NATCOM
Natural-Fiber Thermoplastic Composite Manufacturing

Final Report – June 20, 2024

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Project Scope

This project will advance the state-of-the-art by developing new, lower embodied energy composites comprised of a novel thermoplastic resin and natural fiber reinforcements. This material not only serves as a transformative technology that paves the way for advances in composite recycling, but the insights gained during its development will also enrich the understanding of processing techniques for other thermoplastic resins. Specifically, the project aims to complete a proof of concept for manufacturing processes and characterization of natural fiber reinforced Elium organosheet and other product forms for future scale. This project will also improve process techniques using continuous glass fiber, which will be used for benchmarking comparative data and has broad application in industrial and electrical markets. Provided a successful result, additional investigation and scale up could be conducted in conjunction with the IACMI SURF facility.

Executive Summary

Elium prepreg was manufactured using a pilot-sfale treater system at Western Washington University (WWU). The process proved to be feasible and the next step is to scale this technology at an industrial scale at Norplex-Micarta. Mechanical properties of glass and fiber systems can likely be improved by using an Elium grade more suitable for post-cure consolidation (thermoforming) and by optimizing consolidation parameters.

Task 2: The focus of this task was to develop the optimal curing parameters for the continuous process of producing Elium organosheet. Towards this end, the teams at WWU discovered that the UV photoinitiated/polymerized skin was effective at preventing MMA volatilization using a S5064 8 m/W/cm2 UV lamp. Omnirad 819 was chosen as the photoinitiator to use in subsequent production trials. Optimal feed rates and pinch roller ratios were also determined and will be used in production trials in the 2024 reporting period. A peroxide thermal initiator (Laurox) was required to polymerize residual MMA after sample UV exposure and optimal conditions for its use were determined using DSC. The team recommends a “Go” decision based on the development of a curing package and achieving Milestone 2.1: Documenting development and recommended formulation for trials on prepreg coating line.

Task 3: Each treater run provided the team with data and information pertaining to the quality of the manufactured prepreg. Three main takeaways are as follows: Photo-initiator in the resin mix posed too much of a gumming issue. Approximately 50% resin-to-fiber ratio was maintained with thermal initiator only. The prepreg process parameters from treater run #4 were ideal for the flab fiber material. The team plans on using these key takeaways to further develop the PMMA prepreg pilot-production process.

Task 4: Flax/PMMA prepreg manufactured on a traditional prepreg treater is a viable material. WWU has successfully scaled bench top to pilot production of PMMA based thermoplastic prepreg using a traditional lab scale treater line using flax, fiberglass, and linen fibers. Through mechanical testing of flax prepreg tensile, flexural, and short beam shear data was gathered. Although the manufacturing process to consolidate the prepreg was not optimized, a comparison between the materials can be made. In comparison to fiberglass the flax fibers with a PMMA matrix will perform at approximately half the tensile strength, a third of the flexural modulus, and half the short beam shear strength.

Task 2: Development of curing package and trial of hand-layup organosheet fabrication

This task will develop a curing package consisting of an ultraviolet and/or organic peroxide initiator(s). Preliminary formulations will be evaluated for effectiveness by assessing the degree of polymerization using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the cured organosheet. The curing package will also be evaluated for pot-life to ensure safe handling during pilot-scale production runs.

Objective

Western Washington University partnered with Norplex and Arkema to develop thermoplastic prepreg using a poly(methyl methacrylate) (PMMA) matrix. The primary goal of this research project is to develop a method to manufacture PMMA-based, flax-fiber composites using a lab scale prepreg treater. The period of performance of this work is September 2023 to June 2024. During Fall quarter of 2023, two objectives were met:

- Determine methods for polymerization of PMMA from Elium MMA resin system
- Determine initial process parameters for manufacturing prepreg with the WWU treater

Background

Sponsors

Norplex and Arkema are the sponsors for this research. Norplex specializes in thermoset composite design, development, and manufacturing. Norplex seeks to expand its capabilities to PMMA-based thermoplastic composites. Arkema is a materials manufacturer with headquarters in France. They manufactured and supplied the MMA monomer system used in this project, Elium C595.

Glossary of Terms

Several materials and processes were used in this project, Table 1 outlines the terms and details definitions of each.

Table 1: Glossary of Terms

Materials and Equipment	**Definition**
MMA (Methyl methacrylate)	Acrylic monomer and oligomer, Elium C595
PMMA Poly(methyl methacrylate)	Polymerized Elium
Omnirad 819	UV photo-initiator
PL-032	UV photo-initiator
Laurox	Peroxide thermal initiator
Prepreg treater	Machine to make prepreg material

Materials

Elium C595 was used as the MMA monomer resin system for polymerization to PMMA. Polymerization can occur via UV photoinitiation and/or thermal initiation. Poly(methyl methacrylate), Figure 1, is an amorphous acrylic thermoplastic polymer known for its UV resistance, hardness, abrasion resistance, and dimensional stability.

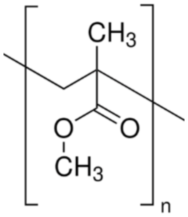

Figure 1: Chemical structure of PMMA repeat unit [2].

Polymerization

For this research, PMMA was polymerized using photoinitiators and a peroxide-based thermal initiator. These initiators have distinct advantages over one another. Photoinitiators polymerize a monomer via free radical generation when exposed to UV light. This is a relatively safe process for operators and safety measures are easily implemented. The photoinitiators used in this research were Omnirad 819 and PL-032.

Thermal initiators begin the polymerization reaction when a resin system is exposed to a temperature sufficient enough to begin free radical generation. The temperature required for this process is unique to the thermal initiator. Additionally, this reaction can be accelerated by increasing the processing temperature. Peroxides are most commonly used as thermal initiators and pose a greater risk to safety due to their high reactivity. The thermal initiator selected to start this research was Laurox, manufactured by Nouryon, due to its increased safety over other choices that react well with Elium C595.

Prepreg Treater

Prepreg is a material made with fibers that are impregnated with resin (matrix). It is frequently used in place of traditional composite layups. One type of prepreg manufacturing equipment is called a treater. Western Washington University’s (WWU) lab-scale prepreg treater (Figure 2) facilitates testing material processing parameters, which can help validate material performance and mechanical properties. The lab-scale prepreg treater is comprised of a resin bath, two industrial ovens, a ventilation system, and a take-up section (Figure 3).

The lab-scale treater is currently configured to process thermoset materials. A single roll of fiber material is drawn through a thermoset resin bath, consolidation rollers to control resin concentration, and into two industrial ovens for B-staging the matrix. The take-up section applies a poly-film layer to the final product to maintain the material's quality during storage. Typically, prepreg treaters are used with thermosetting resins and are designed to bring the resin to B-stage, or partially polymerized stage, so the prepreg material is tacky and can be draped and further cured. Unique to this study is the goal of not utilizing poly-film as a backing/carrier material during thermoplastic prepreg manufacturing, as well as polymerizing a liquid thermoplastic resin (instead of a thermoset) on the treater line.

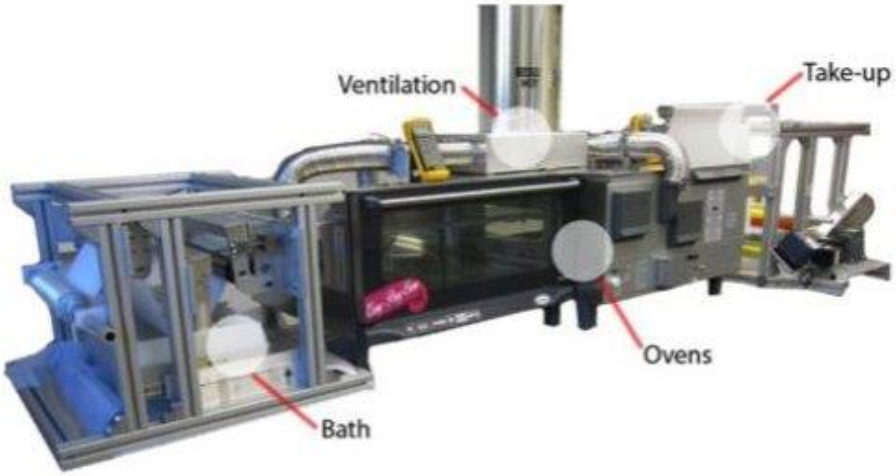

Figure 2: Treater used in WWU's Polymer Materials Engineering labs [1]

Figure 3: Simple 2D diagram of Current Treater Configuration

Results and Discussion

MMA Volatilization (Poly-film vs. Skin)

Elium resin is volatile and the MMA monomer will evaporate if left with sufficient surface area open to the atmosphere. The volatilization of MMA monomer will affect formation of the polymer chains and, thus, the properties of the resulting composite. To reduce evaporation of the MMA, a poly-film can be applied to the top and bottom of the wet-out fibers in a treater line. However, applying poly-film would add complexity to our treater line and introduce extra waste in the manufacturing process. To determine a method for reducing the vaporization of MMA, a study of weight loss as a function of time was conducted using neat Elium MMA resin and fiberglass, Elium and fiberglass sandwiched between poly-film sheets, and Elium and fiberglass photoinitiated with UV to create a polymerized skin. For the UV polymerized skin, two UV lamps were used; a S5064 and PIZHLO UV lamps. Photoinitiated Elium resin samples were mixed with 3% by weight photoinitiator, PL-032, and exposed to UV for 1 min and 3 min. This was prepared in a speed mixer at 1000 rpm for 2 minutes. 6 Elium/fiberglass samples were manufactured in total, stippled with resin, and then weighed for 10 minutes with the mass of each sample recorded every minute to calculate the mass loss rate (g/min).

Table 2 details the results of this study, suggesting that a UV polymerized skin on the material acts as a sufficient barrier against MMA vaporization. The sample with the lowest MMA mass loss rate (0.0001 g/min) was the photoinitiated skin sample using the S5064 UV lamp for 3 minutes. The same mass loss rate of MMA was observed by the photoinitiated skin sample using the PIZHLO lamp for 3 minutes. These results indicate that a UV polymerized skin is better at preventing MMA vaporization than applying a poly-film, 0.0001 g/min versus 0.0058 g/min respectively. Incorporation of UV lamps to the WWU lab-scale treater is needed as the manufacturing process is scaled up.

Table 2: Results of MMA vaporization study

Sample	**Mass Loss Rate (g/min)**
MMA on Fiberglass	0.0092
MMA on FG w/ poly-film	0.0058
MMA PL032 1 min (PIZHLO)	0.0025
MMA PL032 3min (S5064)	0.0001
MMA PL032 1min (S5064)	0.0055
MMA PL032 3min (PIZHLO)	0.0001

UV Lamp Selection

It was shown that UV photoinitiators aided in forming a polymerized, PMMA, skin on the Elium/fiberglass sample, preventing volatilization of MMA monomer. The S5064 and PIZHLO UV lamps were used in the MMA vaporization study. The S5064 UV lamp has a higher illumination than the PIZHLO UV lamp, but the PIZHLO UV lamp is more cost effective. The S5064 UV lamp had a “top only” configuration which means that it polymerized a skin onto the samples asymmetrically. With two PIZHLO UV lamps, it was possible to symmetrically illuminate samples in a “top and bottom” configuration. A DSC experiment was performed to determine which of the UV lamps more effectively polymerized the skin on an Elium/fiberglass composite (Figure 4). Note that in Figure 4 the Old UV refers to samples polymerized using the S5064 UV lamp (top only) and the New UV refers to the samples polymerized using the PIZHLO UV lamps (top and bottom).

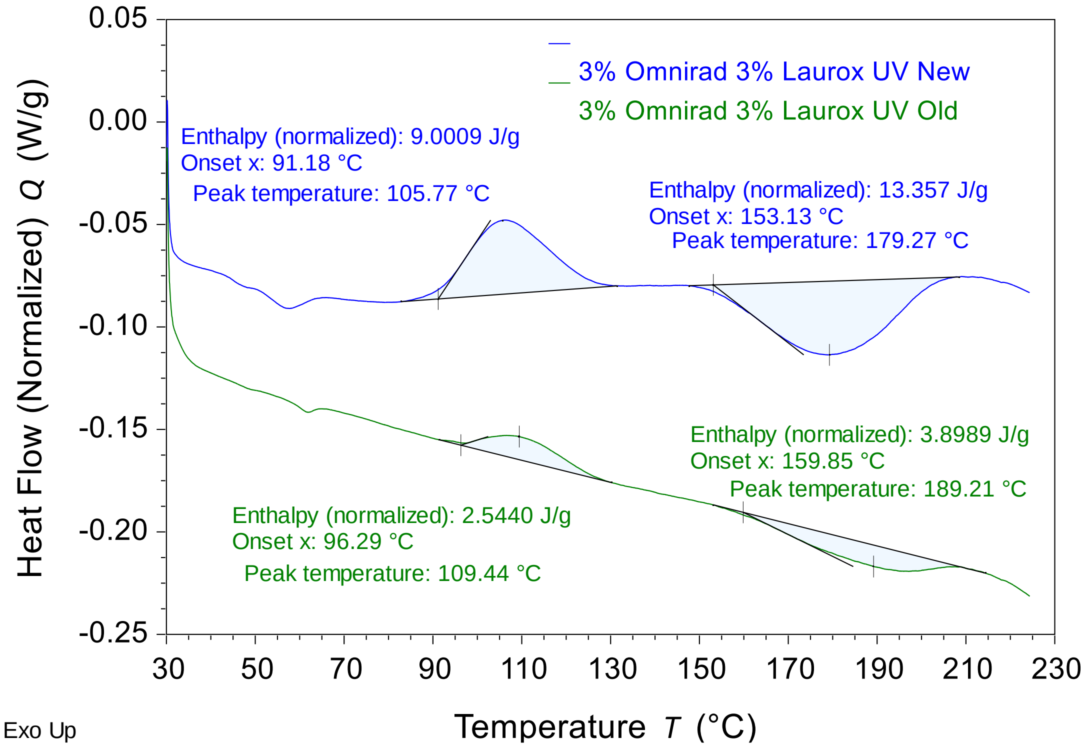

Figure 4: A DSC curve comparing the Old UV lamp setup (S5064) and the new UV lamp setup (PIZHLO). Both samples use 3% Omnirad/3% Laurox.

The DSC thermograms show decreased enthalpy of reaction (exotherms centered at ~100 °C) for the S5064 UV lamp sample vs the PIZHLO UV lamp sample. Similarly, there is a decrease in the enthalpy of vaporization (endotherms centered at ~185 °C) for the S5064 UV sample vs the PIZHLO UV lamp sample. The larger enthalpy values from the PIZHLO UV lamp sample suggests that more MMA monomer remains in the sample (greater endotherm) and that a greater extent of reaction is needed from the thermal initiator, Laurox (exotherm), indicating the PIZHLO UV lamps produced a less polymerized skin than the S5064 lamp. Thus, all further development will utilize the S5064 lamp moving forward.

Thermogravimetric Analysis (TGA)

TGA was conducted to determine the degradation onset temperature of each polymerized system (photoinitiated and thermally initiated). Three initiators were tested using multiple preparation methods. Two photo-initiators were used, Omnirad and PL-032. One thermal initiator was used, the peroxide,

Initial tests targeted understanding the impact of UV photoinitiators under static UV illumination versus pulling a composite sample under a UV lamp (dynamic), simulating pull rates of the WWU lab-scale treater. These tests were performed using 3 wt% Omnirad and 3 wt% PL-032 with UV exposures of 3, 5, and 7 minutes as well as dynamic pull tests of 1, 2, and 3 inches per minute. The resin systems for these samples were homogenized using a speed mixer at 1000 rpm for 2min and all composite samples utilized the S5064 UV lamp.

Additionally, the thermal initiator, Laurox, was tested. The concentration of Laurox was varied between 1 wt% and 3 wt% with a constant concentration of Omnirad photoinitiator of 3 wt%. Two different UV lamp systems were utilized, the S5064 and the PIZHLO.

The results of degradation onset temperature from the above samples are listed in Table 3. The degradation onset temperatures of the samples range from 241.53 °C to 255.76 °C. The average onset temperature was 250.14 ± 4.02 °C.

The TGA results suggest that the initiator type does not significantly impact the degradation temperature of the polymerized PMMA.

Table 3: Degradation onset temperatures (°C) recorded for each initiator.

