Effect of surface treatment of microfiberlated cellulose fibers on biocomposite properties and additive manufacturing process

[a,c]Halil L. Tekinalp, [a]Darby Ker, [a]Xianhui Zhao, [a]Bowie Benson, [a]Melanie Buziak, [c]Vlastimil Kunc, [c]William Peter, [a,b]Soydan Ozcan

[a]*Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN 37830*

[b]*University of Tennessee, MABE, Estabrook Rd, Knoxville, TN 37916*

[c]*Manufacturing Demonstration Facility, ORNL, 2350 Cherahala Blvd, Knoxville, TN 37932*

ABSTRACT

Polymer additive manufacturing (AM) is a rapidly growing technology and it is transitioning to become an advanced manufacturing technique with the introduction of fibrillar reinforcing materials such as carbon and glass fibers into polymer feedstock. As a result of increasing environmental and long-term sustainability concerns, there is an increasing interest in using bio-derived cellulose fibers to reinforce composites instead of carbon and glass fibers. Melt extrusion/fused filament fabrication method is the most commonly used polymer AM technique which enables direct digital manufacturing of parts with complex geometry with a controlled anisotropic distribution of reinforcing phase. However, there are multiple factors that affect the mechanical performance of the final part such as the dispersion and orientation of the reinforcing fibers, the adhesion between the fibers and the polymer matrix, and the porosity/defects present in the part. Chemical modification of the surface of the reinforcing fibers is an effective way of improving the fiber-polymer interaction. Furthermore, the improved adhesion between the fibers and the polymer can also enhance the fiber dispersion, improve the rheological behavior of the molten feedstock and minimize the formation of porosity during the printing process, which is one of the major issues in AM. In this study, we are investigating the effect of silane surface treatment of micro-cellulose fibers on the thermal, rheological and mechanical properties of cellulose-PLA biocomposites and on the 3D-printing process. X-ray photoelectron spectroscopy results confirmed the increase in amine and silane groups on the surface of modified fibers, indicating successful functionalization. Thermal and mechanical characterization of modified fiber-PLA composites showed significant increases in storage modulus, glass transition temperature, and complex viscosity compared to neat PLA.

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INTRODUCTION

The interest in the use of bio-based polymer composite systems has increased dramatically in recent years due to sustainability, cost and environmental impact. Polymer composites are used in many areas from automotive to aerospace, from sporting goods to buildings. One of the recent area of interest for polymer composites is additive manufacturing (AM), also as known as 3D printing [12]. Polymer composites usually consist of polymer matrix and a reinforcing phase material such as glass fibers and carbon fibers. Instead of these fibers, the use of natural fibers like cellulose, the most abundant polymer on the planet, can be extremely beneficial for their low cost, recyclability, biodegradability, and relatively low density. Cellulose is already being used in many industries such as pulp&paper and textile production [1-4]. Furthermore, cellulose fibers are the component that gives the rigidity and strength to many plants and trees, and therefore, can be good candidates for reinforcing polymers provided that they are processed and integrated properly. Cellulose nanofibers (CNF) have been previously shown to reinforce thermoplastic and thermoset polymers [5], including bio-based resin systems such as polylactic acid (PLA, a bio-based resin derived from corn starch). To illustrate, a study showing that a PLA composite containing 30 wt% cellulose microfibers (CMF) demonstrated a ~100% increase in elastic modulus compared to the base resin was reported [6].

One of the key issues for using bio-based fibers in polymer composites is poor adhesion at the interface between the fiber surface and polymer due to hydrophilic nature of the cellulose fibers and hydrophobic nature of most polymer resins. This poor interaction not only impacts the dispersion of these fibers inside the polymer matrix and the mechanical properties of the composite, but it will also impact the melt rheology and processability of the material system. Cellulose is a semicrystalline polysaccharide in which D-glucopyranose units are linked together by β-(1-4)-glucosidic bonds [7]. Cellulose is naturally hydrophilic due to the large amounts of hydroxyl groups, which causes poor interfacial adhesion with hydrophobic polymer matrices [8]. This incompatibility reduces the potential for cellulose fibers to act as reinforcing material, so improving the interaction between the fibers and the polymer matrix via chemical treatments can significantly improve adhesion. Chemical modification agents have the potential to react with hydroxyl groups on the fiber surface and introduce new functional groups that can promote interaction with the polymer matrix. This study aims to modify surface functionality of cellulose microfibers to improve interfacial adhesion between cellulose fibers and PLA matrix and to investigate its impact on rheology, printability and composite properties. This is a continuation of the work done by Tekinalp et al. to produce PLA composites for large scale additive manufacturing [9]. A silane compound was used as the coupling agent for the solution-based surface treatment on commercially available CMF’s of average size [10].

