Autodesk and Stereolithography 3D Printing:

Bio-inspired Resins for Better Human and Environmental Health

Chen Cheng, Ann Dennis, Lee Ann Hill, Coleman Rainey, and Brian Rodriguez
University of California, Berkeley — Greener Solutions

Final Report

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1. Executive Summary

Stereolithography (SLA) is a three-dimensional (3D) printing technique that uses computer-aided and photo-initiated layered construction to produce three-dimensional objects. Though 3D printing has the potential to revolutionize modern additive manufacturing, materials used in 3D printing processes also pose potential hazards to people and the environment. As an active innovator in 3D printing, Autodesk has committed to making additive manufacturing safe and sustainable by developing 3D printing materials and processes that are less hazardous to people and the environment

With help from Autodesk and the Berkeley Center for Green Chemistry, we explored biologically-inspired design principles, which guided our search for alternative resin materials. Using biologically inspired design principles, we also sought to improve the overall safety of the current resin product. In this report, we identify five alternative strategies and evaluate each for their technical feasibility, hazard potential, and potential use cases. We also highlight data gaps and further considerations for each alternative strategy. Through these alternatives, we aim to introduce modifications for improved safety of current 3D printing resins. We also aim to provide a framework for looking beyond current resin materials. Finally, our overall goal for this project report is to explore, identify, and evaluate biologically-inspired materials for safer stereolithography 3D printing resins.

2. Introduction

With increased pressure on industry for efficiency, waste reduction, and sustainability, many manufacturers are now exploring new methods of production. Additive manufacturing, for example, builds three-dimensional products layer by layer rather than using "subtractive" methods of manufacturing, such as injection molding. Additive manufacturing can reduce overall waste in the manufacturing process, as well as cater to a market for customized products.

Three-dimensional (3D) printing is the most common additive manufacturing method used today. One type of high resolution 3D printing is stereolithography (SLA). SLA is a materials processing technique that converts a liquid resin to a solid polymer product, layer by layer, using computer-controlled UV light. SLA allows for customized printed products, and can tune and transform simple prototypes to full-scale production. SLA 3D printing can also distribute high resolution manufactured products outside of factory walls, and into households. 3D printed products have a wide range of uses cases, including prototypes, wearables, and biomedical applications.

SLA 3D printing has the potential to revolutionize modern manufacturing and rapidly pattern various customized, functional, and hyper-local products. However, materials used in 3D printing processes may pose potential hazards to people and the environment. The primary hazards stem from the liquid resin and uncured liquid resin in the final printed object. SLA printers have six common resin types including acrylates, thiols, alkenes, vinyl ethers, epoxides, and oxetanes. Of these, acrylates are the most common because they are very effective and considered the safest (Mulvihill, 2015). Despite being considered the safest, acrylate monomer's reactive properties still pose hazards to human health.

As an active innovator in 3D printing, Autodesk has committed to making additive manufacturing safe and sustainable by developing 3D printing materials and processes that are less hazardous to people and the environment. As a first step in promoting innovation in the 3D printing industry, Autodesk has adopted an open source platform in Spark. Through this open source platform, Autodesk aims to proactively shape 3D printing's future, as well as redefine the future of making things. This fall, Autodesk also began collaborating with Berkeley Center for Green Chemistry to identify alternative resin materials that will improve the bio-friendliness of their resin product, Photopolymer Resin (PR48).

2.1 Current Product

Autodesk's current Photopolymer Resin (PR) 48 consists of reactive oligomers, reactive monomers, a photoinitiator, and a UV-blocker (Table 2-1). PR 48's photoinitiator, Esstech TPO+, is used to initiate the polymerization process at a 405 nm wavelength. Reactive oligomers and monomers are used for cross-linking. UV blocker, Mayzo OB+, ensures that there

is high resolution polymerization in the localized areas dictated by the computer software and projector. The PR48 resin relies heavily on the acrylate-based monomer, which easily forms double bonds to create polymers, but is a potential hazard to human health and the environment.

In California, uncured resin is considered hazardous waste and must be treated and disposed of as uncured paint or coatings. Additionally, the 3D-printing process does not fully cure; in most cases 20 - 30 % of uncured resin remains bioavailable in the print. Exposure to uncured resin can cause skin sensitization after repeated exposure (Mulvihill, 2015a). Additional hazards of the PR48 resin are shown in Table 2-1.

Modifying and redesigning the resin formulation can reduce overall hazard, and may also increase the structural and functional capabilities of the product. Thus, by understanding the components and limitations of the current product, we aimed to efficiently and effectively target interventions based on Autodesk's needs.

Table 2-1. Ingredients, functions, and hazards of current Autodesk Ember Photopolymer (PR) 48 Resin.

	Ingredient	%	Function	Hazard(s)
Reactive Oligomers	Allnex Ebecryl 8210	39.78	Crosslinking	Reproductive & Developmental Toxicant Skin Sensitizer Skin & Eye Irritant Aquatic Toxicant
	Sartomer SR 494	39.78		
Reactive Monomer	Rahn Genomer 1122	19.88	Crosslinking	Skin & Eye Irritant Aquatic Toxicant
Photoinitiator	Esstech TPO+	0.4	Polymerization: Initiation	Reproductive Toxicant Skin Sensitizer Aquatic Toxicant
UV-blocker	Mayzo OB+	0.16	UV light penetration control	Skin & Eye Irritation Persistent

3. Approach

The Greener Solutions team, through the Berkeley Center for Green Chemistry, is comprised of graduate students with varied academic backgrounds, including chemistry, public health, and architecture (see Appendix A). The primary aim the Greener Solutions team was to explore, identify, and evaluate biomimetic, green chemistry, and life-cycle solutions for less hazardous SLA 3D printing resins.

Our approach involved a broad, extensive process of inquiry and a thorough evaluation of alternative resin materials. We aimed to build upon Autodesk's previous work, while incorporating research and perspectives from a diverse set of external resources. Our iterative approach included the three primary steps, depicted in Figure 3-1.

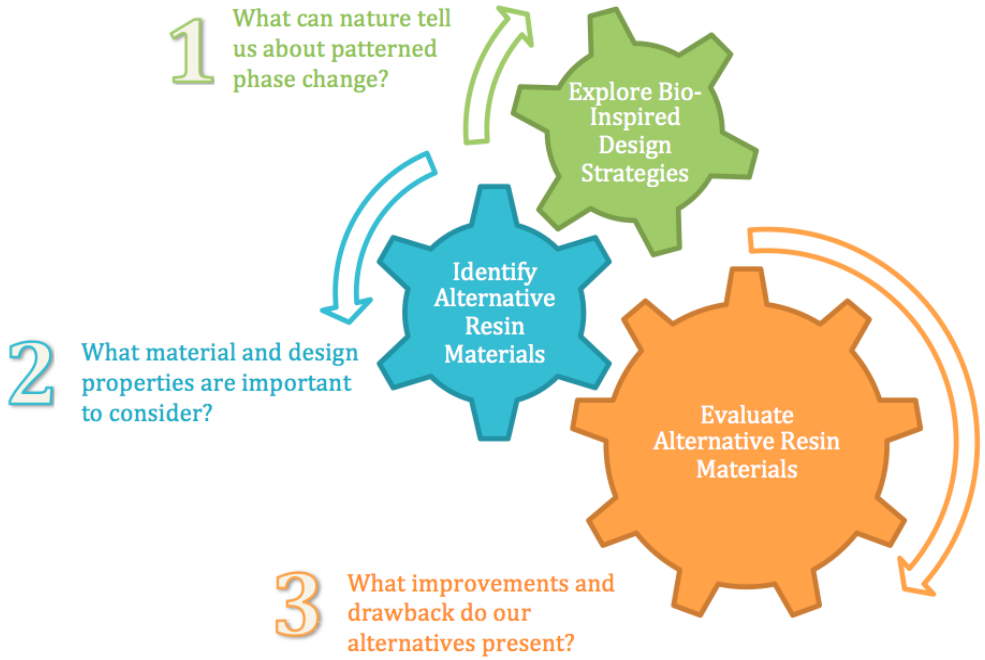


Figure 3-1. Our approach to investigate potential alternatives for SLA resin materials.

We explored previous biologically-inspired design principles to begin identifying alternative resin materials. We then evaluated our proposed alternatives by considering technical feasibility, hazard potential, and potential use cases. This was an iterative process, and we considered three primary questions as we completed this project (Figure 3-1).

Biological Inspiration

Previous work by Tom McKeag, Justin Bours, and Martin Mulvihill guided our biological inspiration for alternative resin materials. The biological design principles, shown in Table 3-1, considered themes from nature specific to material manufacturing and guided our materials selection approach. Additive manufacturing has great promise for making products that resemble natural form, and these design strategies provide inspiration for ways to reduce or eliminate

hazards. These design strategies also promoted the use of functional products that could consist of minerals, polysaccharide, protein, and bio-based synthetics (Mulvihill, 2015b).

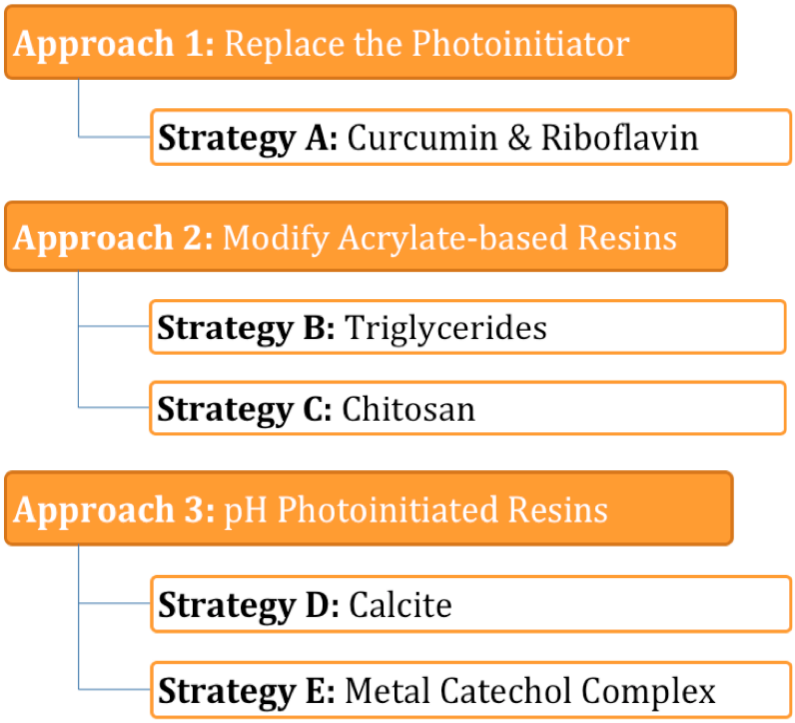
Table 3-1. Biological design principles prepared by Mulvhill, 2015. These strategies include modular, hierarchical construction, self-organization, composites and functional grading of material. These strategies also relate to both the natural phenomena inspiring the principle and possible applications in additive manufacturing.

