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Benjamin D. Mitchell University of Louisville

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## EFFECTS OF SIZING AGENTS ON MECHANICAL PROPERTIES OF CARBON FIBER–POLYMER COMPOSITES VIA FUSED FILAMENT FABRICATION ADDITIVE MANUFACTURING

By Benjamin D. Mitchell B.S. in Mechanical Engineering, University of Louisville, 2021

A Thesis Submitted to the faculty of the J.B. Speed School of Engineering of University of Louisville In Partial Fulfillment of the Requirements For the Degree of

> Master of Engineering in Mechanical Engineering

Department of Mechanical Engineering University of Louisville Louisville, Kentucky

April 2022

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### **DEDICATION AND ACKNOWLEDGEMENTS**

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#### **ABSTRACT**

# <span id="page-8-0"></span>EFFECTS OF SIZING AGENTS ON MECHANICAL PROPERTIES OF CARBON FIBER–POLYMER COMPOSITES VIA FUSED FILAMENT FABRICATION ADDITIVE MANUFACTURING

Benjamin D. Mitchell

April 28, 2022

This study demonstrated the effects of changing the sizing agent parameter during the preparation of carbon fibers on the mechanical properties of composite made with acrylonitrile butadiene styrene (ABS) as the matrix material and carbon fibers as the fiber material. Three types of sizing agents produced by Allnex were used to coat three different batches of carbon fibers that were mixed with a torque rheometer and extruded with a barrel-style melt extruder into continuous spools of 1.75 mm filament for use with commercial 3D printers. Tensile tests were conducted on the filaments and tensile bars printed from the materials. Results showed that mechanical properties improved for each sizing agent when compared to nominal properties for ABS, but when compared to previously studied properties for fibers sized with an epoxy-based agent, modulus was not as high but tensile stress was around the same. This indicated that the physical limitation of the properties of the tensile strength of the fibers is independent of sizing agent chosen, but tensile modulus changed accordingly with the sizing agent chosen. Further studies should be done to document effects of a wider library of sizing agents on the mechanical properties of carbon fiber composites.

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#### **INTRODUCTION**

<span id="page-21-0"></span>The design and manufacturing of composites has been a major focal point for materials engineering innovation. The idea of interspersing a mundane low-cost material with parts of a valuable high-cost material with limited availability, in order to "borrow" its superior properties at a lower price, has found a wide range of applications, from structural uses where compressive and tensile strength is important, to the field of smart materials where piezoelectric or material self-healing properties are desired. One of these sought-after materials, carbon fiber, has been hailed as a possible addition to the low-density, highstrength materials that has the potential to revolutionize how structural, load-bearing components of buildings and moving assemblies are envisioned.

Recently, the use of 3D printing to create more complex geometries from composites has been considered. At this point, for carbon fiber composites, there exist many different PLA or ABS filaments that have been filled with carbon fibers and that are being manufactured and sold in bulk as generic composite material in various online marketplaces. Study and documentation of the processing of such composites is an ongoing effort, however, as industrial application and experimental use of carbon fiber polymer composites seemed at one point to have totally outpaced the research of these materials. A body of working research knowledge is growing, as one study by Dou et. al. focused on varying many different printing parameters in a slicing software to document the effects on tensile testing of printed carbon fiber composite samples, including layer height, nozzle temperature, extrusion width, and print speed [\[5\]](#page-70-1). This research is growing not only in quantity, but also in breath: there is even work that has investigated the sustainability of carbon fiber composites by testing their recyclability over multiple regrind and re-extrusion cycles. Significantly, one cycle in the study was found to increase mechanical properties of the composite material in a very rare non-downgrade recycling process [\[7\]](#page-70-2). For ABS, the effects of composition of fibers by weight percent and their orientation within the matrix has been examined by Tekinalp et. al. [\[6\]](#page-70-3). Work with ABS-carbon fiber composites in this study will be compared to this data as a baseline reference, and all manufacturing and printing process conditions cited in the paper for the composite material were preserved for this study.

In order to properly disperse the carbon fibers through the matrix as a fiber material, sizing agents must be used. Pure carbon fibers normally have an inert surface that has poor wettability, which has been expected to lead to poor interfacial adhesion consequently when mixed into a polymer composite on their own [\[8,](#page-70-4) [9\]](#page-71-0). To solve this problem, a simple technique called sizing is used, where fibers are coated with a thin film of special adhesivetype polymer that directly target the interfacial adhesion aspect of the carbon fibers and matrix material [\[9\]](#page-71-0). These polymers are known as sizing agents. Sizing agents tend to be polymer specific, especially those distributed by specialized manufacturers [\[2,](#page-70-5) [3,](#page-70-6) [4\]](#page-70-7). These sizing agents tend to thermally degrade easily when typical polymer melt temperatures are reached, making it challenging to guarantee the full adhesive properties of a sizing agent within the resultant composite. One category of sizing agent that has been used is polyurethane dispersants (PUDs), which have been shown to significantly increase interfacial adhesion between fibers and matrix by more than 90% [\[9\]](#page-71-0). In the work of Tekinalp et. al. [\[6\]](#page-70-3), carbon fibers in the composites used were sized with epoxy resin.

The use of certain formulations of epoxy-based resin seems to be part of the standard

treatment process to produce carbon fiber composites. However, unfortunately for the body of knowledge contained within research databases, these formulations and the testing done on them are usually kept a trade secret by producers in the carbon fiber manufacturing industry [\[9\]](#page-71-0). Testing of the effects of many other materials used as sizing agents for the carbon fibers on the mechanical properties of parts made with fused filament fabrication has only been studied to a limited extent in academic and research settings. This paper aims to help facilitate a new avenue of research that could potentially allow the true potential to be reached of not just carbon fiber composites, but a wide range of composites that use compatible fibers as their strengthening material within the matrix.

#### **MATERIALS AND METHODS**

<span id="page-23-0"></span>The process of materials in this study was based on the work done by Tekinalp et. al. [\[6\]](#page-70-3). Differences in data obtained in this study should mostly stem from the difference choice of sizing agent, since all other manufacturing process parameters of the resultant carbon fiber polymer composite that were specified in this previous work were kept identical.

Pellets of pure unfilled ABS, specifically CYCOLAC<sup>™</sup> RESIN EX58, were obtained from SABIC Plastics and used as the matrix material of all 3 composites. Relevant properties of the CYCOLAC™ ABS are presented in

<span id="page-24-0"></span>**[Table](#page-24-0)** *1*.

Property	Value
<b>Tensile Stress</b>	39 MPa
<b>Tensile Modulus</b>	2.080 GPa
Melt Viscosity at 240 C	15500 P
Density	1.03 $g/cm^{3}$

<span id="page-25-0"></span>**Table 1**. CYCOLAC™ RESIN EX58 material properties considered in this paper.

Carbon fibers were provided by Oak Ridge National Laboratory, who prepared them for this study by coating them with 3 different blends of sizing agents produced by Allnex: Daotan® TW 6450/30WA, Daotan® TW 6490/35WA, and Duroxyn® SEF 968w/25WA. Relevant properties of each sizing agent are presented in **[Table 2](#page-25-1)**, **[Table 3](#page-25-2)**, and **[Table 4](#page-25-3)**.

<span id="page-25-1"></span>**Table 2**. Daotan® TW 6450/30WA material properties considered in this paper.

Property	Value
<b>Dynamic Viscosity</b>	$50$ mPa-s (max)
Density	1.04 $g/cm^3$

<span id="page-25-2"></span>**Table 3**. Daotan® TW 6490/35WA material properties considered in this paper.



<span id="page-25-3"></span>**Table 4**. Duroxyn® SEF 968w/25WA material properties considered in this paper.



Each group of coated fibers, having an average fiber length of 3 cm, were then blended with melted ABS pellets using a Brabender Intelli Plasti-Corder Torque Rheometer that

was set to 220°C. For each composite, 10 weight percent of fibers (21.57 grams) was collected and blended with 194.16 grams worth of ABS pellets. 10 weight percent was chosen as the fiber loading composition because there was reference data in the work of Tekinalp et. al. [\[6\]](#page-70-3) with a manufacturing process detailed that could be matched against as a control condition without sizing agents. To avoid the torque from going too high and causing damage to the Brabender machine, the speed was lowered and progressively raised in steps to help thoroughly mix the material by the end of the process. Plastic was then scraped from the machine and fed through an industrial grinder, which produced grinded pellets of composite material.

To produce composite filament that could be used for printing, a Filabot Extruder Setup was used that included a Filabot EX2 Filament Extruder, a Filabot Airpath, and a Filabot Spooler. The continuous turning barrel of the Filabot EX2 Filament Extruder was set to a constant temperature of 220°C, and the micrometer included within the Filabot Spooler was utilized to help ascertain that each produced spool of composite material did not exceed 1.75 mm in diameter.

Next, a modified Creality Ender 3 printer was used to produce printed parts with 1.75 mm diameter filament from each spool of composite material. The dimensions called out by ASTM D638 were followed to print tensile test specimens of Type V. A hardened steel extruder stepper motor gear was used to feed the material into the PTFE tube through to the hotend; however, this gear had a slightly larger diameter than the stock brass gear that came with the printer. As a result, sometimes enough force was generated to totally strip the filament if it experienced too much resistance to push filament through. This caused the gear to lose its grip and become unable to extrude further material without user intervention if the printer was not monitored for occasional clogging of the nozzle. The stock white PTFE tube from the printer was replaced with a dark blue Capricorn brand PTFE tube that had more resistance to thermal degradation at the elevated temperatures used to print the material. A borosilicate glass bed with a rough texture on top was used as the surface for the print bed. A coating of Vision Miner's Nano Polymer Adhesive was applied to the bed before each print for extra adhesion and to help combat the natural tendency of ABS to warp at the corners from the bed during printing.

