Final Report

Faludi Lab Group:

Eco-friendly 3D Printable Materials

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ENGS 24

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I. Introduction

This paper investigates the tensile strength of eco-friendly 3D printed materials via ASTM D638 – 14 Standard Test Method for Tensile Properties of Plastics, type IV[1], as well as looks at the microstructure of the materials at the point of failure and on outer surfaces via scanning electron microscopy (SEM). The three materials tested are as follows: a mixture of sodium silicate (water glass) with pecan shell flour (PF + WG), sodium silicate with pecan shell flour and oyster shell (PF + OS + WG), sodium silicate with oak wood sawdust (Oak + WG). These materials were chosen for their small environmental impact over their lifecycle, and because they can be printed at room temperature, reducing energy consumption.

Fused deposition modeling or fused filament fabrication 3D printing, a novel and useful process for rapid prototyping and the creation of intricate geometries, is an additive manufacturing technique that deposits material from a nozzle onto a surface (the bed) and builds up in layers. The nozzle has freedom in the x and y directions, while either the platform that is being printed on or the nozzle itself has freedom in the z direction, allowing full control in 3D space to deposit material. Material can only be put on top of previous layers, with the possibility of some additional overhang.[2]

In traditional 3D printing, the nozzle is heated to heat the material to be printed above its glass transition temperature so that it can bond to the layers it prints on and can be shaped as the print head moves. This material coming out of the nozzle usually comes from a spool to allow for continuous printing, and materials used are traditionally certain

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[1] ASTM International, "ASTM D638-14 Standard Test Method for Tensile Properties of Plastics."

[2] Spoerk et al., "Effect of the Printing Bed Temperature on the Adhesion of Parts Produced by Fused Filament Fabrication."

plastics, such as PLA or ABS, as these extrude well and have reasonable glass transition temperatures. To prevent part warping and help with adhesion to the bed, the bed is often heated well above room temperature.[3]

Environmental impacts from 3D printing are primarily from energy use during printing[5] from heated beds and nozzles, with toxicity of printing materials and material waste being secondary (figure 1),[6] as environmentally harsh plastics are used. Eco-friendly materials mitigate both of these costs by printing without heated nozzles or beds and consist of compostable materials with little environmental impact over their lifecycle, such as flour or wood-based filaments, which bond chemically rather than thermally. The Faludi lab group found a 75% decrease in energy when chemical bonding was utilized though these pecan flour or oak based materials or similar organic compounds,[7] printing at room temperature with no heated parts.

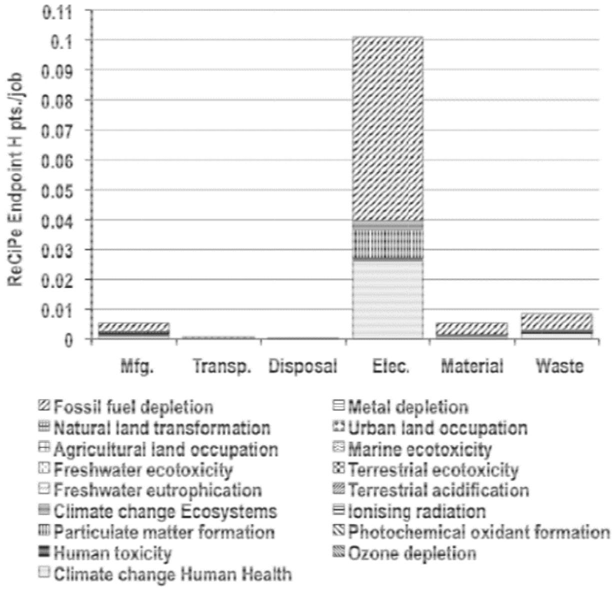

Figure 1: A breakdown of the environmental impact per job for a large FDM machine at maximum utilization, printing ABS. Environmental impacts measured according to the ReCiPe model, where lower is less environmentally taxing.[4]

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[3] Spoerk et al.

[4] Faludi et al., "Does Material Choice Drive Sustainability of 3D Printing?"

[5] Faludi et al.

[6] OECD, *The Next Production Revolution*, 204.

