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Colorimetric evaluation of 3D printing polymers exposed to accelerated aging for Cultural Heritage applications

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Abstract
3D printing has become a widespread technology that allows the creation of physical objects from different materials. The conservation and restoration of Cultural Heritage field has recently introduced this technology as a complement to its traditional methods. However, the main concern in the application of 3D printing in this context is the long-term behavior of the materials used. The key objective of this research was the identification of the suitability of 3D printing filaments for conservation purposes. The methodology followed in this study consisted of a selection of 13 3D printing filaments for Fused Deposition Modeling (FDM) technologies, which were tested and exposed to an accelerated aging procedure. In order to classify and recommend the materials that present better results, the properties of color, the glossiness, the pH and the Volatile Organic Compounds emission were investigated. This paper collects the results of the analyses carried out, focusing discussion on the colorimetric behavior. The results demonstrate the usefulness of some of the materials studied, highlighting the performance of EP as one of the most stable and reliable materials while Flex is one of the most changeable ones in the Cultural Heritage context. Even though this research provides an overview of the aging of the materials studied, further analyses should be performed to understand the chemical composition and its behavior when exposed to a long-lasting aging process.

KEYWORDS
3D printing, accelerated aging, colorimetry, Cultural Heritage, fused deposition modeling

1 | INTRODUCTION

Technologies and materials used in 3D printing have been drastically developed in the recent decades. The accessibility to these machines and the decrease in the fabrication prices have boosted the rapid prototyping to become a new tool at the service of the conservator of Cultural Heritage.

The applicability of 3D printing in a large amount of research fields has improved the knowledge of these technologies in different subjects.[1–4] In the literature, many research papers related to the characteristics of

3D printing materials for the industry field can be easily found.[5–8]

The 3D fabrication technologies are divided into two great groups depending on the creation process.[9,10] On the one hand, subtractive fabrication machines are based on the elimination of material from a solid bulk, using abrasive tools as drills, milling machines, rasps, and so forth.[11] On the other hand, the additive manufacturing printers are based on the creation of the object with the layer by layer deposition of the melted material.[12–15]

Specifically, this study is focused on Fused Deposition Modeling (FDM) techniques, which consist of melting a 3D printing filament and extrude the material to create a 3D object layer by layer.[16] Depending on the characteristics of the 3D printer, they can be generally classified in open or closed machines and direct or indirect extruding. Normally, these technologies are affordable, easy to use and present great results, highlighting this equipment among others. As a drawback, the resolution of FDM printed parts is not usually under 0.1 mm, which means that layers can be seen at first sight. In addition, increasing the resolution results in higher production time.

However, the accessibility to FDM printers have boosted their application in the artistic creation[17] and conservation-restoration of Cultural Heritage areas.[18] In conservation, some of the main applications of printing materials concern the creation of replicas[19–21] or the restoration of missing parts.[22–26]

For all those printers, there already exist numerous 3D printing materials in the market that could be applied to the conservation and restoration of cultural assets. Particularly for FDM 3D additive manufacturing, there is a wide variety of polymer-based printing materials with different fillers, such as wood, stone or metal dust.[27,28] Currently, the development of new 3D printing materials is focused also on the sustainability, looking for recycled and greener resources.[29–32]

A priori, the chemical composition datasheets and the behavior information of the materials are unknown data for the heritage application context. Few papers deal with the characteristics and long-term performance of these materials for conservation purposes.[33,34] Aura-Castro et al.[35] recently published their research concerning the characterization of a selection of FDM 3D printing materials. Nevertheless, the study of historical plastics and other polymer-based materials commonly used in the Cultural Heritage field is a regular practice.[36] For all this, it is necessary to analyze the behavior, the long-term aging and the compatibility of those materials in order to guarantee the harmlessness and the respect of the original materials.

One of the most important aspects regarding the conservation field is the evolution of the materials added during the intervention of any cultural object. Because of this, accelerated aging is one of the main techniques to assess the changes produced in a specific material when exposed to different ambient conditions.[37,38] This way, color and glossiness are optical properties that may determine the selection of a certain material for cultural heritage, as these alterations indicate other chemical degradation taking place in the material. Likewise, from a durability point of view, a material with low color modification may be more suitable for restoration or artistic creation purposes.

2 | MATERIALS AND METHODOLOGY

For this study, a total of 13 different 3D printing materials based on a wide range of polymer matrices and fabricated with FDM technologies were selected. All the FDM filaments were shaped in two $7 \times 7 \times 0.5$ cm sheets. This sample design proved suitable for the analysis techniques proposed in this research.

In particular, the samples were provided by SmartMaterials 3D[39] in the form designed for this study. In Table 1, the printing parameters used for this step are detailed. Furthermore, the layer height was set in 0.2 mm and the infill reached the 100% for all the materials.

In order to evaluate some properties of the selected materials, the analysis techniques were performed before and after the exposure to the specific combination of aging conditions (radiance, temperature and relative humidity). The characteristics measured were the color, the brightness, the pH and the emission of volatile organic compounds (VOCs).

All the samples were exposed to an accelerated aging procedure in a Xenon-Arc Solarbox 3000 e RH equipment with a window glass filter (ASTM D4459 and UNE-EN ISO 4892). The ambient conditions selected were a total of 300 h of continuous exposition with 50% relative humidity, a temperature of 40°C and 550 w/m^2 of irradiance.

