UV Curing Effect(s) on Colorimetric Properties of Test Specimens Created via Stereolithography

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Abstract: This paper presents the results of observing colorimetric change obtained by the impact of UV curing. The test specimens were made by stereolithographic process from photopolymer materials with the addition of cyan, magenta, and yellow dye. To better understand the impact of UV curing on colorimetric permeability properties, specimens were made in five different thicknesses (1 mm, 2 mm, 3 mm, 4 mm, and 5 mm). The UV curing time was divided into eight intervals of 15 minutes, at the end of which spectral and colorimetric values of each specimen were measured. The difference in color change was defined and shown using the CIELab color system. The conclusion of the conducted tests indicates that specimens with smaller thickness have a greater color change. The correlation between the time interval of UV radiation and the direction of color change was determined.

Keywords: color distance; color quality; stereolithography; UV curing

1 INTRODUCTION

Additive manufacturing technologies are increasingly used in areas where the visual properties of the obtained 3D prints are essential. Research on materials used in additive manufacturing technologies is mainly focused on testing mechanical properties. Prior research on materials in the stereolithographic process of additive manufacturing has studied the relationship between mechanical properties and the degree of polymerization. Studies have shown that increasing the time interval of curing with UV radiation changes the material's mechanical properties. Y. Yang et al. (2019) investigated the influence of UV radiation on the tensile strength and hardness of test specimens. Materials with longer intervals of UV curing by UV radiation change the mechanical properties to increase their tensile strength and hardness to a certain extent. After a longer UV curing interval (16 hours), the tensile strength and hardness decrease. Based on these findings, a mathematical model was developed to predict the mechanical properties of the material. In addition, Y. Yang et al. (2019) investigated the anisotropy of the material, and the orientation of the model during additive production has a significant influence on the mechanical properties of the material [1]. In their study, Puebla et al. (2012) presented the influence of model orientation on mechanical properties and material aging degradation on photopolymer resins [2]. Statistical analysis of DOE proved that the materials are not isotropic. The mechanical characteristics of the test specimens differed depending on the orientation in regards to the model on the building platform of the additive production device. Puebla et al. investigated the effects of accelerated aging of the material on the mechanical properties of test specimens. Application of accelerated aging over 50 days does not show a significant difference in the material properties. In their work by DSC analysis, Mansour et al. (2007) showed the influence the degree of polymerization has on mechanical properties of the material when exposed to accelerated aging. [3].

Due to rapid developments in the additive production industry and the spread of its agency to new applications, the standards do not cover all areas of additive production [4], [5]. There are currently no standards and guidelines for the visual or colorimetric properties of materials. The color of the obtained 3D prints is an essential element in their user's experiences, and the stability and durability of 3D print's colors need to be experimentally determined. There are standard ways of defining and measuring color in the graphics industry to control and adjust reproduction [6]. A study by Stanic et al. (2012) examined the reflective colorimetric properties of 3D prints. The influence of accelerated aging on color properties, colorimetric stability, and colorfastness on a 3D impression expressed by the additive binder imprinting process on materials was investigated. After exposing specimens to accelerated aging, significant color changes expressed as a ΔE_{00} value were measured on the 3D print. Changes in brightness, chromaticity, and tone were observed. The changes vary depending on the thickness of the ink coating and the final type of 3D print processing [7, 8]. The influence of aging on the properties of color, and colorimetric stability and durability of a 3D impression made by the additive process of binder jetting materials, was investigated. Coon et al. (2016) conducted a study on the protective covering for prototypes made by additive manufacturing technologies in which experts from the field of product design and development participated. The study showed that 68% of respondents believe that a physical print is more valuable than a digital record, and 81% of respondents noticed changes in the 3D print over a more extended period of time [9]. Also, due to physical damage, material, and color degradation, 84% of respondents said they would like to replicate and create new 3D prints. M. Neumüller et al. (2014) explores the application of additive technologies in the protection of cultural heritage, where visitors are provided with a multi-sensory and especially haptic experience using 3D prints. One of the crucial aspects of multi-sensory is the color of 3D prints. The visual properties of the material, due to degradation and discoloration of the material in additive manufacturing, are an essential factor in the choice of reproduction technology, and they need to be investigated further [10, 11]. Yuan et al. (2018) describe six

procedures of additive manufacturing technologies and their colorimetric properties when outlining possibilities of making 3D color prints [12]. The paper describes the indicators for assessing the color quality of 3D prints: color measurement, color specification, and color reproduction. In addition, color stability and consistency are essential properties for 3D prints, especially when 3D prints are applied as final products (functional prototypes and museum exhibits). Current research in color in additive manufacturing technologies focuses are on using classical colorimetric methods and their application to the 3D print.

