



A NEW METHOD FOR PREPARING 3D ACRYLIC PHOTOPOLYMER PATTERNS FOR INVESTMENT CASTING

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BACKGROUND

The stereolithographic 3D printer is rapidly becoming a common way to produce patterns for investment casting of jewelry items. The concept for this 3D printing method was first demonstrated in the early 1980s by Hideo Kodama,¹ and in 1984 Charles Hull coined the term and received a patent for the process of stereolithography.² In this process a CAD file for the 3D object is sliced into layers in the Z axis and the slices are projected with short wavelength visible (blue) and/or UV light onto a liquid photopolymer resin that is selectively cured by this exposure in a layer-by-layer fashion to build a replica of the 3D object. There are two different classes of device to produce parts by stereolithography (SL):

- Direct writing with a laser
- Projection writing using DMD (Digital Micro-Mirror Device)

In direct writing, the laser is selectively scanned over the surface of the resin to expose the slice cross section on the layer of resin. With projection writing, a digital micro-mirror device is located between a strong light source and the photopolymer. The micro mirrors in the DMD are directed so that only the image of the slice of the desired cross section of the layer is passed through the projector lenses to expose the resin.

Over the 30 years since Hull's initial patent, there has been a wide variety of machines developed that can produce stereolithographic parts in a multitude of resins, with new developments in machines, process and resin chemistry occurring at a staggering rate. The use of stereolithography has become an increasingly popular means of producing patterns for investment casting, either as masters for rubber molding to produce wax injection molds or as patterns for direct burnout and casting.

PHOTOPOLYMERS

The photopolymers that are grown in the 3D printer are long-chain molecules which result from the linking and cross linking of monomer and oligomer molecules. In stereolithography the polymerization reaction is initiated by the formation of free radical molecules from the breakdown of a photo-initiator molecule that has been irradiated by the blue/UV light. These free radicals kick off the linking of the monomer and oligomer molecules into chains, transforming

the liquid resin into a solid. There are several families of photopolymers used in SL printers: Acrylate, epoxy and urethane resins are used in the process. Acrylates resins, derived from acrylic acid, are used for growing patterns for direct burnout in investment casting. These resins are similar to methyl methacrylate (MMA), the resin used to make the glazing material that we typically think of when we hear the word acrylic. That clear plastic sheet is polymethyl methacrylate (PMMA), the polymerized form of MMA. However, the SL photopolymer resins are typically more complex molecules than MMA. The composition of the resins used in the 3D printer is typically closely held information, but one manufacturer has released one of their resin formulas³ as an open source material. Figure 1 gives us an idea of what the resin's composition might look like.

PR48 Resin

- Photoinitiator: 2,4,6-Trimethylbenzoyl-diphenyl-phosphineoxide (TPO) 0.40%
- UV blocker: 2,2'-(2,5-thiophenediyl)bis(5-tert-butylbenzoxazole) (OB+) 0.16 %
- Reactive diluent: Genomer 1122, 19.89%
- Oligomer: Ebecryl 8210, 39.78%
- Monomer: Sartomer SR 494, 39.77%

Figure 1 Open source resin formula

Monomer and oligomer molecules make up about 80% of the formula, which are the building blocks of the final polymer. The monomer molecule is the repeating element in a polymer chain, and the oligomer molecule is composed of multiple monomers with a specific structure that links between the polymer chains. The oligomer molecule is chosen to improve the polymer's properties and may even bring other types of polymer families like epoxies or urethanes into the resin in a form that will cross link into the polymer chain. A reactive diluent is used to reduce the viscosity of the monomer/oligomer solution to a useable consistency, basically a different monomer molecule that has a lower viscosity. This way the reactive diluent is linked into the structure by polymerization rather than having to evaporate like a solvent would; it makes up about 20% of the formula. The photo-initiator that kicks off the polymerization of the monomer and a UV blocker to limit the penetration of UV make up the balance of the liquid resin.

PROBLEMS WITH PHOTOPOLYMER RESINS AND BURNOUT

Polymer resins have been used for making patterns for direct burnout for many years. The most common one is polyethylene; it is well known as carving "wax." It is available in different hardness formulations and colors to facilitate its use

as a directly carved pattern material. In a different formulation it is injected into metal molds to make “plastic” patterns. It is easily melted, vaporized and then combusted in the burnout process; it flows out of the cavity formed by the casting investment around the pattern at a reasonably low temperature in a similar fashion to waxes. With continued application of heat, the polyethylene will decompose into smaller molecules, such as propane, propene, ethane, ethene, and other similar compounds, that are easily combusted.⁴ It does require a bit more care and attention in the burnout process than a wax, but in general it can be treated like a wax pattern. Polyethylene is close enough to wax in its properties that it is also used to modify the properties of many wax formulations.