A hardened steel 0.5 mm nozzle was used to print from the composite; however, in Ultimaker Cura, the parameters for an expected 0.4 nozzle diameter were selected to account for the increase in effective viscosity from the presence of the adhesive sizing agent on the fibers interacting with the flowability of the ABS matrix material through the nozzle. When the preloaded settings for a typical 0.5 nozzle diameter printing experience was selected in Cura, it was harder to extrude the composite material through the nozzle used, because even at elevated temperatures, it did not flow as easily as pure unfilled ABS. In addition, choosing the downsized 0.4 mm nozzle diameter parameters meant that the lines that came out of the actual nozzle were drawn more closely together on the physical print, allowing more geometry from the edges of existing lines to melt into the new drawn lines. It was understood that this helped to bridge the selected 100% print infill as close to a cross section of pure material as possible for tensile testing, with infill line directions being oriented 0° longitudinally parallel to the direction of loading.

A very slow print speed of 7.5 mm/s and a layer height of 0.2 mm were selected for use with all replicates produced for tensile testing of the carbon fiber composites at a nozzle temperature of 260°C and a bed temperature of 110°C, which were the maximum selectable hardware temperatures by the Ender 3's Marlin firmware. These high temperatures with slow print speeds were determined to help mitigate most of the nozzle clogging issues that were encountered. Since ABS was used as the matrix material, it was expected that warpage could prove to be an issue if it was not considered during printing preparations. Therefore, the Ender 3 was placed inside of an enclosure that was generously provided to the lab by Shenzhen Warmy Industrial Co. Ltd., which was found to heat to 43.2°C on average from the ambient air of the bed heat alone during prints. It was later found while troubleshooting that under these thermal conditions, reliable printed parts could be obtained at faster nozzle travel speeds. Future testing should help determine the highest print speed that can be used with these composites without filament slippage and nozzle clogging occurring.

<span id="page-29-0"></span>**[Table](#page-29-0)** *5* summarizes the critical parameters selected in Cura that, through trial and error, proved to yield the most repeatable method to successfully print high-strength tensile testing specimens with all three blends of composite fibers, in addition to other physical parameters that were present during printing. With all print settings applied, the estimated total print time displayed in the Ultimaker Cura slicer was 48 minutes per tensile bar with an estimated print mass of 2 grams.

<b>Process Parameter</b>	Setting
Printer Model	<b>Creality Ender 3</b>
Nozzle Diameter - Actual	$0.5 \text{ mm}$
<b>Nozzle Material</b>	<b>Hardened Steel</b>
<b>Bed Material</b>	<b>Borosilicate Glass</b>
<b>Bed Adhesive</b>	<b>Vision Miner Nano</b> Polymer Adhesive
Nozzle Diameter- <b>Ultimaker Cura</b> Selection	$0.4 \text{ mm}$
<b>Nozzle Temperature</b>	$260^{\circ}$ C
<b>Bed Temperature</b>	$110^{\circ}$ C
Layer Height	$0.2 \text{ mm}$
<b>Print Speed</b>	$7.5$ mm/s
<b>Infill Density</b>	100%
<b>Infill Pattern</b>	Lines
<b>Infill Direction</b>	[90, 90]
Enclosure Temperature	$43.2$ °C (ambient from bed)

<span id="page-30-1"></span>**Table 5**. Printer process parameter settings used to print composite tensile testing bars.

Each ASTM D638 Type V tensile bar and unprinted composite filament was tested for tensile strength using a Instron 5569A electromechanical test machine. For every testing case, the gauge length was set to 20 mm, and shear pin-based clamps were used.

## **RESULTS AND DISCUSSION**

<span id="page-30-0"></span>The Brabender Intelli Plasti-Corder Torque Rheometer was successfully used to produce hardened material for each of the three composites that was grinded and pelletized using an industrial grinder. When these pellets were then fed into the Filabot Extruder Setup, the diameter of the resultant filament varied and was difficult to control before the rollers that stabilized the filament for measurement with the micrometer were moved to a position that induced less tension on the hardened filament. Results at each step of the process are shown below.



<span id="page-31-0"></span>**Figure 1**. Torque and feedstock temperature within the Brabender equipment versus time during the mixing operation for the composite sized with Daotan TW 6490/35WA, where mixing speed was increased at intervals when torque approached equilibrium at each speed.

<span id="page-31-1"></span>

**Figure 2**. Sample of one category of sized carbon fibers from Oak Ridge National

## Laboratory.



<span id="page-32-0"></span>Figure 3. Sample of one of the resulting composites from the torque rheometer mixing, placed into a sheet of aluminum foil to safely cool for handling before further processing.

<span id="page-33-0"></span>

**Figure 4**. Insertion of a hardened composite sample into the industrial grinder.



**Figure 5**. Pelletized material for the composite with fibers sized with Daotan TW 6490/35WA.

<span id="page-34-1"></span><span id="page-34-0"></span>

**Figure 6**. Filabot Extruder Setup that was used to create the composite filament with sized carbon fibers (different polymer pictured).

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**Figure 7**. Filament produced with fibers coated with the Daotan® TW 6450/30WA sizing agent.


**Figure 8**. Filament produced with fibers coated with the Daotan® TW 6490/35WA sizing agent.



**Figure 9**. Filament produced with fibers coated with the Duroxyn® SEF 968/25WA sizing agent.



**Figure 10**. Enlarged photo of the surface of the sized carbon fiber composites.

<span id="page-38-1"></span>To help characterize the input material, a pycnometer was used with compressed helium gas to measure the density of the grinded feedstock used to produce the filaments. Returned densities were compared to nominal values of interest in **[Table 6](#page-38-0)**.

<span id="page-38-0"></span>**Table 6**. Measured density of each composite compared to densities of ABS and of sizing agent.

Parameters	Measured Density $(g/cm^3)$	<b>Difference</b> from ABS	Difference from sizing agent used
$ABS + 10wt\% CF$ [Daotan <sup>®</sup> TW 6450/30WA]	1.0546	2.36%	1.39%
$ABS + 10wt\% CF$ [Daotan <sup>®</sup> TW 6490/35WA]	1.0601	2.88%	1.39%
$ABS + 10wt\% CF$ [Duroxyn® SEF 968w/25WA]	1.0529	2.20%	2.36%

Measured densities did not seem to have any correlation to trends observed in the tensile testing results. However, the manufacturing processes used helped to pack the fibers and ABS together more tightly than standalone ABS as seen by the comparison in density values, indicating that porosity may not have been an issue in the feedstock used. As a result, the quality of each filament material was high upon visual inspection. No voids or pockets of air were observed on the surface or in the cross section of the filament produced, and surface quality was very smooth, shown in **[Figure 10](#page-38-1)**. To verify sufficient packing of material within the volume of the filaments, SEM images were obtained for the crosssectional view of the filament, shown below.



**Figure 11**. 500 µm scale view of SEM imaging performed on the cross section of the carbon fiber composite filaments (Duroxyn® SEF 968w/25WA sized composite used).



**Figure 12**. 200 µm scale view of SEM imaging performed on the cross section of the carbon fiber composite filaments (Duroxyn® SEF 968w/25WA sized composite used).

Voids were very small and difficult to notice at the 500 μm zoom level. At the 200 μm zoom level, these voids were small and spaced evenly throughout the material. These voids are understood to be the locations of the carbon fibers evenly dispersed in the matrix material, since most of the holes were uniformly sized. Thus, porosity of the feedstock material used for printing tensile bars was demonstrated not to be an issue and was not considered when analyzing test results for either filaments or tensile bars.

Cooled filament that was spooled was structurally solid in the longitudinal direction, but any transverse force applied to the filament caused it to whiten and shear very easily for all three types of composites. Generally, pure ABS filament is weaker in the transverse direction, especially during bending, than other standard filaments used for most prints such as PLA in the transverse loading direction, so it could be considered that the resultant composite materials were brittle in nature with respect to their fracture mechanics. This transverse loading weakness also observed for printed tensile bars during testing.

Each composite filament also underwent tensile testing, in addition to the Type V tensile bars that were printed with the filament. Gauge length used was 20 mm for all tensile tests conducted. Filament diameter was inconsistent between samples, so an average diameter of 1.6 mm was used for all cross-sectional area calculations performed for stress. Moduli for each tensile test of the filament and tensile bars was determined by taking the slope between two points that best described the entire elastic region of the test, given by

$$
E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}
$$
 Equation 1

where σ was a chosen stress data point and ε was its corresponding strain location. Yield strength was analytically found by setting an arbitrary point x on the plot far away from the line, and finding what a new point y would be if the destination of the line were offset

by 2% by using

<span id="page-41-0"></span>
$$
y = Ex(1 + 0.02) - Ex(0.02)
$$
 **Equation 2**

. Tensile strength was taken as the highest stress value that the material gave during the entire duration of the tensile test until fracture. Results of the data obtained from tensile testing the filaments of each composite material are tabulated below.

