

## Article

# Hybrid Bio-Based Composites: Enabling Cellulose Nanofiber (CNF) Incorporation into Composites via Macroscale Natural Fiber Carriers

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## Abstract

Cellulose nanofibers (CNFs) have significant potential in composites as additives to improve mechanical properties, melt rheology, and more. However, agglomeration of CNFs is a key challenge in composite melt processing as obtaining nano-level dispersion of CNFs often requires cost- and energy-intensive processes (e.g., solvent exchange or freeze drying) due to the strong hornification tendencies of CNF. Herein, we avoid these challenges by using a natural fiber carrier method to integrate CNF into thermoplastic composites. Fibers are co-dried to create a hybrid fiber feedstock for compounding in which natural fibers are decorated with dispersed nanofibers. The hybridized fibers result in up to a 24% increase in tensile strength and up to a 35% increase in Young's modulus compared to composites only containing natural fibers. The lignocellulosic nanofibers are found to outperform their purely cellulosic counterpart, which is theorized to be due to either an increased propensity for fibrillation of the lignocellulosic fibers or the increased hydrophobicity of the fibers due to the presence of lignin. Surface analysis of fiber feedstocks, via streaming potential measurements and dynamic light scattering (DLS), confirmed a significant change in the feedstock hydrophobicity before and after hybridization. While mild additions of CNF (1 wt.% on the macroscale fiber) do not impact the composite melt viscosity, the viscosity is found to increase at higher CNF loadings (5 wt.% on the macroscale fiber), indicating its utility as a rheology modifier. Lastly, use of these materials as novel feedstocks for medium-scale additive manufacturing in high-fidelity part production was demonstrated.

**Keywords:** cellulose nanofiber; polymer composites; hybrid; bio-based; natural fiber



Academic Editor: Jordi Puiggali

Received: 19 May 2026

Revised: 16 June 2026

Accepted: 23 June 2026

Published: 30 June 2026

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## 1. Introduction

Poly(lactic acid) (PLA) is a bio-based polyester known widely for being renewable and bio-compostable as well as an excellent candidate for 3D-printing. However, its low ductility and brittleness often limit its industrial applications despite its easy processing. Various solutions have been proposed to improve the mechanical performance of PLA, including chemical modifications [1], alloying [2–4], and reinforcement with microscopic or nanoscopic fillers to create a composite [5–7]. Composite production can be quite effective, as miscibility issues between constituents are avoided. PLA composites have been produced with a wide variety of fillers including glass fiber (GF) [8], natural fibers (NFs) [9], and carbon fiber (CF) [10] as well as nanomaterials like carbon nanotubes [11] or cellulose nanomaterials (CNMs) such as cellulose nanofibrils (CNFs) or cellulose nanocrystals

(CNCs) [12]. For example, the literature has shown that only 1.3 wt.% of CNF in PLA improved stiffness by 200% for the as-made material and  $\leq 600\%$  with orientation of the anisotropic CNF [12]. Cellulosic reinforcements like NFs, CNF, or CNC are of particular interest for PLA as these materials preserve the compostable attribute of the composite while improving its mechanical performance. Renewably sourced composites made of natural fibers, CNMs, or their hybrids are of growing interest in many industries, including automotive applications that would benefit from high specific stiffness and strength [13,14], plastic packaging [13,14], and large-format additive manufacturing (LFAM) applications in buildings and precast concrete tooling, which require lower cost feedstocks [15,16].

Natural fiber-reinforced composites (NFRCs) have been investigated for PLA containing a variety of NFs, including coir (coconut) fiber [17], hemp fiber [18,19], and flax fiber [20], as well as wood-based cellulose like wood flour [21] or bleached pulp [22]. While continuously oriented NFRCs can be prepared, many investigations focus on short, discontinuous NFRCs, which have been used for compression molding [9], injection molding [9], and 3D-printing [23]. Discontinuous NFRCs are widely used because of the inherently discontinuous nature of natural fibers. Typically, the higher the strength and stiffness of the NF, the better the reinforcement in the polymer. NFs from varying sources have inherently different chemical compositions (i.e., cellulose, hemicellulose, and lignin content) [20], morphologies, and aspect ratios. NFs such as hemp or flax are high in cellulose content and relatively dense; consequently, these materials tend to have superior mechanical properties. For example, Sanivada et al. demonstrated that neat PLA has a tensile strength of  $\sim 50$  MPa, and a composite prepared by melt compounding followed by compression molding with 30 wt.% flax fiber yielded PLA composites with a tensile strength of 60.1 MPa [20]. Similarly, randomly oriented 30 wt.% hemp fiber/PLA composites have exhibited up to 75 MPa tensile strength [9]. PLA composites with wood pulp can produce similar improvements at high fiber loadings as tensile strengths of 67.9 MPa, and modulus values of 5.3 GPa have been reported for 30 wt.% recycled paper pulp/PLA composites; meanwhile, PLA composites with 30 wt.% wood flour (WF) result in a tensile strength of 58.8 MPa and a tensile modulus of 6.22 GPa [9]. Despite these improvements, differences in hydrophobicity between natural fibers and PLA can result in poor interfacial adhesion and thus result in a loss in tensile strength or poor reinforcement, brittleness, etc. [9]. Chemical surface treatments (e.g., mercerization or alkali treatments) or increases in surface roughness can improve or recover lost tensile strength in NF composites due to chemical interactions at the filler/matrix interface or mechanical interlocking, respectively [9,14].

Mechanically fibrillated CNFs are long, flexible nanoparticles with dimensions of 20–100 nm diameter and lengths on the order of microns [13]. Commercially, CNFs are widely available and use bleached soft kraft pulp or other refined, 100% cellulose biomass as a feedstock. However, there is growing interest in lignocellulosic CNF (LCNF) and CNC, which would enable a wide variety of byproducts and waste streams to be incorporated into this high value product [24]. While these materials are not the stiffest or strongest class of CNMs, their reinforcing potential has been demonstrated in various composite applications, including PLA. For example, freeze-dried CNF bundles have been melt compounding in PLA at concentrations up to 50 wt.%, with tensile strength improvements from  $\sim 55$  MPa to  $\sim 95$  MPa with 40 wt.% addition of CNF into PLA [25]. Like other natural materials, the chemical compatibility of CNF and other CNMs with polymer resins is a challenge due to the difference in hydrophilicity; polymers like PLA, polypropylene, etc., are less hydrophilic than CNMs [13]. While many chemical grafting methods have been explored to improve the compatibility of CNMs with polymer resin, an alternative method may simply be to use LCNF as lignin is more hydrophobic than cellulose [26–28]. LCNF has shown significant potential to improve the mechanical properties of PLA composites where

increasing lignin content results in enhanced tensile strength (+37%) and modulus (+61.1%) at concentrations of up to 9% lignin in LCNF compared their controls [29].

