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Oak Ridge National Laboratory Mineral-Ground Micro-Fibrillated Cellulose Reinforcement for Polymer Compounds

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Manufacturing Science Division
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ABSTRACT

Additive Manufacturing (AM) is quickly becoming a mainstream, energy efficient manufacturing technique for complex and custom components. ORNL has taken polymer AM into the next level with Big Area Additive Manufacturing (BAAM). However, we need to develop the strength of AM materials (specifically polymers) to satisfy the mechanical requirements of structural parts. Also, it is crucial that the developed process can easily be scaled up to have a significant impact in the manufacturing industry of US. Furthermore, renewable, bio-derived AM materials are desirable from a sustainability perspective.

In the first phase of this project the mechanical properties of polymer AM components were significantly improved developing a micro fibrillated cellulose (MFC)-reinforced composite material system that is derived from biomass and compatible with BAAM. Unfortunately, the improvements were observed only with freeze-dried MFCs, and freeze-drying is a very slow process and is not industrially scalable. Furthermore, MFCs were not available in large quantities at low cost. However, FiberLean has reached 12,000 tons/year capacity (60,000 tons/year including the minerals). FiberLean offers MFCs at a scale and order of magnitude lower price than current market participants.

With their recently developed novel (patent pending) drying process FiberLean can achieve over 50% solid content commercially. In the 2nd phase of the project, the original objective was to investigate this new novel drying process along with compounding with different formulations to optimize and adapt to large scale additive manufacturing. However, the compounded materials prepared via this approach were very brittle and demonstrated poor mechanical performance. Therefore, the project was focused more on a scalable chemical surface modification of MFCs to enable their drying via conventional oven process with minimal agglomeration and better dispersion in PLA polymer matrix.

Fiberlean and ORNL have worked together in this project to develop mineral-ground microfibrillated cellulose (MFC) - reinforced additive manufacturing feedstock materials with significantly improved mechanical properties. Properly surface modified and dried Fiberlean cellulose microfibrils led to tensile strength increases up to ~40% and elastic modulus increases up to 70% with the addition of 30% MFC into PLA matrix. The work has led to a high impact journal article and a provisional patent. Opportunities for a follow up work to demonstrate the technology in large scale and application of it to AM applications are currently being searched.

1. MINERAL-GROUND MICRO-FIBRILLATED CELLULOSE REINFORCEMENT FOR POLYMER COMPOUNDS

FiberLean Technologies is the global leading microfibrillated cellulose (MFC) producer that utilizes minerals for their fibrillation process. FiberLean is a recent spin off company of one the largest mineral companies in the world, Imerys, and is a veteran run small business. FiberLean has already established a new FiberLean facility on a large paper mill site in the eastern US. Six full-time staff members with competitive wages, benefits, and health insurance were hired to operate the plant. Also, during the year of design and construction, seven full time engineers and 38 full time construction workers were employed. Furthermore, the local economy benefited additional revenues in the areas of industrial equipment purchases, bulk transportation (trucks, tankers), local food and hospitality, car rental, airport etc.

In the first phase of a collaboration project with FiberLean (then Imerys), the team demonstrated that use of mineral-ground MFCs can dramatically improve mechanical properties of commonly used thermoplastic polymers such as Acrylonitrile Butadiene Styrene (ABS) and Polylactic acid (PLA) (see Fig.), provided that the fibrils are properly dried and have the right morphology.This phase II technical collaboration project (MDF-TC-2015-067) began on April 1, 2019 and was completed on February 15, 2021. FiberLean Technologies is a large microfibrillated cellulose (MFC) producer that utilizes minerals for their fibrillation process. MFCs are natural wood-based products that can offer great benefits for reinforcing polymer composites; however, drying these fibers without causing agglomeration, redispersing dried fibers in polymer matrices and poor compatibility between these hydrophilic fibers and hydrophobic polymer matrices are technical challenges that need to be solved to enable their use in composite applications.

