Investigate Methods to Increase the Usefulness of Stereolithography 3D Printed Objects by Adding Carbon Nanotubes to Photo-Curable Resins

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This paper aims to inform the reader about the aspects of compositing carbon nanotubes in photo curable resin that is commonly used in stereolithography 3D printers. The focus is to increase the strength of the resin to allow for a greater range of objects to be printed with SLA printers. The paper will look at the different types of carbon nanotubes that can be used, what weight percent of nanotubes in resin will most likely work best in a printing environment based on surface hardness and cure time, and comparative destructive testing. It was shown with a small sample size that the carbon nanotubes composite had lower strength but greater toughness over pure neat resin.

1. Introduction

There has been an increase in popularity of 3D printing in recent years. 3D printing may also be poised to become a disruptive technology in the near future according to 3dprinter.net.

3D printing is the creation of real world objects (at this time, usually made from some sort of resin, ceramic or metal) by a computer-controlled process similar to that of a 2D document printer. 3D printers are capable of producing arbitrary shapes without any sort of mold or special model-dependent tooling. This is accomplished by printing material in many successive "2D" layers fused together to produce a 3D shape.

3D printing can be done in a variety of ways and using a variety of materials. Stereolithography 3D printing can produce high resolution but generally weaker, brittle objects. By adding small amounts of CNT from .1-5.0 wt. (%) to resin, it has been shown to improve the mechanical properties. With the addition of multiwalled carbon nanotubes a reported 35% increase in Young's Modulus has been viewed with .5 wt. (%) MWCNT [5]. This project proposes to explore ways to mitigate these negative qualities by compositing SLA resin such as WaterShed™ 11120 with carbon nanotubes. By expanding the range of applications that SLA 3D printing is suitable for, technology can become even more versatile than it already is.

By adding .25% by weight coiled carbon nanotubes to WaterShed™ 11120 resin, it was viewed to have a toughness increase of 11.4% and a lower max tensile strength over pure WaterShed™ resin. This may be desirable for some printed objects where a greater overall toughness is needed but lower peak strength.

2. Research Methods

2.1. Evaluation of Carbon Nanotubes for Use in UV-Resin

Composites containing isotropic oriented nanotubes possess lower mechanical properties than do composites with aligned nanotubes. Also to increase the strength of CNT and the polymer matrix, the bond between the surface of the CNT and polymer should be maximized [1].

Single walled Nano-tubes (SWNT) have a high Young Modulus of around 1TPa. To fully exploit the properties SWNT, they should be homogeneously dispersed and aligned within a polymer matrix. By functionalizing the carbon nanotubes, it has been shown to produce direct bonding between the nanotubes and the polymer. It has shown to produce high dispersion of nanotubes with sonication [1].

Coiled carbon Nano-tubes have a high young modulus of around .7TPa. This is comparable to the approximately 1TPa of straight single walled CNT. The configuration of coiled CNT surface should enhance the bonding strength between the CNT and the polymer by means of mechanical interlocking. This may create better load transfer between the polymer and CNT in comparison to straight CNTs. Single walled CNT have to consider the way they are functionalized and dispersed in the polymer more than alternatives such as coiled CNT because they do not have any means for mechanical interlocking with the polymer. Multi-walled CNT even with properly functionalized outer wall will have the outer wall of the nanotubes separate from the inner layers as seen in the polymer after a tensile test [3].

Looking at the information presented. Coiled carbon Nano-tubes was chosen for use in the photopolymer because of the ease of interlocking the CNT with the polymer without having to do additional steps such as functionalizing the CNT. A way to alignment of the nanotubes within the composite would be ideal, with the constraint of time and money this will not be looked into. Coiled nanotubes shape is an ideal geometry for use in composites. The coil shape will allow for the resin to flow between the CNT coils and interlock it with the resin and allow for better load transfer. The nanotubes are spring-like, this can increase the fracture toughness of a polymer based nano-composite [3].

Coiled multi-walled carbon nanotubes were purchased from nanoamor.com [6].