Patterns from a stereolithographic printer are a different story. Unfortunately, polyethylene is not available in a form that can be utilized in stereolithography. Though many refer to these resins as waxes, they do not behave like waxes in a number of ways. They have a higher coefficient of thermal expansion which can adversely affect the durability of the investment.^{5,6} The SL acrylic resins don't really melt like a wax or polyethylene. They remain solid until the heat applied is in the range of 300°C-400°C (572°F-752°F), when they will begin to decompose. As the resin decomposes some of the polymer chains depropagate (unzip) or split in the middle, breaking down into smaller polymer or other compounds, then back into monomers and oligomers which can volatilize and burn. The oxygen from the air and hydrogen from the resin will form peroxides, hydroxyls and other reactive compounds. Those compounds, along with free radicals still present in the resin, cause some of the monomers to polymerize again only to be decomposed later with the rising temperature. This may happen multiple times during the decomposition process. Eventually, a tar-like mass forms that is a mix of monomer, polymer and other compounds formed in the decomposition process. With continued heating this material eventually breaks down into volatile compounds that combust and turn into CO₂ and water vapor, which exit the cavity.

Some of the pattern's mass will remain behind as a solid char. This char may be 15%⁷ or more of the original mass of the pattern. Char is the solid residue from the decomposition and is carbon compounds that can't volatilize. This char takes a long time to burn out of the mold cavity due to the limited availability of oxygen and the upper temperature limitation of gypsum-bonded investment. To completely remove the char, the flasks typically require a burnout schedule with a long dwell at a temperature near the breakdown point of gypsum investment. If the char is not fully combusted in the burnout process, it will show up as black inclusions in the casting. With many resins there is also some “ash” left behind as well that is not combustible and ends up as inclusions occupying some of the mold volume and reducing the fidelity of the casting. There are burnout schedules for gypsum investment, special formulations of and additions to the investment mix that seem to improve the pattern removal process, but there still seems to be no consensus on what is the best process.^{5,8,9,10,11}

The Positive Defect

Beyond burnout schedules and investment formulations, there is a persistent problem in the burnout of the photopolymer pattern that seems to be hard to eliminate. It is the mold-surface degradation that leaves a raised positive defect on the surface of the casting, increasing the volume of the casting beyond the perimeter of the original pattern. It can range from a significant roughening of the surface and loss of detail to just occasional bumps where the face of the mold has spalled away. It appears to be some form of resin-mold reaction that is affected by burnout schedule and the degree of post-grow pattern cure. If you invest and burn out a pattern that has only been rinsed to remove uncured resin from the surface, the results will be a very degraded casting surface. The more complete the curing of the pattern, the less this type of defect presents in the casting.

It is very clear from empirical evidence that exposing the investment to uncured or under-cured resin definitely degrades the surface of the resulting investment mold. It has been suggested that a chemical reaction between the investment and the monomer in the uncured resin interferes with the setting or structure of the investment in the area of contact, resulting in a reduced-strength investment where it touches the pattern. The degraded investment, coupled with the high thermal expansion rate of the acrylic pattern, is put forward as the cause of the observed casting defects. However, given that the resin breaks down into a monomer several times in the thermal decomposition process, it would seem that all molds from photopolymer resins would be adversely affected if this were the case.

I would like to suggest an alternative hypothesis. I believe that what is happening is that the uncured and under-cured resin is impregnating the investment at the interface with the pattern. It starts when the pattern is exposed to water in the investment during the mixing and setting process and the initial stages of burnout. I believe the vacuum applied during the investing process is also helping to draw the uncured resin out of the pattern. These resins are miscible in water, so this would lead to a resin presence in the uncured investment at the interface between pattern and the investment. During burnout, as the investment is dried out and the temperature begins to rise, I believe the resin-impregnated investment is essentially cemented to the pattern by the curing of that resin by heat. With the rising temperature the pattern will eventually begin to shrink as the volatile components escape. I am suggesting that the shrinking pattern pulls the resin-impregnated, cemented investment off of the surface of the mold cavity, resulting in the positive surface defects seen on the cast pieces.

