EFFECTS OF PRINT AND POST-CURE PARAMETERS ON MECHANICAL PROPERTIES OF 3D PRINTED PARTS

NewPro3D

Abstract

The production of 3D printed parts via selective solidification of photopolymers is a complex process with many variables that can be adjusted to achieve optimal mechanical properties from a printed object. This paper will explore existing 3D printing systems and how they compare to NewPro3D technology, while also investigating the parameters that can be adjusted in the production of a 3D printed part using the NewPro3D process, from printing to post-curing, and how they affect the final mechanical properties of a 3D printed object.

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INTRODUCTION

NewPro3D has developed a 3D printer that produces solid parts from liquid resins at speeds and resolutions that meet or exceed the world's top 3D printing technologies. NewPro3D develops and produces printers that are able to produce isotropic objects at high-speeds with their patented Intelligent Liquid Interface technology.

Traditional methods of producing 3D printed parts by means of additive manufacturing produces parts that are limited in their applications due to the anisotropic nature of their mechanical properties and slow print times. These anisotropic material properties and slow print speeds can be attributed to the inherent flaws of these printing processes, and the dependence of material properties on the direction in which the part was printed.

Using Digital Light Processing, the NewPro3D process is a technology that converts liquid resins into solid parts, layer by layer, by selectively curing cross-sectional slices of a 3D object using a process called photopolymerization. NewPro3D technology is able to produce parts much faster than existing technologies such as Stereolithography and Fused deposition modelling, while also producing anisotropic parts with superior part resolution.

. This report will answer the following questions related to the NewPro3D printing process:

1. Are 3D parts produced using DLP isotropic?
2. Are material properties dependent on vertical resolution of print?
3. How does heat affect mechanical properties of a finished part during the post-curing process?
4. How does UV radiant flux affect mechanical properties of a finished part during the post-curing process?

This report will also discuss:

- Existing 3D printing technologies the mechanical properties of the parts they produce
- The polymerization process of photopolymers

Existing Stereolithography (SLA) Systems

The closest relative of the NewPro3D process is an Upside-Down (Inverted) SLA printer. Inverted SLA printers use a laser to selectively cure a 3D object one point at a time by drawing it's cross-section through a transparent, PDMS (silicone) window. The build platform on an SLA printer descends into a vat of liquid resin, leaving a gap between the build platform and the transparent window equal to one layer thickness. When the laser has finished curing one slice, the build platform raises, detaching the part from the PDMS window. A recoater blade then sweeps across the build platform, refreshing the widow with resin for the next layer. Upon sweep completion, the build platform descends, lowering the printed part one layer thickness above the PDMS window and the above process repeats until the print is complete.

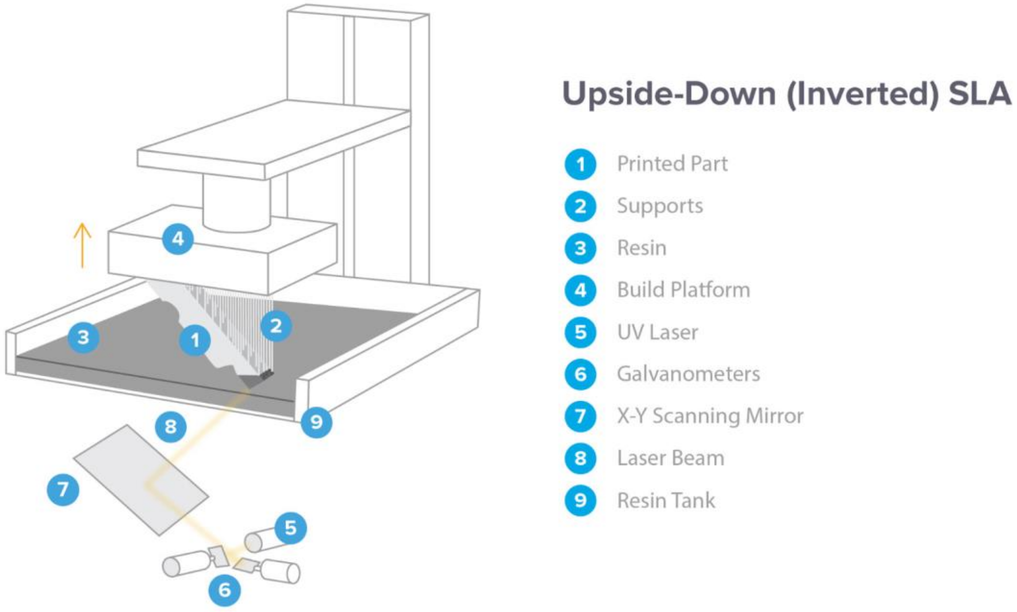

Figure 1: Upside –Down (Inverted) SLA printer – Formlabs

There are several disadvantages to printing with a traditional SLA process:

