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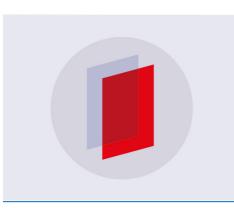
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3d printing technologies:
are their materials safe for conservation treatments?

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Abstract. 3D printing technologies have been definitively introduced in conservation treatments. Despite the advantage of not requiring direct contact with the artwork, allowing the preservation of fragile objects, the printed item is located in direct contact with the object and the characterization of the filament used for the printing is not often taken into consideration. The following study was undertaken as an evaluation of filaments possibly employed for conservation treatments. The characterisation of the components was carried out through infrared spectroscopy, thermal and chromatographic analyses. Moreover, it was investigated whether such materials release volatile organic compounds (VOC) during their degradation process. Indeed, all of them released styrenic and alkyl compounds, all solvents for materials that can be found on artworks, employed by both, artist and conservator.

1. Introduction

In the last few years, 3D printing technologies have been introduced in conservation treatments as solution for different issues. Among 3D techniques, fused filament fabrication (FFF) method has found several applications in the field, in particular employed for the creation of reconstructions or integrations [1-7] and reinforcement structures [8] for fragmented art pieces. Surely, one of the advantages is that creating an object, starting from a CAD 3D model, does not require a direct contact with the artwork. In fact, the model can be drawn from artwork pictures reworking or from its laser scans. This allows preserving fragile objects, without inducing further damages as for the creation of a mold, which needs a direct contact with the artwork. On the other hand, in such cases, the printed item is located directly on the object and, despite that, the characterization of the filament used for the printing is not an aspect taken into consideration. Filaments are, mainly, based on polymers and are not tuned for conservation purposes, therefore their formulations might contain additives such as plasticizers, flame retardants, stabilizers, whose molecules, smaller than the macromolecular structure, can migrate towards the surface with time. These products can affect materials they are in contact with, changing their properties and their aspect, thus creating damage. Another issue could be the release of volatile organic compounds (VOC), derived from the degradation process of the polymer itself. Also in this case, these molecules may act negatively on other materials.

It is clear that on a large market it is not necessarily considered how the base-material will act with the ageing or will interact with artist materials, both questions to be considered though according to the contemporary conservation theories that articulate how conservation products must be reversible and chemically stable with time [9]. Such rules were at the base of a deep characterization of products more often employed in the conservation field or the research of specifically tuned formulations (e.g. Paraloid®B72 or BEVA®371) [10, 11].

Filament-producers tend to keep undisclosed the chemical composition of their products and their datasheets focus mainly on mechanical properties (e.g. deformation, elongation, tensile strength) and printing parameters, in particular temperatures of working plate and nozzle, together with the

suggested printing speed. Nevertheless, missing parameters such as melting points and degradation-processes beginning temperatures are important information too.

Following this line of reasoning, the work here introduced aims at suggesting the elaboration of a list of potential materials that can be safely used on artworks. The project has started with the characterization of several filaments already used or ready to be used in conservation treatments. Only a multi-analytical approach, from infrared spectroscopy to thermal analysis and chromatographic techniques, has allowed to detect different chemicals, either components of the material or products released already in environmental conditions. Furthermore, some of them can potentially compromise restored objects. Indeed, results have underlined the need of having a full awareness of the composition of all involved materials in order to avoid further damages and continuous restoration treatments in a short time-frame on the same artwork.

2. Materials and methods

2.1. Filaments

Fourteen filaments were chosen on the base of the experience of three printing laboratories that had collaborated with conservators in the creation of integration of real artworks. The first material selection was based on the aesthetical aspect, since related with the final result other than on the ease of printing and following smoothing; base materials were not considered. Since the composition of some products is proprietary, production series names and manufacturers are not mentioned. Therefore, filaments are named as general samples, followed by their colour and producers are approximately indicated in order to gather filaments (Table 1).

Table 1. List of characterised filaments, together with their manufacturing; producers have been identified by abbreviation, due to confidential compositions

Filaments	Producers
Filament 1 – white	TF
Filament 2 – white	TF
Filament 3 – white	TF
Filament 4 – light red ochre	TF
Filament 5 – yellow ochre	TF
Filament 6 – light grey	TF
Filament 7– dark grey	TF
Filament 8 – dark red ochre	TF
Filament 9 – light wood	Unknown
Filament 10 – dark wood	CF
Filament 11 – bronze	CF
Filament 12 – transparent uncoloured	TO
Filament 13 – yellow	TO
Filament 14 – white	TO

Chemical characterization of printing materials was the focus of this first part of the work, especially changes induced already by natural ageing. All filaments were characterized through infrared spectroscopy, thermal analysis and gas-chromatography.

