https://doi.org/10.24867/GRID-2022-p46 Professional paper

REVIEW OF PHOTOPOLYMER MATERIALS IN MASKED STEREOLITHOGRAPHIC ADDITIVE MANUFACTURING

Alan Divjak [1], *Mile Matijević* [2], *Krunoslav Hajdek* [3]
[1] *Algebra University College, Zagreb, Croatia*
[2] *University of Zagreb, Faculty of Graphic Arts, Zagreb, Croatia*
[3] *University North, Koprivnica, Croatia*

Abstract: *Among the many types of additive manufacturing, stereolithography (SLA) stands out as one of the most versatile technologies, especially in the production of large prototypes of extremely high surface quality. The basic working principle of this technology has not changed for almost thirty years, but the recent rapid development of the mask-based variant of stereolithographic 3D printing technology (MSLA) has significantly increased its popularity and made it available to a wider range of users. This is especially true for MSLA 3D printers that use liquid crystal displays (LCD) for mask forming. These 3D printers are characterized by large build volume, high resolution and speed of model production, and low price. These factors make them extremely attractive for rapid prototyping or small-scale serial production. However, although they are superior to classical laser-based stereolithography in many technical aspects, their current main drawback is the smaller range of available materials. The development of modern stereolithographic technology has clearly shown that the capabilities of 3D printers themselves are just as important as the materials from which the models are made, the diversity of their mechanical characteristics, available colours, and optical properties. The materials used in all variants of SLA technology are liquid thermoset polymers that are sensitive to UV light (photopolymers). A wide range of areas of application requires a wide range of materials that meet the specific needs of each application. MSLA, as a newer technology, still does not have the same range of materials as 3D printers based on the laser variant of stereolithography. The situation is significantly improving with the increase in the number of available MSLA 3D printers, their popularity, and improved technical characteristics, and it can be said that this is the last step in legitimizing MSLA technology as a competitor to laser stereolithography. The aim of this paper is to analyse the material market for MSLA technology, categorize the supply of materials and objectively compare the available materials with those offered by reputable manufacturers of materials for classic SLA 3D laser printers. Special emphasis is placed on the quality and scope of technical specifications of MSLA materials, which is crucial for their professional use. In addition, the impact of thermoset polymers on user health and the environment is an especially important topic, so an overview of plant-based materials was also made.*

Key words: additive manufacturing, stereolithography, materials, photopolymers

1. INTRODUCTION

There are currently only two additive manufacturing (AM) technologies available to broader range of desktop and professional users that are not willing to pay exorbitant amounts of money to produce their parts. These are Fused Deposition Modeling (FDM) (Chennakesava & Narayan, 2014) and Stereolithography (SLA) (Kafle et al., 2021).

It should be noted that FDM is a trademarked name of Stratasys corporation, one of the leading manufacturers of 3D printers. FDM is also commonly known as Fused Filament Fabrication (FFF) (Singh et al., 2020), which is just a different name for FDM that was coined by the open-source RepRap project. RepRap is credited for popularizing FFF technology and AM in general, since their open-source printers inspired by the expired Stratasys FDM patent was the first AM machine that was available and financially accessible to broader set of users. FFF went down in history as the first consumer desktop AM technology available.

FFF 3D printers are known for their low cost, ease of use, extensive selection of different models, large build volume and a wide range of available materials. Success of any AM technology is based upon cost and performance of 3D printers and the range of available materials. FFF scores high in both categories, but the latter is especially important and goes in favour of FFF. There are many thermoplastics that can be fed into an FFF 3D printer, from low-cost PLA to flexible and elastic ones, to high performance carbon fibre reinforced PEEK composites. Most importantly, almost all these materials can be printed on sub-