	Omnirad	*PL032*	*Omnirad 1% Laurox*	*Omnirad 3% Laurox*
Static 3 min	244.36	251.32		
Static 5 min	253.36	254.14		
Static 7 min	253.40	250.70		
Dynamic 1 in/min	246.57	243.04		
Dynamic 2 in/min		241.53		
Dynamic 3 in/min		249.06		
PIZHLO UV	248.76	252.41	249.57	250.54
S5064 UV	248.83	255.76	254.76	254.36

Bench Scale Simulation of Treater

A small-scale version of WWU's prepreg treater was created to simulate PMMA composite production and further determine the initial process parameters when scaling up. Some of the parameters include pinch roller spacing and feed rate. This bench-scale simulation of the treater is also referred to as the mini treater. Figure 5 shows an annotated photograph of the mini treater. The process for producing an Elium/fiberglass prepreg is as follows:

- The fiberglass is soaked in an Elium resin bath (Left Figure 5, red arrow).
- The soaked fiberglass is pulled through the pasta roller, simulating pinch/consolidation rollers, to get a homogeneous distribution of resin into the fiber.
- Poly-film is added to the bottom of the soaked fiberglass to prevent contamination of the surface inside the fume hood (Middle Figure 5).
- The soaked fiberglass with poly-film on the bottom is pulled through a UV lamp setup (S5064) which polymerizes the skin of the laminate (purple arrow).
- The prepreg is rolled after it is pulled through the UV lamp setup.

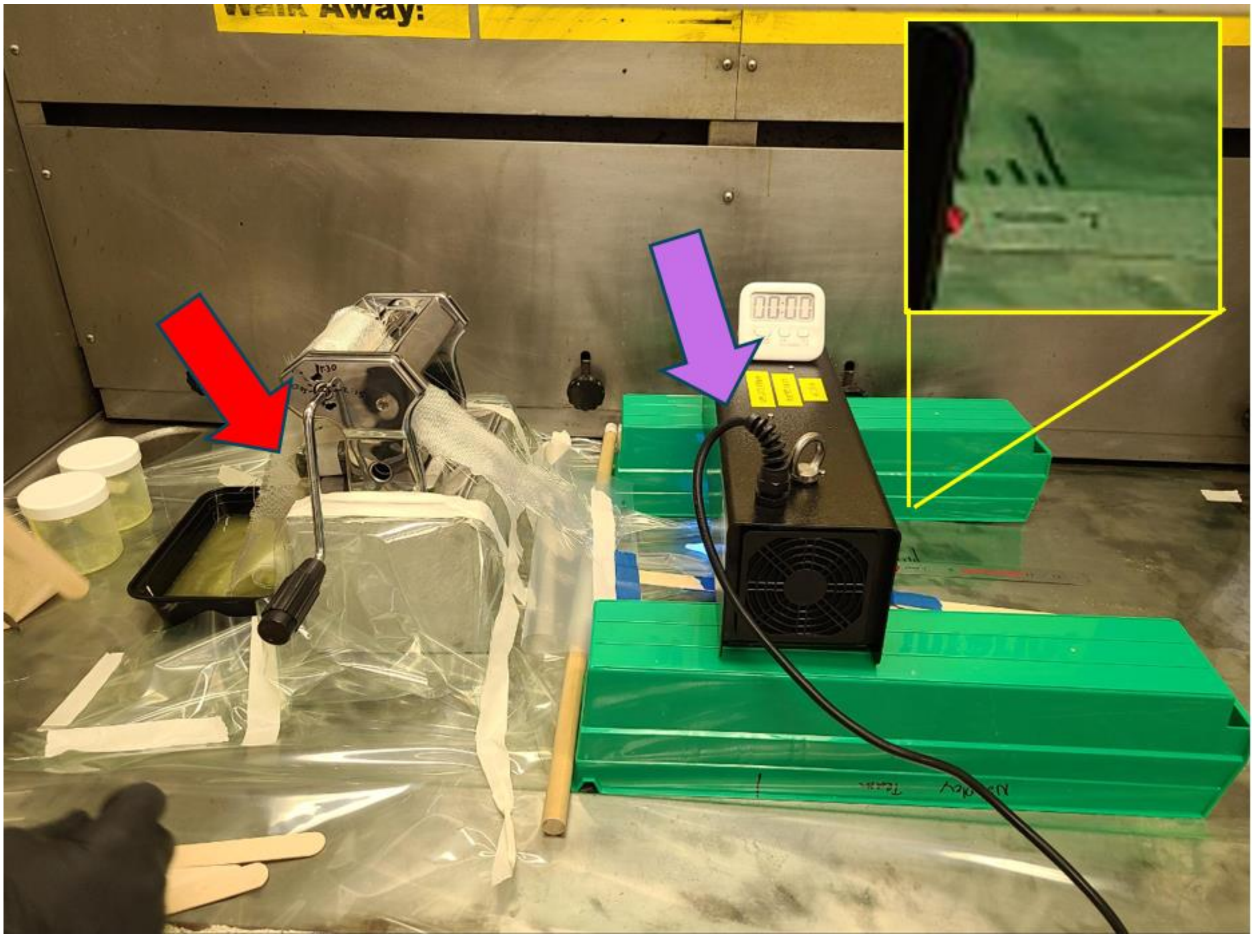

Figure 5: Bench-scale simulation of the WWU treater. The red arrow indicates the resin bath & pasta roller, the purple arrow indicates the UV lamp, and the yellow box indicates the spaced hashmarks for accurate feed rate.

Fiber feed rates were tested on the mini treater. A 1 in/min and a 3 in/min feed rate were tested. The 3 in/min feed rate was too fast to provide sufficient UV exposure to polymerize a skin. To ensure the minimum feed rate of the WWU treater would yield a sufficient UV polymerized skin, a pull rate of 1 in/min was used. This proved successful, therefore a feed rate of 1 in/min will be attempted initially when scaling up the process to the WWU treater.

A pinch roller spacing of 0.012 in was selected because it did not leave the fiber dry or overly saturated with resin. Thermogravimetric analysis was performed on the samples manufactured with the 0.012 in pinch roller spacing to determine the fiber to resin ratio. Norplex recommended a target resin content of 38-42%. The TGA of these samples is shown in Figure 6. The data demonstrates a fiber content of 38% by weight, as indicated by the high temperature plateau after degradation. A pinch roller spacing of 0.012 in will be used with the WWU treater as a starting point to produce a resin content of 38%.

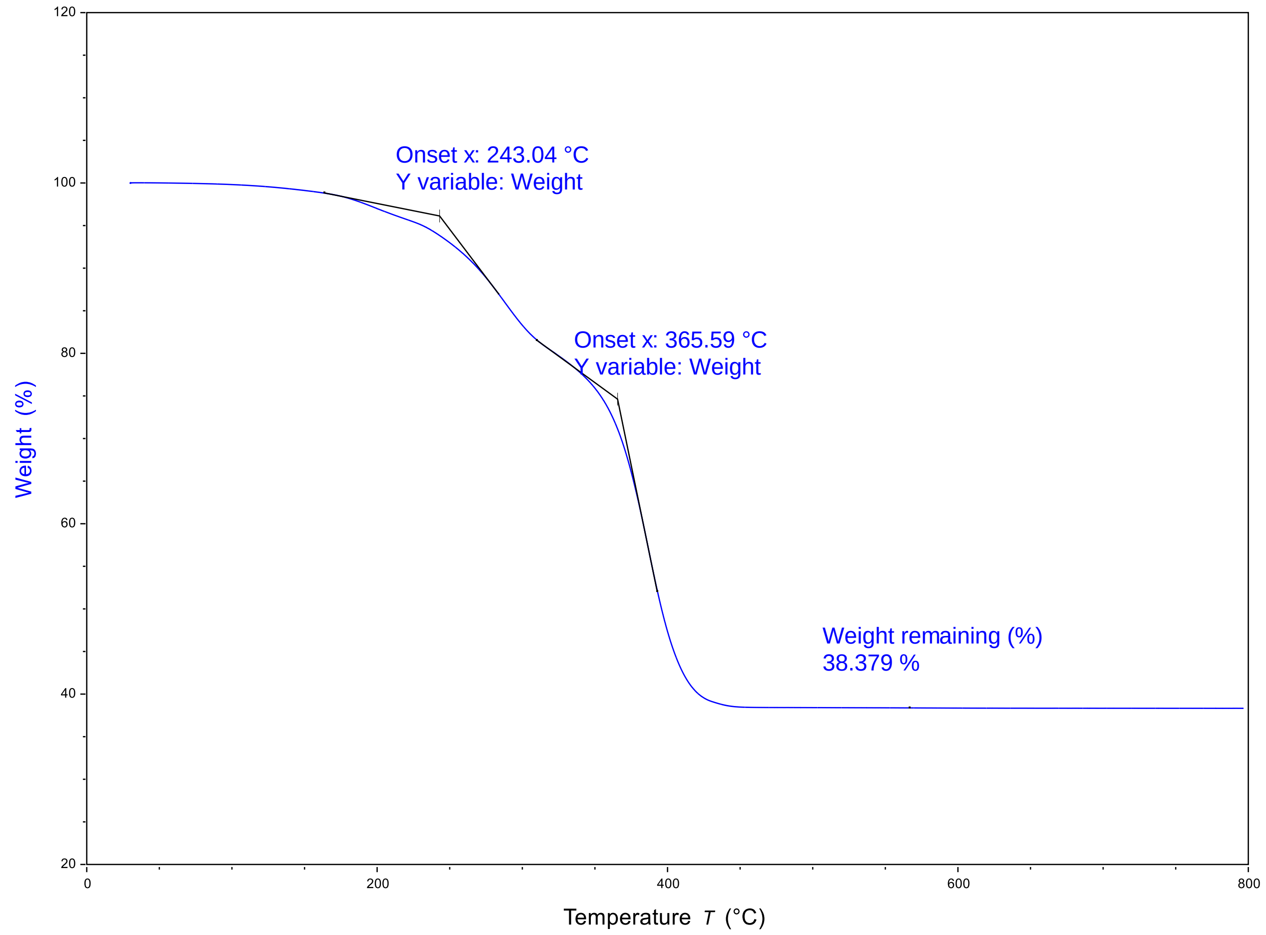

Figure 6: TGA performed on 0.012 in pinch roller spacing sample. Test was performed in N_2 to degrade PMMA but leave behind glass fibers.

Photoinitiator Selection

As previously mentioned, utilizing a photoinitiator with our Elium resin system allows for polymerization of a skin on the prepreg, reducing MMA volatilization. Two different photoinitiators were used, Omnirad 819 and PL-032. Figure 7 shows a DSC thermogram of a PL-032 photoinitiated Elium/fiberglass sample. On the first heat (blue line) an endothermic region was observed between 47-70 °C. This is melting of the photoinitiator and evaporation of residual MMA. T_g can be seen in the second heat (green line) at 96.69 °C, confirming polymerization of Elium MMA into PMMA.

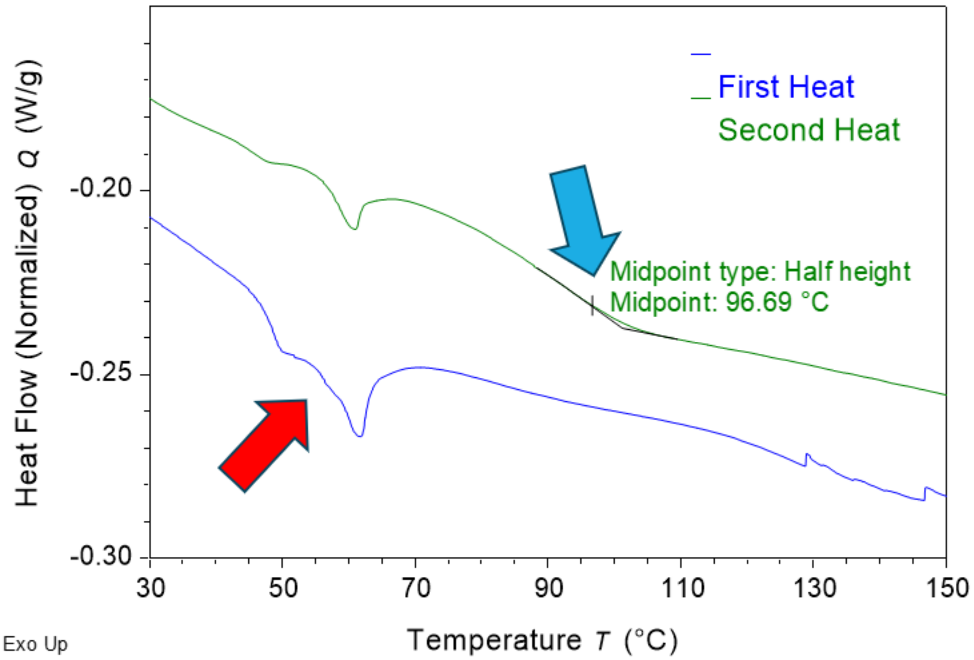

Figure 7: DSC of PL-032/Elium at a static 3-minute UV exposure time. The red arrow highlights the region where melting of the photo-initiator and volatilization of MMA monomer is present. The blue arrow highlights the T_g of the PMMA skin on the composite.

Figure 8 shows a comparison of Omnirad-819 and PL-032 photoinitiated Elium/Fiberglass samples. The 40-100 °C endotherm region is highlighted to demonstrate the difference in enthalpies. Both Omnirad and PL-032 samples show there is melting of residual photoinitiator and volatilization of MMA. However, Omnirad has a lower total enthalpy of 0.396 J /g versus PL-032's enthalpy of 1.054 J/g. The decreased enthalpy in the Omnirad sample suggests that more MMA was instantiated into polymer chains than that of the PL-032 sample. As more MMA is polymerized into a PMMA skin, less monomer remains, reducing the endothermic vaporization. These results indicate that Omnirad was a more effective photoinitiator for creating a PMMA skin on the composite samples and was chosen as the preferred photoinitiator.

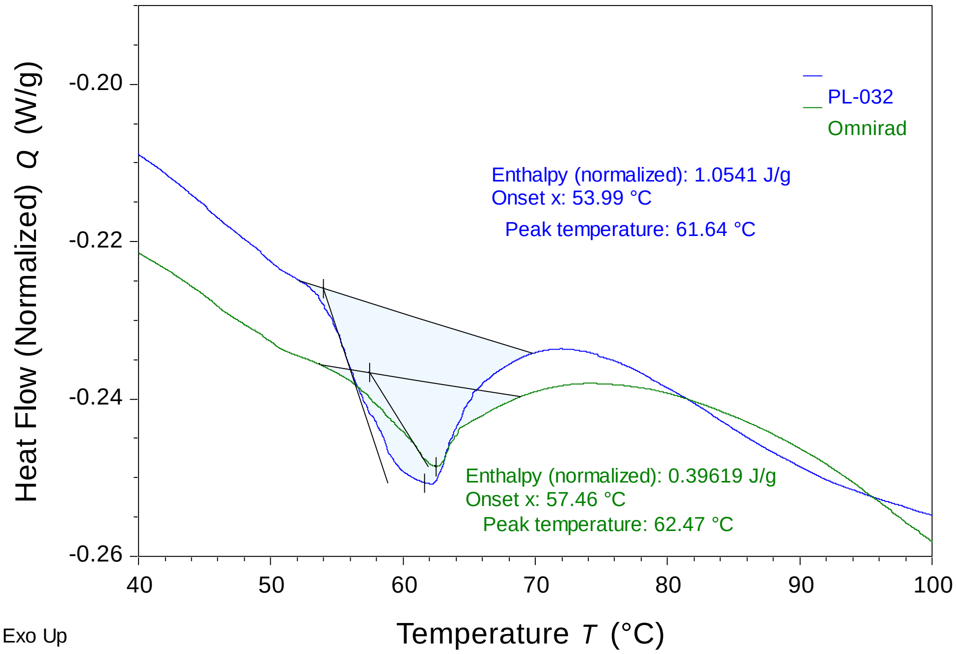

Figure 8: Overlay of DSC experiment portion of the first heat between Omnirad and PL-032 3% by weight.

Thermal Initiator Selection/Implementation

Residual MMA seen in the thermograms from photoinitiator testing indicated that an additional polymerization was needed. The thermal initiator, Laurox was selected for its compatibility with polymerizing the Elium MMA resin system and its relatively high self-accelerating decomposition temperature (SADT) of 50 °C [3]. The high SADT of Laurox reduced the risk of improper handling and increased overall lab safety at WWU.

DSC was performed to study the glass transition temperature (T_g), melt temperature (T_m), and qualitative degree of polymerization of the PMMA matrix. Each sample was run through a heat-cool-heat cycle with a 4 °C/min ramp rate from 25 °C - 225 °C. Figure 9 shows an Elium sample that was prepared with 3 wt% Omnirad photoinitiator, 3 wt% Laurox thermal initiator and subjected to the S5064 UV lamp for 3 minutes to polymerize an MMA skin.

The first heat (blue) in Figure 9 displays a small endothermic event at 40 °C, likely the melting of unreacted Omnirad photoinitiator. An exothermic event occurs between 65 °C and 120 °C. This is the exothermic polymerization of unreacted MMA and the Laurox thermal initiator.