Table 1. Properties of Coiled Carbon Nano-tubes from nanoamor.com [6], [3]

Purity	>60%
Outside Diameter	100-200 nm
Length	1-10 um
SSA	>50 m^2/g
Density at 20°C	~2.1 g/cm^3
Tensile	~.7 TPa

2.2. Mixing Methods

Tip-Sonication mixing is the process where a transducer with a high-pressure sound field that will cause voids in the resin. The voids implode with a localized energy release. This causes high-energy particle collisions that can cause particle surface damage. Using this method it is generally advised to pre-disperse the CNTs with a low viscosity liquid before mixing with a high viscosity resin. There is then the problem of removing the solvent and may weekend the resin matrix. There is also bath sonication where the energy distribution amount the resin is uniform, but provides less energy for distributing CNTs. For low or medium viscosity systems a flow cell may be an effective method for dispersion of CNT since the flow is directed through a high intensity field at the tip of the unit [2].

The density of the resin WaterShed™ 11120 to be used in the experiment is 1.12 g/cm^3 and a viscosity at 30 degree Celsius is 260 cps. The low viscosity liquid makes dispersion of the CNT easier than a higher viscosity fluid. It was then chosen to use traditional shear mixing for pre-dispersion and bath sonication for the full dispersion.

2.3. Initial Testing

A common UV black light from Menards home improvement store of 2' length was used for curing the test samples to determine the best weight percent of coiled-CNT's. Samples with 0, .25, .5, .75, 1 wt. (%) were used in the UV resin for curing. The samples were produced with 10 grams of resin and the weight percent of CNT. They were mixed for 5 minutes using a small hobby paint mixer. The purpose of the test was to determine what concentration of CNT could be used without affecting the cure time of the resin substantially. The samples were approximately 2mL droplet size place onto HDPE and a Distance of 1.5inch from the UV tube. The samples were then allowed to cure until the control sample CNT is viewed to be completely cured. The samples were then evaluated by the standard test method for film hardness by pencil test ASTM D3363 as suggested by ASTM D3732 Standard Practice for Reporting Cure Times of Ultraviolet-Cured Coatings. The samples were evaluated between 6B and 6H with Derwent Graphic Pencils. The different pencil grades are achieved by adding various amounts of graphite to clay. "H" denotes hardness and "B" denotes blackness. The more graphite that is added the softer the pencil softness will be. ASTM D3363 surface hardness test procedure is to prepare the pencil tip as defined by the standard and score the surface of the film at a 45˚ angle. Starting with the hardest pencil lead of 6H and working down to the softest lead of 6B until marking of the surface is not viewed.

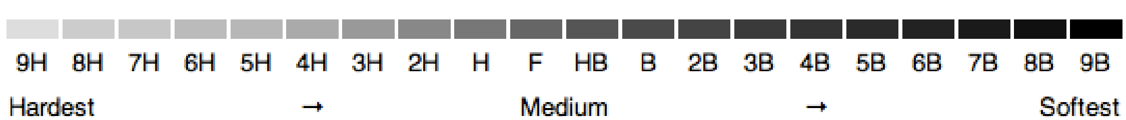

Figure 1. Pencil graphite hardness scale [7]

Table 2. Film hardness after only shear mixing

5 Min Shear Mixing	
Sample Mixture	Surface Hardness
Watershed™	HB
.25% w.t.	B
.50% w.t.	2B
.75% w.t.	3B
1.0% w.t.	3B

The samples of uncured resin remaining were put into a Branson 2510-DTH ultrasonic cleaner or bath-sonicator to further disperse the CNT. The samples were put in for 15 minutes each. Below are the Results of the second test with additional CNT dispersion.

Table 3. Film hardness after shear and ultrasonic mixing

5Min Shear + 15 Ultrasonic Mixing	
Sample Mixture	Surface Hardness
Watershed™	HB
.25% w.t.	B
.50% w.t.	2B
.75% w.t.	3B
1.0% w.t.	3B

It was shown that after bath sonication, the coiled carbon nanotubes retained same surface hardness. From visual inspection under a microscope, it was shown that the ultrasonic mixed film surface had increased the homogeneous dispersion of the carbon nanotubes. Fewer agglomerates were viewed on the surface of the film and over all dispersion was viewed to be improved.