While CNMs can provide excellent reinforcement in polymer composites at even low concentrations, dispersion of the nanomaterial into the polymer is often a challenge [13]. Previous research has depended on time consuming, costly, and energy-intensive multistep processes such as freeze drying or spray drying to retain the nanofibrillar structure prior to composite incorporation [13]. However, these methods typically produce poor dispersion of CNMs due to the formation of strong hydrogen bonds during the drying processes, which causes aggregation [13]. Solvent exchange of CNMs into a good solvent for the polymer tends to produce excellent dispersion; however, PLA is only miscible in hazardous solvents such as dichloromethane or chloroform [30], which can limit the scalability of this method. Other processes have used liquid carriers to distribute and disperse nanomaterials into PLA during melt compounding [12,31,32]. For example, Herrera et al. pumped a suspension of CNC, triethyl citrate (TEC), water, and ethanol into PLA during twin screw extrusion to create plasticized PLA/20%TEC/1%CNC composites [31]; while polyethylene glycol (PEG) has been used as a carrier for CNF [12] as well as cellulose whiskers [33]. In these processes, the carrier serves as a processing aid, plasticizer, and compatibilizer between the nanomaterial and resin. However, the objective of this study was to determine if macroscopic, natural fibers could be used as carriers for the incorporation of CNMs into thermoplastic composites without labor- or energy-intensive methods while maintaining their nanofibrillar morphology.

NFRCs are an important class of composites due to their high specific stiffness and specific strength, properties essential to weight reduction in structural applications. CNMs can further improve mechanical properties, even at small concentrations, in these types of composites, provided the critical issue of agglomeration is addressed. The first objective of this work was to investigate a method to overcome CNF agglomeration in melt-processed polymers without using solvents or low-throughput, potentially costly drying methods like spray drying. The method used was a co-drying method in which the NF acted as a carrier for the CNF, resulting in a NF with fibrillated nanoparticles decorating the surface. The carrier fibers were flax fiber, wheat straw, and bleached soft kraft pulp (BSK), and their CNF counterparts, which were used to create PLA/NFRC hybrid composites. While the most common CNFs are mechanically fibrillated wood pulp, the present study also investigated LCNF from flax fiber and wheat straw, which are unique, non-wood CNFs. Hybrid fiber morphology and surface charge were analyzed. The second objective was to understand the benefits of synergizing CNF sources (i.e., mechanically fibrillated non-wood CNF and wood CNF) with the macroscopic carrier fiber; thus, the thermomechanical performance of the hybrid composites was thoroughly characterized. It should be noted that no additional chemical treatments (e.g., mercerization [34,35], silane [36,37], maleic anhydride [38,39]) were utilized throughout this study.

## 2. Materials and Methods

### 2.1. Materials and Sample Production

**Materials Sourcing:** All polylactic acid (PLA) used throughout this study was purchased from NatureWorks, LLC (Plymouth, MN, USA), as Ingeo 4043D and used as received. The flax fibers (i.e., macroscale fibers) were purchased from MiniFIBERS, Inc. (Johnson City, TN, USA), as 3 mm length fibers, the creafill named Createch T750 was provided by Creafill (Chestertown, MD, USA), and the wheat straw was provided by the University of Maine (Orono, ME, USA). All macrofibers were dried in an oven at 60 °C overnight prior to use; biomass compositional analysis for the three macroscale fibers used throughout this study can be found in Table S1. All CNF suspensions were secured from the

Process Development Center at the University of Maine (Orono, ME, USA) and additional information about these suspensions can be seen in the previously reported literature [24]. In short, the BSK-sourced CNF was produced on a pilot-scale disk refiner and was processed to 90% fines (as measured using a Techpap MorFi fiber analyzer, Gieres, France). The flax- and wheat straw-based CNF materials were produced using a supermasscolloider (MKCA6-2 Masuko Sangyo Co., Ltd., Kawaguchi City, Japan) and were processed to a net energy of 7000 kW.h/MT and 10,000 kW.h/MT, respectively, based on the dry weight of the material. The resulting fines of the non-wood CNFs were ~97% and ~99% for the flax- and wheat straw-based CNFs, respectively. The percent fines are the percentage of fibers under 0.2 mm long. The flax- and wheat straw-based CNFs were produced from the same source of macroscale fibers noted above.

**Fiber and CNF Mixing:** The NF/CNF mixture was produced by first diluting the CNF suspension with DI water by approximately half to reduce its viscosity. The natural fibers were placed into a large bowl, and the diluted CNF suspension was poured over the natural fibers incrementally and mixed by hand to ensure uniform wetting and dispersion until the entire suspension was added to the fibers. Macrofibers and CNF were weighed prior to mixing to target final hybrid fiber formulations of 99 wt.% macrofiber, 1 wt.% CNF for each combination of BSK, flax, and wheat straw with CNF, fCNF, and wsCNF. Each batch yielded approximately 10 g of hybrid fibers. After mixing, the fiber/CNF/water mixture was spread onto a shallow aluminum dish and dried in an oven at 60 °C for a minimum of 48 h. The fiber/CNF materials were noticeably stiffer upon drying and were physically broken into smaller pieces by hand prior to compounding. Additional samples were then made with BSK and flax macrofibers and BSK-based CNF with CNF at 5 and 10 wt.% with respect to the weight of the macrofibers. Finally, large batches (~4 kg) of hybrid BSK/CNF and flax/CNF at 5 wt.% CNF were prepared for large-scale compounding trials.

**Composite Manufacturing:** Composites were produced using a Brabender Intellitorque compounder (Ashland, VA, USA) at a mixing temperature of 180 °C and speed of 60 rpm. The macroscale fiber concentration was kept constant at 20 wt.% and the CNF concentration on the macroscale fiber was kept constant, unless otherwise stated, at 1 wt.% with respect to the weight of the macroscale fiber. These concentrations (e.g., 20 wt.% macrofiber of the total composite weight) were selected based on the previous literature and as a means to maximize mechanical performance without detrimentally increasing composite embrittlement, melt viscosity, or cost [17,21,40–43]. In a typical melt compounding procedure, PLA was placed into the mixing head and processed for 2 min prior to the addition of the natural fiber or natural fiber/CNF hybrid, after which the composite was mixed for a further 5 min to ensure uniform dispersion. It should be noted that the processing parameters (i.e., compounding temperature, time, RPM) were selected based on visual inspection of the composites to ensure uniform filler dispersion. In all cases, the composites were then compression molded (Carver Hydraulic Press, Wabash, IN, USA) at 180 °C into flat sheets of ~1 mm thickness and then cut into strips prior to being compression molded into rectangular bars ( $l \times w \times t$ : 60 mm  $\times$  10 mm  $\times$  3 mm). Compression molding was performed by first equilibrating the sample and mold temperature at 180 °C for ~5 min prior to applying 4 metric tons of pressure for 5 min, then cooling to room temperature under pressure with forced water/air cooling.