Design Principle	Biological Inspiration	Application to SLA
Unity within Diversity: *Minimum parts for maximum diversity*	Organisms are comprised of similar components that combine differently to create vast diversity of life	Components of resin can be combined via SLA process to polymerize in countless formations
Multitasking Monomers: *Relationships matter*	Systems are ubiquitous in nature, and outcomes are influenced by relationships between components	Consider all parts and SLA process involved in the making of the final object
The Optimal Activator	The environment can become the trigger that activates the response	Air, light, temperature and pressure are all present in the SLA process
Taking Advantage of Gradients: *Making Delta do Work*	Interrelationships of environmental conditions reveal energy gradients	Energy associated with a phase change, from liquid resin to solid polymer can be used
Shape is Strength	Forms in nature arise from natural selection towards structural advantage	Shape optimization in SLA saves materials and time; layer adhesion is key.
Self Organization	Self-assembly has structural implications at smaller scales, and often utilizes the polarity of molecules	Photo-initiated polymerization in SLA as a form of self-assembly at the molecular scale
Bottom-Up Construction	Molecular level construction to produce emergent properties, like growth, repair, and adaptation	Elements at the molecular level can be combined to produce emergent properties.
Hierarchy Across Linear Scales	Multiple scale construction allows for strength, durability, and resistance to structural stresses	Resin ingredients polymerized sequentially, possibly through self-assembly
Functionally Graded Materials	Parts are changed across space to respond to stresses or structural challenges	Local composition control (LCC) can save materials and energy in manufacturing
Composite Construction	Balancing strength of mineral matrix and flexibility of protein or polysaccharides to address structural challenges at different scales	Shift in AM from prototyping to higher performance parts
Water is the Universal Medium	Biology is water-based; living things benefit and are limited by water	Water-based materials may allow for extreme recyclability, multiple functionality, common sourcing.

3.1 Approaches categorized by level of intervention

We identified three approaches for exploring less hazardous SLA resin materials and organized them by level of intervention (Figure 3-2). First, we recommend modifying PR48's formulation by substituting the photoinitiator. Second, we propose modifying PR48's acrylate based components with biopolymer backbones. Lastly, we propose a non-acrylate based resin that utilizes light and pH induced phase change for polymerization.

Figure 3-2. Approaches organized by level of intervention. Approach 1 provides a strategy for functional substitution. Approach 2 aims to modify the acrylate based resin with biopolymer backbones. Approach 3 explores opportunities for developing non-acrylate based resins.



4. Alternative Recommendation: Replace the Photoinitiator

4.1 Overview

One of the more hazardous ingredients in the PR48 resin is the chemical that initiates the polymerization process, *diphenyl (2,4,6-trimetyl benzoyl) phosphine oxide* or TPO. This photoinitiator is a Category 2 Reproductive Toxicant and is expected to damage fertility (H361F). TPO also causes skin sensitization and is an acute and chronic ecotoxic.

4.2 Strategy A: Curcumin and Riboflavin

Curcumin is a natural yellow-orange dye derived from the rhizomes of turmeric or *Curcuma longa* plant. It is most commonly used as a cooking spice, but is also applied in photobiological and photosensitizing systems. These features make curcumin particularly relevant to SLA printing. Riboflavin or B2 is a water soluble vitamin generated by plants and many microorganisms. It is most commonly found in dairy products and often used as a yellow dye in foods. Both compounds have been studied as effective photoinitiators for free radical polymerization (Zhao, 2015; Kim, 2009), and curcumin is a well known photosensitizer at wavelengths in the near-UV spectrum (Crivello and Bulut, 2005).

4.2.1 Biological inspiration

TPO's main function in the PR 48 resin formulation is to initiate the polymerization reaction between acrylate monomers. In considering this role, we explored ways through which the environment could be used as the optimal activator for the SLA printing process. Because of technological constraints, however, our curcumin-riboflavin strategy is slightly more nuanced than using environmental factors, like air, light, and temperature as activators in the printing process. Instead, we explored materials sourced from nature that could serve as optimal activators and ultimately reduce hazard.

4.2.2 Technical Feasibility

Curcumin contains photolabile benzyl rings that are sensitive at near-UV radiation. The Ember printer operates at 405 nm, and curcumin has exhibited peak absorbance at 417 nm in hexane (Zhao, 2015). Hexane is a non-polar organic solvent similar to the oligomeric PR 48 formulation, thus we expect curcumin to act as an effective photosensitizer in the Ember system. Although it also possesses an absorbance in the near-UV range, riboflavin requires a co-initiating electron donor in order to be an effective acrylate or vinyl polymerizing agent. Thus, because curcumin is a reducing agent and efficiently loses electrons after photo excitation, we propose using curcumin and riboflavin in tandem as a photo-initiating system.

Figure 4-1 illustrates the proposed reaction mechanism. First, a photolabile curcumin molecule will reach an excited state with the incidence of light. In the presence of riboflavin, curcumin will donate an electron, and the two charged intermediates will facilitate the protonation of a carbonyl group. This produces a radical by which free radical polymerization of the acrylate monomers can proceed. Therefore only the initiating step in polymerization will be affected by this ingredient replacement.

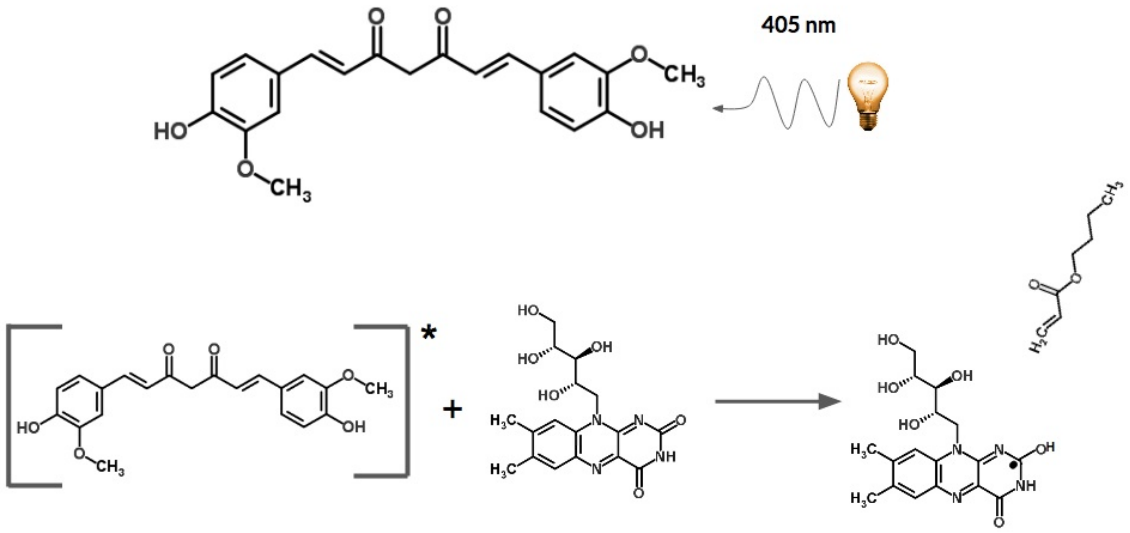


Figure 4-1. An illustration of how curcumin and riboflavin could work in tandem to photoinitiate the production of a radical for acrylate polymerization. Curcumin will reach an excited state through photo excitation, donate an electron, then donate a proton. Riboflavin will subsequently produce a free radical.

The feasibility of this strategy is not only evident in scientific journals, but in our own lab work and correspondence with researchers, as well. During his laboratory work at Lawrence Berkeley National Laboratory, Coleman synthesized a resin with equal loadings of curcumin and riboflavin equalling ~.01% of the total formulation, holding all other PR 48 ingredients constant. Simulating the layered UV-curing of the Ember printer, he was able to cure a 100 micron layer of curcumin-riboflavin initiated resin in approximately an hour. Although polymerization speed is slower than the current PR 48 resin, Chris Venter of the NanoBio team at Pier 9 has suggested that concentrations less than .01% could result in higher polymerization speed. We hypothesize that polymerization speed is being reduced because riboflavin is a highly efficient radical initiator. Therefore, in close proximity to unexcited riboflavin molecules, the excited riboflavin molecules may be terminating their free radicals. By decreasing the concentration of curcumin and riboflavin far below the levels found in PR48, we believe that this photo-initiating system could reach speeds comparable to the current formulation.

4.2.3 Hazard Potential

Our curcumin-riboflavin photo-initiating system consists of two components with different functions, photosensitization and initiation. Therefore, we evaluated the individual hazard profiles of curcumin and riboflavin. In our hazard assessment of curcumin, we found that curcumin does not exhibit carcinogenic activity in male rats. Ames tests have also concluded that curcumin is a non-mutagen. Estimates show that curcumin's log octanol/water partition coefficient (Kow) is 3.29, meaning it is not likely to bioaccumulate. Similarly, curcumin has an estimated bioconcentration factor (BCF) of 68, indicating that it has a moderate potential for bioconcentration in aquatic organisms.

In our hazard assessment of riboflavin, we found that there are no data showing that riboflavin is a developmental toxin in animal fetuses and newborns. Though we found data gaps on riboflavin's potential reproductive toxicity, we found that riboflavin is known for its role in regulating human growth and reproduction. In terms of its absorption and excretion within the human body, riboflavin is rapidly excreted through urine and has a low potential for gastrointestinal absorption, leading to its low hazard profile at high oral doses. Log Kow estimates of riboflavin (-1.46) also show that it has low potential for bioaccumulation.

Finally, in order to accurately assess the hazard of the curcumin-riboflavin system, it is important to consider both potency and dose. For example, though curcumin is known to produce carbon oxides under fire conditions, and to cause skin, eye, and respiratory irritation, we predict that at concentrations between .0001 to .001% of the total formulation, curcumin-riboflavin will have a lower hazard profile than TPO.

4.2.4 Potential Use Cases

Because we are proposing a direct functional substitution to TPO, we anticipate that our strategy's potential use cases will remain the same - jewelry and artistic applications. This strategy is a straightforward fix for reducing hazard in the current formulation. Moreover, if acrylate based monomers could also be altered to decrease their hazard profile, incorporating them alongside a curcumin-riboflavin initiator could provide new use cases.

4.2.5 Future Considerations

Given that polymerization speed at an experimental concentration level of .01% is a technological barrier, we recommend evaluating speed at different concentrations. It is also important to acknowledge that acrylate monomers still comprise the majority of the resin, and will largely dictate the hazard profile of the final product. Therefore, only replacing TPO with our curcumin-riboflavin system will not significantly alter potential hazards in user handling and

disposal exposure scenarios. However, we do believe that our recommendation provides an avenue for incrementally reducing the hazard profile of PR 48.

Moreover, because curcumin and riboflavin are significantly cheaper than TPO, Autodesk could decrease the production cost by using them in the current PR 48 resin. Lastly, there are a host of food additives that can serve as effective photoinitiators and photosensitizers. Therefore, there are multiple iterations of food-additive based photoinitiators that can be explored as functional substitutes.

5. Alternative Recommendation: Modify Acrylate-based Resins

5.1 Overview

Because the photo-curable monomers comprise >99% by weight of the current PR 48 formulation, we believe that an improvement in the hazard profile of the monomers will lead to a significant decrease in the overall hazard profile of the resin formulation.