Regarding the conservation of the 3D printing material joined to the original cultural asset, one of the main concerns was the degradation products that might migrate to the original material and accelerate any degradation reaction. Because of this, the study of the 3D printing filaments aimed to identify whether any compound may change the pH or remain present in the air conditions. The determination of the presence of VOCs was also crucial considering the objective of applicability of these materials in the cultural heritage field. Storage and restoration may be the main applications of these filaments so the original asset may share space

TABLE 1 3D printing parameters of filament samples.

Material	Color	3D printer	Extrusion temperature (°C)	Bed temperature (°C)	Printing speed (mm/s)	Adhesion product
ABS	Natural	Ultimaker 2+	240	90	40–45	Dimafix
ASA	Natural	Ultimaker 2+	250	100	40–45	Dimafix
Boun	Natural	Artillery Genius	220	40	35–40	—
EP	Ivory White	Artillery Genius	220	50	40–45	—
Flex	Ivory White	Artillery Genius	225	50	25–30	—
Glace	Natural	Artillery Genius	220	55	35–40	Dimafix
Nylstrong	Natural	Ultimaker 2+	255	85	40–45	Dimafix
Olive	Natural	Artillery Genius	220	50	40–45	—
Oyster	Natural	Artillery Genius	220	50	40–45	—
PETG	Natural	Artillery Genius	235	70	40–45	3DLac
PLA	Natural	Artillery Genius	210	50	40–45	3DLac
PP	Natural	Ultimaker 2+	215	50	30	Smart Stick
PVA	Natural	Artillery Genius	195	45	35–45	3DLac

with the 3D printed part in a low air circulation cabinet or room.

PH was determined measuring the aqueous extract following the methodology of UNE-EN ISO 3071:2006. A total amount of 1 g was immersed in 50 mL of pure water and displayed in a magnetic stirrer during 1 h. The pH was measured before the immersion of the sample in the water and after the agitation. Similarly, the same measurements were performed before and after the accelerated aging. A Hanna Combo resolution with 0.01 pH – 0.01 mS/cm – 0.01 ppt – 0.1°C and precision ±0.05 pH ± 2% F.S. (EC-TDS) ± 0.5°C and a Hanna HI 99104 with resolution 0.01 pH and ± 0.2 pH accuracy were used with this purpose.

The presence of volatile organic compounds (VOCs) was determined using an Oddy test.[40,41] The procedure consisted of the exposure of 2 g of sample in a hermetically closed ambient with a source of humidity and three different metal coupons (silver, copper and lead). This sample preparation was introduced in an oven for 28 days with 60°C temperature conditions. Finally, the results were collected with a visual inspection of the metals' surface. Further information related to the 3 in 1 Oddy test is described in Díaz, I and Cano, E.[42]

On the other hand, color variability of the samples' surface was analyzed using the Mean Color Difference from the Mean (MCDM) and the differences in color were registered with the aim of relating these parameters with the degradation during the aging process. This information allowed us to extract some conclusions and review the performance of the printing materials studied.[43]

The equipment needed for this study included a Konica-Minolta CM-2600d spectrophotometer with the following measurement conditions: diffuse lightning geometry and 8° detection, specular component excluded (SCE), target mask (measurement/illumination area) with a diameter of 8 mm; UV 0% lightning option; CIE D65 standard illuminant[44] and CIE 1964 standard colorimetric observer.[45] The acquisition step was performed by the Spectramagic TM NX Pro Color Data Software of the spectrophotometer provided by Konica Minolta. The instrument calibration was performed by using a white calibration plate CM-A145 for the maximum lightness and a Zero Calibration Box CM-A32 for the minimum lightness, which were also provided by the manufacturer of the spectrophotometer.

The methodology for the colorimetric study involved the measurement of 10 different values of each sample, respecting the same positions (five in the front and five in the back) in order to determine the chromatic values according to the CIELAB color space –CIE 1976 L^*, a^*, b^*–.[46,47] This consists of an approximately uniform color space (represented in Figure 1) where coordinates are nonlinear functions of the X, Y, Z tristimulus values[48] and the numerical values represent the relative magnitude of the color differences which could be described by Euclidean distances in the color space or also by recently updated equations such as CIEDE2000[49] applied in this study.

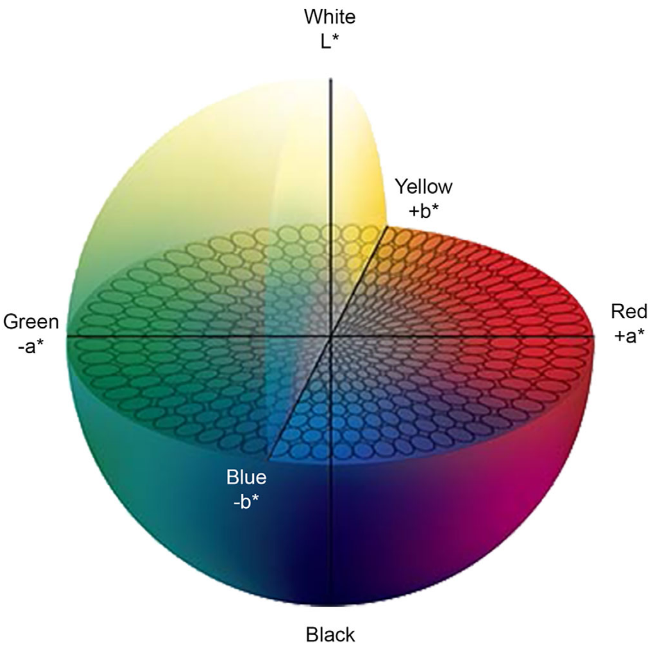

FIGURE 1 CIELAB color space representation.[50]

