Tea. Earl Grey. Hot. - About Materials in 3D Printing

Since the late 1980s 3D printing has been used to transform digital data into physical models and prototypes.[1] In recent years, 3D printing technologies are no longer exclusively used for the fabrication of models and prototypes, but also for the production of small object batch series or single unit projects by the industry and maker scene. Some people call it the 3rd industrial revolution, others can hardly wait to order "tea, Earl Grey, hot" from a 3D printer like Captain Picard did from the Star Trek replicator.

Today, designers and artists are using these technologies in myriad ways, and consequenctly, 3D printed art and design objects, as well as architectural models, have become part of museum and private collections. Conservators are now challenged by a variety of questions about the technology and ageing stability of these objects.

This article is partly based on my MA thesis from 2011, which deals with the applications, technologies, and ageing properties of objects in contemporary art, architecture, and design made by rapid technology.[2] It summarizes the results of the light and dark ageing tests of 3D printed samples performed in 2011 and goes on to describe current trends of material development in 3D printing.

3D printing methods and materials

In order to understand material formulations and their ageing behaviour it is necessary to understand the various 3D printing technologies and their requirements. Today, stereolithography (SLA), selective laser sintering (SLS), fused deposition modelling (FDM), and inkjet powder printing (3DP) are the most popular methods used for rapid technology. In addition to these, layer laminate manufacturing (LLM), material jetting (Polyjet), and paste extrusion are used for large volume objects, material combinations, large-scale machines, printing pens, and foodstuff printers.

A wide range of materials can be used in 3D printing (Gebhardt 2007: 1). Synthetic polymers are often found in the fabrication of industrial prototypes and functional models in design and architecture, metals are commonly applied in the aerospace and tooling sector, and ceramics are widely used for medical applications (Gebhardt 2007: 264 ff.; 305 ff.). But these distincions are lost in the fast growing maker scene, artists and designers who undertake experiments with industrial techniques and materials in order to break them down for home printer solutions.

Table 1 summarizes the techniques mentioned above and gives examples of materials. (Horsch 2014: 27, 73; FormFormForm ltd 2014; Gebhardt 2007: 202f.; i.materialise 2014; Koenig 2014; RepRapWiki 2014; Warnier et al. 2014: 10-15, 47, 49, 56, 124, 142, 146, 150, 170). One must keep in mind that this table only gives an overview and that the materials used in 3D printing are not limited to those mentioned.

The material formulations developed for the different 3D printing processes can be rather complex, e.g. for stereolithographic applications with its high requirements in photosensitivity.[3] Furthermore, some techniques/ materials are difficult to identify because they require postproduction treatments. For example 3DP models have need of stabilization by using wax, resins, or UV coatings, whereas 3DP ceramics have to be consolidated by kilning before they can be glazed (Horsch 2014: 31f.; Warnier et al. 2014: 12).

Colour stability of 3D printing materials

When I began the task of investigating the ageing behaviour of 3D printing materials, I became aware that most studies dealing with the ageing stability of 3D printed objects were performed in regard to industrial applications. They mainly focused on testing the materials' hydrolytic and thermal ageing or the influence of ageing on the 3D prints' mechanical stability.[4]

Prior to 2011, little was known about the long-term ageing behaviour of 3D printed objects if stored or exhibited in museum conditions. A variety of conservators and technologists then began to observe that some polymer based 3D printing materials tend to yellow within a short period of time.

Based on these observations I started light and dark ageing experiments to examine the colour stability of synthetic polymers typically used for 3D printing in industrial and/or home user systems. These experiments were carried out on 3D printed samples, including material formulations based on epoxy resin (EP) for SLA, polyamide powder (PA) for SLS, and acrylonitrile butadiene styrene (ABS) for FDM.[5]

For each of the tested 3D printing materials, pieces were stored in the dark in climate-controlled storage rooms (85 days, 23 +/- 3° Celsius; 50 +/- 5 % RH). An equal number underwent the simulated light ageing procedure (91 days, glass-filtered daylight fluorescent lamps). Before and after, the colour and brightness of all samples were monitored by colorimetric measurements.

