Materials Development and Formulation Document

Consumer printheads are designed for jetting OEM ink. Jetting non-standard fluids requires both material engineering and optimization of hardware control signals. Our main goal is to streamline this development process. Here, we outline the main steps:

Formulation: First, we define the desired characteristics of the material. Then, we choose the appropriate raw materials: monomers, oligomers, additives (surfactants, dispersants), and particles such as pigments, and photoinitiators. Based on the technical datasheets for each raw material, we formulate a material with the appropriate viscosity, surface tension and stability. At this stage, any additional particles can also be dispersed within the materials.

Viscosity, Surface Tension, and Density Measurement: Next, we measure the viscosity, surface tension, and density of the material. These properties are crucial to ensure that the material can be reliably jetted. The viscosity is measured using a DV-1 Prime viscometer and the surface tension is measured using a DataPhysics DCAT 11. Based on these values we can calculate the Ohnesorge number that describes the physical properties of the liquid to be jetted. This number should be between 0.1 and 1 [Derby et al. 2010]. If the value is too high, viscous forces will prevent droplet formation. If the number is too low, additional smaller (satellite) droplets will form. If the Ohnesorge number does not fall within the required range then we modify the formulation.

UV-curing: Next, we test the surface curing of the materials, then manually dispense a thin layer of the material on a glass slide, and we expose it to the UV LEDs for a specified time period (e.g., 1 second). We then check whether the surface of the layer is completely solid. If the surface is still wet, the quantity of the photoinitiator is modified.

Jetting Optimization: We use a droplet visualization system (JetXpert) to verify key parameters: satellite drop formation, drop velocity, size, and stability. The system images jetted droplets at high speeds using a pulsed illumination source. Our printhead driving circuit enables arbitrary control of the waveform shape. For each material and each desired droplet size, we adapt the drive waveform (Figure 1). This process is necessary to ensure good droplet quality. In order to make this easier, we have developed an interactive application to aid users in finding optimal waveforms (Figure 2).

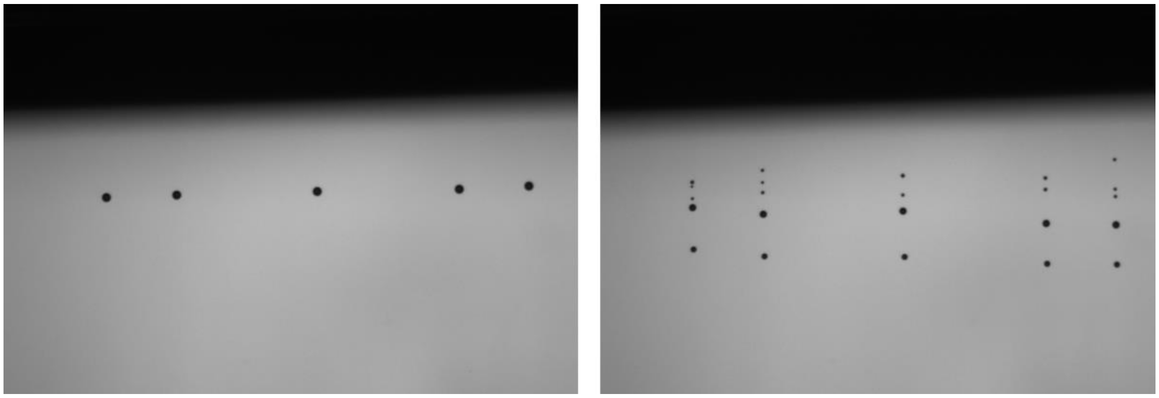


Figure 1. *The droplets with the optimized waveform are shown on the left. The droplets with the default, non-optimized waveform are shown on the right. The right image shows satellite droplets forming.*

