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The Mechanical Properties of Photopolymer Prepared Via 3D Stereolithography Printing: The Effect of UV Curing Time and Anisotropy

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Stereolithography is a high accuracy additive manufacturing process that uses a laser beam to cure photopolymer resin according to the computer-aided design file. Anisotropy in mechanical properties is one of the major challenges that are faced by additive manufacturing technologies. This study is conducted on PR 48 photopolymer samples using FORM 2 SLA printer. Elastic modulus and hardness of printed samples of 50 and 100 μm resolutions were tested at 0°, 45° and 90° orientations using nanoindentation testing machine. The samples were cured using UV, and the effect of UV curing time was investigated. Results for 100 μm print resolution showed that elastic modulus and hardness for 0° orientation is higher than 45° orientation by 35 % and 390 % for 90° print orientation. For 50 μm print resolution, elastic modulus and hardness for 0° orientation are higher than 45° orientation by 106 % and higher by 92 % for 90° orientation. The results show a strong dependency of mechanical properties on print orientation, resolution and UV curing time and temperature.

1. Introduction

3-Dimensional printing, also known as 3D printing, is a versatile and rapidly growing field. It has a variety of applications in prototyping, jewellery, dentistry, pharmaceutical products and customized manufacturing. It uses a layer-by-layer building of objects of any geometry, from a Computer-Aided Design source file. Its flexibility and reproducibility make 3D printing one of the most promising techniques for rapid prototyping and customized manufacturing. 3D printing technology makes manufacturing of complex designs easier, reduces the production cost and time in addition to minimizing the material waste (Ponce et al., 2014).

The 3D printing market is rapidly growing at a yearly rate of around 14 % and is expected to exceed 8 billion USD by 2020. In terms of material volumes, the global demand for 3D printing materials reached approximately 2 Mt in 2013 and expected to continue growing (Chong et al. 2015).

So far, 3D printing is used mostly in producing prototypes rather than functional parts. This is mainly due to low speed and inferior properties and anisotropy of the printed parts (Ligon et al., 2017). The challenges that are facing 3D printing can be summarized as: void formation between the layers that leads to porosity and thus inferior mechanical properties, anisotropic microstructure and mechanical properties, inaccuracy of implementation and defects especially in curved surfaces and layer by layer texture which affects the appearance quality of the surface (Ngo et al., 2018).

Stereolithography is one of the important 3D printing processes. It produces parts by polymerizing reactive resin using photoinitiators that are activated by the light source, which is a laser beam that moves to cure the layer being printed. This method can produce high-resolution parts with a good surface finish (Bose et al., 2018).

Mechanical properties are affected by printed layer thickness, where printing thinner layers leads to better cohesion and improve mechanical properties, but it requires longer build time (Janusziewicz et al., 2016).

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In stereolithography, the polymerization reaction is not complete and individual layers are kept in a semi-reacted "green state" with polymerizable groups between them. This helps in bonding layers with each other as it provides layers for further polymerization in a later stage where to post-curing processes are used to complete the reaction and covalently bond the subsequent layers (O'Neill, 2018). Figure 1 shows the mechanism of polymerization between layers interphase to produce bonding between layers. UV is usually used as a post-curing process as it provides energy to activate the photoinitiators and complete the polymerization process.

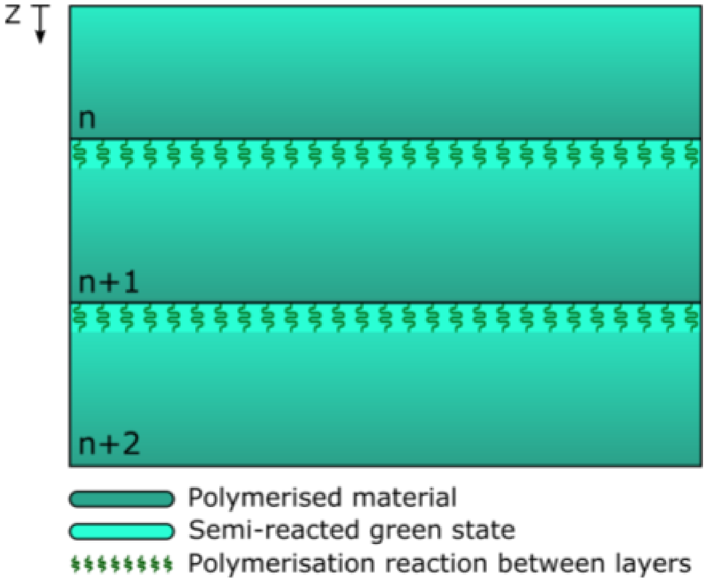


Figure 1: The semi-reacted green state of the layer interface enables layers to covalently bond together (O'Neill, 2018).