Under these conditions, I observed that a variety of the tested materials underwent changes in colour in dark storage as well as in daylight exposure.

The most notable changes were in all tested epoxy resin based samples after 91 days of light ageing as those significantly turned from white to yellow-brown. It is remarkable that most of the epoxy resin samples also showed significant colour changes after 85 days with exclusion of light.

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Table 1

Overview of 3D printing techniques, materials, and appearance

SLA sterolithography	liquid (often permeable to light) acrylics epoxy resins (EP) polyvinyl ethers	photo polymerisation	highly accurate
SLS selective laser sintering	powder polyamide (PA) alumide® (PA with aluminum) polystyrene (PS) polyethylene (PE) polypropylene (PP) thermoplastic polyurethane (TPU) silica sand	fusing	inaccurate
FDM fused deposition modelling	solid (pre-extruded) acrylonitrile butadiene styrene (ABS) polyethylene (HDPE) polyphenylsulfone (PPSF) polylactide (PLA) polycaprolactone (PCL) polyvinyl alcohol (PVA) polyamide (nylon) polycarbonate (PC) silicone (sugru®) thermoplastic elastomers (TPE) thermoplastic binder with wood, metal or ceramics as a filler	fusing and applying	accurate (rounded corners)
3DP inkjet powder printing	powder (substrate) and liquid (binder) gypsum starch clay ceramics glass metals wood paper salt cement	binding	accurate
LLM layer laminate manufacturing	sheets, adhesives sheets: paper coated with polyethylene polyester foils fibre reinforced composites adhesive films polystyrene and unplasticized polyvinylchloride sheets adhesives: EP, PE, acrylics, methacrylics	cutting and glueing	accurate
paste extrusion	solids cement concrete clay foodstuff bio materials	solids	extrusion
material jetting (Polyjet)	liquids see SLA (an object can be made out of different materials/colours)	photo polymerisation	highly accurate

All ABS samples, as well as the polyamide pieces, similarly underwent colour changes after accelerated daylight ageing. The corresponding colorimetric data revealed a shift into yellowing.

Reasons for the photo-oxidative ageing of 3D printing materials

One possible reason for the observed colour change is the presence of oxidation-sensible components in the material. Such components are aromatic molecules like biphenyl A in the epoxy resin based 3D prints or the typically oxidation-sensitive butadiene content in ABS (Gaechter and Mueller 1983: 48; Krebs 1999: 81). It is also important to note that the printing process itself can initiate a pre-oxidation of 3D printing materials. It is well known that such a pre-oxidation can accelerate the future oxidative ageing of plastics (Zweifel 2011: 3).

Pre-oxidation can be initiated during the heat impact caused by the extrusion process during FDM (e.g. of ABS) or Laser Sintering (e.g. PA), but also by the radiation energy used for hardening stereolithographic resins (e.g. EP resins). Moreover, with stereolithographic printing, residues of catalysts or monomers can remain in the material with the potential to speed up oxidative ageing.

Development of 3D printing materials by contemoorary artists and designers

3D printing has experienced an extraordinary degree of development within the last three years, not least due to the expiring of the first 3D printing patents from the 1990s. Therefore, my tests performed in 2011 could already appear slightly out of date.

Nevertheless, the objective here is not giving precise statements about the long-term stability of single materials, but to provide some background on the nature and technical environment of those materials. I also would like to provide some examples of 3D printing experiments made by artists and designers since that time.

Besides conventional 3D printing techniques some tendencies can be observed: use and imitation of natural materials, recycling printed plastics, and combinations of different synthetic polymers.

Various artists and designers have imitated and dealt with natural materials that already hold their own cultural significance.

For example the project *L'Artisan Électronique* by Studio Unfold and Tim Knappen uses paste extrusion to print ceramics (Warnier et al. 2014: 48, 56ff.).

Eric Klarenbeek has experimented with the same 3D printing process. He mixed up powdered straw with water and coated it with a bio plastic polymer (Fig. 1). A mycelium of fungi then grew, substituted more and more water and stuck the printed substrate together (Warnier et al. 2014: 152ff.).