The current Autodesk Ember resin contains ~40% Allnex Ebecryl 8210, ~40% Sartomer SR 494, and ~20%. Sartomer SR 494 and Rahn Genomer 1122 are a tetrafunctional and monofunctional acrylate-containing molecules (Figure 5-1). While the exact chemical structure of Allnex Ebecryl 8210 is unknown, we suspect that it is also an acrylate-containing molecule. The acrylate moiety is needed for the radical polymerization that transforms a liquid mixture of monomers and oligomers into a solid, crosslinked material.

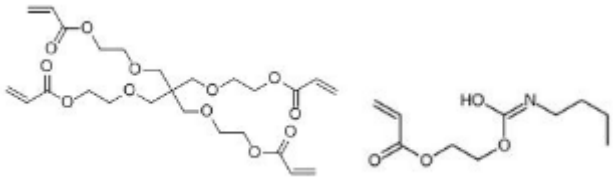


Figure 5-1. Sartomer SR 494 and Rahn Genomer 1122.

The main hazards associated with 3D-printing resins are caused by the presence of the acrylate groups. If absorbed into cells, acrylates can intercalate into the DNA through conjugate addition, rendering acrylates potential mutagens, as well as reproductive and developmental toxins. In light of their hazard profile, many acrylates are also regulated under California Proposition 65. In addition, acrylate monomers in the current PR 48 resin also exhibit moderate to severe aquatic toxicity, and requires that users properly dispose of the resins and rinse waste.

The main route of exposure to acrylate is through skin absorption during monomer production and 3D-printing. Because the monomers have high boiling points and low vapor pressure at room temperature, inhalation of volatilized monomers is unlikely. A second route of exposure is through skin absorption or ingestion during print handling because uncured monomers can leach onto the surface of the 3D-printed objects.

Our approach in reducing the hazard of acrylate monomers involves reducing the bioavailability of the monomers by increasing their molecular weight while maintaining the polymerizable functional groups. It is known that in general, small, polar, and uncharged molecules can easily penetrate the skin and the cell membrane, whereas nonpolar and large molecules do not easily penetrate the skin barrier. Based on the empirical “500 Dalton rule” (Bos 2000), we propose to

increase the molecular weight of the acrylate-based monomers to above 500 dalton to minimize skin absorption.

5.2 Strategy B: Triglycerides

We hypothesize that increasing the molecular weight will reduce the hazard profile of the acrylate monomers. Similarly, adjusting the structure and attachment methods of side-chains could help improve performance. We chose two synthetic formulations to illustrate how increasing the molecular weight of the material could reduce the hazard profile, and adjusting the structure and attachment methods of various side-chains could improve performance.

5.2.1 Biological Inspiration

The most straightforward method to combine a high-molecular weight backbone with acrylate moieties involves reacting a heavy alcohol with acrylic acid or acryloyl chloride. Inspired by the abundant examples of naturally occurring polyols, we decided to first investigate alcohol-containing triglycerides, also known as fats. Triglycerides are molecules composed of glycerol and three fatty acid chains, and the chemical structure of the fatty acid chains dictates the physical and chemical properties of the triglyceride. Specifically, we focused on the triglycerides derived from castor oil, because 85-95% of the fat content in castor oil is made up of ricinoleic acid, which is a fatty acid containing a hydroxy group on C12 (Figure 5-2). This hydroxy group allows the attachment of the acrylate moiety.

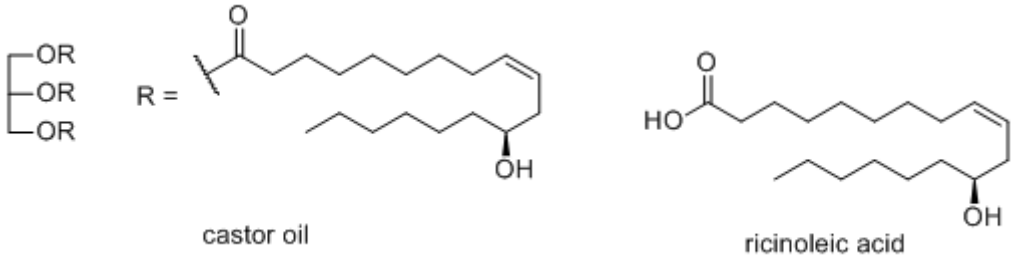


Figure 5-2. Castor oil, major component (R = H) and ricinoleic acid.

5.2.2 Technical Feasibility

We propose constructing monomers containing castor oil-derived backbones with acrylate as the active polymerizable functional group. The target monomer can be synthesized by reacting the major component of castor oil bearing three hydroxy groups with three equivalents of acryloyl chloride (Figure 5-3).

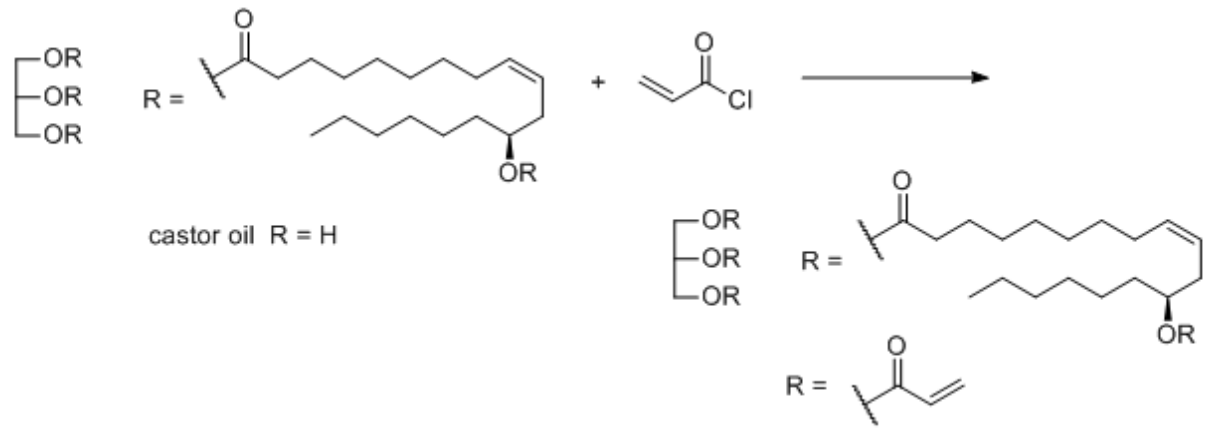


Figure 5-3. Grafting acrylate functionalities to castor oil.

Because the acrylate functionality is the same as the active functional groups found in the current resin (PR48), we expect the new monomers to be compatible with existing hardware. We do acknowledge that because the molecular weight of the monomers is higher than that of the monomers in PR48, viscosity is a potential challenge for monomer handling and mass transport during polymerization. However, this can be potentially addressed by changing fatty acid chains to decrease the melting point and the viscosity. This potential technical barrier can also be addressed by blending in reactive diluents.

5.2.3 Hazard Potential

Our initial hazard assessment of PR 48, demonstrated that health endpoints of interest are skin sensitization and irritation. Through our research, we found that an important measure for assessing dermal absorption and bioavailability is molecular weight. Specifically, we found that 500 dalton is the peak molecular weight at which molecules are readily absorbed and bioavailable (Bos, 2000). Thus, because the molecular weight of our proposed monomers exceeds 500 dalton, we expect reduced skin absorption and entry through the cell membrane. Though we also expect that our proposed monomers would be less bioavailable and hazardous to aquatic organisms compared to PR 48, it is important to note that the molecular weight cutoff for bioavailability through mucosa membrane is 1200 dalton (Bos, 2000).

5.2.4 Potential Use Cases

The use cases of polymer materials depend primarily on the mechanical and physical properties of the polymers, which depend on the chemical composition and the microarchitecture of the materials. Because we propose to construct monomers from triglycerides, we expect the degree of crosslinking to decrease compared to the current PR48. We expect this decreased crosslinking

because of reduced acrylate density. As a result, the 3D-printed objects may be softer than objects printed from PR 48. However, with decreased potential for skin absorption and material softness, there may potential applications in industries that require a high degree of customization, such as hearing aid devices.

Lastly, because our proposed monomers depend on using triglycerides, we can easily tune the physical properties of the monomers and polymers by incorporating different fatty acid side chains. For example, a fully saturated fatty acid may lead to a monomer with higher melting point.

5.2.5 Further Considerations

In addition to reducing the hazard of the current monomers, another advantage of using naturally occurring polyols is that the raw material is bio-based and sustainable, in contrast to the petroleum-based monomers used in PR48.

Castor oil is also relatively inexpensive. Indian castor oil sells for ~$0.05/kg (http://www.commodityonline.com/commodities/oil-oilseeds/casteroil.php), compared to crude oil that currently trades at $0.40/kg. Thus, castor oil is an economically viable source of raw material for producing bulk resin materials. In fact, castor oil is already used for grafting polyurethanes (Thomas 2005).

Finally, the hydroxy functionalities of ricinoleic acid can be used as chemical handles for grafting other polymers, such as polylactic acid (PLA), which itself is a biorenewable and biodegradable polymer. Such chemical modification can be introduced before or after polymerization as means to modulate the mechanical properties of the polymers, as well as for coating.

5.3 Strategy C: Chitosan

Chitosan is another biopolymer backbone to which a methacrylate functional group can be grafted. Chitosan has been used in dentistry because it prevents the formation of plaque and tooth decay (Elizalde-Peña et al. 2007). Chitosan can also regenerate the connective tissue that covers the teeth near the gums, and offers possibilities for treating gingivitis and periodontitis (Pena 2007). In past studies, Chitosan has also been chemically modified to produce advanced functional materials. Specifically, chitosan has been blended with hydroxyapatite to create bone-filling paste for bone substitute and dental composite filling (Elizalde-Peña et al. 2007; Tamura et al. 2011). Chitosan's biocompatibility, biodegradability also make it a suitable material in biomedical applications (Tamura et al. 2011; Bhardwaj and Kundu 2010). For instance, Chitosan

hydrogels are used to develop scaffolds and membranes for applications in tissue engineering and wound dressing (Tamura et al. 2011).

5.3.1 Biological Inspiration

In nature, chitin provides structural and material strength in the exoskeletons of many insects and crustaceans (Azuma et al. 2014). Chitin is also a critical component in the the cell walls of fungi and yeast (Azuma et al. 2014). In identifying another compatible biopolymer for modifying acrylate-based resins, we were drawn by chitin molecules' ability to self organize and create a material necessary for protecting vital functions within organisms. Therefore, our second strategy for modifying acrylate-based resins aimed to replicate chitin molecules' ability to create a protective material, through the use of chitosan. Chitosan is a deacetylated derivative of chitin, and has been used as a photopolymerizable material through methacrylation (Romano et al. 2015; Arakawa et al. 2014; Amsden et al. 2007).

5.3.2 Technical Feasibility

Our second modified acrylate based resin is Methacrylated Glycol Chitosan (MGC) (Figure 5-4). Chitosan is well known for its biocompatibility, biodegradability, and relatively low toxicity (Amsden et al. 2007; Tamura et al. 2011). However, one barrier to using chitosan as a photopolymerizable material, is its poor solubility at pH > 6 (Tamura et al. 2011; Amsden et al. 2007; Arakawa et al. 2014). Therefore, researchers have proposed modifying chitosan's solubility through the addition of a glycol group (Romano et al. 2015; Arakawa et al. 2014; Amsden et al. 2007). In doing so, researchers have been able to solubilize glycol chitosan with a 1M NaOH solvent at pH = 9.0 (Romano et al. 2015). MGC can be produced by reacting a solution of glycol chitosan with glycidyl methacrylate. Romano et al. 2015 reported that 3% degree of substitution occurs by reacting glycol chitosan solution with glycidyl methacrylate for 24 hrs. However, it is important to note that degree of substitution can be manipulated through incubation time (Arakawa et al. 2014).