While the technology used to dry MFCs in phase 1 (i.e., freeze drying) yields fibrils with low bulk density (i.e., loosely packed) and right morphology, unfortunately it is an industrially slow process and not scalable. Other drying approaches such as oven and spray drying yield densely packed fibril agglomerates/chunks that cannot be redispersed due to strong hydrogen bonding among individual fibrils. OH-rich functional groups on the surface of fibrils form strong hydrogen bonding almost irreversible during drying process preventing utilization of fibrillar form of MFCs with high aspect ratio. Therefore, one of the biggest obstacles in front of use of MFCs in polymer reinforcement is water removal and dispersion of the fibrils in polymer matrix. Once this problem is overcome, large number of new area of applications will open up including additive manufacturing in large scale.

Towards this direction, FiberLean has recently developed a technique that can achieve over 50% solid content of MFC, and has already filed multiple patents. However, compounding of MFCs dried via this approach with polymer matrices PP and PLA yielded brittle composites with poor mechanical performance. Therefore, the project was focused more on a scalable chemical surface modification of MFCs to enable their drying via conventional oven process with minimal agglomeration and better dispersion in PLA polymer matrix.

Developing the right strategy to modify surface functionality and dry MFCs and utilizing these surface modified MFCs as a reinforcing filler, up to 38% increase in tensile strength and up to 71% increase in elastic modulus were achieved for the composites compared to neat feedstock material, i.e., PLA. These results demonstrate the value and the need of the surface modification of the MFCs. Also, a feedstock material prepared using a masterbatch of MFC-PLA was used in large scale printing studies of a VARTM mold using MFC-reinforced composites.

STATEMENT OF OBJECTIVES

To evaluate the efficiency of the novel drying and compounding approach of MFC and to optimize the process, Fiberlean produced MFC cake using their recent mineral and drying technology, as well as provided ORNL with the MFC slurry for surface modification studies. The dispersion of the MFCs in the polymer and their effect on thermal, mechanical, and rheological properties of the polymer was investigated. As dispersion of nanomaterials is critical for performance in composites, surface treatments were applied to improve the dispersion of the MFCs throughout the polymer matrix. Characterization of MFC, MFC/polymer composites, mechanical testing specimens were carried out. Successful implementation of the project to lead to full commercialization will require the reduction/elimination of nano and microscale agglomerates in the matrix due to the nanofibrils and fillers in the composite, and therefore will require scaling up of the surface treatment. The performance targets of the composites is 20% increase in tensile strength and 50% increase in elastic modulus. ORNL and Fiberlean collaborated to understand and potentially eliminate the agglomerations while understanding the underlying cause. In the end, VARTM mold was 3D printed in a BAAM system using mineral-ground MFC-reinforced PLA.

BENEFITS

FiberLean's capability to produce Fiberlean MFC in industrially large scale (60,000 tons/year capacity with minerals) and being able to offer it at commodity prices will enable the use of MFCs for polymer reinforcement and use of these feedstock materials in AM will extend the proven energy efficiency benefits of AM into new applications for which polymer AM currently cannot be used. This process not only can provide low cost MFCs for large scale composite applications such as BAAM, but also can stimulate new products and revenue sources for the US forest products and mineral industries. Micro-fibrillated cellulose is a wood-based renewable resource; and from the perspective of national competitiveness and security, micro/nano-cellulose and bio-resins are likely to be domestically sourced, creating US jobs especially in rural areas. We estimate up to one job created per 1000 ton of annual nanocellulose demand. Furthermore, feedstock from renewable and biocompatible resources will minimize America's dependency on petroleum products.)

TECHNICAL DISCUSSION

In this project, we developed a surface modification strategy to functionalize MFC to solve the challenge of drying MFCs with minimal agglomeration and the incompatibility between nanocellulose and polymer matrix. A water-based transesterification reaction was used to modify MFC and the oven-dried MFC was further used as a reinforcement filler for PLA. Remarkably, this oven-dried, vinyl laurate–modified MFC improved the tensile strength by 38% and Young's modulus by 71% compared with neat PLA. Our results suggested improved compatibility and dispersion of the fibrils in PLA after modification.