The CIELAB space—employed for the graphical representation of the color coordinates values—allow us to calculate the CIELAB (L^*_{10}, a^*_{10} y b^*_{10}) Cartesian coordinates. The L^* (lightness) coordinate corresponds to the luminosity of a surface compared to another white reference with the same lightning conditions. For non-fluorescent samples, the values can be measured between 0 (totally dark surface) and 100 (ideal reference blank). The a^* coordinate corresponds to the red-green system with origin in 0. The b^* coordinate refers to the yellow-blue system. The value for these coordinates may be positive or negative: $a^* > 0$ represents the red component while $a^* < 0$ corresponds to green; likewise, $b^* > 0$ matches with yellow and $b^* < 0$ with blue.

The rectangular coordinates could be almost correlated with the corresponding cylindrical ones (lightness L^*_{10}, chroma $C^*_{ab,10}$, and hue angle $h_{ab,10}$), according to the equations:

$$L^* = 116f\,(Y/Y_n)3 - 16$$

$$C^*ab = [(a^*)\,2 + (b^*)\,2]\,½$$

For achromatic stimulus the corresponding value is 0 and, in general, it does not exceed 150 even though for monochromatic stimulus it is possible to reach the quantity of 1000.

$$h_{ab} = \arctan\,(b^*/a^*)$$

The h_{ab} value is comprised between 0° and 360°: 0° ($+a^*$) = red; 90° ($+b^*$) = yellow; 180° ($-a^*$) = green; 270° ($-b^*$) = blue.

Analogously, differences in color have been calculated according to the equation for color difference CIEDE2000[49]: ΔE_{00} (total color difference) which can also be expressed as differences of the components CIEDE2000 lightness (ΔL_{00}), chroma (ΔC_{00}) and hue (ΔH_{00}).[51]

The CIELAB color-difference formula is useful and commonly employed in the cultural heritage research field.[52–57] However, in this case, CIEDE2000 color-difference formula was chosen as a standard following the latest recommendation made by CIE and ISO.[49,58,59] In fact, CIEDE2000 was initially recommended for a set of "reference conditions" (e.g., uniform samples with CIELAB color differences below 5.0 units) that are different from the current ones. However, several authors have employed the CIEDE2000 color-difference formula under many different viewing conditions apart from the "reference" mentioned before.[60–62]

In order to determine the variability of the measurements carried out in the samples surface, the MCDM value was calculated resulting in a CIELAB unity amount using the following equation[63]:

$$\mathrm{MCDM} = \left(\frac{1}{N}\right)\sum_{i=1}^{N}\left[\left(L_i^* - \overline{L^*}\right)^2 + \left(a_i^* - \overline{a^*}\right)^2 + \left(b_i^* - \overline{b^*}\right)^2\right]^{1/2}$$

Where the "i" subscripts represent the color coordinates in each N measure and the horizontal bars correspond to the average value. The MCDM allows us to represent the dispersion of the three CIELAB coordinates using just one number. Therefore, variability of the measured colors in different spots of the same non-homogenous sample can be estimated: the lower the MCDM value, the lower the variability of the color measured is (homogenous sample). The MCDM values expressed in CIELAB units average numbers (AVG) and the standard deviation (*SD*) of the samples measured are provided in the results section.

Finally, the glossiness was also measured before and after the aging process. For this, a Konica-Minolta MULTI GLOSS 268 glossmeter was used. This device performs three different measurements with diverse geometries (angles): 20° (specific for glossiness higher than 70 GU, registered at 60°), 60° (glossiness between 10 and 70 GU, recorded at 60°) and 85° (when glossiness is lower than 10 GU at 60°). In our case, as the values registered were not completely homogeneous, the intermediate geometry of 60° was used to calculate the differences following the UNE 53036:2001 standard. A total of 10 measures in different directions of the front and back surfaces were collected to compare the average values and evaluate the changes of the material. In addition, a neutral gray X-rite background was displayed under the samples during the measurement in order to avoid ambient contaminations.

TABLE 2 Results of Oddy Test. Permanent (P), Temporary (T) or Unsuitable (U). Highlighted the results referred in the text.

Sample	Silver	Copper	Lead
ABS	P	T	P
ASA	P	T	P
Boun	**U**	P	U
EP	**P**	**P**	**P**
Flex	P	T	T
Glace	P	T	U
Nylstrong	P	T	T
Olive	P	**U**	**U**
Oyster	P	T	P
PETG	P	T	T
PLA	P	**U**	P
PP	P	T	P
PVA	P	P	U

Note: The bold values are the most important results discussed in the text.

3 | RESULTS AND DISCUSSION

First, the results of the analysis of pH, glossiness and Oddy Test are presented, followed by the colorimetric study which will be thoroughly described.

