

Dielectric Performance of low viscosity UV-Curable Piezo-inkjet resins for dielectric coating applications

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Abstract

UV-curable piezo inkjet is a useful mechanism to deposit electronically insulating layers for printed and flexible circuit boards. The material development for these print heads require a unique set of expertise in resin formulation, knowledge of application and processing, and resultant end-use properties. They can operate over a wide range of temperatures, are resistant to humidity/moisture as well as some solvents, and can survive hand soldering for rework. This work outlines the dielectric optimization of a base resin package that can be used with colorants for a tailored solution into this market and compares this performance vs. an incumbent UV-curable piezo inkjet dielectric material.

Introduction

Low viscosity resins are being developed for electronic applications as the drive for better dielectric properties meets the need of faster processing speeds. Many commercially available low viscosity dielectric resins feature high dielectric losses, which affect the resultant signal transmissionⁱ. They can also be brittle, contain solvents, contain toxic compounds, as well as skin irritants. The polarity of the material is also a good indicator of moisture uptake. For electronics applications, very hydrophobic materials with good hydrolytic stability are essential to limit any property shift as well as loss of insulation over time.

Low viscosity droplet on demand (DOD) inkjet dielectric inks are used to encapsulate and insulate electrical components in printed electronic applications. They can be used in multiple layers in tandem with conductive inks to make multilayer circuits with insulating crossoversⁱⁱ. The latest trends in this industry is the move from conventional mercury-based UV lamps to Light Emitting Diodes (LED) that emit UV radiation and are much more energy efficient. They also have the added benefit of less energy consumption longer lamp life, and less heat generation, which is important for low glass transition temperature substrates like Polyethylene terephthalate (PET).

In this paper, a new low loss dielectric resin called ELECTROJET 1 was benchmarked against an incumbent low D_k dielectric resin referred to as Competitive Resin A with similar performance goals to be used in printed electronics-type applications.

Experimental Setup

Film samples were cured with a broadband Dymax flood lamp (5000-EC) at 250 μm thick for 30 seconds on both sides to ensure a full cure. The samples conditioned prior to testing by heating to approximately 25 $^{\circ}\text{C}$ below the material's glass transition temperature (T_g) to remove any absorbed moisture. Cured film thickness was measured using a Heidenhain gauge accurate to $\pm 0.2 \mu\text{m}$. Three locations in a 1.0 cm^2 area were chosen for film thickness measurement prior to screen printing of conductive ink and their average was used for the dielectric constant and volume resistivity calculations.

Dielectric Constant and Loss were measured using an LCR meter at room temperature via the ASTM D-150 standard after sample drying at 60 $^{\circ}\text{C}$ in vacuum. One side electrode of the capacitor was

connected to the high voltage and high current terminals of the LCR meter, and the other electrode of the capacitor was connected to a low voltage and low current terminal. A 2 V_{AC} bias was applied to each sample during the measurement. The high frequency measurement was performed using a Network Analyzer with a split cavity resonator per IPC test method TM-650 2.5.5.13 near 10 GHz with the average of 5 samples reported.

Breakdown strength of cured films was measured using the ASTM D-149 standard, ramping at 500 V/s. This test utilizes a 6.35 mm stainless steel ball on a brass substrate in 25 °C silicone oil to minimize the electric field non-uniformity and the chances of a film defect being present at the test location. The cured film thickness was measured and recorded in each breakdown location prior to breakdown. Twenty measurements were made on each film and the dataset was fit using a 2-parameter Weibull distribution with a 95% confidence interval.

Surface and Volume Resistivity were measured on five samples each using a Keithley 6517B and 8009 fixture at room temperature via the ASTM D-257 standard. An alternating polarity of ± 100 V was applied to the cured film for 10 seconds with a 2 nA current range prior to measurement to ensure a net zero charge.

Moisture absorption was performed using the ASTM D570-98 method using a 60 °C cure for 48 hrs. for drying followed by a 50 °C immersion in distilled water for 48 hrs. The increase in weight percent is shown in Equation 1 below.

$$\text{Increase in weight, \%} = \left(\frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \right) * 100$$

Equation 1. Moisture uptake as per ASTM D570-98.

Flexibility of the coatings was tested according to ASTM D522, which uses a coated tin panel. The conformal coating material is flood cured onto the tin panel to ensure a full cure and optimal adhesion. The samples were drawn down to a thickness of 75 µm and bent around a conical mandrel from 38 mm to 3.1 mm. Pencil hardness was measured as per ASTM D3363-74 H.