Synthesis of VL-MFC and characterizations

Chemical modification of MFC with VL was conducted through a transesterification reaction in the aqueous phase,[1] as shown in Figure 1a. After reaction, the product was separated, and oven dried to remove water. The reaction was confirmed by ATR-IR spectra (Figure 1b) in which a peak at 1,730 cm^{-1} belonging to the C=O group appears after modification. SEM results (Figures 1c–d) show that VL-MFC retains its fibril structure after modification. XPS of MFC and VL-MFC also confirmed the successful modification.

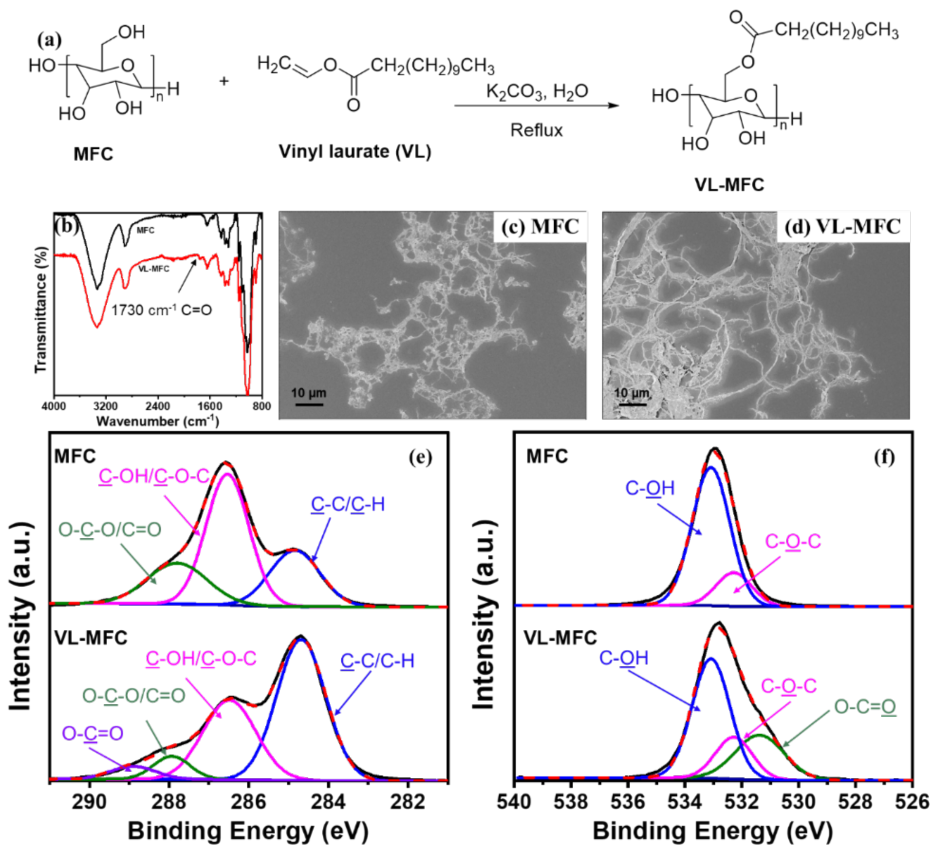

Figure 1. MFC surface modifications and characterizations. (a) Possible reaction scheme to prepare VL-MFC; (b) ATR-IR of MFC and VL-MFC; (c) SEM images of MFC; (d) SEM images of VL-MFC; (e) XPS spectra of C1s in MFC and VL-MFC; and (f) XPS spectra of O1s in MFC and VL-MFC.