Time

Due to the fact that SLA 3D printing systems draw the cross-section of a part using a laser, SLA technology is much slower than DLP as it can only solidify one point on an object at a time whereas DLP technology can solidify an entire cross section of a part at once. SLA print times are therefore limited in both the vertical build height of an object as well as the XY cross-sectional area of the print. In addition to speed restrictions due to the laser technology used in this process, SLA printers must also complete a series of mechanical steps in between each layer which can take anywhere from approximately 10 to 45 seconds [1].

Supports & Part Deflection

Every new layer that is solidified in an SLA process bonds to both the previous cross-sectional slice of the part being printed as well as the PDMS print window. Because of the forces required to de-bond the printed cross-section from the PDMS window, many part supports are required in traditional SLA printers to prevent the part from detaching from the build platform.

In addition to supports required to maintain bonding to the build platform, additional supports are required to prevent part deflection during de-bonding from the PDMS window. Parts with features approaching 90^{o} relative to the vertical axis of the print require many supports to de-bond that feature from the part window as well as to prevent deflection of the feature in finished print.

Build Cross-Section

Due to the relatively high adhesion forces between the printed part and the PDMS window, the build size is restricted in terms of its cross-sectional area as large parts can de-bond from the build platform and/or cause print jams. "Peel forces also limit the use of more flexible materials – Shore hardness below ~70A, because the support structures become flexible as well [1]."

The Polymerization Process

Liquid resins can be made up of monomers or oligomers. Monomers consist of a single repeating carbon molecule whereas oligomers consist of several different repeating carbon molecules, resins can consist of chain lengths ranging from 1 carbon to several thousand carbons; the longer the chain length, the more viscous the resin.

Photoreactive resins designed for 3D printing contain three key ingredients that enable the conversion of liquid resin to solid plastic parts while achieving high resolution prints. These ingredients are monomers and oligomers, photoinitiators, and additives.

Monomers and Oligomers are the backbone of the resin. These form the carbon chains in the finished part that give it strength and stiffness.

Photoinitiators are UV sensitive molecules. When these molecules are exposed to UV light, they break down into two very reactive free radicals. "These molecules transfer the reactive radicals to the active groups on the monomers and oligomer chains, which in turn react with other active groups, forming longer chains [1]."

Additives can come in many forms. Some resins contain pigments or dyes that give the resin a desired colour. All photoreactive resins designed for 3D printing also contain UV blockers. UV blockers decrease how far UV light can penetrate the resin which in turn results in parts with a more precise finish as it prevents the scatter of UV light that would otherwise solidify resin that is supposed to remain liquid.

When photoreactive resins are exposed to UV light, "the photoinitiator molecule breaks down into two parts, and the bond holding it together becomes two very reactive radicals. These molecules transfer the reactive radicals to the active groups on the monomers and oligomer chains, which in turn react with other active groups, forming longer chains [1]." As the monomer and oligomer chains lengthen and begin to crosslink, the resin turns from liquid into a solid part. The more crosslinked a polymer chain is, the stronger and more rigid it becomes.

Do 3D Printed Parts Exhibit Isotropic Properties?

What's the difference between isotropic and anisotropic materials?

Materials that are anisotropic exhibit varying physical properties dependent on the direction in which a property is measured. The bending strength of wood, for example, is highly dependent on the direction in which a load is applied relative to the direction of the wood grain.

Materials that are isotropic exhibit physical properties that are independent of the direction in which a load is applied. Isotropic materials are generally preferred to anisotropic materials since they allow more design freedom and do not require additional support or structure dependent on their geometry. Metals, for example, are isotropic materials that exhibit physical properties independent of the direction in which they are measured.

Anisotropic nature of existing FDM 3D printers

Fused deposition modelling (FDM) printers produce 3D parts by heating a plastic filament through an extrusion nozzle where it is melted and deposited onto the previous layer; each layer in an FDM model bonds to the previous layer via thermally driven diffusion welding. The weld bond between each layer in an FDM model is relatively weak for several reasons:

Volumetric Shrinkage

Filament is extruded from the print nozzle in an FDM part at temperatures ranging from 165°C to over 300°C [2]. Because of the filament changing state from liquid to solid, as well as experiencing a substantial reduction in temperature, FDM parts experience significant volumetric shrinkage upon cooling. When the deposited material cools and shrinks, it stresses and weakens the interlayer bonds, causes high porosity and reduces the load bearing area [3].