	Tensile	Standard	Coefficient
Parameters	Modulus	Deviation	οf
	(GPa)	(GPa)	Variance
$ABS + 10wt\% CF$			
[Daotan <sup>®</sup> TW	3.09	0.29	9.28%
6450/30WA]			
$ABS + 10wt\% CF$			
[Daotan <sup>®</sup> TW	3.73	0.34	9.06%
6490/35WA]			
$ABS + 10wt\% CF$			
[Duroxyn® SEF	3.49	0.41	11.72%
968w/25WA]			

**Table 7**. Tensile modulus data obtained (n=5) for each type of composite filament strand.

**Table 8**. Yield strength data obtained (n=5) for each type of composite filament strand.

	Yield	Standard	Coefficient
Parameters	Strength	Deviation	οf
	(MPa)	(MPa)	Variance
$ABS + 10wt\% CF$			
[Daotan <sup>®</sup> TW	42.75	4.23	9.89%
6450/30WA]			
$ABS + 10wt\% CF$			
[Daotan <sup>®</sup> TW	41.66	3.57	8.58%
6490/35WA]			
$ABS + 10wt\% CF$			
[Duroxyn <sup>®</sup> SEF	40.96	4.36	10.64%
968w/25WA]			

	Tensile	Standard	Coefficient
Parameters	Strength	Deviation	οf
	(MPa)	(MPa)	Variance
$ABS + 10wt\% CF$			
[Daotan <sup>®</sup> TW	45.36	3.79	8.35%
6450/30WA]			
$ABS + 10wt\% CF$			
[Daotan <sup>®</sup> TW	48.15	2.79	5.79%
6490/35WA]			
$ABS + 10wt\% CF$			
[Duroxyn® SEF	48.05	4.19	8.71%
968w/25WA]			

**Table 9**. Tensile strength data obtained (n=5) for each type of composite filament strand.

**Table 10.** Percent elongation at fracture data obtained (n=5) for each type of composite filament strand.

Parameters	Percent Elongation at Fracture (% )	Standard Deviation (% )	Coefficient of Variance
$ABS + 10wt\% CF$			
[Daotan <sup>®</sup> TW	1.85	0.22	12.00%
6450/30WA]			
$ABS + 10wt\% CF$			
[Daotan <sup>®</sup> TW	2.09	0.19	8.97%
6490/35WA]			
$ABS + 10wt\% CF$			
[Duroxyn <sup>®</sup> SEF	2.23	0.28	12.54%
968w/25WA]			

Of the three materials, the composite that was mixed with the carbon fibers sized with Daotan® TW 6450/30WA proved to be the most difficult material from which a consistent diameter that fell below 1.75 mm was obtained. The full length of the fan setup and some applied tension (with no slack in the line of self-suspended filament above the fans) was required to stretch the material enough as it came out of the barrel to shrink it to a small enough diameter for use with 1.75 mm diameter filament printing methods.

Tensile testing results showed that tensile modulus was not statistically different across

the three different composite filament categories tested. The filament made with Daotan® TW 6490/35WA produced the highest value for tensile strength, while Daotan® TW 6450/30WA produced the highest value of yield strength. This higher yield strength value for Daotan<sup>®</sup> TW 6450/30WA is thought to be correlated to the difficulty that was experienced in extruding it as feedstock during manufacturing and from the nozzle during printing.

Plotted stress versus strain curve data for the strongest specimens from each of the three composites are shown below.





Slippage occurred at the onset of tensile testing that caused prolonged regions of zero stress to exist that frontloaded each curve, but fortunately this only had a minor impact on the readability of the data. Well-defined elastic deformation regions and plastic deformation regions existed within all the samples that were tested, which led to the straightforward collection data presented in the immediately preceding tables. Relative to the material properties for pure ABS, the properties of the composite filaments straight out of the Filabot Extruder Setup showed improvements, which was a good sign that the sizing agents were working to increase interfacial adhesion within the composite as intended.

Using the process parameters identified in

**[Table](#page-29-0)** *5*, three replicates of each tensile bar test case were successfully printed.

Dimensions and images of the printed replicates are shown in

## **[Table 11](#page-45-0)**, **[Figure 14](#page-46-0)**, **[Figure 15](#page-47-0)**, and **[Figure 16](#page-48-0)** and compared to the original ASTM

D638 dimensions for Type V tensile bars.

		Width		Thickness		<b>Total Length</b>	Remarks
Parameters	Measured (mm)	Percent Difference from CAD	Measured (mm)	Percent <b>Difference</b> from CAD	Measured (mm)	Percent Difference from CAD	
	3.31	4.01%	2.66	$-24.42%$	62.43	$-1.68%$	Vertical gaps observed in samples in the
$ABS +$ 10wt% CF	3.23	1.56%	2.66	$-24.42%$	62.47	$-1.62%$	geometry transition between infill and inner
[Daotan <sup>®]</sup> TW 6450/30WA]	3.31	4.01%	2.71	$-22.59%$	62.47	$-1.62%$	wall embedded in the clamp points. Known Cura slicer issue that occurs with under- extrusion of material.
$ABS +$ $10wt%$ CF [Daotan <sup>®]</sup>	3.28	3.10%	2.57	$-27.81%$	63.27	$-0.35%$	Seems under-extruded at the clamp points, but middle tensile testing area appears fine.
TW	3.31	4.01%	2.48	$-31.29%$	63.27	$-0.35%$	
6490/35WA]	3.35	5.21%	2.44	$-32.88%$	63.3	$-0.30%$	
$ABS +$ 10wt% CF	3.34	4.91%	2.32	$-37.76%$	63.28	$-0.33%$	
[Duroxyn <sup>®]</sup>	3.35	5.21%	2.33	$-37.35%$	63.34	$-0.24%$	
<b>SEF</b> 968w/25WA]	3.32	4.31%	2.32	$-37.76%$	63.3	$-0.30%$	
<b>ASTM D638</b> Type V Bar		3.18		3.4		63.49	

<span id="page-45-0"></span>**Table 11.** Measured dimensions of each tensile bar used before tensile testing.

<span id="page-46-0"></span>

**Figure 14**. Printed replicates of ASTM D638 Type V specimens from the ABS composite with fibers sized with Duroxyn® SEF  $968w/25WA$ .

<span id="page-47-0"></span>

**Figure 15**. Printed replicates of ASTM D638 Type V specimens from the ABS composite with fibers sized with Daotan® TW 6450/30WA.

<span id="page-48-0"></span>

**Figure 16**. Printed replicates of ASTM D638 Type V specimens from the ABS composite with fibers sized with Daotan® TW 6490/35WA.



**Figure 17**. Side view of one of the printed tensile bar samples.

It was observed that each sample consistently differed significantly from the nominal thickness of ASTM D638 Type V tensile bars. After further testing with printing the same geometry with other materials, it was determined that the cause of the issue was an advanced setting for the Z-axis steps per millimeter value of the Ender 3, which was set by factory default to a value slightly below what it should have been in practice. Results of the data obtained from tensile testing these prints are tabulated below. Gauge length used was 20 mm for all tensile tests conducted. Also, plotted stress versus strain curve data for the strongest specimens from each of the three composites are shown.

Parameters	Tensile Modulus (GPa)	<b>Standard</b> Deviation (GPa)	Coefficient of Variance
$ABS + 10wt\% CF [Daotan@]$ TW 6450/30WA]	3.19	0.49	15.39%
$ABS + 10wt\% CF [Daotan@]$ TW 6490/35WA]	1.84	0.64	34.80%
$ABS + 10wt\% CF [Duroxyn@]$ SEF 968w/25WA]	2.39	0.21	8.91%

**Table 12**. Tensile modulus data obtained across three replicates for each type of ABS composite tensile bar.

**Table 13**. Yield strength data obtained across three replicates for each type of ABS composite tensile bar.

Parameters	Yield Strength (MPa)	Standard Deviation (MPa)	Coefficient of Variance
$ABS + 10wt\% CF [Daotan@]$ TW 6450/30WA]	41.57	6.00	14.43%
$ABS + 10wt\% CF [Daotan@]$ TW 6490/35WA]	35.94	11.62	32.34%
$ABS + 10wt\% CF [Duroxyn@]$ SEF 968w/25WA]	50.15	2.85	5.68%

**Table 14**. Tensile strength data obtained across three replicates for each type of ABS composite tensile bar.



Parameters	<b>Percent Elongation</b>	Standard	Coefficient of
	at Fracture $(\%)$	Deviation $(\%)$	Variance
$ABS + 10wt\% CF [Daotan®]$ TW 6450/30WA]	2.34	0.29	12.44%
$ABS + 10wt\% CF [Daotan®]$ TW 6490/35WA]	2.86	0.41	14.17%
ABS + 10wt% CF [Duroxyn <sup>®</sup> SEF 968w/25WA]	2.96	0.39	13.06%

**Table 15**. Fracture strain data obtained across three replicates for each type of ABS composite filament.

Standard deviation was high in the data obtained for the composite Daotan® TW 6490/35WA because the printed bar on the left seen in **[Figure 16](#page-48-0)** was under-extruded. As a result, it was weaker and failed earlier than the other specimens. If the outlier data from this sample is removed from consideration, the mean tensile modulus for this category improves to  $2.17\pm0.53$  GPa, and the mean tensile strength improves to  $47.45\pm0.00$  GPa, which is still weaker than the results obtained from tensile bars containing the other two sizing agents. The aforementioned observed material weakness in transverse loading for these composites may help to explain the early onset of failure for this part if the cross section of the neck was not totally uniform, as imperfections may cause a slight net bending moment to be generated when the center of loading for the bar is shifted away from the axis along which its true center of mass lies.

