

Development of a Photopolymer-Based Dielectric Nanocomposite for High Resolution Direct-Write Processes

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Abstract

A UV curable dielectric ink composition, which enables adaptable and high-resolution direct ink writing, is presented. The UV curable dielectric ink composition is designed using non-hazardous, low cost, commercially available ingredients. The ink manufacturing procedure was devised to require only fundamental lab equipment, without the need for complex reaction conditions or harmful processes. The UV dielectric ink composition was engineered to meet a range of direct ink writing application specific needs. These needs include a tailored rheology, cured film rigidity, dielectric performance, and adhesive ability. The versatility of this ink composition is demonstrated through the fabrication of dielectric bridges for printed coplanar waveguides, bare die chip integration, and interconnects between printed circuit board regions.

Key words

Additive Manufacturing, Dielectric Materials, Electronic Packaging, Material Preparation, Polymer Films

I. Introduction

Direct ink writing has demonstrated great potential in electronic packaging applications, including complex high frequency device assemblies. Current research in this field has shown how commercially available conductor inks, typically a silver or copper dispersion, can be printed with a high degree of precision to yield sophisticated designs and geometries with high resolution [1,2]. This approach offers a prototyping and package form factor that is not achievable with subtractive manufacturing approaches. To build on this form factor, multiple layers of material can be printed on top of one another, further increasing device complexity. A bottleneck, however, exists when it comes time to select a dielectric material for high resolution direct ink writing. The list of commercially available dielectric inks which can be printed with a direct write printer is limited [3]. Furthermore, there has yet to be a commercially available UV curable dielectric ink that is specifically designed for direct ink writing printed electronics applications, including the appropriate dielectric and mechanical properties and desired viscosity values. Instead, the dielectric inks that have been adopted by this field are inks repurposed from their intended applications [4].

In this work, the development of a photopolymer-based dielectric nanocomposite specifically engineered for high resolution direct ink writing processes is presented. The progression of an application specific formulation process is discussed in detail, and ink formulation modifications are presented in relation to specific application needs. The versatility of the formulated material is demonstrated through three separate electronic packaging applications: dielectric bridges for coplanar waveguides, bare die chip integration, and printed gaskets for interconnects.

The formulation process begins with a comparison of molar absorptivity values for a series of photoinitiators using UV-vis spectroscopy. Specifically, radical type I, type II, and cationic photoinitiators are tested for use in acrylate and epoxy photopolymer formulations [5,6]. Photoinitiator absorptivity is studied within the range that is applicable to common additive manufacturing exposure equipment, and a set of photoinitiators which effectively absorb within this range are selected for further formulation. Following photoinitiator selection, a series of acrylate and epoxy-based photopolymer mixtures are formulated using the selected photoinitiators. Adhesion values are used to compare photopolymer mixtures, with each mixture being tested on

Kapton polyimide and PEEK substrates. Standard ASTM cross hatch testing is used to evaluate adhesion strength. Once a monomer-initiator mixture with superior adhesion is selected, hexagonal boron nitride (BN) nanoparticles are added to the mixture. BN is a natural lubricant, enabling a homogenous mixture to be batched with minimal force. BN is also an opaque white powder, which increases film opacity and facilitates laser surface topology mapping downstream. Lastly the BN particles possess a high aspect ratio, which resulted in a highly thixotropic mixture when added to the photopolymer [7-10]. Thixotropic behaviour causes the viscosity of the mixture to decrease as shear is applied, then increase in viscosity as shear is removed resulting in high resolution printing. Finally, in the last stage of the formulation process, Dynamic Mechanical Analysis (DMA) is used to investigate the effect of crosslinker and BN additions on modulus. The area under the tan delta curve is used to judge the amount of energy released during relaxation. Because certain applications call for the direct ink writable dielectric to be used for printed interconnects, minimizing relaxations will ultimately increase interconnect durability.

II. Formulation

A. Initiator Selection

The first stage in formulating the UV curable direct ink write composition was to select a suitable initiator. The most frequently used UV exposure units in the additive manufacturing ecosystem rely on either a mercury halide bulb or LED arrays, radiating between 310-400nm. To determine which initiator would absorb most effectively within this range, molar absorptivity values were measured using UV-Vis. Radical type I and type II photoinitiators as well as cationic photoinitiators were tested.