## 2.2. Mechanical and Thermal Characterization

**Thermogravimetric Analysis (TGA):** A TA Instruments TGA 5500 (New Castle, DE, USA) was used for all thermal stability testing. Samples (~10 mg) were heated from room temperature to 600 °C at a temperature ramp rate of 10 °C min<sup>-1</sup> in an air environment. The thermal stability for all samples was determined by the onset of thermal degradation

( $T_{onset}$ ) as well as the  $T_{2\%}$  and  $T_{5\%}$ , corresponding to the temperatures at which 2 wt.% and 5 wt.% of the composite mass was lost, respectively. Composites should not be heated above the  $T_{2\%}$  value to ensure no material degradation occurs.

Differential Scanning Calorimetry (DSC): A TA Instruments DSC 2500 (New Castle, DE, USA) was used for all testing under an argon environment. Samples (~5 mg) underwent heat-cool-heat thermal cycling from 0 °C to 200 °C at a rate of 10 °C min<sup>-1</sup>. The glass transition temperature ( $T_g$ ) was recorded as the inflection point of the step change seen in the second heating curve, while the cold crystallization temperature ( $T_{cc}$ ) and the melting temperature ( $T_m$ ) were taken as the maximum and minimum value of the second heating curve, respectively. The crystallinity ( $X_c$ ) was calculated using Equation (1):

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f^\circ \phi} \quad (1)$$

in which  $\Delta H_c$  and  $\Delta H_m$  indicate the enthalpies for cold crystallization and melting, respectively.  $\Delta H_f^\circ$  indicates the melting enthalpy of a purely crystalline PLA (taken to be 93 J g<sup>-1</sup>), and  $\phi$  represents the mass fraction of PLA [44]. The crystallinities were recorded from the second heating curve of DSC [44].

Tensile Testing: Tensile testing was performed using a servo-hydraulic test frame (MTS, Eden Prairie, MN, USA) with a 500 lb-f load cell with Type V dogbones according to ASTM D638. Each specimen was elongated at 1 mm/min until fracture, and elongation was recorded using a 0.3" axial extensometer (Epsilon, Jackson, WY, USA). At least five specimens of each material were tested.

Dynamic Mechanical Analysis (DMA): A TA Instruments DMA 850 (New Castle, DE, USA) was used for testing all composite samples molded to 60 mm × 10 mm × 3 mm ( $l \times w \times t$ ). Temperature sweeps were performed using a dual cantilever fixture under an air environment in which samples were heated from room temperature to 100 °C at a rate of 3 °C min<sup>-1</sup>, frequency of 1 Hz, and amplitude of 15 µm. Heat deflection temperature (HDT) experiments were also performed in the DMA using a three-point bending fixture in which samples were heated from room temperature to 100 °C at a rate of 2 °C min<sup>-1</sup> under a constant stress of 0.455 MPa; HDT experiments were performed according to a modified ASTM D648 procedure, and the HDT was recorded as the temperature at which the sample reached a deflection of 0.121% strain [45]. A minimum of three samples were performed for all experiments to ensure statistically significant results [45].

Rheology: Samples were compression molded following the procedure described above to produce disks 25 mm in diameter and approximately 1.2 mm in thickness. Rheological measurements were performed using an oscillatory rheometer (ARES G2, TA Instruments, New Castle, DE, USA) equipped with 25 mm parallel plates in a forced convection oven. Each material was measured at 180 °C with a 1 mm gap. Amplitude sweeps were first performed on each material at a frequency of 1 Hz and strain ranging from 0.005 to 50%. Strain amplitudes were selected within each material's linear viscoelastic envelope in which strain and stress are in-phase. Frequency sweeps were then performed using the selected strain amplitude for each material at frequencies ranging from 0.1 to 628 rad/s. At least two frequency sweeps were performed for each material of interest.

### 2.3. Fiber Characterization

Streaming Potential: Zeta potential as a function of pH was obtained for macroscopic fillers from streaming potential measurements acquired by an Anton Paar SurPASS 3 Electrokinetic Analyzer (Ashland, VA, USA) equipped with a Cylindrical Cell. Samples (0.4 g of respective fibers) were loaded into the sample holder and compressed to form a porous plug through which a probing electrolyte solution was flushed. The fibrous

sample material was fixed in place within the cylindrical flow channel by thin membrane sheets and plastic, permeable support discs edged with sealing gaskets. Aqueous 1 mM KCl solution was used as the electrolyte. A series of streaming potential measurements was performed, beginning at ~pH 10 and ending at ~pH 3, for each experiment. The pH of the electrolyte solution was adjusted by the addition of 0.05 M HCl or 0.05 M KOH solution. During testing at each pH condition, the sample was rinsed four times with the electrolyte solution before three streaming potential measurements were collected. The electrolyte solution was purged with nitrogen throughout the duration of the measurements to prevent the dissolution of carbon dioxide. The zeta potential,  $\zeta$ , was calculated according to Equation (2) [46]:

$$\zeta = \frac{dU}{dP} \times \frac{\eta}{\varepsilon \varepsilon_0} \times K \quad (2)$$

where  $dU/dP$  represents the linear slope of streaming potential vs differential pressure with a minimum  $R^2$  value of 0.97 to be considered a valid measurement,  $\eta$  is the electrolyte viscosity,  $\varepsilon_0$  is the permittivity,  $\varepsilon$  is the dielectric coefficient of the electrolyte, and  $K$  is the bulk conductivity.

**Dynamic Light Scattering (DLS):** DLS measurements were taken on a Malvern Zetasizer Pro (Westborough, MA, USA) using CNF suspensions diluted to a concentration of 0.0014 wt.%. The refractive index and density for cellulose was assumed to be ~1.47 and ~1.4 g cm<sup>-3</sup>, respectively. A minimum of three samples were tested per material to ensure statistically significant results.