EXPERIMENTAL

1. Materials

Cellulose microfibers (TC750) were obtained from CreaFill™ (Chestertown MD). CreaFill™ TC750 micro fiberlated cellulose fibers are specified as 20-30 micron in width and approximately 700 microns in length. The loose density of the fibers is 20-30 g/L. The dry-base fibers are also specified by the manufacturer as to be approximately 99.6% pure cellulose. For the chemical modification, (3-aminopropyl) triethoxysilane (APTES) 98% was used as received from Sigma-Aldrich® (St. Louis MO). 190 proof ethanol from Decon Laboratories (King of Prussia PA) and ASTM 1 deionized water were used to formulate the solvent used for the chemical treatment. Neat PLA pellets (Ingeo Biopolymer 4043D) were obtained from Natureworks (Savage MN).

2. Surface Treatment

The cellulose microfibers were dried at 80 °C for a minimum of four hours before any treatment to reduce moisture content. The surface treatment used in this experiment followed a similar procedure used by Gwon et al. [10]. 15:1 solution/fiber ratio by weight was used. A mixture of 95 wt% ethanol and 5 wt% deionized water was used as a solvent. 3wt % APTES was slowly added to the solution with magnetic stirring at 25 °C to allow the compound to hydrolyze for one hour. After hydrolysis, the dried cellulose microfibers were added to the solution and magnetically stirred. The fibers were soaked in the solution for 2 hours to allow for silane coupling. The fibers were then vacuum filtered and dried at 80 °C for 24 hours.

3. X-Ray Photoelectron Spectroscopy

Samples of unmodified and surface modified TC750 fibers were analyzed with X-ray photoelectron spectroscopy (XPS). Each fiber collection was pressed onto double-sided tape and fixed to glass slides, which were then introduced into the analysis chamber through a vacuum pumped load-lock. To identify the elements present on the surface of the fibers, a wide energy range survey scan was acquired. A set of narrow energy range core spectra was acquired for specific elements to identify chemical bonding changes on the modified fibers.

4. Compounding & Sample Preparation

Modified and unmodified TC750 fibers were dried along with PLA pellets at 80°C for a minimum of four hours to reduce moisture content. The materials were fed into a Brabender Intelli-Torque Plasti-Corder high-shear mixer and compounded at 170°C for 5 minutes at 60 rpm. This type of mixing allowed for fiber clump breakup and dispersion within the molten polymer matrix. Composites with modified and unmodified cellulose were formulated at a range of 10-30 wt% fiber content. Each composite formulation was then melted in a plunger-type batch extrusion unit at 170-190°C. A slit-shaped die was used to extrude the composites into slit preforms. The slit preforms were measured and cut to predetermined weights and compression molded at 170-190°C into uniform bars based on ASTM standard D4703 [11]. The samples were initially pressed at 170°C, but composites with higher fiber content (i.e. 30wt%) did not uniformly melt and flow and subsequently had to be pressed at higher temperatures. Each composite formulation was also pressed into 1.0mm films for rheological testing and thermal characterization using the aforementioned compression molding procedure.

ASTM Type V dogbone tensile samples were 3D printed using a Lulzbot Taz 6 with a 0.8 mm diameter nozzle. The composite filament was made using the plunger-type batch extrusion unit with a 1.75 mm diameter die. In order to accommodate the rheological and melting properties of the material, as well as inconsistencies in the filament, the printing parameters had to be adjusted to the specifications shown in Table 1.

Table 1: Specifications for 3D printing parameters for PLA-TC750 Composite filaments

Printing Temp.	*195 °C*	Layer Height	*0.4 mm*
Build Plate Temp.	*60 °C*	Line Width	*0.9 mm*
Flow	*100%*	Wall Thickness	*1.0mm*
Print Speed	*30 mm/s*	Top/Bottom Thickness	*0.8 mm*
Wall Speed	*15 mm/s*	Top/Bottom Layers	*3*
Outer Wall Speed	*30 mm/s*	Top/Bottom Pattern	*Lines*
Inner Wall Speed	*35 mm/s*	Initial Layer Speed	*15 mm/s*
Top/Bottom Speed	*30 mm/s*	Initial Layer Travel Speed	*87.5 mm/s*
Travel Speed	*175 mm/s*	Skirt/Brim Speed	*15 mm/s*

5. Thermomechanical Characterization

Dynamic mechanical analysis (DMA) was carried out on each formulation using the compression-molded bars. Each bar had 35.0 x 9.8 x 2.8 mm approximate dimensions. A TA Instruments Q800 dynamic mechanical analyzer was used in dual cantilever mode. Measurements were performed at a temperature range of 30°C to 120°C at a heating rate of 3.0°C/min with a constant frequency of 1.0 Hz and strain amplitude of 0.5%.

Thermogravimetric analysis (TGA) was carried out on each sample using a TA Instruments Q500. Approximately 10-25 mg sample pieces were cut from the 1.0mm films to use as test specimens. A temperature range of 30°C to 600°C was used with a heating rate of 10°C/min in nitrogen atmosphere.

