

Hot Lithography - High precision 3D printing of flame retardant photopolymers for the electronics industry

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Introduction

Additive manufacturing (AM) has gained wide acceptance in R&D departments of companies in major industries (e.g., mobility, electronics, medical, aerospace, tooling) and their strategic initiatives towards industrial production solutions greatly contribute to the AM industry's recent upswing. Global sales of AM products and services showed double-digit growth rates from 1990 to 2020, highlighting this great potential. From the most prestigious AM industry annual report (Wohler's Report 2020¹), photopolymers (from resin-based 3D printing processes) occupy the most important class of materials in the AM market, accounting for more than 30% of total material-related sales. Above all, however, photopolymers are also already being used in AM-based industrial production (e.g., for personalized orthodontic splints or hearing aid shells), although here still exclusively as molded samples or for components subjected to little mechanical stress. The technical use of AM components primarily as a product development solution in the performance evaluation of later series parts represents the most promising entry of AM polymers into industrial part production, yet it cannot be successfully implemented at the present stage due to a lack of either i) part quality or ii) material performance of the available AM components.

Resin-based stereolithography (SLA), which can achieve very high surface quality ($R_a < 10 \mu\text{m}$), is an excellent candidate for the production of industrial-grade polymer components. SLA uses light-curable resin formulations that are cured layer-by-layer using either a laser or a digital projector, which allows polymers to be fabricated with excellent precision.²

However, the SLA materials currently available on the market are not particularly suited for industrial use as functional components, as they tend to exhibit brittle material behavior and are lacking the necessary functional properties (e.g., flame resistance, long term stability).

Cubicure GmbH developed and patented a new SLA process, Hot Lithography[®] (Figure 1). The concept behind it is to take advantage of a light-based SLA technology and provide solutions to the associated material obstacles. In order to introduce more functionality (e.g., toughness, heat deflection temperature, durability, flame resistance) to SLA materials, a number of parameters need to be addressed, but these changes typically lead to challenges related to processing of the respective resin formulations. Reducing the crosslink density of the photopolymer network via use of high molecular weight or oligomeric derivatives, introducing intermolecular forces into the resin backbone (e.g., urethane groups), or the option to process composites (e.g., organic or inorganic fillers), for example, are

strategies that have a positive impact on the final performance of the material, but have dramatic effects on the reactivity and resin viscosity of the light-curing systems.

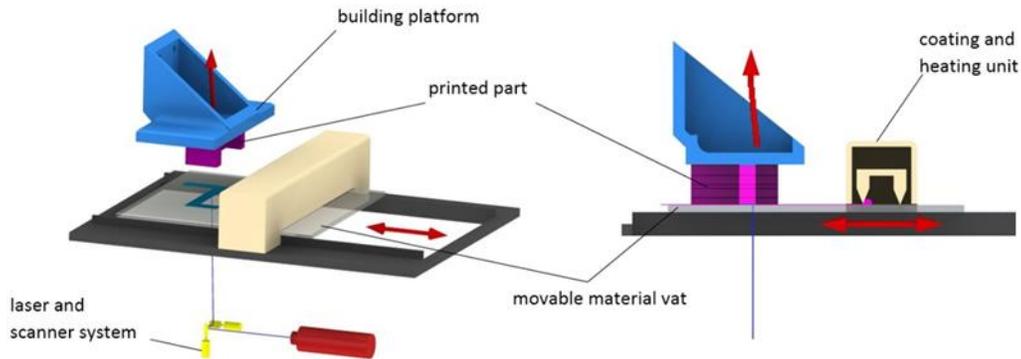


Figure 1: Hot Lithography set-up³

Resin optimizations that could lead to higher material performance (e.g., toughness or heat deflection temperature) and smoother processing (e.g., reduction of polymerization shrinkage) are severely limited in standard lithography-based AM technologies due to a rather narrow processing window (e.g., viscosities $< 2 \text{ Pa s}$ and processing temperatures $< 60 \text{ }^\circ\text{C}$). These limitations are overcome with Hot Lithography by enabling higher temperatures during the printing process (up to $120 \text{ }^\circ\text{C}$) and opening the process to higher resin viscosities (up to 20 Pa s at processing temperature). Thus, Hot Lithography offers unique opportunities for material development by dramatically expanding the processing window for new material solutions and 3D printable resin formulations (see Figure 2).