The T_g of the sample is obscured by the polymerization event in the first heat, which was expected to occur around 100 °C. The T_g of the sample was determined during the cooling step (green) and second heat (red). T_g was found to be 91.67 °C, and 94.91 °C respectively.

The next sample tested used the same resin system as the first sample previously described, however it was placed in an oven at 80 ºC for 27 minutes after UV skin formation to polymerize the unreacted MMA. The heat exposure of 27 minutes was selected from the mini treater determined feed rate of 1 in/min and the 27-inch long oven available on the WWU treater.

From the DSC thermogram of the 80 °C sample (Figure 10), a smaller exotherm was observed in the first heat (blue). This indicates that the addition of a heating step in the sample preparation process increased polymerization of the Elium initiated by Laurox as less residual monomer remained to react. The T_g for this sample was determined to be 92.04 °C from the cooling step (green) and 90.65 °C from the second heat (red).

The third sample was prepared identically to the second, however it was heated at 100 °C for 27 minutes. The DSC thermogram shown in Figure 11 displays a smaller exotherm starting at 65.97 °C in the first heat (blue). The T_g determined from the cooling step (green) was 95.04 °C and 94.84 °C for the second heat (red). The total enthalpy for the 100 °C heated sample from the exothermic polymerization that occurs on the first heat is nearly 10x less than the total enthalpy of the exotherm in the 80 °C sample. This suggests that the 100 °C, 27-minute heat step, is more effective in fully polymerizing the remaining MMA after UV exposure/skin formation.

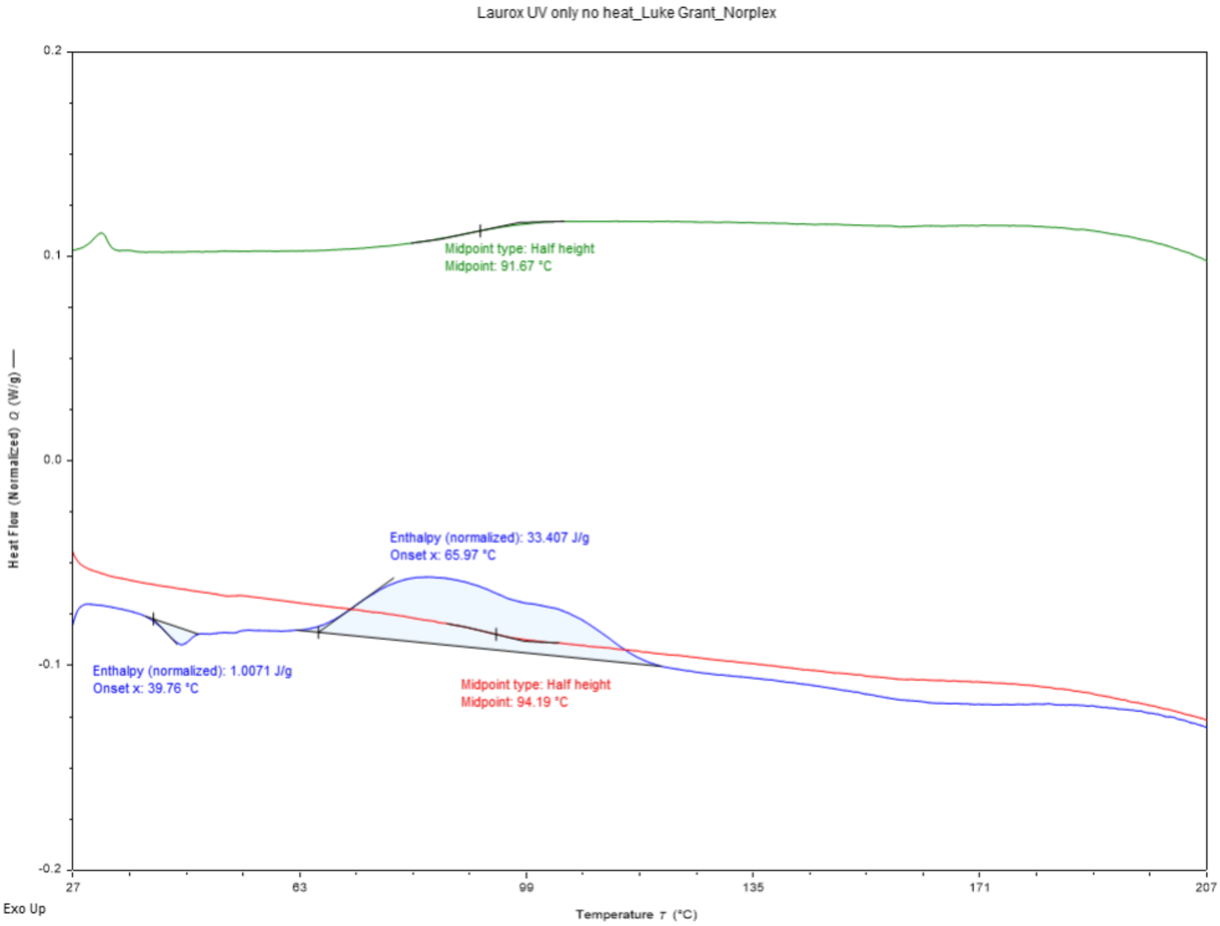

Figure 9: DSC thermogram of PMMA with 3% Omnirad and 3% Laurox after UV skin polymerization, without a heating cycle.

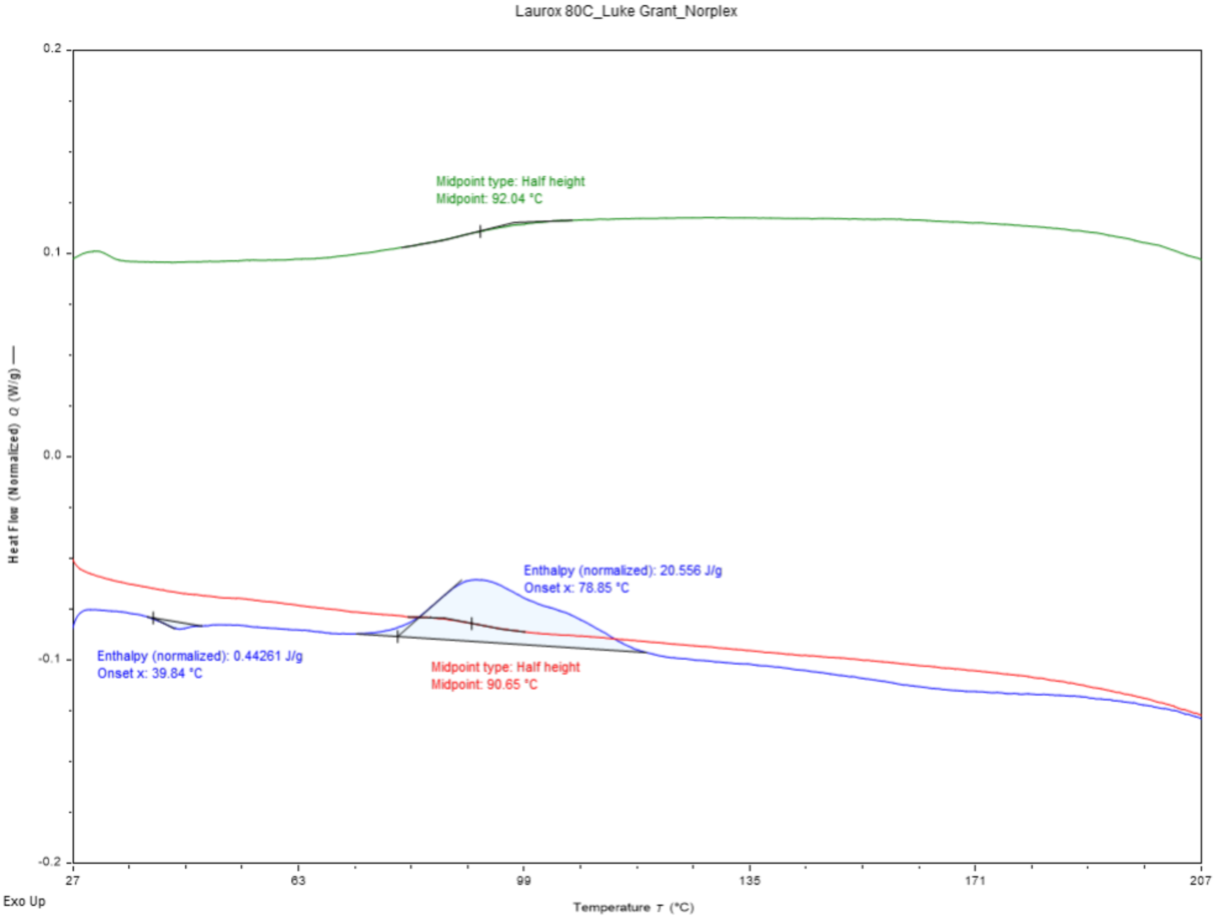

Figure 10: DSC thermogram of PMMA with 3% Omnirad and 3% Laurox after UV skin polymerization, heated to 80 °C for 27 minutes.

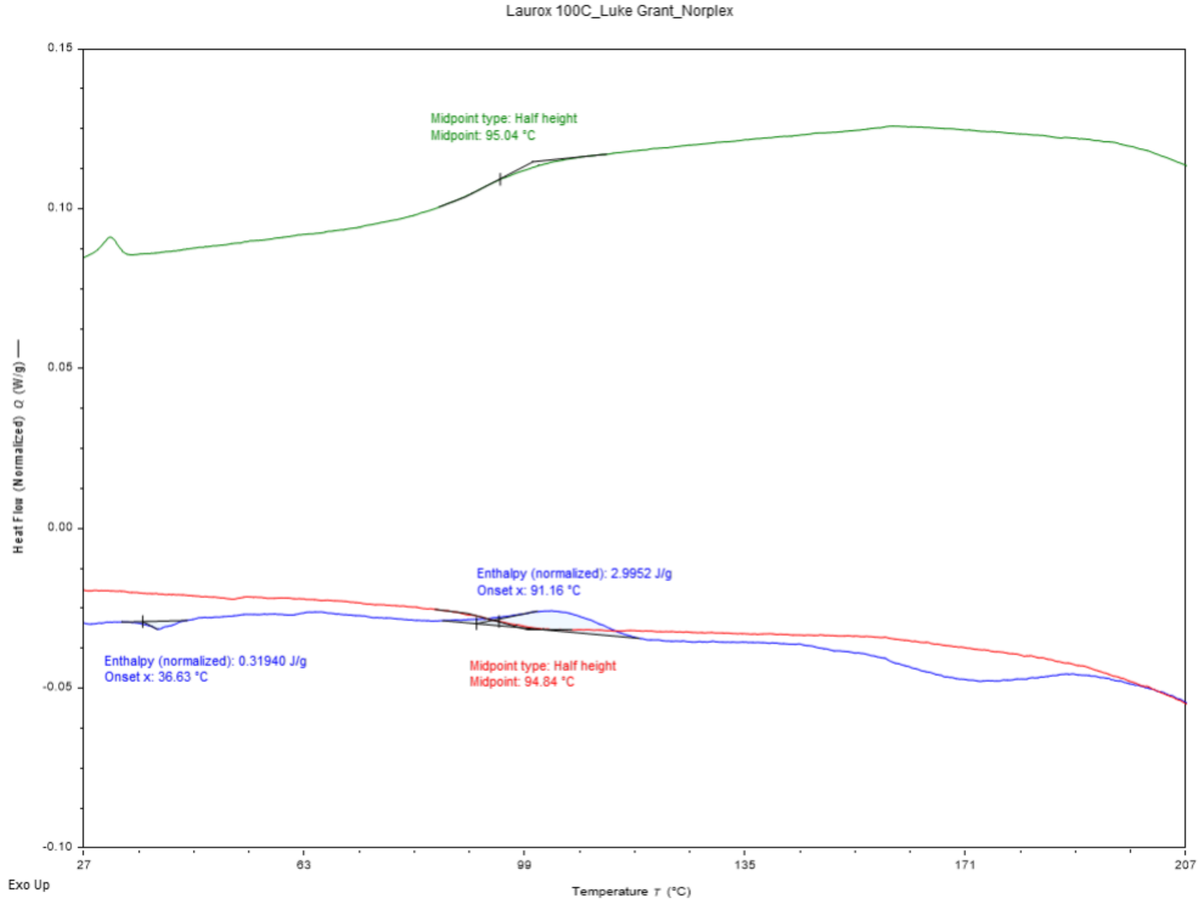

Figure 11: DSC thermogram of PMMA with 3% Omnirad and 3% Laurox after UV skin polymerization, heated to 100 °C for 27 minutes.

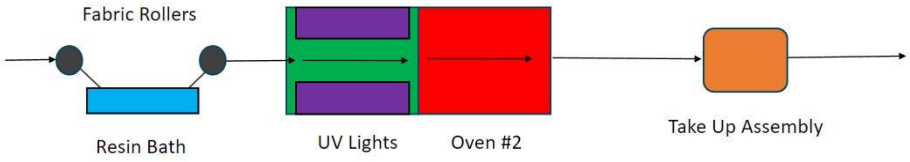

Figure 12: WWU Lab-Scale Treater, Modification Option 1

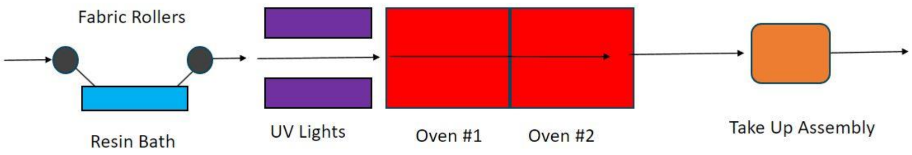

Figure 13: WWU Lab-Scale Treater, Modification Option 2

After modifications are made to the treater, the team will conduct preliminary prepreg manufacture on the WWU treater. The results from the Fall Quarter work will be implemented as initial treater parameters. As prepreg is fabricated from the treater, material characterization will be preformed which will include resin content, resin flow, tensile, compression, short beam shear, and impact testing.

Conclusion

The WWU research team had four major decision points over Fall quarter. First was determining if applying poly-film or a photoinitiated PMMA skin was more effective at preventing MMA volatilization. Second was identifying the most effective photoinitiator and UV lamp setup for producing a PMMA skin. Third was selecting a pinch roller spacing that yields a 60:40 fiber to resin ratio. Fourth, was determining the concentration of thermal peroxide (Laurox) and oven temperature that produced reacted/polymerized PMMA matrix. In addition, the team has planned to begin treater testing next quarter with option #1 for the UV lamp configuration. These will require an additional S5064 UV lamp and mounting them inside oven #1. The key takeaways from the research conducted during Fall Quarter are as follows:

- The UV photoinitiated/polymerized skin was effective at preventing MMA volatilization
- The S5064 UV lamp was most effective at reducing MMA volatilization via skin formation
- Omnirad photoinitiated more MMA to PMMA
- The optimal feed rate for UV exposure was 1 in/min
- The pinch roller spacing to produce a fiber to resin ratio of 60:40 was 0.012 in.
- A peroxide thermal initiator (Laurox) was required to polymerize residual MMA after sample UV exposure
- The processing temperature most effective at polymerizing MMA in the 27 min time constraint (1 in/min feed rate) using Laurox was 100 °C.
- Option #1 selected as initial UV lamp configuration for WWU lab-scale treater

References

[1] N. Larson *et al.*, “Developing a Lab Scale Solvent-Based Prepreg Treater,” Western Washington University, Bellingham, WA, Jun. 2015.

[2] Poly(methyl methacrylate) Sigma Aldrich, www.sigmaaldrich.com. https://www.sigmaaldrich.cn/CN/product/aldrich/182230 (accessed Dec. 12, 2023).

[3] Nouryon. Laurox Product Data Sheet. http://www.nouryon.com. June 7, 2022.

Appendix (Task 2)

Procedures

Individual Sample Preparation

Sample preparation included mixing the resin and stippling the resin mixture onto 4”x 4” poly-film-backed fiberglass sheets. The resin mixture was weighed and mixed in a speed mixer at 1000 rpm for 2 minutes. Each poly-film backing was labeled according to the sample parameters. Samples were stored in zip-lock bags after samples were processed.

Individual Sample Description

A static test exposed the entire sample to UV radiation for a given time limit. The time limits were 3, 5, and 7 minutes. A dynamic test comprised of manually pulling the sample under UV illumination at an estimated rate. These rates were 0.5 and 1 inch per minute. A scale of ¼” hash marks and a timer were used to estimate the pull rate.

