

Application of spectrophotometric methods for the determination of spectral features and color differences to qualify and quantify the color of ABS polymers

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Received November 20, 2022

UDC 677.017.55.535.66:678.7

Original scientific paper

In order to contribute to research focused on objectifying color in 3D printing and monitoring the influence of 3D printing parameters on the subjective and objective color parameters, this paper a research of the influence of 3D printing resolution and layer thickness on color values of ABS filament samples. The process of 3D modeling of test objects based on Johannes Itten's color circle model in the Rhinoceros computer program was carried out as well as the printing of test objects from colored ABS filaments. Three different printing speeds, resulting in three different printing resolution have been tested. The steps for manufacturing a 3D FDM objects are explained in details, in the experimental part, with the definition of the adjustable and constant print parameters. After the production the colors of the 3D objects were objectively analysed based on spectrophotometric measurement and the analyses of spectral (remission) and colouristic parameters. The results confirm that in order to achieve the best possible 3D printing results, it is necessary to analyze the effects of individual printing parameters on the overall performance of the finished 3D object, including color, using appropriate test methods. In this paper, the color values of the 3D printed samples from the original ABS polymer are examined. Based on the tests performed, the influence of the surface structure of the test objects on the visual and objective properties of the colors is confirmed.

Key words: additive manufacturing; 3D printing; ABS filament; print resolution; printing speed; color objectification

Izvorni znanstveni rad

U svrhu doprinosa istraživanju objektivizaciji boje u 3D ispisu i praćenju utjecaja parametara 3D ispisa na subjektivne i objektivne parametre boje, u ovom radu analiziran je utjecaj rezolucije 3D ispisa i debljine sloja na vrijednosti boje uzoraka ABS filamenta. Proveden je proces 3D modeliranja ispitnih objekata prema modelu kruga boja Johanna Ittena u računalnom programu Rhinoceros te ispis objekata od ABS filamenta u boji. Ispitane su tri različite brzine ispisa, što je rezultiralo s tri različite rezolucije ispisa. U eksperimentalnom dijelu detaljno su objašnjeni koraci za izradu 3D FDM objekata, uz definiranje promjenjivih i konstantnih parametara ispisa. Nakon izrade, boje 3D objekata objektivno su analizirane na temelju spektrofotometrijskog mjerenja te analize spektralnih (remisijskih) i kolorističkih parametara. Rezultati potvrđuju da je za postizanje najboljih mogućih rezultata 3D ispisa potrebno analizirati učinke pojedinih parametara ispisa na ukupnu izradu gotovog 3D objekta, uključujući boju, korištenjem odgovarajućih ispitnih metoda. U ovom radu ispitane su vrijednosti boja 3D ispisanih uzoraka iz ABS polimera. Na temelju provedenih ispitivanja potvrđen je utjecaj površinske strukture ispitnih objekata na vizualne i objektivne karakteristike boja.

Ključne riječi: aditivna proizvodnja; akrilonitril/butadien/stiren; 3D ispis; rezolucija ispisa; brzina 3D ispisa; objektivizacija boje

1. Introduction

In additive manufacturing (AM), 3D objects are produced directly from three-dimensional model data by applying polymer material layer by layer. Additive manufacturing is finding more and more applications every day in various areas of industry, but also in art and culture, and there is almost no area where AM is not present (medical applications, automotive industry or a wide range of consumer products). Additive processes belong to the advanced production technologies, the so-called Key Enabling Technologies (KET), and have been developed and applied since the second half of the 1980s [1, 2]. AM has multiple advantages such as flexibility with complex geometries, high production efficiency, resource conservation and environmental friendliness, and therefore plays an important role in Industry 4.0 and has the potential to revolutionize the industry [3, 4]. Among the many AM technologies, fused deposition modeling; (FDM) is the most widely used today. The principle of this technology is that a thermoplastic filament is extruded from a heated nozzle and applied layer by layer to form the component. [5, 6]. The most commonly used materials are acrylonitrile/butadiene/styrene (ABS) and polylactic acid (PLA). Due to its good specific properties, such as mechanical properties, chemical resistance, fine surface treatment and a good possibility of further processing, ABS is increasingly used in various industries. One of the main obstacles to the introduction of FDM into functional components is the lack of standards for manufacturing and testing the materials [2, 5]. For this reason, scientists and industry researchers are investing significant efforts in researching and determining the influence of certain 3D printing parameters on the overall properties of a 3D printed product, and it is certainly one of the properties that significantly influences the development of low-budget devices and cheaper materials to bring additive processes closer to any individual who wants to explore the possibilities of these technologies [7, 8].