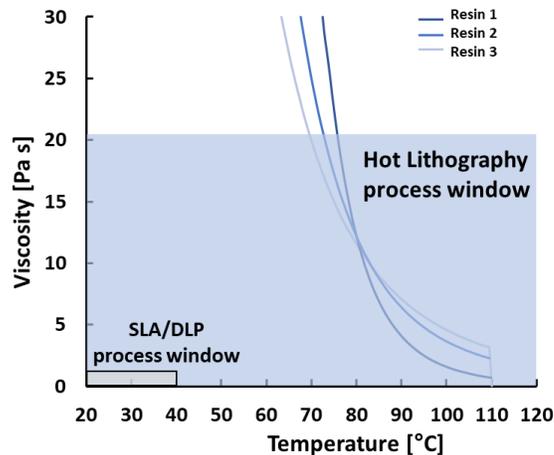


Figure 2: Process window for material development of photopolymers using Hot Lithography compared to state-of-the-art resin-based processes (e.g., stereolithography- SLA or digital light processing - DLP).

Thus, Hot Lithography makes it possible to develop functional AM photopolymers and, from them, AM components with high potential for industrial applications. This is ideally realized through a strong interaction between the AM process and material development. Already successfully developed tough AM photopolymers (e.g., combined tensile strength $> 40 \text{ MPa}$, elongation at break $> 15\%$ and heat deflection temperature $> 70 \text{ }^\circ\text{C}$) with additional high surface quality of the AM components (e.g., resolution of $10\text{-}50 \text{ }\mu\text{m}$ depending on laser spot and layer height, roughness $R_a < 10 \text{ }\mu\text{m}$) and additional key properties like flame resistance show the high potential of this AM technology (see Figure 3).

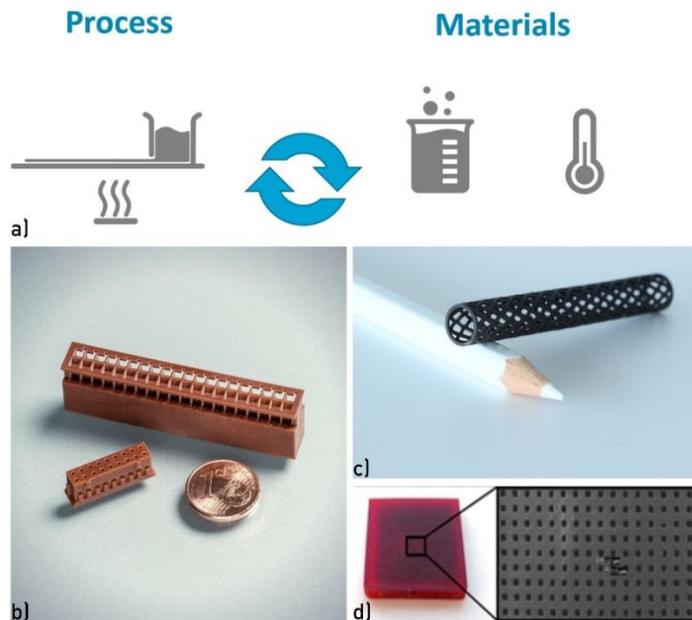


Figure 3: a) Hot Lithography - a platform with strong interaction between process and material development for industrial AM material solutions, b) flame retardant photopolymers made of Cubicure Resin Evolution FR (e. g., for electronic components), c) parts with high complexity made of Cubicure Resin Evolution, d) highest precision (e.g., micro screen with open channels $\approx 120 \mu\text{m}$) made of Cubicure Resin Precision SF.

Polymer part manufacturing for the electronics industry needs to support specific material performance, high manufacturing precision and surface quality. Clearly, lithography-based AM technologies (e.g., SLA, DLP) offer such critical performance characteristics yet available materials still fail to support industrial expectations. In this paper, methacrylate-based photopolymers with flame retardant additives are studied for their suitability to print flame retardant photopolymers via Hot Lithography.

Results and Discussion

Methacrylate-based photopolymers with flame retardant additives

Herein, the influence of flame retardant additives on the flammability and on the final (thermo)mechanical properties of 3D printed photopolymers are investigated. A base resin formulation (Matrix – resin formulation Evolution provided by Cubicure) together with five different flame retardant additives was studied. The flame retardant additives differed in their aggregate state and in their mode of action (FR1 – liquid phosphorous-based, FR2 – liquid, halogen-based, FR3 – liquid, oligomeric phosphorous-based, FR4 – solid, inorganic mineral filler, FR5 – solid, intumescent).