Nanoindentation, or depth-sensing indentation is one of the important techniques in measuring mechanical properties of the materials. It measures the penetration of an indenter into the surface of the material during application and release of the load. Hardness and elastic modulus are derived from the load-displacement curve that is plotted based on nanoindentation data points as shown in Figure 2. The main advantage of this technique is the ability to find mechanical properties from local deformation in a small sample size (Díez-Pascual et al., 2015).

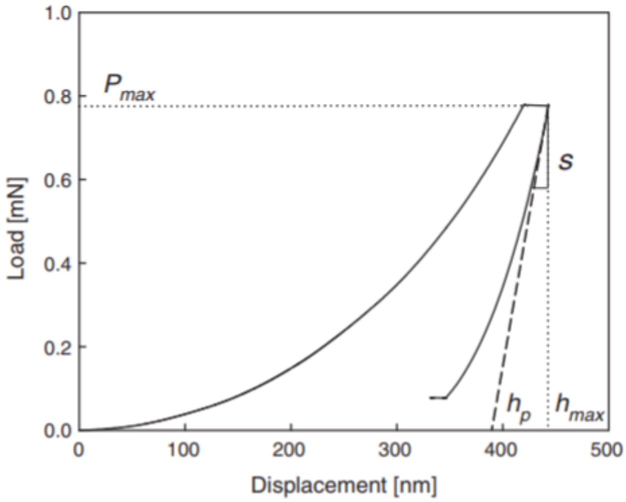


Figure 2: Typical nanoindentation curve for polymeric material (Díez et al., 2015)

Researchers in a previous study printed specimen in different print orientations and layer thicknesses using SLA printer. The printed specimen was tested using a universal testing machine to measure elastic modulus and ultimate tensile strength. The study found no significant effect of build orientation on the mechanical properties of 3D printed photopolymer specimen. The same study found that increasing the layer thickness from 25 μm to 100 μm resulted in 30 % decrease in elastic modulus and 21 % decrease in ultimate tensile strength (Naik and Kiran, 2018).

The aim of this study is to verify the influence of print orientation, layer thickness, UV post-curing time, and post-curing temperature on the mechanical properties of the printed samples. Nanoindentation was used to evaluate elastic modulus and hardness of the samples.

2. Materials and methods

2.1 Materials

Photopolymer resin grade PR 48 was obtained from Autodesk, USA. The PR 48 is an acrylate-based photopolymer resin that was used as printing material. PR 48 resin consists of EBECRYL 8210, an aliphatic urethane acrylate, (39.8 wt%) and SR 494, Ethoxylated pentaerythritol tetraacrylate, (39.8 wt%). Being enriched with double bonds, they are suitable for the polymerization reaction. Diphenyl(2,4,6-btrimethylbenzoyl)phosphine oxide (TPO 0.4 wt%) was used as photoinitiator. A monofunctional urethane acrylate, Genomer 1122 (19.8 wt%) was used as a reactive diluent to reduce the viscosity of the base resin. It reacted with other constituents and influenced the final properties of the printed parts. UV blocker 2,2- (2,5-thiophenediyl)bis(5-tertbutylbenzoxazole) (0.16 wt%) was used in PR48 resin to control the light penetration depth, which is needed to confine cured layer thickness. PR48 initiating system is free radical polymerization that is suitable for a UV lithography (Skliutas et al., 2018).