2 EXPERIMENTAL PART

The stereolithographic process of additive manufacturing was selected for the production of test specimens. Stereolithography is the oldest commercially available additive production technology [13, 14]. The 3D impression obtained by the stereolithographic process visually shares visual similarities with the characteristics of the products similar to the products obtained in classical manufacturing processes such as injection molding. It is characterized by a very smooth surface, and the development of new materials improves the material's mechanical properties. Furthermore, dimensional accuracy is very precise, which allows the production of small details. Therefore, this additive manufacturing process is well accepted in the early stages of development, development of functional prototypes, and applicable products.

Colorimetric properties of materials were investigated in the stereolithographic process of additive manufacturing. The photopolymer materials used to create the 3D impression are in a liquid state before the photopolymerization process. Such a fluid state of the photopolymer allows us to interact with colors and pigments to produce 3D color prints. The stage of 3D printing is then followed by additional processing required by the stereolithography additive manufacturing process before obtaining the final product. Firstly, the model needs to be rinsed with a liquid that will remove all unpolymerized material from the surface of the 3D print. Additional UV curing is then required to complete the polymerization process. The duration of exposure to UV radiation was divided into specific time intervals to enable tracking of the effect each period has on the mechanical and colorimetric properties of measured specimens. Because of the need for strict measurement tolerances Computer-aided design - CAD environment is used to make a 3D model of test specimens.

Test plates were made in thicknesses of 1 mm, 2 mm, 3 mm, 4 mm, and 5 mm. Formlabs photopolymer RS-F2-PKG-CR was used for the stereolithographic process, in which dyes cyan (RS-F2-CRCY-01), magenta (RS-F2-CRMA-01), and yellow (RS-F2-CRYL-01) were added. Test 3D specimens were created using Formlabs Form 2. The Formlabs Form 2 stereolithographic additive manufacturing device uses a 405nm UV laser with a power of 250 mW. All models were oriented along the Z-axis to make better use of the build platform surface. The height of the fabrication layer (Z-axis) was set to 0.1 mm. The mixing ratio of the based photopolymer and dye was defined by the ratios prescribed by the manufacturer in order not to disturb the mechanical properties of the material [2]. The scheme of experimental work is shown in the Fig. 1.
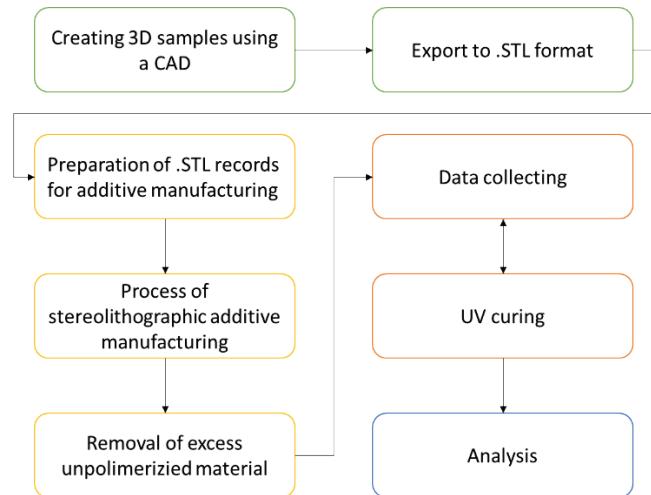

Figure 1 The scheme of experimental work is shown

After the test specimens were made by the stereolithographic additive production process, they were washed in a solvent to remove residual unpolymerized materials. Colorimetric and spectral properties of the test specimens were measured before the UV curing procedure using a spectrophotometer. The test specimens were then dried at 15-minute intervals using a UV chamber with controlled measurement conditions. After each UV curing interval, the colorimetric and spectral properties of the test specimens were measured to determine the effect of UV curing on the material. An analysis of the influence of UV radiation on the colorimetric properties of 3D prints was made based on the measured spectral and chromatic data. The difference in the color of the test specimens is shown as a ΔE_{00} value with a description of the direction of the tone change. The evaluation of the colorimetric color difference is shown in Tab. 1.

