

Powder Bed Fusion of Polymers with Ultraviolet Light Emitting Diode Energy Sources

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Abstract

Powder bed 3D printing of polymers often uses broadband near-infrared (NIR) emitters and selectively printed fusing agents with absorption spectrum matching the emission of selected IR energy source. However, due to few available NIR absorbers that can be formulated into printable agent, printed 3D parts often have limited application due to regulatory concerns or unwanted color. Shifting the emitter's spectrum to a narrow, near-ultraviolet band (wavelength > 350 nm) can provide more absorber candidates while minimizing the potential UV-induced damage. Choice of the printable absorber span from inorganic metal oxides (TiO₂, ZnO, CeO, etc.) to organic absorbers that may include commercial UV absorbing ingredients used in paints, vitamins, food derivatives, cosmetic and pharmaceutical components. Some absorbers, being colorless or white, enable printing parts with the original polymer powder color or white base for desired coloring of the printed objects.

Introduction

Powder Bed Fusion 3D polymer printing relies on the selective fusing/melting of the powder's surface layer while printing stack of layers to form the desired 3D object. In one version of this process, printing is achieved by irradiating the entire surface of the bed with near-infrared (NIR) sources, and selectively depositing a fusing agent ink consisting of strongly absorbing moieties within the emitted spectral range [1-3]. Thus, the region where fusing agent is present heats more rapidly compared to the surrounding ink-free areas. In fact, sufficient overlap between the emission spectrum of energy emitter and absorption spectrum of the fusing agent is one of the key requirements of an effective polymer printing.

The described printing process commonly uses high-power, low-cost halogen lamps as energy sources emitting mostly in the NIR and visible ranges. Unfortunately, the number of absorbers with good absorption-to-emission match to halogen lamps and suitable for ink formulation is limited. Most of them are inorganic particles used in pigmented inks with limited absorber concentrations. They often have broad absorption spectra extending into the visible range and producing printed parts with an unattractive grey appearance. These absorbers can be further limited by their potential environmental impact, regulatory limitations, or toxicity [4,5]. Selected metal oxides and carbon black are the best-known examples of NIR absorbing ink (Figure 1).

Polymer powder NIR absorption may be another challenge. Print selectivity requires that ink-free powder area absorbs significantly less irradiated energy than the ink coated powder. Excessive absorption of NIR energy and consequently heating of the ink-free polymer powder (Figure 1) may limit the quality of the printed parts. This challenge can be addressed by applying the second printed agent that selectively reduces powder heating (e.g., "detailing agent" used in the HP Multi Jet Fusion) but at an added cost [3].