2.2 Equipment

Form2 SLA 3D printer (Product of Formlabs, USA), which uses 250 mW laser beams to polymerize the photopolymer, was used to print the samples. FormCure unit (Product of Formlabs, USA), which uses heat and 405 nm light, was used for UV post-curing of the samples at room temperature and at 80 °C

2.3 Preparation of samples

Samples of 20 × 20 × 3 mm were designed using online Tinkercad 3D design tool. Samples were printed in horizontal, inclined and vertical orientations as shown in Figure 3. Samples of 50 μm and 100 μm resolutions were printed. Printed samples were washed with ethanol to get rid of any unreacted resin. Different post-curing process using UV at room temperature and UV at a higher temperature (80 ºC for 150 min) were introduced on the printed samples which were initially polymerized using laser beam and their effects on the mechanical properties of the samples were studied.

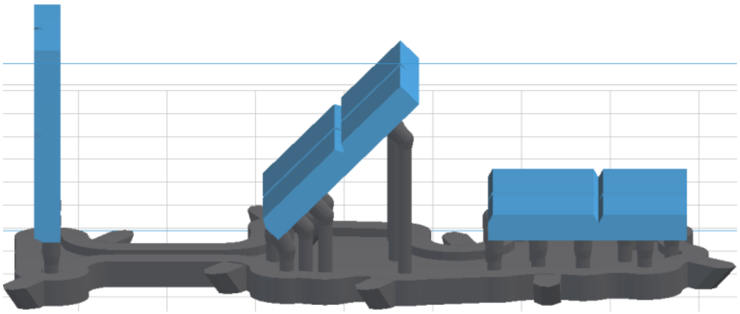


Figure 3: Sample print orientations in 0°, 45° and 90°.

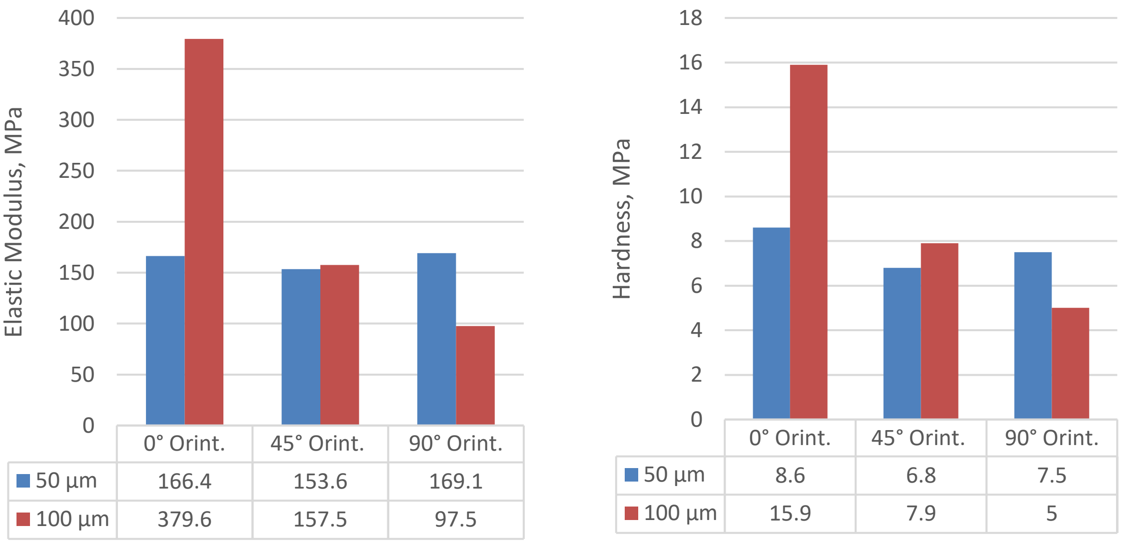
2.4 Characterization

The nanotest 3 nano-indentation platform (Product of Micromaterials, UK) was used to determine elastic modulus and hardness values of the samples. The load was measured as a function of deformation depth. Berkovich type diamond indenter was used with a maximum load of 20 mN. The experiment was done in the following sequence: (1) approaching the surface, (2) loading to the peak load of 20 mN at rate of 5 mN/s, (3) holding the indenter at peak load for 30 s, (4) unloading from the peak load at rate of 20 mN/s. Holding step was included to eliminate the effect of creep. Elastic modulus and hardness values were obtained through the analysis by Nanotest software.