[7] Faludi et al., "Can Novel Materials Improve Environmental Impacts of Additive Manufacturing While Retaining Quality?"

Conventional 3D printing has the potential to either have a high or low environmental impact. Some implementations have found 70% less impact than comparable injection molded parts according to the ReCiPe method for life-cycle impact assessment,[8] which is a sustainability metric that looks at environmental impacts on a global scale.[9] 3D printing has also been estimated to have up to 500% the environmental impact of injection molding if implemented according to current industry practices.[10] This large variation is also due to the fact that the impact of 3D printing is difficult to compare to that of injection molding, as material waste, energy used, and environmental impact varies with batch size and geometry of the part being made, as well as machine utilization and other factors.[11] In general, it has been found that economies of scale win out for injection molding for batches of high number, but there are cases where on small scales (hundreds of parts or less), 3D printing can have less impact per part.[12] With the use of the novel materials tested, organic and compostable parts were found to have up to 82% less impact than the same ABS printed parts, according to ReCiPe endpoint H analysis.[13]

For popular extrusion-based 3D printers, the Organization for Economic Co-operation and Development (OECD) recommends expanding the use and selection of compostable bioplastics to make the material used more ecofriendly, and to chemically solidify materials rather than melt and solidify thermoplastics[14] to save on energy. A step

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[8] OECD, *The Next Production Revolution*.
[9] Netherlands National Institute for Public Health and the Environment, "LCIA: The ReCiPe Model."
[10] OECD, *The Next Production Revolution*, 204.
[11] Kreiger and Pearce, "Environmental Life Cycle Analysis of Distributed Three-Dimensional Printing and Conventional Manufacturing of Polymer Products."
[12] Kreiger and Pearce.
[13] Faludi et al., "Can Novel Materials Improve Environmental Impacts of Additive Manufacturing While Retaining Quality?"
[14] OECD, *The Next Production Revolution*, 199.

towards this is the commercially successful PLA (polylactic acid), a compostable bioplastic with a lower melting point than other thermoplastics and does not require a heated bed,[15] which lowers its energy usage, although it still does require above-ambient temperature heated extrusion to print and is only industrially compostable.[16] More radical examples of sustainable 3D printing would be inkjet printing with salt (without epoxy re-enforcement), which has had a lower impact by up to a factor of 38 compared to similar machines using different materials.[17] Similar approaches that use organic materials with a binder have also been done, such as spruce chips and gypsum or sodium silicate, but these had less than ideal mechanical performance and were found only to be appropriate for non-structural use.[18]

Materials that are known to be compostable, such as wood, pecan shells, or oyster shells, reduce environmental impact over a lifecycle by providing both safe disposal via composting and environmentally safe production of the material by harvesting available natural materials. Materials printed at room temperature require a modified 3D printer that has no heated bed, and nozzle that can accept a paste as the feed material rather than continuous filament. The ideal material would print at room temperature, have a small environmental impact over its lifecycle, and retain the strength of more traditional plastics. Conventionally printed PLA has been found to have an average tensile strength of 56.6 MPa over multiple layer heights and orientations when using the same ASTM tensile testing

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[15] Faludi et al., "Does Material Choice Drive Sustainability of 3D Printing?"
[16] van Wijk and van Wijk, *3D Printing with Biomaterials: - Towards a Sustainable and Circular Economy*.
[17] Faludi et al., "Does Material Choice Drive Sustainability of 3D Printing?"
[18] Henke and Treml, "Wood Based Bulk Material in 3D Printing Processes for Applications in Construction."

used in this experiment;[19] a material with similar properties that prints at ambient temperature to lower energy consumption would be ideal.

The body of literature focuses on energy and environmental metrics. In this report, we analyze our mechanical and material testing data from the organic compounds outlined above to see what applications are appropriate for their use.