During printing, the composite filament made with Daotan® TW 6490/35WA put up much resistance to extruding, and external force had to be applied to the filament to give the extruder gear enough strength to force sufficient material through the nozzle. The most significant reason this occurred was because of the inconsistent diameter of most of the filament extruded, causing some portions of the filament to be larger than 1.75 mm in diameter and resulting in a very difficult fit through the PTFE tube. This effect also occurred in the under-extruded sample shown in **[Figure 16](#page-48-0)**. However, resistance, albeit

less significant, was still experienced with a second batch of material extruded with tighter control on the filament diameter. This could have been influenced by a higher viscosity of the sizing agent used, with the reported maximum value for viscosity of this sizing agent listed in **[Table 2](#page-25-0)** to be 50 mPa-s, higher than the average viscosity of either of the other two sizing agents tested in this study, but other reasons are more likely than this. Although all sizing agents were diluted with water during the preparation of the fibers, the interaction of the individual constituent particles the comprise each sizing agent with the flowability of the ABS matrix material through the nozzle could have had some impact that led to the printing resistance experienced.

Stress-strain curves are plotted for each category of composite tensile bar specimens below.





Relative to conventional curves for pure ABS tensile testing, the specimens tested produced stress-strain curves that behaved differently. Once pure ABS reaches yield strength, it normally cannot sustain the high stress and falls to a lower stress state while plastically deforming. However, the sized carbon fiber composite samples that were tested survived stresses that were higher than the yield strength, and they continued to rise in stress while plastically deforming. This illustrates that the addition of sized carbon fibers to unfilled ABS improves its mechanical performance behavior under axial loading conditions.

Data from tensile testing the tensile bars was compared to the nominal properties for CYCOLAC EX58, cited in

**[Table](#page-24-0)** *1*, and to the results obtained by Tekinalp et. al. [\[6\]](#page-70-0) for 10 wt% epoxy-sized carbon fiber loading, shown below. This information, along with comparisons with filament performance, is visually conveyed in bar charts plotted below.

**Table 16**. Tensile modulus data for tensile bars from each sizing agent composite studied compared with properties for the pure ABS used and for the epoxy-sized composite from literature.

Parameters	<b>ABS</b> Tensile Modulus	Difference from Nominal Value	Tekinalp et. al. Tensile Modulus	Difference from Nominal Value $(\%)$
$ABS + 10wt\% CF$ [Daotan <sup>®</sup> TW		42.2%		$-83.2888$
6450/30WA]				
$ABS + 10wt\% CF$ [Daotan <sup>®</sup> TW	2.08	4.30%	7.75	$-112.455$
6490/35WA]				
$ABS + 10wt\% CF$				
[Duroxyn <sup>®</sup> SEF		13.7%		$-105.853$
968w/25WA]				

**Table 17**. Yield stress data for tensile bars from each sizing agent composite studied compared with properties for the pure ABS used.

Parameters	<b>ABS</b> Yield <b>Stress</b>	Difference from Nominal Value $(\%)$
$ABS + 10wt\% CF$		
[Daotan <sup>®</sup> TW		6.38%
6450/30WA]		
$ABS + 10wt\% CF$		
[Daotan <sup>®</sup> TW	39	$-8.17%$
6490/35WA]		
$ABS + 10wt\% CF$		
[Duroxyn® SEF		25.0%
968w/25WA]		

**Table 18**. Tensile strength data for tensile bars from each sizing agent composite studied compared with properties for the pure ABS used and for the epoxy-sized composite from literature.





**Table 19**. Percent elongation data for tensile bars from each sizing agent composite studied compared with properties for the pure ABS used.



<span id="page-56-0"></span>

**[Figure 19](#page-56-0)** shows a summary of the tensile modulus data obtained in this study. For composite sized with Daotan® TW 6450/30WA, mean filament tensile modulus was 3.09 GPa with a standard deviation of  $\pm 0.29$  GPa, while mean tensile bar tensile modulus was 3.19 GPa with a standard deviation of  $\pm 0.49$  GPa. Mean tensile bar tensile modulus was 3.3% better than mean filament tensile modulus, which was exceptionally good for

comparisons of this kind and illustrated excellent performance of the printed tensile bars in this category. Filament made from this composite performed 39.1% better than the nominal value of 2.08 GPa for ABS and 86% worse than the nominal value of 7.75 GPa for epoxy-sized composite from literature, whereas the tensile bars printed from the composite filament performed 42.2% better than ABS and 83.3% worse than the epoxysized composite from literature.

For composite sized with Daotan® TW 6490/35WA, mean filament tensile modulus was 3.73 GPa with a standard deviation of  $\pm 0.34$  GPa, while mean tensile bar tensile modulus was 2.17 GPa with a standard deviation of  $\pm 0.53$  GPa. Mean filament tensile modulus was 52.8% better than mean tensile bar tensile modulus, which indicated significant inconsistencies in the quality of the printed tensile bars. Filament made from this composite performed 56.7% better than ABS and 70.1% worse than the epoxy-sized composite from literature, whereas the tensile bars printed from the composite filament performed 4.3% better than ABS and 112.5% worse than the epoxy-sized composite from literature.

For composite sized with Duroxyn® SEF 968w/25WA, mean filament tensile modulus was 3.49 GPa with a standard deviation of  $\pm 0.41$  GPa, while mean tensile bar tensile modulus was 2.38 GPa with a standard deviation of  $\pm 0.21$  GPa. Mean filament tensile modulus was 37.5% better than mean tensile bar tensile modulus. Filament made from this composite performed 50.6% better than ABS and 75.9% worse than the epoxysized composite from literature, whereas the tensile bars printed from the composite filament performed 13.7% better than ABS and 105.9% worse than the epoxy-sized composite from literature.

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Yield Strength (MPa)

<span id="page-58-0"></span>**Figure 20**. Clustered column chart of yield strength data for both filaments and tensile bars from each sizing agent composite studied compared with properties for the pure ABS used.

**[Figure 20](#page-58-0)[Figure 19](#page-56-0)** shows a summary of the yield strength data obtained in this study, which was obtained with the help of **[Equation 2](#page-41-0)**. For composite sized with Daotan<sup>®</sup> TW 6450/30WA, mean filament yield strength was 42.75 MPa with a standard deviation of  $\pm$ 4.23 MPa, while mean tensile bar yield strength was 41.57 MPa with a standard deviation of  $\pm 6.00$  MPa. Mean filament yield strength was 2.8% better than mean tensile bar yield strength, which was exceptionally good for comparisons of this kind and illustrated excellent performance of the printed tensile bars in this category. Filament made from this composite performed 9.2% better than the nominal value of 39 MPa for ABS, whereas the tensile bars printed from the composite filament performed 6.4% better than ABS.

For composite sized with Daotan® TW 6490/35WA, mean filament yield strength was 41.66 MPa with a standard deviation of  $\pm 3.57$  MPa, while mean tensile bar yield strength was 35.94 MPa with a standard deviation of  $\pm 11.62$  MPa. Mean filament yield strength

was 14.7% better than mean tensile bar tensile strength, which was better than average for comparisons of this kind. Filament made from this composite performed 6.6% better than ABS, whereas the tensile bars printed from the composite filament performed 8.2% worse than ABS.

For composite sized with Duroxyn<sup>®</sup> SEF 968w/25WA, mean filament yield strength was 40.96 MPa with a standard deviation of  $\pm 4.36$  MPa, while mean tensile bar yield strength was 50.15 MPa with a standard deviation of  $\pm$ 2.85 MPa. Mean filament yield strength was 20.2% worse than mean tensile bar yield strength, which indicated some inconsistencies in the quality of the composite filament that was tested. Filament made from this composite performed 4.9% better than ABS, whereas the tensile bars printed from the composite filament performed 25.0% better than ABS.



Tensile Strength (MPa)

<span id="page-59-0"></span>

**[Figure 21](#page-59-0)** shows a summary of the tensile strength data obtained in this study. For

composite sized with Daotan<sup>®</sup> TW 6450/30WA, mean filament tensile strength was 45.36

MPa with a standard deviation of  $\pm 3.79$  MPa, while mean tensile bar tensile strength was 55.03 MPa with a standard deviation of  $\pm$ 5.35 MPa. Mean filament tensile strength was 19.3% worse than mean tensile bar tensile strength, which indicated some inconsistencies in the quality of the composite filament that was tested. Filament made from this composite performed 40.8% better than the nominal value of 30 MPa for ABS and 11.7% worse than the nominal value of 51 MPa for epoxy-sized composite from literature, whereas the tensile bars printed from the composite filament performed 58.9% better than ABS and 7.6% better than the epoxy-sized composite from literature.