Table 1 Evaluation of colorimetric color difference

$\Delta E^* < 1$	a deviation that is not noticeable
$\Delta E^* = (1\text{-}2)$	very small difference; noticeable only to the experienced to the observer
$\Delta E^* = (2\text{-}3,5)$	mean difference; noticeable even to the inexperienced to the observer
$\Delta E^* = (3,5\text{-}5)$	great difference
$\Delta E^* > 6$	a very big difference

The total color change is shown as the value of ΔE_{00}, and the color difference equations are specified in Eqs. (1) through (4). The change in lightness between two test specimens is expressed by Eq. (1), change in chromaticity is expressed by Eq. (2), and change in hue is expressed by Eq. (3).

$$\Delta L' = L'_b - L'_s \tag{1}$$

$$\Delta C'_{ab} = C'_{ab,b} - C'_{ab,s} \tag{2}$$

$$\Delta H'_{ab} = \left[2\left(C'_{ab,b}\, C'_{ab,s} \right)^{0.5} \sin\left(\frac{\Delta h'_{ab}}{2} \right) \right] \tag{3}$$

$$\Delta E_{00} = \left[\left(\frac{\Delta L'}{k_L S_L} \right)^2 + \left(\frac{\Delta C'_{ab}}{k_C S_C} \right)^2 + \left(\frac{\Delta H'_{ab}}{k_H S_H} \right)^2 + \right.$$
$$\left. + R_T \left(\frac{\Delta C'_{ab}}{k_C S_C} \right) \left(\frac{\Delta H'_{ab}}{k_H S_H} \right) \right]^{0.5} \tag{4}$$

3 REASERSCH RESULTS WITH DISCUSSION

The research results show color change differences between the specimens before and after UV curing. Test specimens are translucent solid materials. Data represented in tables show color change through different curing intervals and CIE values of L^* a^* b^* C^* h before and after UV curing. UV curing intervals spaced by 15-minute increments.

Tabs. 2, 3, and 4 show the total color changes expressed as the ΔE_{00} value for the test specimens with cyan, magenta, and yellow dye. The tables show the color changes described as ΔE_{00} for eight UV curing intervals of 15 minutes for test specimens 1 mm, 2 mm, 3 mm, 4 mm, and 5 mm thick. Tabs. 2, 4, and 6 show that the most significant color change occurs after the first curing interval. It can be seen that the most significant total color change expressed as the value of ΔE_{00} occurs in the test specimens with cyan dye, while the smallest changes were recorded in the test specimens with magenta dye. Tab. 6 shows that the yellow dye test specimens have a uniform color change expressed as a ΔE_{00} value, regardless of the thickness of the test specimens.

Table 2 Color change through different curing intervals for cyan dye specimen tests

Cyan	ΔE_{00}				
Interval	1 mm	2 mm	3 mm	4 mm	5 mm
1	1.22	0.99	1.44	1.14	0.57
2	1.51	1.72	1.86	1.4	0.63
3	1.8	2.12	2.05	1.38	0.56
4	1.85	2.72	2.43	1.97	0.78
5	2.05	2.95	2.65	2.16	0.77
6	2.1	3.08	2.83	2.32	0.83
7	2.29	3.4	3.11	2.53	1.06
8	2.16	3.57	3.2	2.59	1.11

Table 3 Color change through different curing intervals for magenta dye specimen tests

Magenta	ΔE_{00}				
Interval	1 mm	2 mm	3 mm	4 mm	5 mm
1	0.84	0.42	0.62	0.84	0.79
2	1.01	0.59	0.59	0.94	0.82
3	1.07	0.64	0.66	0.96	0.82
4	1.09	0.75	0.63	1.07	0.84
5	1.11	0.8	0.58	0.9	0.69
6	1.19	0.85	1.64	1.06	0.86
7	1.11	0.76	0.69	1.01	0.95
8	1.21	0.9	0.79	0.88	0.85