Figure 1: *Mycelium Project 1.0 - Myceliumchair* (2013/14) by Eric Klarenbeek.

Other designers have discovered simple natural materials for 3D printing and carried out experiments. *Saltygloo* by Rael San Fratello Architects is architecture printed with salt from natural deposits. *degenerate chair* by Daniel Widrig was created by binding together layers of a mixture of plaster and sugar with japanese rice wine (Warnier et al. 2014: 178f.; Widrig 2014).

The *SolarSinter* by Markus Kayser is another example of unconventional thinking with using silica sand, SLS, and solar energy to build glass objects (Fig. 2; Warnier et al. 2014: 47, 54, 188f.).

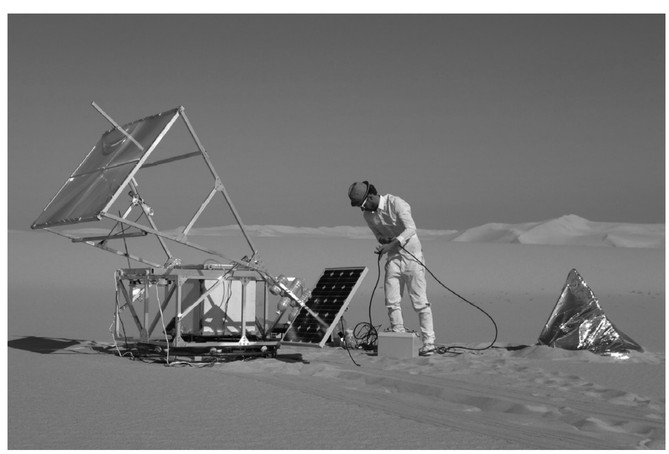

Figure 2: *SolarSinter* (since 2008) by Markus Kayser

Scott E. Hudson has modified a typical personal printer to invent a machine that is able to handle wool and wool blend yarn. In doing this he has combined the traditional felting of wool with modern 3D printing techniques.[6]

Nendo, a Japan based design studio, has created *Lacquered Paper Objects* made with LLM and has imitated a wooden surface by grinding manually and lacquering (Warnier et al. 2014: 116f.).

Another widespreqad trend within the 3D printing community is recycling plastic material from industrial products as well as 3D printed objects.

Dave Hakkens and Dirk Vander Kooij have created two different ways to reuse material from objects of every day life. Hakkens has build a series of small machines for recycling plastic material with a self-made shredder called *Precious Plastic*. PE, PP, and other thermoplastic polymers can be easily granulated and prepared for reuse with a 3D printer.[7] Dirk Vander Kooij has assembled a discarded robotic arm to extrude thick layers of melted plastic (from old refrigerators) via paste extrusion (Warnier et al. 2014: 120f.).

The Potato Eaters by DUS Architects works with paste extrusion as well, even though the material differs. Instead of plastics the architects use potato starch recycled from fries to produce tableware (Warnier et al. 2014: 163).

A further approach is the combination of different plastics by 3D printing. Form Nation and Jan Habraken have created the project *Chairgenics*. Their chairs are fabricated by SLA using epoxy resins and afterwards filled with polyurethane foam for stabilization (Warnier et al. 2014: 134ff.).

Marloes ten Bhoemer has combined two 3D printing technologies to assemble hard with soft materials (Fig. 3). Her *Rapidprototypedshoe* is made out of acrylic and elastic photopolymers with Polyjet and laser sintering techniques (Warnier et al. 2014: 128.).

Figure 3: *Rapidprototypedshoe* (2010) by Marloes ten Bhoemer.

Conclusion

3D printing is a very recent technology and technical developments are ongoing. It demands a high level of attention to current trends and tendencies in order to stay up to date. The results concerning the colour stability of 3D printing materials presented here should be understood as a snapshot of a fast changing and innovative technology.

The composition of 3D printing materials is complex.[8] In particular, minor components in the formulations (e.g. catalysts, ageing stabilizers, residual monomers in SLA parts) are not fully documented by datasheets or in specialized literature.