Mini-Teater Procedure

A small pasta roller, bath, and UV light apparatus simulated the WWU prepreg treater. The bath mixture was mixed in the speed mixer following the same procedure as in the sample preparation section. To collect the sample, a bottom poly-film layer (used as a manual transport mechanism) was rolled onto a wooden dowel and pulled along with the wet fiberglass through the UV light source. The pinch rollers were set to a 0.012” spacing, and tension was maintained by pulling the fiberglass-poly-film combination by hand. A timer was used to estimate the pull rate and UV light exposure as the fiberglass-resin mixture was drawn through the pinch rollers.

Task 3: Pilot Scale Coating of Natural Fibers with Elium Resin

Objective

Western Washington University partnered with Norplex and Arkema to develop a thermoplastic prepreg using a poly methyl methacrylate (PMMA) matrix. The main goal for Winter Quarter 2024 was to examine and determine the process parameters to manufacture the PMMA-based, flax-fiber composite, using Western's lab-scale prepreg treater (Figure 1). The period for this quarter ranged from January 2024 to March 2024.

Prepreg Treater Modifications

The prepreg treater underwent several modifications this quarter to facilitate the manufacturing of the thermoplastic prepreg material. The team carried out two major changes to the prepreg treater. Both modifications were justified from testing results and observations during the fall quarter. All modifications to the treater system were done in a reversable fashion. The team wanted the ability to reconfigure the lab-scale treater to its original configuration.

The first modification that the team completed was mounting the top and bottom UV lights, see Figure 3. Framing rails and brackets were used to mount the UV lights in front of the resin bath to decrease the length between pinch rollers and UV lights. The goal of the top and bottom UV lights was to evenly polymerize a photo-initiated skin on the prepreg. This was an attempt to effectively trap monomer volatiles during the thermal polymerization process to better control the resin-to-fiber ratio of a prepreg sample.

The second modification that the team completed was reconfiguring the prepreg take-up assembly, see Figure 3. The take-up assembly required converting from a thermoset prepreg configuration to a thermoplastic configuration. Poly-film sheets were not needed with the thermoplastic prepreg manufacturing process, and so the poly-film roller assembly was removed from the treater system, see Figure 1. The speed and tension control of the treater system were initially omitted due to the unknown malleability that a manufactured prepreg sample would have.

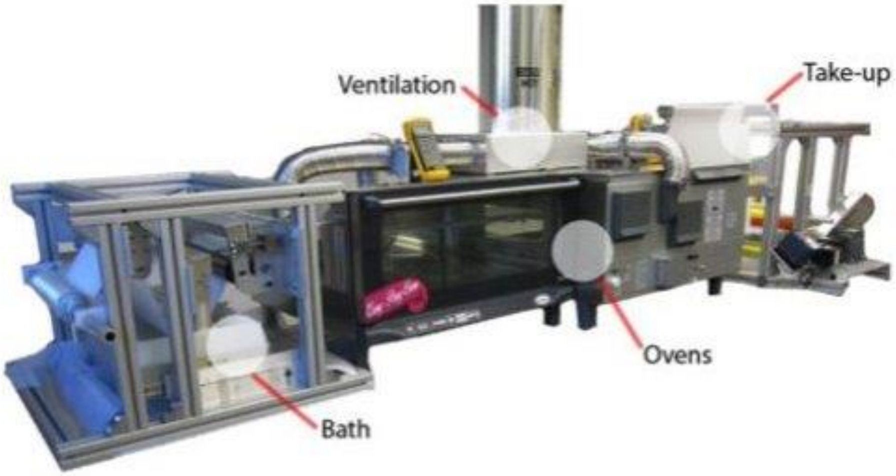

Figure 1. Prepreg Treater used in WWU’s Polymer Materials Engineering lab.

Figure 2. Simple 2D diagram of Treater Configuration for Thermosets.

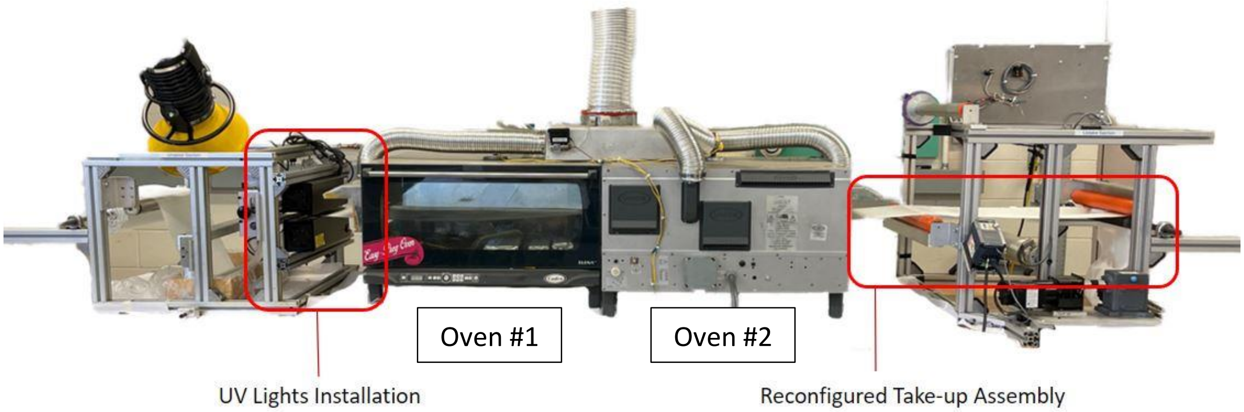

Figure 3. Prepreg treater modified for first lab-scale run.

Treater Run #1

Treater Modifications

Before the first lab-scale treater run, it was expected that the polymerized prepreg would be too stiff to be spooled in the take-up section. To combat this, the take-up spool was replaced with two conveying rollers to pull the prepreg sheet through the treater (Figure 4). The bottom roller was linked to the spool drive motor so speed control could still be used, the top roller (free spinning) was pushed against the drive roller to convey material. The assumption of the prepreg stiffness to also led to the omission of the tension roller for this initial run. For the treater system to operate, the speed signal must be functional. To maintain the function of the speed controller and signal, rubber belts were run from the drive roller to a rotary encoder roller, visible in Figure 4 below.

Figure 4. Conveying rollers installed on the take-up section of treater.

Two identical ultraviolet lights were mounted in front of the pinch rollers to activate the photo-initiator and form a skin on each side of the prepreg fabric before entering the ovens (Figure 5). These lights were initially positioned as close to the fabric as possible to maximize light intensity, however the bottom light ended up being positioned farther away from the fabric due to drooping and fluttering from the convection oven.

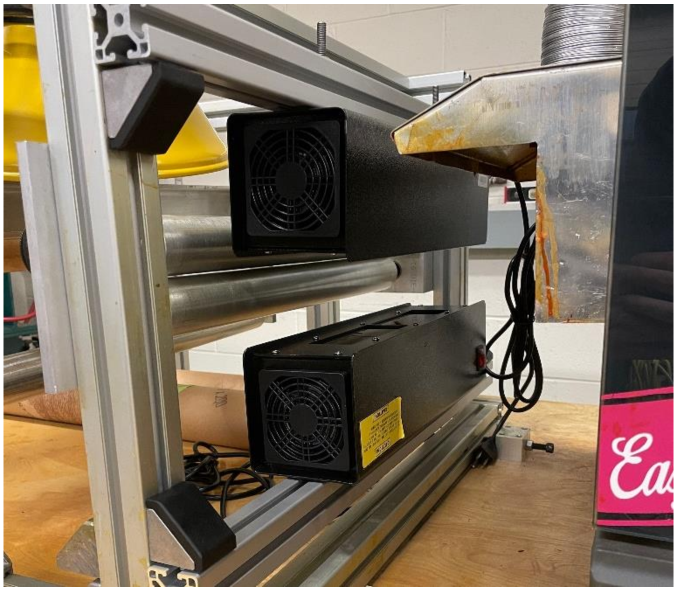

Figure 5. UV lights mounted next to pinch rollers.

Operating Parameters

Table 1. Operating parameters for treater run #1.

Resin	C595 Elium (3.808 kg) 3% Laurox Peroxide (115g) 3% PL32 Photo-initiator (115g)
Fabric	Fiberglass
Feed Rate	1.4 ipm, 6.5 ipm
Pinch Roller Spacing	0.012” (0.025” by end of run)
UV Light Spacing	0.5” from top 1.5” from bottom
Fabric Tension	Tensioner not used
Oven Use	Oven #2 (100 °C)

Results and Discussion

The goal of this initial run was to determine baseline processing parameters on the lab-scale treater. While the fiberglass plain weave fabric was not entirely representative of the flax fiber, the team was able to familiarize themselves with the operation of the treater and practice manufacturing techniques for future runs. Below is a summary of the successes and issues faced during the first treater run.

Pros

- MMA is mostly polymerized before entering oven
- Polymerized prepreg flexible enough to be rolled
- Ventilation worked (no volatile or explosive hazard)

Cons

- Significant gumming of resin on pinch rollers and dip roller
- Peroxide not dissolved into resin
- Tension control not possible without spooling on take-up
- Resin content very low
- Uneven photo-initiation due to UV light pattern

During the run, the team noticed significant gumming of Elium resin on the pinch rollers, which continued to build up for the duration of the run. The resin became thick and tacky across the width of the rollers, with the consistency of rubber cement. It was noted that the gummed resin had a yellow hue, matching the color of the polymerized prepreg. For this reason, it was suspected that UV light bleed was causing the photo-initiator to polymerize the resin on the surface of the pinch rollers during production. An example of this can be seen in figure 6 below, note that this photo was taken early in the run and does not represent the full extent of the gumming issue.

Figure 6. Resin gumming on pinch rollers.

It was also noticed that the projection pattern of the UV light fixtures left a strip of unexposed area at the middle of the fiberglass, shown in Figures 7 and 8 below. Thermal analysis of the discolored strip showed a very slight polymerization peak, however further testing would be required to confidently determine a difference in degree of polymerization.

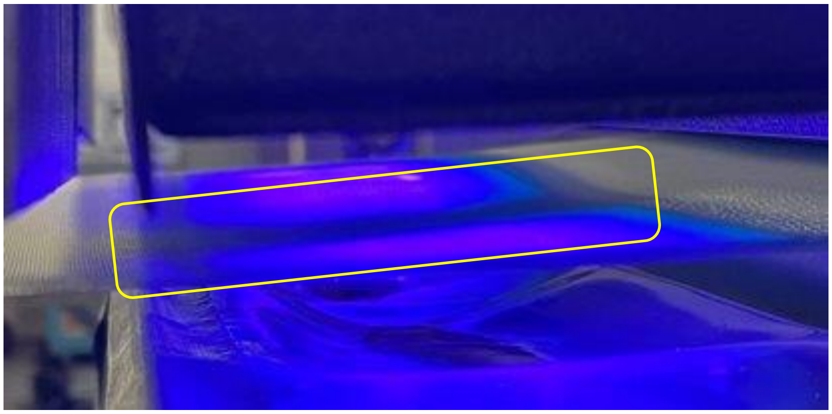

Figure 7. Unexposed area of fiberglass prepreg.

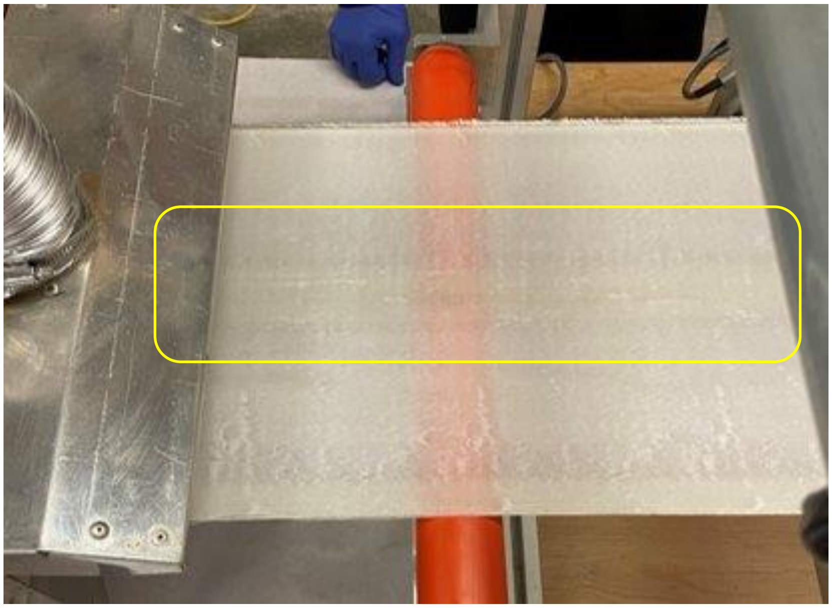

Figure 8. Corresponding unexposed strip of resin on fiberglass prepreg.

Thermal Analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were performed to study the resin wight % content and the degree of polymerization of the prepreg respectively.

For the first treater run, the TGA experiment was performed with the following parameters:

- Ramp rate: 50 °C/min to 700 °C
- Sample mass: 4.573 mg
- Pinch roller spacing: 0.012 “
- Feed rate: 1.4 ipm

The results of this experiment are provided in Figure 9 below. From this graph, it can be calculated that the resin content of this prepreg is 23.9 % resin.

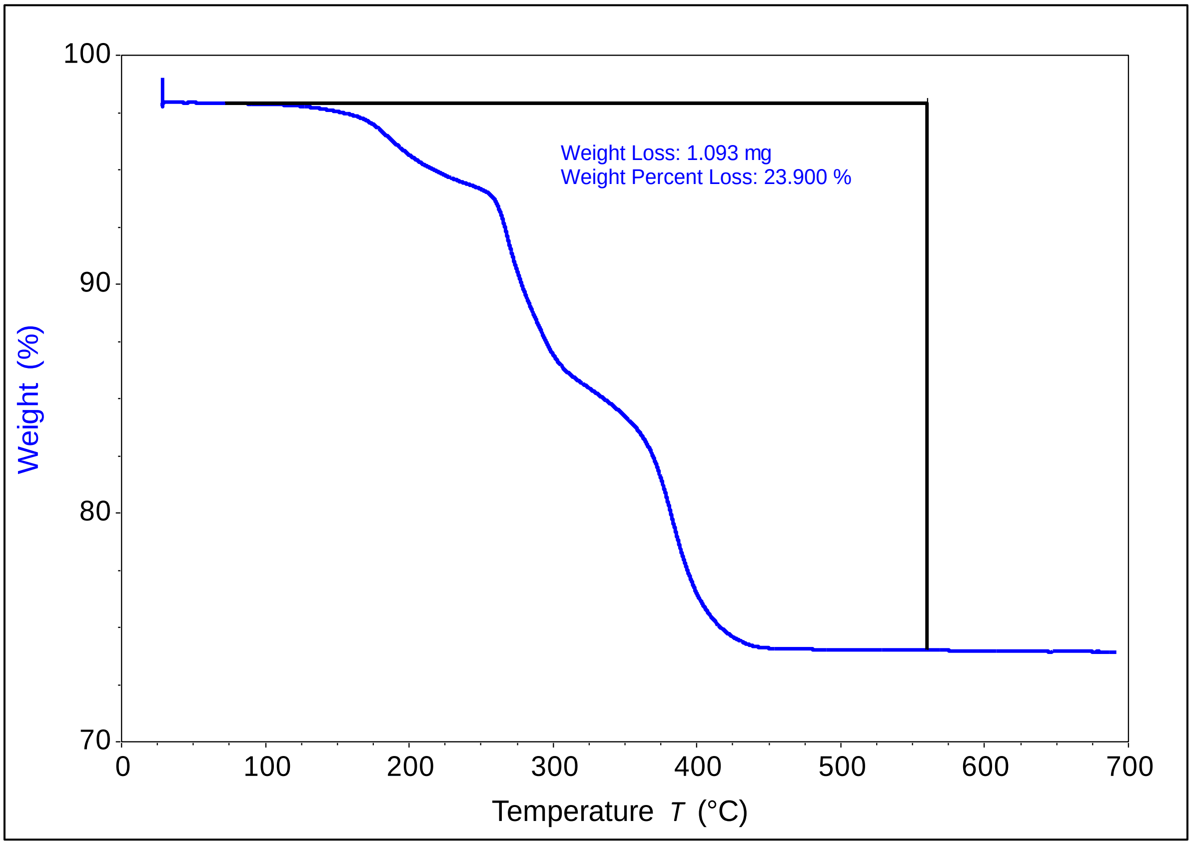

Figure 9. TGA curve from the center of the prepreg sheet.

A heat-cool-heat DSC experiment was performed on this material using the following parameters:

- Heat: 20 °C - 350 °C @ 5 °C/min
- Cool: 350 °C - 20 °C @ 5 °C/min
- Heat: 20 °C - 350 °C @ 5 °C/min
- Sample mass: 4.41 mg
- Pinch roller spacing: 0.012 “
- Feed rate: 6.4 ipm

The results of this experiment are provided in the thermogram in Figure 10. The most notable takeaways from this experiment are seen in the first heat (blue). There is no polymerization exothermic peak present in this sample, which suggests that the sample, which is taken after UV before the ovens, is fully polymerized. These results suggest that the UV or oven line is not needed for the current parameters of the treater. This thermogram is an example of the target thermogram that should be collected from properly polymerized prepreg.