After reactions, the VL-MFC surface became less hydrophilic as evidenced by the contact angle results (Figure 2a-b), where the MFC CA increased from 25° (MFC) to 50° (VL-MFC). After grinding under the same conditions, MFC becomes a powder (Figure 2c), whereas VL-MFC becomes a fluffy, porous fibrillar material (Figure 2f). SEM images of ground MFC (Figures 2d–e) and VL-MFC (Figures 2g–h) also confirm that ground MFC turns into particles and loses its fibrillar structure. These particles are aggregates of MFC, whereas VL-MFC retains a fibrillar structure with partial agglomeration. These results suggested that surface modification of the MFC reduce the agglomeration.

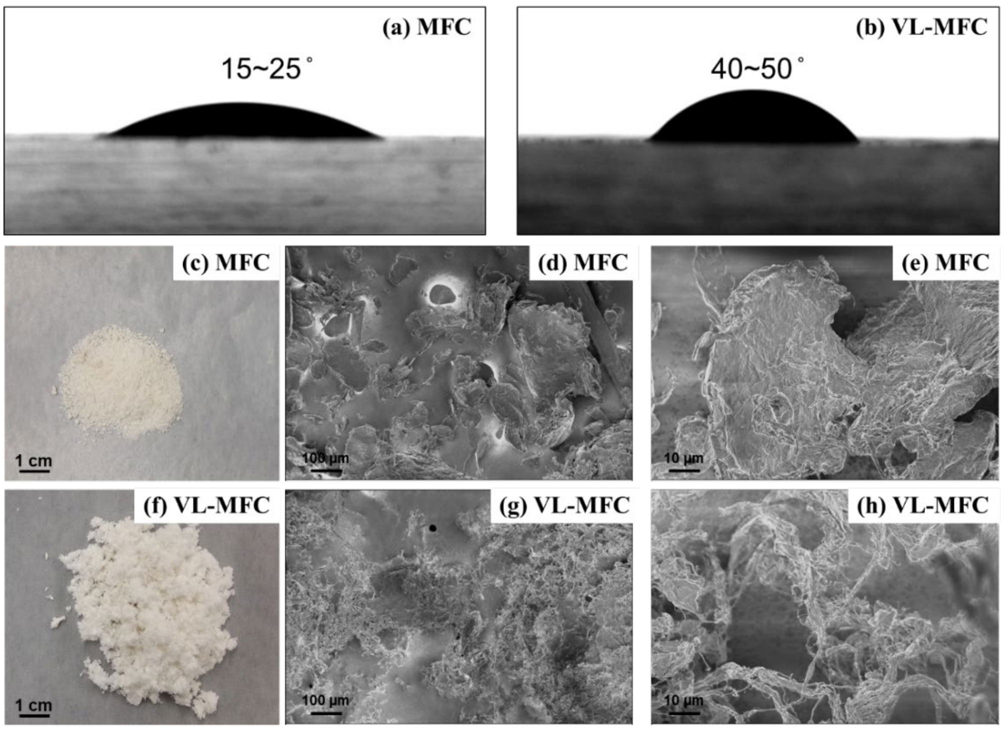

Figure 2. Contact angle of (a) MFC and (b) VL-MFC. Picture of (c) 1 g of MFC and (f) VL-MFC after grinding. SEM images of ground (d–e) MFC and (g–h) VL-MFC.

Reinforcement effect of surfaced modified fibers

After confirming the successful modification of MFC, VL-MFC and MFC were used as reinforcement fillers for PLA. For MFC-reinforced PLA (Figure 3a), the tensile strength decreases as the MFC content increases, dropping by 25% at the MFC content of 30% (45 MPa) compared with neat PLA (60 MPa). Young's modulus of the MFC-reinforced PLA increases slightly by around 12% compared with neat PLA.

These results suggest that oven-dried MFC is unsuitable as a PLA reinforcement due to the MFC agglomeration and the incompatibility between the hydrophilic MFC and hydrophobic PLA matrix. For VL-MFC reinforced composites, the tensile strength increases from 60 to 70 MPa (Figure 3a) after 5% VL-MFC was added. The tensile strength of PLA composites increases with increasing VL-MFC content, reaching 82 MPa after the addition of 30% VL-MFC—an increase of 38% compared with neat PLA and 82% compared with PLA/30% MFC. Young's modulus of PLA/30% VL-MFC composites increases by 71% compared with neat PLA, suggesting that oven-dried VL-MFC provides an excellent reinforcement effect.