Post-Curing of the Patterns

Patterns produced on SL printers are not fully cured by their exposure to the blue/UV light in the printing process. To provide enough exposure to fully cure each layer would result in a loss of resolution as the light scattered outside the intended exposure area would cure a larger spot than intended. Mechanical issues are also presented by a greater degree of curing while printing. The resin shrinks as it cures, straining the layer-to-layer bond and distorting the shape of the cured

resin. It can also make freeing each freshly cured layer from the growth surface difficult as the resin is an excellent glue. Therefore, the resin is cured just enough to have the strength to retain its shape and allow it to be pulled off of the growth surface.

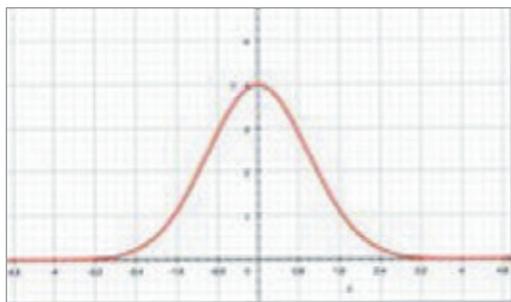


Figure 2 Light beam power distribution

There is an additional issue in the exposure and curing of the pattern that results in uncured resin in the pattern. The beam of light used to cure the resin does not cure a nice, clean cube of resin as it is exposed but produces a volume with a cure gradient, a roughly Gaussian distribution (Figure 2) of degree of cure in the cross section of each voxel or along each raster line.^{12,13} This results in a small volume of uncured resin throughout the matrix of the pattern (Figure 3). Longer exposure to achieve a greater cure would degrade the resolution of the pattern by scattering of light, which would cure unintended volume around and above the desired volume. Since high resolution is one of the main goals in 3D printing patterns, the printer exposure parameters for each resin are typically tuned to minimize curing of unintended volume.

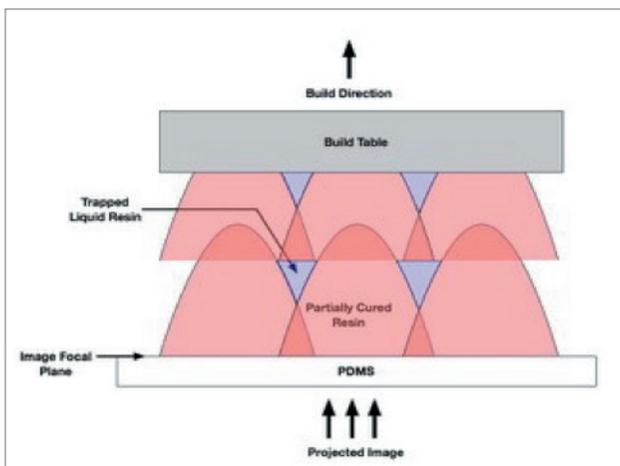


Figure 3 Cured and uncured resin

Post-Print Curing with UV

Post curing of the patterns is intended to complete the curing of under-cured and uncured resin in the pattern. Resin manufacturers typically specify a post-print exposure of the cleaned pattern in a chamber brightly illuminated by UV-emitting lamps or LED's. Post-print UV exposure has a couple of problems, though. First is oxygen: The free-radical process, which is how most of the resins used for direct burnout are polymerized, is inhibited by the presence of oxygen. From the surface of the pattern to the depth of several microns, the resin is under-cured due to this inhibition, resulting in the slightly tacky surface of these prints. Oxygen's inhibition of curing is used to an advantage in the printing of the pattern. The transparent surface that the resin is grown on, the projector image plane or focal point for the scanning laser in the printer, is typically polydimethylsiloxane (PDMS). The PDMS is somewhat oxygen permeable, so with exposure to air there is oxygen present on its surface, which oxygen inhibits the resin from bonding to the surface of the PDMS. However, this also leaves an oxygen-inhibited surface on each layer of the print that will react with the investment. Secondly, the resin has components to limit the penetration of the UV light into the resin to allow for production of high-resolution prints. Without the blocking material the scattering of light into the volume above and around the current slice degrades the resolution of the print. This same blocking material also limits the penetration of UV into the pattern for post curing, leaving areas of thicker section or those less exposed to the UV under-cured.

