WHITE PAPER

EXPANDING THE PROCESSING WINDOW OF DLP ADDITIVE MANUFACTURING

FORTIFY

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INTRODUCTION

Vat photopolymerization 3D printing has been around for a long time. In fact, one the earliest used 3D printing technologies is Stereolithography (SLA) – the first use of which was documented in the 1980s. Since then, companies have innovated on the technology across the board ranging from hardware to software to materials.

One such innovation is called Digital Light Projection (DLP) 3D printing. DLP is a type of vat photopolymerization process not far in spirit from SLA. The primary difference is in how the light is applied – where SLA uses a UV laser to scan and cure each layer, the DLP technology leverages projector technology to pattern and cure an entire layer with a single image exposure. As a result, exposure time per layer is reduced when compared to an SLA process, while also maintaining high resolution.

Other innovations like improved software workflows, better hardware designs, and clever peel force reduction techniques have kept photopolymerization-based 3D printing techniques at the forefront of polymer 3D printing. Yet, despite coming so far, vat photopolymerization techniques continue to face significant barriers to adoption by much of industry as a manufacturing method. The reason for this is the lack of available high performance, multi-functional high-performance materials.

Fortify has innovated in hardware, software, and materials to fill the current void in the market that neat, unfilled photopolymers have left unsatisfied. By piggybacking on the innovations happening in neat photopolymers, Fortify can add functional particle additives to introduce a step change in material performance, tackling the unmet needs of the industries including injection molding, aerospace, 5G, electronics, and more.

This white paper will present the following:

- A suite of problems that engineers, and material scientists face when developing particle filled photopolymer systems
- Customer-ready Flux Developer toolsets that engineers use to solve these problems and print novel, high value materials quickly.
- Examples of how Fortify and Fortify's partners and customers have used the Flux Developer toolsets and methodology to develop high value, technical particle-filled photopolymer materials to tackle real world problems.

1.1 THE CHALLENGE OF FILLED PHOTOPOLYMERS

The challenge of printing filled photopolymers is best embodied by four phenomena:

1. Rheology
2. Sedimentation
3. Alignment
4. Scatter

1.1.1 ADDING PERFORMANCE-BOOSTING PARTICLE FILLERS COMPLICATES RESIN RHEOLOGY

The practical nature of adding particle [ER1] [ER2] to a resin is that the rheology, the resin viscosity and flow behavior, changes significantly. Particle to particle interactions impact the flow characteristics of the resin system, thickening the resins and greatly increasing their viscosity, which leads to situations where increased forces are needed to make the resin flow. Thick resins can make DLP printing very challenging as a lot more force is required for a build plate to plunge through the thick resin to reach the desired layer height.

1.1.2 SOME PARTICLES DON'T LIKE TO STAY SUSPENDED

Sedimentation is another challenge with which particle filled resins are faced. If left to sit idle, the kinds of particles in a resin system will settle to the bottom of suspension creating regions within the resin of higher particle content and, thus, higher filler content, viscosity, light adsorption, and photoscatter. When this happens, the printing process and the resultant printed part will suffer from a greater likelihood of build failure and a part that doesn't meet the part specifications. Proper dispersion and suspension of particle additives is imperative to the health of both the printing process and the final printed part.

1.1.3 ANISOTROPIC PARTICLE ALIGNMENT IMPACTS BEHAVIOR

Not all particles are spherical (isotropic). Particles of any non-spherical shape (anisotropic) naturally adopt an alignment in the printer generally from resin flow. In some cases, alignment may be considered non-critical or undesirable. In other cases, alignment may be imperative to the resultant material properties. Therefore, understanding the alignment of the particles in the resin systems is important[ER1] to the benefit the properties of the final part.

1.1.4 UV LIGHT SCATTERS OFF PARTICLES

There are a variety of photonic phenomena that occur during the UV curing of a filled photopolymer – and one that needs special consideration is how fiber additive interacts with incoming UV light. In a neat polymer system, an engineer may only need to consider resin characteristics like color or refractive index to manage incoming light. However, when solid, micron-scale inorganic, irregularly shaped particles are added to the resin, the photons tend to reflect and refract off those particles and end up in undesired regions within the printing process.

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ADDRESSING THE CHALLENGES OF FILLED PHOTORESINS WITH FORTIFY'S FLUX SERIES 3D PRINTERS

Fortify has developed and incorporated several core technologies and capabilities in our printers that are designed specifically to tackle the challenges that come with processing particle filled photopolymer resins including the following:

1. Continuous Kinetic Mixing
2. Robust Plunging
3. Magnetic Fiber Alignment
4. Flux Developer

2.1 CONTINUOUS KINETIC MIXING (CKM™)

Continuous Kinetic Mixing is included on every model of Fortify's FLUX Series 3D printers. CKM is designed to circulate, heat, mix, and keep particles suspended and dispersed throughout the build. By heating the resin, CKM aids to reduce the overall resin system viscosity, making the material easier and faster to print.