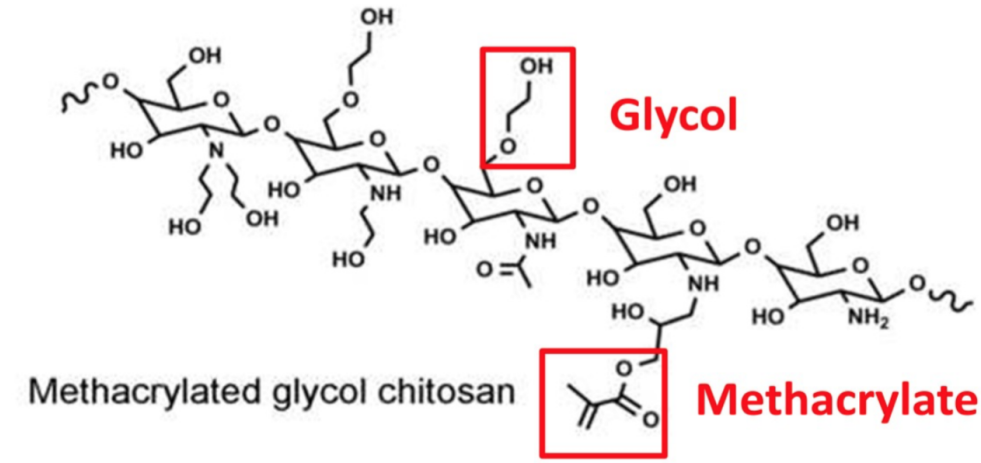


Figure 5-4. Adapted from Arakawa, 2014. Molecular structure of methacrylated glycol chitosan. Adding a glycol group modifies chitosan so that it can be solubilized at pH = 9.0. The methacrylate functional group allows for photopolymerization.

5.3.3 Hazard Potential

There are significant data gaps in the hazard profile of MGC. Therefore, our first approach in understanding the potential hazards of this alternative material was to first look at glycidyl methacrylate. In our hazard assessment of glycidyl methacrylate, we found that health endpoints of concern are: mutagenicity, eye irritation, skin irritation and sensitization, and acute and chronic aquatic toxicity.

In assessing, MGC's hazard profile, we cannot accurately assess hazards related to carcinogenicity, mutagenicity, and reproductive and developmental health. Similarly, though we know health hazards associated with using glycidyl methacrylate, we cannot reliably extrapolate those hazards to MGC because of many factors. For example, given that degree of methacrylation can be manipulated, it is important to first determine how much methacrylation is needed to make MGC compatible with the Ember printer. Secondly, degree of methacrylation also falls in line with dose and potency considerations. By knowing the required degree of methacrylation, we can also determine the concentration levels of methacrylate in the resin formulation. One final consideration for assessing MGC's hazard profile, is the potential for risk shifting. For instance, the highest risk is present in the handling of glycidyl methacrylate. pre Therefore, it is important to consider the setting under which MGC is prepared. If MGC is prepared under controlled settings, then the hazard potential of glycidyl methacrylate can be significantly decreased.

Though there are significant hazards data gaps related to key health endpoints, there are some important starting points in understanding the MGC's hazard profile. For instance, prior studies have assessed the cytotoxicity of MGC. In particular, Amsden et al. 2007 found that MGC's toxicity threshold in chondrocyte cell lines was 1 mg/mL. Similarly, Romano et al. 2015

measured MGC's biocompatibility through mouse fibroblast cells (NIH3T3), and reported cell proliferation up to 85%. As a result, these measures give us information about MGC's cytotoxicity in connective tissue.

5.3.4 Potential Use Cases

There are many unknowns in MGC's hazard profile. However, given the extensive biomedical research on its biocompatibility, we recommend that MGC can be used in applications for which there is available cytotoxicity data. In particular, given MGC's low hazard profile in chondrocytes and connective tissue, we recommend that MGC can be safely used in skin and cartilage regeneration applications.

5.3.5 Further Considerations

To summarize, MGC is a well researched photopolymerizable material that is currently used in biomedical applications. Given the many unknowns related to other important health endpoints, like reproductive and developmental toxicity, we recommend that Autodesk first establish the appropriate concentrations of MGC in order to understand dose and potency. Moreover, given the potential for risk shifting in materials manufacturing, we recommend that Autodesk further consider other exposure scenarios in which risk may be elevated. Conversely, it is important that Autodesk consider at which exposure scenarios risk are being effectively reduced.

6. Alternative Recommendation: pH Photoinitiated Resins

6.1 Overview

SLA printers have six common resin types including acrylates, thiols and alkenes, vinyl ethers, epoxides, and oxetanes. Of these, acrylates are the most common and considered the safest among the six (Mulvihill, 2015). All six of these resin types use radical polymerization and are the only commercially available and academically proposed technology for 3D stereolithography. Until now, the industry for SLA 3D printing has been defined by Paul Jacobs's seminal book, *Introduction to Rapid Prototyping and Manufacturing*, (1992). Since then there have been advancements in the mechanical properties of the acrylates including a range of rigidity and colors. However, the fundamental process of curing the liquid monomers to solid polymers remains the same.
Thanks to the commitment and stewardship of Autodesk, the industry is motivated to improve the human and environmental health impacts of SLA 3D printing. Given the hazard assessment of the PR48 resin we have prepared along with Justin Bours, the reproductive and aquatic toxicity of acrylates at the materials handling and disposal stage is reason to find a new approach for photopolymerization. In addition to these endpoints, we must remember acrylates are a petroleum-based product and with the rising demands of climate change we are motivated to improve the sustainability of the raw material sourcing and manage a cradle-to-cradle lifecycle of the printed product. This is an exciting, unchartered area to explore that could vastly change additive manufacturing.

SLA printing provides an incredible resolution to produce virtually any design. The software developed at Autodesk opens the door for a future where products from industrial parts to wearables to biomedical implants can be customized and optimized beyond any capability of traditional manufacturing. One hurdle to access all this potential is the materials. While there are many novel material possibilities across 3D printing technologies, we hope to push the boundary of the library available to SLA. We thus propose in this report our blue sky strategy, our vision for a fundamental change, for a breakthrough.

It will take significant investment in engineering and laboratory studies. It is proposing two strategies that have not been tried before. We think it is an opportunity worth advancing.

We looked to Nature for lessons in additive manufacturing, specifically for transforming a liquid to a solid in an organized pattern. When considering alternative materials to mimic these lessons, we reviewed the current literature around 2D and 3D printing and synthesized how we could relate those technologies to our challenge. We also considered the key biomimetic strategies proposed by Marty Mulvihill, Tom McKeag, and Justin Bours. The two strategies that most resonated with us were "Taking Advantage of Gradients" and "Functionally Graded Materials."

The biomimetic strategy “Taking Advantage of Gradients: Making Delta do Work” highlights systems in nature that couple a change in environmental condition to a change in material phase. These deltas, or gradients of dynamic disequilibrium, exist extensively throughout the biological world (Mulvihill, 2015b). The system we are interested in is employing a change in pH, the logarithmic concentration of protons in solution, to manage a change from liquid to solid. This would introduce another parameter of localized control to patterning this phase change under stereolithographic 3D printing. In later sections of this report, we will outline how and why we think this is possible.

Another biomimetic strategy “Functionally Graded Materials” is that idea that the array of the material tunes to the desired stiffness. The basic ingredients remain the same, but their ratios organize to change mechanical properties. The classic example is the squid beak: strong and stiff at its pointed end (due to an increased density of protein) to softer and transitional with the rest of the organism (due to increased density of chitin and water). We seek to incorporate this strategy into our approach.

With these two guiding principles in mind, we propose two strategies inspired by organisms in intertidal ocean zones: the oyster and the mussel. These species, among many other creatures, adhere to rock under tremendous force from the seawater. We can learn from both their process and their materials as it relates to SLA additive manufacturing. As process, they take advantage of the pH change in the seawater to form their adhesive cement. As material, they organize organic and inorganic components in a functionally graded fashion that provides both strength and flexibility to their adhesive. Both examples differ chemically and will be explained in greater detail in the “biological inspiration” sections 6.2.1 and 6.3.1.

From there, we asked ourselves how can pH change be photoinitiated in order to be compatible with SLA? Luckily, there is a whole class of compounds studied extensively in two-dimensional lithography that perform this function: photoacid and photobase generators (PAG/PBG). Most generally, these are compounds containing photolabile structures that cleave with the introduction of a photon to form products that are proton acceptors or donors, respectively. PAGs were first proposed in 1984 by Ito and Wilson at IBM for use as photoresists in the the integrated circuit industry (Ito & Wilson, 2009). PBGs followed shortly thereafter. These compounds are well studied in academics and can be used to precisely pattern anionic or cationic polymerizations with micron-scale precision. PAGs have also been developed for use in nano-scale 3D printing utilizing two-photon initiation (Zhou, 2002). These compounds have been underutilized in stereolithography for largely historical reasons (Jacobs, 1992). There is no fundamental drawback or technological justification for their exclusion from three-dimensional lithography. As we shall touch on later, there is little toxicological or environmental data on PAG and PBGs. As these are largely research chemicals with limited application even within microprocessing, more work needs to be done to evaluate their hazard profile.

We propose two ways of approaching this question that are both technologically feasible and minimally toxic. The first, inspired by the oyster, looks solely at inorganic mineralization. The second, inspired by the mussel, looks at the combination of the organic and the inorganic synthesis. The first illustrates how you can strip down a biological model to its core and make its model work in the Ember. The second builds on that simplicity and is particularly exciting because it introduces tunability and functionally graded ability in its chemical composition.

6.2 Strategy D: Calcite

6.2.1 Biological Inspiration

Oysters use an adhesive to attach to intertidal reefs that provides a model for understanding how nature builds materials through patterned phase change from liquid to solid. Figure 6-1 depicts the most commonly studied oyster species, native to Europe, the *Ostrea Edulis*.

Figure 6-1. Zell, H. *Ostrea edulis*. October 3, 2007. Digital Image. Wikipedia. Accessed December 12, 2015. https://commons.wikimedia.org/wiki/File:Ostrea_edulis_01.jpg

Figure 6-2 illustrates how the adhesion between shell and rock occurs. The oyster secretes an organic matrix of phosphorylated proteins (Cranfield 1973). The aromatic amino groups of the

proteins act as nucleating sites for calcium carbonate crystals to precipitate onto out of the seawater (Lopez 2009). Bacteria in the microenvironment of this matrix then convert urea into proton acceptors, creating a local alkaline condition that is favorable for positively charged calcium ions to deposit onto the negatively charged protein amino groups (MacDonald 2010). The carbonate in seawater solution then bonds to the precipitated calcium. Over the course of one night, what began as a soft fibrous gel of proteins became a solidified, incredibly strong mineral matrix (Cranfield 1973). We can learn from both the materials and the process of this biological example as we look to extrapolate methods for SLA 3D printing.