Post-Print Curing with Heat

A second means of post-grow curing is the application of heat to the partially cured patterns. After heat curing, the patterns are harder and no longer have the tacky surface of UV post-cured patterns. Since some photo-initiators can either be activated by UV or heat but not both,¹⁴ there is some question whether the heat is actually initiating the breakdown of the photo-initiator into more free radicals to convert more resin into its polymerized form. One suggestion for why the UV-initiated resins post cure via heat is that the polymerization of the unreacted monomer continues due to greater molecular mobility and increased reaction rate. Elevated temperature allows the unlinked material to come into contact with unterminated polymer chains. In support of this idea, it has been observed that UV post-cured resins lose the tacky surface and increase in hardness if just allowed to age for a few days without doing anything else to them. This indicates that the curing reaction continues to progress at a lower rate until there is no longer any uncured resin; heat just accelerates this activity. In addition, increasing temperature reduces the solubility for oxygen in the resin so less oxygen will be present in uncured portions to inhibit the cure.¹⁵

Heat-cured patterns also exhibit a weight loss from the post-print to cured state of around 3% in these tests so there is some evaporation occurring. The UV-cured prints only lose around 0.5%. I will have more to say about this below.

One drawback to using heat to post cure is greater strain appears to be placed on the pattern in the process than with the UV post cure.¹⁶ As the resin cures it shrinks

as more of the liquid becomes linked into the polymer chains. If the heating rate is too great, a shrinking outer shell is strained by trying to compress the less-cured core of the print. This strain can result in cracks or crazing of the pattern's surface, rendering it unusable for casting. To avoid damaging the pattern, the heating rate must be a relatively slow $1^{\circ}\text{-}2^{\circ}\text{F/minute}$ ($.56^{\circ}\text{-}1.1^{\circ}\text{C/minute}$).

A NEW PROCESS FOR POST-PRINT CURE

In an attempt to remove uncured resin and fully cure the partially cured resin in the patterns without the danger of cracking from heat curing, I decided to try to remove the uncured resin by evaporation. When pressure is dropped, the boiling point temperature decreases and there is greater evaporation rate of volatile materials. I noted that MMA has a boiling point of 214°F (101°C) and vapor pressure of 29 inches Hg, so like water it should boil at near room temperature under a moderate vacuum. I assumed that the acrylic photopolymer used in my 3D printer might have similar characteristics. My studio has a vacuum oven that has a base pressure of 10 millitorr, which should be more than adequate to test the concept.

After placing a cleaned post-grow pattern in the chamber, I began pumping it down. The rate of pressure decrease flattened out at around 300 millitorr, indicating that there was vapor being released by the model. In the low pressure of the vacuum oven there is no convection heating, so radiation and conduction from the walls to the platform in the chamber are the means of heat transfer, which results in a heating rate of around 1°C (2°F)/minute of the platform in the oven. After a period of 1.5 hours, the pressure had dropped to around 20 millitorr with the temperature stabilized at 93°C (199°F). The oven was brought back up to atmospheric pressure and the pattern was examined; it appeared to have similar hardness to heat-cured parts and no tacky surface. When cast, the results were better than either UV or heat post-cure. There were no indications of investment breakdown in the casting. After several more tests, the vacuum/low-heat method was then adopted as the post-print/cure process in my shop.

Experimental Comparison of UV, Heat and Vacuum/Low-Heat Post-Grow Cure Processes

Two sets of patterns were grown for testing. The first was a signet ring (Figure 4) with a range of textures and lettering on the surface to provide a heavy-section piece with some fine detail. The second group of patterns (Figure 5) was a mix of light to heavy sections and simple to more complex detail. Three of these patterns were provided by Frank Cooper from the Jewelry Industry Innovation Centre, Birmingham City University. The pattern geometries were designed to reproduce some of the different features found in jewelry. They have been used in at least one other paper presented at the Santa Fe Symposium[®] to assess the casting of SL printer photopolymer patterns.⁸ The decision to use these models was to allow for comparison to those previously published results. The second group was printed with feed sprues attached to the patterns to allow for more uniform results in the

casting trials. The first set of patterns was post cured as individual pieces (Figure 6). The signet rings in the first set were cut into three sections, including a section of the support base and pattern supports along with each ring. The second set of patterns was processed as a group with five patterns on a single base with their associated supports and gates. Patterns were grown and processed by three post-grow curing methods: UV, heat and vacuum/low heat.



