Photothermal Bleaching of Nickel Dithiolene for Bright Multi-colored 3D Printed Parts

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Article

Keywords:

Posted Date: March 22nd, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1451277/v1

Version of Record: A version of this preprint was published at Nature Communications on February 3rd, 2023. See the published version at https://doi.org/10.1038/s41467-022-35195-4.

Abstract

HP's Multi Jet Fusion (MJF) 3D printing technology utilizes a carbon-based radiation absorber called the "fusing agent" in combination with a near infrared (NIR) light source to facilitate the fusion of polymer powder in a layer-by-layer fashion to generate 3D parts. Most available carbon-based and NIR radiation absorbers have an intrinsic dark color, which as a result will only produce black/gray and dark colored parts. To create white and bright colored parts with MJF, a visibly transparent and colorless radiation absorber is required. In this paper, we designed an activating fusing agent (AFA) that contains a red, strong NIR absorbing dye that can become colorless after harvesting irradiation energy during the MJF 3D printing process. Such a method will not only enable MJF 3D printing of white objects with good performance, but also provide a bright colored part when working with other color agents.

Introduction

3D printing is an advanced manufacturing method that fabricates parts through the conversion of 3D computer aided design (CAD) models into functional objects in a layer-by-layer method[1]. 3D printing offers the ability to produce parts rapidly, at low cost, short runs, and one-of-a-kind[2].

HP's Multi Jet Fusion (MJF) 3D printing technology is a powder bed fusion (PBF) technology that offers speed, quality, strength, and novel functionalities along with the unique ability to produce parts with controllable physical and functional properties on the voxel level within a part[3]. As shown in Fig. 1, MJF 3D printing technology requires the selective jetting of fusing agent containing radiation absorber (NIR material like carbon black) into areas where polymer powder particles will be fused and detailing agent, into areas where the fusing action will be reduced, or into part boundaries to produce sharp and smooth edges. The fusing agent absorbs radiation from the infrared lamps, transferring the light energy to thermal energy and melting the powder particles together in the patterned area. Detailing agent is required in order to avoid thermal bleed by providing evaporative cooling on the edges of parts.

The powder bed is exposed to a fusing energy source (infrared lamps). Selected areas wherein the fusing agent has been deposited by the printheads are fused layer-by-layer to form the 3D part. Parts generated by MJF are black or gray because of the carbon black based fusing agent. To print white and brightly colored parts with the current MJF system, a NIR transparent fusing agent is required. Most available NIR dyes are colored, plagued with poor thermal properties, and have poor stability in aqueous solutions[4].

In this paper, we present a method that enables printing white or intrinsic-colored 3D objects using an activating fusing agent (AFA) that contains a NIR absorbing dye that is red when printed and after harvesting irradiation energy is then bleached during the 3D printing process. AFA is a thermal ink jet formulation containing nickel bis(dithiolene) as the active NIR absorbing material. Nickel bis(dithiolene) complexes are important NIR dyes because of their unique properties, such as photostability, air-stability, thermal stability, intense absorption in the NIR region, easy adjustment of the absorption range with polar solvents, and high electron mobility[5]. These unique properties have enabled their application in thermal imaging, photography, lithography, Q-switch absorber of a laser, optical switching, and antioxidant for polymers[6,7].

Nickel bis(dithiolene) complexes of the general structure shown in Fig. 2 exhibit strong absorption in the 600 to 1600 nm region of the spectrum and are highly soluble in nonpolar solvents like (toluene and chloroform). The strong NIR absorption observed in nickel dithiolene is because of the electron delocalization about the dithiolene ring and the interaction of the delocalized electrons with the empty d-orbitals of the metal center[8].

Methods And Materials

Solvent and Reagents

All chemicals were purchased from Sigma-Aldrich and were used as received unless otherwise stated. Nickel Dithiolene was purchased form Luminochem Budapest Hungary with particle size distribution d_{90} ≤ 50 µm, absorptivity in chloroform 30 L g^{-1} cm^{-1}, absorption region λ = 820–950 nm see Fig. 6

Thermal Inkjet testing

Inkjet-ability was tested using HP internal testing systems for microscopic drop imaging. Figure 3 shows no deflection of drops or solid buildup on the nozzle plate during firing. An elongated column of ink breaks into distinct spherical drops, with a large head and a few smaller satellites. Drop weight and drop ejection velocity ranges between 2–50 nanograms and 5–15 m/sec respectively for thermal inkjet print heads. Our ink formulation performs within the range.

