Plasticizer



Swift Market Assessment for Research & Technology

APRIL 30, 2019

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Foresight Science & Technology's SMART Report provides an unbiased cursory look at the market, competition, IP landscape, and funding opportunities for your idea/technology. This report will help you with: your technology triage process, technology commercialization or funding decision support, assessment of the market for your invention and challenges on its path to the market, identification of potential commercialization partners, and applying for third-party funding. This cost-effective report contains a representative sampling of relevant data collected by experienced technology commercialization professionals.



The Idea/Technology

Reference/Disclosure/Case Number: XXXXXXXXXX

Client Contact: XXXXXXXXX

The technology is a process for adding plasticizers to additive manufacturing (3D printing) polymers in order to alter or customize the properties of the products made or "printed" with them.

What makes this idea/technology innovative?

This invention would allow the end users to customize the mechanical properties (e.g. elastic modulus, yield stress) of stereolithography-produced components by use of one of several resin blends.

What is/are the potential application(s) for this technology?

This technology can be used in 3D printing based on stereolithography. Articles produced using this technology will be significantly less subject to the plasticizer leaching out of the finished material. This makes it suitable in health-sensitive applications such as children's toys and medical appliances. It may also make it valuable in applications where outgassing is an issue, such as vacuum chambers. The reduced leaching also helps ensure longer structural integrity of the finished material.





There are a number of competitive products to consider when comparing this technology to those on the market now. The products described below demonstrate the range of potential substitutes from which customers will be able to choose

Product(s):	Additives for AM
Website:	http://www.ge.com/additive-manufacturing
Company:	GE
Relevance:	GE produces a variety of additive materials for Additive Manufacturing. These include spherical metal powders, and other powdered metals that can be incorporated into the AM process. All of the products appear to be in powder form. ¹
Product(s):	3D photopolymer resins
Website:	http://www.formlabs.com
Company:	Formlabs
Relevance:	Formlabs makes 3D printers and the resins that are used in them. Resin categories include standard, engineering, dental, jewelry, and ceramic. The engineering resins are designed for prototyping that "helps you iterate faster" with resins that are durable, or flexible, or

good for high temps, etc. There is no suggestion that these resins can be used with ionic liquid plasticizers to alter their properties.

¹ "Additive Manufacturing Materials," GE web site, <u>https://www.ge.com/additive/additive-manufacturing/materials</u> (accessed January 13, 2019).

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Product(s): DOW Chemical EVOLV3D[™] USM Universal Support Material

Website: <u>http://www.dow.com</u>

Company: Dow Chemical

Relevance: This is a 3D "support" material that can be used with other 3D filaments to create a variety of structures. The material dissolves in water, leaving a predesigned "gap" that would otherwise be extremely difficult to product with filament and design alone. It is initially available through Taulman 3D.²

Product(s): 3D printing materials

Website: <u>https://www.novoset.com</u>

Company: Novoset, LLC

Relevance: Novoset is a small advanced materials company headed by Dr. Sajal Das, inventor of Primaset while he was at Honeywell. The company develops specialty materials that are printer specific and suitable for 3D manufacturing such as Stereolithography (SLA), Continuous Liquid Interphase Process (CLIP) or other liquid thermoset processes.³

Product(s): Pro Series Flex

Website: <u>http://www.matterhackers.com</u>

Company: Matterhackers

² Tess Boissonneault, "New Evolv3D Universal Support Material by Dow Chemical promises easy, sustainable removal," July 19, 2018, 3D Printing Media Network web site, <u>https://www.3dprintingmedia.network/evolv3d-universal-support-material-dow/</u> (accessed December 27, 2018).

³ "3D printing materials," Novoset, LLC web site, <u>https://www.novoset.com/3d</u> (accessed January 13, 2018).

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Relevance: This filament feels and acts like flexible rubber. It's made in the U.S. 0.5kg of this material sells for \$55.⁴

- Product(s): 3D printer filament
- Website: https://taulman3d.com/index.html
- **Company:** Taulman 3D
- **Relevance:** Taulman produces filament for industrial, technical, medical and artistic uses. It appears the company sells only filament and not liquid resin for stereolithography.⁵

⁴ "Black PRO Series Flex - 1.75mm Flexible TPE (0.5kg)," Matter Hackers web site,

https://www.matterhackers.com/store/3d-printer-filament/proflex-black-tpe-filament-175-05kg (accessed December 27, 2018).

⁵ Taulman web site, <u>https://taulman3d.com/buy-direct.html</u> (accessed January 10, 2019).