However, despite the technical progress of AM technology, there are still a number of problems related to the reliability and variability of the objects produced [9]. All AM techniques generally lead to anisotropy in the microstructure and mechanical properties of the printed parts. This is primarily due to the influence of heat during the deposition process as well as the structure of the diffuse polymer chain. Recent research in this area focuses on the effects of printing parameters on the mechanical properties of printed polymer materials, i.e. layer thickness, extrusion temperature, printing orientation, printing

plate temperature, speed, which directly affects printing time and quality, and sample infill [9-11]. Agnusdei and Del Prete [12] conduct a comprehensive study of the development and evolutionary trends of research directions in this field, focusing on the context of AM technology sustainability. To this end, they conduct bibliometric, online and meta-analyses of the literature. Based on their research, they identify three different clusters in terms of technologies and materials, additive manufacturing for sustainability and additive manufacturing for design [12]. Carutasu, N. L. et al [13] conduct an experimental analysis of the mechanical (tensile and compressive stress) and elastic properties of ABS samples (samples printed by deposition of acrylonitrile/butadiene/styrene filaments), as they identify a certain research gap in this area. They conclude that ABS thermoplastics are stable to environmental influences and show no significant flexing, shrinkage or moisture absorption, and that precise parts are obtained that do not change under environmental influences or over time. They confirm the very low influence of the direction of deposition (horizontal or vertical) and the density of the infill on the elastic and mechanical properties [13]. Kumar and Singh [14] investigate the possibility of blending the polymers most used in AM technology (ABS, PLA and high impact polystyrene - HIPS). They investigated the thermal and mechanical properties of 3D printed (3DP) multicomponents and find that the strain and strength properties of 3DP can be controlled by multi-material printing at predicted input processing settings. It was found that the elongation at break of the multi-component material was lower compared to the single-component ABS or PLA material, and that the breaking load and breaking strength were higher than the single-component HIPS material. 3D printing of multi-component material yielded higher flexural strength than single-component HIPS material, but lower than PLA and ABS. Multi-component printing also resulted in lower thermal conductivity than the HIPS material, which is further confirmation of its usefulness [14]. Markiz, Horvath and Ficzer [15] investigated the mechanical properties of ABS samples, concentrating on the influence of the printing direction. Based on the results of the tensile tests, it was found that the samples printed in the 0° printing direction are for 44.7% higher than those printed in the 90° direction. Furthermore, the printing direction has no influence on the modulus of elasticity. The results obtained show that they are consistent with all research in this area, i.e. all studies have shown that the mechanical properties of 3D-printed polymer samples are stronger at 0° than at 90° [15].

Today, any concept of communication with potential consumers of certain products, services or spaces is no longer conceivable without the built-in concept of aesthetics. Aesthetics is an important dimension of the overall quality of products that contributes to increasing business and market success and business excellence. It is therefore highly important that the aesthetic component of the product is fulfilled in addition to the functional and mechanical properties. An essential part of the concept of aesthetics is color as an inevitable parameter of quality, functional and aesthetic properties and the result of the product for the consumer. Color as a dominant stimulus of visual perception is a powerful means of communication and as such an indispensable quality parameter of any product.