A TA Instruments Q800 Dynamic mechanical analysis was used to measure the T_g using ASTM D4065. Samples were produced in a 3 mm x 12 mm x 17.5 mm, cured using a flood lamp, and ramped from -100 °C to 250 °C at 5 °C/min with the T_g being determined from the Tan Delta peak.

Thermogravimetric analysis (TGA) was completed on a TA instruments Q50 TGA under air using a platinum sample pan. Weight loss as a function of temperature was measured using a ramp rate of 5 °C/min from 40 °C to 600 °C for all samples. Weight loss at device operating temperature (150 °C) was measured by heating to 150 °C at 5 °C/min followed by an isothermal step at 150 °C for 4 hours.

A TA Instruments TMA450 was used with a set force of 0.05 N and a 5 °C/min ramp rate. A thermal anneal was performed to ensure any residual movement due to uncured segments would complete in the measurement range (-70 to 160 °C). The sample was then taken from -70 °C to 160 °C with a

ramp rate of 5 °C/min as per IPC-TM-650 2.4.24.5 after which the Coefficient of thermal expansion (CTE) values above and below T_g were recorded.

Results and Discussion

Two formulations have been analyzed specifically for use in low dielectric constant electronic insulator applications. Competitive Resin A is a conventional off the shelf material designed for droplet on demand printed electronic insulating applications. ELECTROJET 1 is a fully formulated dielectric resin in the same viscosity range that is also geared toward piezo-based inkjet print heads.

The low frequency data, as shown in Figure 1, spans 20 Hz to 1 MHz and is the average of 5 samples tested targeted at 100 pF or greater with error bars showing the minimum and maximum range measured. The dielectric constant data is increasing with frequency for both samples and shows that Competitive resin A has a significantly higher value, which is interesting as it is marketed as a low D_k material. ELECTROJET 1 has a statistically significant decrease in dielectric constant and loss across 20 Hz to 1 MHz operation range. As SiC MOSFETs and IGBTs become more prevalent on the market due to a decrease in on-state resistance ($R_{DS(on)}$), their wide band-gap performance has necessitated a higher operational temperature and frequency. Dielectric loss is effectively the signal loss due to heat that is irrecoverable and must be minimized to maintain maximum transmission. This necessitates the need for lower D_f materials in the 10 kHz up through 1 MHz and demonstrates the performance benefits of ELECTROJET 1 of Competitive Resin A. ELECTROJET 1 has been optimized to significantly reduce the dielectric loss of the material while keeping the dielectric constant stable versus frequency.