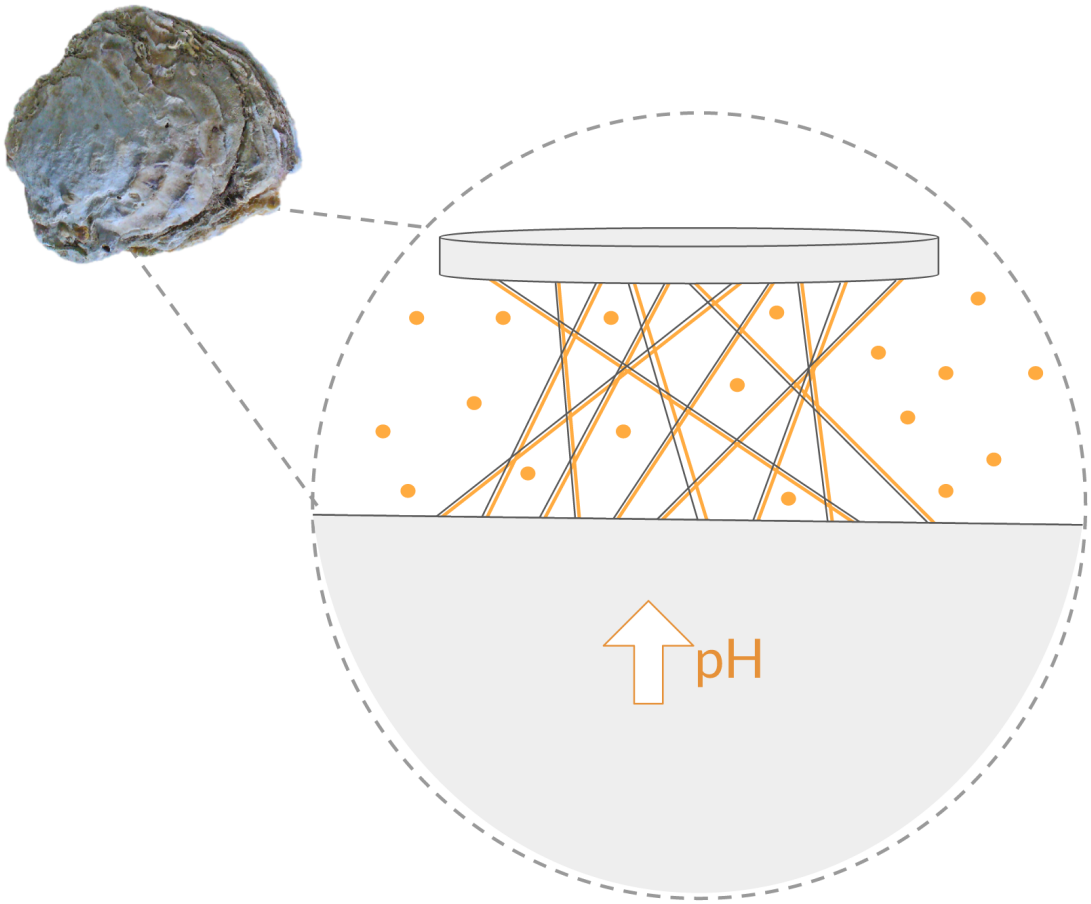


Figure 6-2. *Oyster adhesive between shell and rock.* Personal illustration by Ann Dennis. December 04, 2015. Digital Image. The above cylinder represents the oyster shell and the below surface represents the rock. The black lines extending from the shell represent the extruded protein matrix. The orange dots are calcium and carbonate ions in solution. The increase in pH symbol chronicles a switch to an alkaline environment. The orange lines are then the calcium carbonate ions deposited onto the protein matrix. The image of the oyster is sourced from Figure 6-1.

6.2.2 Technical Feasibility

As a first potential strategy pulling from this example, we can focus solely on the inorganic material, the calcium carbonate mineralization. We expect a crystal lattice of calcium and carbonate ions can be precipitated in the presence of a pH gradient (Figure 6-3).

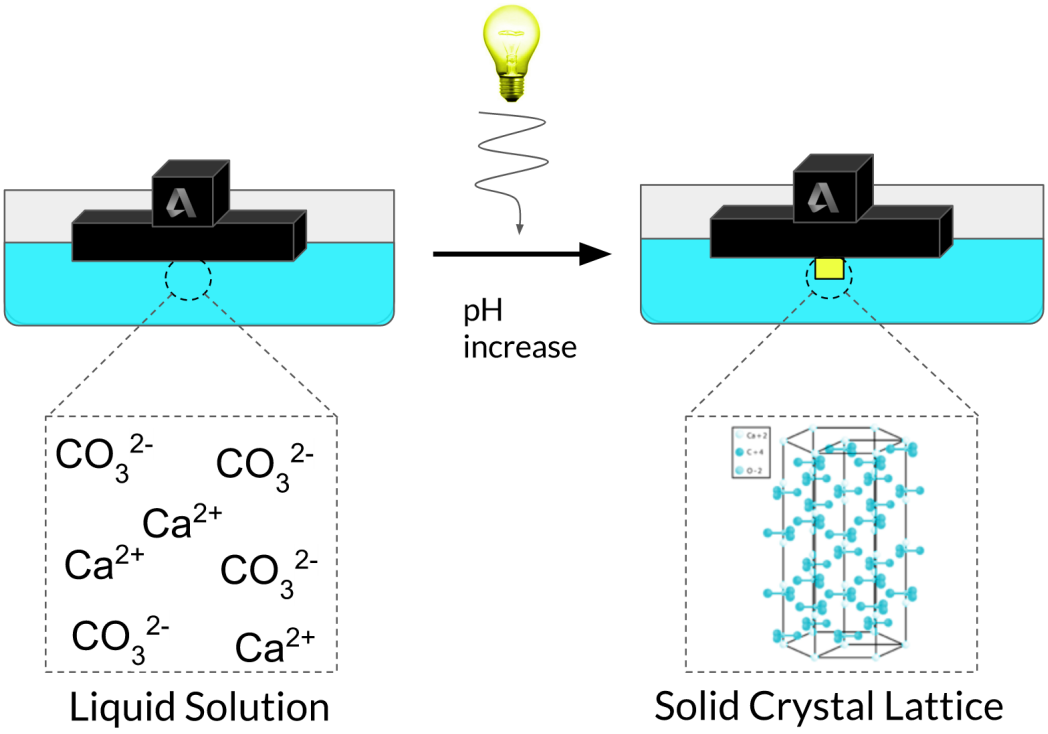


Figure 6-3. Illustration of SLA printer with calcium carbonate in liquid solution transformed by light and a pH increase to become a solid crystal lattice.

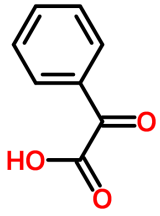
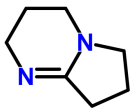
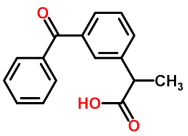
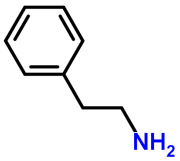
Scientific literature on microbiologically induced cementation and soil remediation details techniques for solidifying calcium carbonate in sand using a pH increase. A rise in pH is equivalent to an increased concentration of proton receptors in solution. This drives the solubility reaction $CaCO_3 \rightarrow Ca^{2+} + H_2CO_3$ to the left, as less protons are available to produce carbonic acid (H_2CO_3). This leads to the rapid precipitation of calcium carbonate, or calcite, at pH levels as low as 8. Mirroring the process of polymerization, the final step required for stereolithographic application is termination. This is evident in two-dimensional use of PAGs, in which the photo-cleaving compounds that release the proton acceptors or hydroxy groups quickly return to equilibrium after irradiation, and are only active in the irradiated regions. (Ito & Wilson, 2009). Photobase generators, the subject of more recent development, have been developed with similar properties. (Suyama, 2008)

The photobase generators we are proposing are tertiary ammonium salts. We have selected these compounds for a number of reasons. First, they are soluble in water. Second, they release strong bases with high efficiency and high quantum yields. This suggests that they can be included in

low concentrations. A number of these PBGs were specifically designed to pose lower risks to environmental and human health, although significant testing is required to validate these efforts.

Table 6-1 shows the components of our proposed PBGs, along with their efficiencies and the pKa values of their conjugate bases. Both phenylgloxylic acid and ketoprofen have been proven to undergo photodecarboxylization with quantum yields as high as $\phi = 0.72$. This means that the double-bonded oxygens are cleaved with the incidence of a photon to form CO_2. In the presence of aliphatic amines, these anions can produce strong photobase generators.

Table 6-1. We propose that these cations and anions can be used in any combination in order to produce quaternary ammonium salts that will act as photobase generators.

Anion	pKa/Quantum efficiencies (if known)	Cation	pKa/Quantum efficiencies (if known)
 Phenylgloxylic acid	$\phi = 0.72$ (Salmi, 2014)	 DBN (1,5-diazabicyclo[4.3.0]non-5-ene)	pKa = 13.5 (Salmi, 2014)
 Ketoprofen	$\phi = 0.75$ (Arimitsu, 2010)	 Phenethylamine	n/a

6.2.3 Hazard Potential

Ketoprofen is used as a nonsteroidal anti-inflammatory drug and often applied as a topical cream. A comprehensive study by the European Agency for the Evaluation of Medicinal Products in 1995 concluded that ketoprofen posed as low risk to mammalian or human health in concentrations as high as milligrams/kg. (EAEMP, 1995) In 1 L of resin, we believe that the concentration of PBG should be held at milligram levels or below, indicating a reasonable level of safety for acute toxic endpoints. Ketoprofen has been identified as mildly irritating to the eyes and skin (GHS, 6.4A, 6.3A). A study on the environmental harms of ketoprofen for persistence,

bioaccumulation, and toxicity conducted by the Canadian Environmental Protection Agency (CEPA) was inconclusive. Phenylglyoxylic acid is a naturally occurring acid that occurs in the metabolization of microorganisms. Although significant data gaps exist, it has been classified by the German FEA as Hazardous to Waters, Class 1, posing a low hazard.

The aromatic amines used in quaternary ammonium salts typically exhibit high hazard profiles. Many are known carcinogens and most are highly basic and corrosive. It is difficult to find photochemically active compounds that release bases and yet retain a low hazard profile. We have identified two amine-based cations, one naturally occurring and one synthetic, that we believe pose the lowest hazard profile possible for such chemicals. Phenethylamine is a natural monoamine alkaloid, found in many different aromatic foods such as cheese and red wine and used as a dietary supplement. In high concentrations it has been found to cause skin irritation (GHS, 8.3A) and eye irritation (GHS, 8.2C), and has even been labeled by the German FEA as Hazardous to Waters, Class 1. DBN, or *1,5-diazabicyclo[4.3.0]non-5-ene*, has also been classified as a skin and eye irritant. Testing of its aquatic toxicity, however, has indicated decreased hazard.