Stress Accumulation

The print geometry and deposition method can result in uneven heating and cooling cycles within the printed part due to accumulation of residual stresses at the bottom surface of a part during fabrication which increases with parts built larger in the vertical direction. FDM printers have also been found to produce high thermally induced stresses along the axis of deposition line. Stress accumulation can be decreased by decreasing the extrusion nozzle radius and thus decreasing the amount of heat transfer between each layer, however a reduction in extrusion nozzle radius will correspond to an increase in print times.

Weld Imperfections

FDM parts commonly produce three types of weld imperfections:

A. Weld cracks (Fig 2-A)
    - Weld cracks are a result of accumulation of thermal stresses within the part upon cooling and reduce the load bearing area each layer

B. Air gaps between welds (Fig. 2-B)
    - Air gaps restrict the part’s ability to dissipate heat after deposition and increase thermally induced stress accumulation while also decreasing the load bearing area of each layer

C. Over-extrusion (Fig. 2-C)
    - Over-extrusion provides the best bond strength between each layer by increasing thermal conductivity between each layer and increasing the load bearing area, however this results in increased bump formation and surface roughness of the finished part

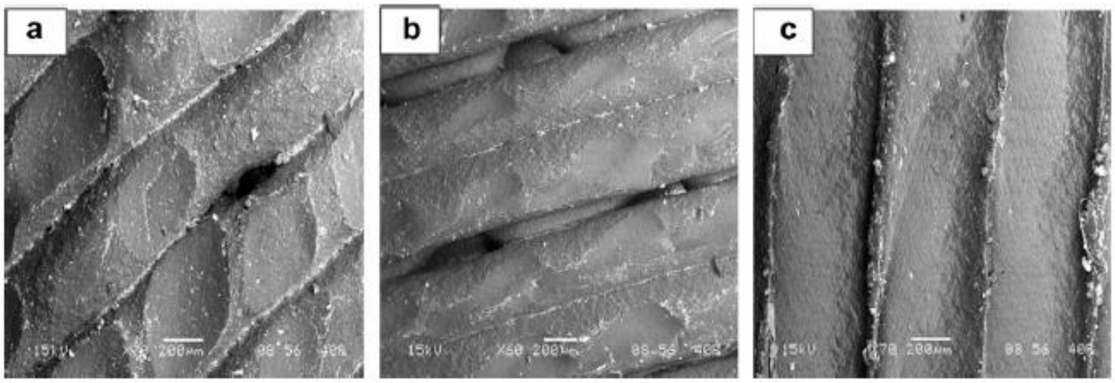

Figure 2: Weld imperfections of FDM parts – Sood Et al.

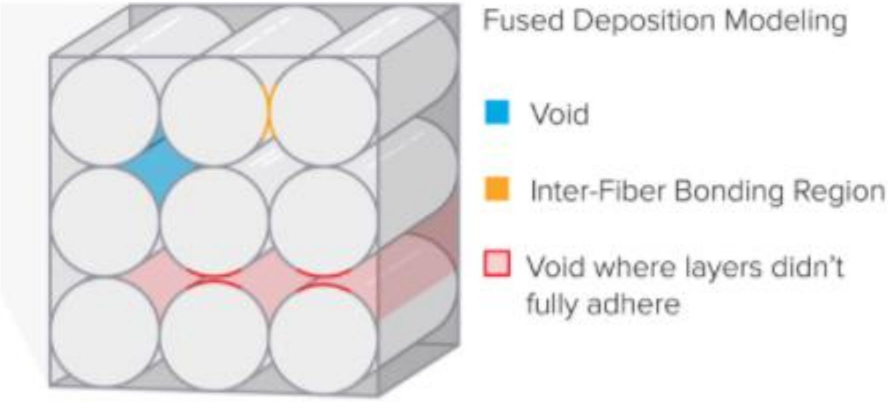

Figure 3: Bonding of Plastic Fibres in FDM Parts – Formlabs

Time & Temperature

The bonding mechanism between layers in an FDM part is inter-diffusion of polymer chains. Diffusion of polymer chains is dependent on time and temperature; increased exposure of adjacent layers at elevated temperatures will result in more inter-diffusion of polymer chains and thus an increase in strength between layers. Stronger bonding can be achieved by reducing extrusion speed and thus increasing the time spent at an elevated temperature, however this results in slower print speeds. FDM parts can also be post-treated in a heated chamber to encourage more inter-diffusion of polymer chains, however this results in significant part shrinkage with no observable increase in strength [4].