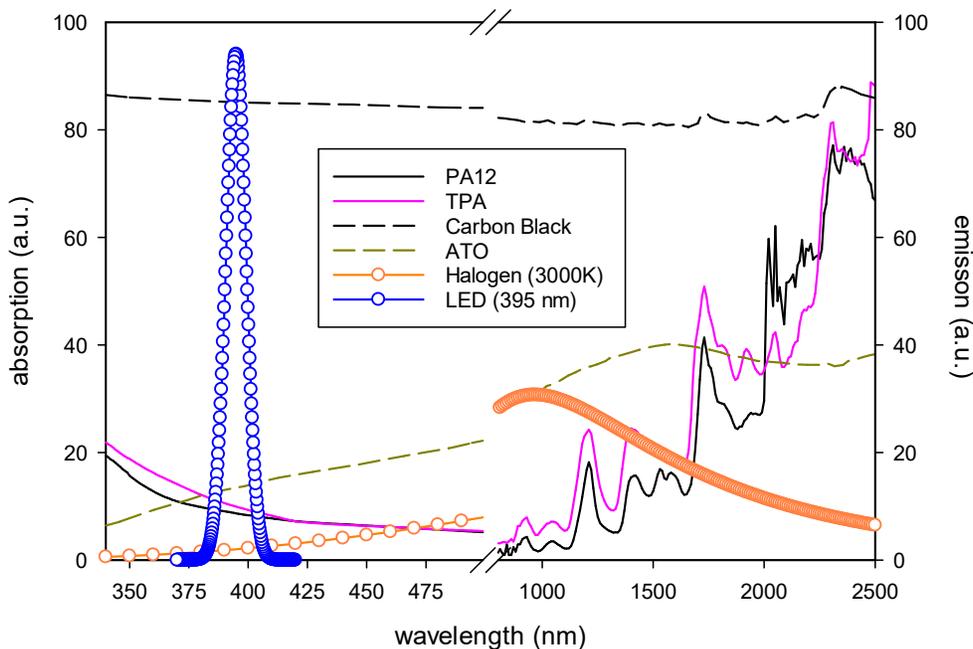


Figure 1. Absorption of selected polymers and fusing agents, and emission of radiative energy source used in present experiment. ATO (Sb-Sn oxide) is an example of metal oxide NIR absorber. Halogen lamp emission was approximated with 3000K black-body radiation. Left vertical axis refers to the absorbers while right axis describes the emitters. For further details – see the supplemental plot below.

Described difficulties can be resolved by shifting the energy source emission to a spectral range where significantly larger number of absorbers becomes available. Some of them may provide pleasing printed color, while others may be colorless, white, or matching the color of polymer powder and, thus, providing an opportunity for further coloring of the printed object with help of a colorant ink printed in parallel with the absorber. A multitude of the absorber candidates provides an opportunity for finding the ones satisfying even the most demanding, product-specific regulatory requirements like, for example, biocompatibility, lack of allergens, allowed skin contact, and food packaging applications.

Shifting the source emission to visible may increase the number of available fusing agents, including common CMY colorants. Prospective sources may include broad-range, high power incandescent and gas discharge lamps, or narrow band arrays of visible lasers and light emitting diodes (LED). However, source emitting the visible radiation implies that the absorber also needs to be visible and have color that may exclude some of the potential applications. It is further shown that shifting the 3D print process into UV may provide an even larger variety of fusing moieties, mostly organic, with high UV absorption due to the rich spectrum of UV driven electronic transitions available in these molecules.

Choice of UV source

Although moving emission deep into UV increases both number of available absorbers and their absorption, care is needed to avoid damage to the polymer material. UV irradiation may cause irreversible changes of the polymer structure. Polymer's damage may scale with the duration of UV exposure and UV photon's energy, and the extended exposure may limit recyclability of the powder and cause damage to material properties of the printed part. Therefore, choice of the UV source needs to be limited to the low-energy end of UV range, where damage is either non-existent or negligible [6,7]. In the present work, UV radiation was selected from the near-UV range (NUV) between 360 nm and 400 nm.

UV heating of polymer powder depends on the intrinsic absorption and concentration of fusing moieties, and on the dose of irradiated energy equal to the product of UV exposure time and irradiation intensity. For the majority of UV absorbers used in this work, and for the UV exposure time limited by desired print cycle time (below few seconds for most applications), the required irradiation intensity needs to exceed 10 to 15 W/cm² uniformly distributed over the entire powder bed.

An array of semiconductor lasers or light emitting diodes (LEDs) is the preferred choice for UV source. Both emit in a narrow spectral range and the emission peak can be selected to match the maximum of fusing agent's absorption. Appropriate UV arrays are commercially available in form of UV lamps with customer-defined formfactors matching the design of the printing system. Since both UV laser and LED arrays can deliver energy sufficient for UV printing, an LED solution may be preferred due to lower cost and less stringent operation requirements. Interestingly, due to the limitation imposed by the electronic nature of available semiconductor devices, the highest intensity UV radiation is achieved for the devices emitting at above 360 nm, which matches the spectral range where polymer damage is minimal.



Figure 2. Proposed UV source – print carriage configurations that can be used in the printer.

Installation of UV source in the printer may follow design used for NIR sources (Figure 2). Mounting the array close to the powder's surface may be preferred due to relatively large divergence of the LED emission. Local irradiation non-uniformities and overall lowering of beam intensity may occur when the LED lamp is placed too far from the bed. This problem can be corrected with the right optics but at a higher overall cost of the UV source.

