Formulating for 3D printing (SLA)

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3D printing is a technique that has been employed for much longer than one would intuitively expect. Lamination-style creation is a well-known type of printing used in the making of 3D objects, for instance, in clay pot construction. Coils of wet clay[1] can be stacked and pressed together to form a taller structure than wouldn't be possible otherwise. Modern 3D printing technology works in a similar fashion, i.e., building layer upon layer, and was first patented in 1984[2], considerably earlier than the current technological explosion ongoing today. Many attribute recent progress to the original patent's expiration[3], but it can also be attributed to the enormous improvement in computing power[4]. This has not only helped the additive manufacturing market, but also the subtractive manufacturing market, with the invention of the CNC machine.

There are two main types of 3D printing, metal and plastic. Most metal printers use a powder bed and intense laser light to sinter parts together[5]. Due to the extreme power requirements of metal 3D printing, this technology is limited to specialized industries that strictly require metal parts. The plastics 3D printing industry is much easier to enter; inexpensive PLA and low hazard machines combine to create a low barrier to entry. Plastics can either be melted and re-deposited onto a growing object, or selectively polymerized to form a plastic thermoset polymer. These two techniques are referred to as fused deposition modeling and vat polymerization, respectively. Formulating theory for vat 3D printing will be the focus of this paper, particularly for SLA-type printing, with a few starting point formulations following the theory and implementation.

Vat polymerization is the umbrella term for SLA, DLP, and CLIP-type 3D printing. These techniques are all employed for their high precision, small footprint, and wide variety of available materials. SLA and DLP printers differ only in their UV exposure technique, but otherwise the underlying mechanisms are identical. In Stereolithographic printing, otherwise known as SLA, a laser draws out a slice of a CAD file, curing the prepolymer resin in the process. The layer is either then peeled off of a non-stick base (constructed of polydimethylsiloxane [PDMS] or fluroethylene propylene co-polymer [FEP]), or the stage is lowered and more prepolymer resin is swept over the cured print[6].

Direct light projection machines, or DLP printers, utilize the same mechanism; however instead of a laser drawing out each slice, a projector exposes the entire CAD slice at once[7] the process continues identically to SLA afterwards. In continuous liquid interface polymerization, or CLIP technology, the print proceeds in a continuous manner[8], as opposed to stepwise in SLA or DLP. This necessitates an upside-down process, as the prepolymer resin needs to be continuously replenished as the curing object moves upward. Because of this, CLIP printers use a projector light source, similar to DLP printers, allowing them to continuously cure the slices of the object.

The mechanics of how each printer works are of utmost importance, as they limit the materials which can be used in each method, according to mechanical properties of the printed part and the compatibility of components. This paper will specifically explore the mechanics of the Form 1+ SLA type 3D printer.

The Form 1+ is an inverted SLA machine, which means that the cured object being built is drawn upward from the prepolymer resin vat. The vat is constructed of acrylic plastic coated with a PDMS layer to act as a non-stick coating and cushion. To begin printing, the vat is first filled with a prepolymer resin, an .stl file is imported into the machine, and a metal stage descends into the resin, compressing the resin into the PDMS. Next, the laser draws out the first slice of the object, and the first layer of the print is cured onto the stage. The vat slowly tilts sideways to peel the first layer off of the PDMS. The metal stage rises up again, the vat tilts back to level, and the stage finally lowers down to stop one layer height above the PDMS. The laser draws the next slice, and the process repeats.

From these mechanical processes, three general formulation constraints are defined. First, all components of the formulation should be compatible with the PDMS and the acrylic plastic vat. The PDMS can and will absorb low molecular weight components, which, if cured while inside the PDMS matrix, will tear it. As an example, PDMS immersed in isobornyl acrylate (IBOA) for 48 hours swells to 187% of its starting weight. This causes severe warping, which leads to print failures and general printer damage. Products should only be used if they swell the PDMS by 10% or less over a 48 hour immersion period. Similarly, the acrylic plastic can be dissolved by certain components as well. The acrylic plastic, if immersed in dimethyl acrylamide (DMAA), will dissolve in 24 hours. This is obviously a serious concern, not only for the preservation of the printer, but also for user safety. Since most print intervals only take a few hours, small quantities of these materials can be used. However, it is highly recommended to look for compatible alternatives. Not all printers use PDMS and acrylic plastic though, so individual considerations will change depending on the printer used.