The radical initiator absorptivity data, Figure 1, showed that both 2-methyl-4'-(methylthio)-2-morpholinopropiophenone and phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide absorb in the target UVA range. 2-Methyl-4'-(methylthio)-2-morpholinopropiophenone contains a tertiary amine moiety, which is known in the art to aid in oxygen consumption.[4] Minimizing the presence of oxygen results in a lower degree of peroxy radical formation, yielding a lower degree of surface cure inhibition. This tertiary amine can also be used as a synergist for a type II radical initiator, such as isopropylthioxanthone or benzophenone. Phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide displayed absorbance past 360nm. This is an attractive attribute for curing with common 365nm and 400nm LED arrays. Because of these advantages, it was decided to continue forward using both initiators.

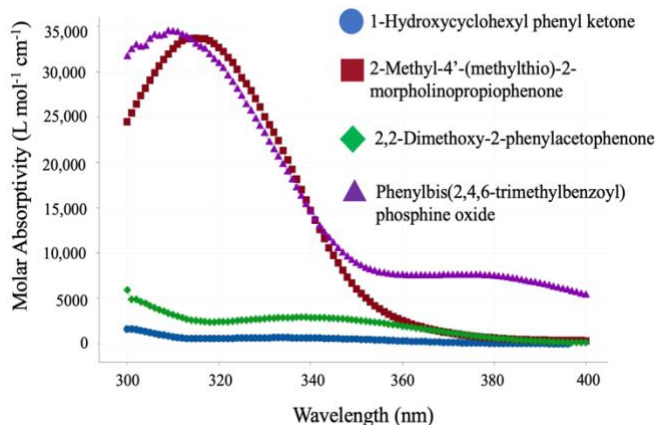


Figure 1: Comparison of radical photoinitiator molar absorptivity, demonstrating the elevated absorbance of 1-hydroxycyclohexyl phenyl ketone and 2-methyl-4'-(methylthio)-2-morpholinopropiophenone between 300nm and 400nm.

For the cationic initiator absorptivity, three initiators showed similar UVA absorbance, Figure 2. Comparing the three candidates, triarylsulfonium hexafluoroantimonate was not used because it contained the toxic heavy metal antimony. Diphenyliodonium hexafluorophosphate was eliminated due to the higher cost compared to triarylsulfonium hexafluorophosphate. Consequently, Triarylsulfonium hexafluorophosphate was chosen as the preferred cationic initiator.

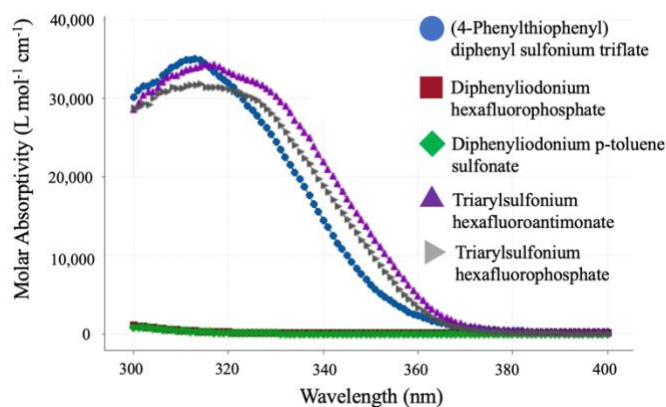


Figure 2: Comparison of cationic photoinitiator molar absorptivity demonstrating multiple initiators which absorb between 300nm and 400nm.

B. Monomer Selection

After a series of suitable initiators had been chosen, monomers were screened. The monomer screening process entailed curing various monomers onto PEEK and Kapton substrates. Specifically, a series of commercially available low viscosity monomer mixtures were tested. A blend of 0.5 w% 2-methyl-4'-(methylthio)-2-morpholinopropiophenone and 0.5w% phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide was used to initiate the acrylate monomer samples. For the epoxide monomer samples, a 2 w% 1:1 mixture of triarylsulfonium hexafluorophosphate and propylene carbonate was used.