Based off the data it was chosen that .25% by w.t. CNT was best for continuation of testing because of the most minimal surface hardness change tested in comparison to the pure WaterShed™ resin.

2.4. Mixture for Tensile Testing

50mL of Watershed 1120 and .125 gram CNT mixed for 5 minutes using hobby paint mixer, then 40 minutes in the Branson 2510-DTH bath-sonicator.

2.5. Coupon Fabrication

Using the ASTM D 638 coupon configuration, it has successfully been used for fabric-reinforced composites and general non-directional laminates. For use with resins and discontinuous fiber composites the coupon is molded to shape. Care has to be taken to ensure the fibers are not preferentially oriented in the mold as to increase the strength of the coupon. Resins tend to be anisotropic so the shaping process may cause particular molecular alignment. The molecular alignment may be an idealization and in result may not show the true strength of the resin given a variety of processing conditions, flow geometry, and specimen geometry.

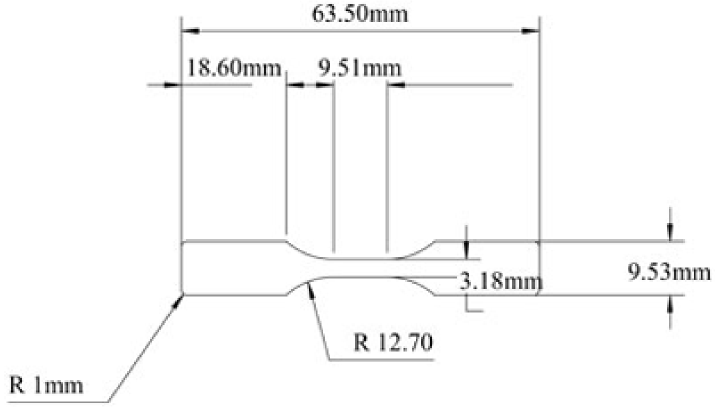

Figure 2. ASTM D638 V Coupon configuration

The amount of material supplied to conduct the tensile tests is a limited amount. It was then chosen to use Type V specimen for evaluation as suggested by ASTM D638 for either large amounts of samples or limited material. The coupon mold was milled out of 5/8 inch thick natural HDPE into the desired coupon shape. 16 coupon samples each 3mm deep were milled out of a single piece. It was viewed that WaterShed 11120 DSM had low adhesion to natural HDPE so it was chosen as the mold material. A Sprayon 511 Dry Film Vydax Mold Release was used to further decrease the adhesion to the mold. The mold was milled out of HDPE using first a ¼" bit and 1/8" bit for final passes of the mold.

Figure 3. HDPE molds with resin and resin mixture

3. Experimental Testing

3.1. Experiment Procedure

The liquid resin samples were filled into the mold using disposable pipettes. One side of the mold was cut off and a temporary piece of tape was then placed over the end of the mold as shown in the photo to allow for easier removal of the coupon. The UV-oven used was made by 3D Systems and is an additional add-on item to their SLA printer. Specific information about the UV oven could not be found, the primary wavelength is in the UV-A region for the oven.