CKM is composed of four primary elements – the wiper, the CKM pump, reserve agitator, and the heater. CKM has two primary embodiments: CKM LV (low volume – shown in Figure 1) and CKM Full (full volume). The main difference between the two CKM types is that CKM LV does not have a reserve agitator.

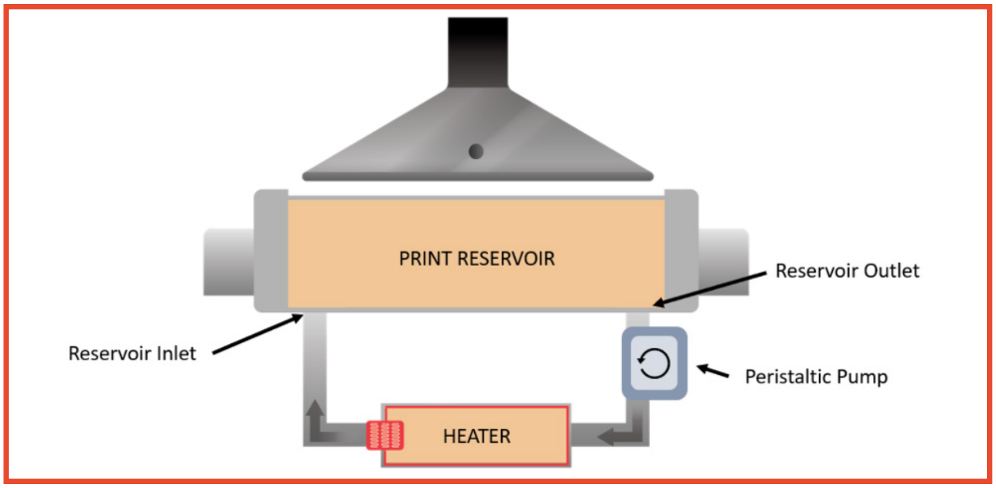

Figure 1: Schematic of the Continuous Kinetic Mixing module for CKM LV.

The reserve agitator, which is part of CKM Full and not shown in Figure 1 continuously agitates several liters of resin during a print. It maintains the suspension of particle filled resins and keeps the material prepared for dispensing to the reservoir.
The heaters in CKM heat the resin system to the desired temperature for the duration of the print, which can be helpful in reducing the viscosity of resins for faster, more effective printing.
The CKM pumps continuously move resin throughout the duration of the build – this helps to maintain the temperature of the resin in the reservoir, as well as prevent any resin from sitting idle for a long enough period for the fiber to sediment out of suspension.
The wiper acts on the film in the reservoir – it can wipe with a layer frequency or time frequency. For resin in the reservoir, the wiper works with CKM to keep the particles in suspension and helps to prevent particle sedimentation that could obstruct UV light in the reservoir.

2.2 ROBUST PLUNGING

CKM was developed to handle viscous resins, but that isn't the only module on the printer that enables high viscosity printing. One major challenge that comes with high viscosity printing is the tough rheological behavior that occurs during the peel and plunge steps in the printing process.

Plunging a partially printed part through thick resin often introduces high plunge forces primarily driven by the resistance to flow that the high viscosity resin exhibits. This resistance to flow can often have non-Newtonian rheological behavior that needs to be accounted for in the plunge and peel steps of the printing process.

Therefore, Fortify developed a plunge and peel system that can operate with 2000 N of force. This high force system, combined with a rigid glass interface in the region of cure, is a critical feature of the printer for processing high viscosity resin systems.

2.3 MAGNETIC ALIGNMENT

As mentioned, anisotropic particle alignment may be critical to the desired behavior of the printed material. To do this, Fortify uses Fluxprint™ – a technology that implements electromagnetic fields to deliberately align in the reservoir. By selectively aligning different regions of a printed part, it is possible to create 3D printed parts with any number of deliberate anisotropic particle alignments. The prerequisite to leverage Fluxprint is that particles need to have some degree of magnetic susceptibility and anisotropy. Nonmagnetic particles can often be made magnetic through doping processes, a route leveraged in some of the materials at Fortify. Anisotropy is satisfied geometrically by fiber or flake shaped particles.

2.4 PARAMETER CONTROLS

For the tools above to work appropriately for a given material, it is necessary to have some control over the individual parameters used to control each toolset – for this, Fortify developed a flexible set of high impact build parameters for Fortify's internal engineers to use to develop and optimize print processes. This is now offered as Flux Developer to users of the FLUX Series 3D printers.

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FLUX DEVELOPER

Flux Developer is a software tool that enables new materials development on the Flux Series of 3D printers. Flux Developer grants users the ability to control all parameters that Fortify's internal materials scientists and process engineers use to develop, on-board, and optimize the printing of new and existing neat and filled photopolymer materials. The effectiveness of Flux Developer shortens the time-to-market for new formulation efforts for users.

3.1 WORKFLOW

When using Flux Developer to design a new filled photopolymer, Fortify engineers typically use the workflow laid out below in Figure 2.