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Polymer Material

All the studies in this paper were conducted using HP 3D high reusability PA12 and HP 3D high reusability PA11 from HP Inc, Palo Alto, CA, USA. The properties of this PA12 and PA11 can be found in Table 1 below.

Table 1
Properties of PA12 powder

Material	Bulk Density (g/cm^3)	Average particle size (µm)	Melting Point (°C)
PA12	0.42	60	187
PA11	0.48	54	202

3D Printing

All printing in this work was performed using an internal advanced MJF print testbed, with the additional capability of printing more than two agents[9]. The production print process includes warming layers, 3D part printing layers, post printing layers, and safety cooling. By the time the build unit is ready to disconnect, the AFA has been at 150^{o}C for the required time to bleach the color from high irradiation absorbing red to colorless. The extracted parts are then sandblasted in a Powershot C (DyeMansion North America Inc., Austin TX, USA) for 15–20 minutes to remove most of the unmolten surface powder.

Mechanical testing

Type V dogbone samples were printed for testing according to the ASTM D638 standard. Tensile tests were performed on these samples using a Lloyd LRX single column testing system (Segensworth East Fareham, Hants, UK) with manual grips and 5kN load cell. A grip separation of 30mm and strain rate of 3mm/min were used. An Epsilon axial extensometer – model 3542 (Jackson, WY, USA) with 10mm gauge length was used for measuring strain.

Density Measurements

The density of Type V dogbone samples were measured using a Mettler Toledo XS205 Dual Range Balance using the Archimedes principle. Room temperature water was used as the auxiliary liquid for buoyancy measurements.

UV-Vis Measurements

UV-Vis spectra were recorded using a Varian Cary 6000i UV-Vis-NIR spectrophotometer with short-wave infrared (SWIR) 800–1800 nm range as well as the UV-visible 175 to 800 nm. Using narrow-band InGaAs detection and a 600 lines-per-mm diffraction grating for improved SWIR sensitivity. The samples were dissolved in chloroform or 2-pyrrolidone at 0.0001%

FTIR Measurement

Infrared measurements were performed on a Thermo Scientific NicoLET iS50 FTIR spectrometer (Waltham, MA, USA) from 3500 to 1000 cm-1 using an ATR diamond crystal.

Result And Discussion

Here, we use nickel dithiolene as the active NIR material in the fusing agent because of its unique properties, and its ability to react with polar solvents containing a tert-amine (DMF, and N-methyl-2-pyrrolidone) which reduces it via electron transfer reaction, and converts it into the mono or dianionic form[10,11] (M(RCSCSR)2-z, z = 1 or 2) as seen in Fig. 4.

The solubility and position of the absorption maximum of nickel bis(dithiolene) complexes is dependent on the solvent polarity and the nature of functional groups attached to the ligand. The reduction is accompanied by a shift in the absorption further into the near-IR region, with up to a 94 nm shift when the solvent is changed from toluene to DMF[12]. A color change of the metal complex from green to red is observed upon reduction[6]. The color of the metal complex solution indicates the oxidation state of the bis(dithiolene) ligand.

Ink Formulation

The agent formulation contained 1 wt % green nickel dithiolene powder, which was reduced to the red state by heating at 100^{o}C for 10 min in a reducing solution, either a thiol or a hindered secondary amine dissolved in 2-pyrrolidone.

After all the green powder was completely reduced to the red state, the stock solution was combined with HP's proprietary ink vehicle to generate a thermal ink jet compatible formulation. The red state can further be reduced to colorless as shown in Fig. 5 by increasing the concentration of the reducing solution and/or heat, depending on the concentration of reduced nickel dithiolene in the solution. A shift in the near-IR peak from 855 nm in the green state to 905 nm the red state was observed, followed by a complete disappearance of the IR peak when the red form is completely reduced to the colorless form see Fig. 6.