**Scanning Electron Microscopy (SEM):** Fibers were sputtered with platinum/palladium and imaged using a Zeiss Merlin field emission SEM (FE-SEM) (Oberkochen, Germany) equipped with a Gemini column at an accelerating voltage of 5 kV.

#### 2.4. Scaled Manufacturing Trials

**Composite Scale-up and Twin-Screw Extrusion:** Compounding of the PLA/BSK, PLA/BSK/CNF, PLA/flax, and PLA/flax/CNF composites with CNF at 5 wt.% with respect to the macrofiber was conducted using a Leistritz ZSE 27 MAXX twin-screw extruder (Allendale, NJ, USA). The 12 heating zones of the twin-screw were set from the inlet to the nozzle as the following: 145–150–155–160–165–170–180–190–185–185–185–185 °C. The composites were compounded using a polymer feed rate of 8 kg/h and a filler feed rate of 2 kg/h for a total composite feed rate of 10 kg/h. The screw was operated at 120 RPM and torque on the screw was ~40% throughout the run. Compounded materials were extruded as filaments and chopped to 3 mm pellets using an in-line pelletizer. Each batch totaled approximately 18 kg.

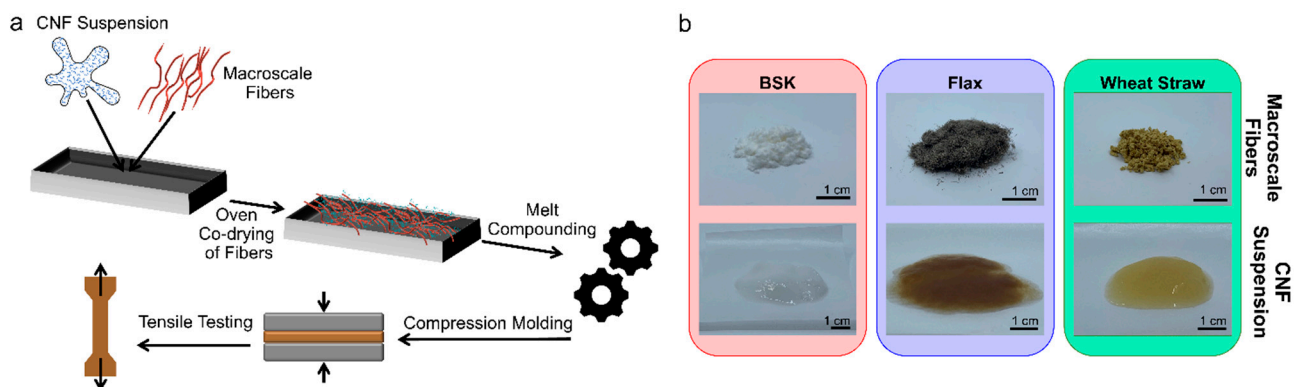
**Additive Manufacturing:** Demonstrative specimens were printed using material compounded via twin-screw extrusion on a pellet-fed gantry-style extruder (re3d Gigabot X2 XLT 900, Austin, TX, USA) with a 1.75 mm nozzle. The extruder comprised three heating zones set to 215 (nozzle), 200 (mid-extruder), and 175 (feeding zone) °C with a bed heated to 60 °C. The specimens were modeled in SolidWorks (Dassault Systems) software, and g-code was generated using Simplify 3D-slicing software (V4). A bead height and width of 1 mm and 2.1 mm, respectively, were used along with a print speed of 2000 mm/min and extrusion multiplier of 1.0. Printed specimens were in the shape of leaves roughly 165 × 100 mm.

### 3. Results and Discussion

#### 3.1. Fiber Preparation

A common challenge with producing CNF-reinforced thermoplastic composites lies in the ability to integrate the CNF into the polymer matrix while retaining its nanofibril-

lar morphology. Conventional oven drying results in aggregated CNF that is practically impossible to re-disperse in solution and results in minimally improved mechanical composite performance, while freeze drying retains the nanofibrillar structure but is time and energy intensive [47–51]. Herein, a hybrid composite approach is taken in which macroscale natural fibers are used as a carrier to disperse CNF into a thermoplastic matrix, and simplistic oven drying allows for the retention of the CNF's nanofibrillar morphology. Initially, diluted suspensions of CNF are mixed with macroscale natural fibers to ensure that the CNF is homogeneously coated onto the surface of the natural fiber prior to oven drying (Figure 1a). Once dried, the CNF is well dispersed onto the natural fibers and maintains its nanoscale morphology while being entrapped onto the fiber surface, allowing for ease of composite incorporation. This hybrid natural fiber/CNF filler is dispersed into a thermoplastic matrix via melt compounding, and the individual macroscale fibers and CNF suspensions can be seen in Figure 1b. Throughout this study the macroscale natural fibers of interest are bleached softwood kraft pulp (BSK), flax, and wheat straw, while the nanofibers of interest are CNF manufactured from BSK (CNF), CNF manufactured from flax (fCNF), and CNF manufactured from wheat straw (wsCNF).



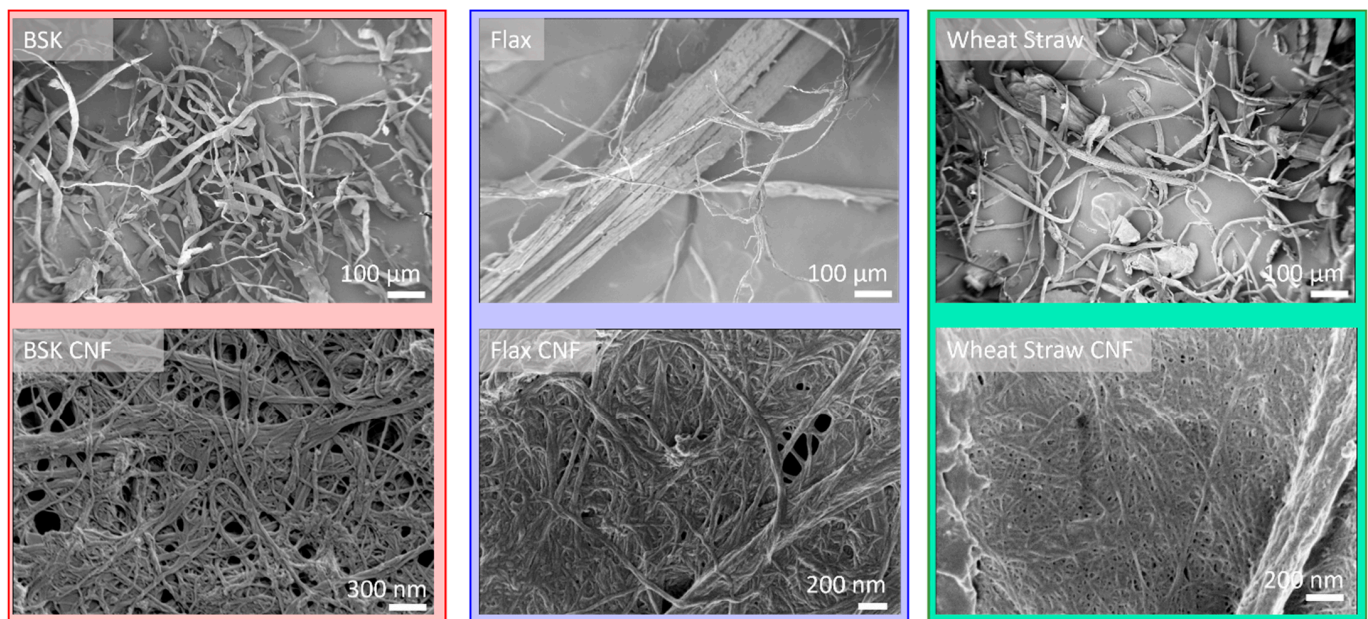
**Figure 1.** (a) A schematic demonstrates how the CNF and macroscale fibers were combined prior to composite incorporation as well as the composite production, molding, and testing steps throughout this study. (b) In addition, both the macroscale fiber (top row) and CNF suspension (bottom row) are shown for all systems with the background colors intended as a guide for the eye.