3D printed parts produced using FDM are limited in their applications because of the anisotropic nature of the finished part, as well as the textured finish of the parts they produce. The thermoplastics that form FDM parts are made of highly entangled polymer chains which produce strong, tough and stiff material properties, however FDM printers are not capable of producing the same level of entanglement of polymer chains between neighbouring fibres which results in parts with significantly reduced strength, toughness and stiffness.

Isotropic Nature of Parts Produced With Digital Light Projection (DLP) Technology

When an object is formed using DLP technology, liquid resin composed of monomers or oligomers forms a crosslinked network of polymer chains that are held together with covalent bonds, one of the strongest chemical bonds. During the printing process, each layer is cured using the minimum dosage of UV radiation required to convert liquid resin into solid. The 3D part that emerges as the part is printing is in a semi-cured “green state” that is much softer and more flexible than the fully cured part.

Because layers are produced in a semi-cured green state and polymerization reactions are not driven to completion, each layer has remaining polymerizable groups on its surface that can then bond to the subsequent layer. As the next layer is formed, crosslinked polymer chains are formed between the current and previous layers forming a polymer network that, on the molecular level, shows no difference between X, Y, and Z directions and is isotropic [1].

The isotropic properties of parts produced using DLP are advantageous over the anisotropic properties of FDM parts due to their consistent and superior mechanical properties, as well as the ability to produce optically clear parts with no visible lines from each layer. Each continuous part printed using DLP technology is a single molecule with no voids or microscopic cracks that can be found in FDM parts.

Are Material Properties Dependent on Vertical Resolution of a Print?

As discussed earlier, parts produced on SLA/DLP printers are isotropic and produce parts that, on a microscopic scale, are one continuous molecule with no interlayer defects. Because of the continuous and isotropic nature of SLA/DLP printing, mechanical properties of printed objects are independent of vertical print resolution. This has been observed by Janusziewicz et al. where objects were printed at vertical print resolutions of 100µm, 20µm and 1µm in X, Y and Z orientations using CLIP (Continuous Liquid Interface Production) SLA/DLP printing technology. Upon testing for tensile strength and Young’s modulus of printed samples and performing one-way ANOVA