Table 4 Color change through different curing intervals for yellow dye specimen tests

Yellow	ΔE_{00}				
Interval	1 mm	2 mm	3 mm	4 mm	5 mm
1	0.95	0.6	0.7	0.76	0.63
2	1.2	0.86	0.84	0.94	0.77
3	1.36	1.01	1.08	1.04	0.91
4	1.33	1.11	0.94	0.89	0.87
5	1.38	1.13	1.17	1.15	1.1
6	1.46	1.28	1.33	1.26	1.21
7	1.49	1.38	1.35	1.24	1.19
8	1.5	1.38	1.42	1.34	1.33

Table 5 CIE values L^* a^* b^* C^* h before and after UV curing the specimens with cyan dye

C	Values before UV curing					Values after UV curing				
	L^*	a^*	b^*	C^*	h	L^*	a^*	b^*	C^*	h
1 mm	46.2	−31.93	−43.03	53.59	233.43	45.59	−34.41	−38.86	51.9	228.47
2 mm	29.61	−23.01	−46.48	51.86	243.66	29.03	−28.63	−40.69	49.75	234.87
3 mm	19.07	−12.98	−43.04	44.95	253.22	18.59	−18.06	−38.35	42.39	244.78
4 mm	11.66	−6.59	−38.06	38.63	260.18	11.25	−10.72	−34.34	35.97	252.66
5 mm	6.31	−2.53	−32.39	32.49	265.53	6.02	−4.35	−30.15	30.47	261.79

Table 6 CIE values L^* a^* b^* C^* h before and after UV curing the specimens with magenta dye

M	Values before UV curing					Values after UV curing				
	L^*	a^*	b^*	C^*	h	L^*	a^*	b^*	C^*	h
1 mm	41.54	68.35	-6.55	68.66	354.53	40.42	66.54	−5.22	66.74	355.52
2 mm	30.15	63.92	16.94	66.12	14.85	29.32	62.85	17.93	65.36	15.92
3 mm	23.41	56.97	30.64	64.68	28.27	22.4	55.83	30.23	63.49	28.44
4 mm	18.7	51.62	30.27	59.84	30.39	17.74	50.59	28.88	58.25	29.72
5 mm	14.91	47.05	25.36	53.45	28.32	14.07	46.08	23.96	51.94	27.47

Table 7 CIE values L^* a^* b^* C^* h before and after UV curing the specimens with yellow dye

Y	Values before UV curing					Values after UV curing				
	L^*	a^*	b^*	C^*	h	L^*	a^*	b^*	C^*	h
1 mm	73.39	−5.02	93.68	93.82	93.07	71.71	−3.54	92.3	92.37	92.2
2 mm	64.57	0.74	91.98	91.98	89.54	63.39	2.47	91.24	91.27	88.45
3 mm	57.42	4.69	87.2	87.32	86.92	56.22	6.21	86.31	86.53	85.89
4 mm	50.87	7.76	80.46	80.84	84.49	49.82	9.08	79.56	80.08	83.49
5 mm	45.74	10.28	74.13	74.84	82.11	44.61	11.27	72.68	73.55	81.18

Tabs. 5, 6, and 7 show CIE L^* a^* b^* and C^* h values for test specimens in the initial green state and CIE L^* a^* b^* and C^* h values after the end of eight UV curing intervals. It can be seen that all test specimens have different colorimetric values depending on the thickness of the pieces. It is also seen

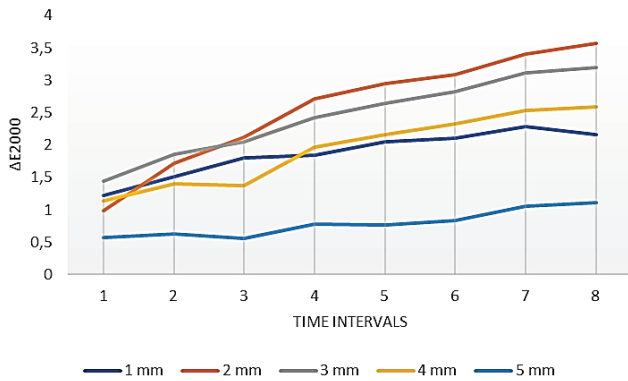that curing reduces the brightness and chromaticity of all test specimens.