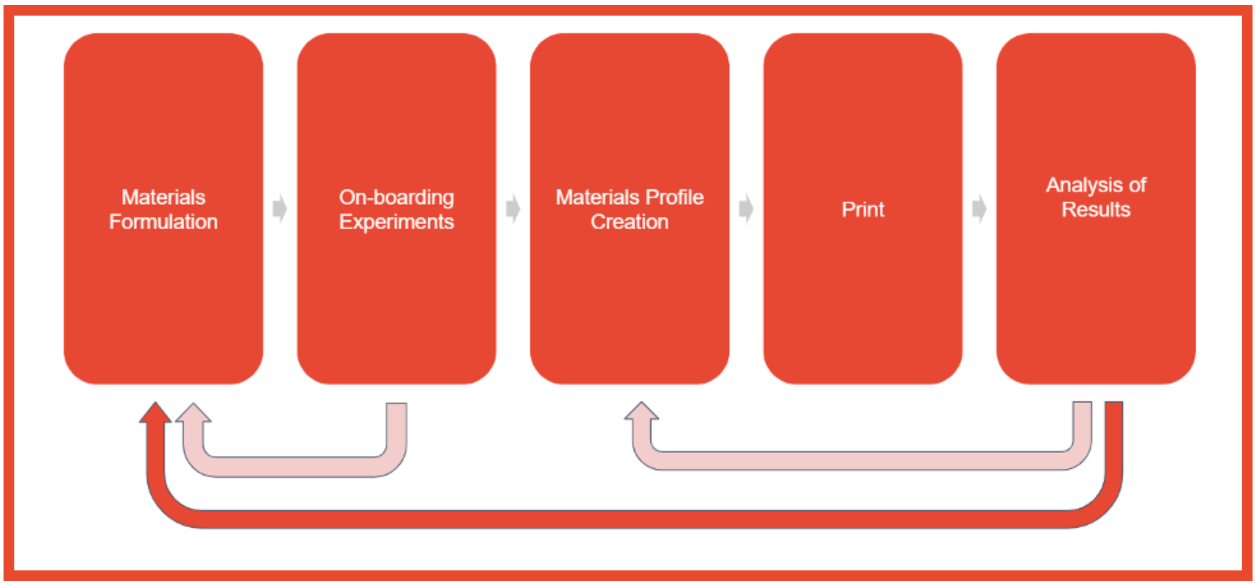


Figure 2: The Flux Developer user workflow

The workflow above walks the users through the high-level steps to develop, on-board, or optimize a particle filled material for printing on a Flux Series printer. Prior to digging into each step in this workflow, understanding the general steps for each printed layer is important as presented in Figure 2.

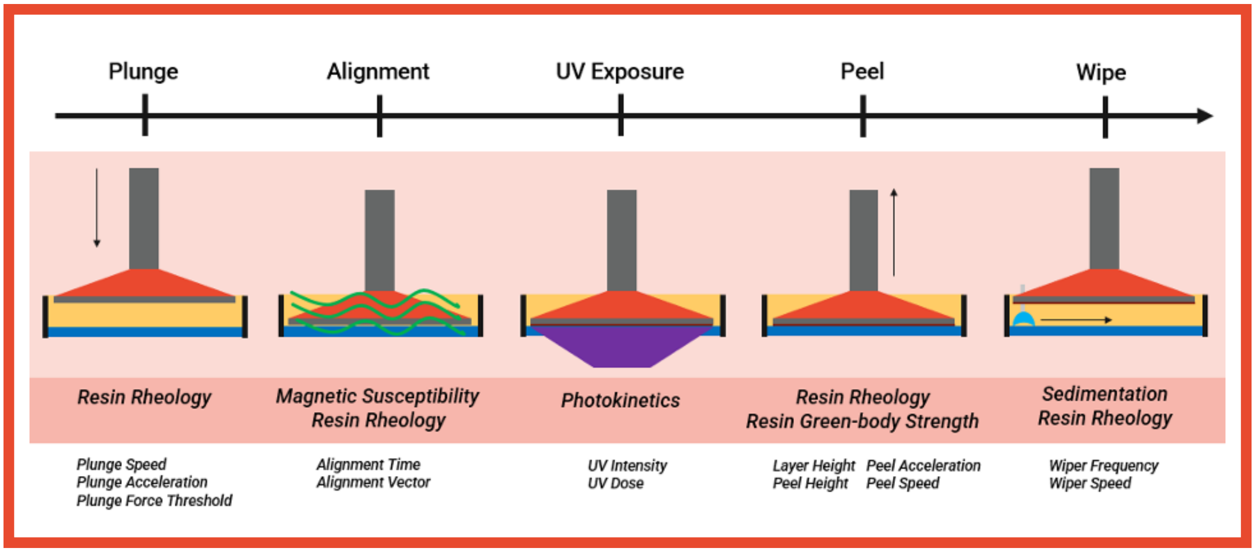


Figure 3: This figure presents the anatomy of a layer. The pictograms show an overview of what is occurring in the step. The dark red row describes the material characteristics that play a critical role in that step, and the bottom row conveys the process parameters that control that process step.