II. Experimental Procedures

Material Production: The laboratory under Dr. Faludi's direction has modified a Makerbot Replicator 2X 3D printer (see figure 2) originally purposed for 3D printing with ABS (acrylonitrile butadiene styrene) filaments. The research team removed the original, heat-driven extruder, and replaced it with pneumatic-driven extruder because their organic filaments do not require heating like traditional 3D printed materials, which come in strands. Instead, the organic 3D filament is loaded as a paste into a disposable syringe with a pressure-driven plunger. The pneumatic setup has a manual air pressure regulator, a barometer, and solenoid valve (see figure 3). The team has two different extrusion heads, 0.58mm and 0.84mm, and uses the larger one for most prints. The Makerbot software program allows them to specify a height of 0.4mm

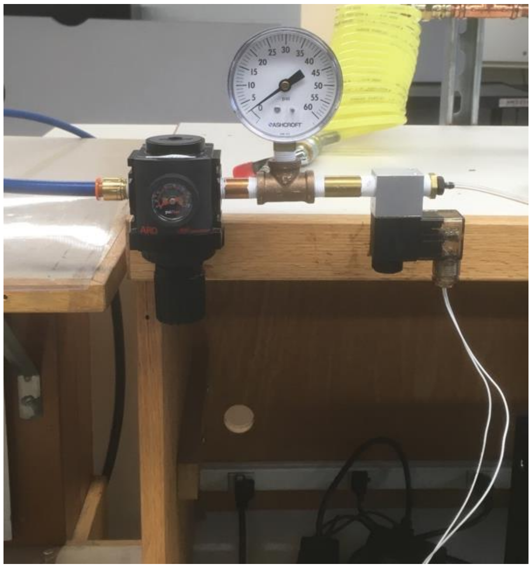

Figure 3: Left to Right: manual air pressure regulator, barometer, solenoid valve

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[19] Tymrak, Kreiger, and Pearce, "Mechanical Properties of Components Fabricated with Open-Source 3-D Printers under Realistic Environmental Conditions"

Figure 4: Mold used for the oak-water glass samples

per layer, with an extrusion speed of 20mm/s. The team places film over the extrusion bed to ensure that prints adhere to the bed's surface. There was only one compound that was not compatible with the customized 3D printing rig: oak and water glass. For this reason, dog bone samples were made with a silicone mold instead (see figure 4).