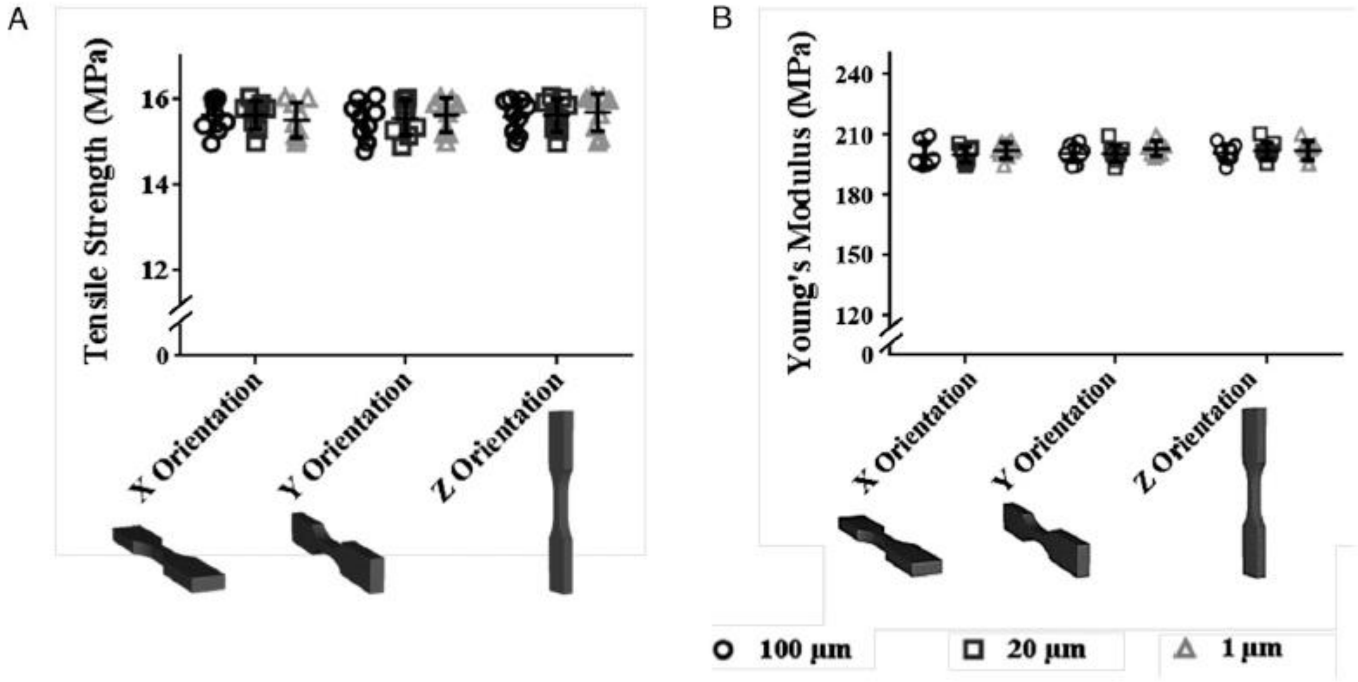

Figure 4: Tensile Strength and Young's Modulus of SLA/DLP Printed Tensile Coupons at Varying Vertical Print Resolutions - Janusziewicz et al.

(Analysis of Variance), no statistical difference was found in the mechanical properties of samples at varying print resolutions [5].

How Does Heat Affect Mechanical Properties of a Finished Part During the Post-Curing Process?

When heat is applied to an object, molecules and atoms vibrate faster which causes the space between them to increase. The application of heat in the photopolymer curing process allows for improvement in the strength and stiffness of an object through an increase in molecule mobility within the polymer network. Curing of photopolymers relies on highly reactive free radicals bonding with open reactive groups within the polymer network. Heat applied to an object during post-curing will increase the mobility of free radicals within the polymer network and increase the likelihood that a reactive free radical will find an unreacted double bond within the network rather than reacting with another free radical which would result in a neutral effect to mechanical properties of the object [6].

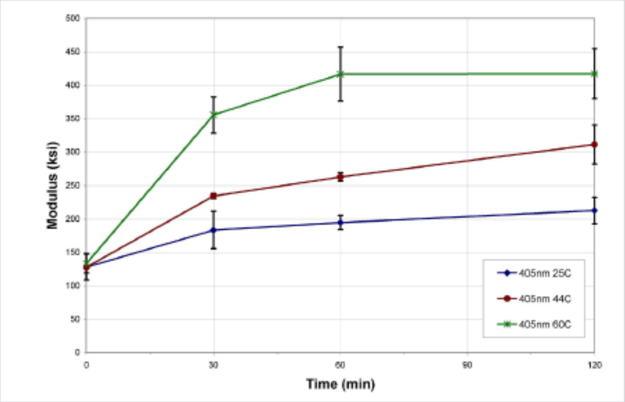

FIGURE 6: EFFECT OF POST-CURE TEMPERATURE ON YOUNG'S MODULUS OF PHOTOPOLYMERS - FORMLABS

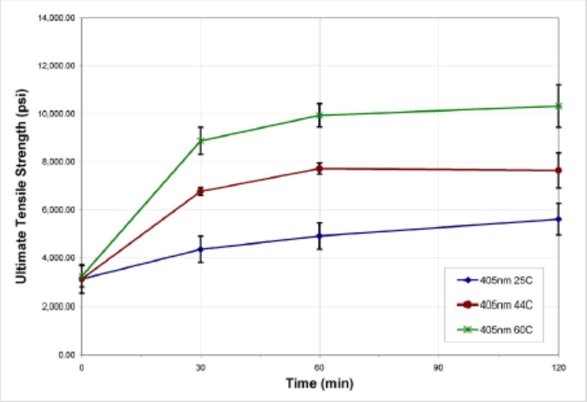

FIGURE 5: EFFECT OF POST-CURE TEMPERATURE ON ULTIMATE TENSILE STRENGTH OF PHOTOPOLYMERS - FORMLABS

Figures 5 and 6 above show that an increase in temperature increases both the degree and rate of cure for photopolymers. Increased temperature during post-curing will decrease the amount of time needed to achieve maximum tensile strength and stiffness, while also increasing the maximum strength and stiffness these materials can achieve.

How Does UV Radiant Flux Affect Mechanical Properties of a Finished Part During the Post-Curing Process?

Radiant flux is defined as the energy emitted, reflected, transmitted or received, per unit time and, in post-curing of photopolymers, is measured in units of mW/cm^2. In the case of photopolymer curing, radiant flux is a measure of the power density of electromagnetic radiation applied to an object. Radiant flux has been shown to have a significant effect on the final mechanical properties of photopolymers as well as the temperature of an object during the post-curing process.