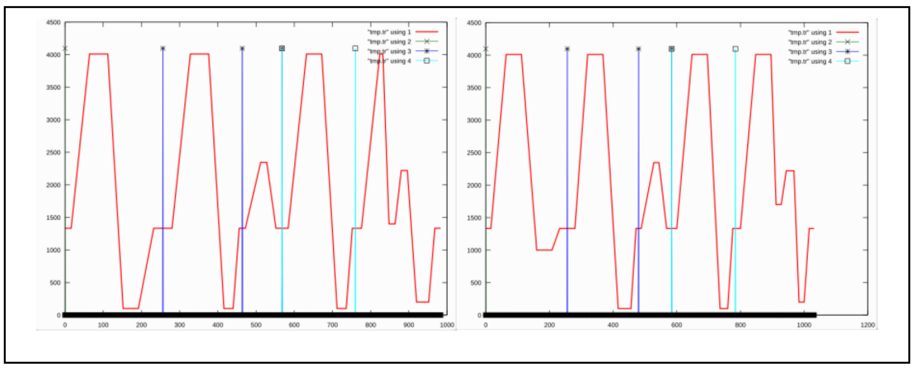


Figure 2. *Our interactive application aids users in finding optimized waveforms for each material. The application is coupled with the JetXpert system to visualize droplets in real-time. The waveform on the left has been optimized for the RIG material while the waveform on the right has been optimized for the ELA material.*

2D Printing: We use a printhead mounted to an XY gantry to print a test pattern composed of straight lines (e.g., horizontal, vertical). We verify the quality of these lines using an optical microscope and a profilometer. We also test the UV-curing of the materials after 2D printing.

3D Printing: After 2D prints can be reliably produced, the materials are tested within the 3D printer. In order to calibrate the layer thickness, we print a 3D material block composed of 100-1000 material layers. We obtain the effective layer thickness by dividing the block height by the number of printed layers. Next, we print a custom 3D chart. We have designed this chart to quickly and visually evaluate the effective resolution of our printer. Both the chart model and a sample single material print are shown in Figure 3.

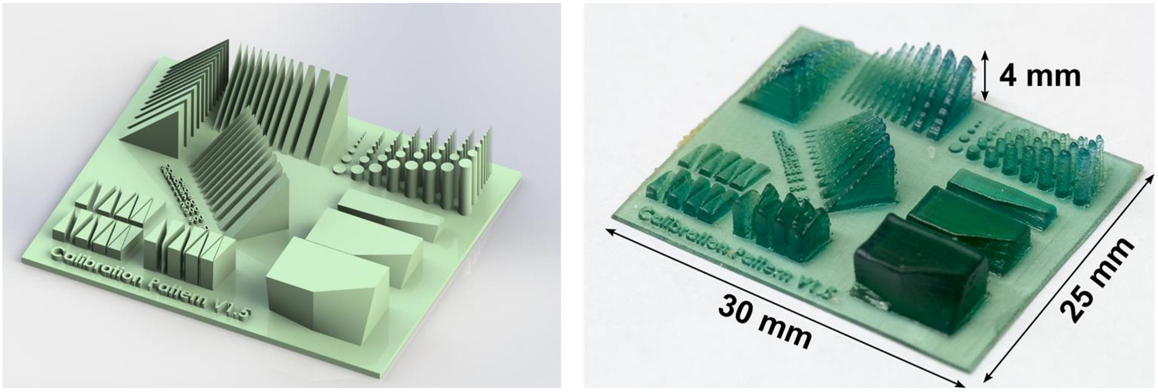


Figure 3. *A rendering of the 3D chart is on the left. A photograph of a printed chart is shown on the right.*

Characterization: We characterize the mechanical, optical, and appearance properties of each 3D printed material by printing appropriate samples for each of these measurements. Instron mechanical tester is used for mechanical properties measurement, and a Varian Cary 6000i spectrometer is used to obtain the spectral distribution of each material. Finally, we use a Kruss Gemstone refractometer to obtain the index of refraction.