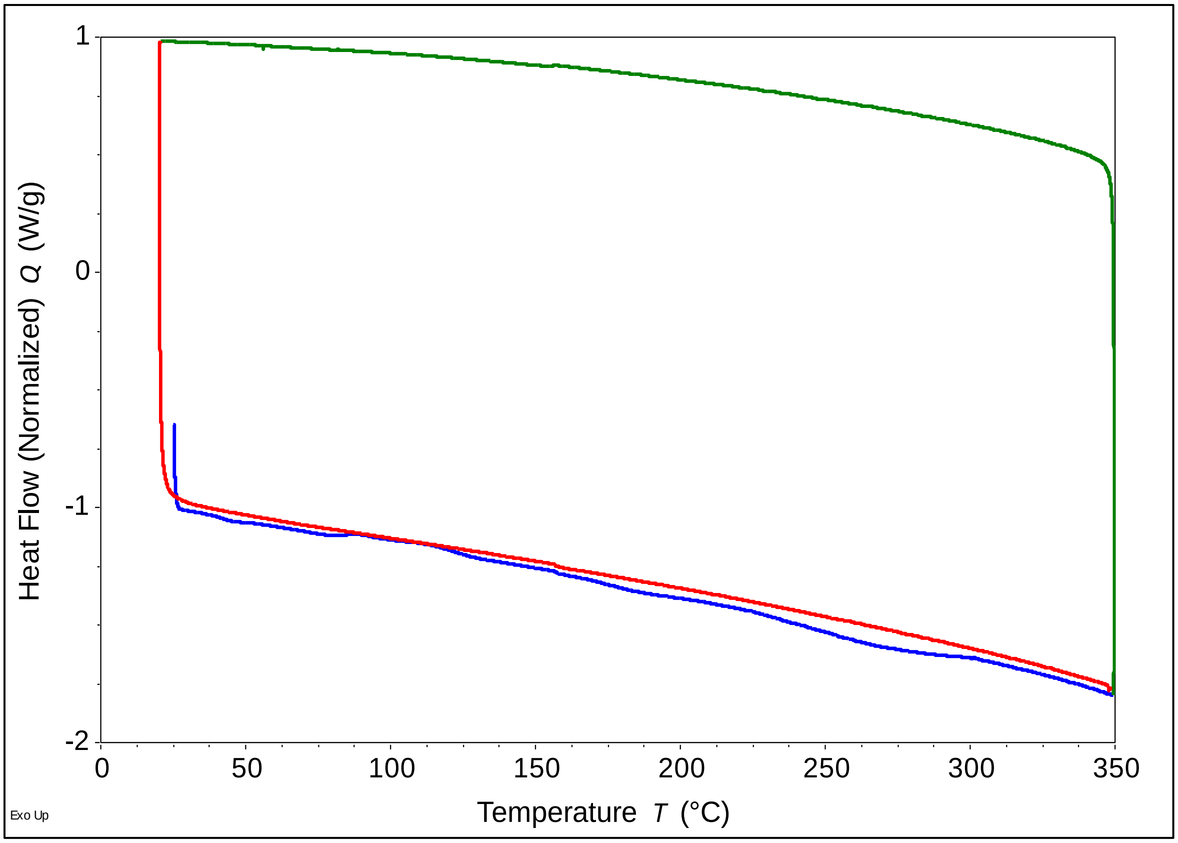

Figure 10. DSC thermogram of a sample taken before oven line in treater.

Treater Run #2

Treater Modifications

For treater run #2, the UV lights were evenly spaced between the fabric material. The distance from the light to the fabric was increased to 3 inches for both the top and bottom lights. The temporary speed control drive belts were removed, and the speed sensor roller assembly was repositioned (Figure 11). This allowed the team to control the speed more accurately. The take up-spool and tension control roller were also reinstated after it was determined that the thermoplastic prepreg was malleable enough to be spooled. To aid in cleanup of the pinch and dip rollers, PVA (polyvinyl alcohol) mold release was applied to the rollers. Finally, a UV light shield was fabricated and placed in front of the UV lights to limit light bleed onto the pinch rollers as an attempt at solving the gumming issue, see Figure 12 below.

Figure 11. Speed sensing roller and tension roller repositioned at take-up section

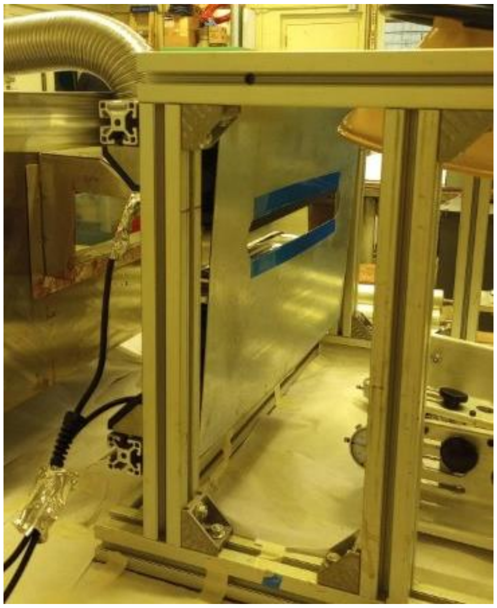

Figure 12. UV light shield installed next to light fixture.

Operating Parameters

Table 2. Operating parameters for treater run #2.

Resin	C595 Elium (3.822 kg) 3% Laurox Peroxide (115g) 3% PL32 Photo-initiator (115g)
Fabric	Fiberglass
Feed Rate	9 ipm

Pinch Roller Spacing	0.018” (0.015” by end of run)
UV Light Spacing	3.0” from top 3.0” from bottom
Fabric Tension	6 lbf
Oven Use	Oven #2 (100 °C)

Results and Discussion

One of the goals for this run was to test the effectiveness of UV light shielding at preventing gumming on the pinch rollers. Another goal was increasing the resin content of the fiberglass prepreg by increasing the pinch roller spacing. With the speed control operational, the team more accurately controlled the federate of prepreg through the treater. The tensioning system ensured that a consistent tension was applied to the prepreg fabric regardless of rolling resistance through the pinch rollers.

Pros	Cons
• Speed control more accurate with take-up spooling	• Excessive gumming of resin on pinch rollers due to UV light bleed and PVA mold release
• Tension control possible	• Peroxide not fully dissolved into resin
• Resin bath liner expedited cleanup	• Did not achieve 40% resin to fiber ratio

The additional space between the UV light fixtures and coated fabric did not significantly improve the polymerization pattern on the prepreg, leaving a line of discolored resin along the middle of the prepreg. The issue of resin gumming on the pinch rollers was not eliminated by the addition of a light shield. It is suspected that the small amount of intense UV light bleeding through the shielding is responsible for the photoinitiation of resin on the pinch rollers. This issue was worsened by the addition of PVA mold release on the pinch rollers, which peeled off the roller and mixed with the viscous resin.

Thermal Analysis

The second treater material was tested in TGA and DSC. For TGA, the following parameters were used:

- Ramp rate: 50 °C/min to 800 °C
- Sample mass: 4.100 mg
- Pinch roller spacing: 0.018 “

- Feed rate: 9 ipm

The results of this experiment are provided in Figure 13 below. From this graph, it can be calculated that the resin content of this prepreg is 19.3 % resin.

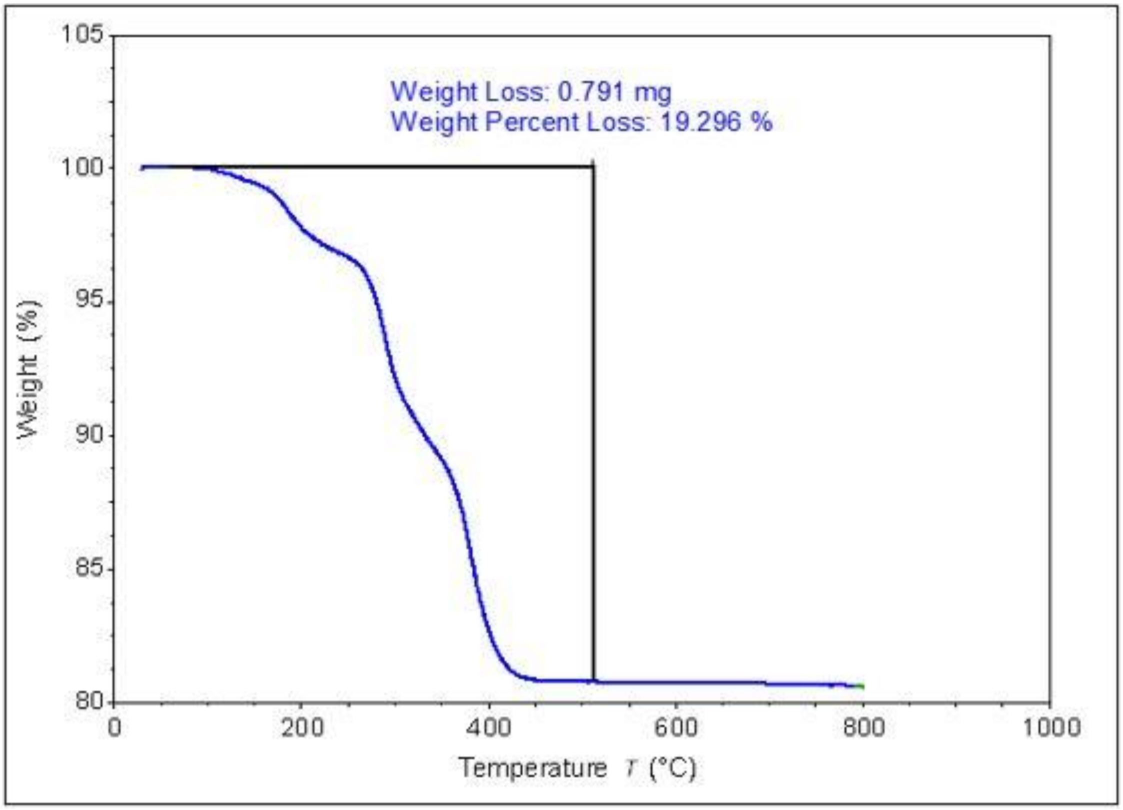

Figure 13. TGA curve from the center of the prepreg sheet.

A heat-cool-heat DSC experiment was performed on this material using the following parameters:

- Heat: 20 °C - 350 °C @ 5 °C/min
- Cool: 350 °C - 20 °C @ 5 °C/min
- Heat: 20 °C - 350 °C @ 5 °C/min
- Sample mass: 4.41 mg
- Pinch roller spacing: 0.018 “
- Feed rate: 9 ipm

The notable results of this experiment are provided in the thermogram in Figure 14. After the increase in UV lamp spacing, which was done to remove the streak in the middle of the prepreg, the material does not see full polymerization before or after the oven line. The reason for this is twofold: There is less energy entering the system from the UV lamps that are now farther away, which causes polymerization to start more slowly, and the increased federate to 9 ipm. This feed rate is fast enough that the time the material spends in the oven can be calculated to be (27 in oven)/(9 in/min) = 3 minutes in heat. This time is not sufficient to fully polymerize the resin in the prepreg, so a small polymerization exothermic peak is observed in the DSC thermogram. This peak will likely shrink over time as the polymerization that was initiated in the oven naturally completes under room temperature. These results suggest that the material requires a slower feed rate.

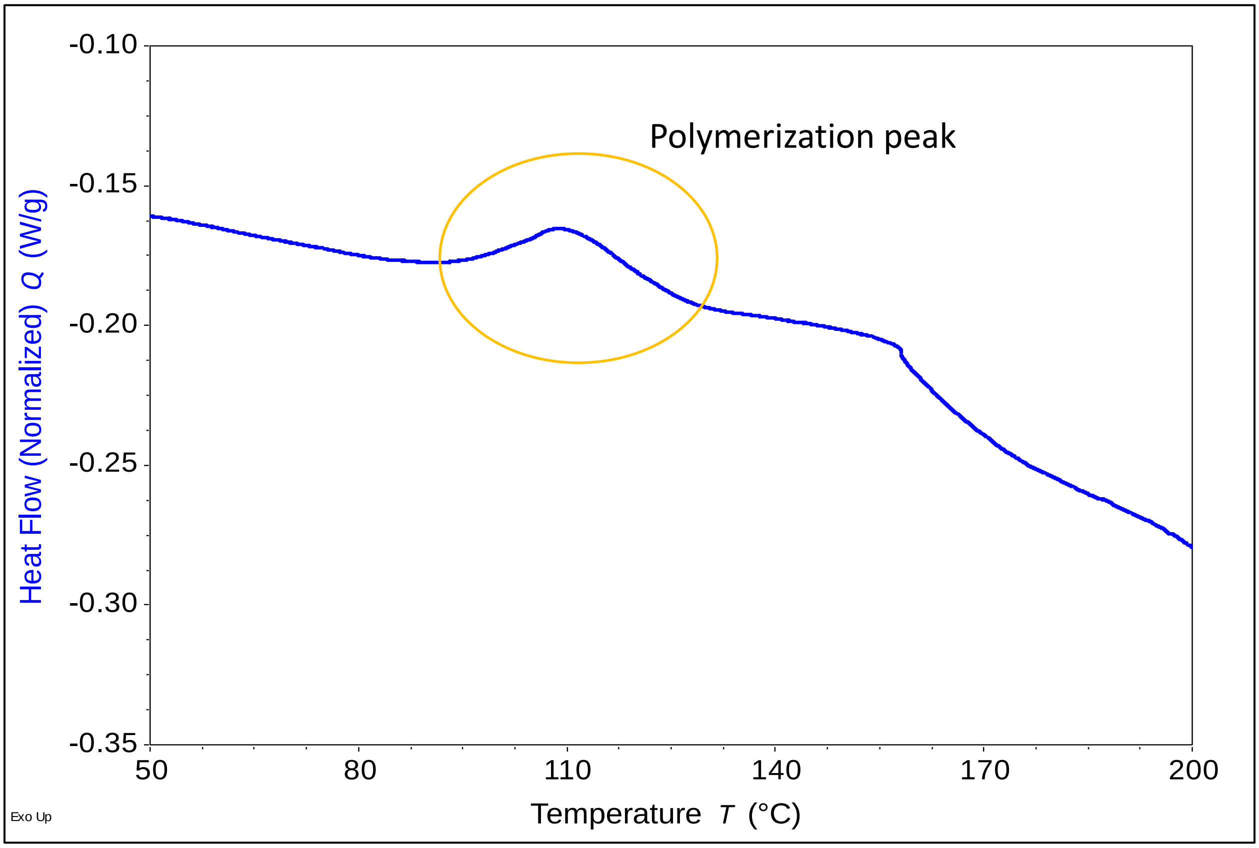

Figure 14. DSC first heat polymerization peak at 110 °C.

Treater Run #3

Treater Modifications

For treater run #3, the team decided to test for resin gumming by omitting the photo-initiator in the mixture. To ensure polymerization with only the thermal initiator in solution, the heat from oven #1 would be needed. The UV lights were removed due to the proximity with oven #1. This was done to mitigate any potential damage to the lights. No changes to the speed control, tension control and take-up assembly were made. No further modifications to the treater system were carried out during this run.

Operating Parameters

Table 3. Operating parameters for treater run #3.

Resin	C595 Elium (4.9 kg)

	3% Laurox Peroxide (150g)
Fabric	Flax plain weave fiber
Feed Rate	9 ipm
Pinch Roller Spacing	0.018” 0.025” (41% resin) 0.030” (52% resin)
UV Light Spacing	UV Lights omitted
Fabric Tension	6 lbf
Oven Use	Oven #1, Oven #2 (100 °C)

Results and Discussion

The primary goal of this treater run was to experiment with the use of flax fiber, and study how its higher absorption properties, compared to fiberglass, would affect the polymerization of the matrix and the resin weight content. The team found that a larger pinch roller spacing was required because the flax fibers are thicker than the fiberglass that was previously used, and because the flax fibers absorbed more resin. To avoid gumming the rollers, the team removed the use of UV photo initiator from the process and opted for only a thermally initiated matrix using both 27-inch ovens at 100 °C.