The monomer and initiator mixtures were each batched as 5g samples in 20mL glass jars covered in aluminum foil. Small Teflon coated stir bars were used to continuously agitate samples for 1 hour at 350 rpms. After 1 hour, each mixture was applied to PEEK substrate using a 50 μ m doctor blade in a 2 x 2 cm area. Immediately after being applied to the PEEK substrate, each sample was UV cured at a distance 3.5 cm below the source for 60s.

Comparing all tested monomers, the acrylate-based bisphenol-A monomer displayed superior adhesion onto the PEEK substrate. This is the commercially available material CN131 sold by Sartomer.

C. Rheology Modification

Initial printing trials showed the monomer and initiator mixture could not be printed with high resolution. The low viscosity and Newtonian behaviour of the mixture resulted in unfavourable wetting and degradation of intended print geometry. To achieve high resolution printing, the ink required rheology modification. Submicron hexagonal BN was used as a rheology modifier for several reasons. BN is a natural lubricant, enabling a homogenous mixture to be batched with minimal force. BN also has a dielectric constant between 4 and 6. With the monomer dielectric constant at 3, adding various concentrations of BN would not significantly alter the dielectric constant of the collective composite, as validated by the dielectric constant and dielectric loss for 15 w% of BN shown in Figure 3. BN is also an opaque white powder. When added to the translucent monomer and photoinitiator mixture, the resulting mixture will become opaque. This is advantageous for downstream processing when the film will need to be mapped by a laser detection system. The final favourable characteristic of hexagonal BN is the morphology. The BN particle possesses a high aspect ratio. Mixing the low viscosity monomer-initiator mixture with the high aspect ratio BN nanoparticles resulted in a thixotropic mixture. The viscosity of the mixture decreased as shear was applied, due to the alignment of nanoparticles in the direction of shear, then as shear is removed the nanoparticle alignment was lost resulting in an increase in viscosity, as shown in Figure 4. The thixotropic effect

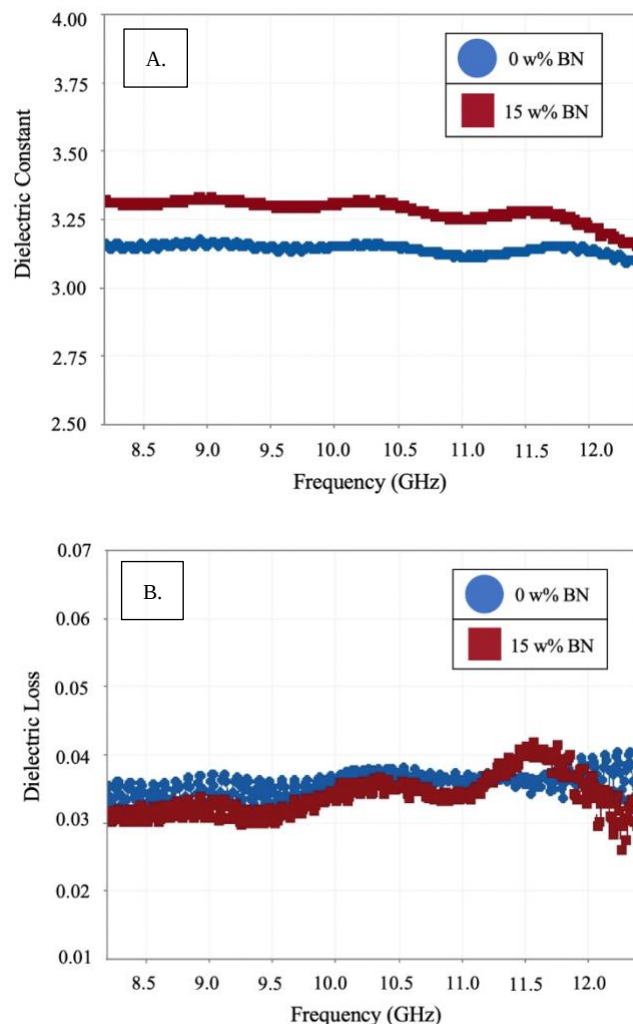


Figure 3: (A, B) The complex permittivity x-band characterization of the two inks using the WR-90 waveguide NRW technique.