The red state can undergo a reversible oxidation to the green state when an oxidizing solvent like water or acetone is added. The colorless state is irreversible. The ink formulation is kept in the red state without oxidizing back to the green state or further reducing to the colorless state by carefully balancing HP's proprietary ink vehicle to keep the amount of water in the formulation at 25%, and still ensure proper thermal ink jetting. This balance is disrupted in our MJF printing process where the red agent is printed, harvests energy to fuse the build polymer powder into a layer of the 3D part, and then reduced to the colorless form after being exposed to 150 ^{o}C for a specific amount of time.

Ink testing and jetting performance

The ink formulation was tested for jetting performance before transferring it to the agent delivery system in our advanced MJF-based testbed to print parts. Figure 3 shows jetting performance on a drop imaging machine using the same printheads used in the 3D printer. Drop imaging shows good performance with most of the ejected material in the leading portion, and the minority in the tail that follows.

3D Printing

The inkjet ink containing 1wt% of the dye was printed to form parts with 0.1 wt% of the dye level ranging from 2–6 picolitre/600 dpi to the desired area that defines the layer of the corresponding 3D object. A halogen lamp with power between 500-750W and color temperature between 2700-3400K was then used as the light energy source to completely fuse the imaged areas with a 20–30 ips fusing speed, after fusing, the residual heat of the build bed allowed the polyamide-12 to further reduce the red form of the nickel dithiolene in the ink to the colorless form, producing a white part having the native color of the powder. When AFA is used with other color inks, the fused area will show the assigned colors see parts in Fig. 7.

Table 2
Mechanical properties of Z- orientation PA12 dogbones printed with AFA

	UTS (MPa)	Elongation (%)	Density (g/cc)
Dog Bone 1	44	24	1.00
Dog Bone 2	44	21	1.01
Dog Bone 3	43	26	1.01
Dog Bone 4	46	38	1.00

Summary

Nickel Dithiolene based near IR materials can be reduced in the presence of common reducing agents like tert-amine (DMF, and N-methyl-2-pyrrolidone via electron transfer reaction into the mono or dianionic form. The reduction of the dye allows formulation into a thermal ink jettable ink. The ink was utilized as a photothermal radiation absorber fusing agent in powder-based 3D printing. After absorbing energy turning into heat, the red color bleaches and turns colorless to generate white and colored parts when used in combination with other colored agents.