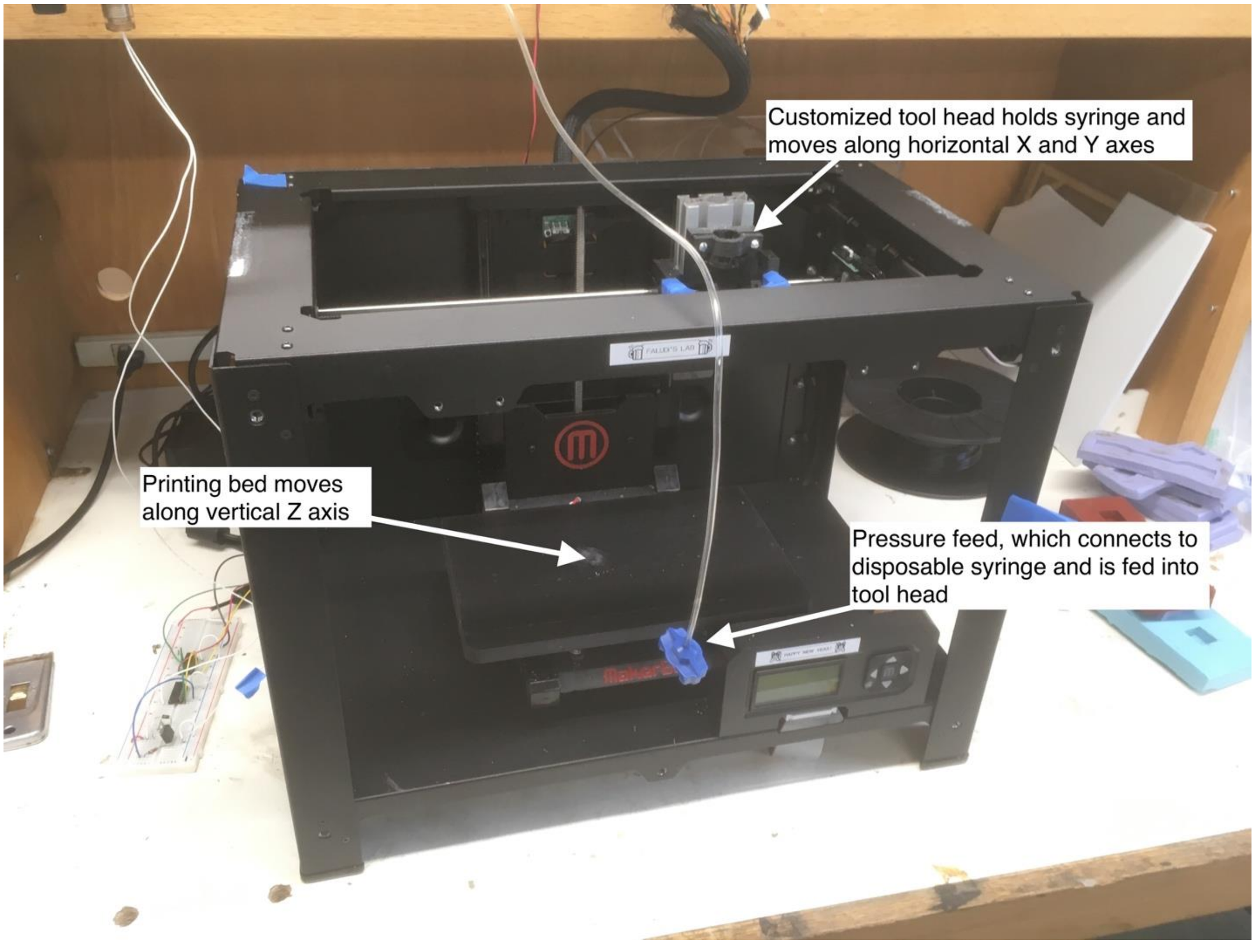

Figure 2: Modified Makerbot Replicator 2X 3D printer

Tensile Testing: We used the Instron 4442 machine in Couch Lab to test the various compounds. The testing was performed at a constant rate of 5mm/s on ASTM standard dog-bone shaped samples. The data was collected as a force-extension curve, which was converted to a stress-strain curve by dividing the force by the cross-sectional at the narrow part of the dog-bone samples. The Instron reported absolute extension, so a gage length of 25mm was used to calculate strain, as per ASTM standards. Using these curves, we were able to calculate the Young's Modulus and ultimate tensile strength of each material. It should be noted that the pecan flour and oyster shell samples were too delicate to be tested using the Instron. The machine's holding jaws crushed them both.

SEM Testing: Each compound material was tested using scanning electron microscopy, a process that probes material surfaces with high energy electrons and captures their scatterings to produce high resolution imaging. This technology is superior to light microscopy because it is not limited by the relatively large wavelength of visible light ($\sim 10^{-6}$m), but instead uses electrons with much smaller wavelengths. Depending on the intensity of this beam, we can explore a sample's material properties at various depths from the surface. An important step in this process is coating the surface of the sample with gold using a Hummer Sputtering System, to increase the sample's conductivity and enable the electron beam's interaction with topological features, rendering sharper images (see figure 5). The imaging was done using a Tescan Vega 3.

Figure 4: A before and after of the gold-coating process on our initial samples

III. Results & Discussion

<u>Tensile Testing:</u> We completed tensile testing for two promising materials with multiple samples of each composition. Figure 6 shows the stress strain curves of the Oak + WG samples and the PF + WG samples.