Materials Library

	Viscosity	Surface Tension	Density	Refractive Index	Modulus	Ultimate Tensile Strength	Elongation at break
	cPs at 25C	mN/m	(g/cm^3)		MPa	MPa	%
RI	170	37.1	1.11	1.49	1550	37.5	7
EL	115	36.5	1.17	1.47	8.5	0.72	175
HR	53.8	40.1	1.05	1.58	261.8	18.2	41.3
LR	22.5	35.3	1.06	1.43	943.7	19.6	2.2
SPT	60.5	40.2	1.09	1.47	N/A	N/A	N/A

Figure 4. *Physical properties of our materials. Viscosity, surface tension, and density are important for jettability, while the other properties are important for functionality of the printed objects.*

We have developed a set of materials that span a range of mechanical, optical, and appearance characteristics. We have also developed a support material. All materials presented in this paper are UV-curable photopolymers. Additional materials such as co-polymers, hydrogels, and solvent-based materials can be adapted to be used within our platform. While we have performed initial experiments with many of these materials, this research is beyond the scope of this paper. Currently, we have rigid material (RIG), elastic material (ELA), high refractive index material (HR), low refractive index material (LR) and support material (SPT). Figure 4 summarizes the mechanical properties of these materials.

Rigid Materials (RIG): The rigid material is composed of UV-curable Bisphenol-A (or its derivatives) and others; all the raw materials are commercially available at low cost. It is mechanically similar to polycarbonate. The basic rigid material (RIG) is optically clear. We have formulated additional versions of the material with different spectral characteristics by adding colored pigments: rigid black (RIG-K), rigid white (RIG-W), rigid magenta (RIG-M), rigid cyan (RIG-C), and rigid yellow (RIG-Y).

Elastic Materials (ELA): The elastic material is formulated with UV curable esters. It is mechanically similar to rubber and it is optically clear. We also created additional versions: elastic white (ELA-W), elastic black (ELA-K), elastic cyan (ELA-C), elastic magenta (ELA-M), and elastic yellow (ELA-Y).

High Refractive Index Material (HR): This material is formulated from several low cost commercially available monomers and oligomers. It is optically clear and its refractive index is 1.58. The material is mechanically rigid.

Low Refractive Index Material (LR): We also formulate low refractive index materials from existing commercially available monomers and oligomers. The refractive index is 1.43. It has similar mechanical properties to the high refractive index material.

Support Material (SPT): Support material is necessary when printing overhangs or very thin features. It can also be used to print a raft at the bottom of the object to even out any platform imperfections. The main requirement for the support material is that it should be rigid and easily removable after the print is completed. The support material is formulated from water dispersible or soluble monomers and oligomers. After printing, the support material can be easily removed from parts manually or through a base water solution.

Presented are the components of the materials used in the printer. Components are mixed in a standard lab stirrer, in a per-weight fashion, for a period of ~3 hours. There are two classes of materials: RIG (rigid) and ELA (flexible). Each class has six different sub-versions of the material that correspond to six colors: white, black, cyan, yellow, magenta, and clear.

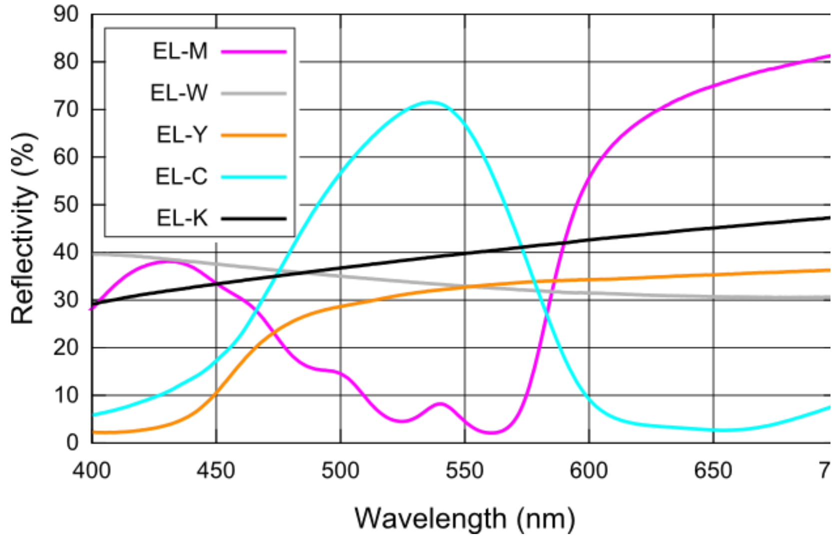
RIG (Rigid)				
Trade Name	**Chemical Type**	**Function in the formulation**	**Supplier**	**Content (%wt)**
Genomer2252/GP25	Bisphenol A epoxy diacrylate in 25% GPTA	Monomer	Rahn USA Corp.	30-50
MIRAMER M300	Acrylic acid ester	Oligomer	Rahn USA Corp.	10-30
Genomer1117	Cyclic trimethylolpropane formal acrylate	Monomer	Rahn USA Corp.	40-60
Irgacure 819	Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide	Photo initiator	BASF	0-5
ITX	2-Isopropylthioxanthone	Photo initiator	Sigma	0-2
MEHQ	4-methylphenol	Photo inhibitor	Sigma	0-0.1
D3410-W6	White Pigment dispersion	Pigment	Rjadispersions, LLC	0-10
D3410-B15:4	Cyan pigment dispersion	Pigment	Rjadispersions, LLC	0-10
D3210-Y150	Yellow pigment dispersion	Pigment	Rjadispersions, LLC	0-10
D3210-R122	Magenta pigment dispersion	Pigment	Rjadispersions, LLC	0-10
D3210-K	Black pigment dispersion	Pigment	Rjadispersions, LLC	0-10