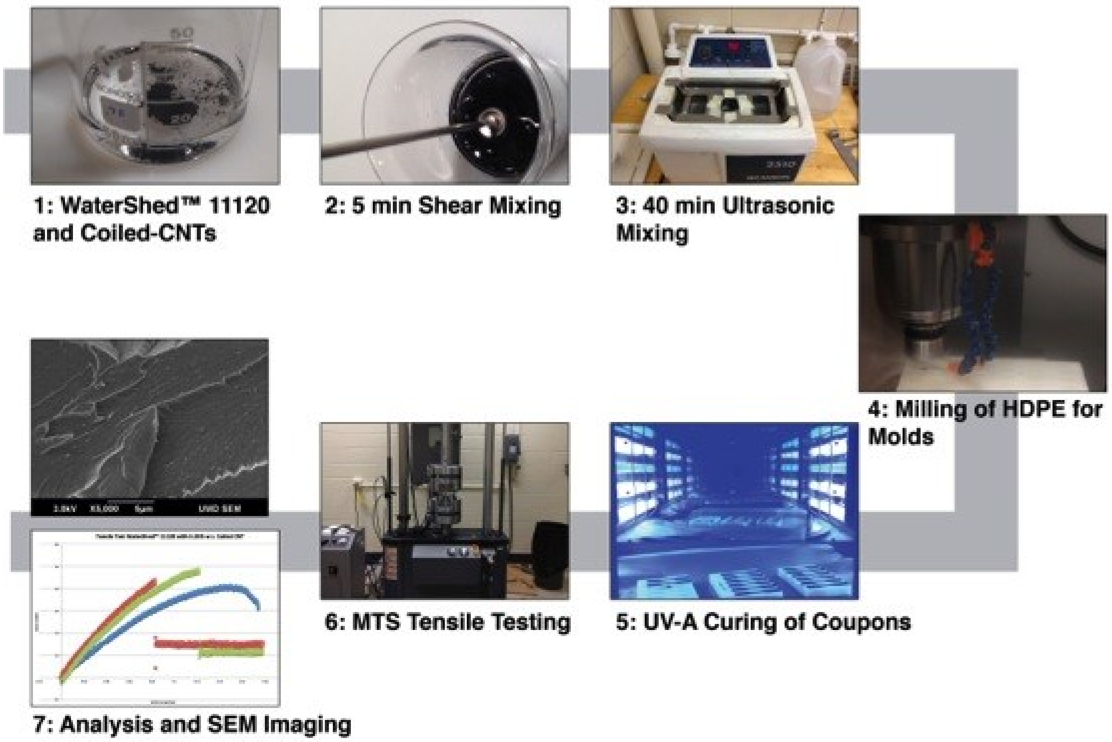

Figure 4. WorkFlow for experimental procedure

Table 4. Cure process for neat WaterShed™ resin and with coiled-CNTs

Composition	30 min	60min	90min	120min
WaterShed 1120 no additives	Sample appeared to be fully cured	Slight yellowing of top resin observed	Similar visual, sample fully cured	Sampled removed from mold and place upsidedown in UV-oven. Continued to be cured.
.25% w.t CNT Ultrasonic Processed	Top fully cured, side test showed gelling in center of sample	Side viewed cured. Partial removal showed slight gumming underneath	Sample cured enough to remove from mold. Slightly hard gel on bottom of sample	Sample removed from mold and place upside down for further curing. Hard gel underside fully cured.
.25% w.t CNT Shear +Ult	Top fully cured, side test showed gelling		Sampled cured enough to remove from mold. Soft Gel bottom.	DNE
.50% w.t CNT Shear+Ult	Increase in gelling over .25%		Hard Top shell and liquid in center of sample.	DNE
.75% w.t. CNT Shear+ult	Increase in gelling over .5%		Hard top shell and liquid in center of sample	DNE
1.0% w.t. CNT Shear+Ult	Increasing in gelling over .75%		Hard top shell and liquid in center of sample	DNE

The .25 wt. (%) CNT resin sample appeared to be the best general weight percent based off the ability to be cured. The pure WaterShed 1120 appeared to be very rigid by general inspection while the .25 wt. (%) CNT sample had more flexibility. Strength of the samples was then evaluated on MTS tensile tester.

3.2. MTS Results

Table 5.
MTS results of tensile test of neat WaterShed™ resin and with coiled-CNTs at a rate 1 mm/s.

Resin Type	MPa	MJ/mm^3	Average Toughness
Neat Resin	56.26	2.09	2.36 MJ/mm^3
	43.92	1.18	
	64.26	3.83	
.25% w.t. CNT + Resin	41.52	3.11	2.63 MJ/mm^3
	44.04	1.82	
	49.05	2.98	

Three samples of the neat resin were made and two of the samples had small air bubbles at the neck of the coupon. Both of the samples fractured at the air bubbles. Six samples of the CNT composited resin were made. Three of the samples fractured at areas other than the neck of the coupon and have a very low tensile strength viewed. Those three results are not taken into account.