Gao et al [1] conduct a study on the influence of the color of ABS and PLA samples on the differences in mechanical behavior (tensile, compressive and flexural strength), since colored filaments are made by mixing natural filament and color additives. The analysis of the test results shows that the color of the material plays an important role in the performance of FDM products. Different colors of filaments affected the properties of the samples to varying degrees. Samples made from the same material but in different colors showed a maximum difference of 29% in mechanical properties (tensile strength) [1]. Tamasag et al [16] come to similar conclusions by investigating the influence of infill parameters, color and pigment distribution on mechanical properties and surface roughness. The results confirm that the most influential parameter on the tensile strength of the parts was the infill density, followed by the material tested, the color pigment and the percentage of coloring. For surface roughness, the infill density was the most influential parameter, followed by the percentage of coloring, the color pigment and the material [16]. Muhamad, Hanifah and Ghani [17] investigated the influence of ABS filament color and temperature on the quality of 3D printing and found that different temperatures must be set for different colors of the same filament type to obtain a product with uniform properties. They also concluded that the temperature parameter has an influence on the strength properties [17].

The fashion and lifestyle industry is, also, one of the unique spaces where Additive Manufacturing is playing transformative role. AM is used in the fashion industry to develop prototypes, innovative examples of haute couture or adaptable personalized creations [18]. The enabling of color 3D printing has opened up a whole range of applications and uses that were not the original application areas of AM processes, particularly in design and art practice, such as 3D

printing of replicas from museum collections, the creation of digitally based art-works, architectural and landscape models, cultural heritage preservation and others. The new application areas have created a need to study and research the properties or characteristics of the color of 3D printed products from the point of view of durability and color stability of the 3D printed product. To answer the question of color stability and durability of color 3D printed products, the behavior of the color during aging must be researched, considering the parameters of the material, 3D printing and the environment [19, 20]. Regardless of whether it is a personalized design, a targeted manufacturing component or a product design, the color characterization of a 3D object is an important tool for communicating color rendering. At present, 3D color printing has a great and significant impact on life and society, but there is still no precise equipment for measuring the structure of the color surface and the characteristics of 3D printed products. Currently, the CIELAB system is most used for color characterization of 3D printed products. In order to describe the color reproducibility of 3D printing and to monitor and control the color output of a 3D printer, professional precision testing equipment and software are required to achieve specific color patterns or tones [21]. Currently, research on the durability and stability of color 3D prints is focused on how to best simulate the aging or alteration of real 3D prints exposed to different environmental conditions. Color consistency and durability are of great interest to artists and designers who use AM technologies for the production of prototypes, artworks, architectural models, scenic models or urban design and require accurate, defined color effects. Color is a fundamental part of any object and the original effects are expected to remain constant over a period. The duration and stability of color depends on various factors, such as light, humidity, temperature and air contact [21]. A literature review shows that the application of 3D printing is becoming more and more extensive, which also has an impact on areas where color is one of the most important parameters for product quality and one of the most important esthetic elements. In order to contribute to research focused on objectifying color in 3D printing and monitoring the influence of 3D printing parameters on the subjective and objective parameters of the color appearance of a 3D object, this paper presents part of a broader research analyzing the influence of 3D printing processing parameters (resolution and printing speed), on color values of ABS filament samples. The process of 3D modeling of test objects based on Johannes Itten's color circle model in the Rhinoceros computer pro-gram was carried out as

well as the printing of test objects from colored ABS filaments with the determination of the color parameters of the 3D printed test objects.

2. Experimental part

In the experimental part of the research, the color parameters of 3D objects printed from ABS filament were tested. The aim was to analyze the influence of the printing layer thickness parameter on the surface structure and thus on the color values of the 3D object. An experimental system was used for the research, consisting of the computer program Rhinoceros for CAD modeling, a 3D printer MakerBot Replicator 2X and ABS filament from MakerBot for printing.

Three groups of 3D printed objects in primary and secondary colors were defined in the experimental setup phase, according to the parameters of resolution and printing speed:

- I group – print layer thickness 0.20 mm (standard printing/middle resolution)
- II group – print layer thickness 0.10 mm (slow printing/high resolution)
- III group – print layer thickness 0.30 mm (fast printing/low resolution).

The steps for manufacturing a 3D FDM object are the same as for all AM processes and consist of creating a CAD model, converting the CAD model into an STL file, transferring the STL file to the 3D printer, setting the printer parameters and manufacturing the products. The creation of the CAD model is shown in Fig.1.