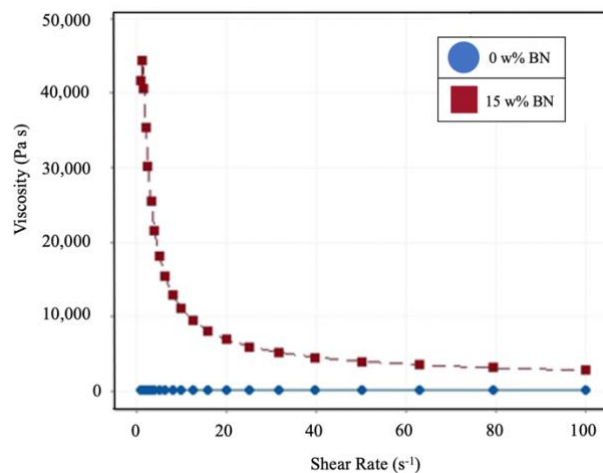


Figure 4: Rheology comparison before and after adding 15 w% BN

resulted in high resolution printing using syringe dispense systems, as shown by Figure 5.

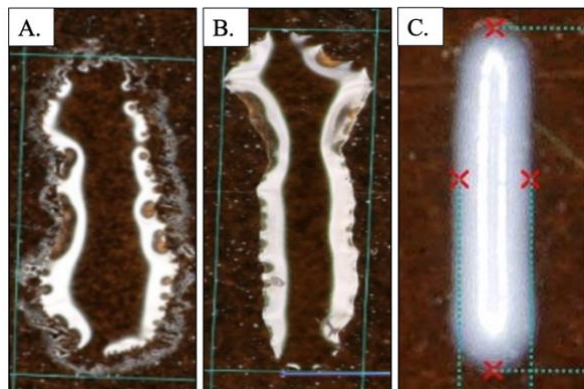


Figure 5: 1-millimeter-long syringe dispense patterns using (A) commercially available photopolymer NEA121, (B) the monomer initiator mixture with no BN addition, and (C) the monomer initiator mixture with 15 w% BN.

D. Modulus Modification

Certain applications require the direct ink writable dielectric to be used as a bridging layer for conductor interconnects. In these applications, the low modulus and thermal relaxations exhibited by the cured dielectric film cause the rigid printed conductor to crack during thermal treatment. To remedy this issue, DMA was used to investigate the effect of crosslinker and BN additions on the modulus. The formulation matrix for various BN Concentrations is shown in Figure 6. Specifically, the area under the tand delta curve was used to judge the amount of energy released during relaxation [5]. By minimizing this area, the silver would be less prone to cracking. The commercially available low viscosity triacrylate oligomer, CN133 sold by Sartomer, was used as the crosslinker.

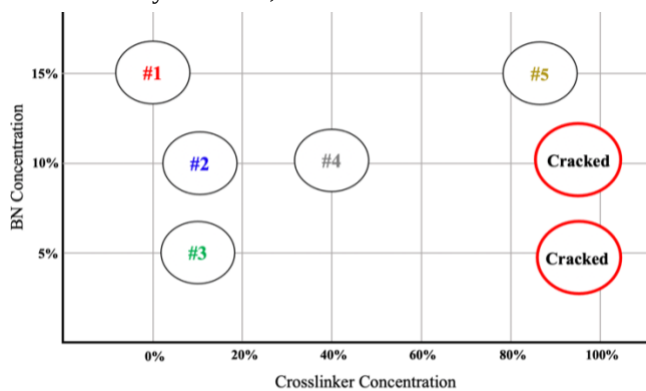


Figure 6: Formulation matrix representing the various BN and crosslinker concentration by w% used to make samples for dynamic mechanical testing.

The DMA data, shown in Figure 7 A. – C., demonstrated that by incorporating BN and crosslinker into the cured film matrix, the thermal relaxation could be minimized. The crosslinker addition proved to be an effective method for lowering the thermal relaxation. Additionally, because the crosslinker is offered as a low viscosity liquid, as opposed to BN which is a powder, adding a crosslinker is a simple and quick method to drastically alter modulus.

