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DEVELOPMENT OF A LOW THERMAL EXPANSION SLA RESIN FOR NICKEL PLATING APPLICATIONS

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Abstract

Stereolithography additive manufacturing is a method of producing parts by stacking layers of a photopolymer resin cured by exposure to UV light . This method of additive manufacturing gives great resolution, but often lacks the material properties of other techniques. One method to increase part performance is the addition of a thin nickel plating to increase strength, heat deflection, and chemical resistance. No solution has been proposed for using nickel-coated parts in harsh environments where the large difference in thermal expansion rates between the nickel plating and base resin cause internal stresses to form. The excellent chemical resistance of the nickel plating would also allow these parts to be used in high-temperature, oxygen-rich environments such as those presented in life support systems. Through the development of a high-performance nanocomposite SLA resin, we hope to achieve parts with good mechanical properties and a CTE similar to nickel.

Introduction

Stereolithography (SLA) 3D printing is a method of additive manufacturing that involves selectively curing thin layers of a photosensitive resin, usually by ultraviolet radiation. By curing one thin cross-section (usually around 50 microns) at a time, a complex part can be fabricated with features that could not be produced using traditional subtractive manufacturing. This technique results in accurate parts with good surface finish and can be achieved through relatively low-cost commercial off-the-shelf (COTS) machines. This method also allows for rapid iteration with the ability to quickly export and print a 3D model with minimal setup time. The drawback of SLA additive manufacturing is still widely constrained by material properties of the photopolymers. Research has been performed on improving the properties of these photopolymers through the addition of different plasticizers and chemistries. Even with these innovations, SLA parts cannot match the strength, chemical resistance, or heat deflection of metal or high-performance fused deposition modeling (FDM) parts. In this paper, we will be attempting to develop a low thermal expansion, high strength resin that can be nickel-plated for increased heat and chemical resistance.

Companies such as Formlabs have experimented with nickel-coated SLA parts, with success for low-temperature applications [1].

Figure 1: Nickel-plated SLA brackets by Formlabs [1]

Although large increases in strength and stiffness at room temperature were recorded, Formlabs recommends that the parts not exceed 150ºC, or be subjected to thermal cycling. If a resin could be formulated with a CTE matching the metal coating, nickel-coated SLA parts could find new use cases in high-temperature applications.

Literature review

Various research has been performed on improving the mechanical properties of SLA resins. Sano and Matsuzaki in 2018 [2] experimented with printing composite materials by adding in ground glass powder, short length fibers, and continuous fiber. The results showed large improvements in mechanical properties for every fiber type.

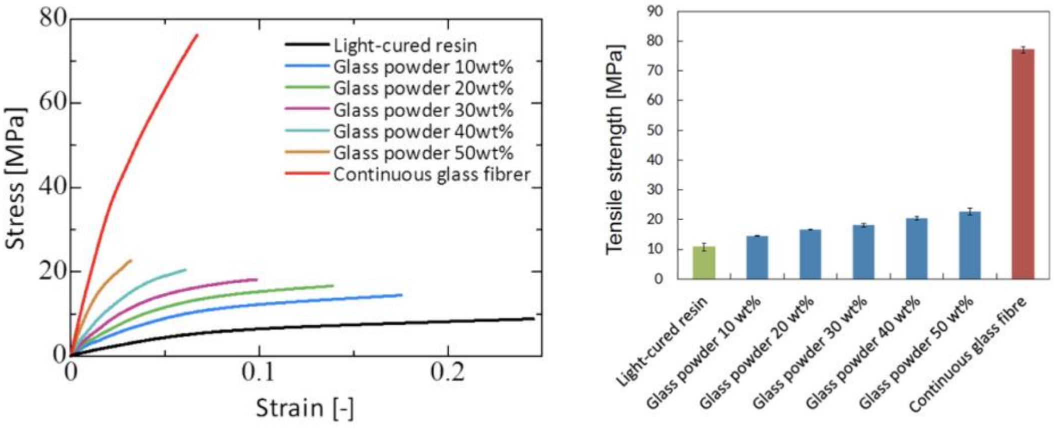

Figure 2: Mechanical properties of glass powder and fiber filled SLA prints [2]

Plasticizers or fillers can also be added to the resin to improve performance. Nanoparticles of silver, silica, copper, and other materials have been used in research to improve part strength, electrical, and thermal conductivity [3]. Very low and even negative coefficient of thermal expansions (CTE's) have been achieved in aligned multiwalled carbon nanotube thin-film composites [4]. However, there is a practical limit to the amount of filler you can add to a resin. In most cases, adding more than 10% by weight of filler can block ultraviolet light from reacting with the resin, causing print failures. Heavy particles such as copper and iron can also begin settling out of the resin and will result in uneven dispersion which can cause stress concentrations within the part and non-isotropic properties which are undesirable. Using nanoparticles of materials with low thermal expansion rates, the coefficient of thermal expansion (CTE) of the resin can be matched as that of the nickel. These nanoparticles will also have to be around the same density as the resin to facilitate good dispersion and reduce settling during printing. The main materials of interest are multiwalled carbon nanotubes (MWCNT's), silicone dioxide nanoparticles, and boron nitride nanoparticles. These additives were chosen for their low coefficient of thermal expansion (CTE) and high young's modulus which are important in reducing the composites overall thermal expansion rate. Carbon nanotubes with a mean diameter of 41 nanometers have been shown to have a negative CTE value between 0º and 100˚ C , roughly *-1* µm/m°C [5]. The goal is to reduce the CTE of the resin down to *13.3* µm/m°C as that of nickel's while using the least amount of filler possible.

K. Shirasu et al. / Composites: Part A 95 (2017) 152–160

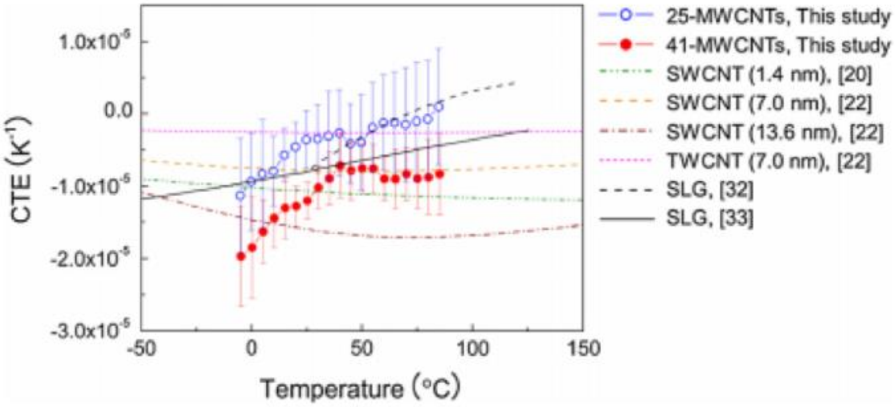

Figure 3: CTE (K^{-1}) comparison of carbon nanotubes [5]

Equipment

The printer chosen for experimentation is a mUVe3d LCD 2k pro for its open-source design and high output UV lamp. The UV LED array can output up to 82 watts of 405 nm UV light across its 5.5 inch 2k resolution LCD display.