The second formulation constraint involves the mechanical strengths of the formulation being printed. The main consideration is given to the overall reactivity of the formulation. Two components with similar ultimate mechanical properties, but differing reactivity, will have dissimilar green strengths if exposed to the same dose of curing radiation. This can be used to a formulator's advantage, as an under-cured object will put less stress on the components of the printer leading to a longer useful lifespan. But, the object must still be cured enough to maintain cohesion during the peeling process. A small addendum to this constraint is that formulations with very low cohesive strengths are difficult to print alone. These formulations typically contain components which have very low tensile moduli (E mod) and low glass-transition temperatures (Tg). Formulations of this nature usually require reinforcement of some kind, or risk failure in the form of delamination.

The explanation for this constraint is found in how printers detach objects from the vat. The PDMS will act as an oxygen source[9] to inhibit direct, mechanical adhesion between the vat and stage. However, the printed/cured layer still adheres slightly. This results from the vacuum-suction effect known as Stefan Adhesion[10] and is the reason why the print is pulled down during the peel process. If the object is to survive and not delaminate from itself or the metal build platform, it needs to be able to withstand these stresses, and have enough structural integrity to detach from the vat. Reinforcement can either come from different, higher Tg, oligomers or monomers, or in the form of inert fillers.

The third general formulation constraint relates to Stefan Adhesion as well, in the viscosity of the formulation. High viscosity formulations drastically increase the forces "pulling" on the print, while low viscosity formulations decrease these forces. Stefan Adhesion can also be affected by the speed of the peel motor, i.e., a faster peel sees greater resistance. From this, it is advantageous to keep formulations near or below 1,000 mPa*s.

Making the jump from theory to practice can be difficult, but following these guidelines can help prints succeed more often than they fail. The first constraint is quite easy to abide, as a preliminary screening of the component absorption is all that is needed to determine compatibility. The second and third guidelines are more difficult to balance from a formulation standpoint, and all of these considerations need to work together toward the final formulation goals. For example, a tough formulation should not use too much brittle monomer, no matter what diluting power it may provide. Or, a flexible formulation should not use too much of a stiff, brittle component, no matter how much reinforcement it will give.

Moving into more applicable theory, the mechanical properties of raw components can be used to significantly influence the final properties of a formulation. There are five integral properties of each component which can determine how it will influence a 3D formulation. These properties are the glass transition temperature, volumetric shrinkage, tensile modulus, tensile strength, and extensibility. All of these properties can be manipulated to make a formulation tough, hard, or flexible. And different combinations of these properties can be extremely useful in preliminary formulation work.

For example, in flexible formulations, low Tg, low E mod, high elongation products show the best results. In hard formulations, just the opposite is needed; a high Tg and high E mod components produce objects with very high hardness. These hard formulations can be brittle though, and so a small amount of high elongation component can be added to prevent shattering and post-cure cracking. Additionally, hard components tend to have high curing shrinkage, which induces additional stress leading to even more brittleness. Low shrinkage and flexible components can help minimize these stresses. To get from a hard formulation to a tough formulation however, brittleness needs to be eliminated, rather than just mitigated. Benchmark tough plastics (e.g. ABS) deform under load before breaking, while brittle materials do not. Thus, tough formulations should be built to emulate this.

Other components may not affect the final mechanical properties of a formulation, but instead will influence how successfully an object prints. These components such as UV blockers, photoinitiator type & concentration, and surface curing additives can all determine whether a formulation will print well, or not.

The first and most important non-resin component is the UV blocker. Blockers are used to decrease the penetrating power of the light, so that fine details and embossings can be printed, i.e., only one layer fully cures at a time and light does not cure any layers beyond the site of exposure. It is important to note that only UV *blockers* are suitable for this application, as stabilizers (e.g. HALS) do nothing to decrease the depth of light penetration. Most pigments will block UV light, and added pigment is the simplest way to add the required blocker for a formulation. Clear formulations can also be made by using fluorescent optical brighteners.

All formulations in this paper will use weight percent of 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene, CAS # 7128-64-5 (referenced here as OB) as the blocker. Less reactive formulations are generally more sensitive to blockers, allowing for predictable improvement in print accuracy. This might be why methacrylates work well in 3D printed formulations, given their lower reactivity and shrinkage compared to acrylates.

The second critical non-resin component is the photoinitiator. Long wavelength photoinitiators are typically used for smaller, consumer grade printers, as the light required to initiate them is less hazardous, and easier to implement. Industrial grade SLA printers are not constrained in the same way, and so have a broader range of photoinitiators from which to choose. The two main photoinitiators used in the consumer world are phenyl-bis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO). Other photoinitiators can certainly be used, and also may help to decrease the surface tack of post-cured objects (such as 1-hydroxycyclohexyl phenyl ketone [CPK], 2-benzyl-2-dimethylamino-4'-morpholinobutyrophenone [BDMM], and thioxanthone [ITX]), however only the two main initiators, BAPO and TPO will be listed in the example formulations.