Varying the feedstock from which the CNF is produced is attractive from an environmental and materials property perspective due to large variances in the embodied energy of the natural fibers (i.e., 37.3 MJ/kg for BSK, 10–12 MJ/kg for flax, and 18.8 MJ/kg for wheat straw) along with favorable fibrillation behavior (e.g., wsCNF reaches nanoscale morphology at lower energy levels compared to the others) [24]. However, it is clear from Figure 2 that regardless of the natural fiber being used, the CNF suspensions exhibit nanofibrillar morphology. Previous analysis of CNFs by Lamm et al. showed that CNF slurries of BSK and wheat straw exhibited lower slurry freeness and higher water retention compared to flax CNF, which suggests that they are more fibrillated than the flax CNF [24]. Furthermore, as previously noted, the LCNFs have a higher fines content compared to the BSK-based CNF, and Ringania et al. has previously demonstrated that increasing fines content from 60% to 90% can result in drying times up to 20% longer [52].

### 3.2. Varying CNF Source/Macroscale Composite Reinforcement

Herein, 20 wt.% of the macroscale fiber and the fiber/CNF mixtures were melt-compounded into neat PLA. The addition of any neat natural fiber into PLA results in a statistically significant decrease in the ultimate tensile strength (Figure 3a) and an increase in the Young's modulus (Figure 3b). This mechanical trend likely indicates a relatively poor fiber/matrix interfacial adhesion, which is not surprising given the hydrophilic nature of

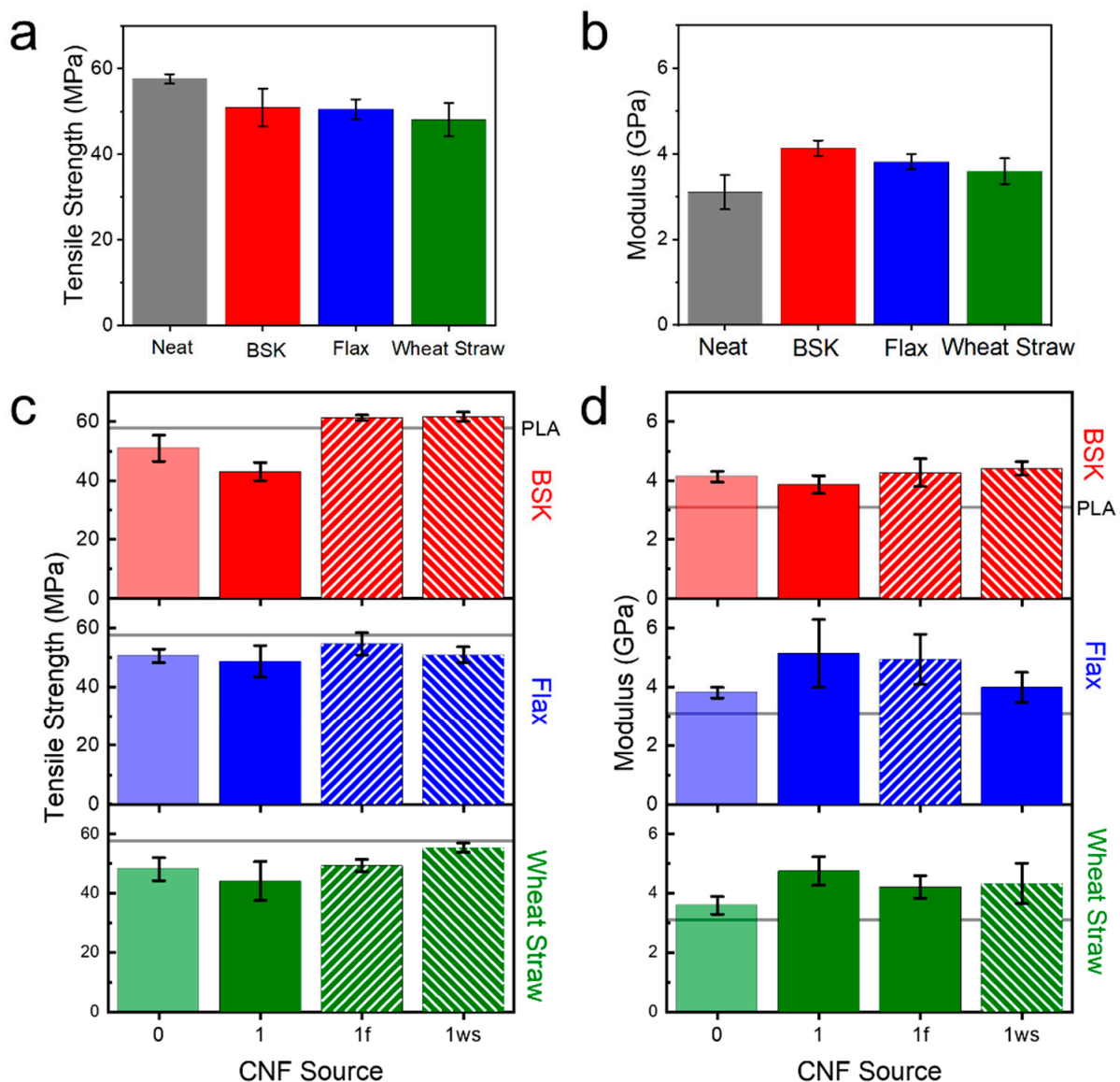
the reinforcing fillers and the hydrophobic nature of the polymer matrix; similar findings have been reported in the literature where there is either no change or a decrease in tensile strength with NF incorporation into PLA [21,41,45,53]. For example, Xanthopoulou et al. reported a 46.2% decrease in tensile strength with the incorporation of 20 wt.% hemp fiber into a PLA blend [40], while Zhang et al. reported no statistically significant change in tensile strength with 30 wt.% flax fiber into PLA [54]. In the case of the three fibers trialed here, BSK outperforms both flax and wheat straw alone as reinforcing fillers with statistically significant 7.7% and 13.1% increases in Young's modulus, respectively, while exhibiting similar tensile strengths regardless of fiber type. There are multiple potential reasons for this observation such as (1) difference in aspect ratio or surface area/volume ratio between the different fiber types, or (2) compositional differences that result in slightly better or worse polymer–fiber interactions due to, for example, lignin content, which is discussed in detail in a later section.