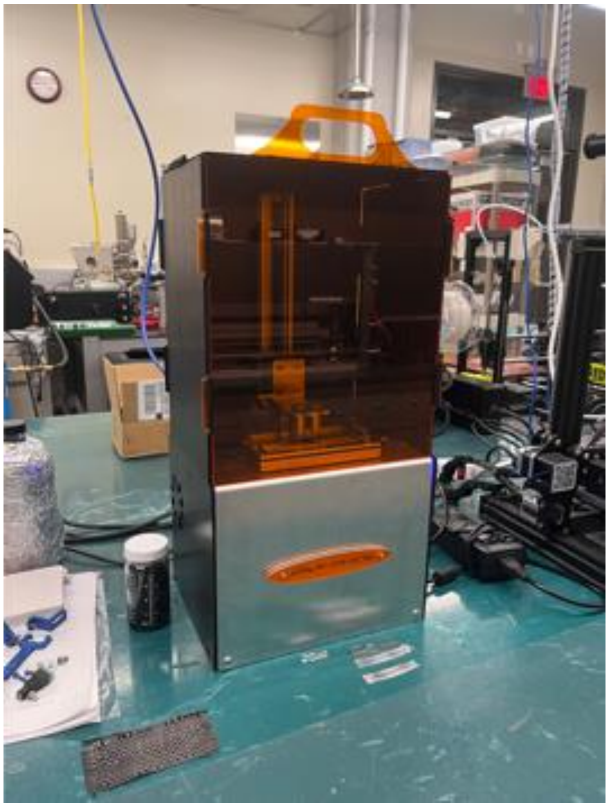

Figure 4: mUVe LCD 2k Pro printer

SLA resins for 3D printing are composed of three main constituents, an oligomer, monomer, and photoinitiator. Oligomers chosen for our formulation include CN154 epoxy methacrylate and Ebecryl 3700 BPA Epoxy resin. These epoxies were chosen for their high hardness and temperature resistance. Monomers, sometimes referred to as reactive diluents, are added to the mixture in order to reduce the viscosity down to a level where it can be easily poured into the resin vat. A low viscosity is also essential as the mixture must reflow under the print bed after every layer, poor flow in a resin can result in voids in the final print. Our reactive diluent is Trimethylolpropane triacrylate, a trifunctional acrylate ester monomer used for its fast cure response and high crosslinking capability. Finally, photoinitiator are used to sensitize the resin to UV light and start the polymerization process.

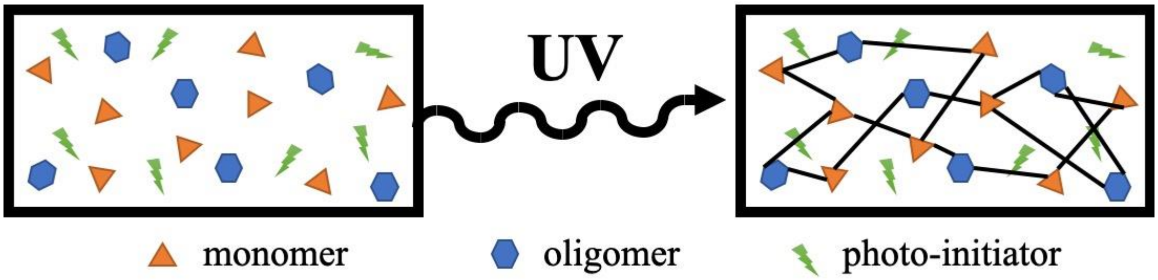

Figure 5: UV resin polymerization [6]

Table 1: Chemicals used in resin formulations

CHEMICAL NAME	**USE**	**SUPPLIER**
CN154 BPA EPOXY METHACRYLATE	Oligomer	Sartomer Americas
EBECRYL 3700 BPA EPOXY RESIN	Oligomer	Allnex
TRIMETHYLOLPROPANE TRIACRYLATE (TMPTA) ACRYLATE ESTER	Monomer / reactive diluent	Allnex
DIPHENYL(2,4,6-TRIMETHYLBENZOYL)PHOSPHINE OXIDE (TPO-L)	photoinitiator	Sigma-Aldrich
PHENYLBIS(2,4,6-TRIMETHYLBENZOYL)PHOSPHINE OXIDE (BAPO)	photoinitiator	Sigma-Aldrich
BYK-W 9010	Dispersing Agent	BYK

Nanoparticle additives include boron nitride, silicon dioxide, and multi-walled carbon nanotubes.

Table 2: Nanoparticle and average particle size

Nanoparticle	*Average Particle size*
Multi-Walled carbon nanotubes	30-50nm outer diameter
Boron Nitride	60-70nm
Silicon Dioxide	80nm

Incorporation of nanoparticles into the resin was achieved through sonication, a well understood technique for nanoparticle dispersion [7]. This is a method where a high frequency transducer is used to create pressure waves in the resin causing cavitation to occur, releasing large amounts of energy into the mixture and dispersing the clustered nanoparticles.

Experimentation

In order to get a baseline resin standard that we can compare to the nanocomposite formulations, a neat resin was created with both of the epoxies.

Table 3: Ebecryl based Neat resin formulation

Chemical	*Amount*
EBECRYL 3700 BPA epoxy resin	40% by weight (20g)
TMPTA	58% by weight (29g)
BAPO	2% by weight (1g)

To reduce the high viscosity of the epoxy resin and make incorporation easier, the Ebecryl resin was heated in a 70ºc water bath. It was then weighed and incorporated into the TMPTA and photoinitiator solution and mixed by hand for approximately 5 minutes. The mixture was then placed under a partial vacuum (-27 inHg) for degassing. Initial test prints yielded good results with great accuracy at a layer exposure time of 8 seconds. We did see some small defects from air entrapment in the mixture, possible due to either inadequate degassing, or air incorporation during the printing process.

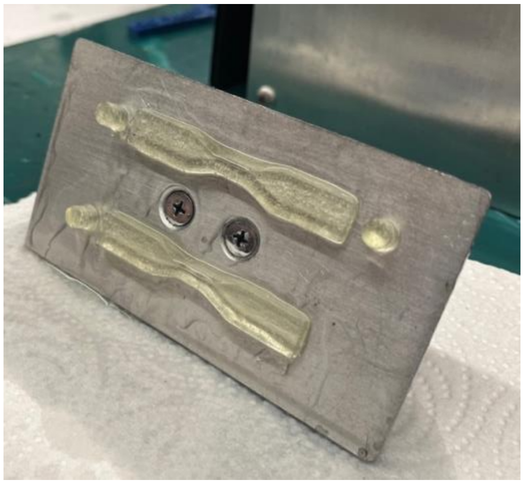

Figure 6: Ebecryl Neat resin test print

A baseline resin using CN154 epoxy was also tested for comparison, this formulation was processed identically to the Ebecryl mixture.