Declarations

Author Contributions

All authors contribute equally to the research

Materials and Correspondence

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Figures

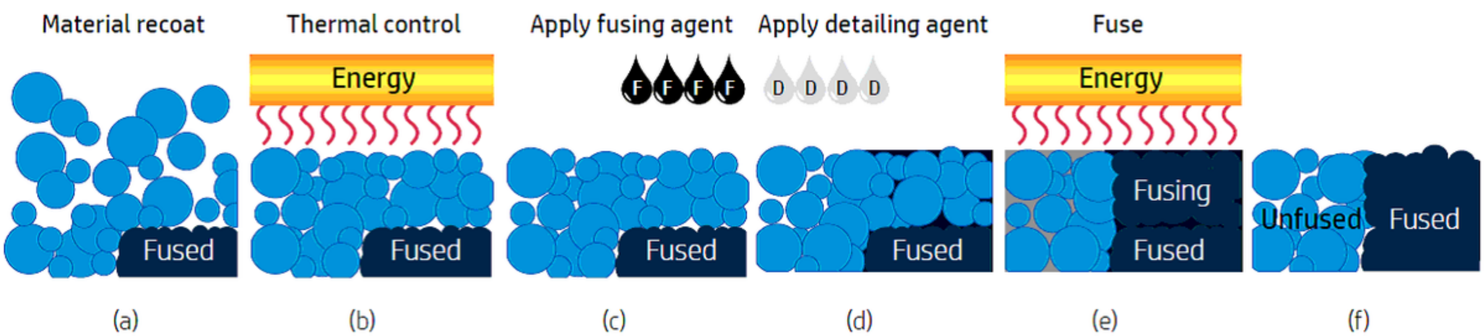

Figure 1

Diagram of additively manufacturing a part using HP MJF technology

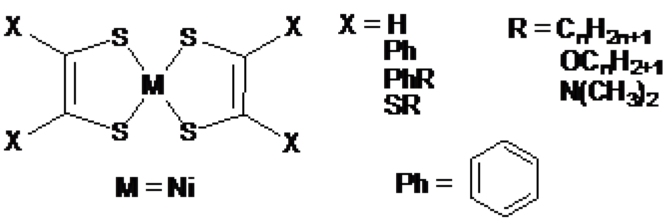

Figure 2