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The following information was found utilizing Derwent Innovations subscription-based data set, Google Patents, Espacenet, and other publicly accessible sources.

These patents and patent applications indicate kinds and range of technology that show up in the patent literature. We emphasize that we look at patents from the standpoint of market competition. We have no opinion on the patentability of your technology. Please consult with qualified legal counsel for opinions on your freedom to operate and extent of Intellectual Property protection. Material in quotes is from the patent abstract unless otherwise noted.

Given this procedure, the following patent or applications were found using the following search string: "liquid AND polymer AND stereolithography".

Patent Title:	High temperature three-dimensional printing compositions
Patent Number:	US20160369040A1
Date:	December 22, 2016
Assignee:	Novoset, LLC
Relevance:	This is a thermoset resin composition that uses ionic liquid catalyst to produce stereolithography objects cured at room temperature but that can withstand high temperatures and is cost effective. The ionic liquids do not appear to be used as plasticizers that modify polymer performance.

Patent Title:	Patterning Material, Patterning Method, and Patterning Apparatus
Patent Number:	US20190009457A1 EP3342789A1
Date:	January 10, 2013



Assignee:	Nagase Chemtex Corporation
Relevance:	This patent produces SLA "patterning material" that improves cure speed and suppresses shrinkage in the 3D shaped article by using diallyl phthalate prepolymer to control those properties. "In the present embodiment, as a result of the patterning material having the above-described composition, it is possible to cause photocuring to proceed efficiently. Accordingly, it is possible to improve the curing speed. In addition, with the use of the diallyl phthalate prepolymer, the shrinkage of the shaped article obtained through three-dimensional stereolithography can be suppressed significantly.
	The proportion of the diallyl phthalate prepolymer in the total amount of the diallyl phthalate prepolymer and the photocurable monomer is preferably 5 to 40 mass % or 5 to 35 mass %, and more preferably 10 to 35 mass %.

Patent Title:	A Multi-Modal Printing System and Method of Operating the Same
Patent Number:	US20180257302A1
Date:	September 13, 2018
Assignee:	Agency for Science Technology & Research of Singapore
Relevance:	This technology seeks to improve the efficient operation of stereolithography (3D printing) equipment specifically related to the human intervention needed to remove printed parts, clean the printer surface, and start the subsequent print job. This recent application suggests that the focus on SLA improvements may still be focused on the equipment itself, and not necessarily the polymer used within it.

Patent Title:	Photopolymer Resins with Solid And Liquid Phases For Polymer-
	Derived Ceramics
Patent Number:	US20190002353A1
Date:	January 3, 2019
Assignee:	HRL Laboratories, LLC

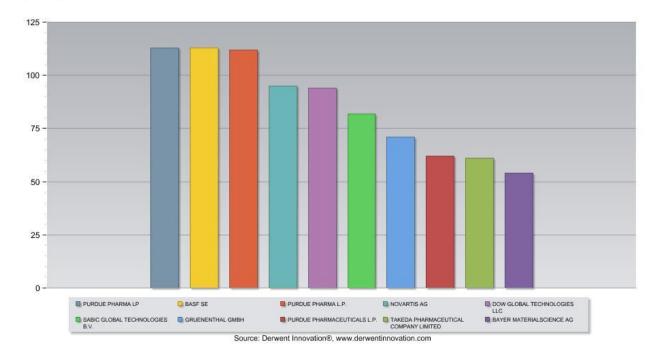
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Relevance:	This is a polymer formulation that provides for 3D printing of ceramic objects that are as strong as traditionally sintered ceramics. "Variations of this invention provide resin formulations and methods which may be used for 3D printing (e.g., by stereolithography) of an intermediate structure followed by thermally treating (e.g., by firing or pyrolyzing) to convert the 3D intermediate structure into a 3D ceramic structure. The monomers and polymeric systems can be converted into potentially complex 3D-printed ceramic shapes with high thermal stability and mechanical strength. The 3D-printed ceramic material may be prepared directly from 3D-printed preceramic polymer material, which contains the dispersed solid polymer fillers. Electromagnetic-radiation curability of the liquid resin formulation enables definition of three-dimensional shapes via 3D printing."