3. Results and discussion

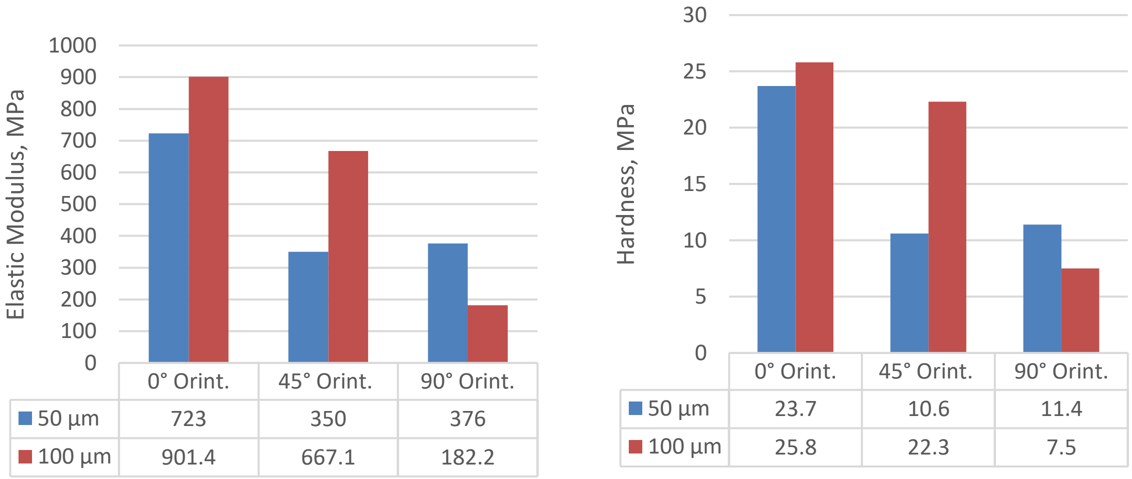
Values in Figures 4a, 5a and 6a show anisotropy in elastic modulus for 100 μm resolution of uncured samples and samples that were cured by UV at room temperature and at 80°C. Horizontally printed samples (0° orientation) have higher elastic modulus and hardness values compared to inclined and vertical print orientations. Figures 4b, 5b and 6b show a similar trend in hardness results for 100 μm resolution samples. Samples with 50 μm resolution show less anisotropy in uncured prints and prints that are cured at 80°C.

When compared to low layer thickness (50 μm), the high layer thickness (100 μm) prints show better elastic modulus and hardness properties in 0° and 45° orientations, and lower properties in 90° orientation. This can be due to having the surface made of a complete layer that photopolymrized by laser beams in case of 0° orientation, while the surface in other orientations consists mostly of semireacted layers in case of uncured samples (Figure 7). These semireacted layers complete the photopolymerization process by UV in postcured samples. This indicates that curing by laser beams results in better mechanical properties compared with layers that cure by UV. 50 μm samples show improved elastic modulus and hardness compared to 100 μm in 90° orientation, as they have lower proportion of semireacted resin due to better penetration of laser beams.



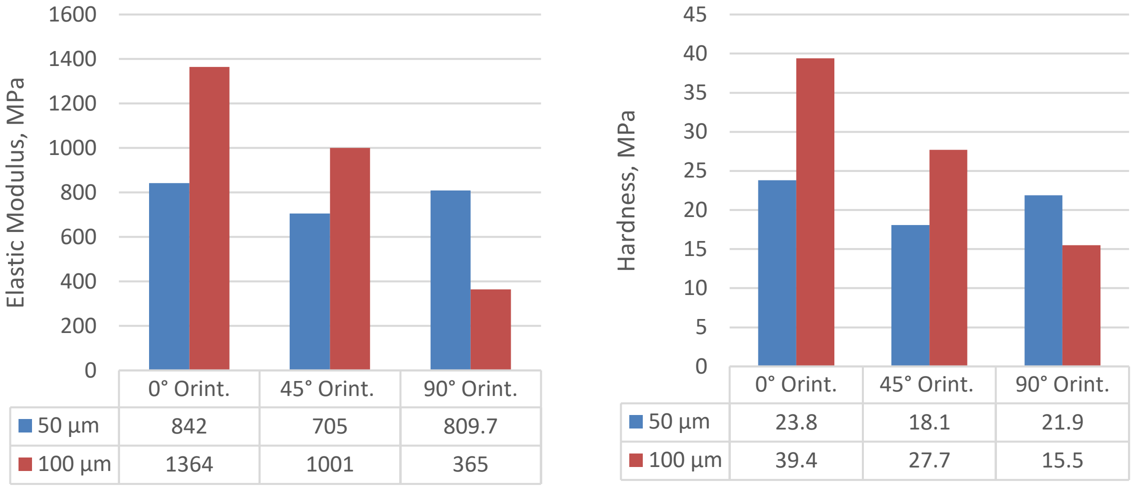
(a) (b)