The datasheet on WaterShed™ 11120 rates the tensile strength evaluated by ASTM D638 from 47.1MPa to 53.6MPa. The experimental results evaluated by the ASTM D638 using V type small sample shown a range of 43.92MPa to 64.26MPa for neat resin and 41.52MPa to 49.05MPa for CNT .25 wt. (%) resin. The results show that one of the neat resin samples had the highest energy absorption. Averaging the three results of the Neat Resin and CNT Resin, the data showed 2.36MJ/mm^3 and 2.63MJ/mm^3 respectively. Showing an 11.4% increase in overall toughness of the material for the set of 3 samples.

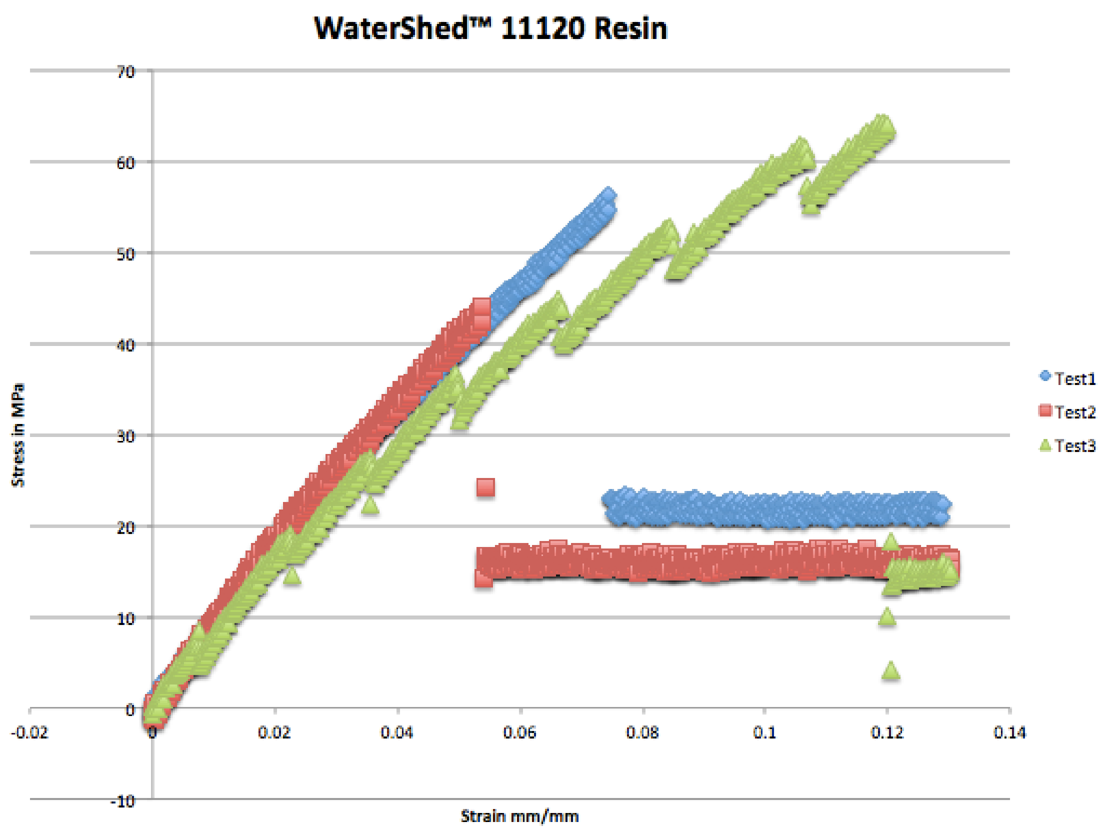

Figure 5. Stress verse Strain for Neat WaterShed™ 11120 Resin

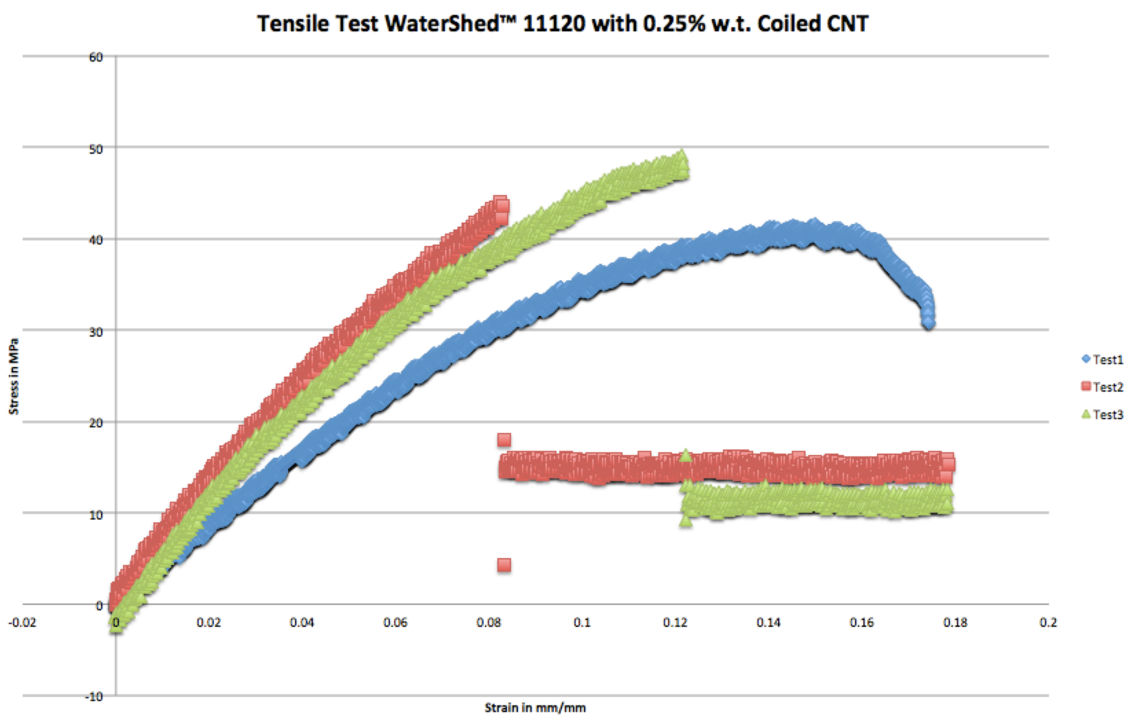

Figure 6. Stress verse Strain for WaterShed™ 11120 and Coiled-CNT Resin

3.3. SEM Imaging

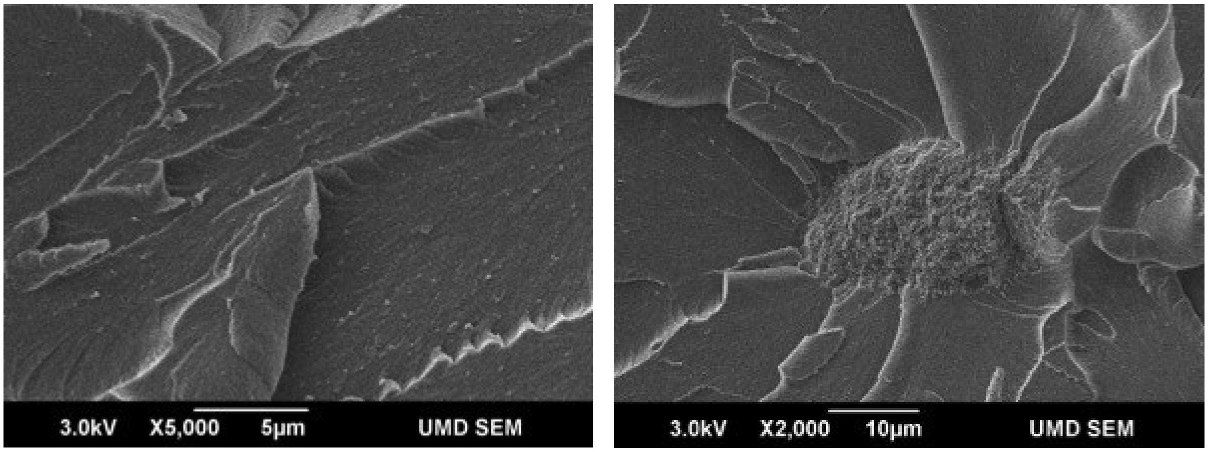

Figure 7. UMD SEM Images of Tensile Test Fracture

The images above were taken with the University of Minnesota Duluth Scanning Electron Microscope of one of the cross section .25 wt. (%) CNT resin samples after fracture. The samples were gold coated to maximize increase the visibility of the carbon nanotubes. The tops of the coiled CNT can be seen at X5000 on the surface of the sample as white dots. Several CNT agglomerates were seen on the surface of the sample fracture like the image shown at X2000 on the right. The average size of the CNT agglomerates was 10-30um.

4. Discussion

After viewing the SEM imaging, the agglomerates suggest either longer or more energy intensive mixing process is needed to homogeneously disperse the coiled CNTs in the liquid resin. Few agglomerates were viewed on the fracture surface, however they appeared to be stress concentrators that would have a negative impact on overall strength of the material.