Figure 2 Color change graph ΔE_{00} with respect to UV curing intervals and specimen thickness for cyan dye specimens
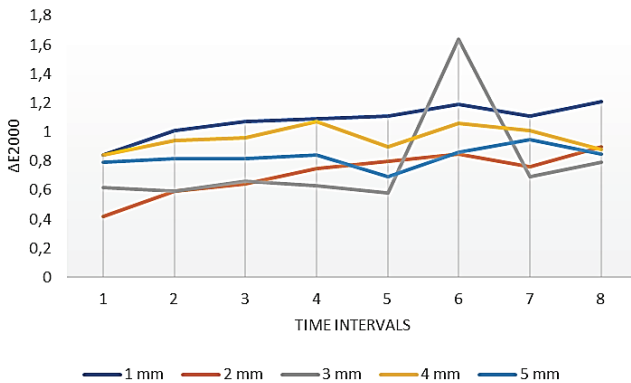

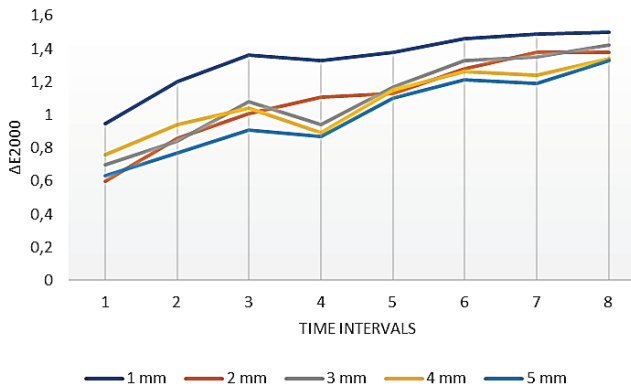**Figure 3** Color change graph ΔE_{00} with respect to UV curing intervals and specimen thickness for magenta dye specimens.

Figure 4 Color change graph ΔE_{00} with respect to UV curing intervals and specimen thickness for yellow dye specimens

Figs. 2, 3 and 4 show the measured total color changes expressed as ΔE_{00} value over eight UV curing intervals of 15 minutes. Fig. 2 shows the changes in the cyan-colored test specimens. The most significant color change is visible in the 2 mm thick test specimen, while a minor color change is seen in the 5 mm thick specimen. Test specimen 5 mm has a slightly noticeable impact of UV curing on color change than other test specimens. Fig. 3 shows the changes of the test specimens with magenta staining. The most considerable color change is visible in the 1 mm thick test specimen, while

a minor color change is seen in the 3 mm thick specimen. A peak is visible for the specimen 3 mm during the 6th drying interval, but the change is still insignificant. However, the peak value of ΔE_{00} after the sixth interval is not large enough for the changes to be noticeable to the standard observer. Therefore, the total color change after the last UV curing interval is less than 1, which according to Tab. 1, color change is not noticeable.

Fig. 4 shows the changes in the yellow test specimens. The most significant color change is again shown in the 1 mm thick test specimen, while a minor color change is seen in the 5 mm thick specimen. It is visible that all test samples have similar color changes during UV curing, except the thinnest specimen.
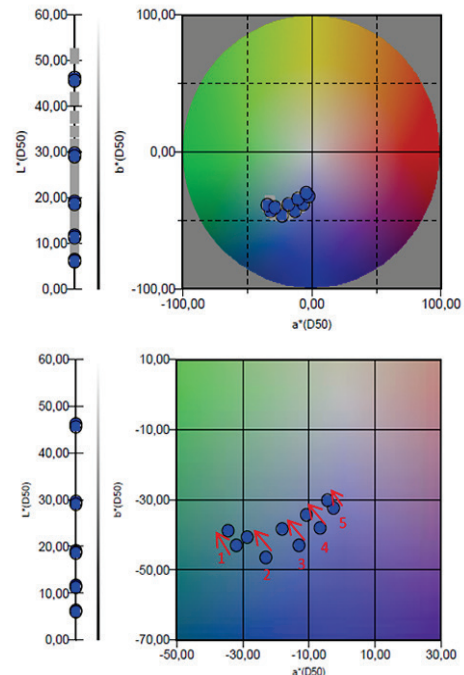

Figure 5 CIELAB colorimetric properties of cyan test specimens

Figs. 5, 6, and 7 show the chromatic values of the test specimens in the CIELAB color system. The initial values and the final values of the color change are shown, in which the direction in which the color changes after a series of curing intervals is visible. Specimens are marked with numbers from 1 to 5, and this number represents the thickness of the test specimens expressed in millimeters.