For each step in the layer anatomy, there is one or several material characteristics that impact that process step. As an example, for the plunge, peel, and wipe steps, resin rheology plays a big role in how those steps behave and how each of the parameters for those steps are defined. To determine what the appropriate parameter value for each available Flux Developer parameter should be for each material system, Fortify has developed a series of on-boarding experiments and software tools for executing smart Design-of-Experiments (DOE) and tracking and recording that data.

3.2 ON-BOARDING EXPERIMENTS

The onboarding experiments can be split into two separate categories – off-machine and on-machine. The goal of the off-machine experiments is to develop a better understanding of the rheology and sedimentation characteristics of the material. The on-machine experiments are designed to characterize the photokinetics and build-plate adhesion behavior.

3.2.1 OFF-MACHINE: RHEOLOGY

Rheology s the study of the flow and deformation of a fluid and is a critical characteristic that needs to be understood to develop robust printing parameters for a given particle filled material – Rheology can more easily be described as the resin thickness, or viscosity. Fortify typically characterizes resin systems using a rheometer with shear and thermal control. With these controls, it is possible to create a dataset that relates the viscosity of a material to inputs like shear rate and temperature. An example dataset for an inorganic particle filled photopolymer resin is presented in Figure 4.

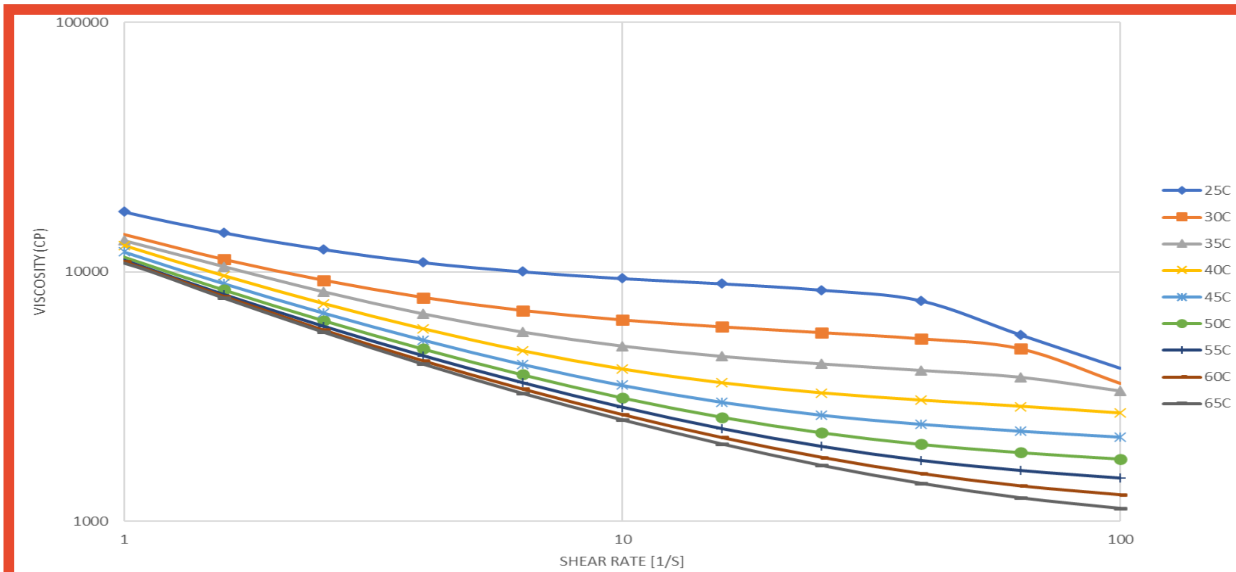


Figure 4: An example rheology curve dataset for a particle filled material

The chart shows the relationship between shear rate and viscosity across a few temperature settings. The results demonstrate the powerful dependence that the viscosity of a resin system has on temperature.

Though rheology of a material system can be impacted by process characteristics like shear rate and temperature, rheology is more significantly impacted by material formulation. Rheology is a function of a variety of material inputs including the base resin, the particle [ER2] content, particle density, particle morphology, and particle size distribution, to name a few. If the formulation of the resin or particle package is an accessible variable in your on-boarding experimentation, resin modification is where an engineer or materials scientist can make the largest impact on resin printability.

3.2.2 OFF MACHINE: SEDIMENTATION

Particle sedimentation is the rate at which a particle settles within the resin. As part of Flux Developer, Fortify offers a particle sedimentation velocity calculator. This calculator provides a first order estimate of the sedimentation rate of a given particle (with a given density, shape, and size) in a neat resin (of a given viscosity and density). This tool helps resin formulators and process engineers to understand what sedimentation velocity to expect and what amount of sedimentation may occur for a given time period of interest. These time periods can be compared against a variety of print process parameters including CKM settings and resin storage conditions.