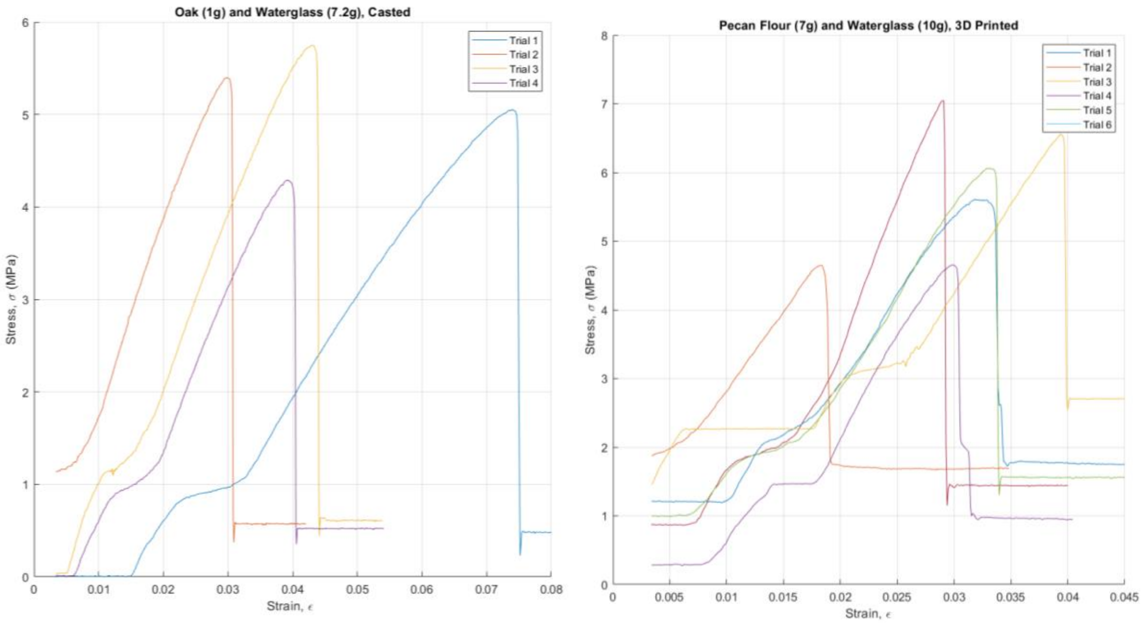

Figure 6: Stress strain curves of four Oak + WG samples (left) and of six PF + WG samples (right)

There was considerable variation in stress-strain curves, owing to the inconsistency of the samples. From these curves, we extracted the Young's modulus, ultimate tensile strength, and toughness of each sample. While the ultimate tensile strengths were consistent across compositions, there was significant variation in Young's modulus and extreme variation in toughness measurements. Table 1 shows the individual readings per sample as well as the average, minimum, maximum, standard deviation, and standard deviation percent.

	Oak + WG			**PF + WG**		
	Young's	UTS	Toughness	Young's	UTS	Toughness
Units	GPa	MPa	MJ/m^3	GPa	MPa	MJ/m^3
	102.3947	5.0541	40.786	426.099	7.0491	549.69
	198.0924	5.3993	656.16	253.2609	5.6077	761.88
	186.9706	5.7521	999.01	229.6583	4.6482	266.77
	177.2427	4.2897	625.52	254.636	6.5648	1025.1
				284.0163	4.6539	486.94
				270.9495	6.0608	152.56
AVG	166.1751	5.1238	580.369	286.4	5.764	540.49
Max	198.0924	5.7521	999.01	426.099	7.0491	1025.1
Min	102.3947	4.2897	40.786	229.6583	4.6482	152.56
STD Deviation	43.365	0.62483	397.57	70.833	0.98819	320.07
STD Dev Percent	26.10%	12.19%	68.50%	24.73%	17.14%	59.22%

Table 1: Tensile testing results (Young's Modulus, UTS, Toughness) for Oak + WG and PF + WG compositions

The Young's modulus of the PF + WG composition was 2.15 times higher than Oak + WG composition. Thus, PF + WG yielded a much stiffer material than Oak + WG. Both materials have two orders of magnitude difference from ABS plastic, which typically has Young's Modulus between 1.4 – 3.1 GPa, and PLA, which has a Young's Modulus of approximately 3.5 GPa. The relatively high Young's modulus of green 3D printed materials would make them potentially valuable where parts may need to keep shape, but will only be useful with sufficiently high tensile strength.

The PF + WG composition demonstrated a higher UTS than the Oak + WG composition. Though the 12.5% increase in strength may seem significant, both materials fall far behind the ultimate tensile strengths of ABS plastic (40 MPa) and PLA (50 MPa). The weakness of these green materials makes them invalid for most structural or prototype applications. However, at their current strength, they could still be viable for aesthetic models. Testing these materials was difficult as many samples set incorrectly and were too weak to be tested.