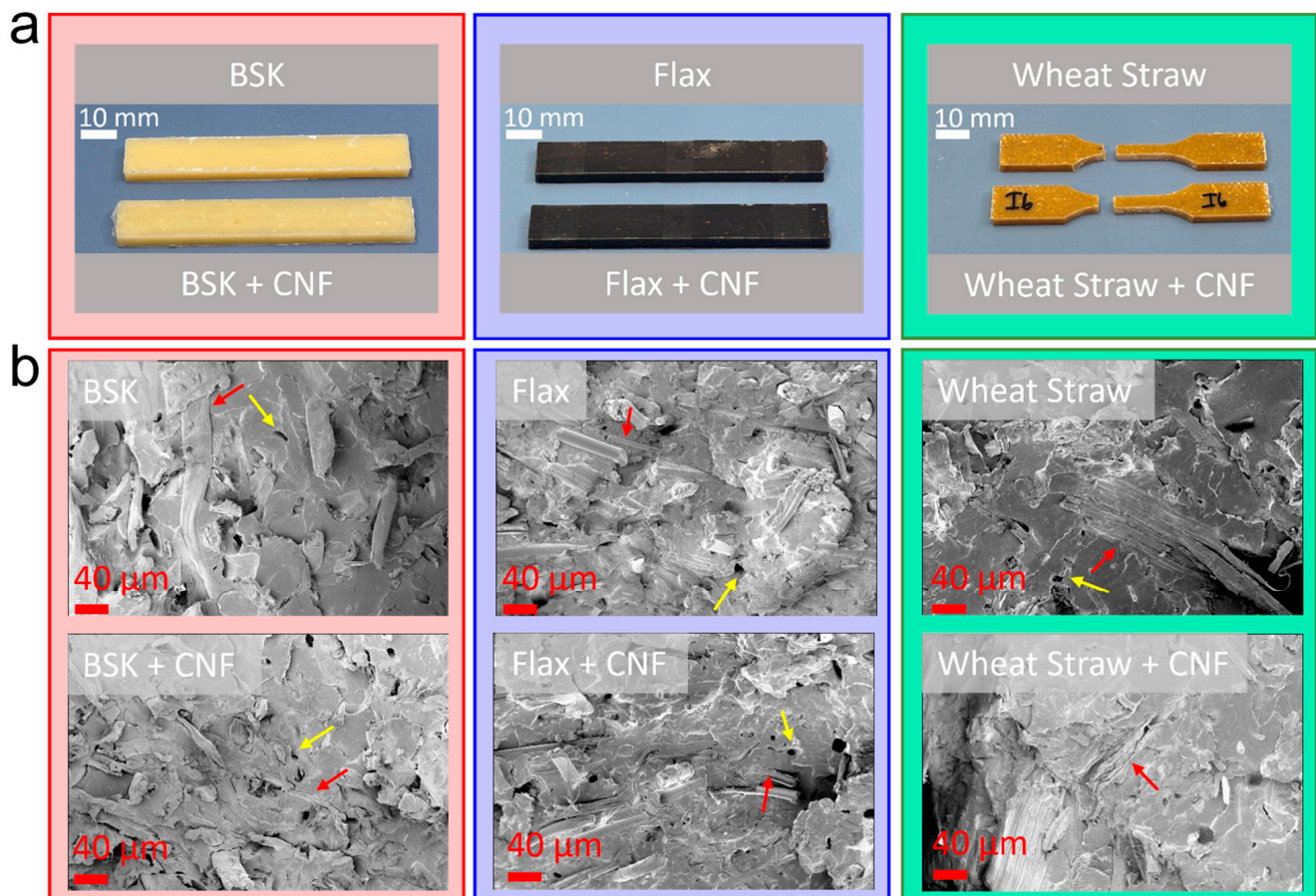
**Figure 2.** SEM images are shown for each macroscale fiber (top row) as well as the corresponding nanofiber (bottom row).

The hybrid fiber/CNF fillers in PLA generally exhibit improvements in tensile properties compared to neat fibers. Hybrids incorporating both macroscale fibers and CNF from the same source (e.g., flax/fCNF) also exhibit a synergistic improvement in properties compared to fiber/CNF from mixed sources (e.g., flax/wsCNF). For example, the sample with hybrid flax/fCNF demonstrates an 8.1% and 29.7% improvement in tensile strength and Young's modulus, respectively, over flax fiber alone. Similarly, the addition of the hybrid wheat straw/wsCNF into PLA demonstrates a 15.0% and 20.6% improvement in both tensile strength and Young's modulus, respectively, over wheat straw alone at the same concentration. It is hypothesized that the identical surface chemistries between the macroscale fiber and nanofiber results in a more favorable filler interaction, enabling the CNF to homogeneously coat the macroscale fiber surface. However, the synergistic improvement in compatibility between the fiber and CNF sourcing does not hold true for the BSK-sourced hybrid filler. The highest mechanical performance of any composite is reported for BSK macroscale fibers hybridized with fCNF and wsCNF, which interestingly provides a 42.5% and 43.2% increase in tensile strength, respectively, compared to the hybrid filler containing BSK-based CNF, and meets or exceeds the tensile strength of neat PLA. It is hypothesized that this is due to the higher fines content of the fCNF (~97%) and

wsCNF (~99%) compared to BSK-based CNF (90%) [24]; the higher degree of fibrillation could increase mechanical interlocking of the hybridized filler with the PLA matrix. Due to the limited availability of nanofiber feedstocks, it was not possible to decouple the impact of fines content and composition. In addition, it should be noted that while all composites with and without filler hybridization appear uniform (Figure 4a), there is evidence of both fiber pull-out (yellow arrows) and fiber wetting (red arrows) present in all tensile fracture surfaces, as seen in Figure 4b. Higher concentrations of nanofiber reinforcement (5 wt.% on the macroscale fiber) were also trialed, the properties of which are shown in Figure S1, which will be discussed in greater detail in a later section. However, there was no significant improvement in mechanical performance with increasing nanofiber concentration. To balance the relatively high cost of nanofiber-reinforcing fillers in comparison to natural fibers, all samples noted herein contain 1 wt.% nanofiber with respect to the weight of macrofiber unless otherwise stated.