For composite sized with Daotan® TW 6490/35WA, mean filament tensile strength was 48.15 MPa with a standard deviation of  $\pm$ 2.79 MPa, while mean tensile bar tensile strength was 47.45 MPa with a standard deviation of  $\pm 0.0038$  MPa. Mean filament tensile strength was 1.5% better than mean tensile bar tensile strength, which was exceptionally good for comparisons of this kind and illustrated excellent performance of the printed tensile bars in this category. Filament made from this composite performed 46.5% better than ABS and 5.7% worse than the epoxy-sized composite from literature, whereas the tensile bars printed from the composite filament performed 45.1% better than ABS and 7.2% worse than the epoxy-sized composite from literature.

For composite sized with Duroxyn® SEF 968w/25WA, mean filament tensile strength was 48.05 MPa with a standard deviation of  $\pm$ 4.19 MPa, while mean tensile bar tensile strength was 53.51 MPa with a standard deviation of  $\pm 4.07$  MPa. Mean filament tensile strength was 10.7% worse than mean tensile bar tensile strength, which indicated some inconsistencies in the quality of the composite filament that was tested. Filament made from this composite performed 46.3% better than ABS and 6.0% worse than the epoxy-

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sized composite from literature, whereas the tensile bars printed from the composite filament performed 56.3% better than ABS and 4.8% better than the epoxy-sized composite from literature.





<span id="page-61-0"></span>

**[Figure 22](#page-61-0)** shows a summary of the percent elongation data, relative to specimen original length, obtained in this study. For composite sized with Daotan® TW 6450/30WA, mean filament elongation was 1.85% with a standard deviation of  $\pm 0.22$ %, while mean tensile bar tensile strength was 2.34% with a standard deviation of  $\pm 0.29$ %. Mean tensile bar elongation was 23.0% higher than mean filament elongation. Filament made from this composite performed 178.1% worse than the nominal value of 32% for ABS, whereas the tensile bars printed from the composite filament performed 172.8% worse than ABS.

For composite sized with Daotan® TW 6490/35WA, mean filament elongation was 2.09% with a standard deviation of  $\pm 0.19$ %, while mean tensile bar tensile strength was 2.86% with a standard deviation of  $\pm 0.41$ %. Mean tensile bar elongation was 23.0% higher than mean filament elongation. Filament made from this composite performed 175.5% worse than ABS, whereas the tensile bars printed from the composite filament performed 167.2% worse than ABS.

For composite sized with Duroxyn® SEF 968w/25WA, mean filament elongation was 2.23% with a standard deviation of  $\pm 0.28$ %, while mean tensile bar tensile strength was 2.96% with a standard deviation of  $\pm 0.39$ %. Mean tensile bar elongation was 27.9% higher than mean filament elongation. Filament made from this composite performed 173.9% worse than ABS, whereas the tensile bars printed from the composite filament performed 166.1% worse than ABS.

It was generally seen that standard deviation for tensile modulus of the filaments was relatively low, with low corresponding coefficients of variable. This is desirable, as it demonstrates that the pure material that was extruded had easily reproduceable mechanical properties. On the other hand, standard deviation for the tensile bars was a bit higher, which makes sense since the occasional difficulties encountered with inconsistent filament diameter and rare nozzle clogging affected the quality of different parts of each print.

Ideally, if 3D printing were a perfect process, trends in mechanical properties would have matched those of the tensile testing data obtained for filaments. However, this was not the case, and the most significant reason for this is the voids formed within the part geometry by the imperfections of material deposition that follows the sliced model path. Although the outermost wall layer stacking will tend to look great from a side view, the extrusion lines on the inside won't form perfect seals as they are laid over each other across

layers, and thin continuous lines of air will exist inside the print. As a rule of thumb, it can be expected that part properties printed from material will achieve around 80% of the pure material properties.

Other minor reasons why results did not match include the observed whitening of the filament induced by the roller system of the Filabot Extruder System that exhibited some transverse stress on the filament, and possibly fracture onset at the microscopic level, as it bent the filament slightly to give the micrometer an accurate reading; the transferring of these cracks in the microstructure to the material that came out of the nozzle, which may have created weak points in the extruded material that cooled into the actual printed parts; and the noticeable holes in geometry between the outer walls and the infill that were partially caused by the Ultimaker Cura slicer software, as seen best in **[Figure 15](#page-47-0)**. Also, since filament diameter was inconsistent, smaller or larger average cross-sectional areas used between composite samples might have influenced their load-bearing capacities, especially since filament area was small compared to printed tensile bar area.

As expected, the material properties for each sample category exceeded the material properties of the ABS used on average, illustrating the ability of the fibers to improve the mechanical properties of ABS when interspersed in a composite as the fiber material. However, the addition of fibers also made the material easier to break after yielding and less compliant during plastic deformation, which led to significantly lower values for percent elongation of both tensile bars and filaments relative to the nominal value for ABS. This is because as the fibers split apart in plastic deformation stress after yielding, residual voids form in the ABS matrix material where the fibers previously were, which rapidly decreases the overall effective cross-sectional area that is available for the tensile bar to

use internally. This continuous decrease in effective cross-sectional area from the formation of voids in the matrix led to the onset of fracture in the samples tested in this study, including the filaments for the composites, much more quickly than in pure homogenous materials.

Comparison indicates that the samples tested in this study had significantly lower moduli than the samples tested by Tekinalp et. al. [\[6\]](#page-70-0), which were sized with an epoxybased agent. This indicates that the adhesive ability of epoxy-based agents on the interfacial adhesion strength for carbon fiber composites with ABS is superior to the effects of the sizing agent blends by Allnex that were tested. However, tensile strength for all composites tested in this study remained similar compared to the study performed by Tekinalp et. al. [\[6\]](#page-70-0), illustrating that although the addition of fibers to a composite does improve the tensile strength over the matrix material in general, the choice of sizing agent does not significantly alter the failure mode within carbon fiber composites, and that there is a physical limitation of carbon fiber composite tensile strength associated with the tensile strength of the fibers themselves.

Furthermore, Minitab statistical analyses were run using the results and compared to results from the study performed by Tekinalp et. al. [\[6\]](#page-70-0) where applicable, and Fisher LSD method pairwise comparisons were performed on results that had p-values less than 0.05. Results are shown below.

<span id="page-64-0"></span>**Table 20**. Conducted single-factor Analysis of Variance on tensile modulus data for tensile bar samples tested, with single-replicate average for epoxy-sized composite included  $(R^2 = 94.58\%)$ .

<b>Source</b>	DF	Adj SS	Adj MS	<b>F-Value P-Value</b>	
		Sizing Agent   3   2.48082×10 <sup>19</sup>   8.26941×10 <sup>18</sup>   29.11			0.001

Error	5   $1.42056\times10^{18}$   $2.84112\times10^{17}$		
Total	$\left(2.62288\times10^{19}\right)$		

<span id="page-65-0"></span>**Table 21**. Grouping information for conducted pairwise comparison on statistical model from **[Table 20](#page-64-0)** using Fisher LSD Method and 95% confidence. (Means that do not share a letter are significantly different.)



**Table 22**. Conducted single-factor Analysis of Variance on yield strength data for tensile bar samples tested  $(R^2 = 46.35\%)$ .

<b>Source</b>	DF	Adj SS	Adj MS	<b>F-Value</b>   <b>P-Value</b>	
Sizing Agent	2		$1.14861\times10^{14}$ 5.74306×10 <sup>13</sup>	2.16	0.211
Error			$1.32973\times10^{14}$ 2.65946 $\times10^{13}$		
Total		$2.47834\times10^{14}$			

**Table 23**. Conducted single-factor Analysis of Variance on tensile strength data for tensile bar samples tested, with single-replicate average for epoxy-sized composite included  $(R^2 = 35.76\%)$ .

<b>Source</b>	DF	Adj SS	Adj MS		<b>F-Value   P-Value</b>
Sizing Agent	3	7.54024×10 <sup>13</sup> 2.51341×10 <sup>13</sup>		0.93	0.492
Error			$1.35431\times10^{14}$ 2.70862×10 <sup>13</sup>		
Total		$2.10833\times10^{14}$			

**Table 24**. Conducted single-factor Analysis of Variance on percent elongation data for tensile bar samples tested  $(R^2 = 35.93\%)$ .



As mentioned above, the tensile moduli were shown to have differences between factor levels that were statistically significant in Minitab. While the composites sized with agents from Allnex all shared a grouping letter in **[Table 21](#page-65-0)** since Minitab did not detect statistically significant differences between these with the data provided from the tensile testing experiments, the epoxy-based composite had a different grouping designation from the factor levels performed in this study, demonstrating that there is a statistical difference in tensile modulus associated with the choice of sizing agent used

for sizing the fibers in a carbon fiber composite.

## **CONCLUSION**

The surface of carbon fibers is inert and does not normally respond well to polymers under load, so sizing agents must be used to prepare carbon fibers for blended composite polymers, which will unlock the true potential of the composite material. Here in this study, it was determined that the choice of sizing agent used during the preparation of carbon fibers had significant effects on the mechanical properties of the resulting composite. If this is true, then even better sizing agents can be developed that further increase the strength of the composite polymer, and the best sizing agent that could possibly exist might bring the composite properties to a maximum threshold where composite properties nearly match the fiber properties in the fiber-loading direction. In applications where high strength, low weight materials like carbon fibers are needed, such as aerospace and formula one racing, new avenues of success can be explored as new and improved sizing agents are developed for carbon fibers.