Finally, the Oak + WG samples exhibited greater toughness than the PF + WG samples. However, it is worth noting that toughness measurements varied the most, with standard deviation percentages of 68.5% and 59.22% for Oak + WG and PF + WG respectively. Thus, with four to six samples, the average toughness calculated likely does not represent the actual average. It is likely that due to the inconsistency of these heterogeneous materials, toughness will vary highly between individual samples. Like ultimate tensile strength, the toughness of these materials is far below that of ABS plastic, which has an estimated toughness of 3500 – 4500 MJ/m^3.

<u>SEM Imaging</u>: We imaged an Oak + WG sample and a PF + WG sample to potentially gain insights as to how each behaved under tensile testing. Figures 7 and 8 compare fracture sites of each composition. The Oak + WG sample appears to form fibers; this would be

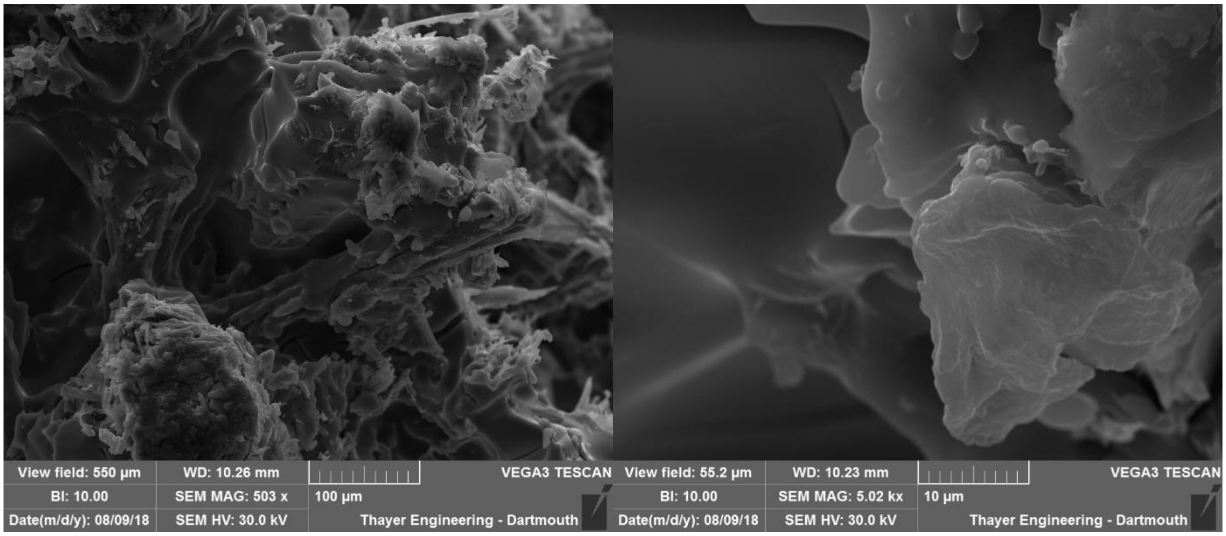

Figure 7: Oak + WG (fracture site)

expected due to its wooden composition. Though we would expect spherical particles due to the nature of ground pecan flour, the PF + WG sample is composed of layers, each comprised of small flakes. With similar binding material (waterglass), we would expect the fibrous composite to have a higher ultimate tensile strength, but this is not the case. This could be because the fibers appear to be randomly oriented. The flakes, however, appear to be aligned in parallel planes. Figures 9 and 10 show views of the top and bottom of the Oak + WG sample. These views show many cracks and holes, which create stress concentrations, likely a major cause of the composition's weakness. The high porosity of these samples similarly creates stress concentrations.