Table 4: CN154 based Neat resin formulation

Chemical	*Amount*
CN154 epoxy resin	40% by weight (20g)
TMPTA	58% by weight (29g)
BAPO	2% by weight (1g)

Table 5: Neat resin print parameters

Print settings	*Layer height (µm)*	*Cure time (Seconds)*	*Pause time before print (Seconds)*	*Bed lift speed (µm / Second)*
Burn-in layers (5)	50	10	1	200
Standard layers	50	8	0.15	200

Nanocomposite mixtures were then created by adding 1 gram of BYK-W 9010 wetting and dispersing agent to the neat resin mixtures along with the nanoparticles. Additionally, nanocomposite mixtures received 1.5 grams of photoinitiator compared to the 1 gram in the neat resin mixtures to ensure sufficient polymerization. For composite mixtures containing multi-walled carbon nanotubes (MWCNT's), an additional 0.5g of TPO-L initiator was incorporated into the resin. The mixtures were then stirred by hand for initial incorporation before being sonicated in in a cold water bath. After every 6 sonication cycles, the process was paused and the resin was hand mixed for approximately 30 seconds. This was done to ensure even heat dissipation and to prevent pockets of resin prematurely polymerizing from excess localized heat. After sonication, the composite resin mixture was degassed under vacuum.

Table 6: Sonication parameters

Number of sonication cycles	24
Cycle on time	10 seconds
Cycle off time	20 seconds
Power	40% (30 Watts)

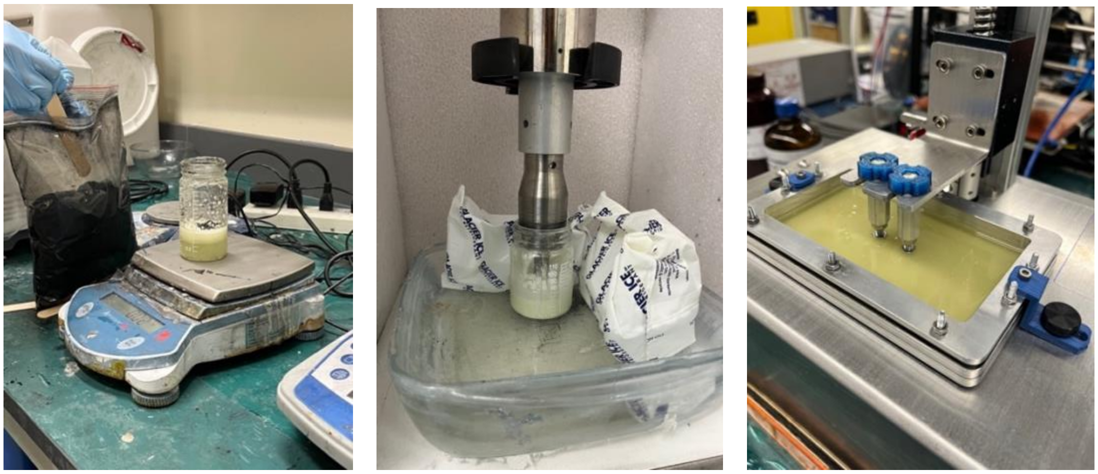

Figure 7: Incorporation, sonication, and printing of nanocomposites

Print parameters for the nanocomposites can be found below in tables 7, 8, and 9. Nanoparticle fillers block ultraviolet light from reacting with the resin matrix and thus require extended cure times versus the neat resin samples. Pause time was also extended slightly to account for the small increase in viscosity with the fillers.

Table 7: Print parameters for boron nitride nanocomposites

Print settings	*Layer height (µm)*	*Cure time (Seconds)*	*Pause time before print (Seconds)*	*Bed lift speed (µm / Second)*
Burn-in layers (5)	50	60	1	200
Standard layers	50	40	0.25	200

Table 8: Print parameters for silicon dioxide nanocomposites

Print settings	*Layer height (µ)*	*Cure time (Seconds)*	*Pause time before print (Seconds)*	*Bed lift speed (µm / Second)*
Burn-in layers (5)	50	35	1	200
Standard layers	50	30	0.25	200

Table 9: Print parameters for carbon nanotube composites

Print settings	*Layer height (μm)*	*Cure time (Seconds)*	*Pause time before print (Seconds)*	*Bed lift speed (μm / Second)*
Burn-in layers (5)	50	160	1	200
Standard layers	50	80	0.25	200

Both resins printed successfully, showing high detail and easily separating from the print bed. CN154 samples were noticeably more optically transparent coming off the printer than the Ebecryl samples. After 5 minutes of UV post cure, both resins became tinted yellow.

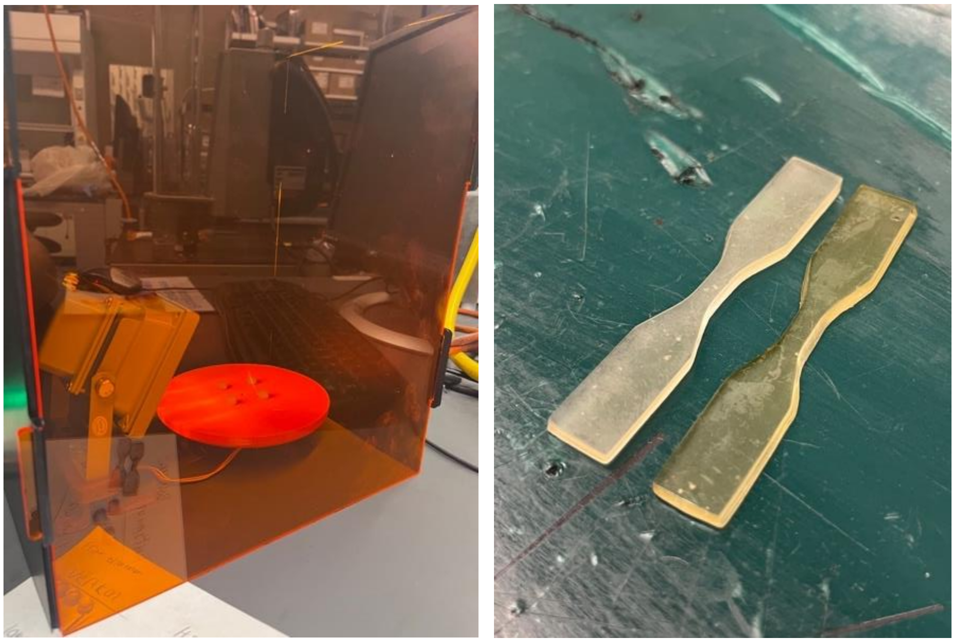

Figure 8: Post print cure, post cure yellowing

Prints containing boron nitride and carbon nanotubes showed large changes in the appearance of the sample. We also observed a small amount of flashing on the bottom of the carbon samples, this is likely from overexposing the initial burn-in layers, causing excess curing outside of the masked area. The boron test samples also grew slightly in all dimensions compared to the other fillers, we suspect this is from UV light reflecting off the white boron particles and causing sample expansion.