Differential scanning calorimetry (DSC) was performed on each formulation using a TA Instruments Q2000 apparatus with a heat-cool-heat procedure. Each sample was equilibrated at 30°C and tested within the temperature range of 30°C to 200°C with a heating/cooling rate of 5°C/min. The crystallinity of each composite was calculated using the following equation:

$$\chi_c = \frac{\Delta Hm - \Delta Hc}{w \times \Delta H_{100}} \tag{1}$$

where χc is the %crystallinity of PLA in the composite, ΔHm and ΔHc are the enthalpies of melting and crystallization of the composites respectively, w is the weight fraction of PLA in the composite, and $\Delta H100$ is the melting enthalpy of 100% crystalline PLA. 93 J/g was the value used for $\Delta H100$.

Rheological properties of each sample (frequency sweep from 0.1 to 100 rad/s) were determined using a TA Instruments Discovery HR-3 at 180 °C in the linear viscoelastic region. Parallel plates of 8mm diameter with a gap of 500 µm were employed for the measurements. Prior to the frequency sweep, a strain sweep (from 0.01% to 50%) at 100 rad/s was performed for each sample to ensure that the strain used was within the linear viscoelastic region.

Displacement controlled tensile tests were performed on the FDM printed samples using servo-hydraulic testing machine. The tensile tester used a 300-lb load cell. A testing speed of 0.01 mm/s was used along with a 10 mm gage-length extensometer.

RESULTS & DISCUSSION

1. Chemical Treatment of Fibers

Due to the rich hydroxyl groups present on their surface, cellulose fibers are highly hydrophilic. In order to promote adhesion and compatibility with the PLA matrix, hydrophobic functionality had to be introduced to the fiber surface. XPS analysis results confirmed that the APTES solution treatment successfully introduced functionalization onto the fiber surfaces.

Table 2 summarizes the relative atomic concentrations of prominent elements found on the cellulose fibers. Unmodified fibers also showed presence of small amounts of N and Si. The modified fibers showed significantly higher N (1-4 at% vs. 0.1 at%) and Si (2-7 at% vs. ~0.5 at%). Cellulose has the chemical formula $(C6H10O5)n$ and APTES is $C9H23NO3Si$, so the increased presence of silicon and nitrogen on the surface of the fibers indicates that chemical modification by silane occurred. The trace amounts of Mg, Na, and Cl are likely due to contamination during fibrillation and processing of the cellulose.

A set of narrow energy range core spectra was also done on the prominent elements present on the surface of the fibers to assess chemical bonding changes. Four separate features were used to adequately fit the curves for the C 1s spectra: hydrocarbon groups at ~284 eV, C-OH bonding at ~286 eV, O-C-O bonds at ~287 eV, and surface carboxyl groups at ~289 eV. Similar measurements were made for the N 1s spectra to account for C-NH-C species at ~399 eV and N-C=O bonding at ~402 eV. For the Si 2p spectra, two different peaks were

Table 2: Relative atomic concentrations of elements found within cellulose microfibers. Modified fibers are denoted with ‘M’.

(at.%)	**C**	**O**	**N**	**Si**	**Mg**	**Na**	**Cl**
TC750	58.1	39.9	0.1	0.6	1.1	0.2	tr
TC750M	56.5	35.6	2.4	4.4	0.8	0.1	tr