2.2. Analytical techniques

2.2.1. Thermogravimetric analysis (TGA)
TGA has been performed to assess the thermal degradation profile of each material and, more specifically, to identify the temperature at which components start to degrade (temperature degradation offset, Tdo), in order to verify the stability of the filaments at the suggested printing temperature. Also, the presence and the amount of inorganic filler in raw materials can be controlled.
Analyses were carried out with a Thermogravimetric Analyzer TGA 2050 (TA Instruments), in nitrogen atmosphere, with a temperature ramp from 40 to 600°C at a rate of 10°C/min. Materials were analysed directly, fragmenting the commercial reel and collecting an amount of sample of ca. 15mg, which was directly put in an alumina pan.

2.2.2. Fourier transform infrared spectroscopy (FTIR) in attenuated total reflection (ATR)
Infrared spectroscopy has been carried out to characterize their chemical nature.
ATR spectra were recorded on a Thermo Nicolet Nexus FTIR spectrometer, with a Smart Endurance ATR accessory with a diamond contact crystal and a ZnSe focusing element. The range investigated was from 4000 to 400 cm-1, with a resolution of 4 cm-1 and the result was the average of 64 scans.

2.2.3. Pyrolysis (Py) gas chromatography/ mass spectroscopy (GC/MS)
Aim of the analysis is a chemical characterization of the material which allows the identification of organic additives such as colorants, flame retardants or stabilizers.
The chromatograph is a 6890N Network GC system (Agilent Technologies) and the analytical capillary column employed has a solid phase made with methyl-phenyl-polysiloxane cross-linked with 5% phenyl methyl silicone (HP-5MS of Agilent Technologies) 0.25μm thick (30m x 0.25mm inner diameter). The coupled mass spectrometer is a 5973 Network Mass selective detector (Agilent technologies) set with the following parameters: interface temperature 280°C, ion source temperature 230°C, quadrupole mass analyser temperature 150°C, electron impact 70eV, scan range 40-600 m/z.
The instrument is connected with a CDS Pyroprobe 1000 with a platinum filament pyrolyzer, supplied by Analytical Inc.. The pyrolysis chamber temperature was 300°C, whereas the pyrolysis temperature was set at 600°C, reached with a ramp temperature of 5°C/ms and held for 10s. The chamber was also fluxed with helium.
Few milligrams of raw material were inserted in a quartz boat and kept in position with some quartz wool. The boat was then put in the pyrolyzer platinum coil and so inserted in the pyrolysis chamber. The pyrolysis and the chromatographic run began at the same moment and the temperature of the column, hold for 2 minutes at 50°C, was heated at 300°C at a rate of 10°C/min.

2.2.4. Solid phase microextraction (SPME) gas chromatography/ mass spectroscopy (GC/MS)
This technique allows the analysis of organic volatile components (VOC) in an enclosed environment. To have semi-quantitative information, ca 1g of sample, cut in small pieces, was sealed and left for one month at room temperature (RT) in a vial with silicone septum, suitable for the insertion of needles. The SPME fibre (65μm diameter, polydimethyl siloxane/divinyl benzene absorbent material, model 57310-U sold by Supelco) is located within a needle which has to be inserted in the vial to collect the volatile components in the inner atmosphere. Sampling was carried out for 30 minutes. The analysis was repeated heating up samples at 50°C for one hour and sampling was conduct in the meantime.
After sampling, the needle was removed and inserted for 2 minutes in the injector (280°C) of the chromatographer (previously described). A ramp temperature from 50 up to 250°C was set, at a rate of 10°C/min. Helium was used as carrier gas, at a constant flow of 1.0 ml/min. Analyses were carried out in split mode (ratio 1/20 of the total flow).
On the basis of the data obtained through FTIR and Py-GC/MS investigations, SPME analysis was limited to one sample per each different material (filament 1-3, 9-13).

