Technical Sciences, 2020, 23(2), 175–184

UNIWERSYTET WARMIŃSKO-MAZURSKI W OLSZTYNIE

Quarterly peer-reviewed scientific journal
ISSN 1505-4675
e-ISSN 2083-4527
TECHNICAL SCIENCES
Homepage: www.uwm.edu.pl/techsci/

DOI: https://doi.org/10.31648/ts.6119

ANALYSIS OF THE INFLUENCE OF UV LIGHT EXPOSURE TIME ON HARDNESS AND DENSITY PROPERTIES OF SLA MODELS

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Received 16 November 2020, accepted 8 December 2020, available online 9 December 2020.

K e y w o r d s: SLA, light-curing resin, hardness, density, UV.

A b s t r a c t

The article analysis the effect of exposure to ultraviolet light on the hardening process of the model made in the SLA technology. Research samples were created with the SLA additive technique using a 10s exposure time. In this experiment, the change in item hardness and density over a 96-hour period was analysed. Light exposure time for details of an item made in SLA technology results in an increase in hardness. At the same time are observed, changes in density and stabilization of both parameters with increasing exposure time to UV light.

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Introduction

Continuous progress and demand for manufacturing unique or short-series items have led to the development of incremental manufacturing techniques. These technologies consist of producing an item by applying one layer after another and bonding them to create the whole model. One of these methods is 3D stereolithographic printing technology or "SLA" for short. This is a new technology that is being used increasingly extensively. It was developed in the early 1980s by Hideo Kodama, a Japanese researcher, who invented it and created the first model based on stereolithography. For this purpose, he used ultraviolet light to cure photosensitive polymers (Bartolo, Gibson 2011, *The Ultimate Guide*… 2017). Since then, there have been rapid developments in the field of positioning and control. This allowed for improvements in this method and the creation of 3D printers for printing models from light-curing polymers.

Stereolithography (SLA) is becoming an increasingly popular low-budget additive manufacturing technology. It has gained particular recognition among artists and engineers as it provides excellent dimensional accuracy and good overall quality of the item compared to its direct and most popular competitor, fused deposition modelling (FDM) (Redwood et al. 2017, Schmidleithner, Kalaskar 2018). Despite the early invention of the first 3D printers (Hull 1998), SLA was not as successful as FDM printers, due to the high cost of consumables, their low availability and durability. At present, multiple problems have been solved and many manufacturers have a wide offer of SLA printing resins for various applications. As a result, models produced with this technology are being increasingly used for mechanical applications due to competitive prices (Cosmi, Dal Maso 2020, Małek et al. 2019).

In SLA technology, an item is produced by bonding successive layers by selective curing of the liquid photopolymerising resin with an actuator in the form of an oriented light wave. The generated light polymerizes a specific network of points forming a model. The liquid material fills a fixed container whose size depends on the working area of the printer. The bottom of the container is formed by a film with a low absorption coefficient. The first layer of the model is fixed to a moving working platform moving in the Z-axis in the direction opposite to gravity. During the whole process, the model is partially immersed in liquid resin at a depth of several millimetres. The immersion is limited by the size of the tank and the amount of resin needed for the process.

Once an individual layer is cured, the printing platform is lifted, which allows the next layer to be peeled off the transparent bottom and fill the space between the light actuator and the already formed layer of the growing model. This process is time-consuming and causes the formation of adhesion forces which may damage the part, hence the need for careful choice of model manufacturing orientation and modelling the support to allow for proper model growth (Liravi

et al. 2015, MELCHELS et al. 2010, PAN et al. 2017, WANG et al. 2018). Greater mechanical strength is achieved by curing by treating the manufactured part with light with a wavelength initiating the photopolymerisation at the end of the printing process (SUN et al. 2008, ZGURIS 2016). The main advantages of stereolithography-based production in comparison with other low-budget 3D printing technologies, e.g. FDM, include high dimensional accuracy, low roughness of the model surface, higher printing speed and isotropic material behaviour (COSMI, DAL MASO 2020).

In addition, the resins used in the manufacturing process are characterised by a wide range of visible light permeability, which enables their use in optics. The finished models can be subjected to additional mechanical processing.

As in most additive technologies, and also in SLA, the models may become distorted during manufacturing, which is, however, insignificant for most types of resins and occurs almost exclusively in the final phase of lighting the finished model (FUH et al. 1997, JACOBS 1992). Some applications preparing a model for SLA manufacturing can predict and compensate for this uniform contraction of the polymerised material (HUANG et al. 2015). Moreover, SLA parts are not porous but waterproof. This guarantees much more control over the internal geometry, mass properties and general characteristics of the printed materials (GIBSON et al. 2010). According to some studies, the physical properties of SLA parts are anisotropic (CHANTARAPANICH et al. 2013, DULIEU-BARTON, FULTON 2000) while more recent studies have confirmed the complete isotropy of the physical properties of these parts (DIZON et al. 2018, DULIEU-BARTON, FULTON 2000, *White paper*… 2018, HAGUE et al. 2004).