Choice of UV absorbers

The first step in UV agent selection was to screen for absorbers with a good match to the emission spectra of the available UV source(s). It is not necessary to exactly align the LED peak emission with the maximum absorption (Figure 3). Due to broad absorption peaks of organic

fusing agents and intense LED emission even partial overlap may be sufficient to heat and melt the polymer powder at high irradiation intensities. In addition, choice of the UV agent needs to follow targeted product requirements. For example, a white printed object requires that fusing agent must be colorless or needs to match the white-colored polymer powder. In some cases, UV fusing agent may need to satisfy stringent regulatory requirements. In others, targeted print product may impose limitation on selection of the fusing agent; for example, it may need to belong to a specific group of products (e.g., a natural product), or it may need to have a required color or surface smoothness without added processing. In another example, the possibility that some UV fusing agents may interact with the incoming UV radiation and become chemically active needs to be considered.

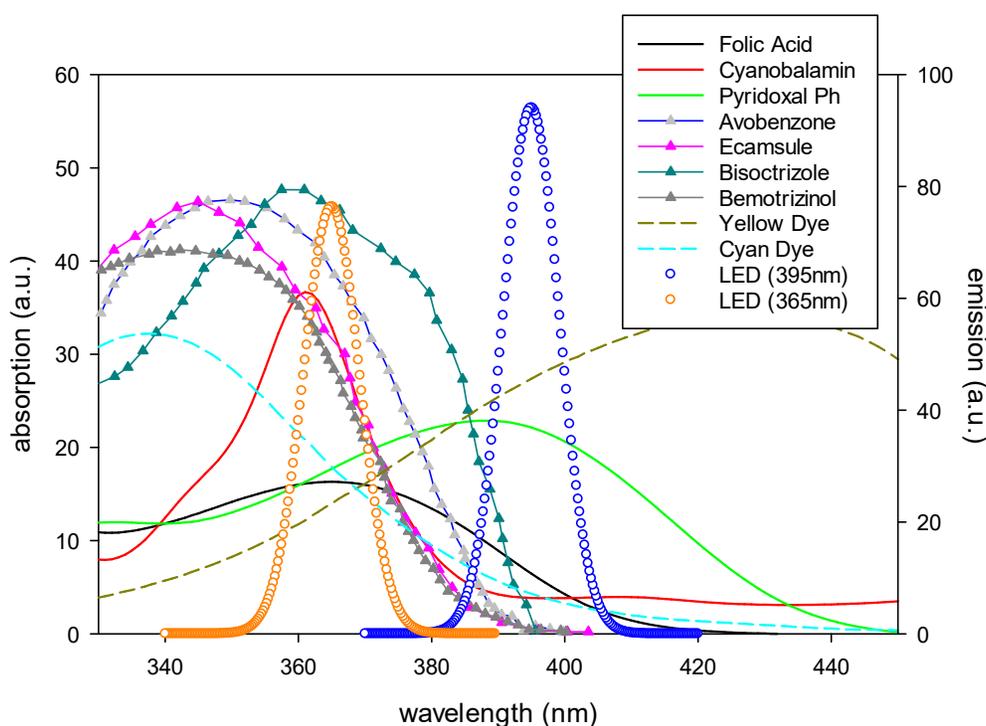


Figure 3. Absorption of selected UV fusing agents (three groups: (1) different forms of vitamin B, (2) UV screens used in cosmetics, and (3) selected CMYK dyes exhibiting NUV absorption, and UV LED sources use in the experiment (365 nm and 395 nm – their different intensities reflect intrinsically weaker emission of shorter wavelength LEDs). Stronger overlap between the absorption and emission curves shows better UV heating. Absorption spectra obtained using aqueous dilution of respective UV absorbing moieties.

In the next step, a reliable fusing agent ink formulation process was developed. This work focused on formulating aqueous inks compatible with HP thermal jet printing. Newly formulated inks were evaluated in a test setup where a thin layer of powder was spread, an ink pattern was printed, and exposed to UV radiation. The solid printed coupons were then evaluated for strength and overall appearance. Finally, the multilayer test structures were printed using the best

performing inks. Polymer powders used in the experiments included: nylons (PA11, PA12), thermoplastic polyamide elastomer (TPA), thermoplastic polyurethane (TPU) which could not be printed due to the high NUV absorption and resulting poor selectivity, and polypropylene (PP). Attempts to print PA12 with added TiO₂ (to improve powder's color) were unsuccessful due excessive UV absorption by the powder (Figure 1). Figure 4 shows examples of printed test coupons.