Figure 4 Signet build layout

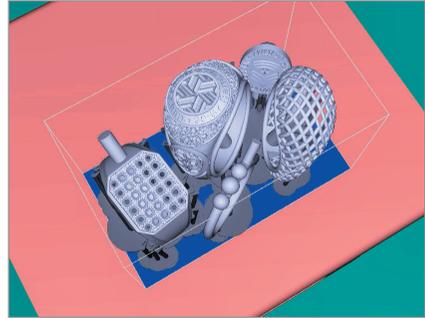


Figure 5 Mixed pattern build layout



Figure 6 Signet test models

Table 1 UV cure weights

Post-grow Weight	Cure Parameters	Post-treatment Weight	Weight Loss
2.368	30 minutes UV	2.365	0.13%
2.325	30 minutes UV	2.315	0.43%
2.362	30 minutes UV	2.353	0.38%
10.108	1 hour UV	9.991	1.16%
7.124	1 hour UV	7.085	0.55%
2.340	1 hour UV	2.307	1.41%
2.232	1 hour UV	2.221	0.49%
2.359	1 hour UV	2.353	0.25%
7.384	1.5 hours UV	7.385	-0.01%
7.783	2 hours UV	7.773	0.13%

UV Post-Grow Cure Tests

The UV curing was performed in a chamber with eight 365 nm 9-watt fluorescent tubes arrayed around the patterns (Figure 7). The patterns were placed on a solar-powered turntable (the UV light powers the turntable) that kept the parts in continuous motion during curing to provide for even illumination of the pattern surfaces (Figure 7). Patterns were cured for times ranging from 30 minutes to two hours. The patterns all retained a slightly tacky surface after exposure. Patterns were weighed before and after curing and exhibited little loss in weight from the curing process. This possibly was just the evaporation of water and/or isopropyl alcohol from the cleaning process absorbed by the patterns as the resins typically do not contain any solvents to evaporate.

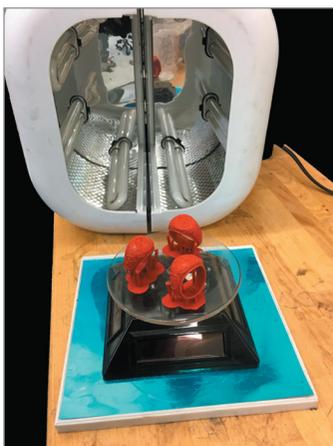


Figure 7 UV box and turntable

Table 2 Heat-cure weight loss

Post-grow Weight	Cure Parameters	Post-treatment Weight	Weight Loss
2.354	50°C 15 minutes, 100°C 15 minutes, 150°C 15 minutes	2.302	2.21%
2.331	50°C 15 minutes, 100°C 15 minutes, 150°C 15 minutes	2.277	2.32%
2.246	50°C 15 minutes, 100°C 15 minutes, 150°C 15 min	2.192	2.40%
2.207	93°C 1 hour	2.149	2.63%
2.3320	93°C 1 hour	2.270	2.66%
2.351	93°C 1 hour	2.290	2.59%
7.807	80°C 1 hour 30 minutes, 90°C 30 minutes, 100°C 15 minutes	7.508	3.83%
7.63	80°C 1 hour 30 minutes 90°C 30 minutes, 100°C 30 minutes	7.508	1.60%
		Average Weight Loss	2.53%

Heat Post-Grow Cure Tests

Heat-curing tests were performed in a countertop convection oven that has been fitted with a digital PID temperature controller and type K thermocouple to measure and control the oven's temperature. Patterns are placed on a metal sheet that sits on the oven rack. Initial tests used a three-step temperature ramp: 50°C (122°F) for 15 minutes, 100°C (212°F) for 15 minutes and 150°C (302°F) for 15 minutes. All patterns were crazed and cracked at the end of the treatment. This type of result was one of the issues that drove me to find a different curing method. During the testing I found some suggestions in online forums that patterns left for too much time in the isopropyl rinse after printing were more prone to cracking (Figure 8). It was suggested to either not use any isopropyl alcohol and just use water with a bit of detergent followed by a clean water rinse or to just briefly rinse the prints in isopropyl, then immerse in water with detergent followed by a rinse in clean water for final cleaning. I switched to the brief isopropyl alcohol rinse followed by detergent and water in the ultrasonic for five minutes, then rinsed in clean water for the final cleaning.