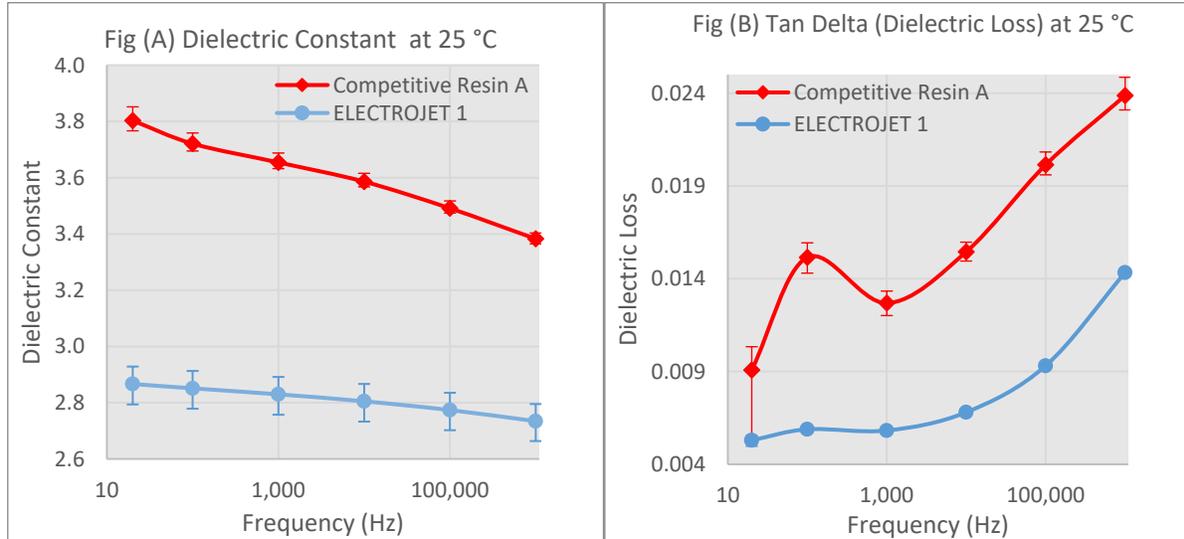


Figure 1. (A) Shows ELECTROJET 1 and Competitive resin A having the same trend in dielectric constant vs. frequency as measured with the LCR meter at 25 °C. Figure (B) outlines a dielectric loss, which increases in both samples with increasing frequency, but has much lower values across the measured frequency spectrum for ELECTROJET 1.

High frequency dielectric constant and loss was also performed on both samples as measured by IPC test method TM-650 2.5.5.13 near 10 GHz. Table 1 below shows a decreased dielectric constant and loss at high frequency for ELECTROJET 1 vs. Competitive Resin A.

	Dk (10GHz average)	Df (10GHz average)
ELECTROJET 1	2.575695	0.010505
Competitive Resin A	2.883075	0.015735

Table 1. Shows the dielectric constant and loss measured near 10 GHz for ELECTROJET 1 vs. Competitive Resin A.

The breakdown strength of both materials was measured using the ASTM D-149 standard as described in the Experimental Setup section above. Figure 2 shows the results of the 2-parameter Weibull analysis at 25°C. A statistical difference in dielectric breakdown strength can be seen with Competitive Resin A having approximately 140V/μm greater dielectric strength but having more low voltage breakdowns < 200 V/μm. This tail can be worrisome in insulating dielectric applications and is most likely caused by Competitive Resin A being more brittle (crack propagation) and having a higher likelihood of generating pinholes. Materials used as ink-jettable insulators are usually deposited in at least 2 layers to help mitigate the chance of pinholes aligning in each layer.