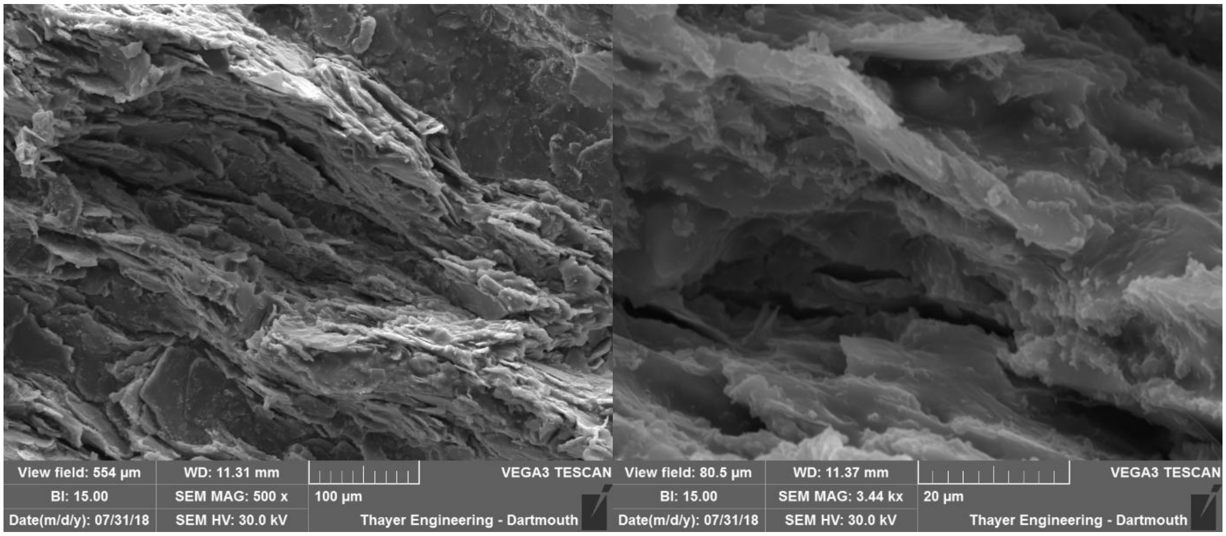

Figure 8: PF + WG (fracture site)

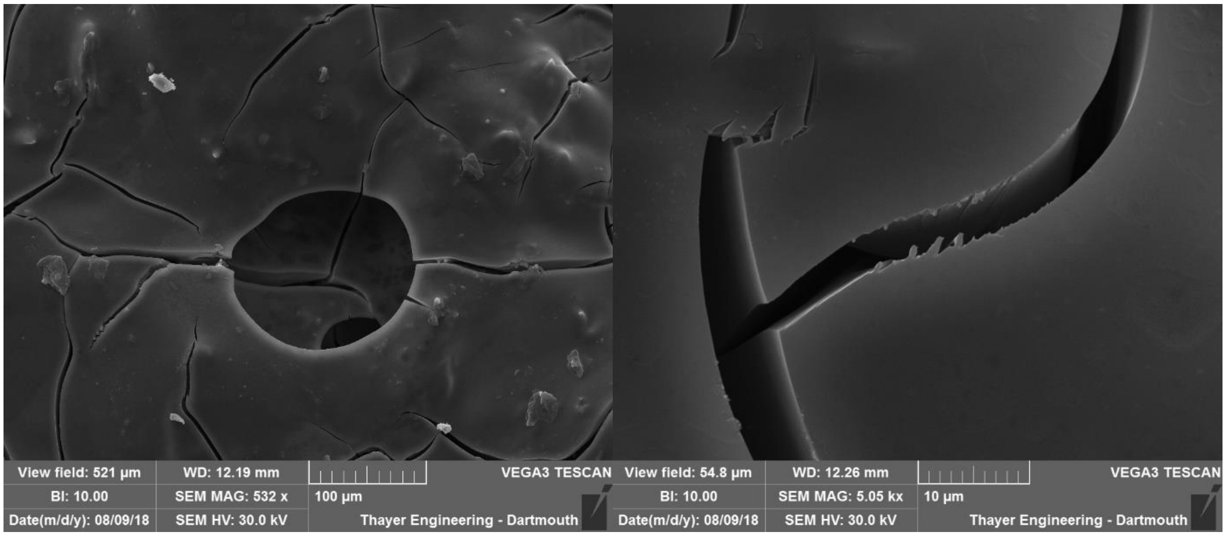

Figure 9: Oak + WG (top of sample)