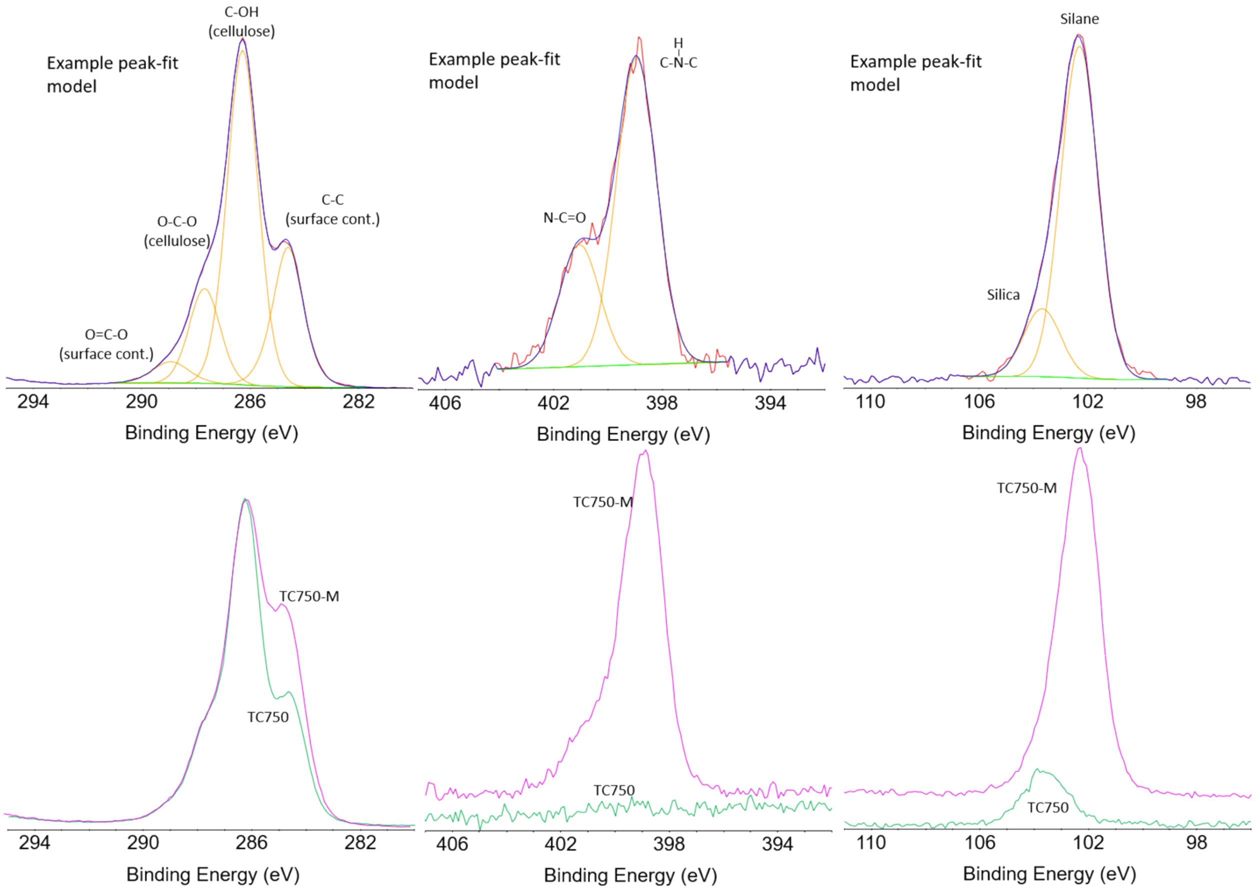

Fig. 1. XPS analysis showing peaks for prominent bonding on the C 1s, N 1s, and Si 2p spectra for modified and unmodified TC750 fibers.

measured: silane species at ~102 eV and silica at ~104 eV. The increased amine group and silane bonding on the modified fibers is particularly significant, as they indicate successful surface modification. **Fig. 1** shows the differences in bonding concentrations for these groups between the modified and unmodified TC750 fibers.

2. Impact of Surface Treatment on Thermomechanical Properties of Biocomposites

Thermal and mechanical characterization was carried out on both modified and unmodified cellulose-PLA composites with varying fiber content (10-30 wt%) to investigate the effect of modification. Thermogravimetric analysis (TGA) was performed to observe any changes in degradation behavior within the composites. Each sample was ramped at a constant heating rate to temperatures up to 600 °C, while their weight changes were monitored. Virtually no difference between the degradation behavior of the modified and unmodified fiber composites were observed, and only slight variances between the composites with higher fiber concentrations (see **Fig. 2**). This indicates that the chemical modification did not have a significant impact on the degradation behavior of composites.

Based on dynamic mechanical analysis (DMA) results, increase in storage modulus with increasing fiber content was observed for both set of composites. Particularly at temperatures above glass transition temperature (Tg), such as 80℃, the modified fiber composites showed significantly higher moduli than unmodified fiber composites (**Fig. 3**). This is an indication of the modified composites dissipating significantly less energy than neat PLA at higher temperatures. DMA results also showed a significant decrease in Tan Delta peak value and shift in peak location (i.e., Tg) with increasing fiber content. While this trend was observed with both set of composites, the surface treated cellulose composites showed larger shifts both in peak height and peak location (**Fig. 4**). This indicates hindrance of segmental polymer chain motion at the macro level, which can be attributed to greater polymer-fiber adhesion.

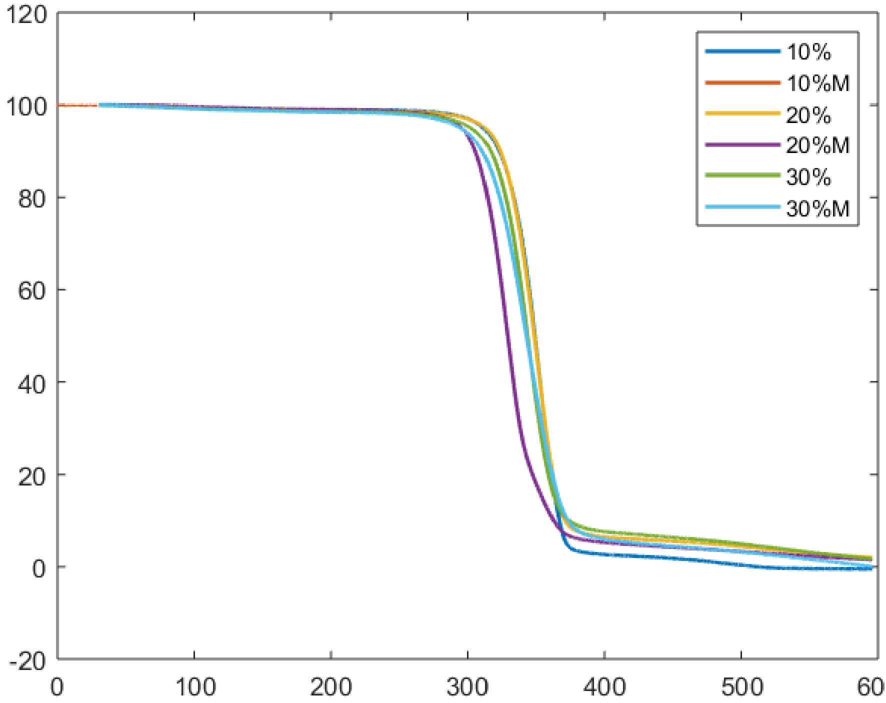

Fig. 2. Thermogravimetric analyses (TGA) showing degradation behavior of PLA composites with modified and unmodified TC750.