Once the CAD model has been defined, the STL file is created. An STL file is a standard format that is used for data transfer when creating 3D printed objects. The STL file of the modeled 3D objects is shown in Fig.2. The 3D printing of the test objects was done with a MakerBot Replicator 2X printer using ABS MakerBot filament with a diameter of

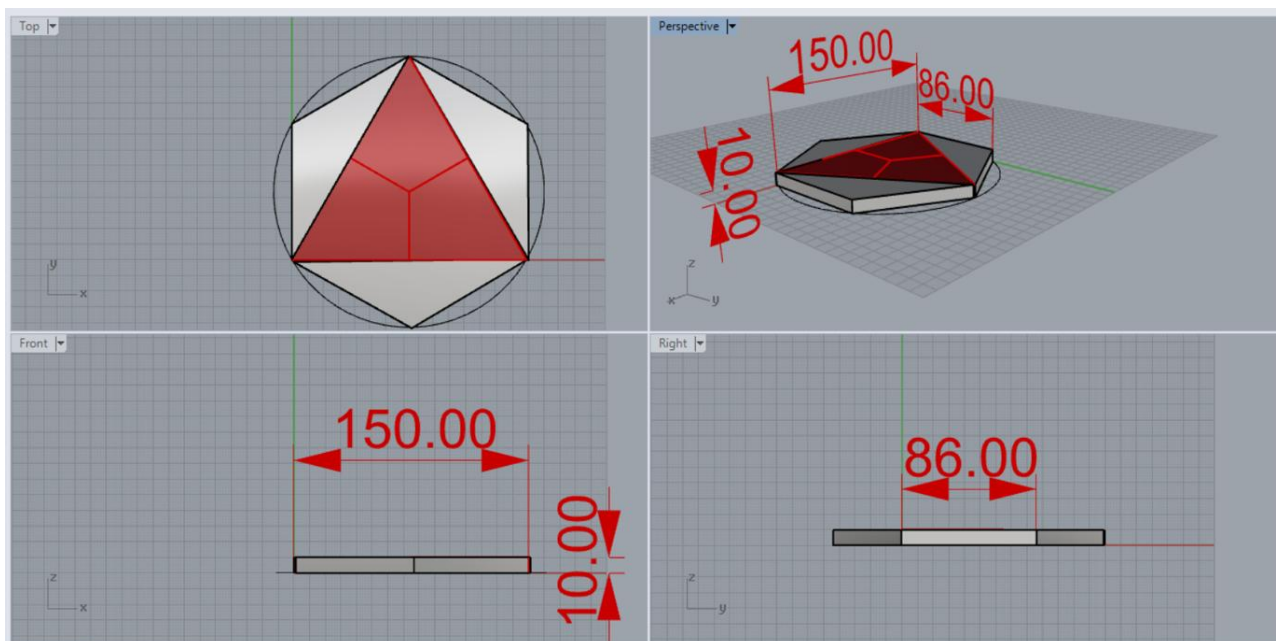


Fig.1 The creation of the CAD model of 3D objects

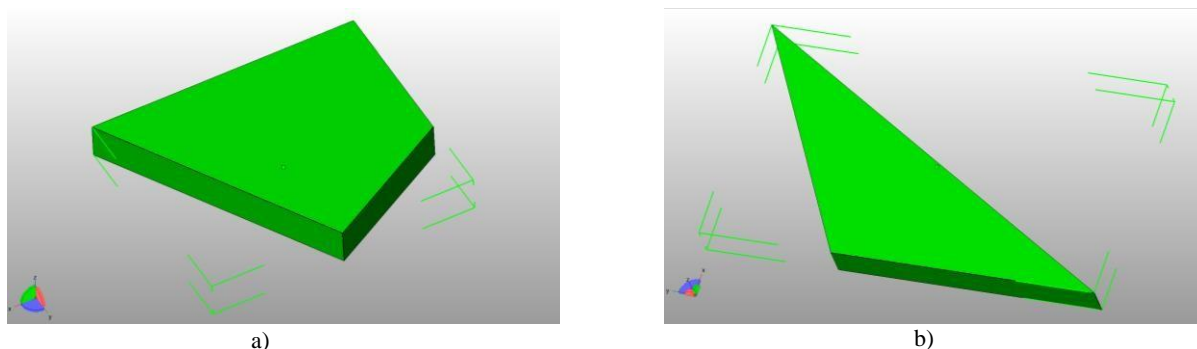


Fig.2 STL files of the test objects: a) internal rhombus, b) an equilateral triangle

1.75 mm, in the colors red, yellow, blue, orange, green and purple. The software of the printing device (MakerWare) enables certain infill patterns: linear, hexagonal pattern, Moroccan star pattern as well as cat and shark infill patterns, whereby the hexagonal or honeycomb pattern was selected for printing the test objects. The selected adjustable and constant print parameters are listed in Tab.1.