Table 1. UV absorbers

Category	UV absorbers	Aqueous ink type / max absorber concentration	Comment
Metal oxides	TiO ₂ , ZnO, CeO ₂	Pigment / < 10%	White. Photocatalytic behavior degrading polymer. May require dedicated antioxidant
Carbon black	Carbon black	Pigment / < 5%	Black. Commercial ink.
Colored inks	Yellow colorant, grey color mixture	Dye / < 5%	Commercial color inks. Yellow and Cyan exhibit strong UV absorption
Vitamin B (various forms)	Cyanobalamin, Folic Acid, Riboflavin, Pyridoxal Phosphate, Pyridoxal HCl, Pyridoxine HCl	Dye / < 3%, concentration depends on the vitamin type	Mostly colorless, some are colored
Food derivatives	Curcumin, ground coffee, beta-carotene, and lycopene in carrot juice.	Dye or pigment / < 4%	Colored. Coffee – finely ground and dispersed in ink vehicle
Ag metallic ink	Ag nanoparticles	Pigment / < 2%	Black. Absorption due to surface plasmon resonance
Fluorescent dye	Pyranine	Dye / < 2%	Colored. Commercial product
UV sunscreen used in cosmetics	Ecamsule, Avobenzones, Phenolic Benzotriazole (Bisotrizole, Octrizole), Benzophenone derivatives (Oxybenzone, Sulisobenzone, Dioxybenzone), Bemotrizinol	Dye or pigment / < 4%	White or colorless. UV-A absorbers selected due to UV range limitation.
Commercial UV absorbers	Tinuvin, Tinosorb, Parsol, Meroxyl, Hostain, Uvinul	Dye or pigment / < 4%	Commercial names are listed.

Table 1 lists selected UV fusing agent candidates evaluated in this study. They are grouped into several categories depending on the specific product demands. It is worth noting that UV printing was achieved even for some “exotic” absorbers originating from natural products (vitamins, food products). Commercial UV absorbers are a separate group of candidates likely employable for a large-scale UV printing. All listed absorbers were formulated into Thermal Ink Jet aqueous inks and printing was done using either 365nm or 395nm UV LED lamps irradiating the powder’s surface for about 0.5 to 1.5 seconds.

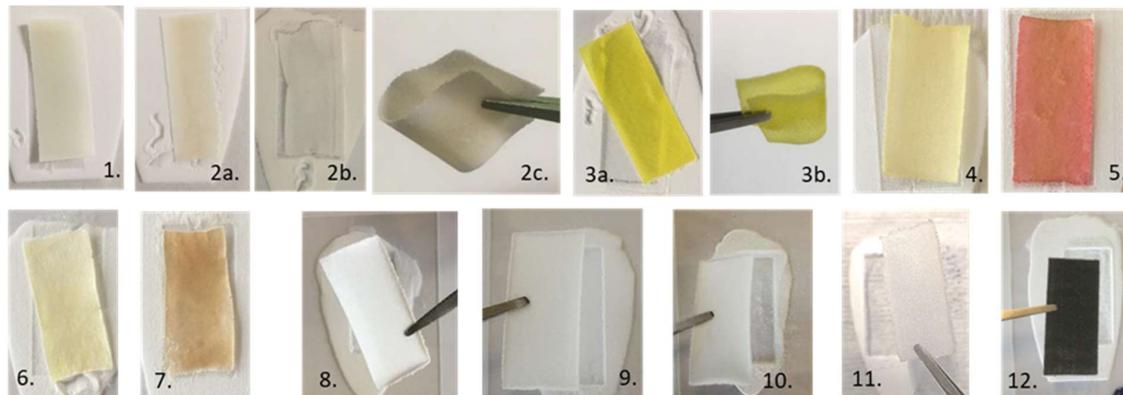


Figure 4. Examples of printed test coupons with the following UV fusing agents: 1. ZnO, 2a. TiO₂ – visible darkening due to photocatalytic reaction, 2b. and 2c. TiO₂ – photocatalytic darkening suppressed with antioxidant, 3a. and 3b. - Common yellow dye, 4. Folic acid, 5. Cyanobalamin, 6. Curkumin, 7. Ground coffee beans, 8. Octrizole, 9. Bisoctrizole, 10. Bemotrizinol, 11. Ecamsule, 12. Carbon Black.