General structure of nickel bis(dithiolene) complex

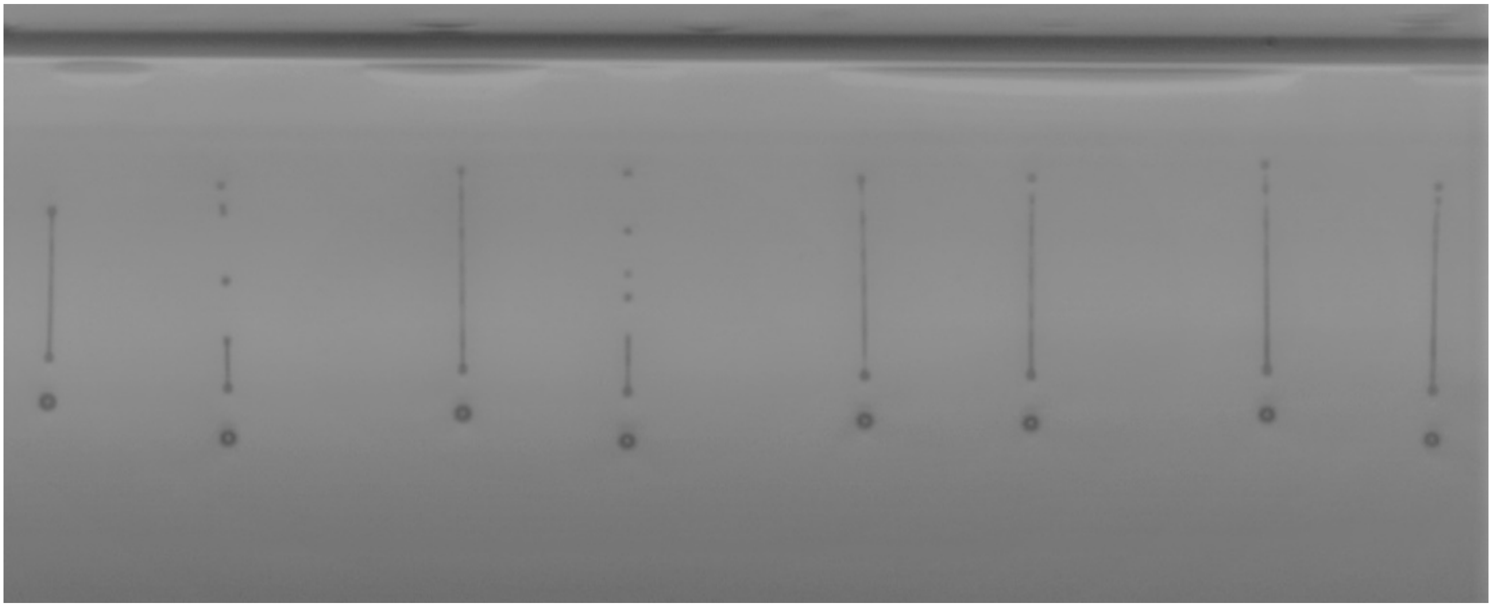

Figure 3

Image of drops-in-flight

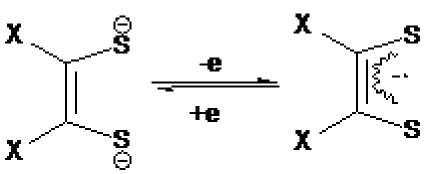

Figure 4

Redox reaction of nickel dithiolene

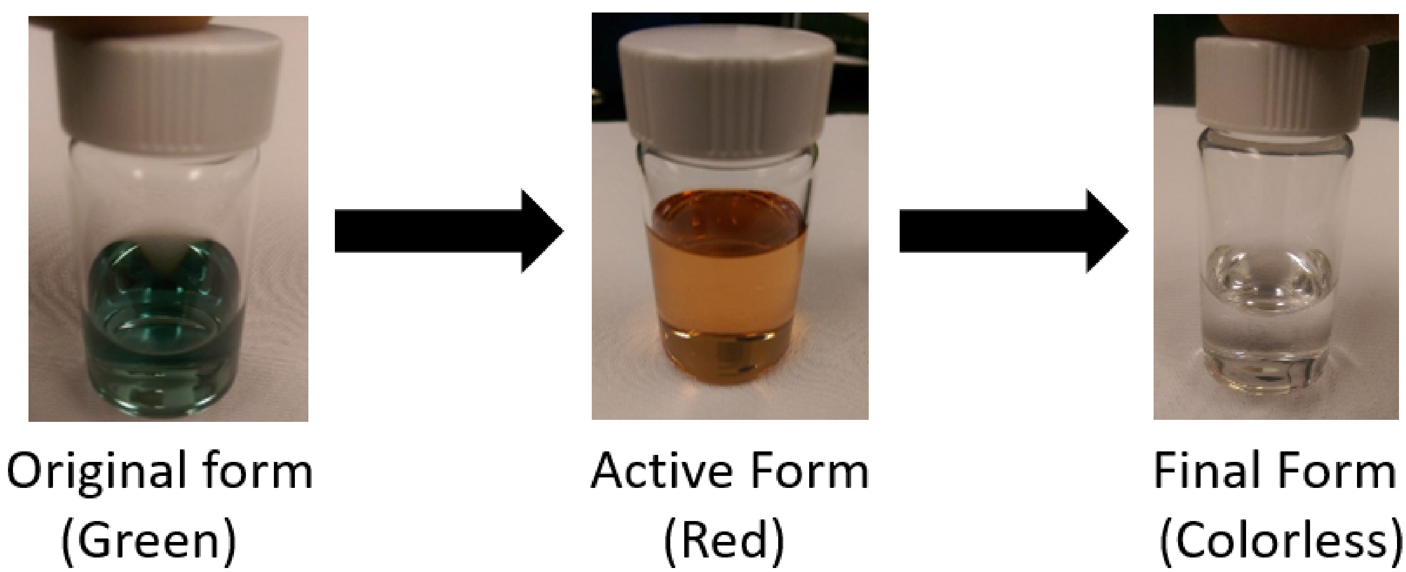

Figure 5

Reduction of nickel dithiolene from original green to red to colorless.