Differential scanning calorimetry (DSC) analyses were carried out to observe the effect of surface modification on crystallization behavior of composites. The second heating cycle was used to examine the specimens to eliminate the impact of previous thermal history.

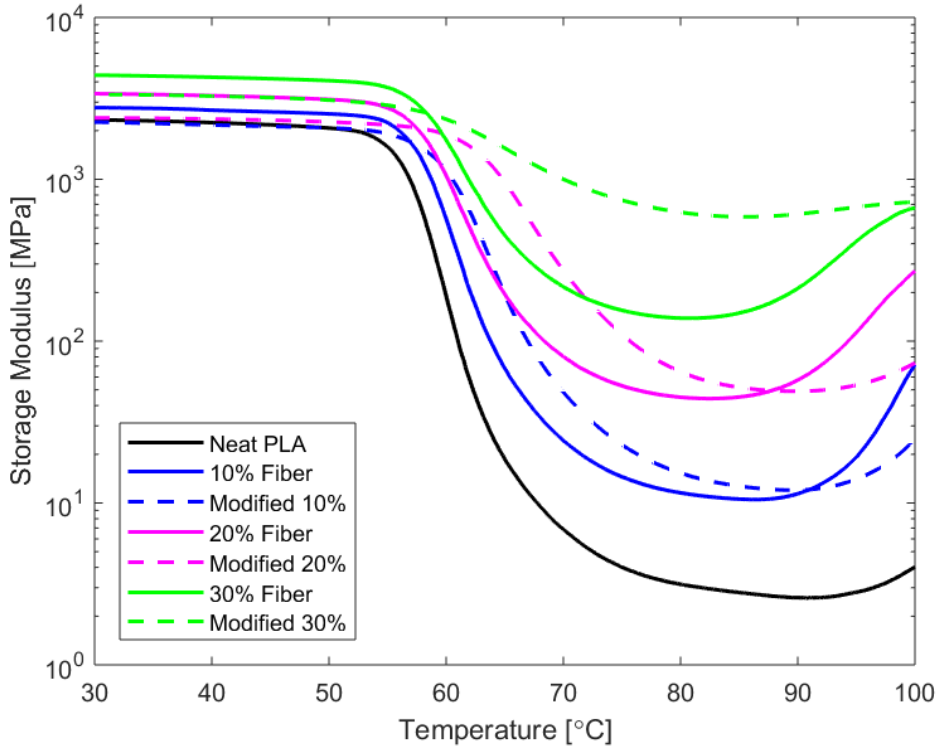

Fig. 3. Dynamic mechanical analyses (DMA) showing storage modulus of PLA composites with modified TC750, unmodified TC750, and neat PLA.