6.2.4 Potential Use Cases

The potential use cases of this proposed strategy would be similar to the current use cases of PR48 and expand upon the profile of applications. Prototyping, educational models, art and design would all benefit from safer products to touch, interact with, and dispose of properly. If feasible to print calcium carbonate at a resolution similar to the current Ember printer, these would strongly rival calcium carbonate products printed using powerbed or fused deposition printing or other forms of manufacturing. Since these other methods use a powder of calcium carbonate with a binder, the array of molecules is at a larger scale as clumps of particles are adhered together using a 2nd ingredient, a glue. The ability to bond the calcium carbonate ions to themselves on the molecular level is not only more similar to how biological organisms manufacture it, but can provide the self organization and mechanical strength of a crystal lattice found in naturally occurring calcite.

The biomedical applications of calcite, the primary composition of bone, is obvious. A Dutch company, Xilloc, 3D prints calcite for non-load bearing artificial bone transplants (Figure 6-4).

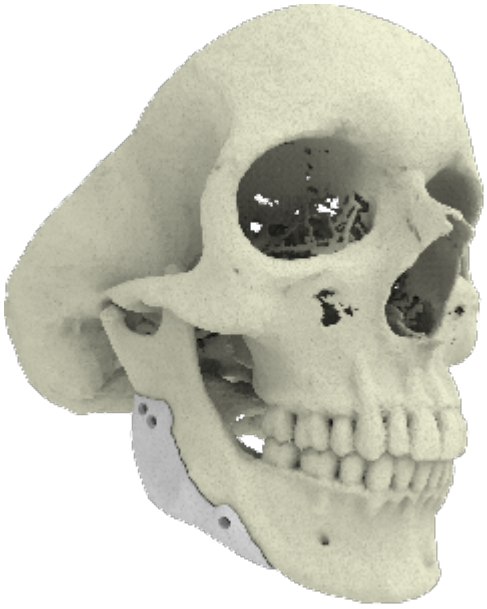


Figure 6-4. "CT-Bone | 3D Printing Real Bone | Xilloc." 2015. Accessed December 18. http://www.xilloc.com/ct-bone/. Image of artificial bone implant.

If a patient has facial or cranial trauma that needs reconstruction, this is still typically done using aluminum or different plastics modeled by hand. How the body accepts these materials has been successful, but there is risk that the body rejects the implant complicating the procedure. With calcium carbonate, the hope would be not only less risk integrating the artificial implant into the body, but improved integration where cellular regrowth could occur around and within the scaffold. CT-Bone believes in these advantages; however, more research is needed. A research group from Munich 3D printed a hydroxyapatite scaffold in a FDM printer with 500µm resolution (Figure 6-5).

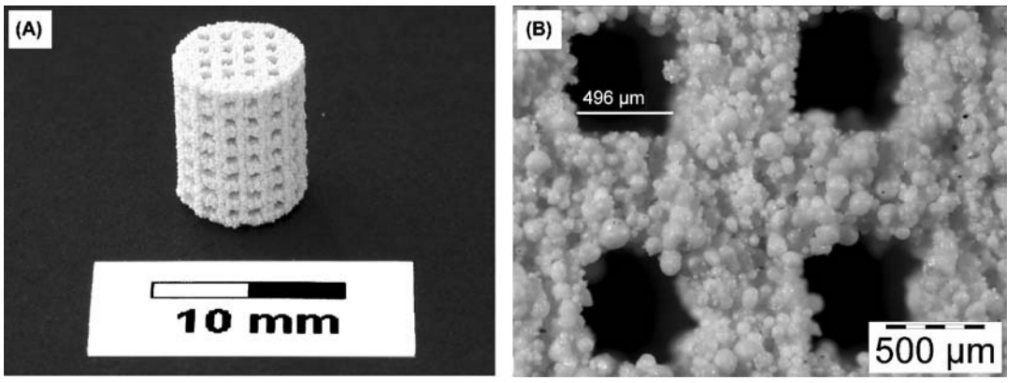


Figure 3 3D printed testpart with interconnecting channels. (a) Whole structure. (b) Detail view of the interconnecting channel structure with diameter of about 500 μm. The remaining granule structure is visible.

Figure 6-5. Leukers et al. 2015. Image of 3D printed hydroxyapatite bone scaffold.

They performed cellular tests and found cells proliferated deep into the structure with success. The advantage of manufacturing this in SLA is the potential for higher precision and therefore better suited for the delicacy of the artificial bone. The ember is currently capable of 50µm to remind the comparison though we cannot report definitely what the resolution is anticipated for this strategy.

The potential hazard of the photobase generators would need more research for biomedical applications. If they are not retained in the final product or there is a post-processing wash that further ensure their removal this would be less of a concern, but it would need to be carefully determined.

Further research developing this strategy would reveal to what degree the final product would shrink. We know that products that need post-processing heat treatment shrink 20-30% as well as products that are water-based hydrogels. This mineral latticing strategy would not need heat treating and would not retain water like a gel that then dries. If this strategy did not shrink as much as competing technologies, the advantage for all use cases is clear.

Research in developing this resin would reveal more about its mechanical properties. This product could potentially be very strong or very fragile and brittle. While there is question of how the calcium carbonate would organize at the molecular scale from something of a sand castle to something of a stone, it will only ever be calcium carbonate meaning this final product will be mineral-based. It will not be a flexible or tunable product capable of being a wearable or other use cases where these material traits would be desired.

6.2.5 Further Considerations

There are many aspects to consider about the technical feasibility of this resin in the Ember printer. How well would the support beams support the printed design? How would it peel from the base? Would the oxygen permeable layer be necessary? How localized can the photobase generators determine its precipitation? Would the calcium carbonate precipitate as predicted? What concentrations of ingredients is needed? Development of this strategy in the laboratory would surely raise more questions and hopefully answer in support of its feasibility.

Like the current product and other alternatives, this one is an opportunity to continue to think about additive manufacturing with light patterning as a means to change phase from liquid to solid at the molecular level, a precision and purity unique to stereolithography. It is an opportunity to additively manufacture in a process closer to biological systems which take advantage of naturally occurring gradients and find strength in the repetition of monomer by monomer addition. Unlike acrylate-based resins, it is an opportunity to think and create beyond free radical polymerization. It is an opportunity to improve the effect on human and

environmental health while sourcing from waste streams and recycling the material in a cradle to cradle fashion.

6.3 Strategy E: Metal Catechol Complex

Our final strategy proposes a stereolithographic and composite material of organic, protein-mimetic macromolecules and inorganic minerals. Further imitating biological systems that produce rapid phase change in the intertidal zone requires the incorporation of both organic and inorganic materials. A close look at another organism, the mussel, offered an exciting model for composite construction. This approach offers the potential for producing functionally graded materials that far exceed the layered tunability of current acrylate-based systems.

6.3.1 Biological Inspiration

Mussels produce strong adhesive thread known as byssus in intertidal zones by taking advantage of the alkaline environment of seawater. The mussel has been well studied by a number of labs around the country, most notably Phillip Messersmith of UC Berkeley Materials Science and Engineering Department. First, the mussel secretes a water-soluble byssus precursor into a groove close to the substrate. These precursors are rich in dihydroxyphenylalanine (DOPA)--approximately 10 to 15 molar percentage. When these proteins are introduced to the alkaline sea-water environment, the catechol becomes deprotonated and coordinates to an iron metal-center (Holten-Andersen, 2008). These metal-catechol complexes can take mono-, bis-, or tris-formations dependent upon the pH and the amount of deprotonation that occurs. This is illustrated in Figure 6-6. This complexes possess among the highest known stability constants of metal-ligand chelates (Holten-Andersen, 2011). By forming these strong byssus threads, the mussel is able to withstand intertidal forces and adhere to substrates with remarkable strength.

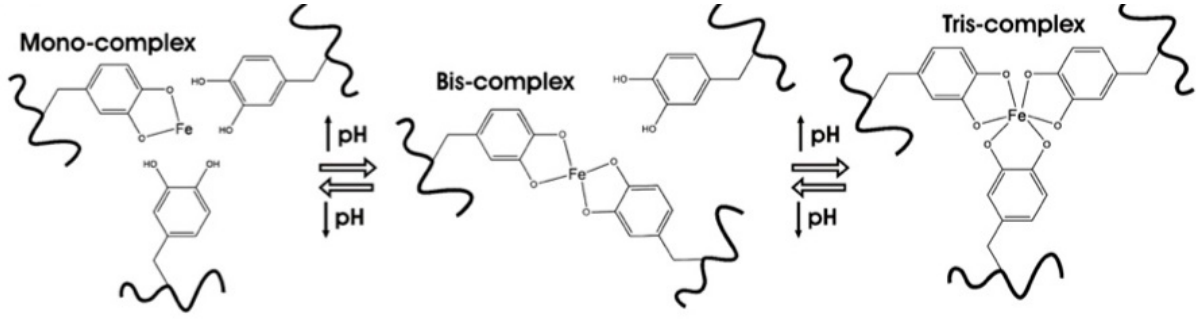


Figure 6-6. The mono-, bis-, and tris- formation of metal-catechol complexes is dependent upon the pH of the system. For the mussel, this is dependent upon the natural environment and the rapid introduction of alkaline seawater. In a SLA system, the tris-complex may not be formed until pH reaches levels as high as ~12.

6.3.2 Technical Feasibility

This process has already been imitated in labs around the country to produce strong, fracture-resilient, hydrogel adhesives. A wealth of academic work has already been done to construct hydrogels and materials that mimic these systems for biomedical and industrial applications (Lee, 2002). Efforts towards understanding the composition of amino acids, proteins, and minerals in mussel and oyster shells have generated pathways for patterning their biomimetic counterparts (Lee, 2006). Biocompatible and 3D printed hydrogels have also been fabricated (Hong, 2015). However none of these research endeavors have produced systems suitable for additive manufacturing or stereolithography.

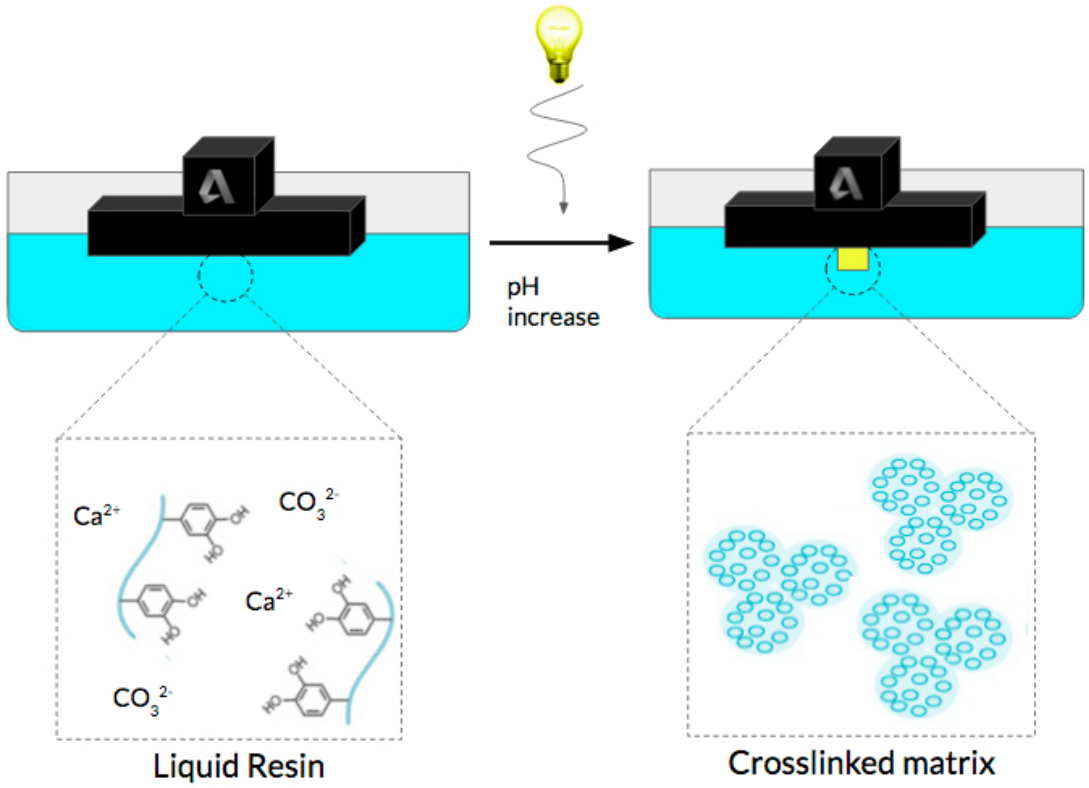


Figure 6-7. A schematic of how we envision a metal-catechol resin to operate in a stereolithographic system.