UV absorption by polymer powders

The ratio of energy absorbed within the ink-coated region and outside of this area can be used as a measure of print selectivity. Low absorption of the polymers within the NUV range (Figure 1) suggests better selectivity when using UV irradiation rather than NIR energy source. However, a large temperature difference between the fused powder area and surrounding ink-free region may also cause potential problems due to thermal stresses deforming the fused region and interrupting printing of subsequent layers. This difficulty can be resolved by printing a narrow “low-stress” band of low concentration UV absorber surrounding the fused, high absorber concentration regions, as shown in Figure 5. Powder from the band region can be recycled with the remaining powder when the selected fusing agent is colorless and kept at a low concentration within the band. In addition, distribution of the UV fusing agent within the “stress band” can be designed to suppress the stresses while minimizing agent’s content.

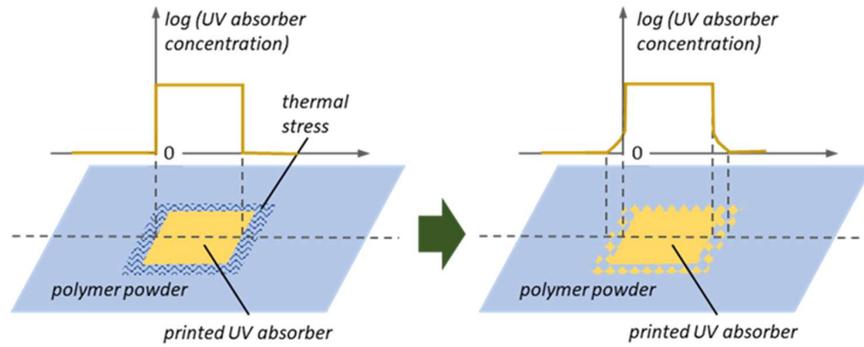


Figure 5. Printing low-concentration band of colorless UV absorber around the edges of fused region reduces thermal stresses.

Printed objects - examples

Figure 6 presents results of the multiple mechanical tests of selected UV printed objects. Comparable results were obtained for several fusing agents qualified for multiple layers printing. Measured mechanical performance equal to, and occasionally exceeds data reported for commercially printed parts of the same polymers.