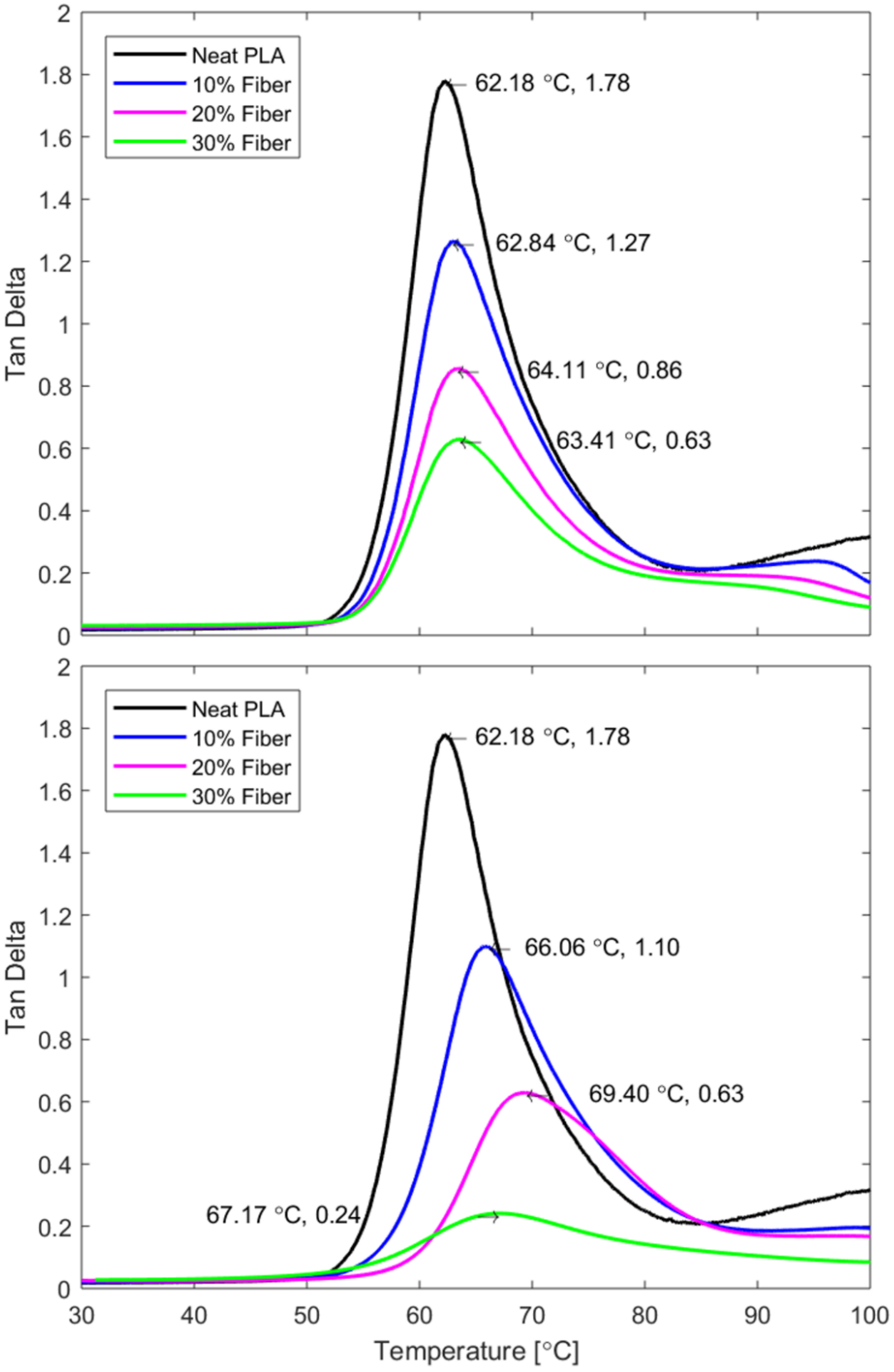

Fig. 4. DMA showing Tan Delta peak values for a) unmodified and b) modified TC750-PLA composites.

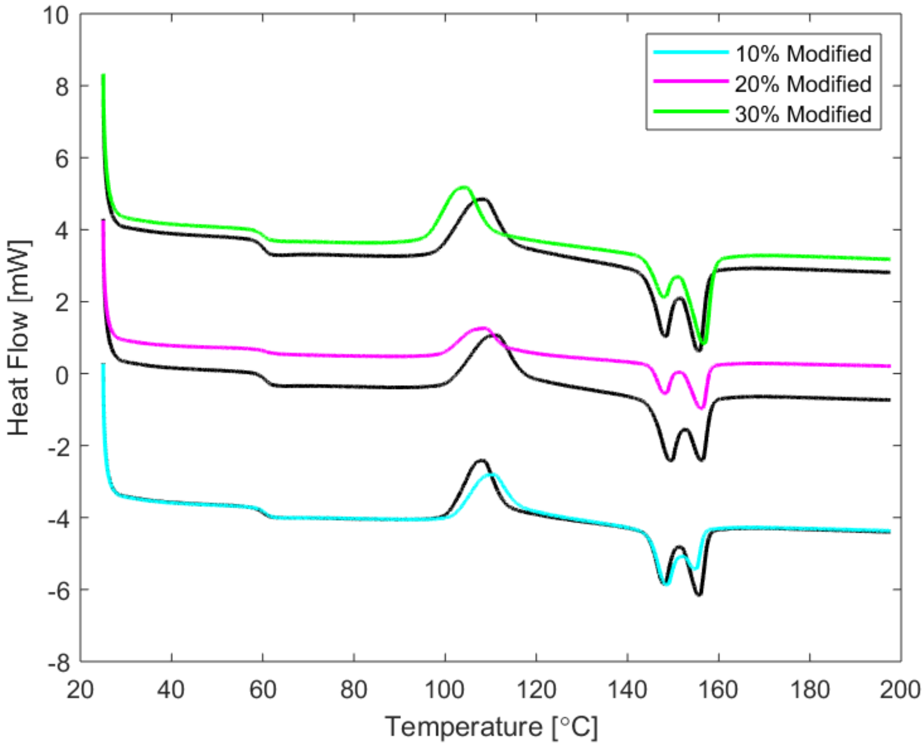

Fig. 5. DSC of the TC750-PLA composites. Each modified fiber composite is plotted with its corresponding unmodified fiber composite (black) according to wt%.

As it can be seen from **Fig. 5**, there is only minimal variation in crystallization behavior between the modified and unmodified fiber composites. If the surface modification was drastically changing the crystallization behavior of the polymer matrix, shifts in peaks corresponding to the glass transition, recrystallization, and melting would be seen. However, each of these peaks remained relatively unchanged with both increasing fiber content and the addition of modified fiber. This also suggests that even though polymer-fiber adhesion is being improved, its impact on the polymer is only at the macro level.