3. Results and discussion

TGA, FTIR and Py-GC/MS allowed a first classification of selected filaments and data are introduced in table 2. Whenever the producer declared the composition of the product, analytical data added some additional details.

Table 2. Summary table of filaments main components, investigated through FTIR and Py-GC/MS. * data obtained by X-ray fluorescence (XRF), not introduced in the previous section due to the employment for this sample only

Filament	Polymer	Tdo [°C]	Filler	Flame retardant	UV-stabilizer	Antioxidant	Plasticizer
F 1	PS	245	$CaCO_3$ (10%)	Dicumene			
F 2	SAN	213	$CaCO_3$ (10%)		Tinuvin P		Dehydroabietic acid methyl ester
F 3	PA 12+PS	419	$CaCO_3$ (20%)		Tinuvin 770	» n.33 » SWP	
F 4	PS	234	$CaCO_3$ (15%)	Dicumene			
F 5	PS	234	$CaCO_3$ (15%)	Dicumene			
F 6	PS	234	$CaCO_3$ (15%)	Dicumene			
F 7	PS	280	$CaCO_3$ (20%)	Dicumene			
F 8	PS	234	$CaCO_3$ (15%)	Dicumene			
F 9	PLA+PS	225			Tinuvin 770		
F 10	PLA	258			Tinuvin 770		
F 11	PLA	290	Copper powder (80%) *		Tinuvin 770	Nocrac M17	Diethyl phthalate (DEP)
F 12	Acrylic polymers blend: P(S-MMA), PBA, PEA	250			Tinuvin P		
F 13	ABS + PTFE (or other fluorinated polymer)	350			Tinuvin 770		
Filament 14	ABS	230			Tinuvin 770		

Legend: PS polystyrene, SAN styrene-acrylonitrile, PA polyamide, PLA polylactic acid, MMA metylmetacrylate, PBA polybutyl acrylate, PEA polyethyl acrylate, ABS acrylonitrile-butadiene-styrene, PTFE polytetrafluoroethylene

TGA results, in terms of comparison of the T_{do} with the suggested printing temperature, highlighted how these two values are often close to each other and so how easily the printing process can be a kickoff of thermal degradation, endangering the workability of the object.

Polylactic acid (PLA), polystyrene (PS) and styrene-based polymers (acrylonitrile-butadiene-styrene, ABS, and styrene-acrylonitrile, SAN) were found as main components of most filaments. In some cases, more polymers are blended together, as for filaments 9, 12 and 13, where, it is assumed, this increases the processability of the material, more than its stability with time.

Filament 3 is mainly made of polyamide (PA). The characterization through Py-GC/MS allowed the identification of the main polymeric component as PA 12 thanks to the presence of laurolactam, which is the starting monomer. Furthermore, the technique highlighted the presence of PS, a component in lower concentration since it was not detected by IR spectroscopy, that it is probably added to provide stability to the formulation.

UV-stabilizers were often found in the formulations, especially Tinuvin P® and Tinuvin® 770, a UV absorber (UVA) and a hindered amine light stabilizer (HALS) respectively. Thus, it is possible to think of these materials as suitable for outdoor application. Other additives detected are flame retardants, antioxidants and plasticizers. In particular in filament 11, diethyl phthalate balances the high percentage of filler (copper, 80% w/w) added in the material. Beside the metal power, calcium carbonate was found as filler, in a concentration range between 10 and 20% (w/w).

Neither pigments nor colorants were identified. Organic colorants are added to polymeric formulations in low concentration, thus it is difficult to detect their presence with the techniques here involved. Only for white filaments the origin of the colour was linked to the addition of calcium carbonate, filler and pigment in the meantime. Wooden-aspect filaments reached their aesthetical aspects with the addition of wooden powder only in one of the two cases studied. Thanks to the VOC emission of furfural and other wooden derivates, it was possible to hypothesize the presence of lignin and cellulose in filament 10; on the contrary filament 9 did not released polysaccharide markers.

SPME-GC/MS results are listed in table 3.