ELA (Elastic)				
Trade Name	**Chemical Type**	**Function in the formulation**	**Supplier**	**Content (%wt)**
CN3105	Low viscosity oligomer	Oligomer	Sartomer	30-50
SR504	Ethoxylated Nonyl-Phenol Acrylate	Monomer	Sartomer	10-30
SR440	Isooctyl acrylate	Monomer	Sartomer	40-60
Irgacure 819	Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide	Photo initiator	BASF	0-5
ITX	2-Isopropylthioxanthone	Photo initiator	Sigma	0-2
MEHQ	4-methylphenol	Photo inhibitor	Sigma	0-0.1
D3410-W6	White Pigment dispersion	Pigment	Rjadispersions, LLC	0-10
D3410-B15:4	Cyan pigment dispersion	Pigment	Rjadispersions, LLC	0-10
D3210-Y150	Yellow pigment dispersion	Pigment	Rjadispersions, LLC	0-10
D3210-R122	Magenta pigment dispersion	Pigment	Rjadispersions, LLC	0-10
D3210-K	Black pigment dispersion	Pigment	Rjadispersions, LLC	0-10

SPT (Support Material)				
Trade Name	**Chemical Type**	**Function in the formulation**	**Supplier**	**Content (wt%)**
SR610	Polyethylene glycol diacrylate	Oligomer	Sartomer	0-20
SR551	Polyethylene glycol acrylate	Oligomer	Sartomer	10-30
PEG400	Polyethylene glycol	Swelling agent	Sigma	50-70
Irgacure 819	Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide	Photo initiator	BASF	0-5
ITX	2-Isopropylthioxanthone	Photo initiator	Sigma	0-2
MEHQ	4-methylphenol	Photo inhibitor	Sigma	0-0.5

HR (High Refractive Index material)				
Trade Name	**Chemical Type**	**Function in the formulation**	**Supplier**	**Content (wt%)**
CN9167US	Polyurethane oligomer	Oligomer	Sartomer	0-30
BPADA	Bisphenol A epoxy diacrylate	Monomer	Sigma	0-30
Ebecryl 114	2-Phenoxyethyl Acrylate	Monomer	Allnex	40-70
Irgacure 819	Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide	Photo initiator	BASF	0-5
ITX	2-Isopropylthioxanthone	Photo initiator	Sigma	0-2
MEHQ	4-methylphenol	Photo inhibitor	Sigma	0-0.1

LR (Low Refractive Index Material)				
Trade Name	**Chemical Type**	**Function in the formulation**	**Supplier**	**Content (wt%)**
SR256	2 (2-ethoxyethoxy) ethyl acrylate	Monomer	Sartomer	40-70
CN9006	Aliphatic urethane acrylate	Oligomer	Sartomer	10-40
SR454	Ethoxylated trimethylolpropane triacrylate	Crosslink agent	Sartomer	10-30
Irgacure 819	Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide	Photo initiator	BASF	0-5
ITX	2-Isopropylthioxanthone	Photo initiator	Sigma	0-2
MEHQ	4-methylphenol	Photo inhibitor	Sigma	0-0.1



Reflectivity of different pigmented EL materials.