Concerning the pH, three different samples of each material were prepared and tested. The aim was to corroborate the absence of any soluble substance that could modify the state of conservation of the original object. Thus, the pH of the aqueous extract was measured before and after the aging process following the methodology explained previously. Overall, the results obtained determined a slightly decreasing variation of the pH, less than 0.2 average in most cases after the exposure. Olive was the material which demonstrated a higher decrease value around 0.42. Furthermore, even though some materials such as Boun, EP, Nylstrong and Oyster generated a decrease in the pH after the aging, initially, an increase around 1 was registered for these materials (pH 5.6 at the beginning, 6.5 after agitation) while PVA was the sole material which decreased the pH around 1 (pH 5.5 at the beginning, 4.6 after the agitation).

The Oddy Test revealed interesting information related to the VOCs emission of the materials selected. After the exposure of the metallic coupons, the results were collected through visual inspection of the surfaces and transformed in a classification of the materials as permanent, temporary or unsuitable recommendation for each metal. According to this, the material was determined permanent when there were no visible corrosion

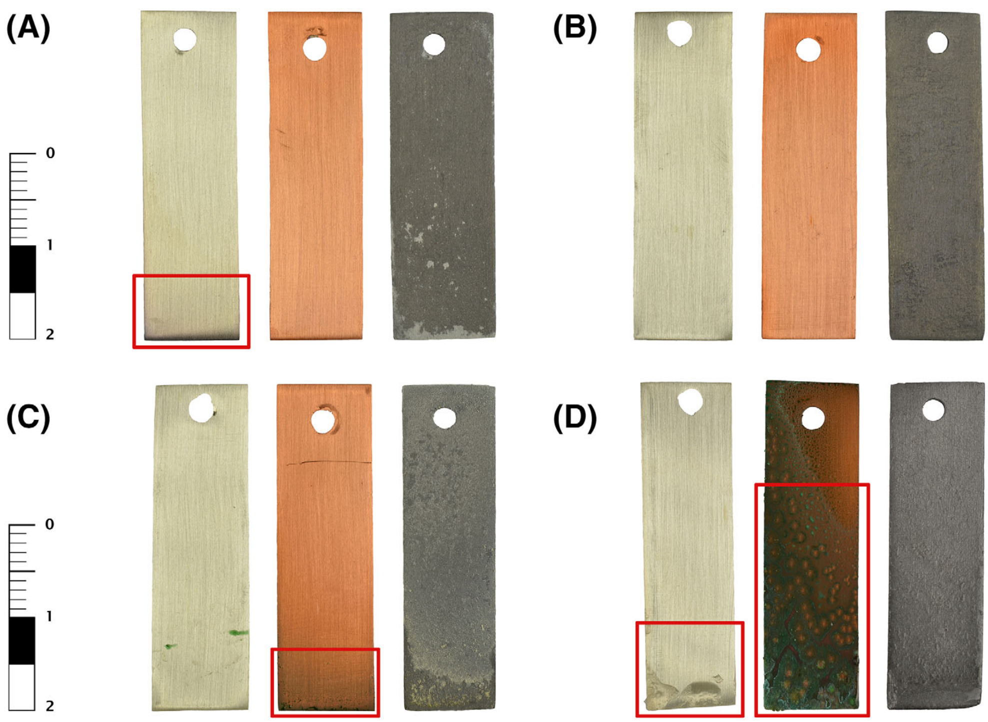

FIGURE 2 Silver, copper and lead coupons of Boun (A), EP (B), Olive (C) and PLA (D).

TABLE 3 Average and standard deviation of MCDM values (CIELAB units) for each sample. Highlighted the results referred in the text.

Sample	MCDM (AVG and SD) Before Aging	MCDM (AVG and SD) After Aging
ABS	0.7 ± 0.1	**8.4 ± 0.2**
ASA	0.4 ± 0.1	1.1 ± 0.2
Boun	0.5 ± 0.3	**0.7 ± 0.2**
EP	**0.3 ± 0.1**	**0.7 ± 0.2**
Flex	0.9 ± 0.2	**19.5 ± 0.2**
Glace	2.1 ± 0.4	**2.0 ± 0.4**
Nylstrong	1.4 ± 0.5	2.4 ± 0.6
Olive	0.8 ± 0.4	2.9 ± 1.0
Oyster	0.5 ± 0.4	1.5 ± 0.4
PETG	1.5 ± 0.2	2.4 ± 0.3
PLA	0.8 ± 0.3	**0.7 ± 0.5**
PP	**4.1 ± 0.5**	4.2 ± 0.7
PVA	3.2 ± 0.5	3.1 ± 0.4
AVG-SD	**1.3 ± 0.3**	**3.8 ± 0.4**