Although a range of such system are possible, we initially suggest incorporating a PBG with Ca^{2+}, CO_3^{2-}, and a DOPA-containing oligomer that mimics the proteins excreted by the mussel. This would produce a photoactive resin capable of curing to solids with high modulus and fracture resilience. Figure 6-7 represents our vision for how this technology could operate. With the introduction of a photon, the photobase generators would produce proton acceptors. This would initiate the deprotonation of the DOPA catechols, which would subsequently coordinate to the calcium. (Stewart, 2004). These calcium-catechol complexes are ionic and not as strong as their iron counterparts, but will still rapidly form tris- complexes with rising pH. (Xu, 2013)

These complexes would act as nucleating sites for the mineralization of calcium carbonate ions. When the component proteins components are neutralized by the calcium ions, they phase separate into spherical aggregates of colloidal droplets. (Stewart, 2004) Composite materials of DOPA-rich proteins and calcite platelets exhibit high strength and regenerative properties (Lin, 2005).

6.3.3 Hazard Potential

The hazard profile of calcite and the photobase generators remains the same as in the above strategy. L-DOPA, the catecholic ligand used to synthesize the protein-like oligomers, is naturally occurring in humans, but has been identified as a developmental toxicant by California's Proposition 65. It has low irritation and cytotoxicity, however, and has been used for biomedical tissue repairs.

6.3.4 Potential Use Cases

This strategy is exciting because it offers the potential for functionally graded materials that far exceed the tunability of acrylate-based resins. While the cross-linking of acrylates can be modulated layer-by-layer depending on light dosage, this technique is imprecise. As the free radical polymerization involved in the PR48 resin is not living, it is difficult to determine the exact level of cross-linking from dosage. In our system, however, there is a clear level of catechol coordination dependent upon pH levels. As the pH is precisely tuned by the irradiated PBG, we believe that the degree of complex formation could be determined at each layer. In addition, the solubility of $CaCO_3$ follows a well-defined pH dependence. The degree of precipitated calcite as a function of dosage could also be dialed in. Calcite is the primary component in many biomaterials, but also found in minerals such as marble. Metal-catechols are adhesive hydrogels. Producing a technology that can span this range of material properties with micron layer precision would represent a significant advancement in SLA technology.

7. Comparison of Alternatives

7.1 Technical Feasibility for SLA

In assessing the technical feasibility of our recommendations, we considered seven metrics (Table 7-1). We determined that our strategies' compatibility with Autodesk's Ember printer was contingent on their respective abilities to initiate, propagate, and terminate a polymerization reaction. Similarly, we acknowledged the critical role that both polymerization speed and viscosity play in the Ember printer's function. Insight regarding technical feasibility for each of the alternative strategies is shown in Table 7-2.

Table 7-1. Technical Feasibility Metrics describing various design considerations for efficient SLA 3D printing resins.

Technical Feasibility Metric	Description
Mechanical & Aesthetic Properties	Tensile strength, compressive strength, color, flexibility, rigidity
Polymerization: *Initiation, Propagation, Termination*	Addition polymerizations like the free radical polymerization exhibited by the acrylate system can be broadly broken down into three steps: initiation, propagation, and termination. We looked for either the same process or similar processes when designing our alternatives for Autodesk.
Speed	Time it takes for the three phased polymerization process to occur and a single layer of polymer to form.
Viscosity	Viscosity impacts the resin handling and polymerization process, as well as compatibility with the Ember printer. Low
Resolution	Minimize layer thickness for higher resolution, dependent on resin properties and SLA engineering.
Layer Adhesion	To form the solid print, the first layer must adhere to the build plate, and subsequent layers must adhere to the previous layer that is polymerized.
Commercially Available	PR48 is comprised of commercially available ingredients. We assessed if our alternative resin materials were also available for large-scale production.
Price	PR48 is priced at $150 per liter bottle. We determined that a price increase or decrease was a key factor to evaluate.

Table 7-2. Summary of technical feasibility details for each of the proposed alternatives.

	Strategy A: Curcumin & Riboflavin	**Strategy B:** Triglycerides	**Strategy C:** Chitosan	**Strategy D:** Calcite	**Strategy E:** Metal-Catechol Complex
Mechanical & Aesthetic Properties	Identical to PR48, monomers are the same. Yellow - red colored resin	More flexible, less rigid and brittle parts.	More flexible, more fracture resistant. Lab proven. (Arakawa, 2014)	Very strong. Lab proven. (Cranfield, 1973)	Very strong. Lab proven. (Holten-Andersen, 2011) Functionally graded materials possible.
Polymerization	Initiation is possible, as confirmed by Autodesk and Greener Solutions researchers.	Propagation and termination may be affected by larger monomer size; proportion of uncured resin could increase.	Propagation and termination may be affected by larger monomer size, uncured resin could increase. Methacrylates are less reactive than acrylates.	PBGs active enough to initiate precipitation? Propagation occurs in many marine organisms. Termination occurs when solution returns to equilibrium.	Metal-catechols have been synthesized in lab using pH gradients. Propagation shown in tube worms (Stewart, 2000)
Speed	Much lower concentration, .001-.0001%, could yield comparable speed	Same as PR48	Slower than PR48, methacrylates less reactive	PBGs require further testing in SLA system	PBGs require further testing in SLA system
Viscosity	Likely more viscous than PR48	Likely more viscous than PR48, higher MW (and hazard) proportional to viscosity	Likely more viscous than PR48	Viscosity could be too low, $CaCO_2$ must be at extremely high concentrations	Viscosity could be too low, $CaCO_2$ must be at extremely high concentrations
Resolution	Same as PR48	Will require further testing in SLA	Will require further testing in SLA	Micron level precision in 2D lithography (Ito & Wilson, 2009)	Micron level precision in 2D lithography (Ito & Wilson, 2009)
Layer Adhesion	Same as PR48	Lower monomer conversion could limit adhesion, requires optimization	Lower monomer conversion could limit adhesion, requires optimization	Require optimization in Ember, can $CaCO_2$ be in high enough concentrations for layer growth	Adhesive properties of metal-catechols could cause jamming
Commercially Available	**Yes**	**Yes**	**Yes**	**Calcite:** Yes **PBGs:** Some but not all	**Calcite:** Yes **PBGs:** Some but not all

7.2 Hazard Potential

We evaluated the hazard profiles of the five alternative resin material strategies using a hazard assessment framework. Due to time constraints, we did not assign formal benchmarks to each of our alternatives. Instead, our main goal in synthesizing all relevant hazard data was to provide all available hazard information that can be used to inform future hazard assessments, like the Biofriendly Assessment Framework created by Justin Bours. We envisioned that the hazard data we were able to gather will also provide Autodesk an opportunity map for further evaluating our five alternative strategies' hazard profiles.

7.2.1. Hazard Framework Methodology

This assessment includes 18 health and ecotoxicity endpoints based on GreenScreen and Biofriendly Assessment Framework by Justin Bours (2015). We included respiratory irritation and general ecotoxicity, which are endpoints not included in the GreenScreen analysis. The table for environmental and human health endpoints are included in Table 7-3. Hazard information for alternative resin materials was compiled from the following sources:

- **Pharos Project Database, Healthy Building Network:** A comprehensive database of health hazard information for chemicals found on authoritative and or screening lists.
- **Safety Data Sheets:** Workplace chemical management documents indicating physical and chemical properties, as well as health endpoints.
- **Peer-Reviewed Scientific Literature:** Scientific literature was used to assess relative hazard information for chemicals for which no toxicological data was commercially available.

Hazard level (high, medium, low) was assigned based on hazard information obtained from Pharos Project. In some cases, enough toxicological or chemical property information was available from other sources to assess the relative hazard, but with a lower level of certainty. Level of confidence was assigned to each indicated hazard level based on the quantity and quality of data used to assign the hazard level. We listed endpoints as unknown hazard if insufficient toxicological information was available. The results of the relative hazard assessment are shown in Table 7-4.

Table 7-3. Hazard endpoint definitions, adapted from Clean Production Action (2013). *,** Additional endpoints added for this hazard assessment framework.

Hazard Endpoint	Definition
Carcinogenicity	Capable of increasing the incidence of malignant neoplasms, reducing their latency, or increasing their severity or multiplicity
Mutagenicity & Genotoxicity	Agents giving rise to an increased occurrence of mutations in populations of cells and/or organisms; agents or processes which alter the structure, information content, or segregation of DNA, including those which cause DNA damage by interfering with normal replication
Reproductive Toxicity	The occurrence of biologically adverse effects on the reproductive systems of females or males that may result from exposure to environmental agents, including alterations to the female or male reproductive organs, the related endocrine system, or pregnancy outcomes.
Developmental Toxicity	Adverse effects in the developing organism that may result from exposure prior to conception (either parent), during prenatal development, or postnatally to the time of sexual maturation.
Endocrine Activity	An endocrine active substance is a substance having the inherent ability to interact or interfere with one or more components of the endocrine system resulting in a biological effect, but need not necessarily cause adverse effects.
Acute Mammalian Toxicity	Refers to those adverse effects occurring following oral or dermal administration of a single dose of a substance, or multiple doses given within 24 hours, or an inhalation exposure of 4 hours
Systemic Toxicity & Organ Effects	Includes all significant non-lethal effects in a single organ that can impair function, both reversible and irreversible, immediate and/or delayed, not included in any other endpoints previously addressed
Neurotoxicity	An adverse change in the structure or function of the central and/or peripheral nervous system following exposure to a chemical, physical, or biological agent
Skin Sensitization	A skin sensitizer is a substance that will lead to an allergic response following skin contact.
Respiratory Sensitization	Hypersensitivity of the airways following inhalation of the substance
Skin Irritation	The production of reversible damage to the skin following the application of a test substance for up to 4 hours
Eye Irritation	Eye irritation is the production of changes in the eye following the application of a test substance to the anterior surface of the eye, which are fully reversible within 21 days of application.
Respiratory Irritation*	Any substance which can cause inflammation or other adverse reactions in the respiratory system (lungs, nose, mouth, larynx and trachea).
Acute Aquatic Toxicity	The intrinsic property of a substance to be injurious to an organism in a short□term, aquatic exposure to that substance
Chronic Aquatic Toxicity	The intrinsic property of a substance to cause adverse effects to aquatic organisms during aquatic exposures which are determined in relation to the life□cycle of the organism
Other Ecotoxicity**	The intrinsic property of a substance to adversely affect an ecosystem
Persistence	The length of time the chemical can exist in the environment before being destroyed (i.e., transformed) by natural processes
Bioaccumulation	Bioaccumulation is the net result of competing processes of chemical uptake into the organism at the respiratory surface and from the diet and chemical elimination from the organism including respiratory exchange, fecal egestion, metabolic biotransformation of the parent compound and growth dilution