1000€ 3D printers, out of the box or with small modifications. This fact alone means that there is a vast array of applications where these low-cost 3D printers can be used.
However, like any AM technology, FFF has certain drawbacks that limits it's usability. Low build speed and low resolution are most prominent. All FFF 3D printers feature a nozzle that extrudes melted plastic. Diameter of nozzle strongly determinates resolution and build speed. Larger nozzles can extrude material faster, but resolution drops significantly, and smaller nozzles increase resolution with drastic decrease in build speed. However, one competing AM technology can offer both high resolution and build speed along with most benefits of FFF technology.
Stereolithography was the first, original AM technology that was introduced in 1980s. Original SLA concept, still used today, uses UV lasers (Stampfl et al., 2008) to spatially solidify a thin layer of liquid photopolymer. This approach to SLA has exceedingly slow build times since laser beam has very small diameter and is mechanically steered. More modern approach is masked stereolithography (MSLA) which uses various techniques to project an entire object cross-section into the photopolymer layer (Potgieter et al., 2008). This results in extremely fast build speed that can exceed 100 mm/h in desktop 3D printers and over 600 mm/h in some professional 3D printers. Resolution of these 3D printers is determined by spatial resolution of light modulator being used and layer thickness. This type of SLA technology drastically mitigates drawbacks of FFF technology as the second AM technology available to desktop consumers
First instance of MSLA was DLP (Digital Light Processing) SLA, where masking was provided by digital micromirror device, based on micro electro-mechanical design (Sampsell, 1994). This variation of SLA has certain advantages, primarily that DLP device can handle high energy light sources in UV band, given that it's micromirrors are made from polished aluminium. This ensured high build speed and device longevity. However, DLP technology is patented and manufactured exclusively by Texas Instruments and as a result DLP device prices are high. Other drawback is limited resolution. Largest DLP device has a resolution od 2560x1600 physical pixels, where every pixel corresponds to a single micromirror. There is a 4K DLP device, but that resolution is achieved through frame blending of images produced by lower resolution DLP array and cannot be considered a true 4K image.
Second instance of MSLA is LCD (Liquid Crystal Display) SLA, and this technology is the topic of this paper. This type of MSLA uses ordinary LCD panel without any back illumination as spatial modulator for layer projection (Wu, Xu & Zhang, 2021). LCD pixels are normally opaque when turned off, but turn transparent when fully switched on. These 3D printers use UV LED arrays to uniformly shine directional light through the LCD panel. Image of a current layer that is to be formed is displayed on the panel. This creates a transparent mask through which UV light passes and spatially solidifies light sensitive resin. This approach to SLA has numerous advantages. LCDs can easily be made large and high resolution. There are already 13-inch panels with 8K resolution available in some high-end desktop LCD SLA 3D printers, and there is no technological reason why size and resolution couldn't increase further. LCD panels are low-cost devices available from many manufacturers, therefore LCD SLA 3D printers are also mostly low-cost devices, even those considered high-end in LCD SLA user community. Only real drawback is that LCD panels are not very transparent at 405 nm wavelength that is predominantly used to solidify resin. Only 2-6% of light passes through the panel, rest in converted to heat (Penczek, Kelley & Boynton, 2015). There is also the problem of LCD panel degradation since strong UV light must be used on account of panel's low transparency in UV band. This causes loss of contrast and light bleeding through opaque pixels. There is no actual data on degree of degradation over time, but manufacturer's estimates vary from 500 to 2,000 hours depending on UV array light intensity and type of LCD panel- This means that LCD panels can be a perishable part of 3D printer that must regularly be replaced if 3D printer is used often.
LCD SLA is the dominant variant of MSLA technology. There are many contributing factors to this. Low 3D printer cost, large number of manufacturers and models, simple use, high-detail and high-speed 3D printing, low maintenance, simple machine design and a large community of users. However, any AM technology is only good as the materials that can be used to build parts and products. It can be said that today most AM technologies are at a point where they are more than capable to producing high quality parts in volume. However, precision, surface quality, build speed and tolerances that a machine can achieve are meaningless if there are no materials suitable for a particular product that needs to be produced. It is therefore of paramount importance that AM technologies can build parts with a very wide range of materials. This presents a problem since products are made from a vast range of materials.
SLA works exclusively with thermosetting polymers (Zhang & Xiao, 2018). User either directly pours resin into the build tank or inserts a resin cartridge into the 3D printer, depending on manufacturer and model. Parts are then produced from that resin. It is immediately obvious that due to working principle SLA