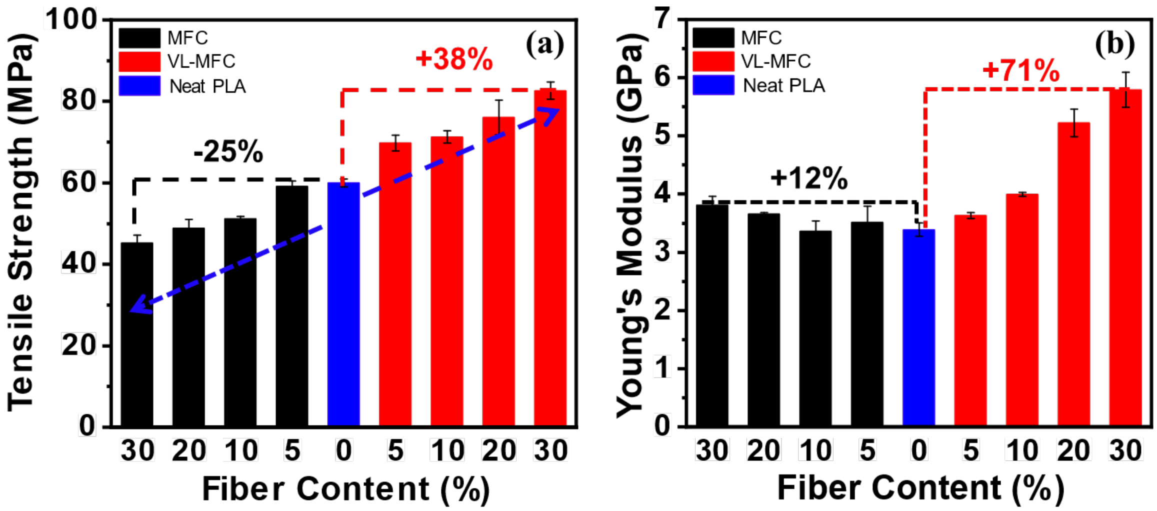

Figure 3. Mechanical properties of PLA composites: (a) tensile strength and (b) Young's modulus of PLA composites with different VL-MFC and MFC contents.

To confirm the reinforcement mechanism, SEM investigated the morphology of the composites. As suggested by Figure 4, neat PLA has a smooth cross section, whereas PLA/MFC composites revealed pronounced MFC agglomeration, suggesting poor MFC dispersion and incompatibility between the MFC and PLA matrix. For PLA/VL-MFC composites, a higher degree of dispersion was observed, as illustrated in Figure 4e,f. A homogenous morphology is observed at 30% VL-MFC contents. The homogenous dispersion of VL-MFC in the PLA matrix results in excellent mechanical reinforcement.