Figure 8 Cracked pattern

Vacuum/Low-Heat Cure

Table 3 Vacuum/oven cure weight loss

Post-grow Weight	Cure Parameters	Post-treatment Weight	Weight Loss
2.365	2 hours vacuum/ 90°C Heat	2.305	2.54%
2.246	2 hours vacuum/ 90°C Heat	2.191	2.45%
2.316	2 hours vacuum/ 90°C Heat	2.272	1.90%
10.09	1.5 hours vacuum/ 90°C Heat	9.897	1.91%
10.34	1.5 hours vacuum/ 90°C Heat	10.087	2.45%
10.687	1.5 hours vacuum/ 90°C Heat	10.316	3.47%
7.38	1.5 hours vacuum/ 90°C Heat	7.134	3.33%
6.975	1.5 hours vacuum/ 90°C Heat	6.75	3.23%
6.815	1.5 hours vacuum/ 90°C Heat	6.613	2.96%
6.783	1.5 hours vacuum/ 90°C Heat	6.597	2.74%
Average			2.87%

This process seems to have greatly reduced the cracking of the prints when heat curing but thick-section prints are still prone to cracking if heated too rapidly. In doing some more research, it appears that heat post-cured prints show greater shrinkage in the XY axis than in the Z, imparting a greater strain on the print than UV post cure.^{14,16}

In contrast to the UV cure, there was a weight loss of an average of 2.5% in these tests from the process of heat curing the patterns. Longer time and higher temperatures produce greater weight loss with as much as 8.9% recorded in one test. More on this will follow.

Vacuum/Low-Heat Post-Cure Tests

Vacuum/low-heat cure tests were performed in a vacuum oven (Figure 9). The patterns are placed in the center of the platform with the oven at room temperature. The chamber is evacuated, and the heat is then turned on. Putting the patterns in the oven at room temperature seems to be a necessary requirement in the process. In the past I have observed that if the patterns are placed directly in the hot vacuum oven, they may crack during the procedure. Occasionally, when patterns were placed in a hot oven, bubbles of resin formed and solidified on the surface of the patterns. They were easily removed but did leave a circular mark on the surface of the pattern. A processing time of 1.5 hours seems to be adequate to produce a low enough level of uncured resin in the testing patterns for clean casting. Though extended time in the vacuum oven will result in additional removal of volatile components, longer times in the vacuum oven can result in the same cracking exhibited by heat post cure.



Figure 9 Vacuum oven chamber

Weight Loss in Post-Grow Cure

The UV post-cured patterns show less than 0.5% weight loss. Both the heat only and vacuum oven processes exhibit greater pattern weight losses (Figure 10). In my tests, depending on exposure time and temperature, I saw between 2% and 9% weight loss. In both heat only and vacuum oven processing, the time and

temperatures that resulted in weight loss of greater than 3% also cracked and crazed, so it appears that too much weight loss is problematic.

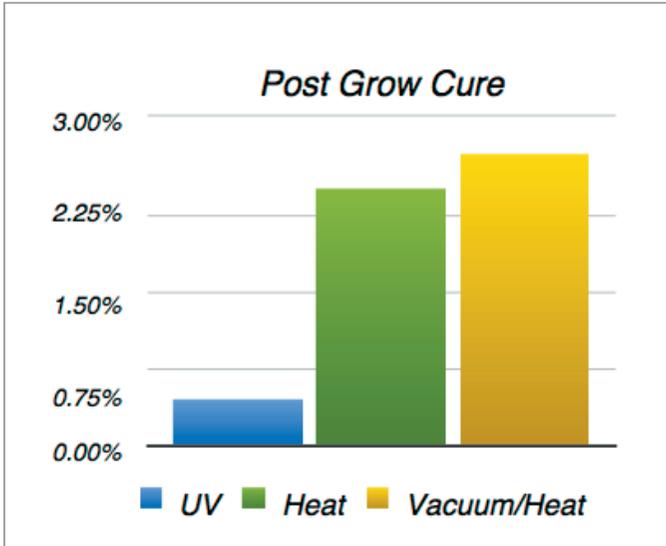


Figure 10 Average weight loss in patterns without cracking

The weight loss is at least in part uncured resin evaporating out of the patterns. It is also very likely some water and isopropyl alcohol absorbed by the print in cleaning also evaporates in either process. In the vacuum oven, this resin vapor freezes out onto the glass door of the vacuum oven and solidifies. The door is insulated from the chamber walls by the rubber gasket so it is considerably cooler than the other chamber surfaces, allowing the resin to condense on it (Figure 11). Enough resin is collected there that it can be scraped off the glass after processing a few prints.