Pros

- Achieved 41% resin content
- Significantly less gumming on majority of pinch rollers – did not build up over time
- Prepreg mostly polymerized when conveyed at 6 in/min
- Prepreg successfully compression molded
- Prepreg mostly polymerized at 9 in/min

Cons

- Slight gumming on edges of fiber on pinch rollers
- Laurox Peroxide did not completely dissolve after 3 days of initial mixing

The flax fibers absorbed and retained resin very well, improving the overall resin weight content to 41 %. This is a success for the team to reach the target resin content of the prepreg. Additionally, the gumming that was previously seen on the pinch rollers was no longer present. This was achieved by the removal of photo initiator from the resin formula so the UV light would not bleed into the resin that is on the rollers, prematurely initiating polymerization, as well as the removal of PVA mold release (see Figure 15). The major challenge the team encountered with this treater run was that the Laurox peroxide did not dissolve fully into the resin mixture despite mixing three days prior to operating the treater. Because of the difficulty in mixing, the team will investigate alternative thermal initiators that dissolve more effectively in Elium.

Figure 15. Pinch rollers no longer exhibiting excessive gumming.

Aerial Weight Resin Content

Due to the thermal degradation temperature of flax fiber being lower than PMMA, the team was unable to determine the resin content through TGA or fiber burnout. To get around this issue, the team came up with a method to compare the aerial weight of the prepreg to that of dry flax fiber. A small (~1.25”) hexagonal stamping die was used to take an array of samples across the width of the dry flax fabric and prepreg material, shown in Figure 16 below. The average mass of samples cut from each material was used to calculate weight fraction of resin in the prepreg material, explained appendix procedure 1.

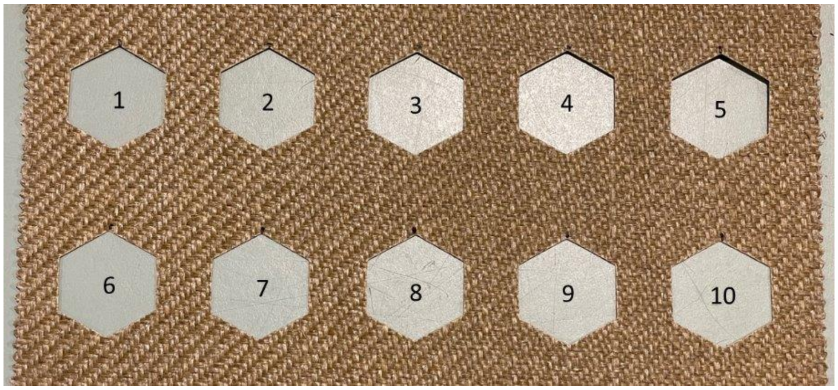

Figure 16. Die cut samples taken from flax fiber prepreg.

Table 4. Prepreg resin content by aerial weight.

Pinch Roller Spacing	Average Resin Content (%)	Standard Deviation (%)
0.025”	40.7	2.2
0.030”	52.5	2.6

Thermal Analysis

A heat-cool-heat DSC experiment was performed on this material using the following parameters:

- Heat: 25 °C - 200 °C @ 5 °C/min
- Cool: 200 °C - 25 °C @ 5 °C/min
- Heat: 25 °C - 200 °C @ 5 °C/min
- Sample mass: 5.64 mg
- Pinch roller spacing: 0.030 “
- Feed rate: 6 ipm

The notable results of this experiment are provided in the thermogram in Figure 17. It can be observed that there is a large endothermic peak at 95 °C, this is caused by evaporation of trapped moisture in the flax fibers that begins to boil off as the polymer matrix softens. Just after this peak, at 110 °C, there is a small polymerization peak that can be seen, which suggests that the material is still not fully polymerized by the end of the treater run. This may be caused by poorly dissolved Laurox thermal initiator or the removal of UV polymerization at the beginning of the treater line.

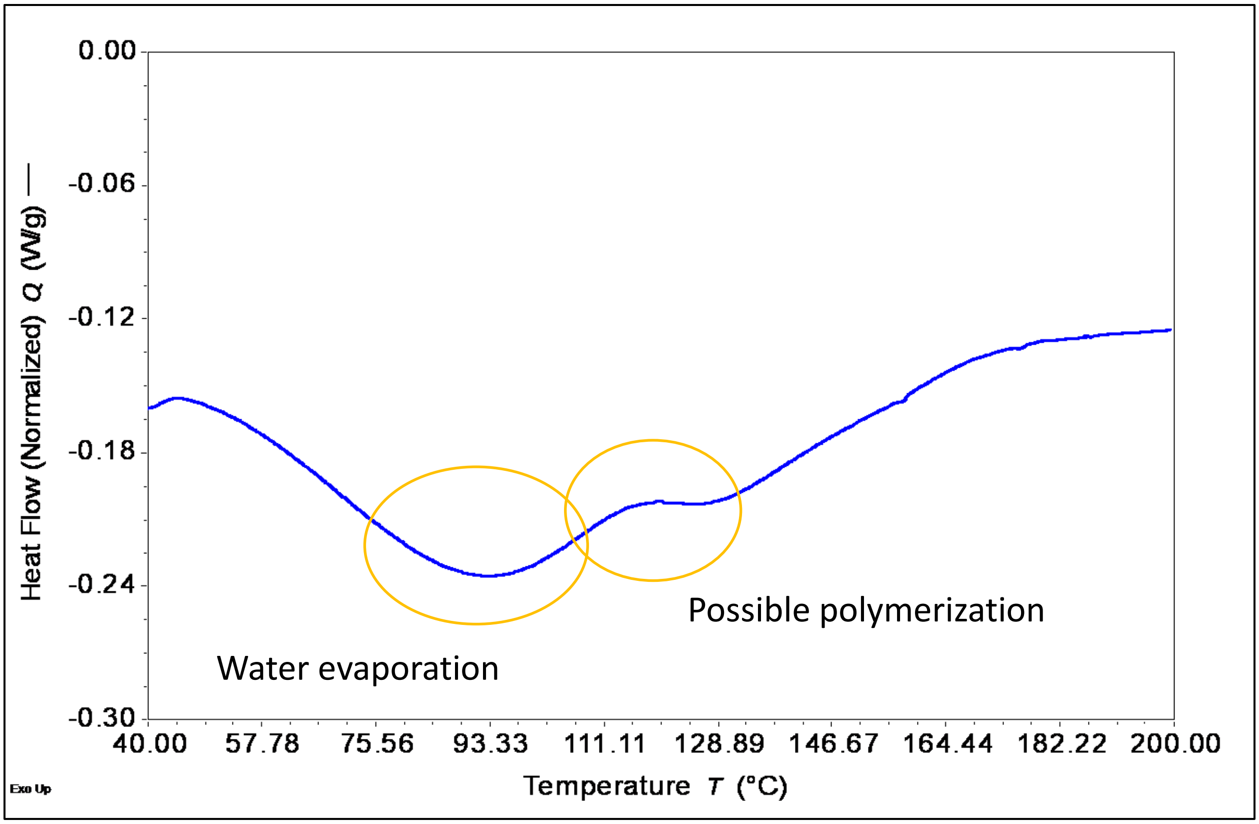

Figure 17. DSC first heat polymerization peak at 110 °C and endothermic evaporation at 95 °C.

Treater Run #4

Treater Modifications

The team operated ovens #1 and #2 at 60° C for the entirety of the run. No further modifications were made to the treater system during this run. The resin bath and take-up sections were kept intact from the previous run.

60 °C was chosen after an initiator study was conducted using the new Perkadox thermal initiator. Three samples were left to isotherm in an oven at 60 °C, 80 °C, and 100 °C. These samples were periodically monitored for polymerization across 30 minutes. After approximately 5 minutes, the 80 °C and 100 °C samples resulted in aggressive foaming, which is likely caused by boiling of MMA monomer in the sample. Figure 18 shows this foaming that was present in the 100 °C sample after 5 minutes at temperature. Because of this foaming, the team elected to use 60 °C for the treater line ovens.

Figure 18. 100 °C sample foamed after 5 minutes at temperature.

Operating Parameters

Table 5. Operating parameters for treater run #4.

Resin	C595 Elium (4.9 kg) 3% Perkadox Peroxide (150g)
Fabric	Flax plain weave fiber
Feed Rate	5 ipm
Pinch Roller Spacing	0.030” (50% resin)
UV Light Spacing	UV Lights omitted
Fabric Tension	8 lbs
Oven Use	Oven #1, Oven #2 (60 °C)

Results and Discussion

The goal of treater run four was to understand the impacts of changing from Laurox to the Perkadox thermal initiator and to identify new parameters for polymerization of the resin, including oven temperature and feed rate.

Pros

- No major gumming on rollers
- Perkadox quickly dissolves in Elium C595 resin
- 0.030” pinch spacing maintained rotation of pinch rollers
- Even resin coverage across width of fabric

Cons

- Resin accumulating on roller, next to edge of fabric
- 0.032” pinch spacing lost rotation of top roller
- Oven dwell time or oven temperature must be increased to fully polymerize prepreg

This treater run proved successful in mixing Elium resin with the Perkadox thermal initiator. Perkadox was found to dissolve rapidly in Elium and does not show signs of re-agglomeration. This alternative peroxide showed large amounts of foaming in the resin bath, but did not foam while in the oven, see Figure 19 for resin bath foam. This foam is very unlike the foam that was observed when mixing Elium with Laurox, and it is determined to have been caused by the Perkadox peroxide initiator. This foaming does not seem to affect the prepreg's quality.

After the oven line, this prepreg was still marginally tacky and smelled like Elium resin. DSC results confirm that the resin was heavily unpolymerized which suggests that the parameters for manufacturing need to be adjusted, specifically the tuning of oven temperature and treater line feed rate.

For this treater run, like run #3, there was very little gumming that was present on the pinch rollers, as seen in Figure 20.

Figure 19. White foam present underneath the pinch rollers in the resin bath.

Figure 20. Pinch rollers featuring little to no gumming.

Aerial Weight Resin Content

The team was able to achieve a resin content of ~50% during this run, as requested by the sponsor. The resin distribution across the width of the prepreg fabric is highly consistent, with a standard deviation of only 1.9%. These results are very encouraging as creating prepreg with flax fiber has been the primary goal for this project.

Table 6. Resin content by aerial weight

Pinch Roller Spacing	Average Resin Content (%)	Standard Deviation (%)
0.030”	50.8	1.9

Thermal Analysis

A heat-cool-heat DSC experiment was performed on this material using the following parameters:

- Heat: 25 °C - 200 °C @ 10 °C/min
- Cool: 200 °C - 25 °C @ 5 °C/min
- Heat: 25 °C - 200 °C @ 10 °C/min
- Sample mass: 8.29 mg
- Pinch roller spacing: 0.030 “
- Feed rate: 4 ipm

The notable results of this experiment are provided in the thermogram in Figure 21. The first heat of this thermogram reveals a very large polymerization peak that stretches from 90 °C to 130 °C. This is likely caused by the switch to the Perkadox thermal-initator. Because this polymerization peak is so large, and the material was slightly tacky and smelled of resin, it can be concluded that the resin was not sufficiently polymerized, and this new thermal initiator needs to be studied more. Either the temperature of the oven needs to be increased, which risks increased foaming of the material, or the feed rate needs to be reduced so the material has more time to polymerize.

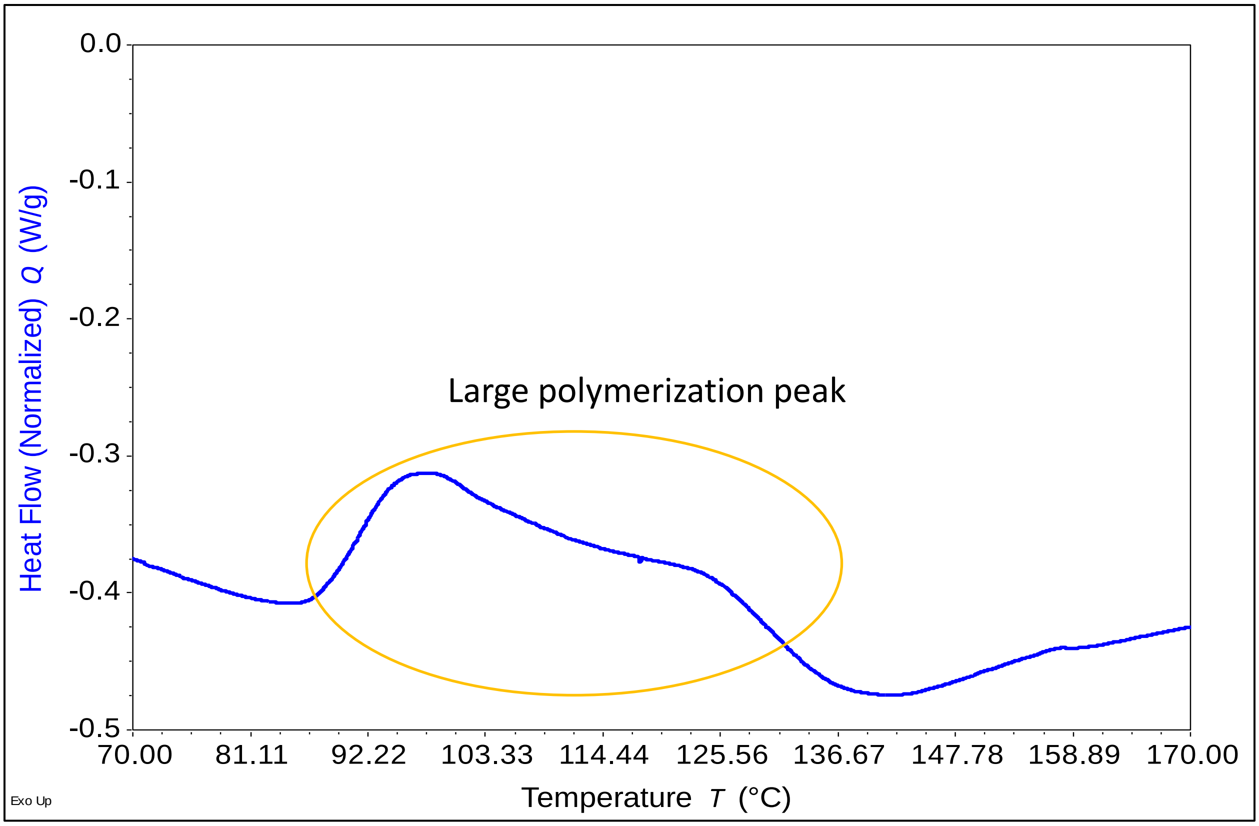

Figure 21. DSC first heat polymerization peak across 90 °C – 130 °C.

Appendix (Task 3)

Procedure 1 – Resin Content by Aerial Weight

1. Cut an 8” long section of polymerized prepreg from the manufactured roll.
2. Cut another 8” long section of dry flax fiber from the same roll used during production.
3. Locate a hexagonal stamping die from the analysis lab and a piece of plastic sheeting (HDPE or ABS) from the soft tooling lab.
4. Bring all materials to the arbor press located in the garage bay of the project lab.
5. Mark an evenly spaced 2x5 array of stamping locations across each section of 8” long fiber (Numbered 1-10).

Figure A1. 2x5 stamping pattern

6. Place the plastic sheeting underneath the fabric or prepreg.
7. Use the hexagonal stamping die to cut out each marked location.

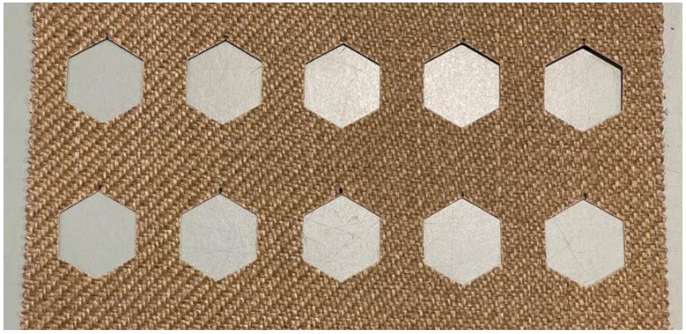

Figure A2. Stamped prepreg sheet

8. Take the numbered cutouts to the analysis lab and record the weight of each sample.
9. Use the equation below to find the average resin content across the width of the sheet.

$$Resin\ content\ (\%) = \left(\frac{M_p - M_f}{M_f}\right) \times 100$$

where:
M_f *= Average weight of dry fiber samples*
M_p *= Average weight of prepreg samples*

10. To find the standard deviation across the sample area, replace the value for M_p in the equation above with the individual weight of each prepreg sample. This will provide a resin content for each sample location, allowing for the calculation of SD across all samples.

Task 4. Material Characterization

Objective

Norplex and Arkema partnered with Western Washington University (WWU) to develop a thermoplastic prepreg using a poly(methyl methacrylate) (PMMA) matrix. The main goal for Spring Quarter 2024 was to compare the mechanical properties of flax, fiberglass, and linen fiber reinforced PMMA prepreg manufactured with the WWU lab scale treater. The time period for this quarter ranged from March 2024 to May 2024.