Figure 9: Boron nitride, carbon nanotube samples

Prints containing silicone dioxide looked very similar to the neat resin samples despite the nanoparticles having a bright white color, similar to the boron nitride before incorporation. This is possibly from the resin and sio2 having very similar refractive index's [8].

Figure 10: Sio2 sample on print bed

Overall, we demonstrated the ability to successfully print nanocomposite resin systems on a COTS SLA printer. Neat resin samples demonstrated very similar exposure times and processing methods to commercially available resins. Nanoparticle composites do require higher exposure times and extra processing steps such as sonication and vacuum degassing, but still demonstrated reliable printing.

Results and Discussion

Tensile testing was performed using ASTM D638 type IV dog bone samples at 1mm/minute on an MTS Exceed universal test system. The slower testing speed was chosen due to the brittle nature of the epoxy resin samples. With the samples being too small for use with an extensometer, sample strain was estimated as a function of crosshead movement. All samples were tested with the layer lines running parallel to the axis of measurement.


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Figure 11: Tensile testing setup

For a baseline standard, the neat resins created with CN154 and Ebecryl were compared to the commercial Stratasys “Digital ABS plus”.

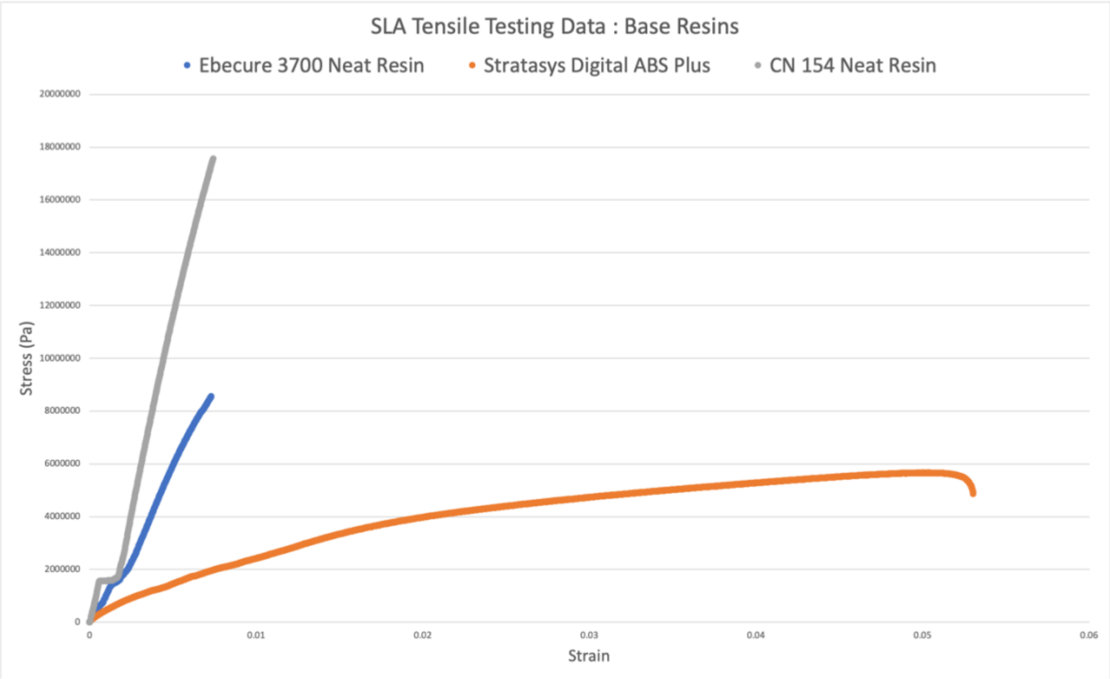

Figure 12: Tensile results of neat resins

Table 10: Neat resin tensile testing

Resin	*Ultimate tensile strength*	*Percent elongation*	*Youngs Modulus*
Stratasys Digital ABS Plus	5.68 Mpa	5.3%	93.3 ± 1.53 MPa
CN154	17.56 Mpa	0.74%	2557.7 ± 1.4 MPa
Ebecryl	8.55 Mpa	0.73%	1241.1± 0.4 MPa

As shown in figure 12, both of the epoxy resins have greater strength and stiffness compared to the commercial Stratasys “Digital ABS Plus” UV resin. CN154 also exhibited a much higher ultimate strength, breaking at 346 newtons compared to the 112 newtons for the commercial system. The combination of a high performance epoxy with the tri-functional monomer results in a stiff, but brittle part.

With the addition of nanoparticles to the CN154 based resin, silica and carbon nanotubes showed increased elongation, but reduced the ultimate strength. Samples containing 1gram of boron nitride showed both decreased strength and elongation.