2. Impact of Surface Treatment on Composite Rheology and Printability

The additive manufacturing process is a rheology dependent process and the improvement in surface interaction/adhesion between cellulose fibers and the polymer matrix is expected to significantly impact the melt flow behavior of the composite system. Rheological characterization of both unmodified and modified cellulose-PLA composites was carried out to further examine polymer-fiber interaction. The addition of fibers in both cases dramatically increased the complex viscosity of PLA (see **Fig 6**). While this increase was much higher at low shear rates (i.e., low angular frequency), it was more moderate at high shear rates. This shear thinning behavior is a desired feature for extrusion based additive manufacturing processes, since low viscosity is needed during the extrusion process under shear, while a high zero-shear viscosity is required so that the material can keep its shape after deposition. The improved shear thinning behavior, higher zero-shear viscosity and lower high-shear viscosity of modified cellulose fiber composites further confirm the improved interaction/adhesion between the cellulose fibers and the polymer matrix with the surface treatment. Although 10 wt% TC750 - PLA composites were also subjected to rheology tests, due to likely degradation of the polymer or contamination introduced during processing reliable data could not be collected; therefore, they were not included, and the tests will be repeated.

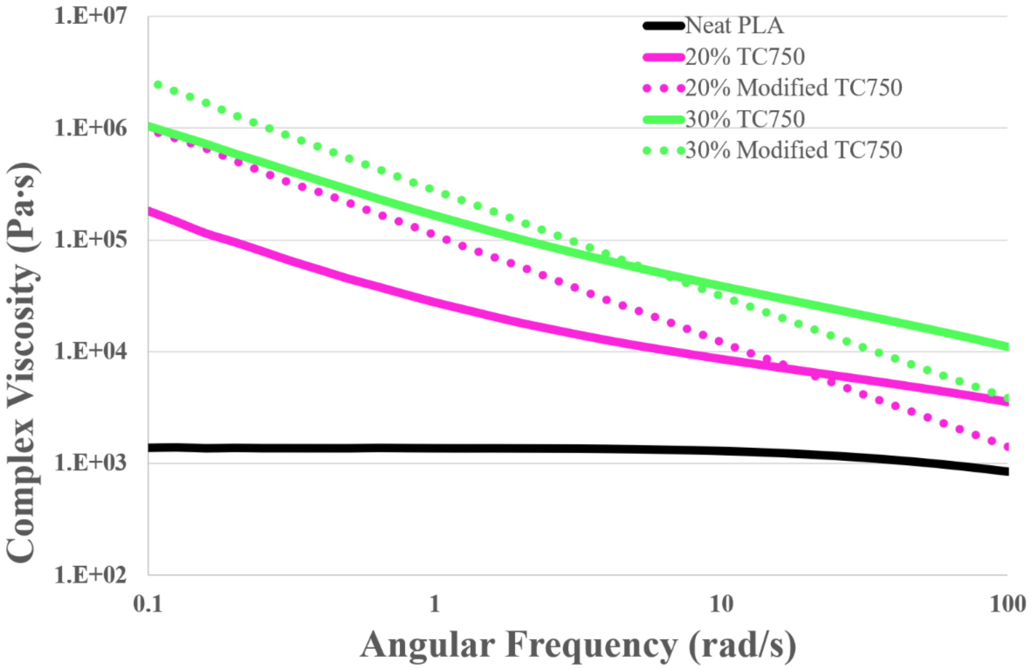

Fig. 6. Viscosity behavior of modified and unmodified TC750 PLA composites.

As previously mentioned, extrusion based additive manufacturing is a rheology dependent process. Therefore, to investigate the effect of surface treatment on the printability of the cellulose fiber-polymer composites, FDM printing filaments containing 10 wt% cellulose fibers (both modified and unmodified) were prepared and used to print tensile testing specimens (ASTM D638 type V, dog-bone specimens [13]). It was observed that surface treatment improved the printability of the cellulose fiber composites and more uniform specimens were printed using modified cellulose-PLA material (see **Fig. 7**). Tensile testing results also showed that treated cellulose fiber composites had relatively higher strength (see **Fig. 8**). Also, it is important to note that the standard deviation observed is significantly low for treated cellulose composites compared to untreated cellulose composites. These results also confirms that the surface treatment can improve the interaction between the cellulose fibers and the polymer matrix and help achieving more uniform processing and printing.