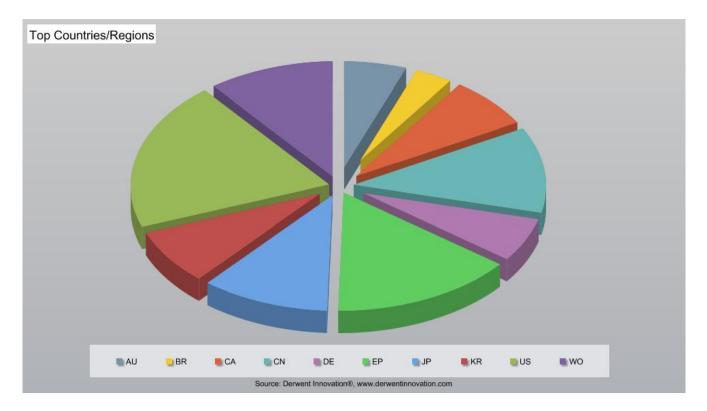
Patent Title:	Tough, High Temperature Polymers Produced by Stereolithography
Patent Number:	WO2018165090A1
Date:	September 13, 2018
Assignee:	Carbon, Inc.
Relevance:	Using CLIP stereolithography, the viscosity of the liquid polymer can affect the properties of the final object that's made. This is important because the technology is being used to produce final parts versus just prototypes. This technology develops the appropriately viscous polymer that solves the problem of it being too viscous (can be difficult to rapidly form into a 3D object) or not viscous enough (can sometimes form low strength, fragile intermediary objects that are difficult to carry through the entire manufacturing process).

The following graphics were obtained from Derwent Innovation analyzing the recent patent activity of "Plasticizer".



Top Assignees by Assignee-Current US









The following provides preliminary findings on the total addressable market for this technology. While market sizes are often hard to estimate, we seek to be as accurate as feasible given the constraints of this report. Below we estimate the approximate total market size, at saturation, for the geographic region, and for all competitors.

Market Niche	Additive Manufacturing (3D printing)
Market Size Indicators	The 3D Printing Plastics Market size was estimated to be \$615.8 million in 2018 and is projected to reach over \$1.9 billion by 2023, with a CAGR (compounded annual growth rate) of 26.1% between 2018 and 2023. The photopolymer segment had the largest share of this market in 2018 and is projected to dominate the market by 2023. ⁶
	The plasticizers market is expected to be worth \$16 billion by 2022, and phthalates is the largest segment. DEHP is not, however, one of the top 4 phthalate plasticizers in this niche. ⁷

⁷ "Plasticizers Market worth 16.15 Billion USD by 2022, Markets and Markets web site, <u>https://www.marketsandmarkets.com/PressReleases/plasticizers.asp</u> (accessed January 13, 2019).

⁶ "3D Printing Plastics Market \$1,965.3 Million by 2023," October 1, 2018, Cision PR Newswire web site, <u>https://www.prnewswire.com/news-releases/3d-printing-plastics-market-1-965-3-million-by-2023-814775846.html</u> (accessed January 13, 2019).

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Market Dynamics

Market Dynamics

Market Drivers	One of the big challenges of using 3D printing for materials is a careful selection of component material with a perfect concentration and an appropriate method. The use of ionic liquids in SLA, or stereolithography, could be a big benefit. ⁸ Because phthalates are not chemically bound to the material they are added to, they can, and do, leach out into water and air. The emission of phthalates occurs during "all" stages of the product's lifecycle. ⁹
	Ionic gels in IL medium have been successfully printed by SLA process with precise structures of microscale resolution. This suggests the approach could be valid. ¹⁰ There is interest in advanced materials within additive manufacturing that alters the polymer once "printed," known as
	4D manufacturing. Thus, continued advancements in changing the polymer material both before and after printing is still quite active. ¹¹

⁸ Kumkum Ahmed, et al, "Ionic liquid in 3D printing (Conference Presentation)," March 27, 2018, Society of Photo-Optical Instrumentation Engineers (SPIE) web site, <u>https://www.spiedigitallibrary.org/conference-proceedings-of-spie/10597/105970W/Ionic-liquid-in-3D-printing-Conference-Presentation/10.1117/12.2296818.short?SSO=1</u> (accessed January 1, 2019).

⁹ Filamentory web site, <u>http://www.filamentory.com/dbp-dehp/</u> (accessed January 13, 2019).

¹⁰ Kumkum Ahmed, et al, "Ionic liquid in 3D printing (Conference Presentation)," March 27, 2018, Society of Photo-Optical Instrumentation Engineers (SPIE) web site, <u>https://www.spiedigitallibrary.org/conference-proceedings-of-</u>

<u>spie/10597/105970W/Ionic-liquid-in-3D-printing-Conference-Presentation/10.1117/12.2296818.short?SSO=1</u> (accessed January 1, 2019).

¹¹ "Advanced materials," 3D Printing Media Network web site,

https://www.3dprintingmedia.network/category/materials/advanced-polymers/ (accessed January 1, 2019).