Curing of photopolymers is an exothermic reaction that can produce significant amounts of heat within an object. In experimental testing of post-cure parameters, Jacobs noted in "Rapid Prototyping & Manufacturing" that large doses of UV radiation over a short time period resulted in a significant exothermic photopolymer reaction that further increased the photopolymer reaction rate and resulted in a substantial temperature increase in regions of thick cross-sections, reaching temperatures of up to 200ºC [7]. Jacobs also noted that temperature increase and maximum temperature during post-curing of a photopolymer resin occurred over 21 minutes after UV lamps had been turned off, indicating that the photopolymer continues to crosslink even in the absence of UV radiation. Jacobs' experiments were performed with a high pofwered mercury arc lamp that produced a radiant flux of 20mw/cm^2. Because of the resultant high reaction rates and temperatures, Jacobs experienced warpage and cracking in his post-cured objects, however, upon finding a lamp at a radiant flux at nearly two orders of magnitude lower, he observed post-cure temperatures of only 40-45ºC and experienced dramatically reduced warpage of 3D printed objects.

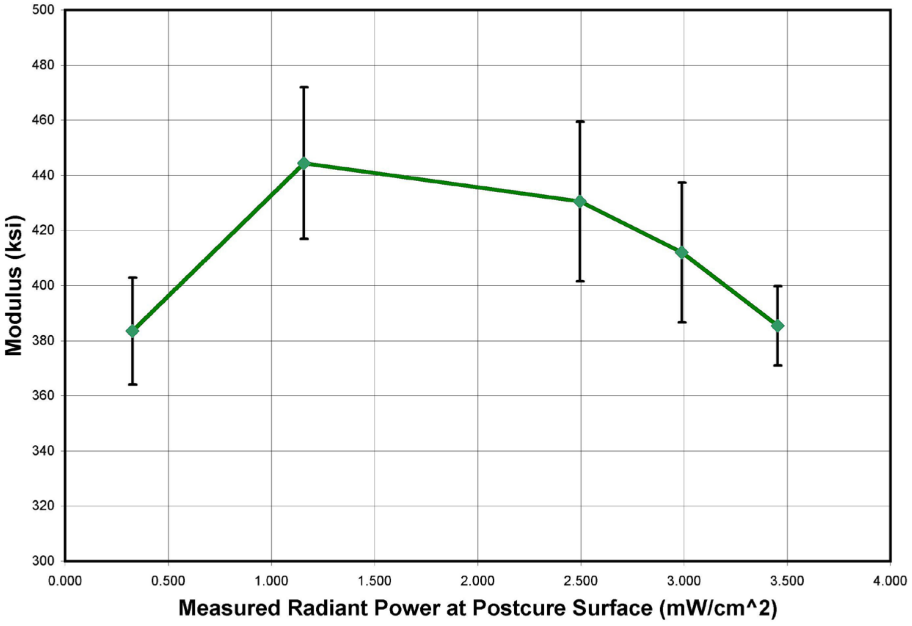

FIGURE 7: EFFECT OF POST-CURE RADIANT FLUX ON YOUNG'S MODULUS - FORMLABS

The NewPro3D process uses a cure chamber with a radiant flux measured at 1.14 mW/cm^2 which is sufficiently powerful to complete the polymerization reaction, while also low enough in power to prevent overheating, warpage and cracking of the part during post-cure. Figure 7 shows that, for a specific material, there is an optimum radiant flux that will produce the greatest material mechanical properties. Not enough power and the resin doesn't fully cure, too much power and free radicals generated by UV will combine with each other and terminate, resulting in no contribution to increased material properties [6] [8]. Material properties are optimized when enough free radicals are produced for the crosslinking reaction to occur, while maintaining a low enough free radical concentration to avoid termination of free radicals with each other. Each resin will have an optimum post-cure radiant flux, further testing of NewPro3D materials will be required to determine at which power level the material achieves maximum mechanical properties.

Conclusions

In summary, the NewPro3D SLA/DLP process is able to produce isotropic parts with material properties that are independent of print direction or vertical print resolution at speeds much greater than those of SLA or FDM printers. It is clear from the research referenced in this paper that both temperature and radiant flux have a significant effect on the final material mechanical properties of a 3D printed object. Further testing of NewPro3D materials will be required to optimize both post-cure temperature and radiant flux as optimized parameters will be material dependent.

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