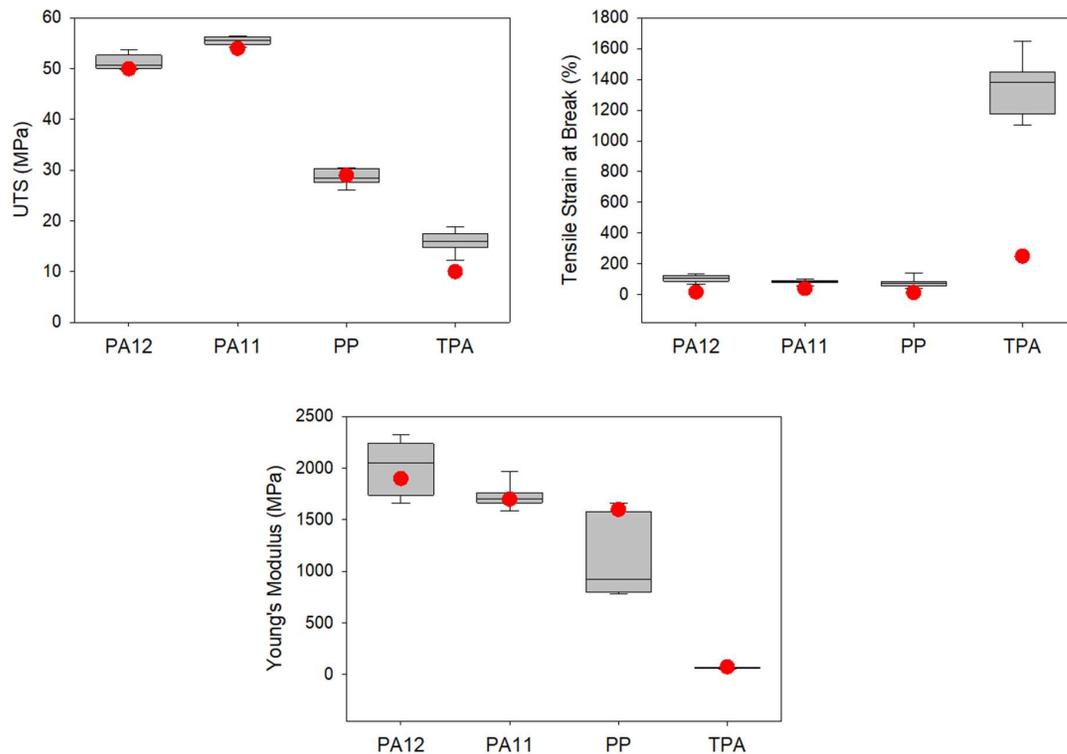


Figure 6. Mechanical properties of PA12, PA11, PP, and TPA white parts printed using Bemotrizinol fusing agent. Red dots represent published commercial values [8].

Examples of printed objects in Figure 7 show the color printing abilities of the UV process. Intentional color printing using standard CMYK inks may not only deliver desired color effects but also expand the color gamut presently available in 3D printing. It is worth noticing that fusing with colorless ink may enable printing translucent objects of selected polymers, as shown in Figure 7.

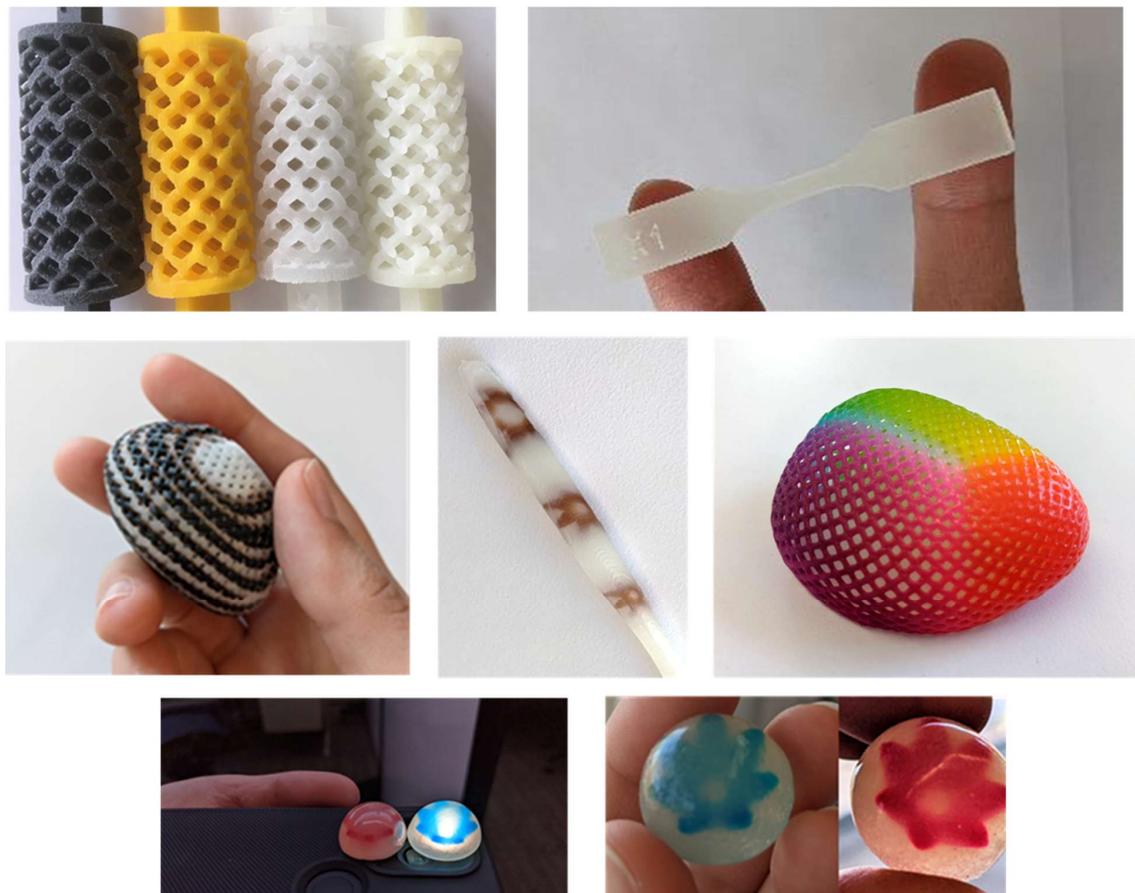


Figure 7. Examples of UV printed objects using either PA12 or TPA polymer powders.