technology can produce only single-material parts. Only exception to this is BCN3D's VLM technology that can use two resins in the same part, but as of now has only been announced as an expensive, professional technology.
Purpose of this paper is to investigate current situation on low-cost resin market (consumer market), as these materials are the ones that are used in consumer LCD SLA 3D printers. LCD SLA 3D printers are a relatively new occurrence and therefore availability of related low-cost resins has generally trailed behind the wide range of professional materials made available for professional SLA printers from industry leading manufacturers. Situation has significantly approved over the last few years, but although there is now a wider range of available materials, they are mostly sold "as-is", meaning there is usually no mechanical data provided. Instead, users must rely on vague manufacturers' descriptions and anecdotal advice from user community when choosing appropriate material for a certain application. This is one of the most important reasons why LCD SLA 3D printers can hardly be used in more serious prototyping and manufacturing role where mechanical properties of produced part are important. It also explains why these 3D printers are still mostly used for miniatures printing and similar high-detail applications and not production of functional parts. Of course, users can still print using professional resins, but that defeats the purpose of using low-cost machines, since professional resins can cost anywhere between 150 and 300 €/kg, whereas low-cost resins are usually in 25-50 €/kg range. This means that just three kilograms of professional resin are more expensive that a large majority of LCD SLA 3D printers and that amount of resin can be used in under a week of consistent printing.

2. METHODS

It must be understood that there is almost no concrete available data on sales volume of individual consumer resin manufacturers, nor is there a clear consensus on where the distinction between manufacturers of professional and consumer resins is. For now, LCD SLA 3D printing can be considered entirely centred on non-professional users that employ these machines for personal projects. It is therefore of little surprise that there is no serious research about this topic.
Given that there are no clear data on popularity or size of consumer resin manufacturers, it was decided to select a representable sample of manufacturers based on their popularity and reputation in user community and websites dedicated to 3D printing. Selection was further narrowed based on Google Trends search popularity over the last 12 month. In the end six manufacturers were selected. Three of those produce 3D printers and resins, while three only produce resins.
Formlabs was selected as a representative for professional side of resin manufacturers and was used as a comparison to manufacturers of consumer 3D printers and resins. Formlabs is a very popular and established company that produces laser-based SLA 3D printera, along with a very wide range of resins. It is considered as an affordable professional SLA solution and is therefore extremely popular with high-end desktop users, smaller companies, research facilities and educational institutions. As was mentioned earlier, it is their wide selection of available resins that make them so appealing. We surmise that Formlabs is an ideal company with which to compare consumer resin manufacturers, as it offers a wide selection of materials with available mechanical datasheets, but is still not considered a highly professional manufacturer like 3D Systems or Stratasys that also offer SLA 3D printers. Importantly, in contrast to those major manufacturers, Formlabs makes prices of their resins available.
Resins of every manufacturer are usually separated in three categories: basic, engineering and specialty. This is how most professional resin manufactures divide their range. Basic resins are designed for purely visual aspect of prototyping. They have high surface quality, print fast and achieve fine details. Engineering resins are used to produce functional parts and therefore have high mechanical properties. They are often meant to simulate other commonly used plastics, such as ABS plastic and therefore have similar mechanical properties to them. Specialty resins are considered those that have some property that is novel or highly specific, such as dental resins that aim to simulate specific type of tissue or plant-based resins that aim to offer low-odour printing that is ecologically more acceptable. Again, there is no clear distinction between these categories and in context in this paper it is based on how professional manufacturers categorize their products.