4 CONCULUSION

To achieve complete photopolymerization, the workflow of stereolithographic additive manufacturing includes the process of curing by UV radiation. During the UV curing process, the extent to which UV radiation affects the colorimetric transmission properties of the test specimens was investigated. Color changes expressed as ΔE_{00} occur in all test specimens and are most pronounced in cyan dye test specimens where ΔE_{00} is greater than 2. Color changes on cyan dye test specimens are visible to the standard observer.
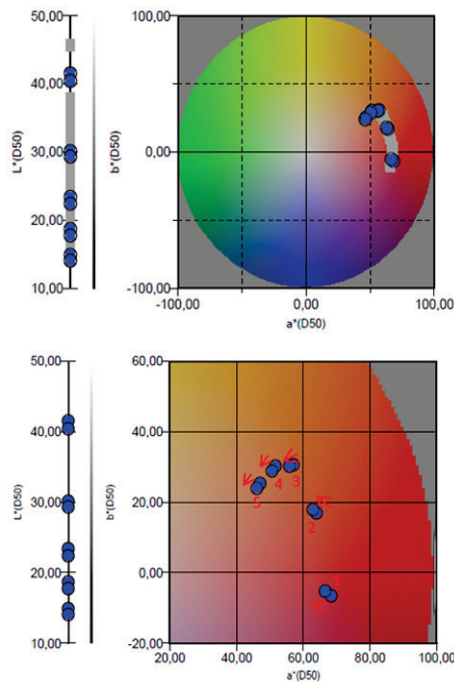
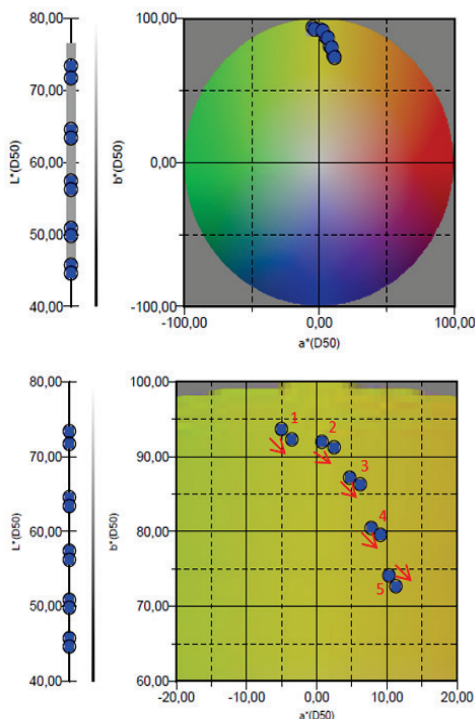**Figure 6** CIELAB colorimetric properties of magenta test specimens

Figure 7 CIELAB colorimetric properties of yellow test specimens

The change in brightness and chromaticity is most salient in the test specimens with the addition of magenta and yellow dye. However, the total color change value of ΔE_{00} is less than 2, so it is not visible to the standard observer. Measurements established a correlation between curing and the direction of color change. All test specimens show that curing reduces the brightness. In test specimens with cyan dye, thinner specimens have a more significant color change. Chromaticity decreases, and the tone changes towards the

green area. For test specimens with magenta dye, change direction is of a different shape than for test specimens with cyan and magenta dyes. The direction of change of thinner specimens is different from thicker specimens. In all specimens, the brightness and chromaticity are reduced, and the direction of the tone change cannot be determined precisely due to too small changes. For test plates with yellow dye, the total color changes expressed as ΔE_{00} are uniform for test specimens of all thicknesses. Brightness and chromaticity decrease equally, and the tone changes toward the orange area. The most significant recorded ΔE_{00} color change occurs after the first curing interval. In this paper, the influence of UV curing on the colorimetric properties of test samples is presented. In most cases, the difference in color change shown as a ΔE_{00} value was not higher than 2. Due to such a slight difference, the color change values would not be noticed. However, additional studies are needed, such as the effect of short and extended aging on colorimetric properties. With such tests, the direction of color change, colorimetric change difference could be determined more precisely.