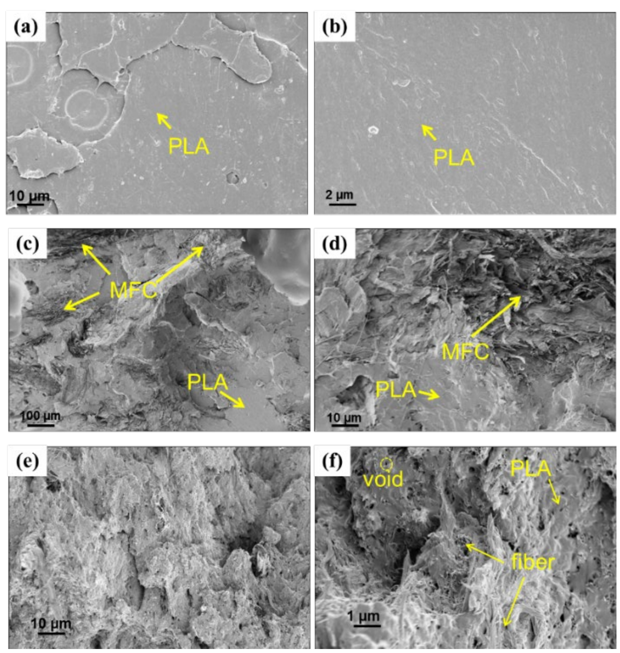

Figure 4. SEM image of the cross section after tensile testing. (a, b) PLA, (c, d) PLA/30% MFC, (e, f) PLA/30% VL-MFC.

Compared with reported studies on nanocellulose reinforced PLA composites, where solution casting [2-6]or solvent based surface modification [7-9] are used, our water based modification and oven-dried VL-MFC can be directly compounded with PLA to make composites, and improve the mechanical performance significantly. These results suggest that combining the surface modification and oven drying of cellulose fiber is a promising strategy for generating dried cellulose fibers for high-performance biocomposite applications. **Also, with these results we have met or exceeded the performance targets (i.e., 20% increase in tensile strength and 50% increase in elastic modulus) suggested in the proposal**.

Large scale additive manufacturing of MFC-composites

As stated in the previous sections, the original plan was to prepare different formulations via a drying technique that FiberLean has recently developed which can achieve over 50% solid content of MFC However, compounding of MFCs dried via this approach with polymer matrices PP and PLA yielded brittle composites with poor mechanical performance. Therefore, the project focused more on developing a scalable chemical surface modification strategy to enable MFCs drying via conventional oven process with minimal agglomeration and better dispersion in PLA polymer matrix. Meanwhile, for the completeness of the project, a masterbatch of MFC-PLA compound provided by Fiberlean was compounded with PLA and wood fibers to investigate large scale additive manufacturing (AM) of MFC composites. Because the quantity of the masterbatch was low, the MFC content had to be kept at 1 wt% to be able to collect sufficient amount of composite feedstock pellets for large scale AM study. Wood fibers (i.e., wood flour) has been added (20 wt%) to improve printability of the formulation. Materials have been compounded by Techmer PM. Approximately, 170lbs of pellets were obtained. Initial printing trials failed, because the pellets were relatively hollow and had large pores in the middle (see Fig. 5a). The pores caused feeding issues possibly breaking in the feeding zone of the extruder leading to a ununiform feeding and material extrusion. Changes in extruder temperature profile and extruder speed did not help and all trials failed in the initial layers (see Fig. 5b).

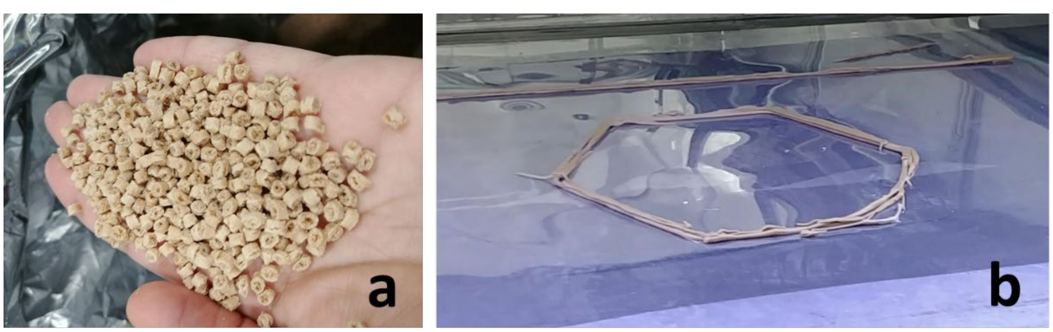

Figure 5. a)Large scale additive manufacturing feedstock pellets with porosity in the center, b) Failed hexagon printing trial due to nonuniform material feeding.