The particle sedimentation calculator is a powerful tool, but as resin systems get more heterogenous, it becomes more practical to run a set of laboratory experiments to better understand the actual behavior of the resin system of interest. Engineers at Fortify tend to run sedimentation experiments that evaluate the sedimentation vs. time under printing conditions such as elevated temperature. When sedimentation isn't addressed with appropriate settings in CKM, the parts may exhibit irregular particle distribution and undesirable characteristics such as the part shown on the left in Figure 5.

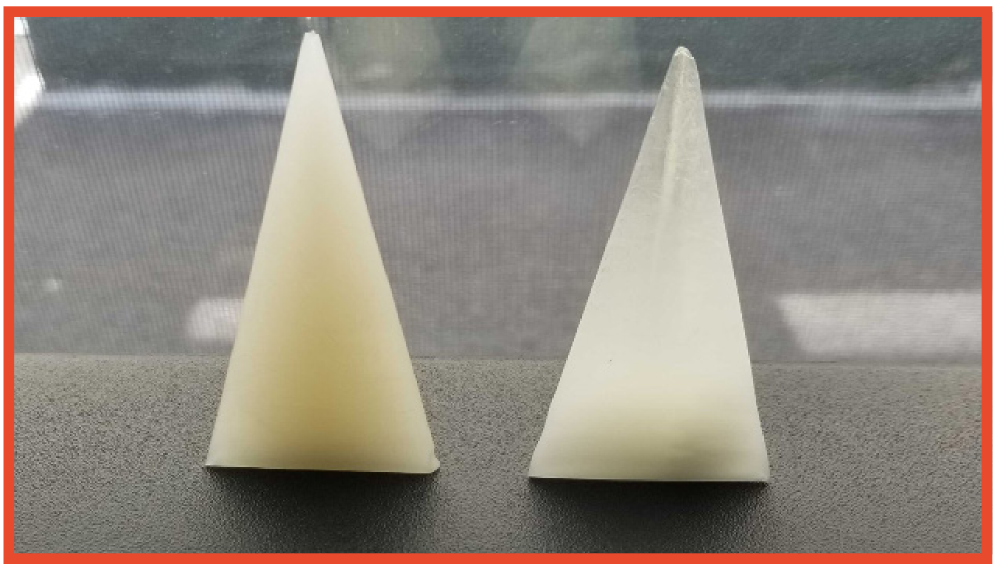


Figure 5: Left part is printed with CKM and exhibits no particle sedimentation. Right part is printed without CKM and shows an uneven distribution of particle filler in the printed part.

3.2.3 ON-MACHINE: SLOT WORKING CURVE

The Slot Working Curve is a customizable experiment that explores the critical relationship between UV energy and resin curing behavior. This is an experiment that is controlled and customized by user inputs on the 3D printer's user interface and creates a series of samples produced by a single light exposure.

ID	Intensity [mW/cm^2]	Dosage [mJ/cm^2]	ID	Intensity [mW/cm^2]	Dosage [mJ/cm^2]
1	2	25	13	10.7	25
2	2	42	14	10.7	42
3	2	59	15	10.7	59
4	2	76	16	10.7	76
5	2	93	17	10.7	93
6	2	110	18	10.7	110
7	6.3	25	19	15	25
8	6.3	42	20	15	42
9	6.3	59	21	15	59
10	6.3	76	22	15	76
11	6.3	93	23	15	93
12	6.3	110	24	15	110

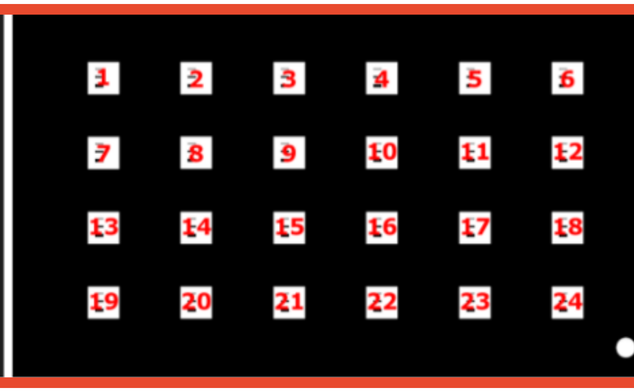


Figure 6: (Left) The input energy and intensity settings for the Slot Working Curve experiment. (Right) The labeled samples that correspond to the selected energy and intensity inputs. (The inputs shown here are demonstrative and are not representative of the example data presented below.)

During the experiment, the printer projector cycles through 4 unique LED input intensities (measured in mW/cm2) and exposes each sample to 6 unique UV energies (measured in mJ/cm2). The result of the experiment is a series of 24 samples, each having received a unique combination of UV intensity and UV energy.

The user can then use a micrometer and a digital microscope to measure the depth of cure of each sample, and the corresponding XY scatter for each sample. Example depth of cure data is plotted in Figure 7, and example scatter data is plotted in Figure 8.