The software of the printing device (MakerWare) enables the positioning and rotation of the file along all three axes, the scaling and determination of the printing nozzle as well as the setting of the printing

parameters. During 3D printing, all test objects are always positioned in the same way on the platform of the printer (Fig.3).

For each thickness of the layer, 6 test objects were printed with primary and secondary colors; a total of 18 test objects were printed. The sample groups of the printed test specimens are shown in Fig.4.

The color measurement was carried out on the printed 3D objects using a DataColor 800 remission spectrophotometer with the measuring geometry $d/8^\circ$, standard light D65 and the size of the measuring aperture 27 mm.

Tab.1 Adjustable and constant printing parameters

	Groups of test objects		
	I	II	III
Printing speed / Resolution	Standard / Standard	Slower / High	Faster / Low
Printing parameters			
Adjustable printing parameters			
Layer thickness (mm)	0.20 mm	0.10 mm	0.30 mm
Infill density	10 %	15 %	10 %
Constant infill parameters			
Infill Pattern	hexagonal	hexagonal	hexagonal
Number of shells	3	3	3
Extrusion temperature (° C)	230	230	230
Platform temperature (° C)	110	110	110



Fig.3 Positioning of test objects on the printer base

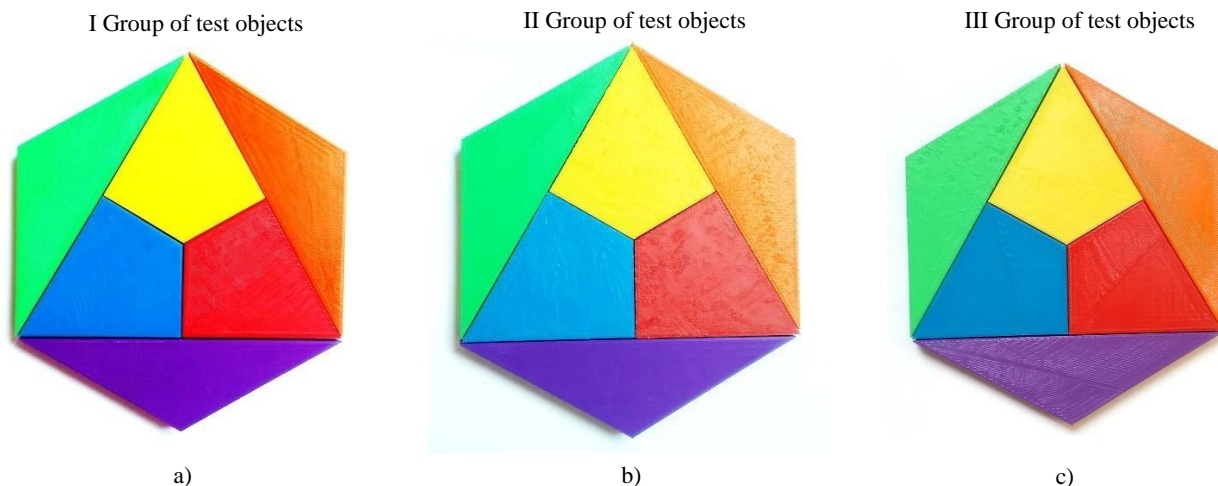


Fig.4 Printed groups of test objects: a) layer thickness 0.20 mm – standard printing/standard resolution, b) layer thickness 0.10 mm – slow printing/high resolution, c) layer thickness 0.30 mm – fast printing/low resolution

All colors were measured for each group of 3D objects. Based on the obtained spectral properties of the colors, the reflectance curves are shown (Fig.5), the positioning of the samples in the a^*/b^* color space is shown and an analysis of the color parameters of lightness (L^*), Chroma (C^*) and hue (h°) is performed. In addition, a numerical evaluation of the color differences calculated according to the CIE76 formula was carried out. The calculation of the color difference is based on the comparison of the reference sample with other samples of the same color, and for this purpose samples of group I were selected as reference (Tab.1).