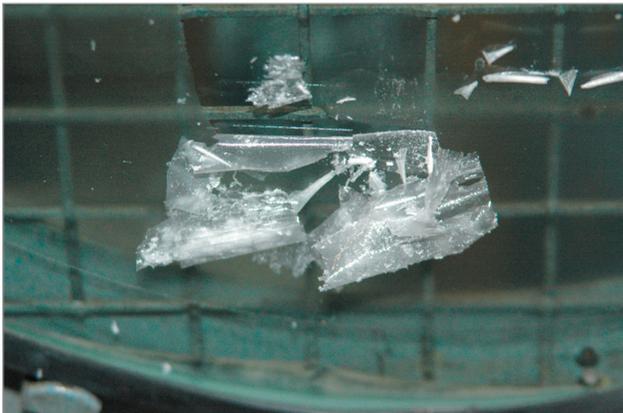


Figure 11 Condensed and cured resin on vacuum oven door

Casting Tests

For each of the casting tests, five patterns were printed. The patterns were cleaned and cured on their foundation without breaking them apart (Figure 12). After printing, the parts were briefly rinsed in isopropyl alcohol for 30 seconds or less. They were then placed in a stainless steel beaker filled with water and a small amount of detergent, placed in the ultrasonic cleaner and run for 30 minutes, then rinsed in clean water and put back in the ultrasonic in a water-filled beaker. After cleaning, they were blown dry and put in an oven at 55°C (131°F) for ten minutes to further dry to attempt to remove any water. The patterns were weighed and recorded. The patterns were cured in one of the following ways:

- UV exposure, 1 hour
- UV exposure, 1.5 hours
- Heated in a convection oven at 93°C (199°F) for 1 hour
- Heated in a convection oven in steps: 80°C (176°F) 30 minutes, 95°C (203°F) 30 minutes, 110°C (230°F) 30 minutes, 125°C (257°F) 30 minutes, 150°C (302°F) 30 minutes, 175°C (347°F) 30 minutes
- Vacuum oven, 93°C for 1.5 hours



Figure 12 Cured patterns



Figure 13 Patterns on tree

For each method of post curing, three flasks were invested and cast. The patterns were placed on a tree as shown in Figure 13. A gypsum-bonded investment developed for plastic patterns was used and allowed to set for at least 3 hours. The burnout schedule that follows was the one described in Andy Anderson's 2011 Santa Fe Symposium® paper.⁹

- Ramp room temperature to 100°C (212°F), 50 minutes, hold for 2 hours 20 minutes
- Ramp 100°C to 177°C (351°F), 50 minutes, hold for 2 hours 20 minutes
- Ramp 177°C to 760°C (1400°F), 6 hours 30 minutes, hold for 3 hours

The flasks were allowed to cool to 537°C (1000°F) and then cast. To ensure enough oxygen for complete burnout of the patterns, the electric furnace door is modified as suggested by Tyler Teague to allow more air flow, and a small air pump is used to introduce a constant stream of fresh air.

Sterling silver was melted in a graphite crucible electric melting furnace with digital temperature control set to 982°C (1800°F). Flasks were poured with vacuum-assist casting, cooled and cast parts removed from the investment.

After clean up, the patterns were examined to gauge the surface quality for each curing method. As seen in Figures 14 and 17, the patterns that were post cured with UV exposure were uniformly of poor quality. The pieces post cured via heat alone were quite a bit better, as seen in Figures 15 and 18. However, each piece had some amount of surface degradation but most could be repaired with a bit of extra finishing. The patterns post cured via vacuum and heat cast with uniformly cleaner surfaces than the two other methods, as seen in the examples in Figures 16 and 19.



Figure 14 Casting result of a UV-cured cage ring



Figure 15 Cast result of a heat-cured cage ring



Figure 16 Cast result of a vacuum oven-cured cage ring



Figure 17 Cast result of a UV-cured signet ring



Figure 18 Cast result of a heat-cured signet ring



Figure 19 Cast result of a vacuum oven-cured signet ring

CONCLUSION

I believe that uncured resin in the pattern is the culprit in the mold surface degradation that plagues direct burnout of 3D-printed patterns. When investing and burning out uncured patterns, the un-polymerized resin comes out of the pattern and infiltrates the surface of the investment in contact with the pattern. As it further heats, the resin polymerizes and bonds the investment to the pattern, creating a composite structure.

In the initial phase of the burnout the resin expands and as the temperature climbs, it begins to decompose, followed by shrinking as volatile decomposition products off-gas. At the same time, as part of the decomposition process, new polymer chains are being formed; the polymer doesn't just unzip and return to a monomer and oligomer form. As the polymer molecule breaks, the ends of the resulting chains can still link to other molecules to form additional polymers. I hypothesize this is when the investment is damaged. The expansion followed by the shrinking of the pattern pulls chunks of the polymer/investment composite in the mold face away from the rest of the mold. As the resin continues to decompose, char begins to form and the remaining mass becomes more tar-like. As decomposition continues, all the volatiles will off-gas, leaving only the char that will slowly sublime with continued exposure to oxygen at the highest temperatures of the burnout process.^{4,7} The spalled investment, which makes up at least some of the "ash" seen in the castings, remains as a powder in the mold cavity. I believe this is the cause of the rough-surface positive defects in the mold face.