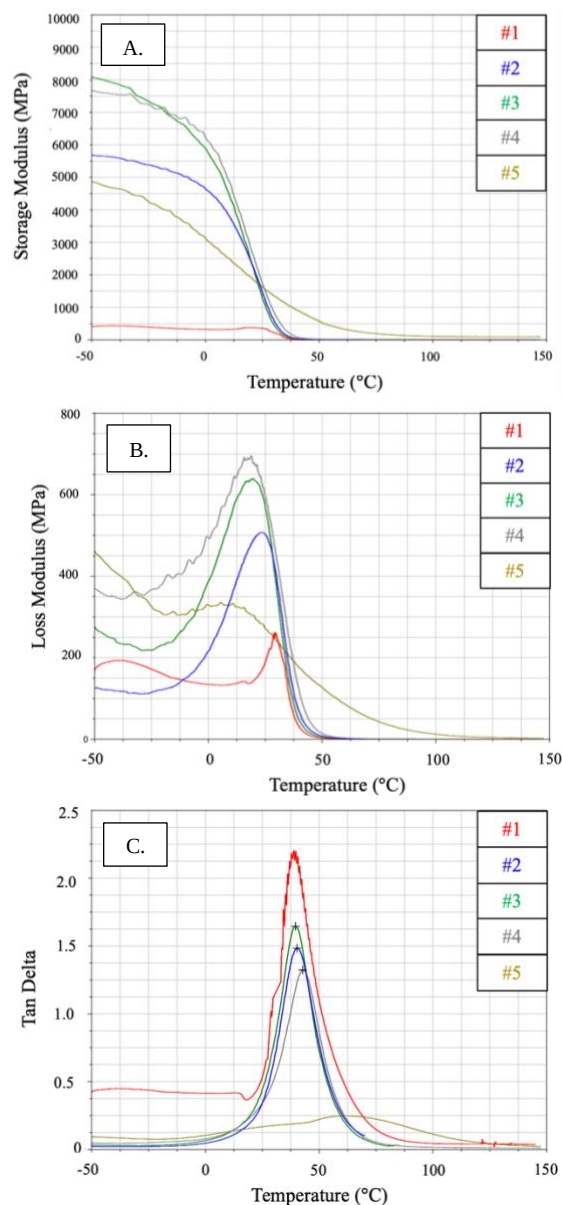


Figure 7: (A-C) Dynamic mechanical analysis measurements taken using a tension clamp at 10 Hz. Measurements were taken from -50°C to 150°C using a ramp of 3°C per minute.

III. Use Cases

A. Bare die chip integration

The first use case of the UV curable ink described by this work is for bare die chip integration. In this example, a cavity is milled out of copper clad board. Following this, a chip is fastened into the cavity. Once the chip has been secured, the dielectric is deposited into the cavity and cured. After curing, conductive traces are printed onto the chip from the surrounding board, using the dielectric as a bridging material. This process is demonstrated in Figure 8 A. – C.