5 REFERENCES

[1] Yang, Y., Li, L., & Zhao, J. (2019). Mechanical property modeling of photosensitive liquid resin in stereolithography additive manufacturing: Bridging degree of cure with tensile strength and hardness. *Mater. Des., 162*, 418-428. https://doi.org/10.1016/j.matdes.2018.12.009

[2] Puebla, K., Arcaute, K., Quintana, R., & Wicker, R. B. (2012). Effects of environmental conditions, aging, and build orientations on the mechanical properties of ASTM type i specimens manufactured via stereolithography. *Rapid Prototyp. J., 18*(5), 374-388. https://doi.org/10.1108/13552541211250373

[3] Mansour, S., Gilbert, M., & Hague, R. (2007). A study of the impact of short-term ageing on the mechanical properties of a stereolithography resin. *Mater. Sci. Eng. A, 447*(1-2), 277-284. https://doi.org/10.1016/j.msea.2006.10.007

[4] ASTM International. Additive Manufacturing Technology Standards. https://www.astm.org/Standards/additive-manufacturing-technology-standards.html#:~:text=Additive %20Manufacturing%20Technology%20Standards%20ASTM %27s%20Additive%20Manufacturing%20Technology,stimul ate%20research%20and%20encourage%20the%20implement ation%20of%20technology.

[5] Chua, C. K., Wong, C. H., & Yeong, W. Y. (2017). *Standards, Quality Control, and Measurement Sciences in 3D Printing and Additive Manufacturing*.

[6] Kipphan, H. (2001). *Handbook of Print Media, 13*(6). Berlin, Heidelberg: Springer Berlin Heidelberg.

[7] Stanic, M., Lozo, B., & Svetec, D. G. (2012). Colorimetric properties and stability of 3D prints. *Rapid Prototyp. J., 18*(2), 120-128. https://doi.org/10.1108/13552541211212104

[8] Chen, G., Chen, C., Yu, Z., Yin, H., He, L., & Yuan, J. (2016). Color 3D Printing: Theory, Method, and Application. *New Trends 3D Print.*. https://doi.org/10.5772/63944

[9] Coon, C., Pretzel, B., Lomax, T., & Strlič, M. (2016). Preserving rapid prototypes: A review. *Herit. Sci., 4*(1), 1-16. https://doi.org/10.1186/s40494-016-0097-y

[10] Neumüller, M., Reichinger, A., Rist, F., & Kern, C. (2014). 3D Printing for Cultural Heritage: Preservation,

Accessibility, Research and Education. In: Ioannides M., Quak E. (eds) 3D Research Challenges in Cultural Heritage. *Lecture Notes in Computer Science*, vol 8355. Springer, Berlin, Heidelberg.
https://doi.org/10.1007/978-3-662-44630-0_9

[11] Pham, D. T. & Gault, R. S. (1998). A comparison of rapid prototyping technologies. *Int. J. Mach. Tools Manuf., 38*(10-11), 1257-1287. https://doi.org/10.1016/S0890-6955(97)00137-5

[12] Yuan, J., Zhu, M., Xu, B., & Chen, G. (2018). Review on processes and color quality evaluation of color 3D printing. *Rapid Prototyp. J., 24*(2), 409-415.
https://doi.org/10.1108/RPJ-11-2016-0182

[13] Bartolo, P. J. & Gibson, I. (2014). History of Stereolithographic Processes. *Compr. Mater. Process., 10*, 19-67.
https://doi.org/10.1016/B978-0-08-096532-1.01001-3

[14] Gibson, I., Rosen, D., & Stucker, B. (2015). *Additive Manufacturing Technologies: 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing, second edition*. Springer-Verlag, New York, XXI, 498.
https://doi.org/10.1007/978-1-4939-2113-3

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