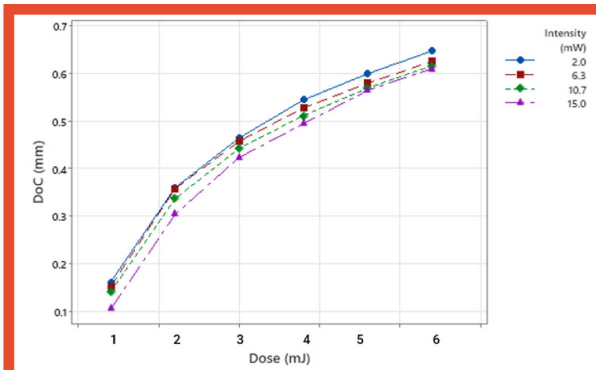


Figure 7: Depth of cure as a function of input energy and intensity for a given resin system (energy inputs obscured for confidentiality purposes).

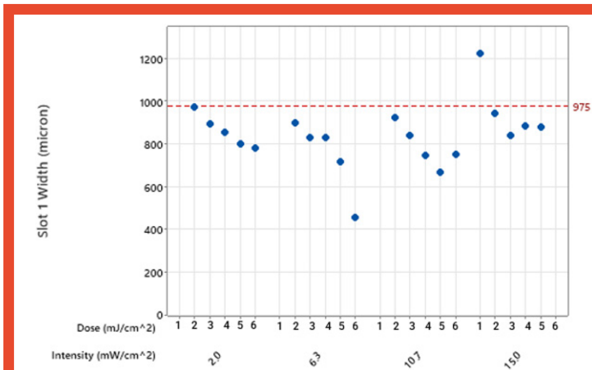


Figure 8: XY scatters as a function of dose and intensity for a given resin system. The measurement taken here is the width of one slot of the Slot Working Curve sample geometry. Values below nominal, defined by the red dotted line in the figure, suggest great over-cure from photon scatter (energy inputs obscured for confidentiality purposes).

Fortify encourages users to consider how their photokinetic results relate to the resin system formulation and the desired application. For example, resin systems that exhibit a high degree of scatter will be challenging to use for parts that require a high degree of resolution. Alternatively, resins that exhibit a very low depth of cure will be challenging to print with high throughput due to requiring thinner layers to print.

Depth of cure and scatter can be impacted by several resin formulation characteristics including, but not limited to:

- Photo-initiator selection and amount
- Particle color, morphology, alignment, and amount
- Inks, dyes, and other light-management agents

3.2.4 ON MACHINE: BUILD PLATE ADHESION

The final on-machine experiment is the build plate adhesion test. In this experiment, the user can define a range of 5 input energies for the first layer of a print. An example of the experimental inputs is shown in Figure 9. The user can leverage this test to determine which energies are required for parts to adhere well enough to the build plate for successful printing while not too well to make part removal challenging.

ID	Adhesion Dosage [mJ/cm^2]	ID	Adhesion Dosage [mJ/cm^2]
1	50	11	275
2	50	12	275
3	50	13	388
4	50	14	388
5	163	15	388
6	163	16	388
7	163	17	500
8	163	18	500
9	275	19	500
10	275	20	500

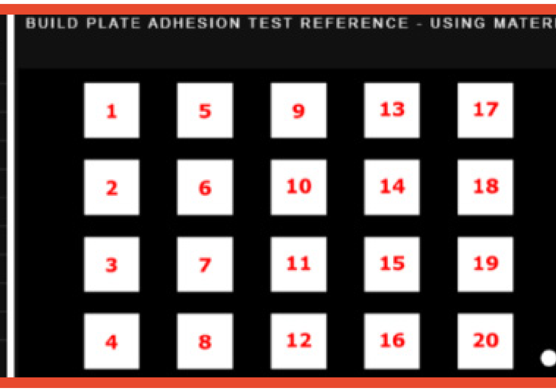
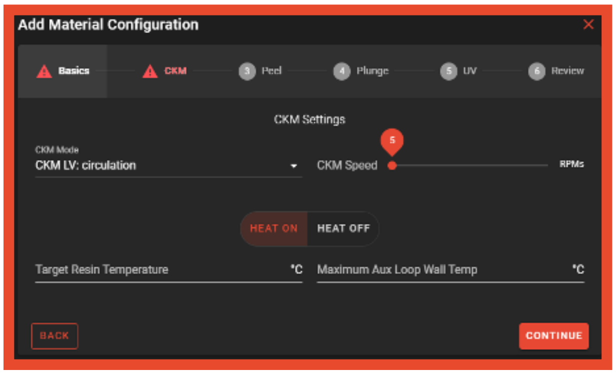


Figure 9: (Left) Experimental inputs for th build-plate adhesion test. (Right) The sample locations that correspond to the experimental inputs.

At this point, the user already has a full set of input parameters to define the peel, plunge, nominal UV intensity and dosage, CKM settings like resin temperature and pump speeds. Therefore, this experiment should be the first 3D printed part in the Flux Developer workflow, while also helping the user to understand what energy is necessary to get a part to stick to the build plate.