The aim of the study is to assess the effect of the exposure time to UV light on the hardness and density of models made in the SLA technology. Determining the influence of the exposure time to UV radiation on the hardness and density of the detail informs about its readiness for use.

Materials and methods

The samples used for the tests were cubes with an edge of 10 mm (Fig. 1). They were made in SLA technology from light-cured resin cross-linking in the light wave range of approx. 405 nm. The exposure time for a single layer was 10 s and its thickness was 50 μm. The ambient temperature during printing was 22°C. The samples were prepared using an Anycubic Photon S Sla printer (Anycubic).

After printing, the samples were treated with light of 400 nm wavelength in a darkened chamber. The lighting time was 1, 4, 8, 12, 24, 48, 64, 72, 96 hours, respectively. The ambient temperature was 22°C. After each irradiation session, the density and hardness of details were measured.

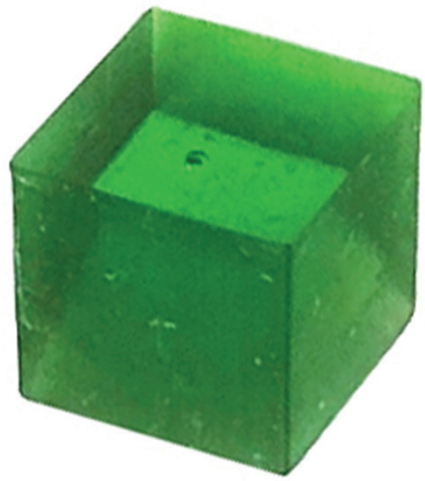

Fig 1. Sample model

The hardness of manufactured parts was measured on the Brinell scale using the "Innovatest Nexus 703A" hardness-meter with an HB 358 N main load value. The measurement was carried out in 10 repetitions.

The density measurement was carried out with the HumiPyc™ Model 1 gas pycnometer (InstruQuest Inc. Scientific Instruments R&D, USA). Helium of purity class 5.0 was used as the measurement gas. Measurements were made at 22 ±0.1°C and 220 kPa. Samples were placed in the measuring chamber where their temperature was stabilised for about 10 minutes. Measurement was made with an accuracy of 0.00001 g/cm^3. Weight was measured using RADWAG AS 62 analytical scales with an accuracy of 0.00001 g. Volume and weight measurements were repeated five times.

Statistica 13.1 software (StatSoft Inc., Tulsa, Oklahoma, USA) was used for statistical analysis of the results. a non-parametric Kruskal-Wallis test was used to assess the differences between the results obtained during the study (at significance level $p = 0.05$).

Results and discussion

Figure 2 shows the hardness of the manufactured parts as a function of the irradiation time. It can be seen that the hardness of the polymer increases as a function of changes in irradiation time. The conducted statistical analysis showed that there are significant statistical differences in parts' hardness depending on the irradiation time (Tab. 1). The p values for irradiation times at which statistically significant differences in hardness were found are marked

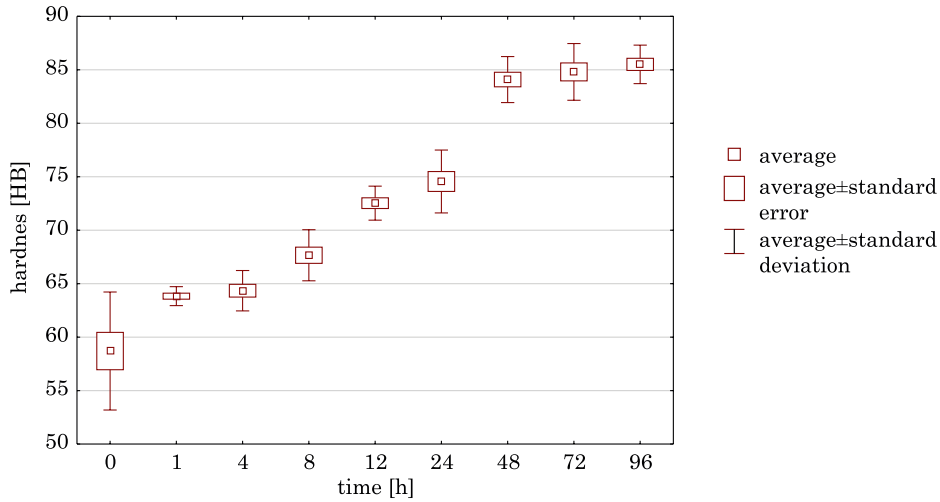

Fig. 2. Changes in element hardness as a function of irradiation time

Table 1

p value for multiple (bilateral) comparisons; Hardness (Sheet1) Independent variable (grouping): Time Kruskal-Wallis test: H (8, *N* = 90) = 81.22954 *p* = .0000