The concentration of photoinitiator is very important in 3D formulations. Too much and prints may overcome the oxygen inhibition of the non-stick film and adhere to the vat. Too little and the prints will not have enough green strength to maintain integrity during the print process. The optimum photoinitiator concentration will depend upon the reactivity of the acrylates utilized, but a typical starting point is between 0.25% and 1% by weight. Moreover, the interaction between photoinitiator and UV blocker can be complicated to predict. At high concentration, photoinitiators can behave as UV blockers, while at low concentrations they can become overwhelmed by the blockers. Sometimes the blocking effect can be used to a formulator's advantage, but at high initiator concentrations prints begin to stick to the vat. Good high-resolution results have been achieved by using higher concentrations of less reactive initiators, such as polymeric photoinitiators, in particular polymeric thioxanthone. The final photoinitiator and blocker concentration will typically need to be determined during the course of formulation screening and optimization.

A note also needs to be made about polymerization stabilizers, which are critical to any UV formulation. These prevent premature gelling of the formulation during packaging and during long prints. In addition to halting unwanted polymerization, stabilizers also contribute to reduced reactivity in general, which has been shown to be advantageous to the long term lifetime of the 3D printers. Typical stabilizer concentrations are near 0.1% by weight of a formulation.

The third critical non-resin component, surface curing agents, can be difficult to optimize. Amines are usually the go-to functionality for improving surface cure in energy curable formulations. However, due to the precision of light exposure required, synergists like amines often do not help. Most prints with added amine components emerge ragged and imprecise, if they don't stick to the vat first. It is speculated that amines may interfere with the oxygen inhibition necessary to allow a print to peel away from a PDMS vat, but that does not explain the raggedness of many amine-containing formulations.

Of course, all formulations are different, and some may end up requiring synergists to properly cure, but as a general rule, amines are not the best way to achieve a tack-free print. A better way to minimize or eliminate surface tack is utilizing a post cure process. A low wavelength photoinitiator can be mixed into formulations, which will remain mostly intact when exposed to visible light from the printer and allow the proper exposure for a successful print. The low wavelength photoinitiator can then be activated by a stronger light source after processing, ideally fully curing the surface.

With all of these considerations in mind, a few general starting point formulations (SPFs) have been developed, though they are not meant to be final solutions for specific applications. They are provided to show that the formulation considerations discussed previously can still be used to develop printed parts with a wide range of mechanical properties for whatever is required. They are also provided to give formulators a place to begin work on a project, with the understanding that each application requires specific individual attention.

Hard SPF: Mon 3

The first 3D SPF is for a general purpose, high definition, hard object. It is comprised of epoxy methacrylate oligomer, which provides the high Tg, high E mod oligomer base; ACMO (acryloyl morpholine), a powerful diluent which also has a very high Tg; and UA 1122, an aliphatic urethane monoacrylate diluent with extremely high elongation. The high elongation component is important to reduce some of the shrinkage stress and temper the brittleness of the other two components, while also reducing the viscosity of the formulation. The formulation is shown below in Table 1.

Table 1. Hard SPF, Mon 3

Product	Mon 3	Tg	E mod	Elongation at Break
Epoxy Methacrylate 97-053	50% wt	114 °C	521,000 psi	5.0%
ACMO	30% wt	148 °C	273,000 psi	Low
UA 1122	19.5% wt	-9 °C	Low	800%
BAPO	0.4% wt	-	-	-
OB	0.1% wt	-	-	-

This general formulation has the stress-strain curve shown in Figure 1, and mechanical data in Table 2. Properties were measured according to ASTM D638-02a, on type VI and V dogbones. The formulation was printed on a Formlabs Form 1+ printer, using the Clear version 2 settings at 0.1mm, and post cured for an hour on each side. The total dose delivered to each side was extrapolated to be 480 mJ/cm^2 of UVA, with no appreciable emission in the UVB or UVC region.