The samples of groups II and III were compared with the samples of the same color of group I. The results of the color differences determined are shown in Tab.3.

4. Results and discussion

Observing the 3D objects of the three groups (Fig.4), slight differences in the properties of the same colors can be subjectively seen depending on the printing parameters of the respective object. In the production of the 3D objects in groups I, II and III, the

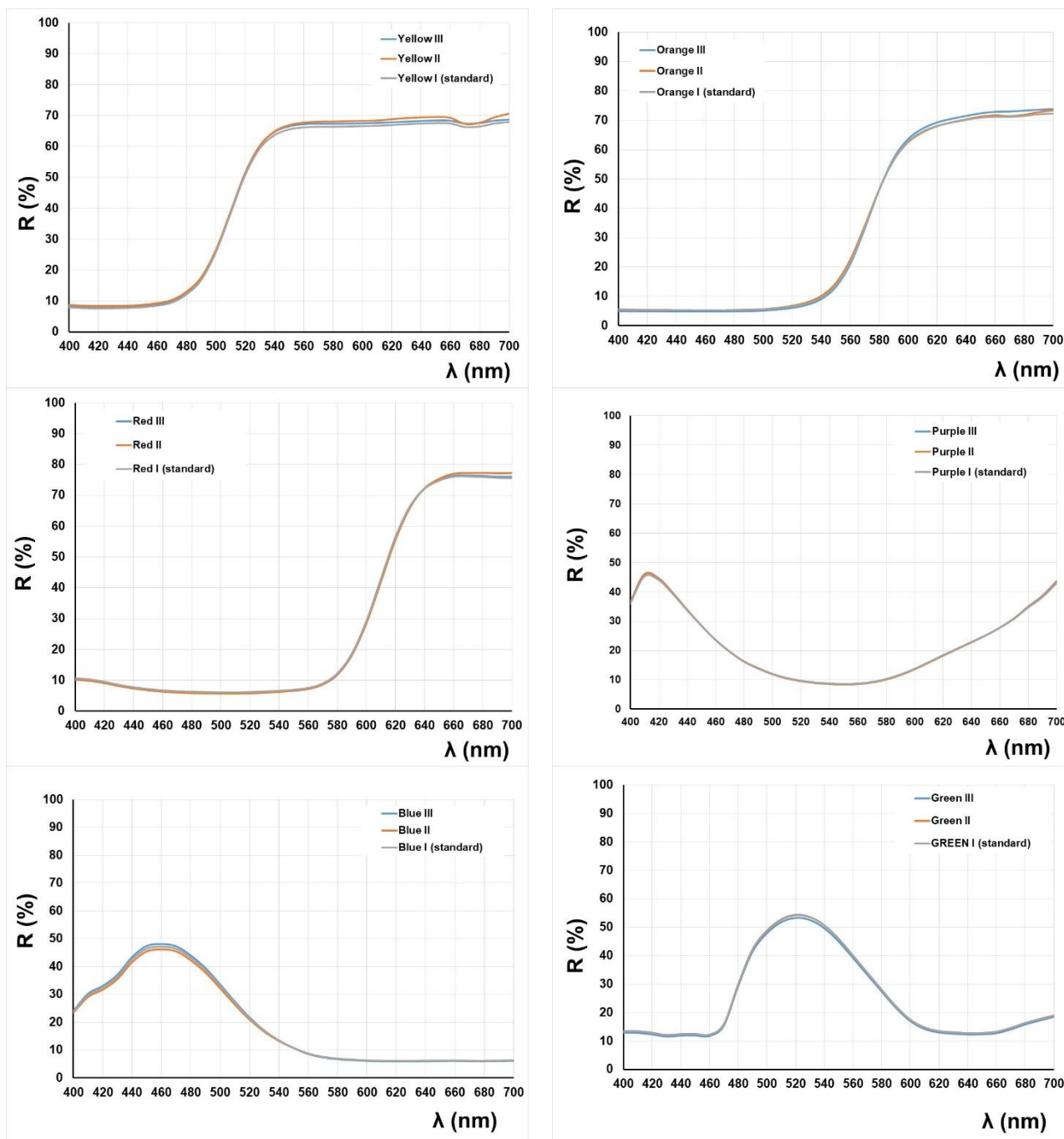


Fig.5 Reflectance curves for coloured 3D objects of three groups (I, II and III)

application of three different printing speeds resulted in three different layer thicknesses. The assumption was that the layer thickness affects the surface structure of the samples and that the expected changes in the structure further affect the differences in the modulation of the incident light, which visually changes individual color parameters. There is a different interaction between the incident light and the surfaces of the objects, which affects the ratio of reflected, absorbed and scattered light and gives the visual impression of a different color appearance. The direction of movement of the reflected light and the scattering determine whether the observed surface appears smooth and shiny or rough and matt. The phenomenon of light absorption is also very complex, and the experience of the surface properties and the color of the surface depends directly on the interaction between absorption and light scattering.

In order to objectively evaluate possible color differences and analyze the nature of these differences, the spectral color characteristics of 3D objects from three groups (Fig.4) were compared by plotting their reflectance curves (Fig.5).