3.3 FLUX PORTAL

Flux Portal is a cloud-based interface for Printer Management & Status, Print History - but most important for Flux Developer is the material configuration development tool. In Flux Portal, Flux Developer users build their material configurations using the parameter values determined during the experiments described earlier (a few screenshots of which is shown in Figure 10.)



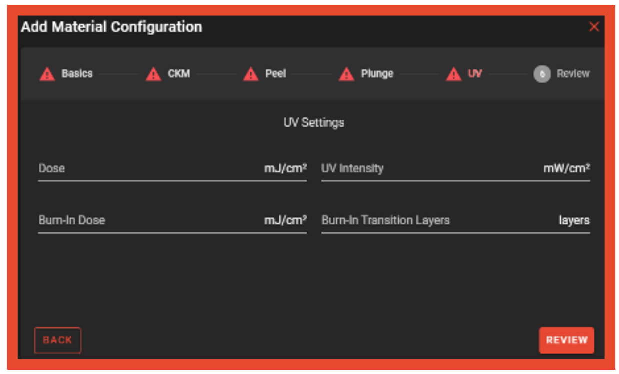


Figure 10: Screenshots from the material configuration development tool in the Flux Portal of the CKM Settings and UV Settings.

4
CASE STUDIES

To demonstrate the utility of the Flux Series of 3D printers combined with Flux Developer, two mini materials development case studies are presented.

4.1 ROGERS RADIX™ PRINTABLE POLYMER DIELECTRIC

Rogers Corporation is a materials partner of Fortify, and recently developed and sells a new line of printable photopolymer dielectric materials called Radix™. When Rogers and Fortify first established their partnership, Rogers had a concept and an initial prototype material they were trying to print. The high-level goal for this material was to develop the capability of scalable manufacturing for new dielectric components like Gradient Refractive Index (GRIN) lenses, waveguides, antennas, and volumetric circuits.

For product goals, there were two primary targets:

- Dielectric Constant of ~2.8 Dk
- Dielectric Loss competitive with Rogers' 4000 series laminates for high frequency applications

With these ideas in mind, Rogers' material development engineers iterated on photopolymer resin system formulas targeting these characteristics. To quickly index against these key characteristics, the engineers leveraged a test fixture called Split Post Dielectric Resonator combined with a Vector Network Analyzer for doing single frequency point characterization of thin film samples at 10GHz (Figure 11). Once a formula with ideal characteristics was established, the engineers began printability characterization using Flux Developer toolsets.

Figure 11: Split Post Dielectric Resonator Testing on early prototype Radix material.

The engineers characterized the rheology, sedimentation, and curing kinetics using the toolsets available in Flux Developer. With that information in hand, a materials configuration was developed on Flux Portal, and the first parts were printed via the Build Plate Adhesion test (Figure 12).

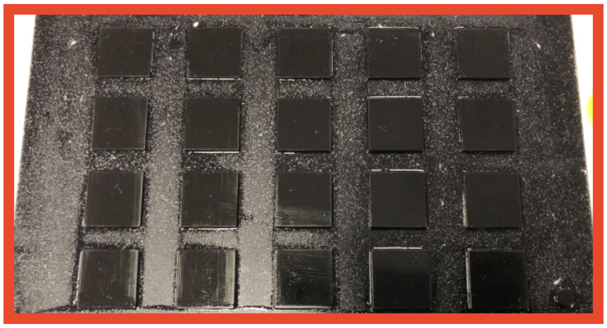


Figure 12: Build plate adhesion test for the Radix 2.8 Dk material

The Rogers engineers discovered that initial material configuration parameters were excellent for printing solid, geometric type parts, but were not successful at printing complex, high resolution lattices. Through some quick experimentation, they observed that by moving the build plate slower during the print process, the lattice features would survive. By using Flux Developer to modify the material configuration parameters, they were able to make a quick adjustment to slow down the build plate movement and reduce build plate acceleration. This led to successful prints for parts containing high aspect ratio features like 225 micron thick walls in gyroid lattices for GRIN lenses, as shown in Figure 13.

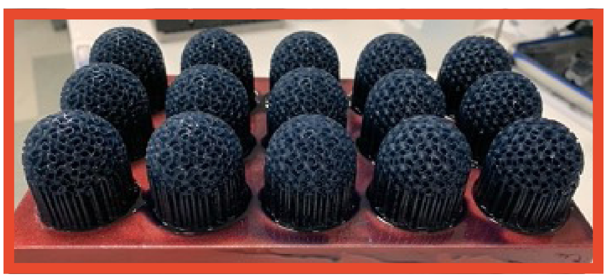


Figure 13: GRIN lenses printed from Radix 2.8 Dk

By being able to print both bulky parts with large cross sections as well as fine featured parts for gyroid-based GRIN lenses, Rogers was able to meet their goal of scalable manufacturing for a wide variety of RF device geometries. The Radix material is an excellent option for a wide variety of high frequency devices that require low loss, low moisture absorption, and the ability to achieve tuned dielectrics via latticing.