If this is correct, the more uncured resin present in the pattern, the more this type of defect will be present. This conclusion appears to be the case from my experimental results and correlates with reports from others.

To achieve the highest quality castings from direct burnout of photopolymer resin patterns, the post-print curing of the resin must be as complete as possible while avoiding the cracking and crazing caused by heterogeneous strain from differing shrinkage rates between the XY plane and the Z axis. Uncured resin present in the pattern results in positive-type surface defects with weight gain and degraded surface quality. These defects require additional time and effort to correct and, if

severe enough, may result in having to scrap the casting. From my tests results I believe that using a vacuum oven to remove the uncured resin by evaporation and finish polymerization of partly cured resin is the most rapid and effective means of producing a pattern that will consistently produce defect-free castings.

REFERENCES

1. H. Kodama, "Automatic method for fabricating a three-dimensional plastic model with photo-hardening polymer," *Review of Scientific Instruments* 52 (1981): 1770-1773.
2. C.W. Hull, "Apparatus for production of three-dimensional objects by stereolithography," US Patent 4575330 (1986).
3. "Autodesk Releases Ember's 3D Printing Resin as Open Source," http://autodesk.blogs.com/between_the_lines/2015/03/autodesk-releases-embers-3d-printing-resin-as-open-source.html.
4. C.L. Beyler and M.M. Hirschler, "Thermal Decomposition of Polymers," *SFPE Handbook of Fire Protection Engineering*, 3rd ed., Chapter 7, ed. P.J. DiNenno (Quincy, MA: NFPA, 2001): 1-110 - 1-131.
5. I. McKeer, "Improvements in the Burnout of Resin Patterns," *The Santa Fe Symposium on Jewelry Manufacturing Technology 2007*, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2007).
6. S. Adler and T. Fryé, "The Revolution of CAD/CAM in the Casting of Fine Jewelry," *The Santa Fe Symposium on Jewelry Manufacturing Technology 2005*, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2005).
7. B. Holland and J. Hay, "The kinetics and mechanisms of the thermal degradation of poly(methyl methacrylate) studied by thermal analysis-Fourier Transform Infrared Spectroscopy," *Polymer* 42, no. 11 (2001): 4825-4835.
8. M. Actis Grande et al., "Quality Excellence in the Direct Casting of RP Resins: Reality or Fiction?" *The Santa Fe Symposium on Jewelry Manufacturing Technology 2011*, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2011): 1-36.
9. A. Andrews, "The Quest for the Perfect RP Burnout," *The Santa Fe Symposium on Jewelry Manufacturing Technology 2011*, ed. Eddie Bell (Albuquerque: Met-Chem Research, 2011): 53-82.
10. J. Tyler Teague, "Investing Resin Models, Tips for Increasing Mold Strength," MJSA Tech Sheet 39; http://www.mjsa.org/publicationsmedia/tech_sheets/investing_resin_models.
11. J. Tyler Teague, "Investing Resin Models, Part 2: New research into preparing a proper mold," MJSA Tech Sheet 42; http://www.mjsa.org/publicationsmedia/tech_sheets/resin_models_part_2.
12. C. Cheah, et al., "Characteristics of photopolymeric material used in rapid prototypes Part I. Mechanical properties in the green state," *Journal of Materials Processing Technology* 67, no. 1 (1997): 41-45.

13. H. Kang et al., "A pixel based solidification model for projection based stereolithography technology," *Sensors and Actuators A: Physical* 178 (2012): 223-229.
14. J.Y.H. Fuh et al., "Curing characteristics of acrylic photopolymer used in stereolithography process," *Rapid Prototyping Journal* 5, no. 1 (1999): 27-34.
15. T. Scherzer and H. Langguth, "Temperature Dependence of the Oxygen Solubility in Acrylates and Its Effect on the Induction Period in UV Photopolymerization," *Macromolecular Chemistry and Physics* 206, no. 2 (2005): 240-245.
16. D. Karalekas and A. Aggelopoulos, "Study of shrinkage strains in a stereolithography cured acrylic photopolymer resin," *Journal of Materials Processing Technology* 136, no. 1 (2003): 146-150.