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	Companies may begin to offer printers at a price that makes them accessible to the everyday hobbyist. ¹² This move would in turn increase polymer use.
	Rize, Inc. has developed a new 3D print technology called APD or augmented polymer deposition. The process, designed for prototyping operations, has one inkjet head that has two separate channels as well as a thermoplastic extruder. With APD, filament and ink can be utilized, layer-by-layer, during the same print-run. The printer can thus lay down functional inks AND release inks. The functional inks can change the material properties, and release inks can make support material removal easier. ¹³ This suggests innovation in the printer itself may have an impact on the ability to alter the properties of the final part.
Barriers to Entry	Little direct evidence of a need or desire to increase the plasticizer percentages in photopolymers used in stereolithography. However, there appears to be an increase in R&D to modify these polymers to alter the final performance of printed objects.
Price of Available Substitutes	0.5kg of material sells for \$55.14

¹⁴ "Black PRO Series Flex - 1.75mm Flexible TPE (0.5kg)," Matter Hackers web site,

¹² Swamini Khanvilkar, "JOSEF PRUSA INTRODUCES A RESIN-BASED 3D PRINTER SLA," September 24, 2018, 3D Printing Industry web site, <u>https://3dprintingindustry.com/news/josef-prusa-introduces-a-resin-based-3d-printer-sla-140370/</u> (accessed January 12, 2019).

¹³ Michael Petch, "RIZE CEO PREVIEWS GAME-CHANGING 3D PRINTING TECHNOLOGY," 2D Printing Industry web site, <u>https://3dprintingindustry.com/news/rize-ceo-previews-game-changing-3d-printing-technology-95453/</u> (accessed January 12, 2019).

https://www.matterhackers.com/store/3d-printer-filament/proflex-black-tpe-filament-175-05kg (accessed December 27, 2018).



Contacts for Potential Partners

Partners may include potential co-developers, licensees, buyers, or other individuals which may be interested in partnering to help bring this technology to market. The individuals listed below have not been validated or contacted by Foresight regarding this technology.

Dow Chemical Company

http://www.dow.com Nathan Wilmot, Associate R&D Director , <u>Nathan.wilmot@dow.com</u> Keith Wilson, Market Segment Manager, <u>Keith.wilson@dow.com</u> *Dow has developed EVOLV3D universal support material for 3D print applications and may be interested in this technology.*

Taulman 3D

http://www.taulman3d.com Thomas Martzall, Owner taulman@taulman3d.com

Taulman is a North American manufacturer and distributor of 3D printing materials. The company works with Dow Chemical and DuPont to provide innovation in the filaments they make and sell for 3D printers. It's not clear if they sell photopolymer, but may be interested if this technology could give them a competitive advantage in that niche.

Eastman Chemical Company

http://www.eastman.com

Alex Dudal, Market Development Rep for 3D filament



423-229-2000

Eastman is a specialty chemicals company and it produces polymers, resins, and plasticizers for 3D printer filament.

Formlabs

http://www.formlabs.com Max Lobovsky, Co-founder and CEO 617-702-8476 This company, spun out of MIT, produces 3D printers and its own library of resins (standard, engineering, dental, jewelry, ceramic).



Funding



Below are some examples of potential funding sources within the area of this technology and/or your geographical region of interest.

National Science Foundation (NSF) SBIR Phase I 2018

https://www.sbir.gov/sbirsearch/detail/1483341

Seeking proposals that permit the manufacturing of complex multi-material, multiscale and/or multi-functional products and services for superior performance and productivity are especially encouraged. This topic includes, but is not limited to, 3D printing, layered object manufacturing, selective laser sintering, selective laser melting, LENS, stereolithography, and fused deposition modeling. Emerging areas in threedimensional printing of complex biological structures for biological and medical applications such as tissue engineering, cognitive technologies, and the study of biomolecular function with the goal of societal benefit and improvement of human potential will also be considered.

Additive Manufacturing Program- Ohio

https://fastlane-mep.org/additive-manufacturing-program/ Funding Available to Help Ohio Manufacturers Try Additive Manufacturing

Office of Naval Research- Materials & Processes for Additive Manufacturing program

https://www.onr.navy.mil/en/Science-Technology/Departments/Code-33/All-Programs/332-naval-materials/additive-manufacturing

Research Challenges and Opportunities: Develop and validate computational approaches for AM materials and processes for engineering applications, Create and



develop AM materials and processes for naval applications, Develop large-scale AM processes for naval materials of interest. Basic Research and Applied Research funding is available.