Exposure time [h] ↓→	0	1	4	8	12	24	48	72	96
0		1.000000	1.000000	1.000000	0.037613	0.008962	0.000002	0.000001	0.000000
1	1.000000		1.000000	1.000000	0.387086	0.119764	0.000088	0.000044	0.000008
4	1.000000	1.000000		1.000000	0.684564	0.227735	0.000237	0.000121	0.000023
8	1.000000	1.000000	1.000000		1.000000	1.000000	0.043082	0.026011	0.007449
12	0.037613	0.387086	0.684564	1.000000		1.000000	1.000000	0.767199	0.305621
24	0.008962	0.119764	0.227735	1.000000	1.000000		1.000000	1.000000	0.887518
48	0.000002	0.000088	0.000237	0.043082	1.000000	1.000000		1.000000	1.000000
72	0.000001	0.000044	0.000121	0.026011	0.767199	1.000000	1.000000		1.000000
96	0.000000	0.000008	0.000023	0.007449	0.305621	0.887518	1.000000	1.000000	

in red. No statistically significant differences in hardness were found between irradiation times in the range from 0 to 8 hours. A similar trend was observed for irradiation times from 12 to 96 h.

The change of parts hardness in the initial irradiation phase could be affected by polymerisation shrinkage, accompanying stress and incomplete conversion of double bonds (DAVIDSON, DE GEE 1984, DAVIDSON, FEILZER 1997). The increasing material hardness may also be related to the continuous cross--linking of the material under the influence of UV light. The degree of polymerisation in cross-linked polymer systems plays a potentially important role

in determining the final physical and mechanical properties of the material. (SOH, YAP 2004). During the first 48 hours of irradiation, the hardness increases and then stabilizes at 84.8 ±0.75 HB, which may be indicative of the end of the cross-linking process. It is worth noting that the initial average material hardness is 58.7 HB with a large standard deviation of about 5.2 HB. a lower cross-linking degree accompanied by higher polydispersity of the material may result in lower hardness, low wear resistance, reduced colour intensity, reduced stability, increased water absorption rate and higher solubility in organic media (FAN et al. 1987, PEARSON, LONGMAN 1989, SHORTALL et al. 1995, VARGAS et al. 1998, VENHOVEN et al. 1993).

Figure 3 shows changes in the density of details as a function of irradiation time. There were no statistically significant differences between the hardness of details for particular irradiation times. In the initial phase, the increase in the sample density may be related to polymerisation shrinkage of the material as a result of initial irradiation. It is accompanied by stress and incomplete conversion of double bonds (DAVIDSON, DE GEE 1984, DAVIDSON, FEILZER 1997). In the period between the 8th and 24th hours of irradiation, a decrease in density was observed, which is the result of the branching of chains already formed during the crosslinking process. The branching of chains can result in a reduction in the packing of carbon atoms in the polymer structure and an increase in the average distances between atoms. This may cause a decrease in the density of the material after eight hours of exposure. However, if the density increases after 24 hours of exposure, several different mechanisms may take place. The resulting branched chains with active terminal groups may undergo such processes as chain closing, recombination, radical transfer and