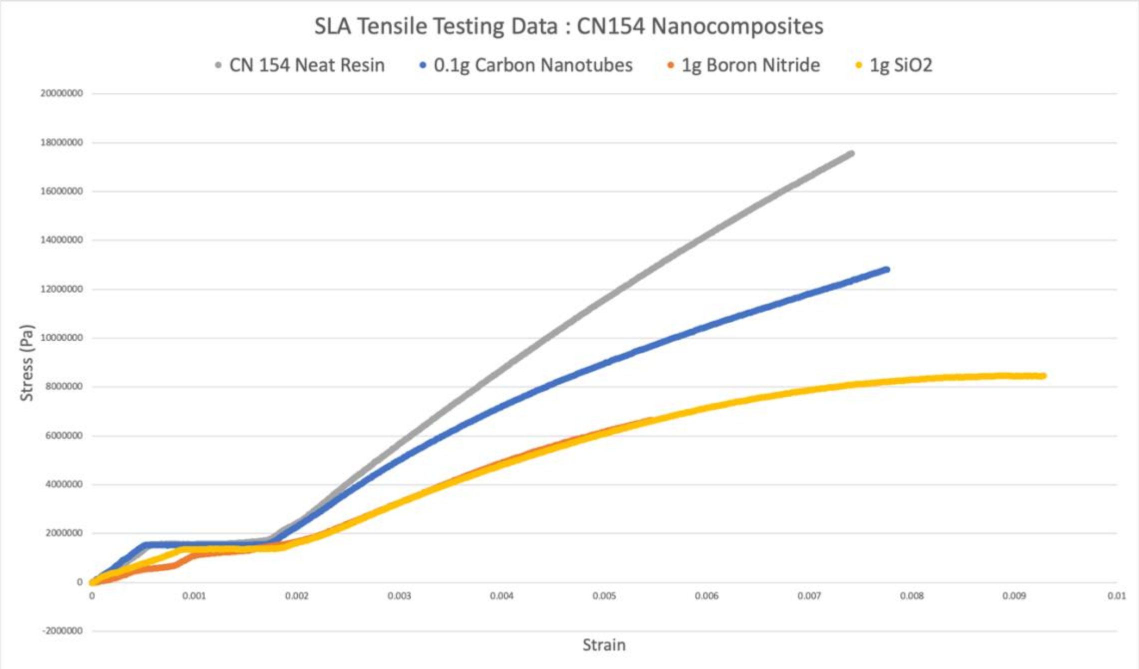

Figure 13: CN154 nanocomposite tensile testing

Table 11: CN154 nanocomposite tensile results

Resin	*Ultimate tensile strength*	*Percent elongation*	*Youngs Modulus*
CN154 Neat	17.56 MPa	0.74%	2557.7 ± 1.4 MPa
CN154 2%wt BN	6.65 MPa	0.54%	2432.9±1 MPa
CN154 2%wt Sio2	8.45 MPa	0.93%	1029.2±0.2 MPa
CN154 0.2%wt MWCNT	12.81 MPa	0.77%	1763.1±0.3 MPa

We believe the slight decrease in performance is due to poor distribution of the boron and carbon in the resin. Over the long print times required, it was observed that clumps of carbon nanoparticles began to conglomerate on the print bed. Poor distribution could cause stress concentrations within the test samples, thus resulting in a decrease in mechanical properties. We also believe that we had poor adhesion between the nanoparticles and resin because samples identically processed using the Ebecryl epoxy resin showed large gains in mechanical properties with the addition of carbon nanotubes.

Figure 14: Carbon nanotube conglomeration on print bed

Ebecryl based silica and MWCNT nanocomposites showed large strength and elongation gains over the neat resin. Samples containing 1gram of boron nitride exhibited almost identical results to the neat resin samples.

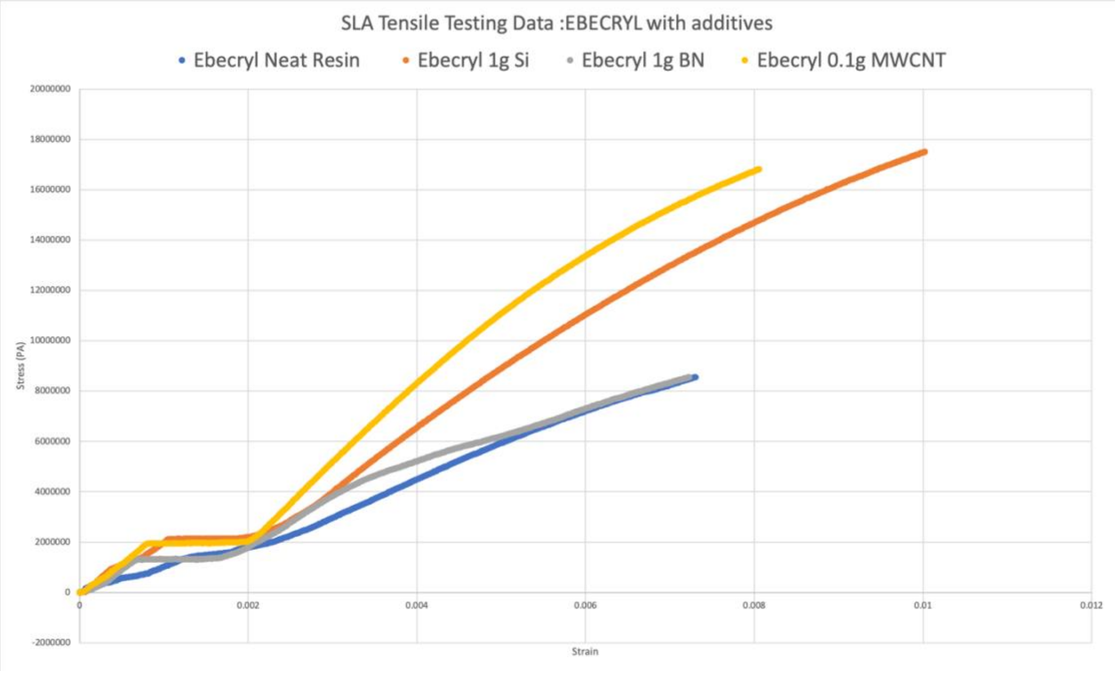

Figure 15: Ebecryl Nanocomposites tensile results

Table 12: Ebecryl nanocomposite tensile results

Resin	*Ultimate tensile strength*	*Percent elongation*	*Youngs Modulus*
Ebecryl Neat	8.55 MPa	0.73%	1241.1± 0.4 MPa
Ebecryl 2%wt BN	8.55 Mpa	0.72%	1231.8±0.9 MPa
Ebecryl 2%wt Si	16.81 Mpa	1.0%	1895.9±0.9 MPa
Ebecryl 0.2%wt MWCNT	17.47 Mpa	0.81%	2319±1.1 MPa

Thermal characterization was performed on a Waters Corporation TA Instruments TMA Q400 using a standard atmosphere from ambient temperature to 150˚ Celsius. CTE was measured by performing an alpha fit operation to find the slope of sample expansion vs temperature in TA Universal Analysis from 60˚ to 140˚C.

Figure 16: CTE sample puck loaded into TMA Q400

Baseline resin samples using Stratasys "DigitalABSPlus" UV resin were printed at a 50-micron layer height and 8 second cure time per layer. TMA measurements showed an average CTE of 203.2 µm/m(m.ºC) from 60-140 ºC in a standard atmosphere for samples with the layer lines running perpendicular to the axis of measurement. Samples with the layer lines parallel to the axis of measurement recorded a 1.5% difference in thermal expansion at 206 µm/m(m.ºC). From this small difference, we can conclude that the unmodified resin samples are thermally isotropic. All CTE samples tested were printed as 5x6mm cylindrical pucks with the layers running perpendicular to the axis of measurement. The epoxy-based resins also showed increased performance in CTE analysis. At 140˚C we did observe sample cracking with the CN154 resin from thermal stress.