The uniformity of the shape of the reflectance curves confirms that the spectral properties of the color do not change in relation to the printing speed, i.e. the layer thickness. The dominant wavelength in the reflected part of the incident light remains the same and there is no change in the color hue. Small differences in the heights of the curve are observed in samples of blue, green and violet hues. For the test objects of yellow, orange and red hues, which were also printed with a different layer thickness, i.e. with a different resolution, the differences are more pronounced, which confirms the position of the curve and indicates certain differences in the chroma and lightness of the measured colors.

Further analysis was performed by showing the location of the measured colors in a^*/b^* color coordinate space (Fig.6).

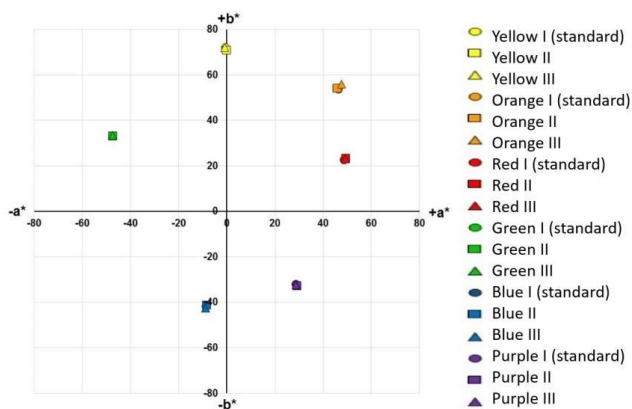


Fig.6 Placement of the measured colours in a^*/b^* color space

By positioning the color samples in the uniform a^*/b^* coordinate space, the hue and chroma parameters are spatially defined, and the relationship between the basic color parameters is monitored and a spatial comparison is performed based on the influence of the objects printing parameters. It can be said that the results of a^*/b^* coordinate values are not completely consistent with the reflectance plot. In contrast to the results obtained for the color remissions, the differences shown in small shifts in position of the same colors are somewhat more visible for the orange, blue and violet hues. Although the differences obtained by comparing the same colors for the different groups (I, II and III) are rather small, they may indicate a certain influence of the parameters of 3D object printing on the comprehensive objective and subjective properties of color.

The values of the basic color parameters (L^* , C^* , h°), (Tab.2), show small changes in the chroma parameter (C^*), which is a consequence of the influence of the surface structure on the ratio between scattering and absorption in relation to the reflectance.