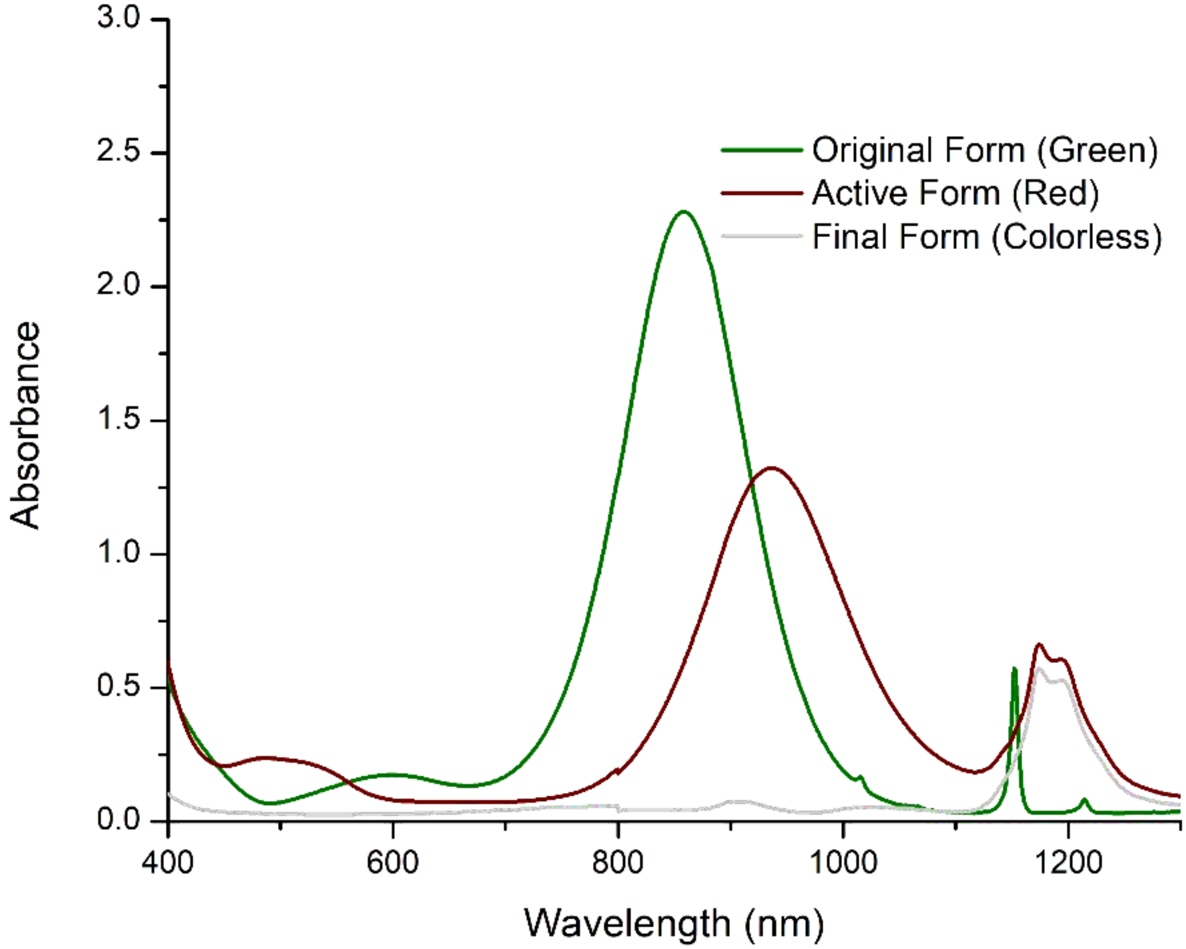

Figure 6

The UV-Vis-NIR absorption spectra of the nickel dithiolene. Green state, red state, and colorless state.

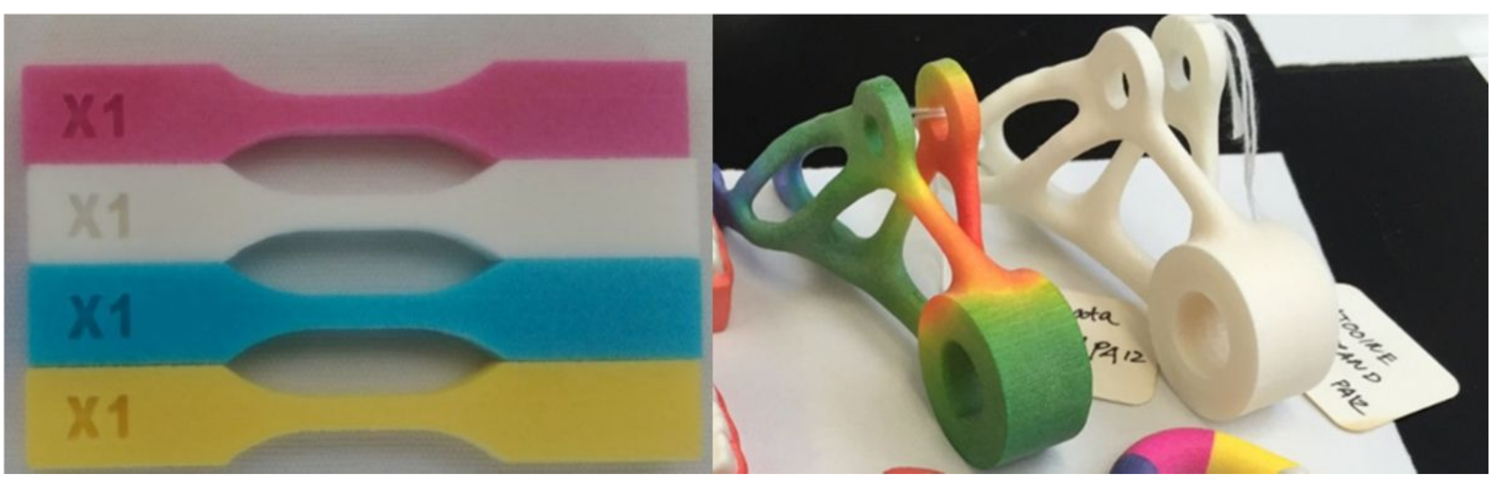

Figure 7

(A) Color ASTM type V dogbones (B) 3D stress analysis bracket printed with AFA agent and PA-12 build material with only sandblast post processing.