## **FUTURE WORK**

With this study, it is currently known that material property data has been obtained for the use of at least four different sizing agents in the preparation of carbon fibers composites. Further studies should be done to document effects of a wider library of sizing agents on the mechanical properties of carbon fiber composites. Additionally, comprehensive data for carbon fiber composites manufactured with unsized carbon fibers should also be

collected, to test the theory of poor expected mechanical performance put forth by Yang, Li, and Yang [\[8\]](#page-70-1). Limited strength data on unsized carbon fibers does exist [\[9\]](#page-71-0), but more information needs to be collected and a set of standard process settings used to make this base composite defined. Not only should this data be collected to verify this assertion, but it will also serve as a control that will help to future researchers easily identify sizing agents that have superior effects on mechanical properties compared to other sizing agents, such as the epoxy-based agent used by Oak Ridge National Laboratory in the preparation of their fibers for their varied weight-percent study [\[6\]](#page-70-0).

Sizing agents tend to thermally degrade at temperatures that are required to blend and extrude most polymers. Chemical engineering research should be done on ways that high temperature-resistant compounds can be implemented to thermally shield the sizing agents used in carbon fibers from damage and degradation during manufacturing processes. Across processes, these extreme temperatures must be reached multiple times (during torque mixing of polymer and fibers, during extrusion of filament material, and during deposition of filament into a printed part), so methods should be devised that such thermal shielding could survive multiple thermal loading cycles.

This study only examined the differences in sizing agent effects as they directly interacted with ABS as the matrix materials. The use of different matrix materials also should be explored with different sizing agents, as a different polymer such as poly-lactic acid (PLA) or nylon might be able to generate different chemical bonds with the sizing agents that were provided for this study by Allnex, which may be either stronger or weaker. Allnex shared that some polyurethane-based sizing agents are designed to work with ABS, but the effects of using a different polymer matrix material than intended has not yet been

demonstrated. There may even exist a polymer that has poor interaction with the industrystandard epoxy-based sizing used for carbon fibers, but excellent interaction with the sizing agents from Allnex. This avenue should be comprehensively explored to expand a possible library of sizing agent effects on carbon fiber composites to include considerations for the effects of varying the polymer used, ranging from many industry-standard polymers such ABS, nylon, and PLA, to more specific polymers such as those smart material polymers that exhibit shape-memory properties.

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# **APPENDICES**

# **APPENDIX A: TECHNICAL DATA SHEETS**

For reference to the manufacturer specifications of the materials used, the provided technical data sheets are included here.



Revision 20210812

# CYCOLAC™ RESIN EX58

**REGION AMERICAS** 

### **DESCRIPTION**

High impact ABS for sheet extrusion and blow molding applications.

### **TYPICAL PROPERTY VALUES**



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**CHEMISTRY THAT MATTERS** 

Figure 23. Page 1 of the technical datasheet for CYCOLAC<sup>™</sup> Resin EX58.





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**CHEMISTRY THAT MATTERS** 





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**CHEMISTRY THAT MATTERS** 

**Figure 25**. Page 3 of the technical datasheet for CYCOLAC™ Resin EX58.

### **TECHNICAL DATASHEET**



# DAOTAN<sup>®</sup> TW 6450/30WA

### PRELIMINARY PRODUCT INFORMATION

#### **TYPE**

Aqueous aliphatic polyurethane dispersion, polycarbonate based

### FORM OF DELIVERY (f.o.d.)

30 % in water (30WA) (also containing 4.3 % Dipropylengly<br>col-dimethylether and 1 % Methoxypropanol)

### **TENTATIVE PRODUCT DATA**

#### Determined per batch:



### **DEVELOPMENT PRODUCT**

This product is serving for trial purposes only. Deviations which might occur<br>during transfer into manufacturing in a commercial scale are possible and do not constitute any material defect.

Neutralization agent approx. 1 % N,N-dimethylethanolamine, as salt

#### SPECIAL PROPERTIES AND USE

Daotan TW 6450/30WA is recommended as the NMP / NEP- free alternative for Daotan (V)TW 1236. Alike latter Daotan TW 6450 is a polycarbonate-<br>based, high molecular weight Polyurethanedispersion. Dried at ambient temperature Daotan TW 6450 is providing clear, crack- free films without further addition of organic solvents or additives. These films exhibit excellent elasticity and mechanical properties as well as very good adhesion to different plastic substrates like e.g. ABS, PC, PA, PVC, PC/PBT, ...

Accordingly Daotan TW 6450/30WA is particularly recommended for waterborne plastic primer and waterborne auto OEM Basecoats with outstanding requirements in terms of stone chip resistance properties. A further use is as modifier resin to improve stone chip resistance properties of e.g. auto OEM primer surfacer formulations.

### **DILUTABILITY**

Daotan TW 6450/30WA provides unlimited dilutability with deionized water, compatibility with organic solvents is limited; e.g. butyl glycol or butyl diglycol cause a strong swelling of Daotan TW 6450. With Proglyde DMM Daotan TW 6450 is completely incompatible. According to our experience<br>Dowanol DPM is a quite suitable diluent. In general it is recommendable to pre-dilute the solvent with deionized water before adding to Daotan TW<br>6450.

### **STORAGE**

At temperatures up to 25 °C storage stability packed in original containers amounts to at least 365 days.

It is important to protect Daotan TW 6450/30WA from frost; at low temperatures it has therefore to be stored under frostproof conditions.

Lowest storage temperature: 5 °C

#### www.allnex.com

Figure 26. Page 1 of the technical datasheet for Daotan® TW 6450/30WA.

### **DISTINGUISHING FEATURES**

Compared to Daotan (V)TW 1236 Daotan TW 6450 provides quicker drying speed at ambient temperature. Properties like adhesion to different plastic<br>substrates, mechanical properties and humidity resistance are in the same range.

#### **REMARK:**

Data contained in this publication are based on careful investigations (and are intended for information only). Due to scale up of this product there is not yet sufficient experience concerning serial production. We can therefore<br>not exclude, that based on future knowledge product data and other indicated properties in upcoming Technical Data Sheets will be subject to change. We reserve the right to leave the product name unchanged, even if<br>product data or other indicated properties will vary from the present product info. Regardless of the data contained in this publication any user is obliged to carry out tests under his own responsibility as to the suitability of<br>the product for a particular use and to investigate the possible violation of industrial property rights of third parties. Information is therefore not binding and cannot be construed as guaranteeing specific properties of<br>products. We apply our General Sales Conditions.

4.0/30.03.2017 (replaces 3.1/30.10.2013)

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Figure 27. Page 2 of the technical datasheet for Daotan® TW 6450/30WA.

### **TECHNICAL DATASHEET**



# DAOTAN<sup>®</sup> TW 6490/35WA

### PRELIMINARY PRODUCT INFORMATION

#### **TYPE**

Waterborne, aliphatic polyurethane dispersion, solventfree

### FORM OF DELIVERY (f.o.d.)

35 % in water (35WA)

### **TENTATIVE PRODUCT DATA**

#### Determined per batch:



### **DEVELOPMENT PRODUCT**

This product is serving for trial purposes only. Deviations which might occur<br>during transfer into manufacturing in a commercial scale are possible and do not constitute any material defect.

**Neutralization agent** approx. 1.0 % triethylamine, as salt

#### **SPECIAL PROPERTIES AND USE**

Daotan TW 6490 is a waterborne, aliphatic polyurethane dispersion, free of solvents and emulsifiers. Dried at ambient temperature Daotan TW 6490 yields transparent, crack-free films.

Coatings based on Daotan TW 6490 provide properties as: - very good adhesion to plastic substrates like e.g. ABS, PVC, PC, PMMA high elasticity and toughness

- excellent mechanical properties (especially stone chip resistance)<br>- little yellowing at elevated temperature

Thus Daotan TW 6490 is recommended for waterborne plastic Primers and<br>Basecoats. Moreover Daotan TW 6490 can be used as modifier resin in waterborne OEM Primer Surfacer recipes to improve stone chip resistance macrossime contribution Dactart TW 6490 needs to be crosslinked<br>with melamine resins (preferably HMMM-grades like e.g. Cymel 303).<br>Optimum results are obtained by using a blending ratio Dactan TW 6490 : Cymel 303 = 85 : 15 (calculated on solid resin).

To further improve water- and chemical resistance properties of coatings dried at ambient temperature Daotan TW 6490 can be crosslinked with<br>- Polyaziridine (e. g. Crosslinker CX-100, Fa. DSM, Netherlands) - Carbodiimide (e. g. Crosslinker XL-701 or XL-702, Fa. Picassian Polymers, Netherlands)

#### **COMPATIBILITY**

Compatibility of Daotan TW 6490 with other resins or additives has to be checked case by case. According to our experience the dispersing additive Additol VXW 6208 and the leveling and substrate wetting agent Additol VXW 6503N lead to excellent results.

#### **STORAGE**

At temperatures up to 25 °C storage stability packed in original containers amounts to at least 365 days.

It is important to protect Daotan TW 6490/35WA from frost; at low temperatures it has therefore to be stored under frostproof conditions.

Lowest storage temperature: 5 °C

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Figure 28. Page 1 of the technical datasheet for Daotan® TW 6490/35WA.