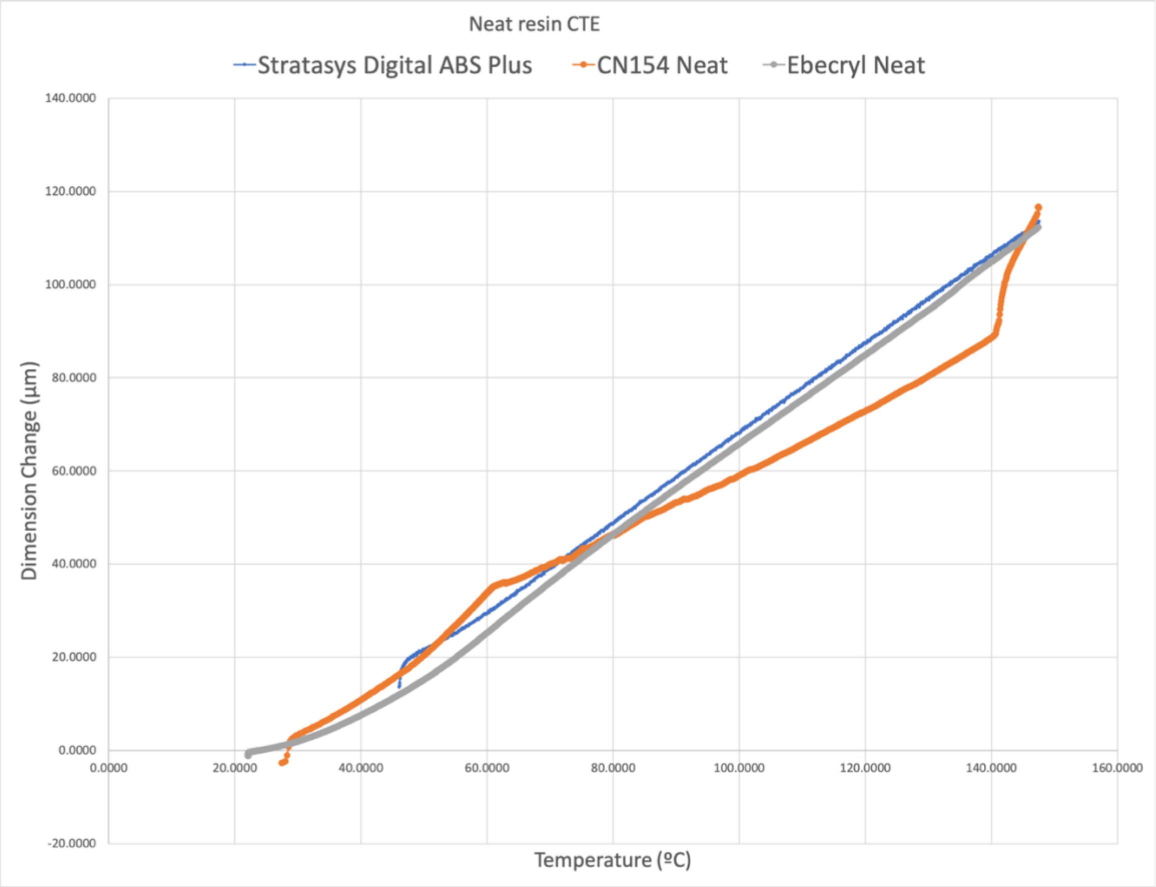

Figure 17: Neat resin CTE results

Table 13: Neat resin CTE results

Resin	*CTE*	*Percent change*
Stratasys Digital ABS Plus	203.2 µm/m(m.ºC)	Baseline measurement
Ebecryl	164.9 µm/m(m.ºC)	18.84% reduction
CN154	126.4 µm/m(m.ºC)	37.79% reduction

CN154 nanocomposites eliminated the stress fracture seen in the neat resin sample. Both the carbon nanotubes and boron nitride samples had an increased CTE compared to the neat resin. With 1 gram of silica, a 5.69% reduction in CTE was measured.

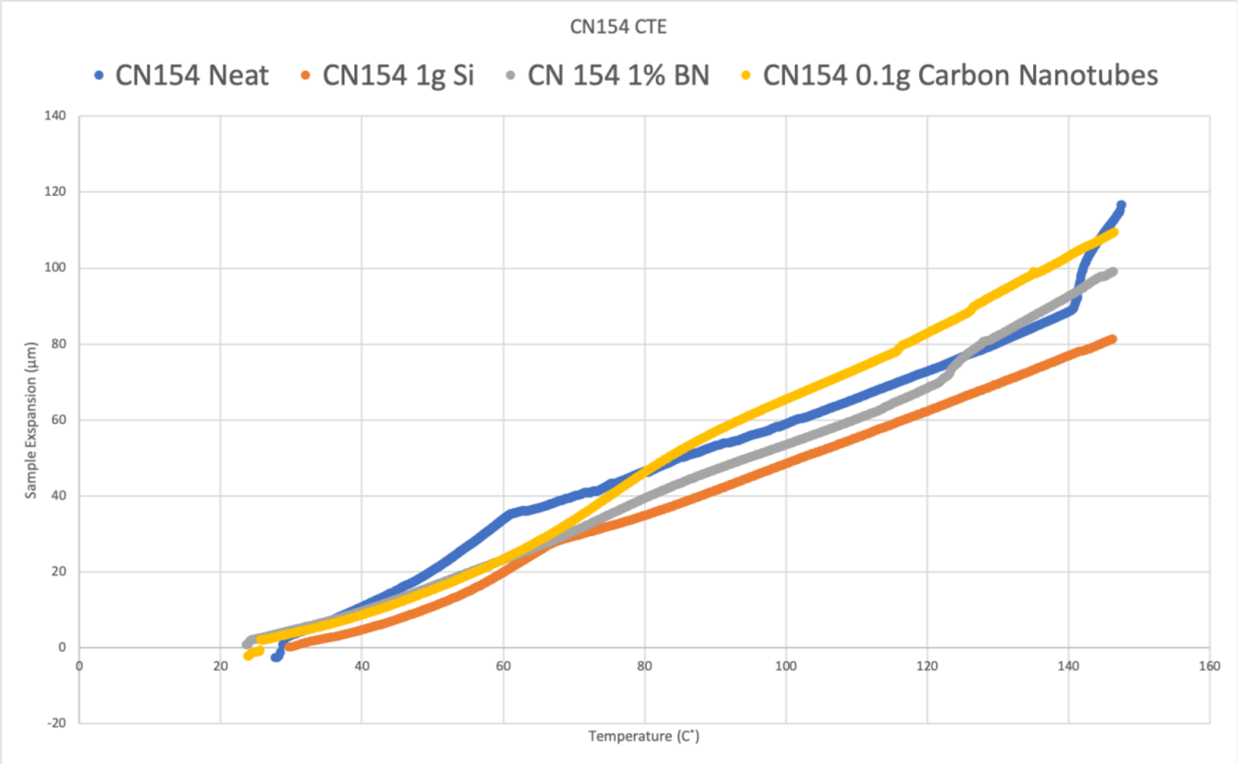

Figure 18: CN154 composite CTE results

Table 14: CN154 composite CTE results

Resin	*CTE*	*Percent change*
CN154 Neat resin	126.4 µm/m(m.ºC)	Baseline measurement
0.2% wt MWCNT	148.2 µm/m(m.ºC)	17.24% increase
2% wt BN	158.6 µm/m(m.ºC)	25.47% increase
2% wt SiO2	119.2 µm/m(m.ºC)	5.69% reduction

CTE results for the Ebecryl based samples showed similar trends to the CN154 samples. Both boron nitride and MWCNT resulted in increased thermal expansion while silica reduced the composite CTE by 7.82%. We observed sample failure at 110ºC in the MWCNT composite with large cracks forming on the surface. To account for the large failure, CTE was measured from 40-100ºC on the carbon sample only.