Figure 4: Uncured samples (a) Elastic modulus results, (b) Hardness results.



(a) (b)

Figure 5: UV cured samples at room temperature for 150 min (a) Elastic modulus results, (b) Hardness results.



(a) (b)

Figure 6: UV cured samples at 80 °C for 150 min (a) Elastic modulus results, (b) Hardness results.

Tables 1 and 2 show percent improvement of elastic modulus and hardness resulting from post-curing processes. The effect of UV curing under high temperature resulted in higher improvement of mechanical properties in all samples compared with the effect of curing by UV at room temperature. This can be attributed to the increased mobility of free radicals in the polymer network which increases the probability of reaction with double bonds instead of reacting with another free radical (Slade, 2019).

Table 1: Effect of UV curing at room temperature and at 80 ºC on the elastic modulus

Sample	% Improvement (UV curing at room temperature)	% Improvement (UV curing at 80 °C)
50 µm, 0°	334.5	406.0
50 µm, 45°	127.9	359.0
50 µm,90°	122.4	378.8
100 µm, 0°	137.5	259.3
100 µm, 45°	323.6	535.6
100 µm ,90°	86.9	274.4

Table 2: Effect of UV curing at room temperature and at 80 ºC on the hardness

Sample	% Improvement (UV curing at room temperature)	% Improvement (UV curing at 80 °C)
50 µm, 0°	175.6	176.7
50 µm, 45°	55.9	166.2
50 µm,90°	52	192
100 µm, 0°	62.3	147.8
100 µm, 45°	182.3	250.6
100 µm ,90°	50	210

The results in Figures 5 and 6 show that horizontally printed samples (0° orientation) have better mechanical properties compared with 45° and 90° orientations. Figure 7 indicates that nanoindentation instrument measures the mechanical properties for a layer that mainly formed as a result of photopolymerization through laser beams of the 3D printer for 0° orientation samples. On the other hand, surfaces of 45° and 90° orientations have some proportion that consists of semi reacted green state interlayer that photopolymerize mainly by UV post-curing process.

It can be observed that the degree of anisotropy is higher in samples with lower resolution (thicker layers), especially for samples that were cured using UV at 80 °C. This can be attributed to higher variation in the extent of photopolymerization by laser beams during 3D printing. Laser beam have limited penetration through the resin layer which results in variation of mechanical properties along the layer thickness.

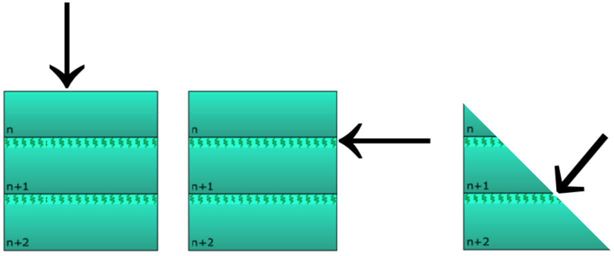


Figure 7: Nanoindentation directions for 0°, 45° and 90°.

4. Conclusions

This study shows anisotropy in elastic modulus and hardness of parts that are 3D printed using stereolithography. Effects of different post-curing conditions were studied and it was found that UV curing under high temperature results in the highest improvement of mechanical properties. Also, the study showed that 100 μm resolution prints have higher mechanical properties compared with 50 μm layer thickness prints in 0° and 45° orientations, lower mechanical properties in 90° orientation.

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