Experimental

Materials

Poly(methyl methacrylate) (PMMA)

Elium C595E obtained from Arkema was used as the MMA monomer resin system for polymerization to PMMA (Figure 1). Polymerization can occur via UV photoinitiation and/or thermal initiation. PMMA is an amorphous acrylic thermoplastic polymer known for its UV resistance, hardness, abrasion resistance, and dimensional stability.

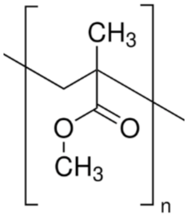

Figure 1: Chemical structure of PMMA repeat unit [1].

Perkadox

Perkadox 16, Di(4-tert-butylcyclohexyl) peroxydicarbonate, was the peroxide thermal initiator used to initiate polymerization of Elium.

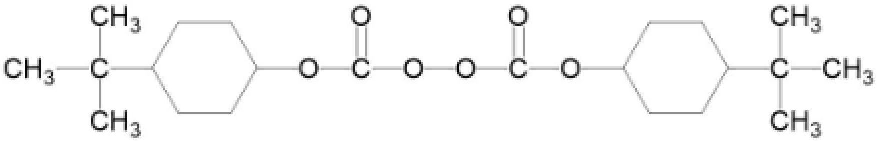

Figure 2: Chemical structure of Perkadox peroxide thermal initiator [2].

Flax

Bcomp ampliTex 5040 is a 2x2 twill weave oriented at 0° and 90°, suitable for composites with low environmental impact compared to carbon or glass. This fabric features a thickness of 0.34 mm. Flax has a tensile strength parallel to fibers of 149.3 MPa, and a flexural modulus of 17.9 GPa. It is notable that flax fibers are known for absorbing large amounts of moisture and resin [3].

Fiberglass

JPS 7628 E-glass plain weave is a tight fiberglass weave with fabric thickness of 0.17 mm. No mechanical properties are reported on JPS provided TDS [4].

Linen

MTV Linen is a 3.8 oz plain weave fabric made with 100% cotton and width of 41 inches [5]. This material was then cut to 14 inches in width for the treater runs. No mechanical properties were reported.

Procedures:

Prepreg Manufacturing

Table 1: Flax prepreg manufacturing parameters

Resin	C595E Elium (4.9 kg) 3% Perkadox Peroxide (150g)
Fabric	Flax fiber
Feed Rate	5 ipm
Pinch Roller Spacing	0.030”
Fabric Tension	8 lbs
Oven Use	Oven #1, Oven #2 (60 °C)

Table 2: Fiberglass prepreg manufacturing parameters

Resin	PMMA
Fabric	Fiberglass
Feed Rate	5 ipm
Pinch Roller Spacing	0.020"
Fabric Tension	6 lbs
Oven Use	2 ovens, 60 °C

Table 3: Linen prepreg manufacturing parameters

Resin	PMMA
Fabric	Linen
Feed Rate	5 ipm
Pinch Roller Spacing	0.020"
Fabric Tension	6 lbs
Oven Use	2 ovens, 70 °C

Resin Content

Resin content for the organic fibers was completed using the methodology that was created last quarter using average dry and wet fiber weights (see Appendix). Resin content for the fiberglass samples were completed using a traditional burn out method.

Degree of Polymerization

Degree of polymerization of Elium resin was measured using TA instruments Discovery X3 DSC. The enthalpy change in exotherm of neat resin was measured as a baseline polymerization. Samples were studied in heat-cool-heat from 25 °C to 200 °C @ 5 °C/min. A comparison was drawn between manufactured prepreg and neat Elium to determine the degree of polymerization as a percentage.

Coupon Manufacturing of Consolidated Material

Coupons were created conforming to ASTM standards [6-8] to measure several mechanical properties of the various prepreg systems. The layout of the coupon is shown in Figure 5. Two plaques were created for each composite in this research as the short beam shear specimens [8] have a larger thickness requirement than the tensile and flexural specimen [6, 7]. The prepreg materials were cut into the size required to create the plaque and then compression molded with two caul plates using the parameters shown in Table 4. It is important to note that the consolidation cycle for plaque manufacturing was not studied and not optimized. Therefore, the resulting mechanical properties are also not optimized.

Figure 5: Layout of composite coupons

Table 4: Parameters set for the compression mold of the plaques

Molding Temperature (°F)	Pressure (tons)	Cycle Time (min)
350	9	15

Tensile Testing

The linen/PMMA and flax/PMMA coupons were cut using a step shear. There were attempts to use a tile saw. Unfortunately, that resulted in extreme amounts of water ingress and the disintegration of the organic fibers. Fiberglass/PMMA samples, however, were cut using a tile saw. The tensile bars were tabbed using Armstrong 2-part epoxy and cut circuit boards. The tensile

Short Beam Shear Testing

Short beam shear testing bars were cut by utilizing a composites band saw for all samples. The short beam shear testing bars followed the ASTM D2344-13 short beam shear testing standard [8].

Flexural bar Testing

The flexural bars were cut using both a step shear for the fiberglass and linen samples and a composites band saw for the flax samples. The ASTM D7264-15 flexural testing standard was followed for sample testing [7].

ASTM Standard Requirements [6-8]:

All mechanical tests conducted in this work followed ASTM standards. The D3039-17 ASTM tensile testing standard was used for tensile testing, requiring a sample thickness of 2.5mm with an area of 254mm X 25.4mm. The D2344-13 ASTM short beam shear testing standard was used for short beam shear testing, requiring a sample thickness of 6 mm with an area of 38.1mm X 12.7mm. The D7264-15 ASTM flexural testing standard was used for sample testing, requiring a sample thickness of 2.5mm, and area of 97.8mm X 12.7mm. Table 5 demonstrates the number of plies that were required to reach the standard thickness of each test run in this study, as well as how closely the widths of the samples meet standard that they must comply to.

Table 5: Measurements of the average thickness and width of the composite coupons

	Average Thickness (mm)	Thickness Standard Deviation (mm)	Number of Plies	Average Width (mm)	Width Standard Deviation (mm)
Flax Tensile	2.62	0.0034	7	27.48	0.042
Flax Flexural	2.73	0.14	7	16.06	1.53
Flax Short Beam Shear	6.92	0.16	17	13.57	0.37
Fiberglass Tensile	2.58	0.0040	13	25.68	0.85
Fiberglass Flexural	2.63	0.033	13	11.35	0.52
Fiberglass Short Beam Shear	6.44	0.13	33	13.53	0.87
Linen Tensile	2.77	0.0029	17	26.77	0.023
Linen Flexural	2.72	0.047	17	12.62	1.93

Results and Discussion

Resin Content

Table 6: Resin content results across prepreg systems

	Flax	Fiberglass	Linen
Resin Content (by weight)	50%	40%	51%

As shown by Table 6, the linen prepreg had the largest resin content by weight. This can be attributed to the absorbency of the linen as linen is 100% cotton. Flax has the second highest resin content due to the organic fiber's ability to absorb resin and retain it. Fiberglass has the lowest resin content by weight because of the tight weave of the fabric that prevents the fiber. To increase the resin content of the fiberglass, allowing for a longer soak time in the bath could increase the potential for the fiberglass to allow for more resin to infiltrate between the tightly woven fibers and thus result in an increase of the resin content by weight.

Degree of Polymerization

A heat-cool-heat DSC experiment was performed on the prepreg systems using the following parameters:

- Heat: 25 °C - 200 °C @ 5 °C/min
- Cool: 200 °C - 25 °C @ 5 °C/min
- Heat: 25 °C - 200 °C @ 5 °C/min

The polymerization exotherm observed on the first heat of the DSC experiments was used to determine the degree of polymerization. The integrated enthalpy of these exotherms were referenced to the heat of polymerization of MMA to PMMA of 57.8 kJ/mol [9]. The integrated enthalpy, peak temperature, and calculated degree of polymerization for the three prepreg systems can be found in Table 7. All three systems yielded similar degrees of polymerization, indicating a repeatable and consistent polymerization reaction of the Elium and Perkadox 16 thermal initiator via the treater manufacturing line.

Table 7: DSC Results

	Peak Temperature (°C)	Enthalpy (J/g)	Degree of Polymerization
Flax	112.84	29.422	94.9%
Fiberglass	123.15	35.172	93.9%

Linen	124.27	45.957	92.0%

Tensile Testing

Flax/PMMA tensile testing results from ASTM D3039-17 [6] are provided in Table 8. Figure 9 shows images of the failure for each bar. Each bar failed with fiber breakage and no delamination.

Table 8: Flax tensile average results across 6 tensile bars.

	Flax Tensile Average Results	Standard Deviation
Modulus (MPa)	4179.44	486.25
Peak Stress (MPa)	133.68	12.09
Width (mm)	27.48	0.042
Thickness (mm)	2.62	0.0034
Gage Separation (mm)	203.2	

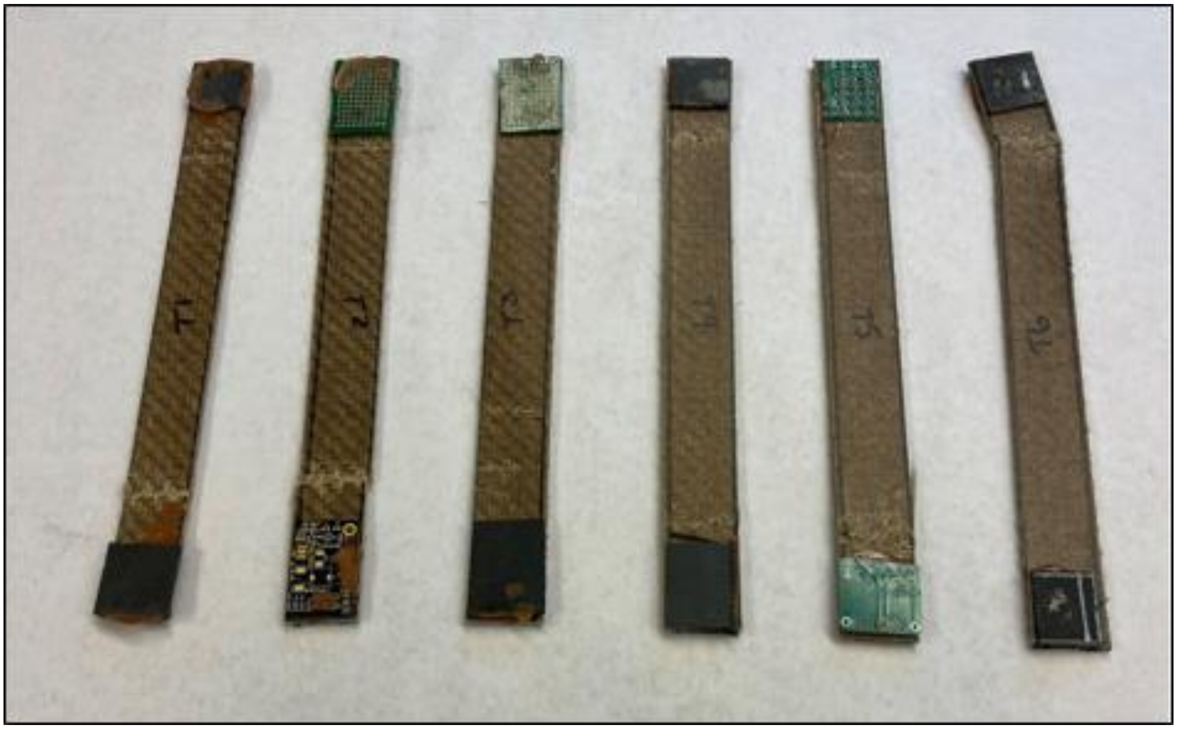

Figure 9: 6 Tensile bars broken, featuring the same failure mode near the grips.

Fiberglass/PMMA tensile testing results from ASTM D3039-17 [6] are provided in Table 9. Figure 10 shows that the bars failed with excessive delamination and some fiber breakage at the interface of the fiber with the tabbing material.

Table 9: Fiberglass tensile average results across 5 tensile bars.

	Fiberglass Tensile Results	Standard Deviation
Modulus (MPa)	5845.53	1894.07
Peak Stress (MPa)	270.91	40.09
Width (mm)	25.68	0.85
Thickness (mm)	2.58	0.004
Gage Separation (mm)	203.2	

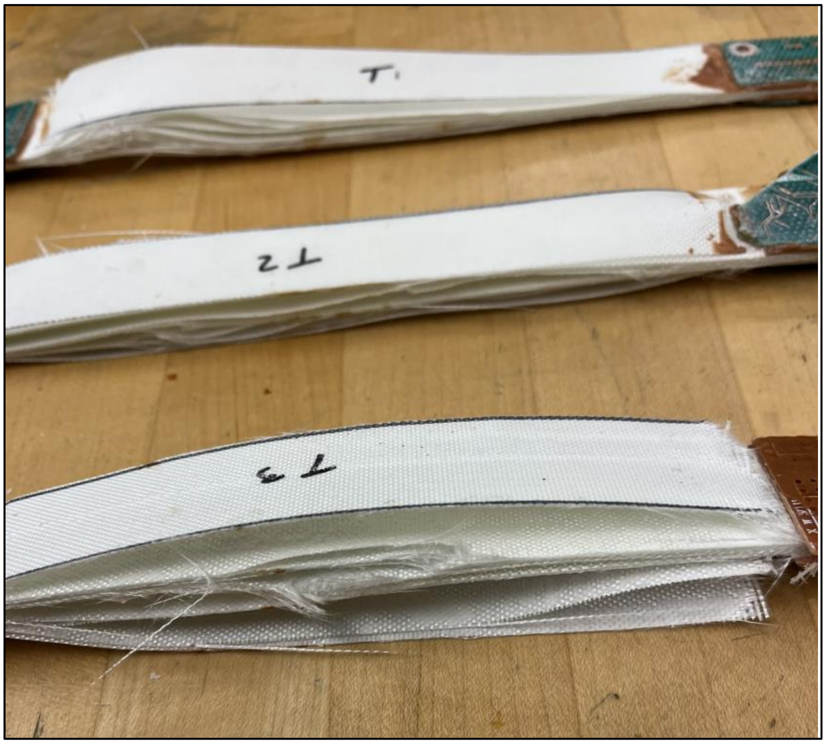

Figure 10: 3 examples of the fiberglass tensile bars after fracture.

Linen/PMMA fiber tensile testing results from ASTM D3039-17 [6] are provided in Table 10. Figure 11 shows that each of the linen bars failed with some delamination and some fiber breakage.

Table 10: Linen tensile average results across 5 tensile bars.

	Linen Tensile Average Results	Standard Deviation
Modulus (MPa)	3676.42	504.38
Peak Stress (MPa)	98.27	6.70
Width (mm)	26.77	0.023
Thickness (mm)	2.77	0.0029
Gage Separation (mm)	203.2	N/A

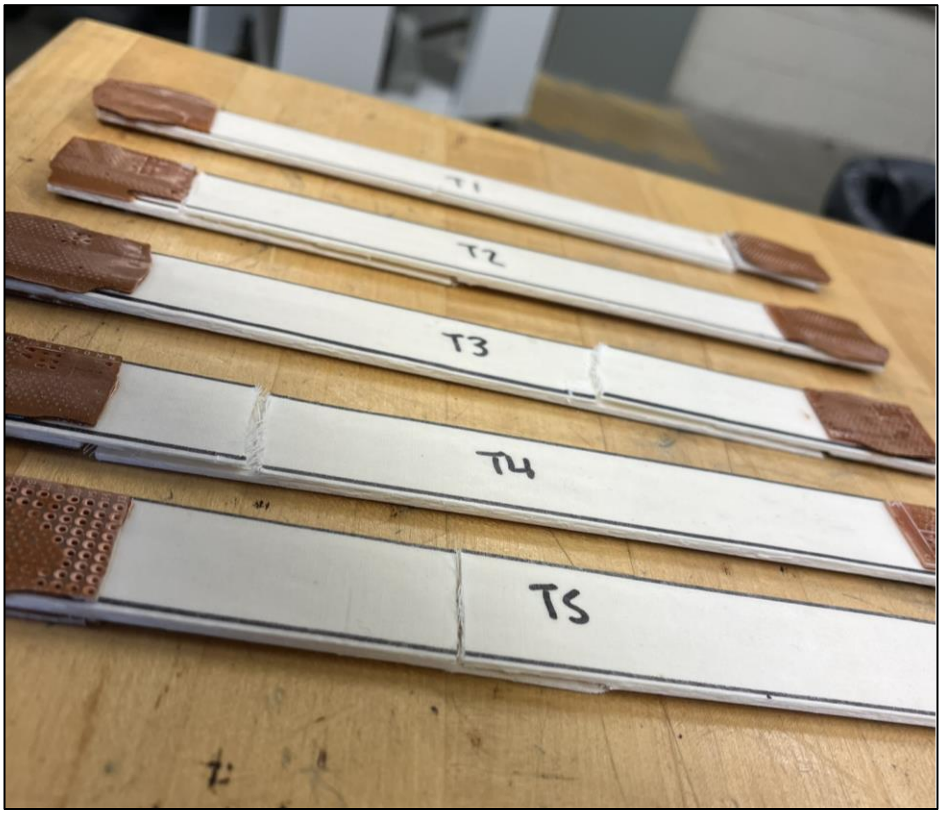

Figure 11: Fiberglass/PMMA tensile bars.