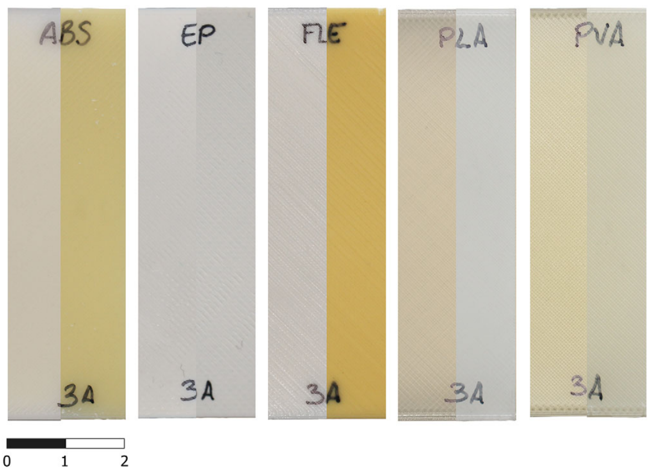

FIGURE 3 Comparison of visual colorimetric changes of ABS, EP, Flex, PLA and PVA before (left) and after (right) the aging.

signs at first sight. Besides, it was unsuitable when huge corrosion products were visible in most of the surface and the temporary recommendation was reserved to localized signs. Following these guidelines, Table 2 summarizes the results.

In Figure 2, the coupons corresponding to the materials Boun, EP, Olive and PLA are shown. In particular, Boun was the only material which altered the silver. The material that presented the best results was EP, probably due to the presence of calcium carbonate in its composition. On the contrary, Olive was the material which altered both the copper and lead, demonstrating the worst results. Finally, the result revealed by PLA was disturbing, as the copper exhibited massive corrosion products and a sticky substance was deposited in the surface of the coupons.

Focusing on the colorimetric results, the color variability (heterogeneity) of the samples, expressed by the MCDM in CIELAB unities based on the aging conditions, is described in Table 3. Likewise, color variation before and after the accelerated aging procedure can be easily compared in a selection of materials in Figure 3.

The results demonstrate that the average color variability (MCDM value) is lower in the samples before aging (1.3 ± 0.3) than the same values after the procedure (3.8 ± 0.4), which indicates a higher dispersion of the color measures in the front surfaces as a consequence of a higher exposure to the combination effect of radiation, temperature and humidity. Only Glave and PLA materials showed a light descent of the MCDM value after the aging.

Before aging, EP sample recorded the lower average MCDM value (0.3 ± 0.1), which means a higher homogeneity between front and back, while PP showed the greatest value, (4.1 ± 0.5) suggesting a higher difference between front and back.

After the aging process, the samples with a lower average MCDM value were Boun (0.7 ± 0.2), EP (0.7 ± 0.2) and PLA (0.7 ± 0.5), while Flex (19.5 ± 0.2) was the material with a higher average MCDM value followed by ABS (8.4 ± 0.2). Therefore, the low homogeneity level

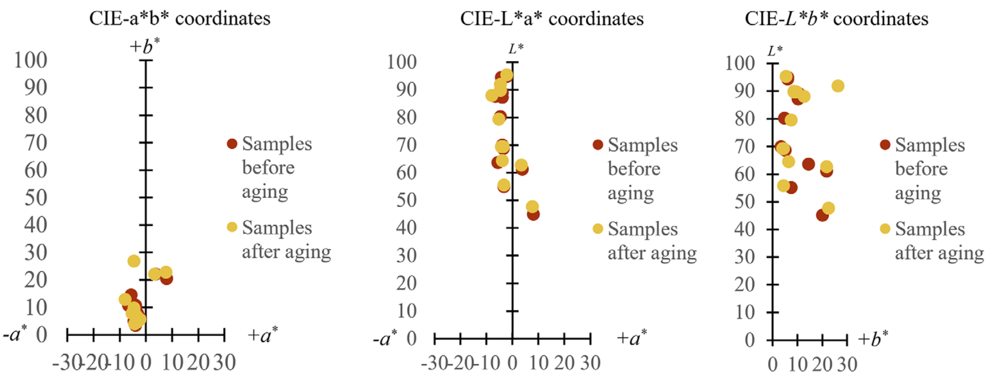

FIGURE 4 Values from the samples before and after aging: CIE-*a***b** (A); CIE-*L***a** (B); CIE-*L***b** (C).

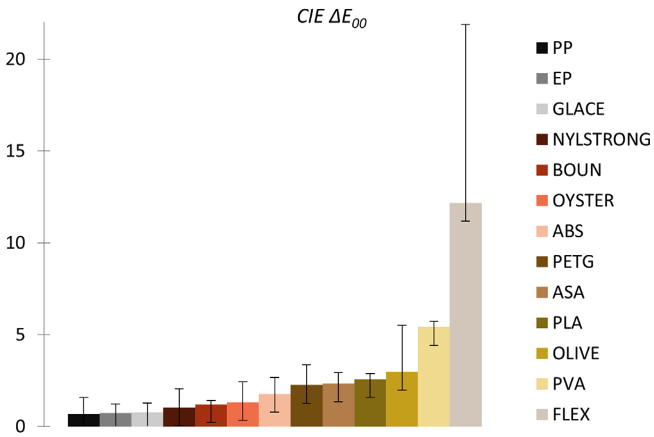

FIGURE 5 ΔE_{00} values of the samples before and after the aging (from lower to highest order).