Tab.2 L^* , C^* , h° values of measured colors for all 3D objects

Sample	L^*	C^*	h°
Yellow I (standard)	79.2	72.1	90.5
Yellow II	79.9	70.9	90.1
Yellow III	79.7	72.1	90.6
Orange I (standard)	58.6	71.1	49.2
Orange II	59.0	70.9	49.8
Orange III	58.7	73.5	49.6
Red I (standard)	45.7	53.9	24.9
Red II	45.2	54.5	25.2
Red III	45.3	54.4	25.2
Blue I (standard)	46.8	42.6	258.2
Blue II	46.4	42.0	258.5
Blue III	46.8	43.6	258.2
Purple I (standard)	41.5	43.0	311.7
Purple II	41.2	43.9	311.7
Purple III	41.5	43.2	311.6
Green I (standard)	66.9	57.9	145.0
Green II	66.9	57.8	145.0
Green III	66.3	58.0	144.9

The change in the surface structure does not lead to changes in the spectral composition of the reflected light, which results in uniform values of the tone parameter (h°). The lightness values (L^*) are also uniform within each group, confirming that the surface structure has no influence on the amount of light reflected from the surface. A further characterization of the differences in relation to the processing parameters of 3D printing was carried out

Tab.3 Color differences (CIE76) of compared samples for same colors, in each group

Color differences CIE 76	dL*	da*	db*	dC*	dh	dE
Yellow I (standard)						
Yellow II	0.76	0.48	-1.12	-1.12	-0.47	1.44
Yellow III	0.49	-0.05	-0.02	-0.02	0.05	0.49
Orange I (standard)						
Orange II	0.26	-0.66	0.78	0.16	1.01	1.06
Orange III	-0.12	1.31	2.57	2.8	0.68	2.88
Red I (standard)						
Red II	-0.46	0.47	0.57	0.67	0.31	0.87
Red III	-0.34	0.39	0.52	0.57	0.31	0.73
Purple I (standard)						
Purple II	-0.32	0.59	-0.68	0.9	-0.01	0.95
Purple III	-0.01	0.05	-0.24	0.21	-0.12	0.24
Blue I (standard)						
Blue II	-0.57	0.24	0.34	-0.38	0.16	0.7
Blue III	-0.17	-0.27	-1.12	1.15	-0.03	1.16
Green I (standard)						
Green II	-0.04	0.09	-0.01	-0.08	-0.04	0.1
Green III	-0.64	-0.03	0.16	0.12	-0.11	0.66

by calculating the color differences using the mathematical formula CIE76. As part of this analysis, the values of the total color difference (dE) and the differences in the individual color parameters were calculated: lightness difference (dL*), chroma difference (dC*), hue difference (dh°) and a*/b* differences (da* and db*). Deviation on the a* axis (red-green axis) is defined with da* value, and db* stands for the deviation on the b* axis (yellow-blue axis). Negative values of the differences of the a* and b* coordinates (-da*; -db*) indicate that the sample is redder or yellower than the reference (standard), while positive da* and db* values indicate that the sample is greener or bluer compared to the reference (standard).

The comparison, i.e. the determination of the color differences, was carried out in relation to the selected standard (sample I, marked as STANDARD referring to the samples of colors in Group I). The results are shown in Tab.3. The color differences confirm rather low influence of the monitored parameters of 3D object printing on the objective properties of the color. Color difference values slightly outside the agreed tolerance ranges, which for the total color difference dE is ≤ 1 , dL* ≤ 1 , dC* ≤ 0.8 and dh° ≤ 0.5 were determined for yellow, orange and blue colors. In the case of the samples mentioned, the reason for the color differences achieved, which are slightly outside the tolerance limits, lies precisely in the increased values of the chroma difference (dC*).

5. Conclusion

The results confirm that in order to achieve the best possible 3D printing results, it is necessary to analyze the effects of individual printing parameters on the overall performance of the finished 3D object, including color, using appropriate test methods. In this paper, the color values of the 3D printed samples from the original ABS polymer are examined. Based on the tests performed, the influence of the surface structure of the test objects on the visual and objective properties of the colors is confirmed. The results obtained confirm the influence of the thickness of the print layer on the appearance of the color. Color characterization is one of the key factors for comprehensive quality assurance of 3D printed products. The integration of an objective CIE system into the quality control processes is essential for the manufacture and control of products where color is an important parameter, as well as for products manufactured with 3D printing technology.

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