Furthermore, a 3D printed object by itself might not be a homogeneous material unit. Not only do designers and artists recycle, but also the industry recycles the support material, in the SLS process for example, and mixes it up with new powder. In addition, there are plenty of processing parameters during 3D printing (e.g. processing temperature, radiation energy) that the manufacturer can change.

This potentially influences the ageing stability of the finished part. Considering this complexity, it becomes obvious that it is not possible to make general statements about the ageing stability of 3D printing materials. Nevertheless, the study from 2011 shows results on the prospective behaviour of the materials used at this time and gives insight into expected deterioration phenomena.

Many of the tested 3D printing materials are not photo-oxidatively stable and tend to change colour in accelerated indoor light exposure. Moreover, a variety of the tested materials showed colour changes even if stored in the dark for a short time (84 days). This indicates the necessity of preventive conservation treatments to slow-down the materials' ageing by oxidation processes.

Possible ways to achieve this could be oxygen-free storage, the use of UV-A filters, or the reduction of illumination time and intensity.

Finally, it is important to note that the development of suitable preservation concepts for 3D printed objects also includes understanding the artists' and designers' position in regard to the desired durability of the 3D printed object, the acceptance of ageing phenomena, and the question of re-printability.

As part of a conservation strategy, it might be necessary to implement protocols to acquire the digital data of the 3D parts (CAD or STL files) and back them up in suitable archival formats.

Most 3D printing materials were originally developed for short-lived prototypes and models. They were not made to last several years. However, the requirements for the material's ageing stability can change drastically if a collector or a museum acquires a 3D printed object as piece of art or design. Then, as this article has shown, the preservation of 3D prints poses an extraordinary challenge.

Endnotes

(1) 3D printing is used as a generic term for all commonly so-called «generative manufacturing processes» which can be described as growing an object by applying and fusing material (e.g. liquid, filament or powder) layer by layer (Bonten 2003: 53 ff.). The term 3D printing must not be confused with inkjet powder printing (3DP).

(2) The thesis was written at the Conservation Department of the Berne University of the Arts in close contact with conservators, artists, designers, and technologists. The main goal was to enlarge the conservators' knowledge about the techniques of objects made by rapid technology and about the prospective ageing behaviour of some current materials in use. The term rapid technology is used to sum up rapid prototyping, rapid manufacturing, and rapid tooling.

(3) The high complexity of these materials is well documented in the patent literature, e.g. Pat. No. US 6,251,557 B1 «Photosensitive Resin Composition for Rapid Prototyping and a Process for the Manufacture of 3-Dimensional Objects» by Stephen Lapin and Michael Sullivan in 2001.

(4) See «Effects of Aging on Epoxy-Based Rapid Tooling Materials» by Xavier Ottemer and Jonathan Colton (2002, Center for Polymer Processing, Rapid Prototyping and Manufacturing, Institute and School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA, USA), «Effect of long-term ageing on the tensile properties of a polyamide 12 laser sintering material» by R.D. Goodridge and R. Hague (2010, in: *Polymer Testing*. No. 29/2010, p. 483-493), and «A study of the impact of short-term ageing on the mechanical properties of a stereolithography resin» by S. Mansour, M. Gilbert, and R. Hague (2007, in: *Materials Science and Engineering* A. No. 447/2007, p. 277-284).

(5) The complete experimental set-up including manufacturers, material descriptions, method of measuring, and evaluation in statistics is published in Madsack 2013: 60 f.

(6) «Printing Teddy Bears: A Technique for 3D Printing of Soft Interactive Objects» by Scott E. Hudson, Human-Computer Interaction Institute, Carnegie Mellon University and Disney Research Pittsburgh, 2014.

(7) http://www.preciousplastic.com/ (last seen 07.09.2014).

(8) See Pat. No. US 6,054,250 «High Temperature Perfomance Polymers for Stereolithography» by Eugene Sitzmann, Russell Anderson, Mathias Koljack, Julietta Cruz, and Chandra Srivastava in 2000.

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