The data collected from tensile testing was consolidated into an overlay graph (Figure 12). Table 11 gives the average stress and modulus for each material type. Fiberglass/PMMA had the highest average tensile modulus of 5.85 GPa and tensile stress of 133.6 MPa. In comparison, linen/PMMA had the lowest tensile modulus (3.68 GPa) and strength (98.3 MPa) of the three.

Table 11: Average tensile results for each material.

	Average Tensile Modulus (GPa)	Tensile Modulus Standard Deviation	Maximum Tensile Stress (MPa)	Maximum Tensile Stress Standard Deviation
Flax	4.18	0.49	133.6	12.09
Fiberglass	5.85	2.08	270.9	40.09
Linen	3.68	0.50	98.3	6.70

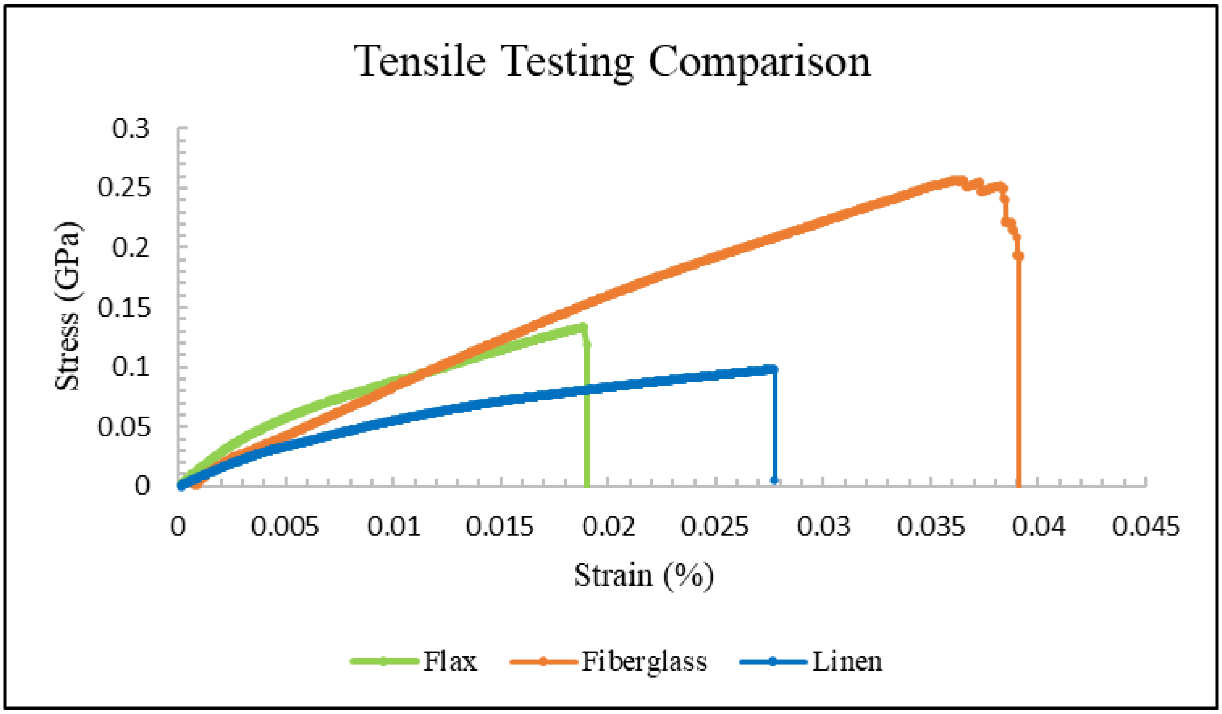

Figure 12: Overlay stress/strain graph of all materials.

Short Beam Shear Testing

All short beam shear testing was performed with a span of 26 mm and was halted after 7 mm of deflection.

Flax/PMMA short beam shear testing results from ASTM D2344-13 [8] are provided in Table 12. Figure 13 shows that each of the samples failed in a similar fashion with no delamination or fiber breakage.

Table 12: Flax short beam shear results.

	Flax Short Beam Shear Average Results	Standard Deviation
Strength (MPa)	4.97	0.27
Width (mm)	13.57	0.37
Thickness (mm)	6.92	0.16

Figure 13: Flax short beam shear failures, top (left) and side (right) views.

Fiberglass/PMMA short beam shear testing results from ASTM D2344-13 [8] are provided in Table 13. Figure 14 shows that each of these samples failed with some delamination on the edges but no fiber breakage.

Table 13: Fiberglass short beam shear results.

	Fiberglass Short Beam Shear Average Results	Standard Deviation
Strength (MPa)	10.50	0.95
Width (mm)	13.53	0.87
Thickness (mm)	6.44	0.13

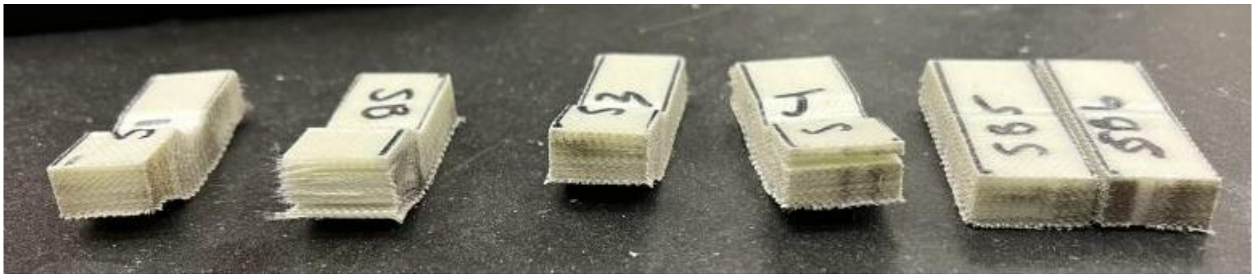

Figure 14: Fiberglass short beam shear failures, displaying delamination on one side of the sample.

Linen/PMMA short beam shear samples were not tested during the extent of this study due to time constraints.

Flexural Testing

Support separation for all testing was 80 mm and all tests were halted after 16 mm of deflection.

Flax/PMMA flexural testing results from ASTM D7264-15 [7] are provided in Table 14. Figure 15 demonstrates that the fibers failed without delamination of the samples.

Table 14: Flax flexural average results across 6 flexural bars.

	Flax Flexural Average Results	Standard Deviation
Modulus (MPa)	49.47	11.25
Peak Stress (Mpa)	2.63	.39
Width (mm)	16.06	1.53
Thickness (mm)	2.73	0.14

Figure 15: 6 Flax flexural bars after testing.

Fiberglass/PMMA flexural testing results from ASTM D7264-15 [7] are provided in Table 15. Figure 16 demonstrates that the coupons failed with both delamination and fiber breakage.

Table 15: Fiberglass flexural average results across 6 flexural bars.

	Fiberglass Flexural Average Results	Standard Deviation
Modulus (MPa)	135.42	8.36
Peak Stress (MPa)	5.67	.29
Width (mm)	11.35	.52
Thickness (mm)	2.63	0.033

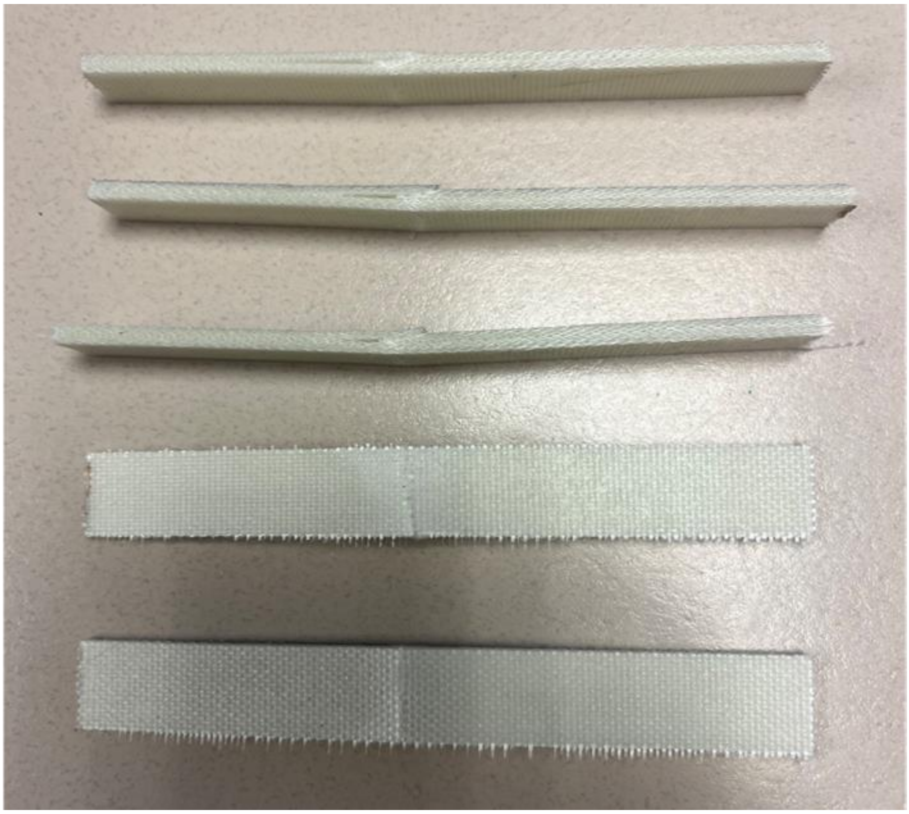

Figure 16: Fiberglass flexural bars.

Linen/PMMA flexural testing results from ASTM D7264-15 [7] are provided in Table 16. Figure 17 shows each sample delaminating and encountering fiber breakage.

Table 16: Linen flexural average results across 5 flexural bars.

	Linen Flexural Average Results	Standard Deviation
Modulus (MPa)	96.32	26.80
Peak Stress (MPa)	5.34	1.084
Width (mm)	12.62	1.93
Thickness (mm)	2.72	0.047

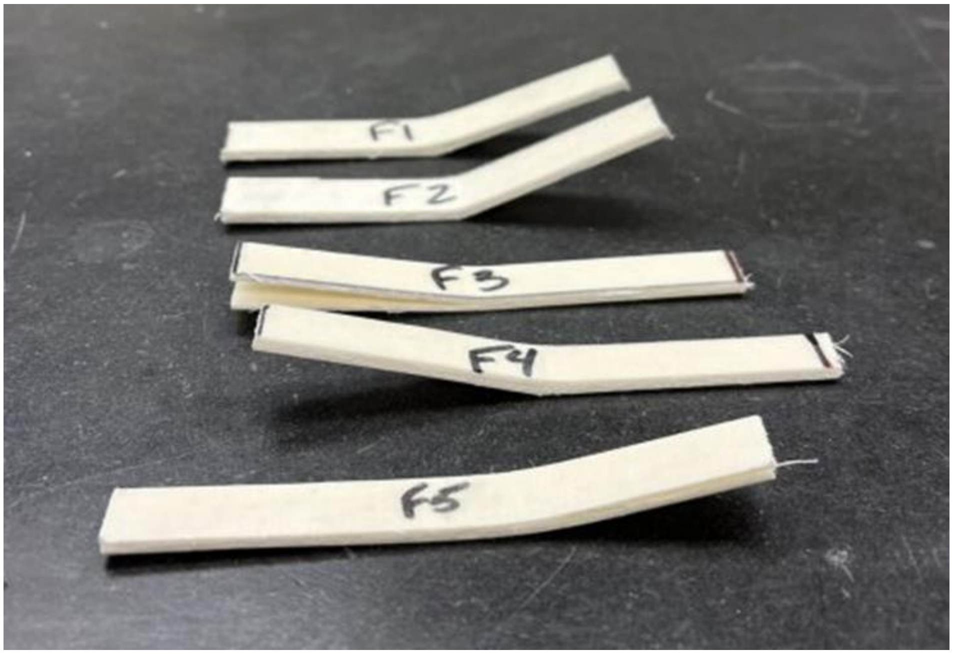

Figure 17: Linen flexural bars.

The data collected from flexural testing was compiled into an overlay graph provided in Figure 18. Average values for each material type are provided in Table 17. Similarly to the tensile testing, the fiberglass/PMMA coupons had the highest properties with a flexural modulus of 135.42 MPa and a flexural strength of 2.63 MPa. Flax/PMMA had the lowest flexural properties with a modulus of 49.47 MPa and strength of 2.63 MPa.

Table 17: Compiled Flexural results for each material.

	Average Flexural Modulus (MPa)	Flexural Modulus Standard Deviation	Maximum Flexural Stress (MPa)	Maximum Flexural Stress Standard Deviation
Flax	49.47	11.25	2.63	0.39
Fiberglass	135.42	8.36	5.67	0.29
Linen	96.31	26.80	5.34	1.08

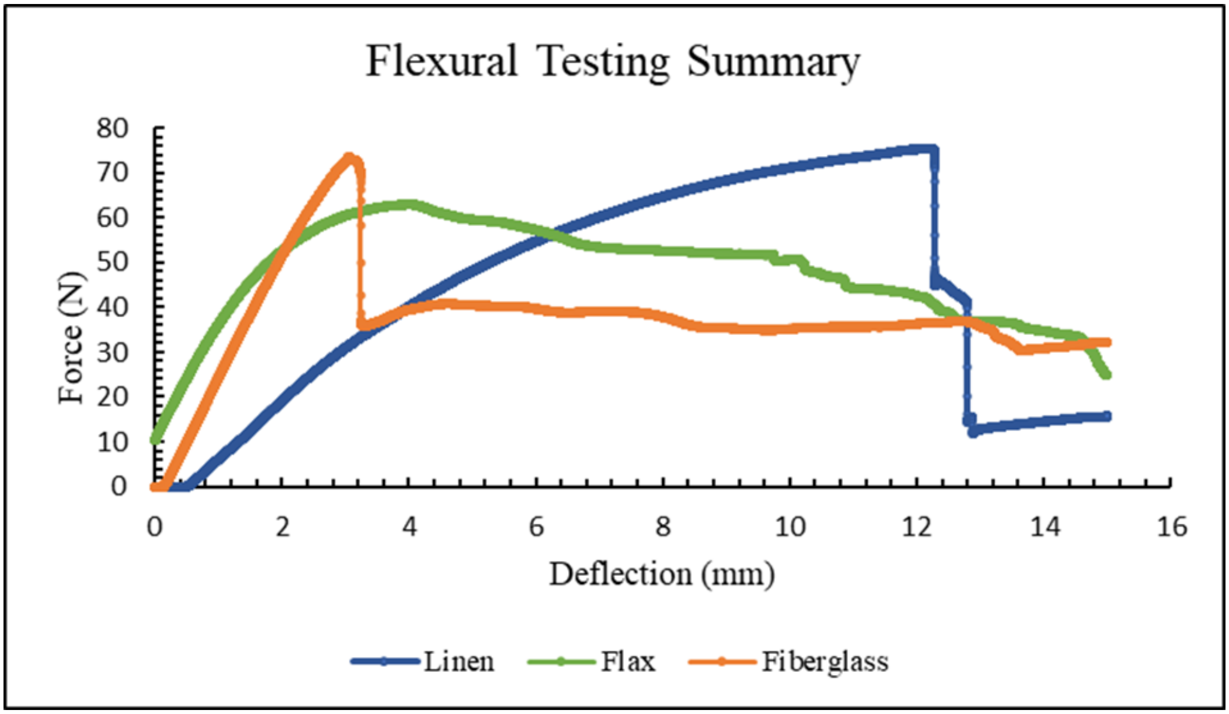

Figure 18: Overlay stress/strain graph of all materials.

Conclusion

Flax/PMMA prepreg manufactured on a traditional prepreg treater is a viable material. WWU has successfully scaled bench top to pilot production of PMMA based thermoplastic prepreg using a traditional lab scale treater line using flax, fiberglass, and linen fibers. Through mechanical testing of flax prepreg tensile, flexural, and short beam shear data was gathered. Although the manufacturing process to consolidate the prepreg was not optimized, a comparison between the materials can be made. In comparison to fiberglass the flax fibers with a PMMA matrix will perform at approximately half the tensile strength, a third of the flexural modulus, and half the short beam shear strength.

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