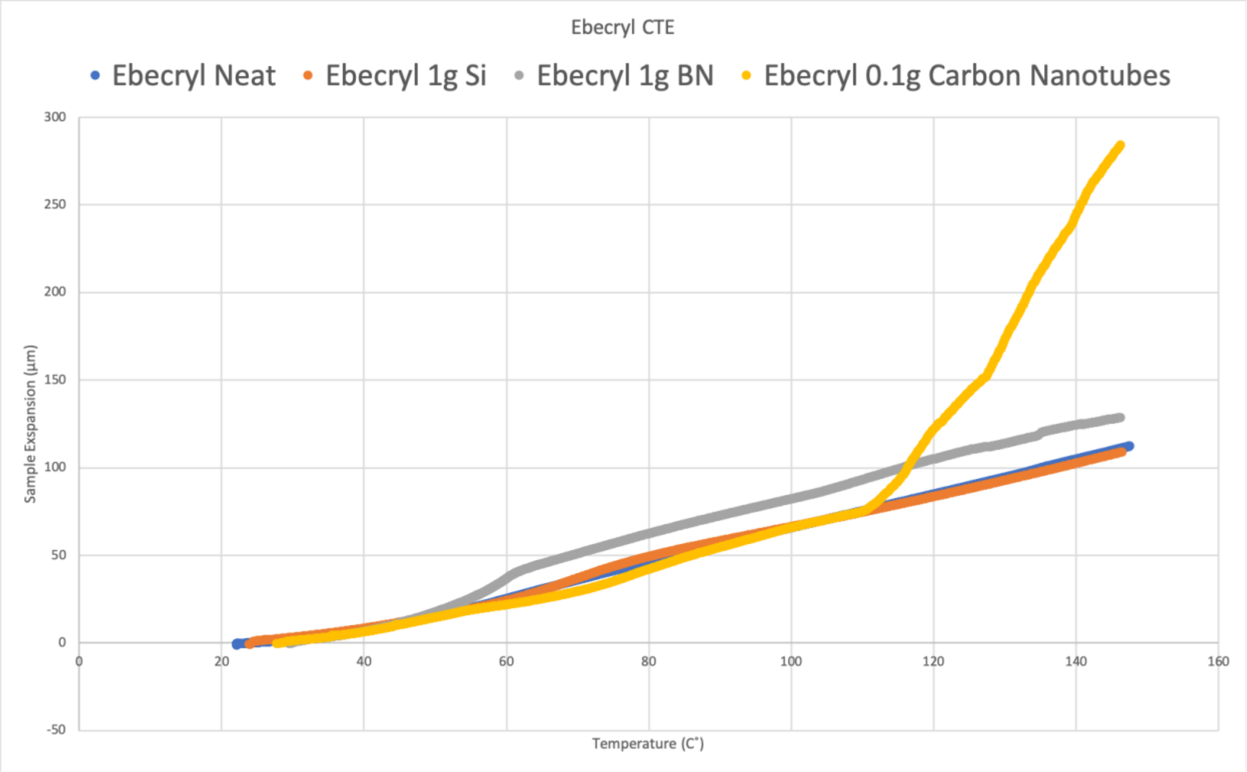

Figure 19: Ebecryl composite CTE results

Table 15: Ebecryl CTE results (*Indicates changed measurement parameters)

Resin	*CTE*	*Percent change*
Ebecryl Neat resin	164.9 µm/m(m.ºC)	Baseline measurement
0.2 % wt MWCNT	174.5 µm/m(m.ºC)*	5.82% increase*
2% wt BN	182.5 µm/m(m.ºC)	10.67% increase
2% wt SiO2	152.0 µm/m(m.ºC)	7.82% reduction

Comparison of all CTE measurements can be found below in table 16. The best performing overall resin system was determined to be CN154 in combination with silicon dioxide nanoparticles.

Table 16: Comparison of all CTE results, compared to nickel

Resin	*CTE*	*Percent change*
Stratasys Digital ABS Plus	203.2 µm/m(m.ºC)	Baseline measurement
Ebecryl Neat	164.9 µm/m(m.ºC)	18.84% reduction
CN154 Neat	126.4 µm/m(m.ºC)	37.79% reduction
Ebecryl 0.2 % wt MWCNT	174.5 µm/m(m.ºC)*	14.12% reduction*
Ebecryl 2% wt BN	182.5 µm/m(m.ºC)	10.18% reduction
Ebecryl 2% wt SiO2	152.0 µm/m(m.ºC)	25.19% reduction
CN154 0.2% wt MWCNT	148.2 µm/m(m.ºC)	27% reduction
CN154 2% wt BN	158.6 µm/m(m.ºC)	21.94% reduction
CN154 2% wt SiO2	119.2 µm/m(m.ºC)	41.34% reduction
Nickel metal	13.3 µm/m(m.ºC)	93.45% reduction

Defects can be observed from the following prints of Carbon and Boron Nitride nanotubes. This is due to the air bubbles that have been occurring during the mixing process of both mixtures of resins. After a direct comparison of both surfaces of each print we notice that there are significantly more defects in the MWCNT prints compared to the Boron Nitride prints. As carbon is an effective absorber of UV light [9], we concluded that the additional defects were caused from incomplete polymerization during the printing process.

