystallinity of the tested PLA systems. This result confirms the observations contained in the work [4], which also did not indicate any significant correlations in these studies. However, other correlations can be observed. There is a negative correlation between Tg and compressive strength (R= -0.62). It is difficult to clearly indicate the reasons for this correlation at this moment.

It is worth noting that only Pearson's linear correlation coefficients were measured. Therefore, it is not possible to exclude the occurrence of nonlinear correlations between the examined parameters, although linear correlation was the most expected here.

Table 6. Determined w_{ma} and w_{ra} parameters for the tested materials

	Δc_p [J/gK]	X -	w_{ma} -	w_{ra} -
natural	1,463	0,13	0,73	0,14
white	0,884	0,16	0,44	0,40
silver	0,930	0,09	0,47	0,44
iron gray	0,555	0,13	0,28	0,59
black	0,752	0,16	0,38	0,46
green leaf	1,622	0,06	0,81	0,13
yellow	1,461	0,19	0,73	0,08
orange	1,425	0,12	0,71	0,17
red	1,327	0,05	0,66	0,29
magenta	1,149	0,17	0,57	0,26
sky blue	0,933	0,10	0,47	0,43
dark blue	0,995	0,09	0,50	0,41

3.7. PLA Structure

Thermal history is an important factor influencing the mechanical properties of polymers [24]. It includes sample aging [32], heating and cooling rates and sample processing [37]. An amorphous layer (interphase) can be distinguished in the semi-crystalline structure of the polymer, directly adjacent to the crystalline structures. This layer is called rigid amorphous (RA), in contrast to the layer not directly adjacent to the crystal structures (mobile amorphous, [MA]). The RA layer partially crosses the crystalline-amorphous boundary, affecting the modulus of elasticity, which is similar to the modulus of the crystalline part. The RA layer is also strongly dependent on the crystallisation temperature (Tc). As the value of Tc increases, the amount of RA fraction decreases. The thermal effects observed near the Tg concern the MA fraction. Thermal effects are observed well above the Tg [30] in the case of the RA fraction, which is significantly limited in terms of mobility. Formulas (2–4) were used to determine the share of the RA fraction [32]. However, it should be taken into account that they do not include the enthalpy values during the sample cooling process (when the formation of the RA fraction is induced at temperatures above Tg), and therefore they do not take into account the entire possible thermal history of the sample.

$$w_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \tag{2}$$

$$w_{ma} = \frac{\Delta c_p}{\Delta c_{p,a}} \tag{3}$$

$$w_{ra} = 1 - w_c - w_{ma} \tag{4}$$

where:
ΔH_m – melting enthalpy of the sample, [J/g]
ΔH_c – cold crystallisation enthalpy, [J/g]
ΔH_m^0 – melting enthalpy of a sample with 100% crystallinity, [J/g]
Δc_p – specific heat capacity increase in Tg, [J/gK]
$\Delta c_{p,a}$ – specific increase in heat capacity in Tg of a 100% amorphous sample, [J/gK]
w_c – weight fraction of the crystalline part (X)
w_{ma} – weight fraction of the MA fraction
w_{ra} – weight fraction of the RA fraction
w_{ma} and w_{ra} parameters determined for the tested materials are presented in Table 6. In order to determine them, the following values ΔH_m^0 and $\Delta c_{p,a}$ were adopted in this work:

- $\Delta c_{p,a}$ = 2.00 [J/gK] as the average value in the range of Tg = 62-66°C [32];
- ΔH_m^0 = 107 [J/g] corresponding to the α' polymorph of PLA [32].

The exothermic crystallisation peak was observed during the cooling stage from 200°C to 50°C only for the *black* and *yellow* samples (Figure 12). The other materials did not show changes in this area in the form of characteristic exothermic effects (such as the *natural* sample in Figure 12). The enthalpy values of the temperature