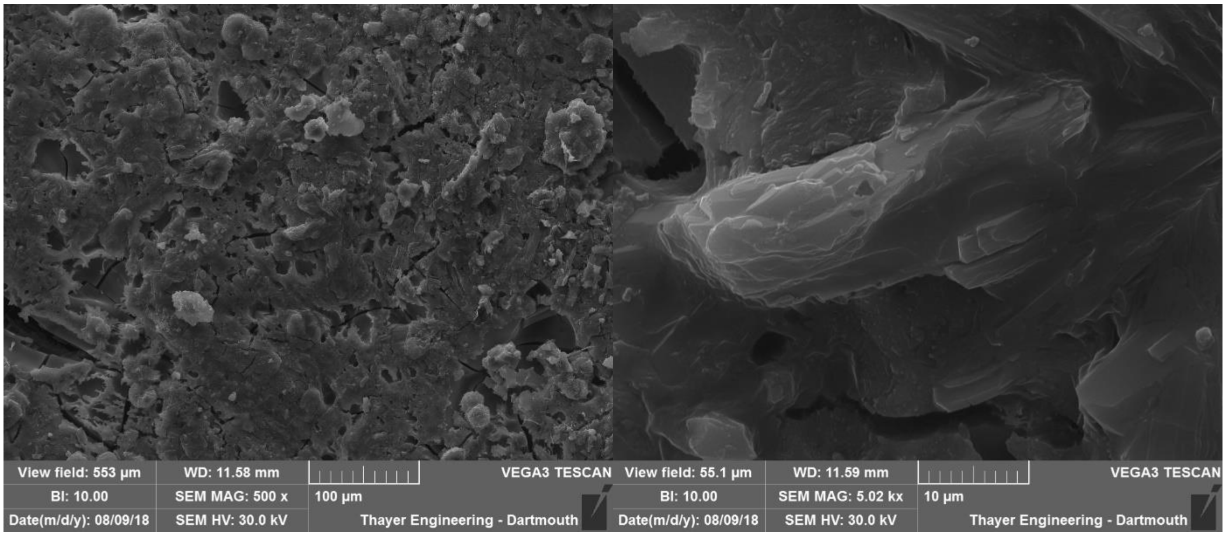

Figure 10: Oak + WG (bottom of sample)

IV. Conclusion/Summary/Future Work

Because our chosen subject is on the cutting-edge of its field, there is little research done on the material properties of composites similar to the ones that we fabricated and tested. Although this limits our ability to quantitatively analyze our data in comparison to other, similar materials, it also means that our results and data could help future researchers in this field.

After creating batches of two different composites, oak with waterglass (Oak + WG) and pecan flour with waterglass (PF + WG), performing tensile testing on them, and analyzing their points of fracture using microscopy, we came to a few conclusions about their material properties. The main takeaway is that while Oak + WG has a 12% higher average ultimate tensile strength and a 70% higher Young's modulus than PF + WG, both are substantially weaker than the materials commonly used for 3D printing. While our materials could be used as a low-energy, environmentally friendly alternative to 3D printing for aesthetic uses, they are not viable alternatives for functioning parts or prototypes.

In order to modify eco-friendly 3D printed materials for more practical purposes, one must first analyze what factors play into their weaknesses. Future testing could include a more in-depth analysis of the correlation between the composition of samples and material properties. By using energy-dispersive x-ray spectroscopy (EDX), one could analyze both the overall concentration and local concentrations of the matrix and filler. This could help determine how microstructure and overall composition affect material properties.

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Appendix: Equipment Description from Midterm Report

Dr. Faludi's lab uses a Makerbot 3D that has been rigged in a way that allows the user to use his or her own custom filament in the printing process. Moreover, an Instron testing machine was used on samples on to test their tensile properties. This testing was done by Dr. Faludi's team initially and the initial samples we received were dog-bone-shaped and subjected to the tensile test.

We ourselves used the samples provided and imaged the break sites using scanning electron microscopy. This process involved coating the samples in gold to increase their conductivity and placing them under an instrument that shoots an electron beam at them and captures that x-rays that bounce of the samples' surfaces.

A before and after of the gold-coating process on our 5 samples

Moving forward, we will conduct our own tensile and compressive tests using the Instron machine in couch lab. We will also perform a Rockwell hardness test, which we learned about during our lab session. As we learned in our tools and techniques session, “The hardness of a material is the measure of a material's resistance to deformation by surface indentation or abrasion. Most hardness tests are considered non-destructive as only a very small indentation is left after the test.”