Since the printing trials were unsuccessful due to pellet issues, the pellets were reprocessed and pelletized by Techmer PM. The new pellets were proper and did not cause any feeding issues. The pellets were dried overnight at 55-60 °C, prior to printing. The printing conditions were optimized and a 5' curl bar (two-bead wall) and a hexagon with a side dimension of 8" were printed (see Fig. 6).

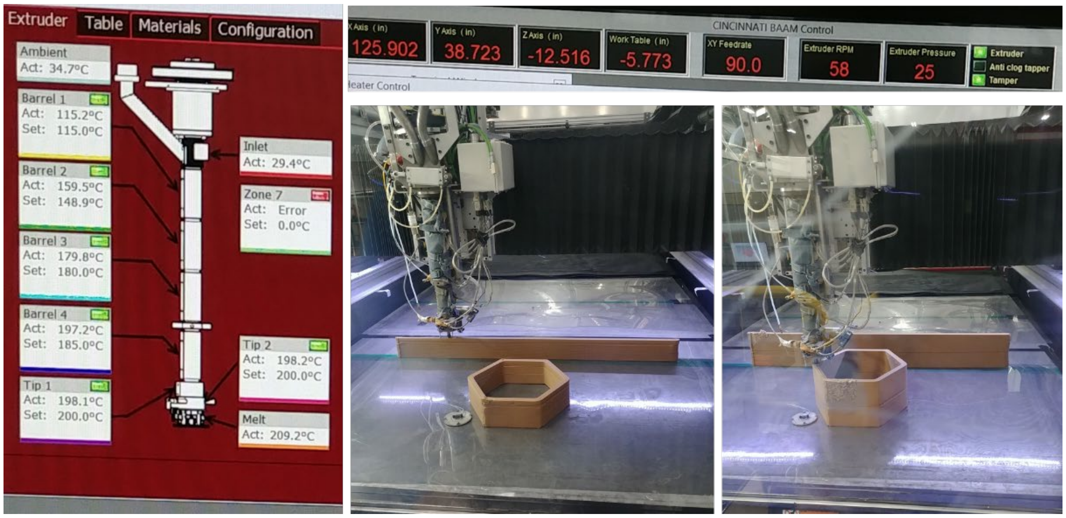

Figure 6. Large scale additive manufacturing of Fiberlean material (1%MFC+20%wood fibers +PLA) and printing condition.

Both the extrusion and the deposition of the material was uniform. During the middle of the print, the temper that flattens the deposited layer broke. Because we had limited material, we continued the print. Although the temper failure caused some imperfections, overall printing quality was still good (see Fig 7). The layer time of 2-2.5min was used. The curl bar was quite flat, only a minor warpage on the edges due to residual stress was observed.

Figure 7. Printed hexagon and a curl bar showing the print quality and slight warpage at the edges.

Upon successful printing of representative parts, a VARTM mold designed for a motorcycle cover was selected. The motorcycle cover, and a CAD design of a representative part is shown in Fig. 8.

Figure 8. Motorcycle cover as selected demonstration mold: Actual part and a selected CAD design.

A female mold design was selected for VARTM process, and it was printed. The printing conditions and the mold printed is given in Fig. 9. During the print we had some vacuum issues which caused some distortions in the initial layers due to solid part design ; however, the print quality in general was good.