The test samples had a large variance in strength and toughness. Only one sample of the 9 samples tested broke in the center of the coupon. This suggests air bubbles or variance in the way the samples were poured into the molds. The data shows an overall increase in toughness of the resin of 11.4% through the addition of CNTs, but because of the small test size and variability seen in the samples, I would not say conclusively that the addition of nanotubes in resin increased the toughness.

5. Summary and Conclusion

3D printing can be done in a variety of ways and using a variety of materials. Stereo Lithography 3D printing can produce high resolution but generally weaker, brittle objects. This project explores ways to mitigate these negative qualities by compositing SLA resin such as WaterShed™ 11120 with carbon nanotubes. By expanding the range of applications that SLA 3D printing is suitable for, technology can become even more versatile than it already is.

By adding .25% by weight coiled carbon nanotubes to WaterShed™ 11120 resin, it was viewed to increase the toughness of the resin by 11.4% and a lower max tensile strength over pure WaterShed™ resin from 650N to 450N peak. This may be desirable for some printed objects where a greater overall toughness is needed but lower peak strength is needed. Problems such as the settling of carbon nanotubes over time will need to be looked into and solved before this solution can become viable for use in SLA 3D printers.

6. Further Research

To evaluate the composite completely for usefulness, more tests involving different types of curing processes and evaluations should be done. The resin was cured using a UV-oven designed for post cure of SLA printed parts. The CNT resin should be better simulated or tested in a actual SLA printer to see if layer by layer build up still has desired strength properties. Building up tensile test samples layer by layer, different orientations of the resin and CNTs will likely be viewed in comparison to the poured mold samples made in this experiment. By building the test sample layer by layer possible higher weight percentage of CNT could be used due to the additional curing of it.