Smooth printed surface

Figure 8 shows yet another application of the printable UV absorber. Polymer parts printed using the described Powder Bed process often exhibit large surface roughness caused by incompletely melted particles embedded into the surface, and they may require additional post-print treatment reducing surface's roughness to an acceptable level. This challenge can be reduced by coating the surface with transparent UV absorbing ink and exposing it to a brief UV radiation after the printing is completed (limited to the top surface when employing it as the last printing step; or coating the entire surface after the printed object is removed from the powder bed). A large concentration of surface UV absorbers can accelerate heating of the thin surface layer, melt the

residual embedded particles, and reduce surface roughness without impacting the sub-surface region of the printed object.

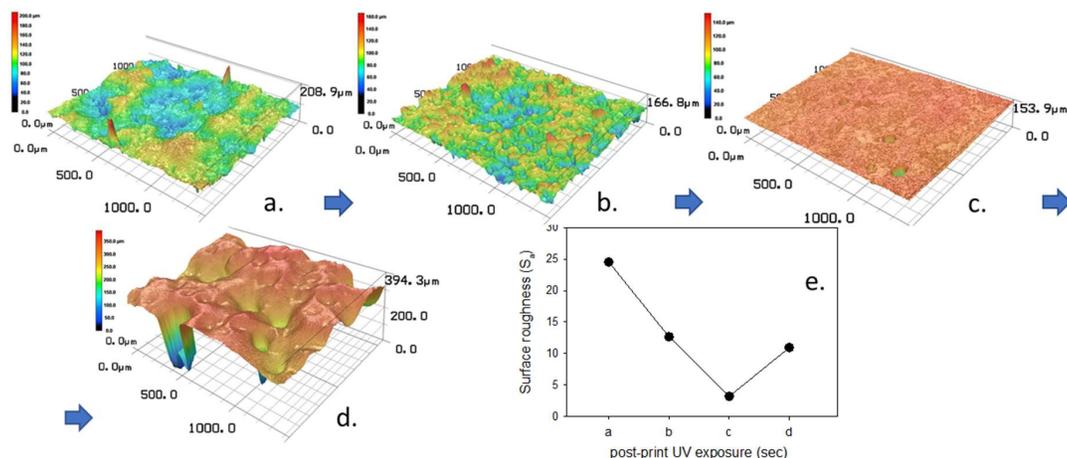


Figure 8. Surface roughness S_a (arithmetical mean average – mapped with Keyence VK-2000 laser profiler) of 3D printed flat PA12 object, and then coated with transparent UV absorbing agent and exposed to post-print UV radiation ($UV=395\text{ nm}, 14\text{ W/cm}^2$). Post-print UV exposure time: (a) 0 sec (immediately after printing), (b) = 0.4 sec, (c) 0.8 sec, (d) 2.0 sec, (e) shows evolution of the surface roughness as a function of UV exposure time. At first (b), UV induced heating of the surface layer causes surface coarsening (surface protrusions become larger but fewer initially decreasing the S_a roughness). With continuing heating/melting (c), surface roughness reaches the minimum. Further heating (d) increases thickness of the molten surface film and starts random convection-driven liquid movement resulting in large variation in surface topography after the layer is frozen upon UV termination.

Summary

Use of UV emitting non-coherent narrow-band radiative energy source in Powder Bed 3D printing process opens the possibility of employing a new set of printable absorbers providing the selective fusion of polymer powder. Several of the new UV absorbers are inorganic, but majority of them are organic moieties with strong UV absorption driven by molecular electronic transitions matching the UV photon energy. Due to their low cost, limited operation requirements, sufficiently high radiation density, and flexible formfactor design, LED arrays are the preferred UV energy source. However, due to potential UV-induced damage to polymer material, choice of the UV source is limited to narrow NUV range of 360 nm to 400 nm. Colorless fusing agent enables printing of white and translucent parts, and a broad gamut of colors provided by additional CMYK inks printed in parallel with the UV fusing agent.

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Supplemental Plot: Comparison of absorption and emission curves.