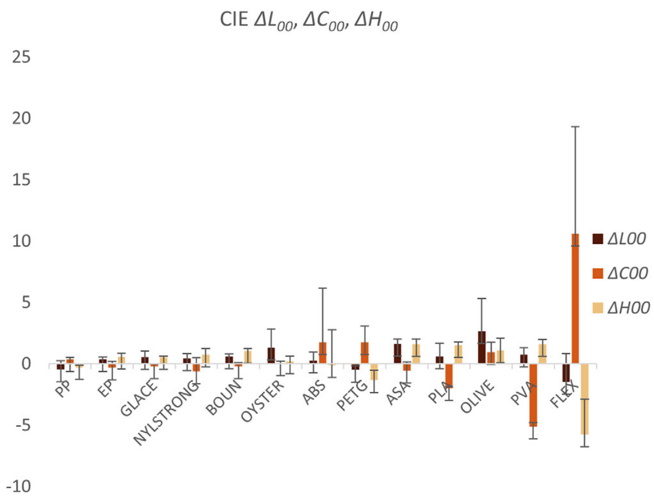

FIGURE 6 CIEDE2000 ΔL_{00}, ΔC_{00}, ΔH_{00} values of the samples measured before and after the accelerated aging (ordered following the ΔE_{00} from Figure 3).

for the last two materials mentioned suggest a chromatic alteration when comparing front and back.

The rectangular coordinates of CIELAB color (lightness L^*_{10}, a^*_{10} y b^*_{10}) are presented in Figure 4.

According to Figure 4A, the average values of a^*b^* coordinates indicate a low intensity slightly greenish to yellow color for most of the samples before aging: average value of $a^* = -2.5 \pm 4.0$ and $b^* = 10.1 \pm 5.7$. Only two of them presented a subtly red tone. After the aging process, the color remains the same with an increase in intensity: average value of $a^* = -2.7 \pm 4.0$ and $b^* = 11.1 \pm 7.7$. However, the higher values of *SD* revealed the variability respect to the average, highlighting the b* coordinate after the aging procedure.

According to Figure 4B,C, the average values for the L^* (lightness) coordinate measures showed an increase after the aging ($L^* = 75.7 \pm 16.2$ before and $L^* = 76.3 \pm 15.7$ after) but with a large *SD* value that demonstrates the heterogeneity of these numbers in respect to the average.

Figure 5 presents the medium values for color difference CIEDE2000 (ΔE_{00}) of the samples before and after the aging process.

For observers without altered color perception, the magnitude of visual color thresholds depends on the location of the reference color in the CIELAB space[64] and, under optimal viewing conditions, this may be even lower than 1.0 CIELAB unit.[65,66] Since there is no scale factor to transform from CIELAB into CIEDE2000 units, for uniform samples, 1.0 CIELAB - difference unit is equivalent to approximately 0.6 of a CIEDE2000 color-difference unit,[67] so this could be considered as the minimum visible CIEDE2000 color difference value.

This way, according to the graph, in all cases, visible differences in color in the analyzed samples are shown

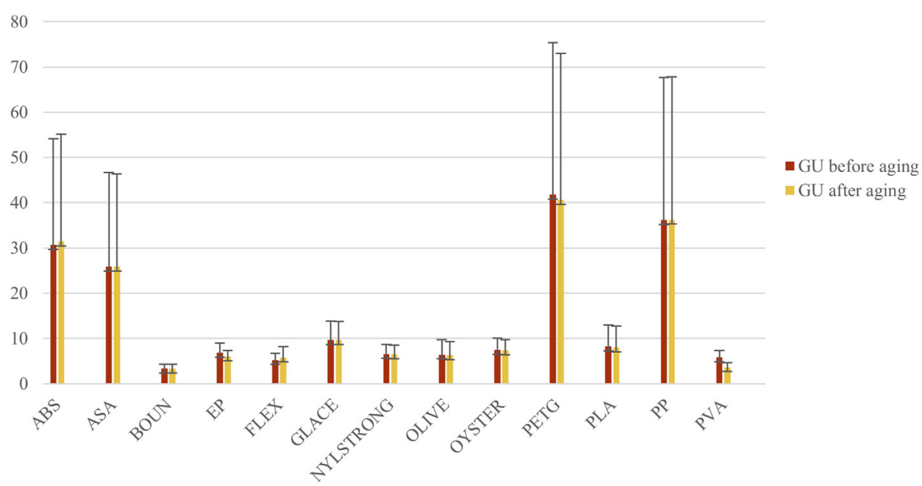

FIGURE 7 Glossiness units (GU) values measured in the samples before and after the accelerated aging.

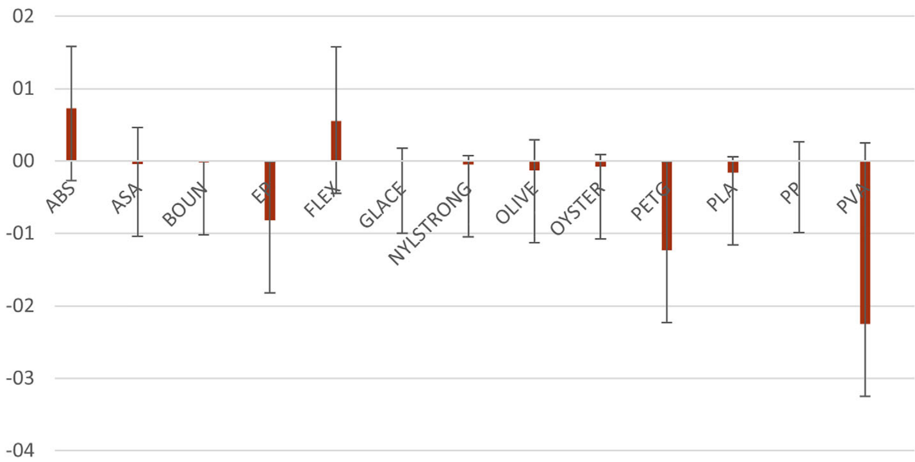

FIGURE 8 Glossiness differences before and after the aging expressed in GU values.

and the magnitude of visual color discrimination with an average value of $\Delta E_{00} = 2.7 \pm 3.1$ is doubled.