3. RESULTS

Based on initial research of user communities (Reddit/3dprinting, Quora/3D printing, 3D Hubs) and dedicated websites (All3DP, 3DPrinting, Clever Creations, TCT Magazine, 3D Insider) we identified seven

most prominent companies that produce both 3D printers and resins. These are Elegoo, Prusa, Peopoly, Flashforge, Creality, Anycubic and Phrozen. Further five prominent companies were identified that only produce resins. These are eSun, Nova3D, Monocure3D, Liqcreate and Sunlu.
Google trends gives further insight into popularity of these companies. The term that was used was *"name_of_the_company resin"*, i.e. *"creality resin"*. Term *"resin"* was included as to discount results advantage that companies offering both 3D printers and resins would have. Results are shown in Table 1.

Table 1: Relative search result share of considered companies

Company name	Offer	Rank	Relative search result share
Anycubic	3D printers and resins	1.	100%
Elegoo	3D printers and resins	2.	90%
Phrozen	3D printers and resins	3.	31.6%
Creality	3D printers and resins	4.	28.4%
eSun	Resins	6.	20%
Prusa	3D printers and resins	5.	14.2%
Liqcreate	Resins	7.	14.2%
Monocure3D	Resins	8.	12.6%
Sunlu	Resins	9.	11%
Nova3D	Resins	10.	7.9%
Flashforge	3D printers and resins	11.	4.7%
Peopoly	3D printers and resins	12.	3.1%

Based on the results Anycubic, Elegoo and Phrozen were selected as representatives of companies offering both 3D printers and resins, while eSun, Liqcreate and Monocure3D were selected as representatives of companies that offer only resins. While these six companies do not represent the whole market, they do hold a significant stake in it and can therefore give a good overview of the general trends.
Material range, pricing and mechanical datasheets were collected for every company. Amount of available data in mechanical datasheets was divided into three categories: *"none"*, *"basic"* and *"extensive"*. *"None"* means that no mechanical data was provided. Purely descriptive or relative terms provided by manufacturers were not taken into consideration since they do not represent any useful information. Resins with only one or two mechanical parameters were also bundled into this category, since this limited set of information is insufficient to derive any serious conclusion on the mechanical behaviour of parts produced from those resins. *"Basic"* category contains resins for which some data was provided and this was limited to 3-6 mechanical parameters since this amount of data is sufficient to predict reasonably well behaviour of parts produced using these resins. Finally, *"extensive"* category was reserved for resins that have 7 or more mechanical parameters provided, meaning that it is possible to accurately predict behaviour of parts produced using those resins. Resin offerings of all manufactures are shown in Tables 2-7.

Table 2: Anycubic's resin range

Resin name	Price (USD/kg)	Mechanical data
Colored	38	none
Plant based	41	basic
Flexible tough	60	basic
DLP Craftsman	45	basic
Water-wash	36	basic
Standard	35	basic
ABS-like	38	basic
Dental	60	none
Average price:	**44.1**	

Table 3: Elegoo's resin range

Resin name	Price (USD/kg)	Mechanical data
Plant based	35	basic
ABS-like	34	extensive
Standard	29	basic
8K standard	30	none
Water-washable	34	basic
8K water-washable	40	none
Thermochromic	40	none
Average price:	**34.6**	

Table 4: Phrozen's resin range

Resin name	Price (USD/kg)	Mechanical data
Aqua 4K	40	extensive
Aqua 8K	50	extensive
Speed	38	extensive
Aqua	38	extensive
Water-washable	38	extensive
Mud-like	140	extensive
Flex	69	extensive
ABS-like	33	extensive
Castable W40	240	none
Castable W20	220	none
TR300	50	extensive
Castable Dental	200	extensive
Protowhite Rigid	80	extensive
Rigid Pro410	70	extensive
Functional TR250LV	38	extensive
Stiff	80	extensive
Tough	78	extensive
Average price:	**91.5**	

Table 5: eSun's resin range

Resin name	Price (USD/kg)	Mechanical data
eResin PLA	60	extensive
eResin PLA Pro	60	extensive
Standard	70	extensive
Water-washable	60	extensive
PM200 PMMA-like	56	extensive
Hard Tough	80	extensive
eResin Flex	120	extensive
Average price:	**72.3**	