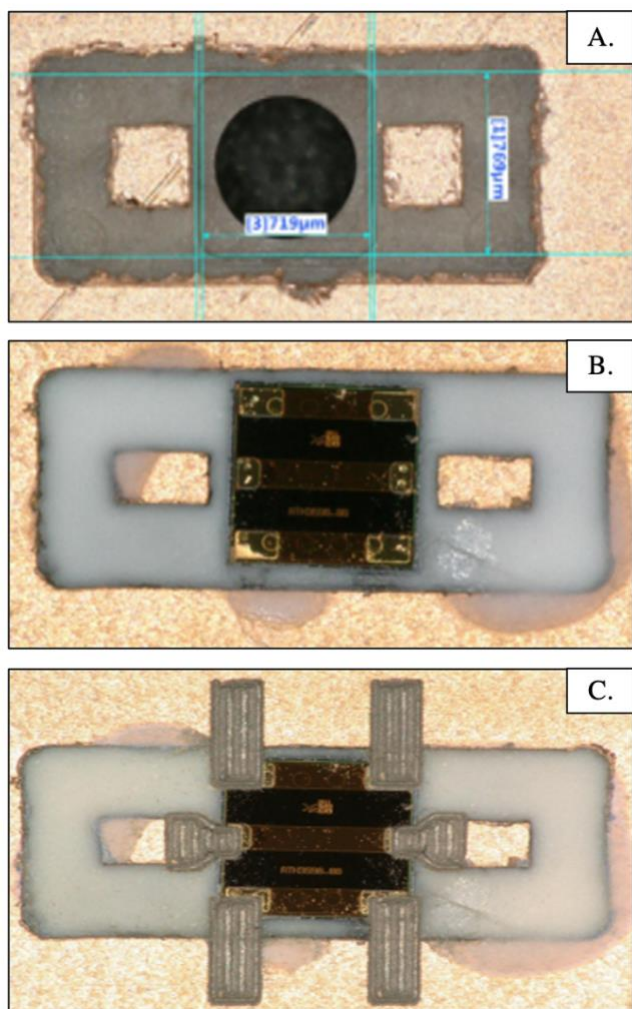


Figure 8: Example of how the dielectric composition was used for bare die chip integration. The dielectric composition was applied in (B.), so that conductive traces could be printed from the die onto the surrounding substrate in (C.).

B. Printed Conductor Interconnects

Similar to the bare die chip integration use case previously mentioned, the ink described by this work has

also been used as a gasket material to fill gaps between regions on a circuit board. In this use case, a structure is placed into a cavity on a circuit board, and then the dielectric ink described in this work is dispensed into the cavity between the structure and the surrounding board, as shown in Figure 9 A. – C. After the dielectric material is applied, conductive traces are printed over the cured dielectric material to make electrical connections between the structure and the surrounding board, as displayed by Figure 9 D.

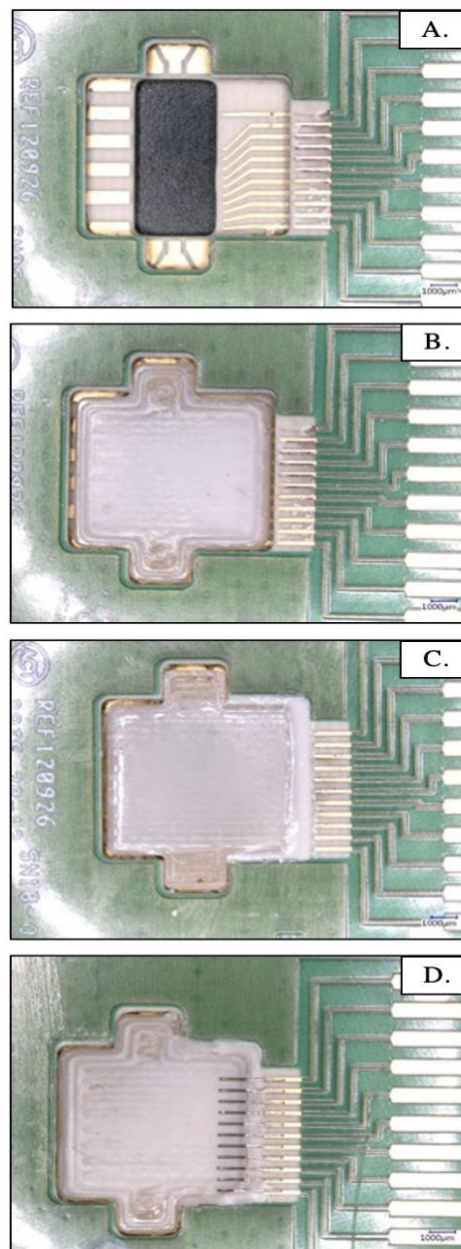


Figure 9: The workflow demonstrating when the dielectric composition is applied (C.) to facilitate the integration of discrete components and allow for printed conductor interconnects between dissimilar materials (D.).

III. Conclusion

This work presents an assessable? and versatile UV curable ink composition, specifically for direct ink write applications. This work demonstrates how the ink composition can be used in a multitude of advanced printed electronic applications, where ink performance and resolution are paramount.

Acknowledgments

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