Flammability testing and (thermo)mechanical properties of flame retardant photopolymers

Photopolymers from the Matrix and from formulations with 10 and 20 wt% added flame retardant additives were molded in a UV-light chamber and subsequent horizontal burning tests were conducted

on the resulting rectangular photopolymers. The flame retardant properties were successfully improved by the liquid flame retardants FR1-3 already at 20 wt% contents (Table 1). Whereas the photopolymerized base resin (Matrix) and all samples containing 10 wt% flame retardant additives burned down completely in the horizontal burning test, the flame extinguished in the burning tests with respective photopolymers containing 20 wt% flame retardant additives. With the solid flame retardant additives FR4 and FR5 no significant reduction in flammability was detected for contents up to 20 wt%. All photopolymerized samples were also manually assessed with respect to their mechanical properties and a potential softening effect via the incorporation of flame retardant additives was recorded. The liquid, phosphorous-based FR1 showed significant softening, which is not desired in the final photopolymer and the liquid, halogen-based FR2 is not desired due to regulatory restrictions for such compounds. Thus, the liquid, oligomeric phosphorous-based FR3 overall showed the best performance with improved flame resistance, lower impact on mechanical properties and good stability and printability of the final resin.

Table 1: Horizontal burning test of the molded base resin (Matrix) and molded photopolymers with 10 or 20 wt% flame retardant additives FR1-3, respectively. * ... All samples burned down in vertical burning tests

Sample	Flame retardant additive	Concentration [wt%]	Softening effect [Y/~N]	Burning Time, horizontal [s]*
Matrix	-	-	-	> 70, burned down
FR1_10	liquid, phosphorous-based	10	Y	> 70, burned down
FR1_20	liquid phosphorous-based	20	Y	~ 50, extinguished
FR2_10	liquid, halogen-based	10	N	> 70, burned down
FR2_20	liquid, halogen-based	20	~	~ 35, extinguished
FR3_10	liquid, oligomeric phosphorous-based	10	~	> 70, burned down
FR3_20	liquid, oligomeric phosphorous-based	20	~	~ 70, extinguished

Subsequently, a combination of FR3 with the solid FRs (i.e., FR4 – solid, inorganic mineral filler, FR5 – solid, intumescent) was tested for potential synergistic effects. In the horizontal burning tests those photopolymers performed significantly better, thus vertical burning tests have also been performed. For the vertical burning tests, the photopolymer specimens were 3D printed from the prepared resin formulations. Synergistic effects could be detected with the liquid/solid combination FR3/FR5_20/20, which even passed the vertical burning tests performed in accordance with UL 94 with 3 mm thick samples (Table 2). This result is giving an indication that such a material concept could pass the industrially relevant UL 94 testing, which is a critical requirement for the electronics industry.

Table 2: Vertical burning test of the 3D printed base resin (Matrix) and molded photopolymers with 20 wt% flame retardant additives FR3-5 and combinations of FR3 with FR4 and FR5, respectively.

Sample	Flame retardant additive	Concentration [wt%]	Vertical burning test in accordance with UL94 [s]
Matrix	-	-	-
FR3_20	liquid, oligomeric phosphorous-based	20	No pass
FR4_20	solid, inorganic mineral filler	20	No pass
FR5_20	solid, intumescent	20	No pass
FR3/FR4_20/20	liquid, oligomeric phosphorous-based / solid, inorganic mineral filler	20/20	No pass
FR3/FR5_20/20	liquid, oligomeric phosphorous-based / solid, intumescent	20/20	Pass for 3mm

Additional to the vertical burning tests, tensile bars and specimens for the assessment of heat deflection temperature were 3D printed as well. Ensuing figures display the influence of the implemented flame retardant additives on the (thermo)mechanical properties of the resulting photopolymers. The green properties or “as printed” (see described softening effect in Table 1) were significantly reduced by all liquid flame retardant additives FR1-3. Thus, higher proportions of the liquid flame retardants were not feasible, since already at 20 wt% FR-content the final tensile strength after post-processing was reduced by > 20-60% and the Young’s modulus by > 40-80%, depending on the flame retardant additive. The heat deflection temperature was reduced by about 30-60%, and the elongation at break was increased by 50-70% (Figure 4).