#### **REMARK:**

Data contained in this publication are based on careful investigations (and are intended for information only). Due to scale up of this product there is not yet sufficient experience concerning serial production. We can therefore<br>not exclude, that based on future knowledge product data and other indicated properties in upcoming Technical Data Sheets will be subject to change. We reserve the right to leave the product name unchanged, even if<br>product data or other indicated properties will vary from the present product info. Regardless of the data contained in this publication any user is obliged to carry out tests under his own responsibility as to the suitability of<br>the product for a particular use and to investigate the possible violation of industrial property rights of third parties. Information is therefore not binding and cannot be construed as guaranteeing specific properties of products. We apply our General Sales Conditions.

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**Figure 29**. Page 2 of the technical datasheet for Daotan® TW 6490/35WA.



# DUROXYN® SEF 968w/25WA

**Technical Datasheet** 

### **DEVELOPMENT PRODUCT**

This product is serving for trial purposes only. Deviations which might occur during transfer into manufacturing in a commercial scale are possible and do not constitute any material defect.

#### **TYPE**

Non-drying epoxy resin ester, water emulsifiable

### FORM OF DELIVERY (f.o.d.)

25 % in water (25WA)

#### **TENTATIVE PRODUCT DATA**

Determined per batch:



#### SPECIAL PROPERTIES AND USE

Duroxyn SEF 968w/25WA is used as binder for fiber sizing (glass and carbon). Duroxyn SEF 968w/25WA can be easily formulated and reduced with water to the required solids content. It can be used as the sole sizing material or formulated with other waterborne sizing components.<br>Final compatibility and sizing bath stability needs to be evaluated. Duroxyn SEF 968w/25WA provides excellent spreading properties of the fibers

#### **STORAGE**

At temperatures up to 25 °C storage stability packed in original containers amounts to at least 180 days.

#### **PRECAUTIONS**

Please notice the information in the material safety data sheet (SDS).

#### **REMARK:**

Data contained in this publication are based on careful investigations (and are intended for information only). Due to scale up of this product there is not yet sufficient experience concerning serial production. We can therefore not exclude, that based on future knowledge product data and other indicated properties in upcoming Technical Data Sheets will be subject to change. We reserve the right to leave the product name unchanged, even if product data or other indicated properties will vary from the present product info. Regardless of the data contained in this publication any user is obliged to carry out tests under his own responsibility as to the suitability of the product for a particular use and to investigate the possible violation of industrial property rights of third parties. Information is therefore not binding and cannot be construed as guaranteeing specific properties of products. We apply our General Sales Conditions.



# Figure 30. Technical datasheet for Duroxyn® SEF 968w/25WA.

### **APPENDIX B: OTHER 3D PRINTING STUDIES**

Other filaments were manufactured with the Filabot filament extrusion machine, too. Ultem 1000 (polyetherimide), which was received from SABIC Plastics, was extruded at different temperatures all in the range of 400°C, and outgassing was observed at elevated temperatures that were too high, causing the resultant extrusion to contain many gas-filled bubbles. These were theorized to be due to either the hygroscopic properties of the polymer feedstock having absorbed moisture from the ambient air before melting, or the extreme temperatures required to fully melt the polymer serving as a catalyst for the polymer to thermally degrade after it exited the nozzle of the Filabot machine.

Additionally, there was a need in lab for more available reliable printing methods of flexible polymers such as Hytrel, TPU, shape-memory polymers, and composites that blend any of these with soybean-husks. An additional Ender 3 V2-type machine was purchased, and it was fitted with a 0.8 mm nozzle with Cura settings expecting a 0.6 mm nozzle to account for resistance from the natural fibers in the composites used. A composite with PLA as the matrix material and soybean husk fibers as the fiber material was tested at 210°C nozzle temperature to print an intended stand for a 3D-printed University of Louisville mascot logo. Results were aesthetically pleasing, and layer height stayed consistent between layers on the first print attempt. Further use of this printer and nozzle to print with soybean husk fiber-based composites will likely see continued good results.



**Figure 31**. Soybean husk fiber with PLA composite successfully extruded from the nozzle of the additional printer that was purchased for use with natural fibers.



**Figure 32**. Successful aesthetic print from the additional Ender 3 printer for a part made from soybean husk fiber with PLA composite. No warping occurred, and final part has great mechanical strength and interfacial layer adhesion while handling. Scale bar shown to roughly illustrate the size of the printed part.

Similar experimental work to the work on sized carbon fiber composites was performed on a batch of regrinded nylon filled with glass beads and glass fibers, obtained from the Campbellsville, Kentucky manufacturing plant location of the Murakami Corporation. Tensile bars were printed at three different nozzle and bed temperature combinations, with a 0.4 mm nozzle, using otherwise identical process settings to the default profile for PLA for Creality Ender 3 series printers in the Ultimaker Cura slicer software. A modified Creality Ender 3 V2 was used to print the nylon-glass composite extrusions: the stock heater assembly was replaced with the Micro Swiss All Metal Hotend Kit to provide better durability protection from the abrasiveness of the glass and to promote better thermal conductivity through the material, and the heater cartridge was replaced with one with more wattage that had the power to heat to higher temperatures much quicker and maintain those higher temperatures during printing much easier. Dimensions of printed bars pre-testing are shown below, along with final images of the feedstock used and filaments obtained from feedstock, as well as the Minitab analyses. Filaments were extruded at three different temperatures, and ASTM D638 Type IV tensile bars (shrunk to 75% of the nominal size dimensions) were printed at three different printer temperature combinations for a multifactor study.

	Width		Thickness		<b>Total Length</b>		
Parameters	Measured	Percent Difference	Measured	Percent Difference	Measured	Percent Difference	
	(mm)	from CAD	(mm)	from CAD	(mm)	from CAD	
Filabot $220^{\circ}$ C	5.04	5.66%	2.51	$-19.36%$	84.82	28.76%	
Nozzle	5	4.87%	2.45	$-21.75%$			
$245^{\circ}$ C Bed 60°C	5.15	7.82%	2.48	$-20.55%$	N/A	N/A	
Filabot $220^{\circ}$ C Nozzle $260^{\circ}$ C Bed 80°C	5.21	8.97%	2.5	$-19.75%$			
	5.16	8.01%	2.24	$-30.56%$			
	5.18	8.40%	2.56	$-17.40%$			
Filabot	5.12	7.24%	2.37	$-25.03%$	84.97	28.94%	
$220^{\circ}$ C Nozzle $255^{\circ}$ C Bed 65°C Filabot $230^{\circ}$ C Nozzle $260^{\circ}$ C Bed 80°C	5.04	5.66%	2.57	$-17.02%$			
	4.9	2.85%	2.4	$-23.79%$			
	4.98	4.46%	2.49	$-20.15%$			
	4.97	4.26%	2.47	$-20.95%$			
	5.09	6.65%	2.41	$-23.38%$			
Filabot $230^{\circ}$ C	5.07	6.25%	2.82	$-7.77%$	N/A	N/A	
Nozzle	4.92	3.25%	2.86	$-6.36%$			
$255^{\circ}$ C Bed 65°C	4.88	2.44%	2.76	$-9.92%$			
Filabot $230^{\circ}$ C Nozzle $245^{\circ}$ C Bed 60°C	5.03	5.46%	2.45	$-21.75%$			
	5.09	6.65%	2.5	$-19.75%$			
	5.03	5.46%	2.45	$-21.75%$			

**Table 25**. Measured dimensions of each nylon-glass composite tensile bar used before tensile testing.



**Figure 33**. Raw regrinded feedstock material for the nylon, glass fiber, and glass bead composite obtained from the Murakami Corporation manufacturing plant in Campbellsville, KY.



**Figure 34**. Filament obtained from the nylon-glass composite feedstock that was extruded at 210°C. Surface finish is too rough to be usable for printing due to the glass fibers and glass beads protruding through the surface and not mixing well enough with the polymer.



**Figure 35**. Filament obtained from the nylon-glass composite feedstock that was extruded at 220°C. Surface finish is rough enough to cause skin injuries when handled roughly due to the glass fibers on the surface, but it is usable for printing.



**Figure 36**. Filament obtained from the nylon-glass composite feedstock that was extruded at 230°C. Surface finish is smooth but is still abrasive enough to cause skin injuries due to some of the glass fibers on the surface. It is completely usable for printing.



**Figure 37**. Tensile bar sample printed from nylon-glass composite extruded at 220°C, with a nozzle temperature of 245°C and a bed temperature of 60°C. Sample was printed on glass with hairspray used as an adhesive. Surface finish is smooth to the touch on the bottom, and visually smooth but rough to the touch on other surfaces exposed to air during the print process. All samples were visually similar to each other between factor levels. Scale bar shown to roughly illustrate the size of the tensile bar.



**Figure 38**. Tensile bar sample printed from nylon-glass composite extruded at 220°C, with a nozzle temperature of 255°C and a bed temperature of 65°C. Sample was printed on glass with hairspray used as an adhesive. Surface finish is smooth to the touch on the bottom, and visually smooth but rough to the touch on other surfaces exposed to air during the print process. All samples were visually similar to each other between factor levels. Scale bar shown to roughly illustrate the size of the tensile bar.



**Figure 39**. Close-up side view of one of the nylon-glass composite specimens printed. Visual smoothness and high aesthetic quality of the exposed print surfaces is readily apparent. Scale bar shown to roughly illustrate the size of the tensile bar.

**Table 26**. Tensile modulus data obtained across three replicates, with two outliers removed, for each factor level of nylon-glass composite tensile bar.



**Table 27**. Yield strength data obtained across three replicates, with two outliers removed, for each factor level of nylon-glass composite tensile bar.