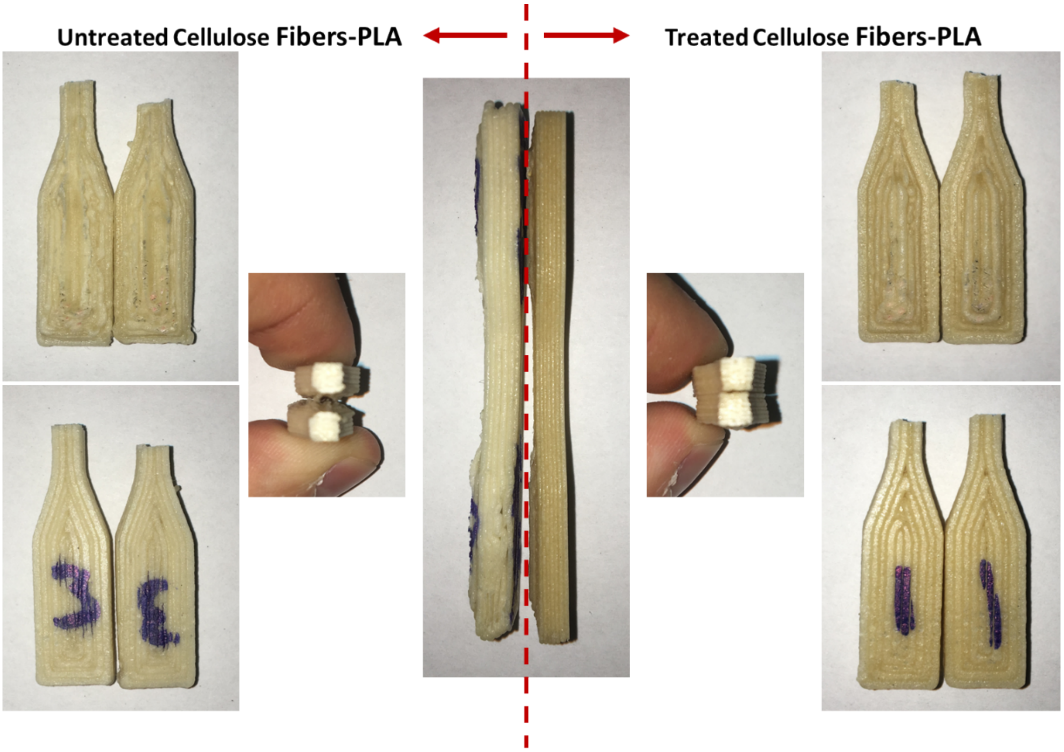

Fig. 7. Images of FDM-printed 10 wt% cellulose fiber-PLA specimens.

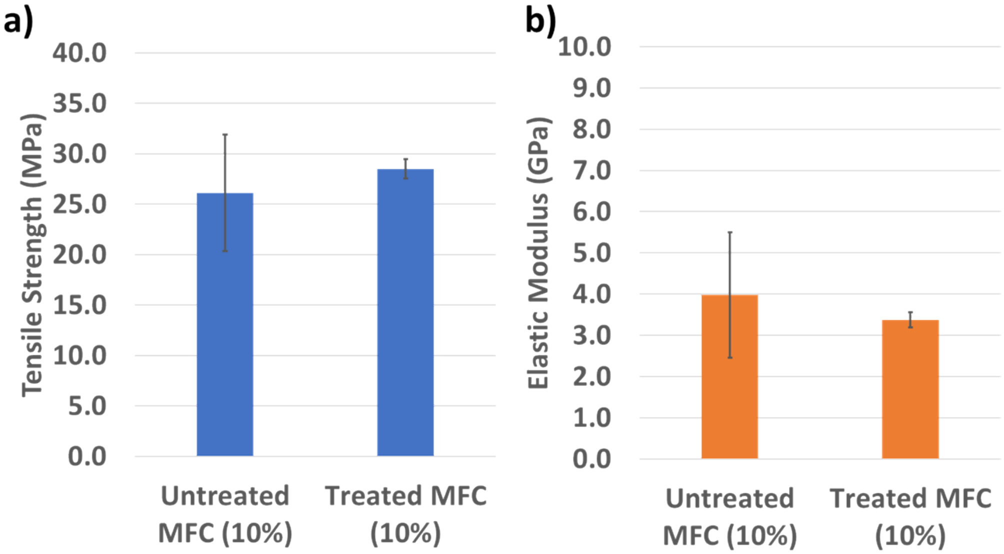

Fig. 8. Tensile properties of FDM-printed specimens; a) tensile strength, b) elastic modulus.

CONCLUSIONS

The surface modification of cellulose microfibers with a silane compound to improve interfacial adhesion and compatibility with PLA bio resin was successfully shown. Initial XPS analysis confirmed the chemical modification of the microfibrillated cellulose surface with silane. The modified fibers were also shown to improve mechanical and thermal properties. DMA results showed higher storage modulus values, indicating that the composites with modified fibers dissipate less energy at higher temperatures. Greater shifts in glass transition temperature were also observed in the modified fiber composites indicating that there is improved fiber-polymer adhesion and greater amounts of energy are required to induce segmental polymer chain movement. Rheological analysis further suggests improvement of interfacial adhesion due to high complex viscosities and higher shear-thinning behavior. Finally, it was shown that the surface treatment can improve the printability, and therefore final properties of the printed fiber composites. Further work needs to be carried out to optimize processing parameters, but surface modification with a silane solution has been shown to improve the functionality of cellulose microfibers and promote compatibility with PLA. The improved properties provided by this treatment may be useful for future work in developing bio-based feedstocks for large scale additive manufacturing.

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