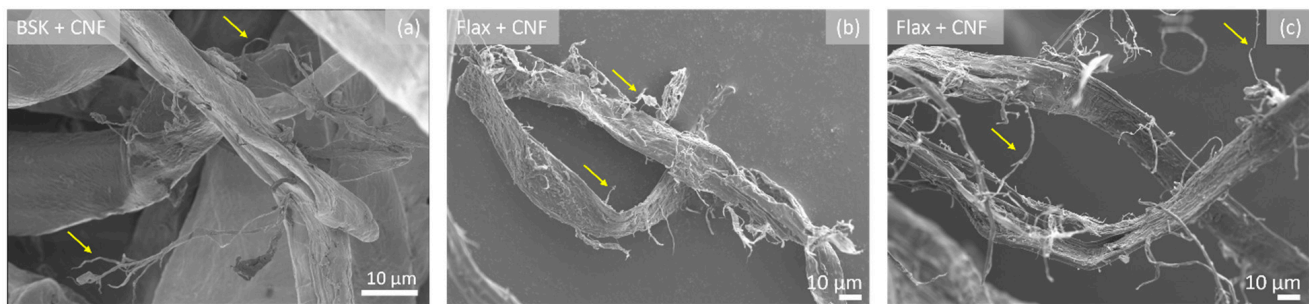
**Figure 3.** (a,b) Tensile properties are shown for all composite systems with only the addition of the macroscale natural fibers at 20 wt.%. (c,d) Tensile properties are shown for all hybrid composite systems where 0 indicates no CNF addition and 1, 1f, and 1ws indicate the addition of 1 wt.% bleached pulp CNF, 1 wt.% flax CNF, and 1 wt.% wheat straw CNF, respectively.



**Figure 4.** (a) Photographs are shown for each composite formulation to demonstrate filler homogeneity. The scale bars represent 10 mm. (b) SEM images are shown of the composite fracture surfaces containing both the macrofiber (top row) and hybrid fibers containing both the macrofiber and nanofiber (bottom row). The yellow arrows indicate areas of fiber pull-out and the red arrows indicate areas of good adhesion between the fiber and matrix. The scale bars represent 40 μm.

The impact of filler hybridization on composite performance is likely influenced by the morphology (i.e., fines concentration, aspect ratio, or surface area) and chemical composition (i.e., presence of lignin, pectin, extractives, etc.) of the individual constituents. Both factors could impact interactions between either the two reinforcing fillers when hybridized, leading to variations in CNF distribution on the fiber, or the fillers and the surrounding polymer matrix due to differences in polarity and hydrophilicity. Furthermore, it is unclear whether the CNF remains on the surface of the macroscale fiber during melt compounding or if it is partially transported into the polymer matrix while undergoing shear. Regardless of hybrid filler type, Figure 5 clearly demonstrates the presence of CNF on the macroscale natural fiber, as indicated by the yellow arrows.

The thermal and thermomechanical performance of each composite was also explored. Table 1 displays the TGA results for all composites. No significant trend is seen when comparing the composite formulations, though there is a minor decrease in thermal stability with the 20 wt.% addition of filler into the PLA matrix. For example, when incorporating the neat BSK, flax, or wheat straw into the composite, there is a 6.3%, 2.9%, and 9.2% decrease in  $T_{5\%}$ , respectively, compared to the neat PLA. However, the addition of 1 wt.% CNF onto the surface of the macrofiber minimally impacts the thermal stability; this is unsurprising due to its relatively small quantity. The wheat straw does appear to be the least thermally stable fiber utilized within this study.

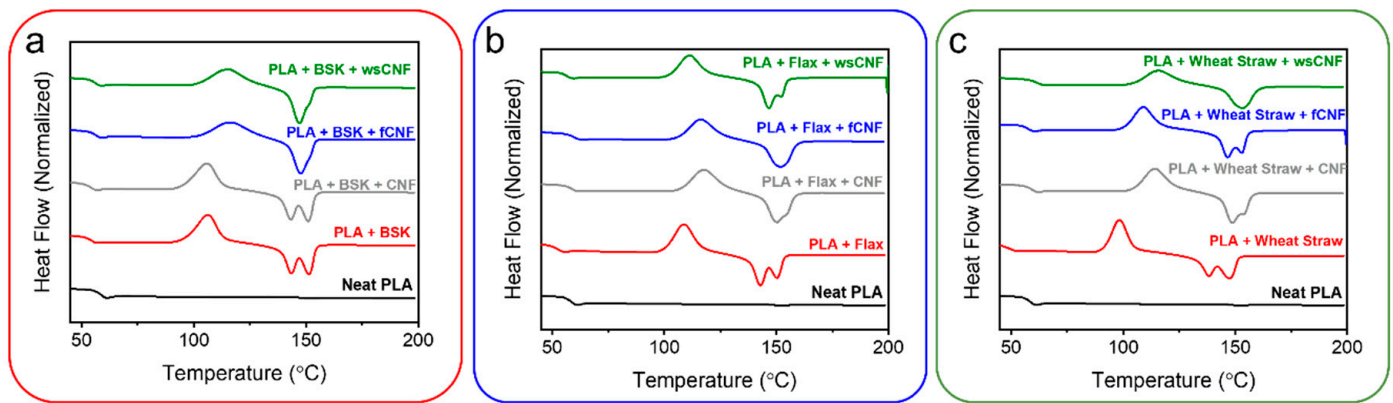


**Figure 5.** SEM images are shown for various hybrid fibers containing both macroscale natural fibers (a) BSK and (b,c) flax, as well as nanofiber. For clarity, the yellow arrows indicate nanofibers that are physically adhered to the surface of the natural fiber. The scale bars represent 10  $\mu\text{m}$ .