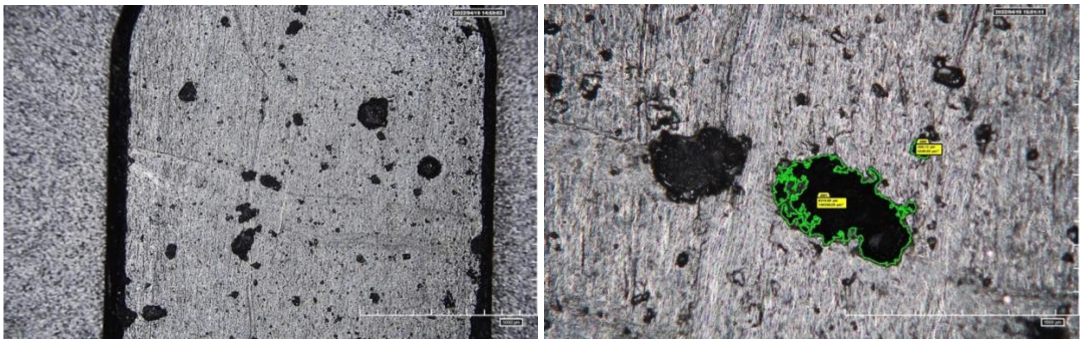

Figure 20: Optical microscope images of MWCNT prints and its surface defects

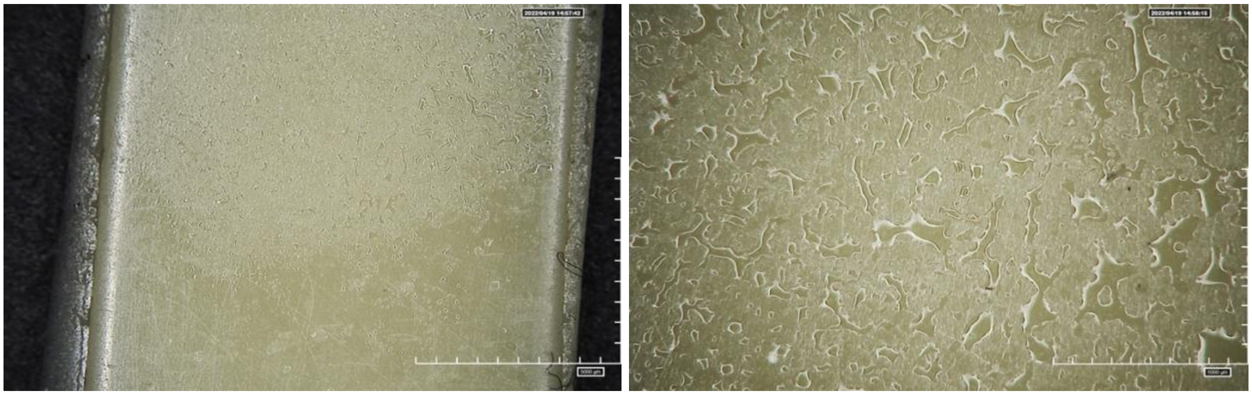

Figure 21: Optical microscope images of Boron Nitride prints and its surface defects

Conclusion

This research demonstrated the ability to modify the mechanical and thermal properties of SLA resin through the addition of nanoparticles. For CTE reduction, silica was identified as the best performing filler, reducing thermal expansion in both epoxy resin formulations. Tensile performance was also improved in the Ebecryl formulation and increased elongation was observed in the CN154 resin with the addition of silica. Sio2 is a very popular additive in epoxy as it demonstrates strong adhesion to the resin matrix as long as good distribution is achieved. This great matrix adhesion explains the increased thermal characteristics in both the Ebecryl and CN154 samples. Multi-walled carbon nanotubes showed great improvements in mechanical testing for the Ebecryl based resin, but did not deliver the same benefits in the CN154 composite. As both mixtures were processed identically, we believe this difference is due to the increased wetting and bonding between the nanoparticles and Ebecryl resin matrix. Even with the addition of BYK-W 9010 wetting and dispersing agent, the CN154 resin failed to properly bond with the nanotubes, resulting in decreased performance. Carbon nanotubes have also been shown to increase the thermal conductance of composite systems [10], a possible explanation for the increase in CTE for both resin systems. This would also explain why we saw sample failures and cracking occur during the thermal testing of carbon samples. Boron nitride nanoparticles failed to increase mechanical or thermal performance in either resin matrix. This probably due to a couple of factors, ceramics such as boron nitride have been shown to decrease cure depth substantially in SLA resins [11]. Decreased cure depth could cause insufficient polymerization during the print, resulting in weaker parts. We could also be experiencing the same wetting problem seen with the carbon nanotubes, as our wetting agent is optimized for carbon fillers and might not be effective in wetting and dispersing ceramics. Boron nitride is also known for being difficult to properly disperse [12]. Poor dispersion of the boron could be from the limited power output of our sonication machine, or could be occurring during the printing process as the low viscosity resin allows the nanoparticles to conglomerate and settle out during the long print times. In total, a combination of these factors could be the cause of the boron nitride being an ineffective filler for SLA additive manufacturing.

References

1. Formlabs, *Strength from Metal: Stratagies and use cases for Electroplating SLA Parts.* 2021.
2. Sano, Y., et al., *3D printing of discontinuous and continuous fibre composites using stereolithography.* Additive Manufacturing, 2018. **24**: p. 521-527.
3. Hu, G., et al., *Nanofillers can be used to enhance the thermal conductivity of commercially available SLA resins.* Procedia Manufacturing, 2019. **38**: p. 1236-1243.
4. Shirasu, K., et al., *Negative axial thermal expansion coefficient of carbon nanotubes: Experimental determination based on measurements of coefficient of thermal expansion for aligned carbon nanotube reinforced epoxy composites.* Carbon, 2015. **95**: p. 904-909.
5. Shirasu, K., et al., *Potential use of CNTs for production of zero thermal expansion coefficient composite materials: An experimental evaluation of axial thermal expansion coefficient of CNTs using a combination of thermal expansion and uniaxial tensile tests.* Composites Part A: Applied Science and Manufacturing, 2017. **95**: p. 152-160.
6. Hanton, J. *PHOTO-CURABLE RESINS FOR SLA (STEREOLITHOGRAPHY) 3D PRINTING:*. 2020 [cited 2022; Available from: http://www.robots.co.uk/?p=501.
7. Huang, Y.Y. and E.M. Terentjev, *Dispersion of Carbon Nanotubes: Mixing, Sonication, Stabilization, and Composite Properties.* Polymers, 2012. **4**(1): p. 275-295.
8. Khlebtsov, B.N., V.A. Khanadeev, and N.G. Khlebtsov, *Determination of the Size, Concentration, and Refractive Index of Silica Nanoparticles from Turbidity Spectra.* Langmuir, 2008. **24**(16): p. 8964-8970.
9. Xiao, J., et al., *Carbon nanotubes as light absorbers in digital light processing three-dimensional printing of SiCN ceramics from preceramic polysilazane.* Ceramics International, 2020. **46**(11, Part B): p. 19393-19400.
10. Han, Z. and A. Fina, *Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review.* Progress in Polymer Science, 2011. **36**(7): p. 914-944.
11. Fei, G., et al., *Scattering Model for Composite Stereolithography to Enable Resin–Filler Selection and Cure Depth Control.* ACS Applied Polymer Materials, 2021. **3**(12): p. 6705-6712.
12. Jiang, H., et al., *Boron Nitride Nanosheet Dispersion at High Concentrations.* ACS Appl Mater Interfaces, 2021. **13**(37): p. 44751-44759.