Table 6: Liqcreate's resin range

Resin name	Price (Euro/kg)	Mechanical data
General purpose	90	extensive
Premium Flex	75	extensive
Premium Model	75	extensive
Premium Black	66	extensive
Premium Tough	75	extensive
Hazard Glow	150	extensive
Tough X	140	extensive
Strong X	160	extensive
Flexible X	130	extensive
Composite X	113	extensive
Clear Impact	130	extensive
Wax Castable	90	extensive
Gingiva mask	140	extensive
Dental model	140	extensive
Average price:	**113.8**	

Table 7: Monocure3D's resin range

Resin name	Price (USD/kg)	Mechanical data
3D Pro Bigvat	119	none
3D Pro Crystal Clear	119	none
3D Pro Deep Black	119	none
3D Pro Glow	141	none
Study	137	none
Precise	160	none
Gingiva	160	none
Tuff	121	basic
3D Rapid	55	none
Flex100	121	none
Average price:	**125.2**	

It should be noted that eSun offers much broader range of resins, 18 in all, but for 11 of those resins pricing was not provided and therefore these were excluded from Table 5.
Formlabs' resin library is considerably larger than any previously mentioned manufactured, containing 36 different resins. Average price of one liter of resin is 263.3 USD. Formlabs provides extensive mechanical datasheets for all resins, with most high-performance resins featuring highly detailed testing data.

4. DISCUSSION

Anycubic, Elegoo and Phrozen are clearly most prominent manufacturers of SLA resins in consumer market. Almost all 3D printers come bundled with some amount of standard resin that is meant to get users going fast. If users get good result with these resins, it is reasonable to expect that they will continue to use the same one. Hence, they purchase the same resin from the same manufacturer. It is therefore not surprising that the most prominent 3D printer manufacturers are also the largest suppliers of SLA resins.
However, resin range of these manufacturers is usually very basic, as shown by the data. Their range mostly consists of standard, water washable, ABS-like and plant-based resins. This is more than enough for casual users that are mainly interested in producing art-based models, such as miniatures, but it is not usable for functional part manufacturing or serious prototyping. ABS-like materials do offer better mechanical properties than standard resins, but availability of detailed mechanical specifications makes it difficult choice to make. In general 3D printer manufacturers offer very scarce mechanical data. Anycubic offers 8 materials, 6 of which have only basic mechanical data available. Elegoo offers 7 materials, 3 of which have basic mechanical data and only one with full data available. Only exception in this category is Phrozen. They offer much broader range of resins, 17 in total. 15 of them have detailed mechanical

specifications available. This is somewhat reflected on pricing – average price per kilogram is 91.5 USD, but this is mostly contributed by expensive castable and dental resins. Price of standard resins is on par with Anycubic and Elegoo. Another difference in their resin range is absence of any kind of plant-based resin.

In contrast, companies offering only SLA resins have a broader range of materials with usually better mechanical specifications provided. They also have higher prices. eSun and Liqcreate offer several high-performance materials that can be easily used to produce functional parts or prototypes. Monocure3D is an outlier in this case, they offer smaller range of resins and provide mechanical data for only one resin. Only two other resins have any mention of mechanical data and they are limited to two parameters. This is disappointing since Monocure3D's prices are comparatively high. I general, it is worth noting that none of these companies offer plant-based resins, which is an interesting situation given their broader range of resins than Anycubic and Elegoo, both of which offer plant-based materials.

Exploring Formlabs range of materials reveals that they have by far the broadest offering of materials and most detailed mechanical datasheets. This is to be expected from a closed, professional systems and highlights how far behind are consumer SLA resin manufacturers. Resin price matches this level of refinement, as Formlabs's materials of similar categories are more expansive than eSun's and Liqcreate's. Of course, this difference makes more sense in high performance materials, but difference between standard materials is vast – Formlabs standard materials (149 USD) are vastly more expansive than Anycubic (38 USD) and Elegoo (29 USD).