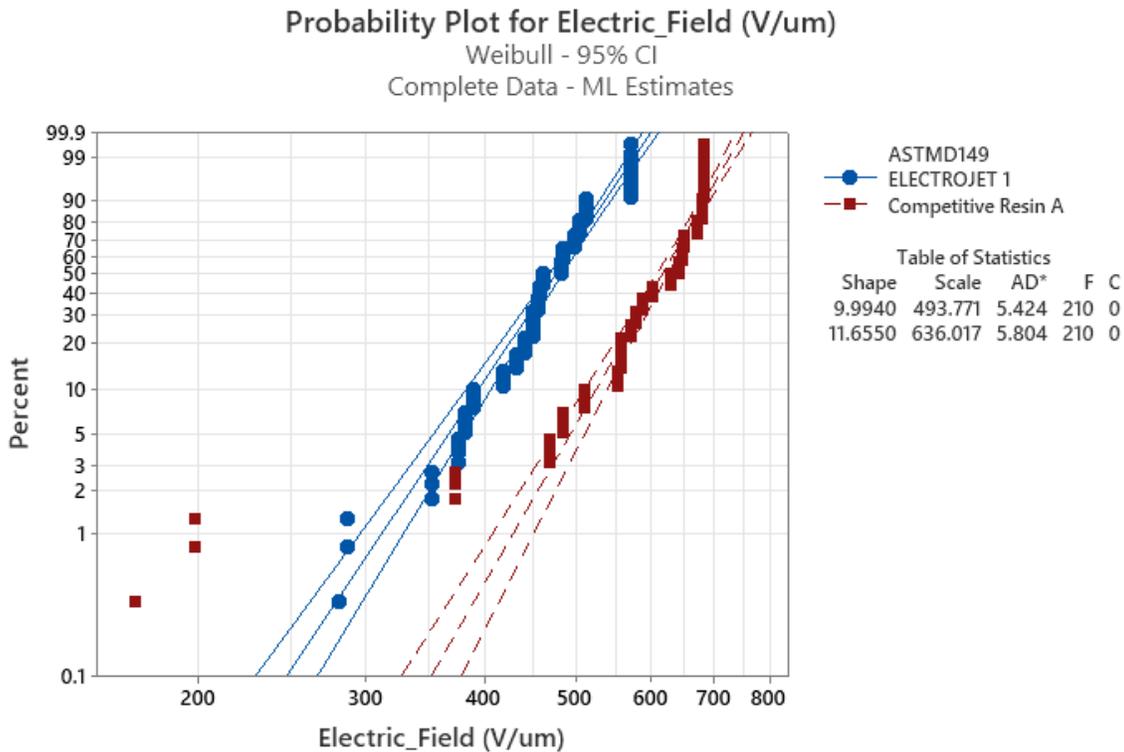


Figure 2. Shows the breakdown strength of ELECTROJET 1 and Competitive Resin A. The Shape parameter describes how the Weibull data is distributed. The Scale parameter determines the spread of the Weibull distribution. The Anderson-Darling statistic (denoted AD*) measures the area between the Weibull distribution line of best fit and the empirical distribution function from the individual data points.

Surface and Volume Resistivity were measured next as shown in Table 2. As the name states, the Surface Resistivity measures the ability of the material to conduct electricity across the surface and its value should be high for a useful electrical insulator. The Volume Resistivity measures the amount of current leakage through the material at a set thickness and voltage, which is then converted to resistance through the equation $V = I * R$. A smaller leakage current value is desired as this directly translates into a high performing electrical insulator.

	Avg. Surface Resistivity (Ω /square)	Avg. Volume Resistivity (Ω *cm)
ELECTROJET 1	2.41923E+16	6.62823E+15
Competitive Resin A	9.9299E+16	1.54467E+15

Table 2. Shows the average Surface and Volume Resistivity of ELECTROJET 1 and Competitive Resin, A which are statistically comparable.

Optimization of dielectric loss is a key factor in many applications like dielectric substrates, device encapsulation, thermoset film capacitors, and potting materials, and one main factor that affects dielectric loss is moisture uptake of the resin. Hydrophobic resin blends have been developed to optimize the low loss needs of these insulating applications while still maintaining good breakdown strength characteristics. Humidity strongly affects the dielectric materials that can absorb moisture, and can increase capacitance and dielectric loss significantly over a range of humiditiesⁱⁱⁱ. This is because water is highly polar and even slight increases in moisture uptake of the material can have a significant effect on the dielectric properties. Table 3 below shows comparable values for ELECTROJET 1 and Competitive Resin A, indicating that the higher Df values found in Competitive Resin A at low and high frequency are a result of the material being much more polar and not due to a high moisture content.

	Moisture Absorption (% increase in weight, ASTM D570)
ELECTROJET 1	0.0058
Competitive Resin A	0.0054

Table 3. Shows the average Moisture Absorption of ELECTROJET 1 and Competitive Resin, A which are statistically comparable.

Flexibility of the coatings was demonstrated by bending the sample around a conical mandrel and is shown in Figure 3 below. Both materials feature a hard surface as shown in the Pencil Hardness data below (Table 4) and are somewhat brittle. The Competitive Sample A shows a significant reduction in flexibility compared to ELECTROJET 1 as seen in the tree-like crack propagation shown, which can limit its end use applications within printed electronics. Especially as the insulating layer thickness and area increase, this can play a significant role in premature failures and open circuits resulting from the lack of flexibility.

A) ELECTROJET 1

B) Competitive Resin A

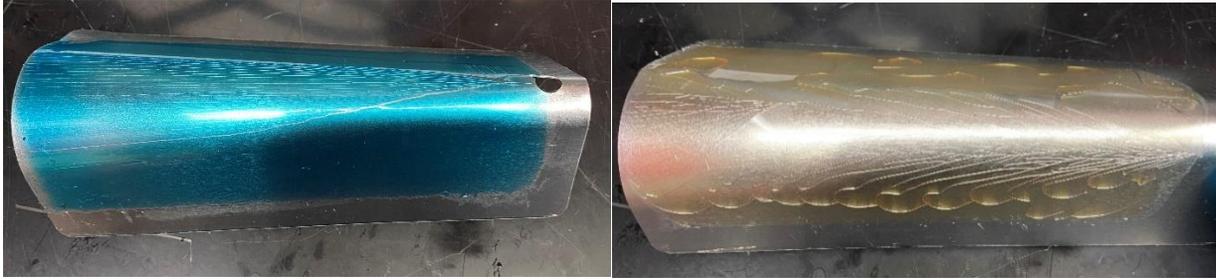


Figure 3. Shows the flexibility differences between ELECTROJET 1 and Competitive Resin A as measured per ASTM D522.