The lowest average value in color difference was registered in PP (0.7 ± 0.9) and EP (0.7 ± 0.5) samples, nearly followed by Glace (0.8 ± 0.5). These materials would result the most stable to aging conditions from a chromatic point of view. Nevertheless, the samples of Flex (12.2 ± 9.2) presented the highest medium values, resulting the material with a larger SD number. These outcomes revealed a great heterogeneity in the difference color measures due to the different exposure to the aging conditions of radiation, temperature and humidity.

For this study, it was useful to consider the three components of the CIEDE2000 micro-space in order to analyze the lightness (ΔL_{00}), chroma (ΔC_{00}) and hue (ΔH_{00}) differences (Figure 6).

After the aging process, CIEDE2000 lightness, chroma and hue difference values were observed in each sample.

The ΔL_{00} reached a positive average value (0.5 ± 1.0), showing a slight lightening of materials. The lowest positive value was presented by ABS (0.2 ± 0.7) and the highest by Olive (2.6 ± 2.7). Only PP, PETG and Flex reported a darkening: the lowest negative value was registered by PP (-0.5 ± 0.7) and the highest by Flex (-1.5 ± 2.3). In general, ΔL_{00} provided an average percentage of 30.4 $\pm$ 31.3% CIEDE2000 color difference, resulting in the component which less contributed to the total color difference. It also presented a high *SD* value, suggesting a noticeable variation between samples.

An increase in the color intensity of the samples after the aging was demonstrated by the ΔC_{00} which reached a positive average value (0.5 ± 3.51). Nevertheless, the ΔC_{00} results ranged from positive to negative. The samples of Oyster (0.0 ± 0.2) presented the best results with no differences in chroma. The lowest positive value was measured in PP (0.5 ± 0.1) and the highest correspond to Flex (19.1 ± 19.3), indicating an increase in the color intensity. On the contrary, the lowest negative value was presented by Boun (-0.2 ± 0.3) and Glace (-0.2 ± 0.2) and the highest by PVA (-5.1 ± 0.3), which results in a decrease of the intensity. The average percentage contributed by ΔC_{00} to the CIEDE2000 color difference was 38.2 ± 34.6%, being the component which contributed most to this parameter. In the same manner of ΔL_{00}, the high value of SD demonstrated a variation between samples.

Finally, the ΔH_{00} presented a positive average measure (0.1 ± 2.0) that represents a negligible hue increase even though negative and positive values were registered.

The lowest positive value appeared in Oyster (0.2 $\pm$ 0.4) and the highest in ASA (1.6 ± 0.4) and PVA (1.6 $\pm$ 0.4). For the first sample, hue differences could be barely appreciated, resulting in a minimum increase of the color intensity. For the others, a turn from yellow to green and a descent in chroma intensity were observed. Lastly, the lowest negative value was obtained in ABS (-0.1 ± 2.9) and the highest in Flex (-5.8 ± 5.9), both presented an increase in chroma but, in the first case, a slight change from yellow to green was perceived and just the opposite circumstances in the second one. In this case, the contribute of ΔH_{00} to the CIEDE2000 color difference was 31.4 ± 22.3%, showing a considerable SD between samples as well.

Focusing on the analysis of the evolution of glossiness, Figure 7 presents the glossiness units (GU) measured in all the materials before and after the exposure to accelerated aging. The results demonstrated a minimum difference between the beginning and the end, in particular, the average glossiness difference was only -0.3 ± 0.6.

Additionally, Figure 8 shows the glossiness differences quantified before and after the accelerated aging of materials expressed in GU values. The samples of ASA (0.0 ± 0.5), Boun (0.0 ± 0.0), Glace (0.0 ± 0.2) and PP (0.0 ± 0.3) did not experience a glossiness variation considering one decimal position. ABS was the sample which demonstrated a greater increase in this property (0.7

± 0.9) and PVA exhibited the higher decrease (−2.3 ± 2.5).

4 | CONCLUSIONS

First of all, the Olive material reported the worst results in the Oddy test and pH values, suffering a slight acidification and producing a harmful ambient for copper and lead. However, EP demonstrated the best results for Oddy test and pH and also revealed one of the lower color heterogeneities (lowest MCDM value) and minor color differences (ΔE_{00}) experienced after the aging procedure.

Generally, a noticeable color difference (ΔE_{00}) (considering 0.6 units in the CIEDE2000 system and approximately 1.0 unit in CIELAB) was appreciated in all the materials studied after the accelerated aging.

TABLE 4 Summary of main findings of the study.