4.2 FORTIFY'S THERMALLY CONDUCTIVE DIELECTRIC

Like Rogers Corporation, Fortify had a resin design goal – create an electrically insulative, thermally conductive dielectric photopolymer resin with a goal of 2 W/m-K. To achieve a high thermal conductivity without electrical conductivity, Fortify material scientists leaned on phononic conduction over the more typical electron conduction to transport heat through printed parts and avoid electrical conductivity. The target application space for a thermally conductive, electrically insulative polymer is in thermal management applications in the presence of electrically active circuits with a high feature resolution requirement.

To index for thermal conductivity, the Fortify engineers leaned on Thermal Interface Materials (TIM) testing equipment. The TIM Tester is capable of measuring through-plane thermal conductivity of both liquids and solids. By being able to test the thermal conductivity of liquid samples, Fortify was able to quickly cycle through formulation concepts while indexing against rheology (an off-printer on-boarding tool) and thermal conductivity without needing to print a test geometry.

Once a few material formulations with promising characteristics were developed, the materials scientists ran the key formulations through onboarding tool to understand the photocuring and rheological behavior of the material and begin printing sample geometries like those in Figure 15.

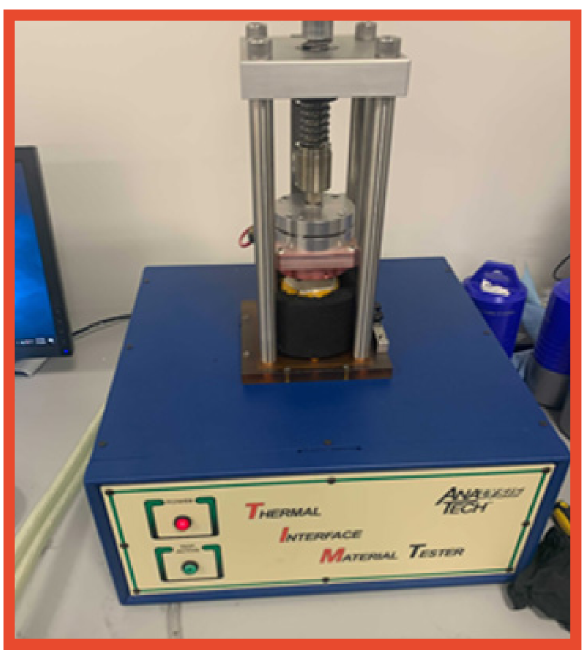


Figure 14: Photograph of the TIM tester used for early screening of material formulations.

Figure 15: Photograph of the TIM tester used for early screening of material formulations.

With printed samples, Fortify engineers were able to verify the thermal conductivity behavior of the solid, printed components met the design requirement of 2 W/m-K with a dielectric strength of 30 kV/mm. Having developed a material that met the primary design requirement, the next step was to optimize printing behavior to achieve geometries that are meaningful for heat sinks, heat exchangers, and cold plates – which for additive manufacturing typically means high surface area lattice-type geometries. Therefore, an example heat sink was designed and used to print as part of process optimization. The results of the parameter and process optimization workflow is the heat sink shown in the photograph in Figure 16.

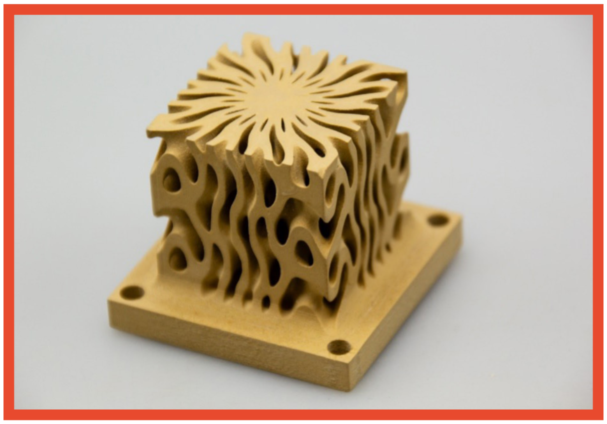


Figure 16: Photograph of a printed heat sink for a thermal management application.

Combined with architected design concepts like graded gyroid latticing, the 3D printed thermally conductive dielectric material is a wonderful technology perfectly suited for all types of thermal management applications where electrical insulation is a must. This material was also just awarded the TCT Materials Innovation Award at TCT 3Sixty in June 2022.

TCT Materials Innovation Award at TCT 3Sixty in June 2022

5

CONCLUSION

With the unique capabilities of the Fortify printers and the flexibility of the Flux Developer toolsets, engineers can quickly design, test, and optimize the printing of new high value, particle filled photopolymer materials. Fortify's staff of highly experienced application engineers, material scientists, and process development experts are available to support your material development efforts. Reach out to Fortify today to get the conversation started and learn more about how you can solve your hard, technical materials development problems with Flux Developer.

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