Abrasion resistance, Pencil Hardness (ASTM D3363-74 H)	
ELECTROJET 1	H
Competitive Resin A	5H

Table 4. Shows the average Pencil Harness of ELECTROJET 1 and Competitive Resin A.

Dynamic mechanical analysis (DMA) was used to measure the T_g using ASTM D4065. The glass transition temperature (T_g) is most typically determined from the Tan Delta peak and can be seen for ELECTROJET 1 (A) and Competitive Resin A (B) in Figure 4 below. The DMA plots for ELECTROJET 1 are very typical for a thermoset-based material. Competitive Resin A does show multiple T_g 's at -69°C and 99°C respectively.

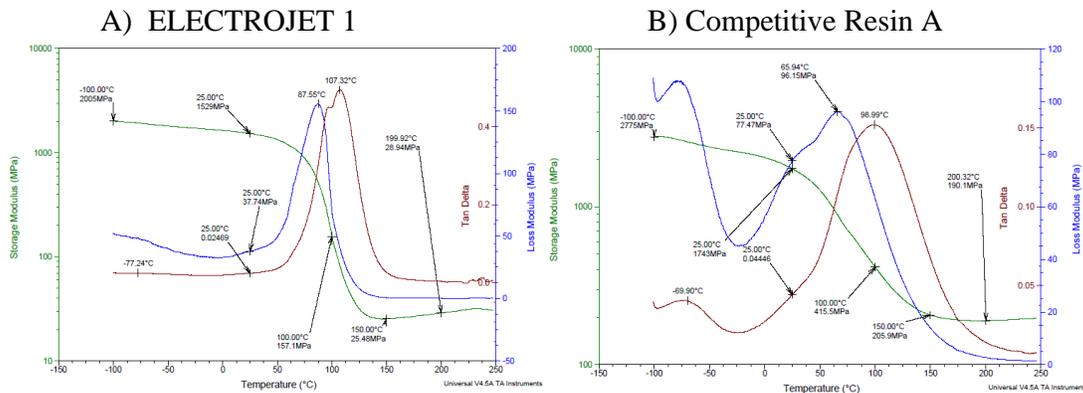


Figure 4. DMA plots for ELECTROJET 1 (left) and Competitive Resin A (right)

Thermogravimetric analysis (TGA) is used to understand the weight loss and decomposition temperature of a material as a function of temperature. Decomposition and weight loss are important to acknowledge for insulating electronic applications where the cured resin can operate at high temperatures ($>150^\circ\text{C}$). ELECTROJET 1 and Competitive Resin A were heated to 600°C and

weight loss is recorded over that temperature range as shown in Figure 5 below. 1% weight loss for ELECTROJET 1 and Competitive Resin A were recorded at 275.4 °C and 332.6 respectively °C. A 4-hour hold at 150 °C was also used to have an idea of the thermal stability of the material at high temperature. These results can be seen in Figure 6 below and show an increased thermal stability at 150 °C for ELECTROJET 1 versus Competitive Resin A in an air environment.

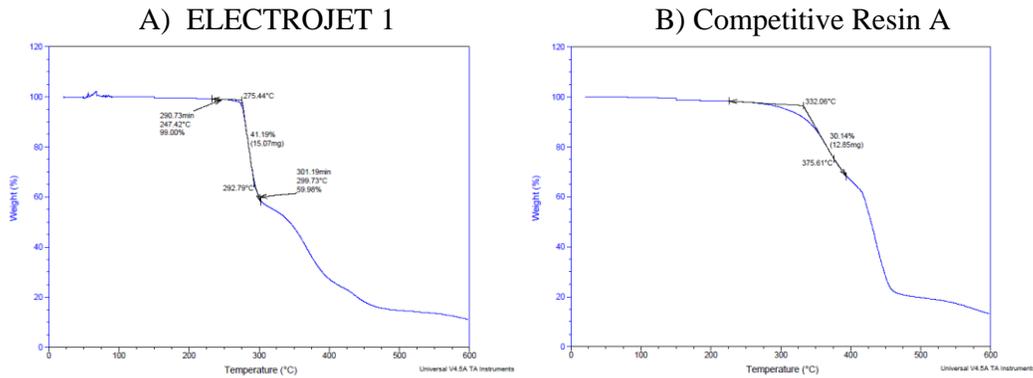


Figure 5. 1% weight loss plots for ELECTROJET 1 (left) and Competitive Resin A (right)