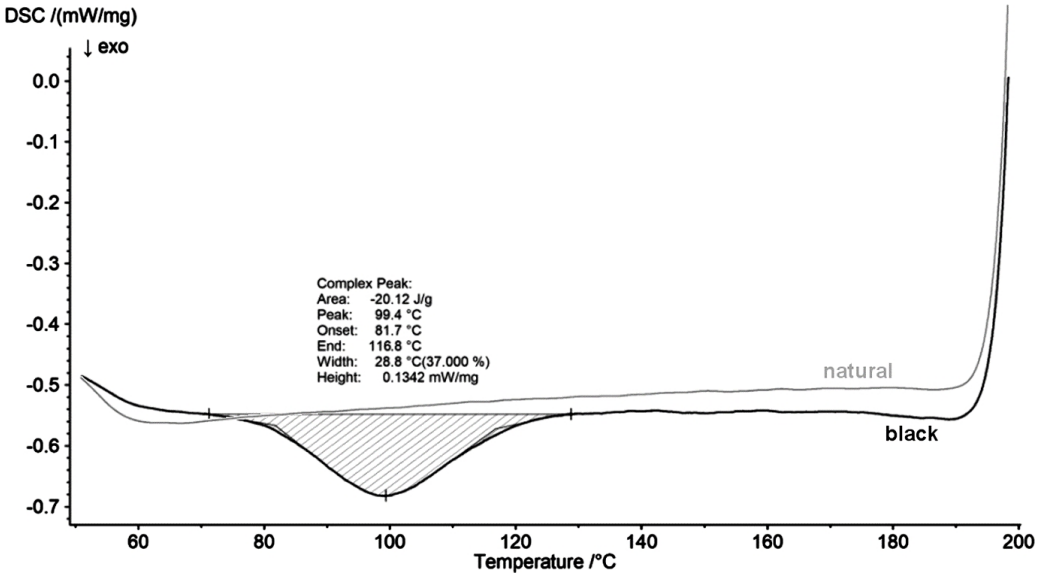


Fig. 12. DSC curve of cooling at a constant rate of 10 K/min for black and *natural* samples; in the case of *black*, one can observe an exothermic peak characteristic of the crystallisation process

peak during cooling for the *black* and *yellow* materials were 20.12 J/g (99.4°C) and 10.66 J/g (96.8°C), respectively. These temperatures significantly exceed the glass transition temperatures (64.6°C and 65.5°C for *black* and *yellow* samples, respectively), but are much lower than melting temperatures observed during the first heating (for *black* sample: T_{m1}=155°C and T_{m2}=148°C, for *yellow* sample: T_{m1}=151.8°C). These effects may be related to the previously discussed RA fraction. These samples show the highest proportion of the crystalline phase among all the tested samples (*black*: 16.8%, *yellow*: 18.5%). Therefore, a large share of RA interphase bordering between crystalline and amorphous structures (MA fraction) can be expected. Furthermore, the lowest temperatures for the cold crystallisation process were observed for both samples during the second heating process (from 50°C to 200°C) amounting to 102.7°C (*black*) and 105.9°C (*yellow*). The temperatures of the cold crystallisation process observed during the second heating oscillated from 113.1°C (*sky blue*) to 131.4°C (*natural*) for the remaining samples without a clear relationship between the observed temperature and the degree of crystallinity. Comparing the values of cold crystallisation temperature from the first and second heating process it can be observed that the highest values of these temperatures are characteristic for the *natural* material (respectively, 106.4°C for the first heating and 131.4°C for the second heating). Reducing the cold crystallisation temperatures in the case of samples with pigments may mean the nucleation of crystal structures at lower temperatures, and thus the acceleration of the processes related to the further ordering of polymer chains and the relaxation of sample stresses.

4. Conclusions

The paper presents the analysis of the influence of the type of pigment in multi-coloured PLA filaments from one supplier on their selected mechanical properties (bending strength, impact strength) and thermal properties (softening point). The results of mechanical tests showed that PLA *natural* (bending), *white* (compression) and *silver* (impact strength) have the highest strength parameters. *Iron gray, natural, dark blue* and *magenta* have the highest heat resistance, although the differences in relation to other materials are very small.

Although the structural tests performed (DSC) did not directly explain the changes in the mechanical and thermal properties of the tested materials

as a function of the type of pigment, the influence of the type of pigment on these properties is indisputable. Differences in mechanical properties between individual materials are very large: the range of results for bending and compressive strength is approximately 20% and impact strength – approximately 45%. Differences in the softening point are in the order of 5%. Such large differences in the properties of PLA filaments indicate that the selection of the wrong material may result in damage to the element during operation, which should be carefully analysed by designers. Although the difference in the degree of crystallinity of the *yellow* and *red* material is fourfold (18.5% vs. 4.5%), the tests showed that the degree of crystallinity *X* was not a significant factor in terms of material properties, what was initially expected.

The test results show that the choice of material in the right colour affects the performance of the product with the desired mechanical and thermal properties. In order to correlate the results of these tests with structural properties, DSC test was performed. The analysis of DSC test results (analysis of R^2 coefficients) showed no significant correlations between the structure (degree of crystallinity), physical properties of materials (such as melting point or enthalpy of melting) and the functional (mechanical) properties of materials. The correlation coefficients were either zero or very small. However, the differences in the mechanical properties of different coloured PLA filaments are so large (20% or even 50%) that these values must be taken into account as one of the critical parameters in the AM datasets. Only then can AM techniques be effectively used.

This article was created in cooperation between Wrocław University of Science and Technology and Częstochowa University of Technology

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Received 2023-03-22
Accepted 2023-06-25