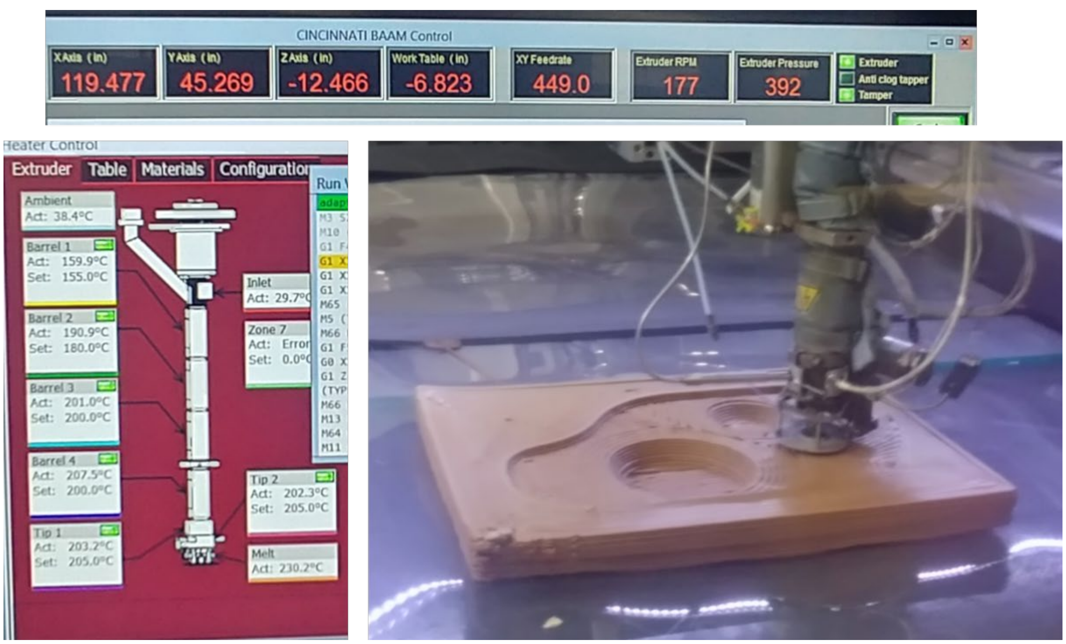

Figure 9. Large scale additive manufacturing of motorcycle cover VARTM female mold using Fiberlean material (1%MFC+20%wood fibers +PLA) and printing condition.

Due to lab access limitations, and running out of funding, machining and testing of the printed mold couldn't be completed by the project completion date. However, as explained earlier, the focus of the project shifted towards development of the surface modification process and composite feedstock with improved material properties.

SUBJECT INVENTIONS

- An U.S. Provisional Application No. 63/051,614 was filed based on the results from this collaboration
- A journal article was published: Carbohydrate Polymers 2021, 256, 117525.

COMMERCIALIZATION POSSIBILITIES

Fiberlean Technology is interested in scaling up the surface modification strategy developed in this project and producing surface modified fibers for producing composite feedstock for large scale AM applications. Additional opportunities are currently being searched for scaling up the process and demonstration the developed materials in large scale AM applications.

PLANS FOR FUTURE COLLABORATION

Another Cooperative Research and Development Agreement (CRADA) or Strategic Partnership Project (SPP) between Fiberlean Technology and ORNL are under discussion for metrology and printing components using modified fiber after scaling up process.

CONCLUSIONS

The results of the project showed that the surface of Fiberlean fibers (mineral-ground microfibrillated cellulose) can be chemically modified via industrially scalable process enabling drying with minimal agglomeration. The surface modified and oven dried fibers have been shown that they have the potential to significantly improve the mechanical properties of a common AM biopolymer resin, PLA, provided that the right chemistry and processing approaches are employed. Using an aqueous-phase modification approach to functionalize MFC, and its oven-dried form, the tensile strengths of neat AM polymer were increased about 38%, while their elastic modulus increased about 71%. Therefore, the project metrics were successfully met. A provisional patent has been applied and a high impact journal article has been published as a result of the project.

After demonstration of the reinforcing potential of the partner's product via an industrially viable process, now scaling up the surface modification strategy to produce large quantity of fibers is needed. Once the process scale up is completed, formulation will be optimized for both the mechanical properties and the suitability for AM in large scale.

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PARTNER BACKGROUND

FiberLean Technologies is a large microfibrillated cellulose (MFC) producer that utilizes minerals for their fibrillation process. FiberLean is a recent spin off company of one the largest mineral companies in the world, Imerys, and is a veteran run small business. Imerys is an Industrial Minerals company and a leading supplier of pigments for paper and packaging. Typical minerals produced by Imerys include kaolin, talc, mica, marble, graphite perlite, diatomaceous earth.