Table 3. Summary table of SPME-GC/MS data

Filament	Polymer	VOC (RT)	VOC (50°C)
Filament 1	PS	Styrene derivatives	=
Filament 2	SAN	Styrene and acrylonitrile derivatives, acetone	=
Filament 3	PA 12+PS	Styrene derivatives and alkanes	=
Filament 9	PLA+PS	Styrene and lactic acid derivatives	=, terpenes
Filament 10	PLA	Lactic acid derivatives, furfural and other saccharide derivatives	=
Filament 11	PLA	Few lactic acid derivatives, in trace concentration	= in higher concentration
Filament 12	Acrylic polymers blend: P(S-MMA), PBA, PEA	Acrylate monomers (MMA, EA), aliphatic aldehydes	=
Filament 13	ABS + PTFE (or other fluorinated polymer)	Styrene derivatives, alkenes	=

Several studies about VOC released by polymeric filaments have been already reported in literature, but mainly with the aim of finding a correlation between 3D printing and human health, with respect to the inhalation of toxic organic volatile components released by the filament during the printing process. Therefore, tests have been carried out at temperatures set for the printing (ca 200°C) [12,13]. Here, the aim was verifying if the addition of printed items directly on an artwork might create further damage to the contact area. Considering that, the release at room temperature of remarkable amounts of styrene and its derivatives represents a danger due to the solvent action that these compounds have on several materials commonly employed by artists and conservators, e.g. natural terpenic resins or polymeric adhesives and consolidants.

4. Conclusion

For this project, 14 filaments for fused filament fabrication were selected among an ample group on the market. The choice of characterizing these materials is due to the always increasing employment of

this 3D printing technique for creating integrations to be placed on fragmented artworks. Aim of the work was investigating the possibility of further damage to the artist object, induced by the insertion.

First classification of the samples was carried out with FTIR and Py-GC/MS: polystyrene based and PLA polymers are the most employed for the creation of such materials, as main component or copolymers in blend with other matrix. As filler, calcium carbonate is often added since its colour and opacity make this powder suitable as pigment or support for organic colorants as well. Organic colorants were not identified, due to the low concentration usually introduced in industrial formulations. Thanks to the chromatographic techniques, a good overview of additives was achieved. In particular antioxidants, UV-stabilizers and one flame retardant have been identified. Moreover, the VOC emission of furfural and other wooden derivates led to the identification of lignin and cellulose as filler and coloured component in one filament. SPME-GC/MS analysis have therefore revealed to be essential for a thorough characterization of the material, even though the aim of performing it was identifying VOC released by filaments components.

Data of VOC emission of the filaments showed for all of them the release of the unreacted monomers and their derivatives; moreover some of them showed also acetone and short-chain alkyl compounds, all solvents for materials that can be found on artworks, employed by both, artist and conservator. The compounds detected at room temperature were unexpected in such a short time of observation although documented in literature, both at room temperature and above. If safety of artworks wants to be preserved, these results should be taken into consideration under the workplace hazards point of view too.

TGA data underlined how the printing temperature is often close to the T_{do} of the material in nitrogen atmosphere, therefore damages during this step cannot be excluded and should be verified.

Another issue related with these materials is that their formulation is often modified and characterising all of them is, in practice, impossible. Therefore, if conservators want to realise the conservation treatment with 3D printing techniques, the choice of the filament has to be made with attention and among a small group of selected materials, finding a fast method to check that the composition has not changed drastically. This aspect has then to be balanced with the needed time, the cost and the value of the treatment itself. Materials traditionally employed for such interventions have been deeply investigated and provide a safe and known answer to the integration issue. On the other hand, new techniques allow modelling pieces with specific software that permit to manage objects pictures in order to create a unique printed piece that perfectly fits on the area to be renovated.

4.1. Further developments

Since integrations on artworks might require a certain resistance to loads or particular forces due to their position on the object, mechanical properties should also be considered to have a complete view of the material wherewithal. Mechanical tests should be carried out on just printed and on aged specimens. Another aspect that was not investigated is the possible swelling and damage induced by water on some of the materials, especially PLA, as suggested by Proikakis [14]. These ageing investigations find reason considering that filaments, as in general conservation materials, should be suitable either for indoor and outdoor environments, or at least chosen with this awareness.

Furthermore, changes in crystallinity degree of just-printed and aged pieces could be investigated through DSC, thermal analysis not introduced here, but carried out to investigate deeper samples thermal transitions.

About VOC release, more information might rise from a calibration of the system in order to give an idea of real concentrations. Finally, tests on mock-ups are suggested, with the insertion of printed pieces on traditional materials (especially organic ones) and observation of the interaction, keeping in mind two of the fundamentals of conservation: reversibility and durability.

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