5. CONCLUSION

It is difficult to gauge entire resin market for consumer MSLA 3D printers. There are many 3D printer manufacturers offering their own resins and there are many manufacturers specialized only in resins. This paper aims to cover most notable companies in both segments and data suggests that the market situation is rapidly becoming more favourable for desktop MSLA users seeking to utilize more advanced resins at a reasonable price. Prime examples of this are Phrozen Liqcreate. Phrozen has a diverse offering of resins at a reasonable price, while Liqcreate offers rather advanced resins like Composite X, albeit at a higher price. However, it is still substantially less expensive than Formlabs's offering of high-performance materials.

Somewhat surprising is the fact that there are very few eco-friendly resins available. Apart from Anycubic and Elegoo, there are no plant-based resins from any other manufacturers considered in this paper. Desktop resin 3D printing is becoming more popular and one of the most negative aspects of this technology is the fact that resins are difficult to work with and hazardous to health. Up until recently, all resins had to be washed in isopropyl alcohol. Today, all resin manufacturers offer water-washable resins that can be cleaned in tap water. While this is much more convenient for users, these resins still present health hazard. As MSLA technology grows in popularity, development of less toxic, eco-friendly resins is of paramount importance for the users and the environment.

It can be concluded that the range of affordable priced resins is substantial, if not yet diverse like in professional SLA 3D printing. Given that MSLA 3D printing is a still a rather new technology, the outlook for further expansion of material range is good. Many of the companies offering MSLA 3D printers and affordable resins are of Chinese origin, and that has historically been viewed as a negative. However, more and more of these companies are achieving recognition in Western markets and this leads to increased sales, which in turn leads to more research and development of new resins. Therefore, the market in rapidly expanding and it will be interesting to see further developments in years to come.

6. REFERENCES

Chennakesava, P. & Narayan, Y.S. (2014) Fused deposition modeling - insights. In: *Proceedings of the international conference on advances in design and manufacturing ICAD&M'14.* National Institute of Technology Tiruchirappalli, p. 1345.

Kafle, A., Luis, E., Silwal, R., Pan, H.M., Shrestha, P.L. & Bastola, A.K. (2021) 3D/4D Printing of polymers: Fused deposition modelling (FDM), selective laser sintering (SLS), and stereolithography (SLA). *Polymers*. 13 (18), p.3101. Available from: doi:10.3390/polym13183101

Penczek, J., Kelley, E.F. & Boynton, P.A. (2015) A general framework for measuring the optical performance of Displays under ambient illumination. *Information Display*. 31 (5), 30 - 35. Available from: doi:10.1002/j.2637-496X.2015.tb00843.x

Potgieter, J., Zyzalo, J.R., Diegel, O. & Xu, W.L. (2008) Layer Curing for Masked Projection Stereolithography: the effects of varying irradiance distributions. In: *2008 15th International Conference on Mechatronics and Machine Vision in Practice*. IEEE, pp. 604 - 609. Available from: doi:10.1109/MMVIP.2008.4749599

Sampsell, J.B. (1994) Digital micromirror device and its application to projection displays. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*. 12 (6), 3242 - 3246.

Singh, S., Singh, G., Prakash, C. & Ramakrishna, S. (2020) Current status and future directions of fused filament fabrication. *Journal of Manufacturing Processes*. 55, 288 - 306. Available from: doi:10.1016/j.jmapro.2020.04.049

Stampfl, J., Baudis, S., Heller, C., Liska, R., Neumeister, A., Kling, R., Ostendorf, A. & Spitzbart, M. (2008) Photopolymers with tunable mechanical properties processed by laser-based high-resolution stereolithography. *Journal of Micromechanics and Microengineering*. 18 (12), 125014.

Wu, X., Xu, C. & Zhang, Z. (2021) Flexible film separation analysis of LCD based mask stereolithography. *Journal of Materials Processing Technology*. 288, 116916. Available from: doi:10.1016/j.jmatprotec.2020.116916

Zhang, J. & Xiao, P. (2018) 3D printing of photopolymers. *Polymer Chemistry*. 9 (13), 1530 - 1540. Available from: doi:10.1039/C8PY00157J