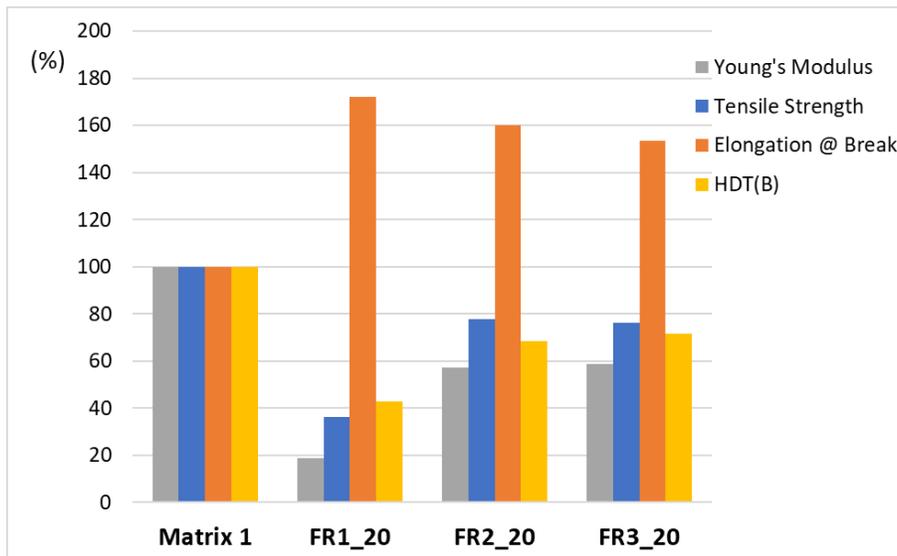


Figure 4: Influence of flame retardant additives on (thermo)mechanical properties with respect to Matrix 1. Matrix 1 neat and Matrix 1 with 20 wt% flame retardant additives, FR1-3_20 respectively.

The addition of the solids FR4 and FR5 in 20 wt% content, respectively together with 20 wt% FR3 resulted in a roughly 20% increase in heat deflection temperature, but the tensile properties were compromised significantly (Figure 5).

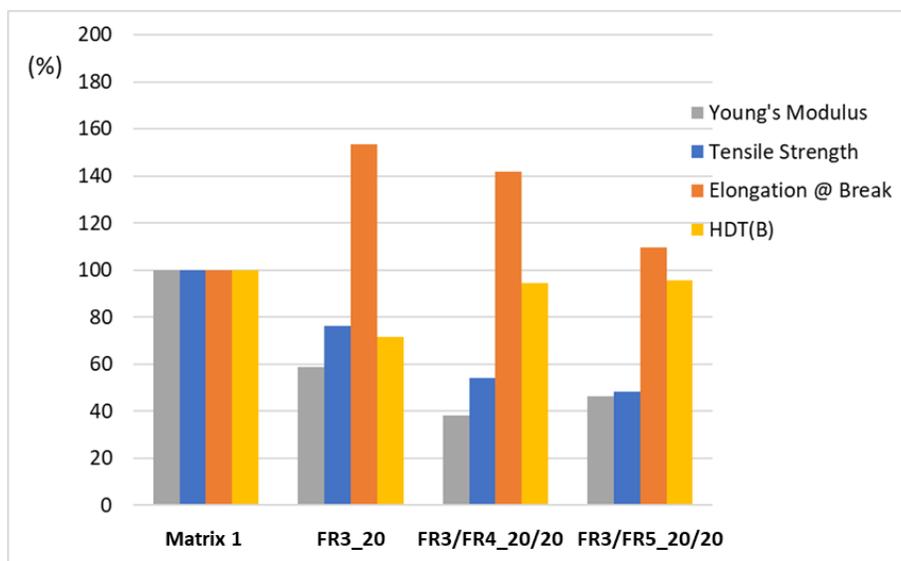


Figure 5: Influence of flame retardant (FR) additives on (thermo)mechanical properties. FR 3: liquid, oligomeric phosphorous-based; FR 4: solid, inorganic mineral filler; FR 5: solid, intumescent.

Materials and Methods

Methacrylate-based photopolymers with flame retardant additives

Formulations and sample preparation:

As base resin formulation, referenced as Matrix, the commercial resin Evolution provided by Cubicure was used. As flame retardant additives, established derivatives from the polymer industry were selected (i.e., FR1 – diphenyltolylphosphat, a liquid phosphorous-based derivative, FR2 – bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate, a liquid, halogen-based derivative, FR3 – a liquid, oligomeric phosphorous-based derivative, FR4 – aluminium hydroxide, a solid, inorganic mineral filler, FR5 – a solid, phosphorous-based intumescent derivative). All flame retardant additives were homogeneously mixed with the Matrix at 70 °C and in the respective contents by weight (e.g., 10 wt% FR3 for sample FR3_10). For the horizontal burning tests rectangular specimens with the measurements 25 x 4 x 2 mm³ were molded in a UV chamber from Uvitron International, Intelliray 600. The used electromagnetic energy ranged from visible to UV light from 250 – 600 nm with a light intensity of 178.8 mW cm⁻² (100%) and samples were cured for 2x5 min and flipped in between irradiation cycles.