Another factors to look into are the viscosity of the CNT resin mix. SLA printers often employ a special squeegee to spread the resin over the part as it is made or else is allowed to flow under the part. If the viscosity is greatly increased this may cause problems with the operation of the printer.

Settling of the CNT was viewed after a period of two weeks. If the resin used in SLA 3D printers is stored in large vats that are located in the printing area, a percentage of the CNTs may separate and settle. This can poise problems if the laser cures the resin from the bottom of the vat as the CNTs would absorb the energy. Solutions to keep the CNTs dispersed in the resin will have to be looked into.

Nanocellulose is a nanomaterial with density similar to Kevlar at 1.5 g/cm^3 and tensile strength one third of that of carbon nanotubes at 10,000MPa [4]. Nanocellulose has the potential to be a great additive material for SLA 3D printing because of the projected low cost of 10 USD /KG from the US Forest Service and its generally clear appearance. UV-curable resin cost is roughly $150 per Liter if buying in low quantity from suppliers such as FormLabs. By adding cheaper nanofiller material the price of the resin may decrease while also increasing the toughness of the resin. Nanocellulose is a clear to white material. This may allow for the UV light to pass through the nanofiller with minimal impact on the curability of the resin. At higher concentrations of CNT this was shown to be a problem. Currently the only available Internet source for nanocellulose was found from the University of Maine Process Development Center at a cost of 450 USD per pound.

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