**Table 28**. Tensile strength data obtained across three replicates, with two outliers removed, for each factor level of nylon-glass composite tensile bar.





<b>Extrusion</b> Temp.	<b>Nozzle/Bed</b> Temp.	<b>Percent</b> Elongation $(\% )$	<b>Standard</b> Deviation $(\% )$	<b>Coefficient of</b> <b>Variance</b>
	$245^{\circ}C/60^{\circ}C$	5.476375	0.183675	3.35%
$220^{\circ}$ C	260°C/80°C	5.974016667	0.498997856	8.35%
	$255^{\circ}C/65^{\circ}C$	7.73055	0.97935	12.67%
	260°C/80°C	6.769716667	1.099368387	16.24%
$230^{\circ}$ C	$255^{\circ}C/65^{\circ}C$	6.168483333	0.574967284	9.32%
	$245^{\circ}C/60^{\circ}C$	10.73988333	0.574967284	5.35%

<span id="page-92-0"></span>**Table 30**. Conducted dual-factor Analysis of Variance on tensile modulus data for nylonglass composite tensile bar samples tested  $(R^2 = 71.75\%)$ .



**Table 31**. Grouping information for conducted pairwise comparison on Extrusion Temperature from statistical model of **[Table 30](#page-92-0)** using Fisher LSD Method and 95% confidence. (Means that do not share a letter are significantly different.)



**Table 32**. Conducted dual-factor Analysis of Variance on yield strength data for nylonglass composite tensile bar samples tested  $(R^2 = 54.89\%)$ .

<b>Source</b>		Adj SS	Adj MS		<b>F-Value   P-Value</b>
Extrusion Temp.		$8.73467E+13$ $8.73467E+13$		4.37	0.063
Printer Temps.		$9.61350E+13$   4.80675E+13		2.40	0.141
Extrusion Temp.*Printer Temps.		$3.84218E+13$   $1.92109E+13$		0.96	0.415
Error	10	$2.00062E+14$   $2.00062E+13$			
Total	15	4.43513E+14			

<span id="page-93-0"></span>**Table 33**. Conducted dual-factor Analysis of Variance on tensile strength data for nylonglass composite tensile bar samples tested  $(R^2 = 59.19\%)$ .



**Table 34**. Grouping information for conducted pairwise comparison on Extrusion Temperature from statistical model of **[Table 33](#page-93-0)** using Fisher LSD Method and 95% confidence. (Means that do not share a letter are significantly different.)





<span id="page-94-0"></span>**Table 35**. Conducted dual-factor Analysis of Variance on percent elongation data for nylon-glass composite tensile bar samples tested  $(R^2 = 83.06\%)$ .

**Table 36**. Grouping information for conducted pairwise comparison on Extrusion Temperature from statistical model of **[Table 35](#page-94-0) [Table 33](#page-93-0)**using Fisher LSD Method and 95% confidence. (Means that do not share a letter are significantly different.)

<b>Extrusion Temp.</b>	N	<b>Mean</b>	Grouping	
$230^{\circ}$ C		0.0789269		
$220^{\circ}$ C		0.0639365		н

**Table 37**. Grouping information for conducted pairwise comparison on Extrusion Temperature \* Printer Temperatures from statistical model of **[Table 35](#page-94-0) [Table 33](#page-93-0)**using Fisher LSD Method and 95% confidence. (Means that do not share a letter are significantly different.)



## **APPENDIX B: RESEARCH PROJECTS IN OTHER LABORATORIES**

Additionally, work was done in the summer of 2021 to assist a Research Experience for Undergraduates (REU) student from Western Kentucky University with conducting a dielectrophoresis experiment in outer space aboard the International Space Station in collaboration with NASA, under the direction of Dr. Stuart Williams. Small glass capillaries whose thinnest dimensions were smaller than 0.2 mm were to be used to transport particles in colloidal suspension with a fluid over top of a belt-powered miniature desktop microscope whose objective lenses could be moved about a stage. 3D printed mounts were to be designed in SolidWorks and used to help suspend the glass capillary slides above the microscope while simultaneously being completely leak-proof and vibration-proof.

Many iterations of designs and print parameters of the desired capillary adapters were tested through the Ultimaker Cura slicing software used to print the tensile bars in the study of this thesis. The successful design for this application is shown below, fully installed with the microscope, and was manufactured on a personal Creality Ender 3 printer with a glass bed to guarantee dimensional accuracy of the cavity product's surface where the capillary is inserted. Interference-fit holes for a conductive pogo pin for use with conductive epoxy were printed on top, and current was successfully generated through the pin into the epoxy. This current was to be used to apply alternating electric fields at high frequencies to the samples inside the capillary tubes to effectively "trap" them in place, inducing the dielectrophoresis effect.



**Figure 40**. Leak-proof glass capillary mounts designed for a dielectrophoresis experiment in collaboration with NASA. Two-part epoxy was used to attach the glass capillaries to the printed products that were designed in SolidWorks, sliced in Ultimaker Cura, and printed on a Creality Ender 3 printer. Also pictured: black printed frame was designed in SolidWorks to mount the capillary adapters above the microscope via metricsized screws from McMaster-Carr that were lined with Loctite.

# **CURRICULUM VITA & RESUME**



ADDRESS: 6340 Pond Lily St., Prospect, KY 40059

DOB: Los Alamitos, CA, USA – October 4, 1998

EDUCATION

& TRAINING: B.S., Mechanical Engineering, University of Louisville (2017-21) M.S., Mechanical Engineering University of Louisville (2021-22)

AWARDS: Mechanical Engineering Department Academic Achievement Award (2019)

Material Handling Systems Most Valuable Co-op (2019)

TRiO Student Support Services Senior of the Year (2021)

Student Achievement Mentorship Award (2021)

Robert C. Ernst Award (2021)

Lewis S. Streng Award (2022)

UofL Cardinal Marching Band Graduating Senior Award (2021)

PROFESSIONAL SOCIETIES:

Tau Beta Pi (2021-Present)

# **Benjamin Mitchell**

(502)-552-1921 legomasterben@aol.com www.linkedin.com/in/benjamin-mitchell-2022

# **OBJECTIVE**

To work for a company that offers fulfilling work that will advance my knowledge and expertise in fields relating to mechanical engineering, automation, or robotics, and provides opportunities to employ creativity in my solutions.

# **EDUCATION**



# **PROJECTS**

## **Master of Engineering Thesis in Mechanical Engineering May 2021-May 2022 - May 2022**

- **•** Explored sizing agent effects on interfacial adhesion within 3D-printed carbon fiber-reinforced ABS.
- **•** Investigated the mechanical properties and sustainability of 3D-printed recycled glass fiber-reinforced nylon.

## **Capstone: Response of Microfluids in Microgravity Aboard the International Space Station** Jan 2021-May 2022

- **•** Communicated with NASA to refine research parameters and satisfy ISS protocol.
- **•** Created SolidWorks prototypes of glass capillary holders and 3D printed them for testing.

## **Redbird Robotics** Aug 2018-Mar 2020

- **•** Independently researched optimal part and system designs for drones in team competition projects such as IARC.
- **•** Created and 3D-printed parts for prototyping the team's designs.
- **•** Facilitated a morning TV news segment featuring the team at the 2019 Louisville Maker Faire.

# **ENGINEERING EXPERIENCE**

## **University of Louisville J.B. Speed School of Engineering** *Louisville, KY Graduate Research Assistant*

Aug 2021-Present

- Provide expertise on 3D printing to partners in industry and fulfill 3D-printed prototype requests.
- **•** Support Dr. Kunal Kate's laboratory research by assembling and customizing 3D printers, manufacturing composite polymer filaments from feedstock, and 3D printing with soy and fiber-based composites.

### **Material Handling Systems** *Mount Washington, KY*

*Mechanical Engineering Co-op* Spring 2019; Fall 2019; Summer 2020

- **•** Won "Most Valuable Co-op" company award in Spring 2019.
- **•** Designed conveyor layouts in 3 different warehouses across the United States.
- **•** Created, formatted, and revised construction-grade AutoCAD/Inventor installation drawings.
- **•** Implemented conveyor railing/supports, implemented safety measures, and collaborated with other mechanical designers to meet critical project deadlines.
- Frequently collaborated with manufacturing to optimize quality control and assembly of conveyor components.
- **•** Used Inventor and Vault to design and revise specialized parts to be manufactured for installation projects.
- **•** Redesigned designer training modules for new hires while taking classes at UofL.

# **SKILLS/COURSEWORK**

- **•** 3D printing with self-owned Ender 3/Ultimaker Cura
- **•** Autodesk Inventor/AutoCAD
- **•** SolidWorks
- **•** Fundamentals of Autonomous Robots

# **ACTIVITIES & HONORS**

- **•** Robert C. Ernst Award
- **•** Lewis S. Streng Award
- **•** M.E. Dept. Academic Achievement Award

# **LICENSES & CERTIFICATIONS**

- **•** Lean Green Belt, ID #17949003
- **•** Fundamentals of Engineering Exam (Pending registration)

## **•** Design of Experiments/Minitab

- **•** LabVIEW
- **•** Fluid Power Systems
- **•** Mechanical Vibrations
- **•** UofL 2021 Cardinal Marching Band
- **•** UofL 2021-2022 Cardinal Pep Band
- **•** 2021 Student Achievement Mentorship Award

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