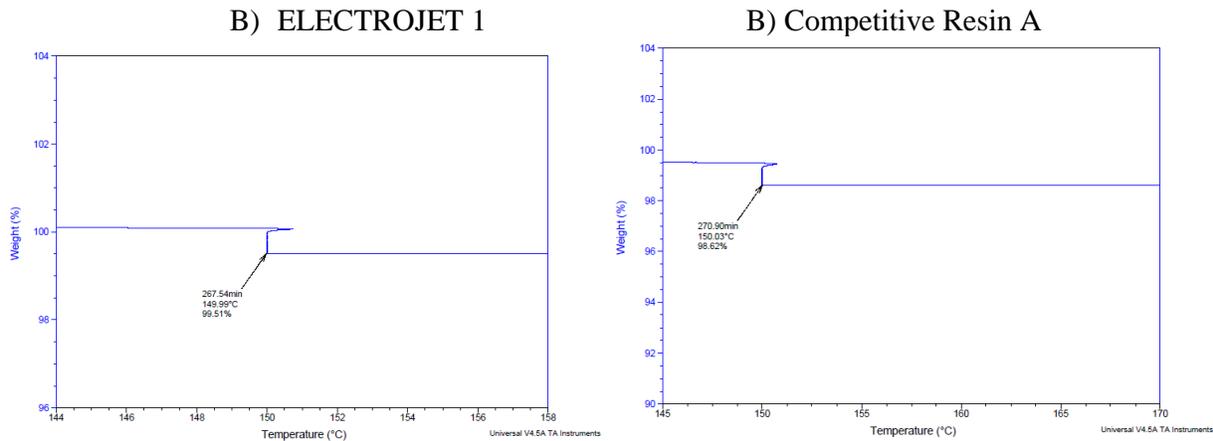


Figure 6. 4 hour hold weight loss plots for ELECTROJET 1 (left) and Competitive Resin A (right)

Thermal mechanical analysis (TMA) was run on all samples to determine the coefficient of thermal expansion (CTE) of each material during heating/cooling. Understanding the CTE of an encapsulating material is important because large expansion in a range of temperatures due to thermal stress can cause conductors to delaminate and lose adhesion, which can shorten the lifetime of the electronic device or even cause failures. It is important to ensure that the encapsulating material has a CTE that is close to the CTE of the electronic components. Materials have a tendency to expand and contract under changes in temperature, especially when the temperature of the environment increases past the T_g of the material. Table 5 shows the TMA data of ELECTROJET 1 and Competitive Sample A when tested in expansion mode. The lower the value for the CTE, the less expansion that occurs over that temperature range.

	CTE (Linear, 20 C below and above T _g , μm/m*°C)
ELECTROJET 1	91.2, 225.7 (T _g 73.48C)
Competitive Resin A	63.87, 155.7 (T _g 42.31)

Table 5. Shows the respective CTE and T_g values for ELECTROJET 1 and Competitive Resin A after the same pre-anneal cycle was used.

Conclusion

Herein we have identified a next generation low viscosity dielectric resin called ELECTROJET 1 that is tailored to solder mask, rigid encapsulation and printed circuit based insulating application. The common themes of these materials include the need for high breakdown strength, low moisture uptake, very low dielectric constant and loss values as well as high surface and volume resistivity values. The ELECTROJET 1 resin featured a dielectric loss that was about half the Competitive Resin A value at 1 kHz and at high frequency. It had similar values for moisture uptake, T_g, shelf life and surface/volume resistivity values. The competitive resin did have a higher hardness value, which also reflected its tendency to crack when flexed. This is a significant limitation for flexible substrates like PET or polyimide, which are common in this space. These examples of new materials show how electronic properties can be optimized specific for an application by optimizing the chemistry of the resin. ELECTROJET 1 mentioned in this article is commercially available through Sartomer by request.

ⁱ Liu, Y, Erika Rebrosova, and Nandakumar Menon. Uv-led dielectric ink for printed electronics applications. WO2018136480A1 Published July 26, 2018.

ⁱⁱ Pfeiffenberger, N. T. Dielectric Performance for Electronic Applications using UV-Curable Chemistries. UV + EB Technology (2021).

ⁱⁱⁱ McKerricher, Garret et al. "Fully inkjet-printed microwave passive electronics." *Microsystems & nanoengineering* vol. 3 16075. 30 Jan. 2017, doi:10.1038/micronano.2016.75