Table 2. Mechanical properties of Mon 3

Mon 3	Imperial	Metric	Standard of Measurement
Tensile Modulus	297,000 psi	2,050 MPa	ASTM D638-02a
Tensile Strength	6,200 psi	42.7 MPa	ASTM D638-02a
Elongation at Break	3.5%		ASTM D638-02a
Work	0.22 lbf	0.30 J	Zwick/Roell integration software
Impact strength	8 lbf/in	430 J/m	ASTM D5420-04
Shore hardness	85 D		ASTM D2240
Viscosity	660 cP	660 mPa*s	Brookfield Viscometer at 1000RPM and 25°C

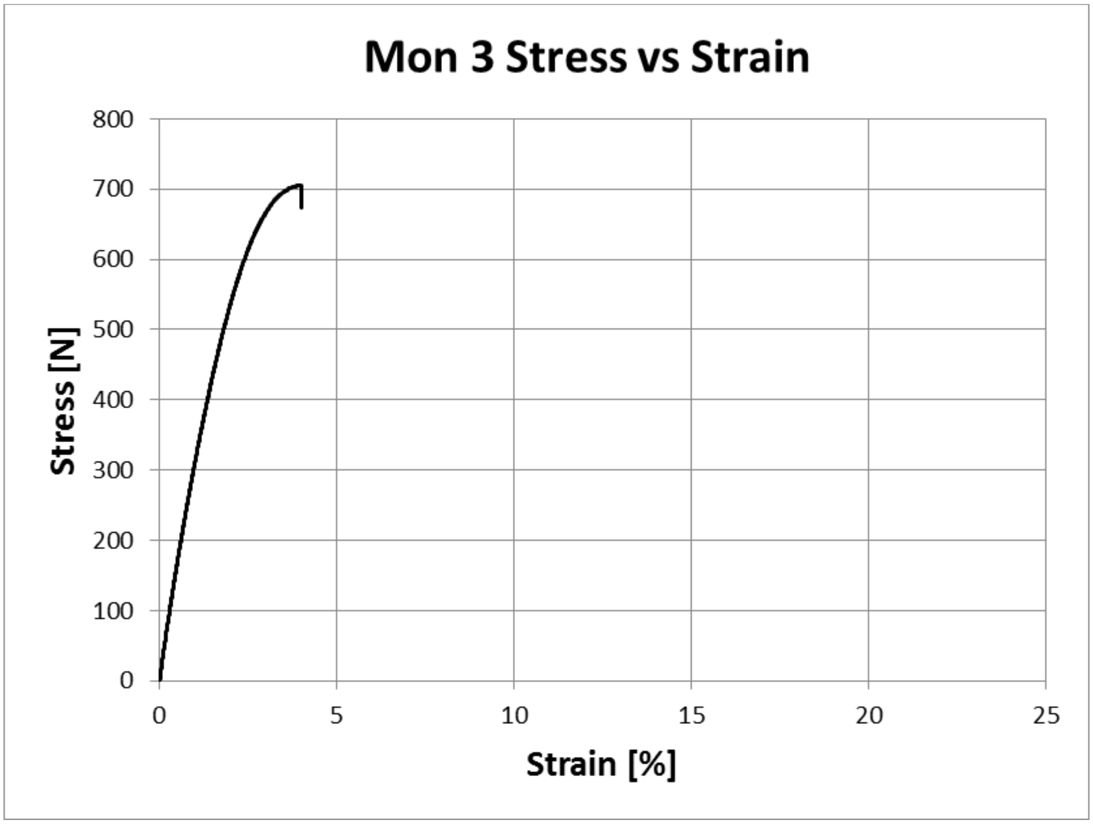

Figure 1. Stress vs Strain curve of Mon 3

Tough SPFs: C3 and C17

The next two SPFs are for tough, engineering type applications. The definition of toughness is woefully imprecise in the 3D printing world, and most formulations will need to be optimized for the specific application. However, the general properties of a tough formulation are high tensile strength, high elongation, and high impact resistance. Toughness is academically measured by the area under the Stress-Strain curve, known as Work, and that is what these formulations strive to maximize, while keeping in mind the previous three considerations. The two formulations each consist of "chunks" of two hard, high E mod components, and two soft, high elongation components. These components either provide the strength and rigidity to withstand high stress, or provide the flexibility to deform with plastic flow, rather than shattering in brittle failure. This results in an object which is very difficult to deform, but which will still stretch and bend significantly before complete failure. The two tough formulations, C3 and C17, are shown in Table 3.

Table 3. Tough SPFs, C3 and C17

C3					C17				
Product	wt %	Tg	E mod	Elongation	Product	wt %	Tg	E mod	Elongation
UA 1122	24.48	-9	Low	800%	UA 1122	24.46	-9	Low	800%
UA 4316	25	7	1,450 psi	47%	UA 4316	25	7	1,450 psi	47%
ACMO	25	148	273,000 psi	Low	DPGDA	25	104	High	Low
Modified EA 2281	25	66	404,000 psi	17%	UA 4302	25	90	202,000 psi	7%
TPO	0.5	-	-	-	TPO	0.5	-	-	-
OB	0.02	-	-	-	OB	0.04	-	-	-

The mechanical properties of both tough SPFs are shown in Table 4. The Stress-Strain curves for both are also shown in Figure 2; C3 is the solid line, while C17 is the dashed. Both formulations were 3D printed, post cured, and tested using the same methods and conditions as the hard SPF, Mon 3.