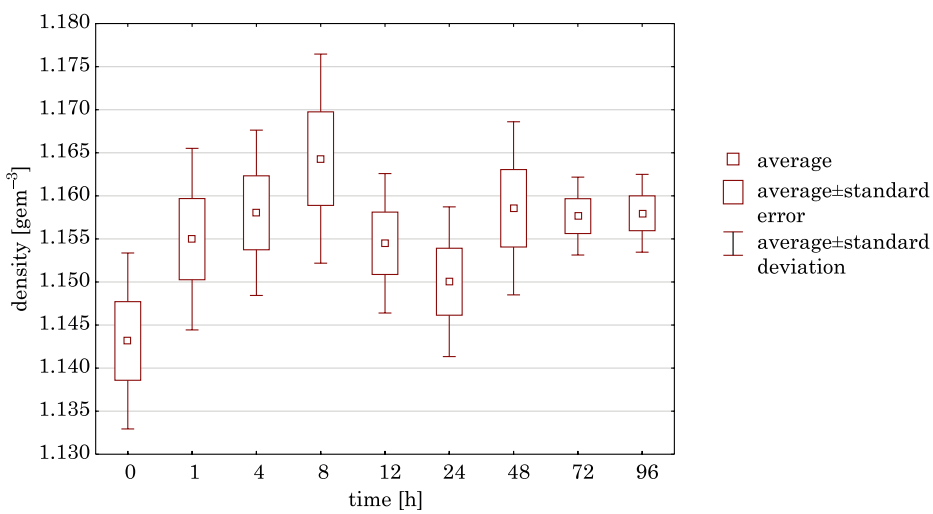

Fig. 3. Changes in element density as a function of irradiation time

linking to another chain. Especially the latter process may cause another increase in density observed after 24 hours of irradiation. The correlated increase in material hardness also supports the hypothesis that such a mechanism occurs. However, none of the above-mentioned processes can be excluded. It is also probable that a radical polymerisation reaction with chain transfer occurs (BOCIONG et al. 2018, CRAMER, BOWMAN 2001, PODGÓRSKI et al. 2015).

Comparison of the trends of changes in hardness and density of the analysed models allows for unequivocally stating that they assume a consistent conservative trend in particular measurement intervals (Fig. 2 and Fig. 3). The point of refraction between the 8^{th} and 12^{th} hour of irradiation provides an exception, where the density decreases from 1.1643 $g \cdot cm^{-3}$ to 1.1544 $g \cdot cm^{-3}$ with further stabilisation of the change tendency observable in subsequent time intervals. During irradiation, the hardness increases by about 24.5 HB and the density by 0.0148 $g \cdot cm^{-3}$ in relation to measurements in samples before irradiation.

It is worth mentioning that hardness is directly related to increasing material density. The values of both parameters assume a growth trend in the initial eight curing hours which may be caused by material shrinkage. At this stage, both parameters depend, among others, on the mutual distance of double bonds (CZECH, MINCIEL 2015, DAVIDSON, DE GEE 1984, DAVIDSON, FEILZER 1997). In his research on curable light polymers, LE XUAN (1993) confirmed the relationship between the time of exposure to UV radiation and the increase in hardness which was attributed to the increase in the crosslinking density of the polymer (LE XUAN, DECKER 1993).

Polymerisation of methacrylate monomers in composite resins creates a strongly cross-linked structure. However, the monomer conversion is never completed and always contains significant amounts of lateral double bonds (FERRACANE et al. 1997). These suspended double bonds can influence the crosslinking density in composites by reacting with propagating radicals to form crosslinking in primary or secondary cycles. a transverse bond is formed when a radical reacts with a double side bond on another kinetic chain. a primary cycle is created when a radical reacts with a double bond hanging on its own kinetic chain. a secondary cycle is formed when a radical reacts with a double bond hanging from another kinetic chain with which it is already cross-linked. Primary cyclisation reactions form microgels and introduce some heterogeneity in the polymer network with loosely cross-linked areas and more strongly cross-linked areas of the microgel coexisting next to one another (ANSETH, BOWMAN 1994, BOOTS, PANDEY 1984). This is confirmed by the behaviour of the samples in the initial irradiation period, which is evidenced by a linear increase in the hardness parameter of the irradiated material. Such cyclisation would promote an increased local conversion because it does not reduce the mobility of the system as much as cross-linking. However, cyclisation may also lead to a reduction in effective cross-linking density, as cycles do not have a significant impact

on the overall crosslinked structure. Reducing the effective crosslinking density of the cured resin would lead to a reduction in its mechanical strength, resistance to solvents and glass transition temperature (ANSETH, BOWMAN 1994, BOOTS, PANDEY 1984), which is responsible for changes in material density during the entire curing process and indirectly translates into hardness.

Conclusions

This study confirmed that material hardness increases with an increase in irradiation time. No statistically significant influence of the irradiation time on the density of manufactured parts was observed. The observed trends indicate that the hardness and density values stabilize after 48 hours. It thus seems reasonable to accept 48 hours of irradiation time with a 400 nm wavelength light as a criterion for element strength stability.

It should be noted that elements manufactured using SLA technology are subject to shrinkage, which may result in the deformation of the elements. However, its extent is very limited, which is confirmed by only a slight change in the density of the parts and the lack of a statistically significant influence of the irradiation time on density. It should also be noted that the exposure time has a positive effect on hardness and density homogeneity in individual elements, as evidenced by the decreasing standard deviation.

ACKNOWLEDGEMENT

This study was partially supported by the University of Warmia and Mazury in Olsztyn (grant No. 16.610.001-300).

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