7.2.2 Hazard Profiles of Alternative Resin Materials

Overall, we found that toxicity information was more readily available for acute hazard endpoints as opposed to chronic endpoints. We also found that skin and eye irritation were consistent hazards across the proposed alternatives. However, it is important to further evaluate the modifications of acrylate based resins because of dose and potency considerations. Likewise, aquatic toxicity also remained a consistent hazard across alternatives that retained acrylate based resins, but there may be improvements in aquatic toxicity for our non-acrylate based strategies. Finally, considering California Prop 65 listings of certain acrylates, we recommend that any reduction in reproductive and developmental toxicity is a significant improvement from a regulatory standpoint. Thus, by further exploring Strategy D, with calcite and low concentration PBGs, we expect to reduce reproductive and developmental hazards currently posed by the PR 48.

7.2.3 Limitations of Hazard Assessment and Future Directions

As mentioned, though this hazard assessment is a useful first investigation into the relative hazards of these alternatives, it does not represent a thorough assessment of hazards for each chemical and each strategy discussed in this report. For instance, hazard largely depends on routes of exposure, exposure dose or concentrations, exposure duration, and synergistic toxicity associated with chemical interactions.

We recommend that future hazard investigation include:

1) Quantifying chemical formulations of final strategies and quantifying impacts of post-processing on reducing toxicity. In order to complete a thorough exposure assessment it is important to quantify chemical formulations. By quantifying chemical formulations, Autodesk can also evaluate regulatory constraints for chemicals listed under authoritative bodies.

2) Evaluating the relevance of available hazard information. For instance, points in life cycles largely dictates the hazards related to the types and routes of exposure. Furthermore, hazard assessments should consider the relevance of this hazard information - we believe Justin's Biofriendly Assessment Framework is a great tool for accomplishing this.

3) Chronic hazard endpoints that were not available for many strategies. We acknowledge that these data may require further collaborations with academic partners.

Table 7.2 Summary of hazard assessment of proposed alternative resin materials.

	Human Health Group I					Human Health Group II								Environmental Health			Environmental Fate	
	Carcinogenicity	Mutagenicity & Genotoxicity	Reproductive Toxicity	Developmental Toxicity	Endocrine Activity	Acute Mammalian Toxicity	Systemic Toxicity & Organ Effects	Neurotoxicity	Skin Sensitization	Respiratory Sensitization	Skin Irritation	Eye Irritation	Respiratory Irritation**	Acute Aquatic Toxicity	Chronic Aquatic Toxicity	Other Ecotoxicity**	Persistence	Bioaccumulation
CURRENT PRODUCT: EMBER PR48 RESIN																		
Oligomer 1: Allnex Ebecryl 8210	U	U	HH	HH	U	LH *	U	U	HH	U	MH	MH	U	HH	HH	U	U	U
Oligomer 2: Sartomer SR 494	U	U	HH	HH	U	LH *	U	U	HH	U	MH	MH	U	HH	HH	U	U	U
Reactive diluent: Rahn Genomer 1122	U	LH *	U	U	U	LH *	U	U	U	U	MH	MH	U	MH	HH	U	U	U
Photoinitiator: Esstech TPO+	U	U	HH	U	U	U	U	U	HH	U	U	U	U	HH	HH	U	U	U
UV blocker: Mayzo OB+	U	U	U	U	U	U	U	U	U	U	MH	MH	MH	LH *	*	U	HH	U
STRATEGY A: CURCUMIN & RIBOFLAVIN																		
Curcumin	LH	LH	U	U	U	U	U	U	U	HH	HH	U	U	MH*	U	U	U	LH
Riboflavin	U	U	U	LH *	U	U	U	U	U	U	U	U	U	U	U	U	U	LH
STRATEGY B: TRIGLYCERIDES																		
Acryloyl Chloride	U	U	MH*	MH*	U	HH	U	U	MH*	U	HH	MH	MH*	MH	U	U	U	U
Triglyceride Acrylate Monomer	U	U	MH*	MH*	U	HH*	U	U	MH*	U	MH*	MH*	MH*	MH*	U	U	U	U
STRATEGY C: METHACRYLATED CHITOSAN																		
Glycidyl Methacrylate	U	HH*	U	U	U	U	U	LH	MH	U	HH	HH	U	HH	HH	U	U	LH
Methacrylated Glycol Chitosan	U	MH*	U	U	U	U	U	LH *	MH*	U	HH*	HH*	U	HH*	HH*	U	U	LH *
STRATEGIES D & E: PH PHOTOINITIATED RESINS																		
Calcite	U	LH *	U	U	U	U	U	U	U	U	U	U	LH	LH	LH	LH	U	U
L-dihydroxyphenalylanine (Levodopa)	U	U	U	HH	U	MH	U	U	U	U	U	U	U	U	U	MH	U	U
Ketoprofen	U	U	U	U	U	MH	U	U	U	U	MH	MH	U	U	U	MH	U	U
DBN (1,5-diazabicyclo[4.3.0]non-5-ene)	U	U	U	U	U	U	U	U	U	U	HH	HH	U	U	U	U	U	U
Phenylgloxylic acid	U	U	U	U	U	MH*	U	U	U	U	HH	HH	HH	U	U	U	U	U
Phenethylamine	U	U	U	U	U	MH	U	U	U	U	HH	HH	U	LH	U	MH	U	U

HH: High Hazard	MH: Medium Hazard	LH: Low Hazard	U: Unknown Hazard

* Classification based information not sourced from Pharos or an authoritative body
** Endpoint not included in GreenScreen hazard framework

8. Conclusions

Additive manufacturing has the potential to create opportunities for improving raw materials sourcing, materials processing, and for preserving the integrity of human and environmental health. Through our partnership with Autodesk, we have investigated five biologically inspired alternatives for safer and more bio-friendly 3D printing resin materials.

Three of our five biologically inspired alternatives can be considered incremental changes to the existing PR 48 formulation. Taking into account available hazard information and data gaps, we believe each of these incremental changes have the potential to be safer resin materials depending on potency and dose. For instance, by determining key criterion like concentration levels, relevant exposure scenarios, and monomer conversion rate, Autodesk can reliably compare these strategies to the current resin formulation. To illustrate, though modifying acrylate monomers with a biopolymer backbones can decrease bioavailability in user handling, manufacturing still requires the use of acryloyl chloride or glycidyl methacrylate. In the end, these strategies still rely on the use of hazardous components, but the risk of exposure and hazards are shifted to a more controlled setting. Additionally, because of significant data gaps on the hazard profiles of our biopolymer based resins it is important to adopt precautionary principles, and identify methods through which the safety of our proposed alternatives can be accurately assessed. For example, EPA has published guidelines for assessing carcinogenicity, mutagenicity, reproductive toxicity, and developmental toxicity.

Beyond functional substitutions and product modification, we also believe it is important to move beyond acrylate-based resins for truly safer and sustainable 3D printing resins. In this report, we also discussed opportunities for non-acrylate based resins utilizing a localized pH change along with light to initiate polymerization. Similar to our incremental alternatives, we emphasize the importance of understanding dose and potency when assessing hazard. Though calcite can be considered low hazard components, PBGs have a high hazard profile, and their risks can only be fully characterized by understanding the concentrations at which they will be used.

Finally, we'd like to emphasize that although this work may offer opportunities, it is up to product designers and manufacturers moving forward to create and implement the most appropriate solutions. Collaboration between industry and academia allows for differing viewpoints and a deeper understanding, and we hope this collaboration can help foster innovation for SLA resin materials that is better for people and the planet.

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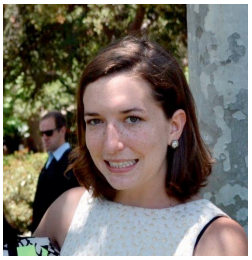
Appendix: About the Authors

Chen Cheng (chch@berkeley.edu) is a 4th-year Chemistry PhD student in the group of Prof. John Hartwig at Berkeley. He received his BS degree in chemistry from UNC-Chapel Hill in 2011 where he conducted research in polymer and organometallic chemistry under the supervision of Prof. Maurice Brookhart. His current work focuses on the development and mechanistic investigation on new catalytic transformations. He's looking forward to applying his technical background to developing more bio-friendly 3D-printing processes.



Ann Dennis (ann.elizabeth.dennis@gmail.com) is in her first year of the M.S. in Architecture, Building Science and Sustainability, program at the College of Environmental Design at Berkeley. She graduated from Pomona College in 2013 with a B.A. in Biology and focused her thesis on the investigation of biological mechanisms for energy and water saving building facades. She is currently studying parametric design while researching performance and structural optimization techniques. She is interested in sustainable directions for additive manufacturing and seeks to improve the impact of architectural materials on human and environmental health. She has enjoyed working Autodesk and is grateful for the opportunity to explore those areas of interest.

Lee Ann Hill (leeann.l.hill@berkeley.edu) is a Master of Public Health student in the Environmental Health Sciences Division at Berkeley. She received her B.S. in Environmental Science from Ithaca College where she researched the fate and transport of heavy metals and endocrine disruptors in soils. While working for the City of Ithaca (NY), she implemented a sampling protocol quantifying emerging organics in local waterways. Currently, Lee Ann works as a Health Intern at Natural Resources Defense Council, where she examines health hazards associated with oil and gas extraction in California. She looks forward to assisting Autodesk in developing safer resins.

Coleman Rainey (colemanwestfallrainey@gmail.com) is a member of polySpectra, a group conducting research at Lawrence Berkeley National Laboratory. They focus on the development of novel photoinitiated polymers with wide-ranging functional group compatibility and potential applications in new lithographic approaches to producing advanced materials. He received his B.A. from Columbia University in Physics where he studied assemblies of ultracold atoms trapped in an optical lattice. He is committed to cradle-to-cradle design practices and expansive thinking in the development of a more just, verdant, and peaceful world.

Brian Rodriguez (rodrib00@gmail.com) is a second year MPH student in Environmental Health Sciences. Brian currently works at the Center for Environmental Health as a research assistant, and makes sure companies comply with their legal agreements related to lead standards. Before enrolling in the School of Public Health, Brian also received his B.S. in environmental sciences at UC Berkeley, and did his senior thesis on mapping air pollution distribution within the East Bay. He's excited to be working with the Autodesk team on this project, and is eager to start helping during this 4-month journey.