Table 4. Mechanical properties of C3 and C17

Tough SPF	C3		C17	
Units	Imperial	Metric	Imperial	Metric
Tensile Modulus	107,300 psi	740 MPa	135,000 psi	930 MPa
Tensile Yield	1,440 psi	9.9 MPa	2,045 psi	14.1 MPa
Tensile Strength	3,040 psi	21 MPa	3,440 psi	24 MPa
Elongation at Break	74%		25%	
Work	2.77 lbf	3.76 J	1.35 lbf	1.83 J
Impact strength	>54 lbf/in	>2,900 J/m	22.5 lbf/in	1,200 J/m
Shore hardness	75 D		77 D	
Viscosity	1,150 cP	1,150 mPa*s	925 cP	925 mPa*s

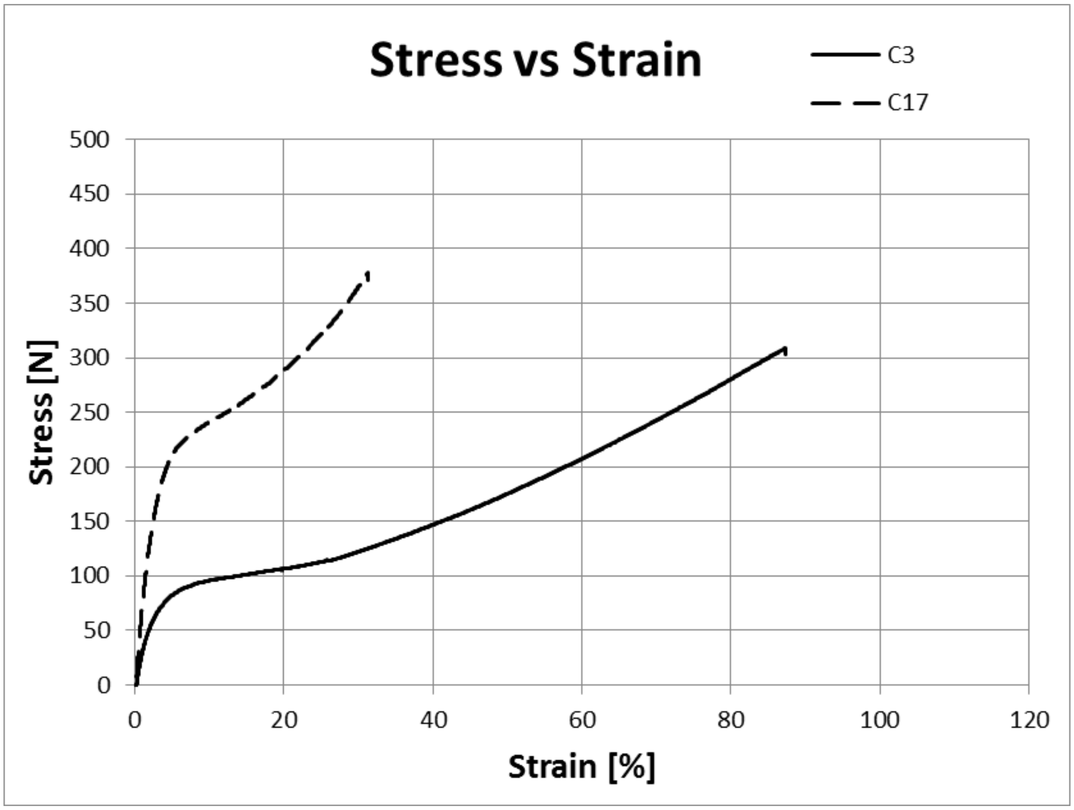

Figure 2. Stress vs Strain curve, C3 and C17

Formulating for 3D printing is a new challenge which proves that the energy curing industry is continually pushing the envelope of material properties, and formulators will need to grow with it in order to keep pace with diverse and demanding applications. With the help of new raw material development and innovative formulation problem solving, the new requirements of 3D vat photopolymerization are completely achievable. The hope is that this paper can provide formulators with enough general background knowledge to begin working with this new technology, or to provide a new perspective on how to achieve mechanical properties comparable to engineering thermoplastics.

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