Material	Analysis Techniques			
	pH	**Oddy Test**	**Glossiness**	**Color**
ABS	Slight variations, not relevant	Suitable for temporary application	Insignificant changes were registered	Noticeable color change. Insignificant Lightness and Hue difference, visible Chroma variation
ASA	Minor acidification after agitation	Suitable for temporary application	Glossiness barely reduced	Minor color change. Perceptible Lightness and Hue difference, minor Chroma variation
Boun	Considerable increase of pH after agitation	Unsuitable for Cultural purposes	Insignificant changes were registered	Almost irrelevant color change. Minor Lightness and Hue difference, insignificant Chroma variation
EP	Considerable increase of pH after agitation	Recommended for permanent use	Glossiness barely reduced	Irrelevant color change. Minor Lightness and Hue difference, insignificant Chroma variation
Flex	Slight variations, not relevant	Suitable for temporary application	Glossiness barely increased	Extremely noticeable color change. Slightly Lightness difference, ultra-high Chroma variation, high Hue modification
Glace	Slight variations, not relevant	Suitable for temporary application	Glossiness barely increased	Almost irrelevant color change. Minor Lightness and Hue difference, insignificant Chroma variation
Nylstrong	Considerable increase of pH after agitation	Suitable for temporary application	Insignificant changes were registered	Minor color change. Slightly variations in Lightness, Chroma and, Hue
Olive	Minor acidification after agitation	Unsuitable for Cultural purposes	Insignificant changes were registered	Minor color change. Moderate Lightness difference, minor Chroma variation, slightly Hue modification
Oyster	Considerable increase of pH after agitation	Suitable for temporary application	Insignificant changes were registered	Almost irrelevant color change. Perceptible Lightness modification, insignificant Chroma and Hue variation
PETG	Slight variations, not relevant	Suitable for temporary application	Insignificant changes were registered	Noticeable color change. Slight Lightness difference, perceptible Chroma variation, minor Hue modification
PLA	Slight variations, not relevant	Suitable for temporary application	Insignificant changes were registered	Noticeable color change. Minor Lightness difference, moderate Chroma variation, slight Hue modification
PP	Slight variations, not relevant	Suitable for temporary application	Insignificant changes were registered	Irrelevant color change. Insignificant Lightness, Chroma and Hue variations
PVA	Considerable acidification after agitation	Unsuitable for Cultural purposes	Glossiness considerably reduced	Very noticeable color change. Minor Lightness difference, high Chroma variation, slight Hue modification

The main dispersion of the color measurements (highest MCDM values) was a consequence of a higher color variation in the exposed faces to the radiation, the temperature and the humidity than the protected ones (less exposed to the ambient conditions). This fact demonstrates the negative effect that these conditions have on the materials studied.

From a colorimetric point of view, the materials which showed less color variations would be more suitable for the Cultural Heritage field. Considering 1.0 CIEDE2000 tolerance units, the order concerning the color stability (from lower to higher ΔE_{00}) should be PP, EP, Glace and Nylstrong while Boun, Oyster and ABS would present a medium stability (ΔE_{00} values between >1.0 and <2.0) and PETG, ASA, PLA, Olive, PVA and Flex would be considered the most unstable materials, highlighting the last one as the most chromatically altered (12.2 ± 9.7).

The CIEDE2000 color system allows us to consider the lightness (ΔL_{00}), chroma (ΔC_{00}) and hue (ΔH_{00}) differences separately, facilitating the evaluation of each component and the identification of the most unpredictable parameter. According to this, the average measures for ΔH_{00} are the most stable with a low positive average value (0.1 ± 2.0). The hue variations involve (in 10 out of the 13 samples) a slight turn from yellow to green and reverse in the others, with both increase or decrease of chroma.

Lightness ($\Delta L_{00} = 0.5 \pm 1.0$) and chroma differences ($\Delta C_{00} = 0.5 \pm 3.5$) were the parameters with higher variations and similar average positive values. In general, this indicates that the samples suffered a slight lightening joined to an increase in color intensity after the aging. Nevertheless, a non-uniform variation was perceived, so that each material should be considered individually. The greater part of the samples (10 out of 13) reached an increase in lightness (a positive value of ΔL_{00}) and only three presented a negative rate. On the contrary, seven materials showed a descent of chroma (negative value of ΔC_{00}) while other five increased the value of this component and one of them remained with the same measure. In any event, the higher absolute values correspond to the samples with the greater increase in Chroma as a result of the exposure.

Concerning the glossiness, this study concludes that this property is closely related to the visual appearance of the material and, in this case, was barely altered during the accelerated aging, so it did not produce significant results.

This way, Table 4 summarizes all the main conclusions extracted from the interpretation of the results obtained in the study.

To summarize, this research gives an overview of some physical aspects of a wide selection of 3D printing materials for their application in the Cultural Heritage field. Nonetheless, it is necessary to carry out further studies regarding the chemical composition and the polymer degradation from a compositional point of view to determine the evolution of these materials and their suitability for these applications.

AUTHOR CONTRIBUTIONS

María Higueras: Conceptualization, Methodology, Writing – Original Draft, Writing – Review & Editing, Visualization. **Francisco José Collado–Montero:** Methodology, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Resources. **Víctor Jesús Medina:** Resources, Writing – Review & Editing, Supervision.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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