3D Printing via Hot Lithography for preparation of (thermo)mechanical test specimens:

Specimens for the vertical burning test (125 x 12.7 x 3 mm³), the heat deflection temperature tests and tensile tests were printed from respective resin formulations on a commercial Caligma 200 printer by Cubicure with a layer height of 100 µm. The Caligma printer is set up with a 405 nm diode laser source. The laser beam is scanned over a 2-dimensional plane using a galvanometer scanning system. All parts that had direct contact with the formulation were heated to 60-80 °C; this includes the material vat, the building platform, and the recoating unit. The laser spot on the surface of the material vat has a diameter

of $\sim 18 \mu\text{m}$ (FWHM). The printed samples were post-processed by cleaning with isopropanol and ensuing thermal curing at $120 \text{ }^\circ\text{C}$ for 2 h and then $150 \text{ }^\circ\text{C}$ for 2 h in a Carbolite Gero LHT oven. Prior to (thermo)mechanical testing, all specimens were placed in a conditioning box for a minimum of 88 h at $23 \text{ }^\circ\text{C}$ and 50% relative humidity.

Horizontal and vertical burning tests:

For a first assessment on flammability the molded photopolymers were clamped horizontally and flamed with a lighter for 5 s. Then the time until the flame self-extinguished was detected or the photopolymers completely burned down (Figure 6). The vertical burning tests on the 3D printed specimens were performed in accordance with UL 94 standard at the LKT – Laboratorium für Kunststofftechnik GmbH in Vienna Austria.

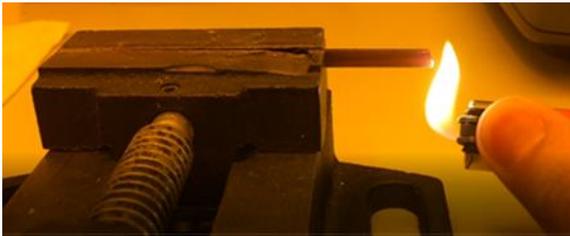


Figure 6: Set-up for the horizontal burning test.

Heat Deflection Temperature (HDT):

Heat Deflection Temperature (HDT) measurements were performed on an HDT/Vicat 3-300 standard. HDT(B) tests were performed according to DIN EN ISO 75. The sample specimens (with a rectangular geometry of $80 \times 10 \times 4 \text{ mm}^3$) were tested flatwise with a loading force of 0.45 MPa for HDT(B). The starting temperature for each measurement was set to $26 \text{ }^\circ\text{C}$ and the samples were subjected to the respective loading force for 5 min. Then, a temperature ramp of 120 K min^{-1} was performed.

Tensile Tests:

A ProLine Z010 TH material tester from Zwick/Roell was used for tensile tests of the 3D printed specimens. The test was performed according to DIN EN ISO 527-2 using 5A specimens. The Young's modulus was measured within 0.05-0.25% of elongation at a strain rate of 1 mm min^{-1} and then the measurement was continued with a strain rate of 10 mm min^{-1} . 5 specimens were tested per sample.

Conclusion

The investigated material strategy shows tremendous potential for the development of flame retardant photopolymers via Hot Lithography for the 3D printing industry. The results highlight, how flame resistance can be efficiently introduced into state-of-the-art methacrylate-based photopolymers for 3D printing by selection of industry-known flame retardant additives, yet detailed experiments for the elucidation of possible synergistic effects and careful selection of formulation components to compensate for possible negative effects on printability and (thermo)mechanical performance need to be taken into consideration. Specifically, the Hot Lithography technology was implemented giving rise to i) unique performance photopolymers (e.g., materials with UL 94 V0 classification) and ii) industrially relevant production throughput & quality (e.g., Cerion production plant), thus enabling flexible production of functional AM-parts optimized for the electronics industry.

Acknowledgements

The authors gratefully acknowledge the financial support by the Austrian Research Promotion Agency (FFG, within the projects “3D HiPerPolymers” - number 874202 and “Polyflame” – number 870576).

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