**Table 1.** The TGA results are presented for all composites.

|     | Macrofiber  | CNF     | $T_{onset}$ ( $^{\circ}\text{C}$ ) | $T_{2\%}$ ( $^{\circ}\text{C}$ ) | $T_{5\%}$ ( $^{\circ}\text{C}$ ) |
|-----|-------------|---------|------------------------------------|----------------------------------|----------------------------------|
| PLA | -           | -       | 338.76                             | 306.02                           | 322.75                           |
|     | BSK         | -       | 328.05                             | 275.25                           | 302.55                           |
|     |             | 1 CNF   | 330.59                             | 280.15                           | 309.93                           |
|     |             | 1 fCNF  | 325.11                             | 285.92                           | 310.10                           |
|     |             | 1 wsCNF | 329.43                             | 285.86                           | 312.72                           |
|     | Flax        | -       | 332.36                             | 258.80                           | 313.26                           |
|     |             | 1 CNF   | 335.46                             | 264.13                           | 316.05                           |
|     |             | 1 fCNF  | 338.28                             | 260.89                           | 316.30                           |
|     | Wheat Straw | -       | 316.74                             | 258.30                           | 292.92                           |
|     |             | 1 CNF   | 308.90                             | 229.70                           | 285.41                           |
|     |             | 1 wsCNF | 309.55                             | 245.62                           | 291.35                           |

Figure 6 and Table 2 display results of DSC testing and indicate that there is no significant shift in the glass transition temperature ( $T_g$ ) among the composite samples with  $T_g \sim 50$ – $55$   $^{\circ}\text{C}$ . In addition, the presence of filler serves as crystallization nucleation agents, decreasing the cold crystallization temperature ( $T_{cc}$ ) from that of neat PLA, shifting from 118  $^{\circ}\text{C}$  (difficult to visualize in Figure 6 due to the magnitude of thermal events in the composite traces) for neat PLA to between 100 and 113  $^{\circ}\text{C}$  for the various composite samples. This variation with the presence of lignocellulosic fillers is also mimicked in the melt temperature ( $T_m$ ) where it decreases from 149  $^{\circ}\text{C}$  for neat PLA to between 139 and 147  $^{\circ}\text{C}$  for the composites. It is theorized that the presence of the lignocellulosic components impacts the nucleation rate or efficiency and crystalline structure in this slow-crystallizing polymer, which accounts for the broadening of the crystallization peak in Figure 6a as well as the fact that only one melt peak is visible with a clear shoulder present. Furthermore, the presence of lignocellulosic macroscale fibers appears to produce the most significant decreases in  $T_{cc}$  (decreases ranging from 12.5 to 18.7  $^{\circ}\text{C}$ ) and  $T_m$  (decreases ranging from 6.2 to 10  $^{\circ}\text{C}$ ) compared to neat PLA; this decrease is minimized for samples containing BSK macroscale fibers, which only demonstrate decreases in  $T_{cc}$  ranging from 5.1 to 14.3  $^{\circ}\text{C}$  and decreases in  $T_m$  ranging from 3 to 6.9  $^{\circ}\text{C}$ . However, it should be noted that the variation in fiber topology could also be responsible for the effects seen on crystallization. There is no statistically significant variation in crystallinity reported as a function of formulation.



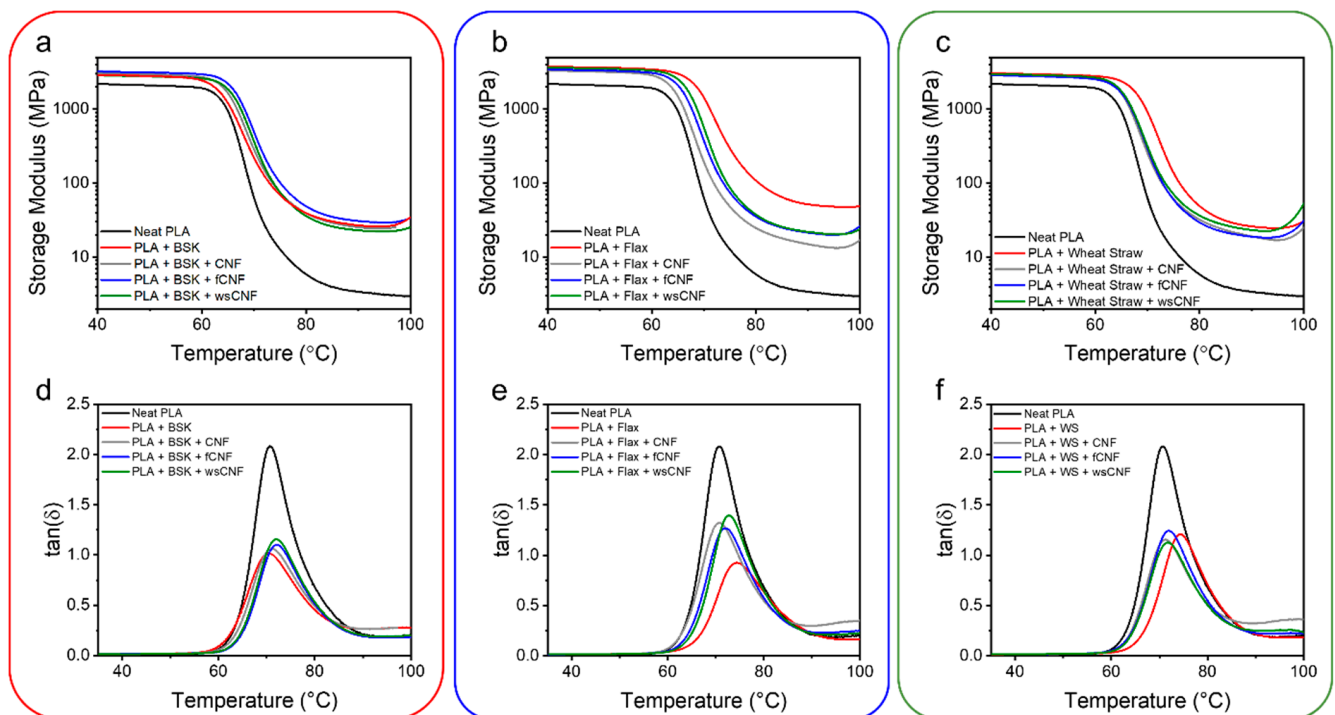
**Figure 6.** DSC second heat curves are shown for all hybrid composites where the macroscale fiber in each case is BSK (a), flax (b), and wheat straw (c).

**Table 2.** The DSC results are reported for all composites.

| Macrofiber | CNF     | $T_g$ (°C)        | $T_{cc}$ (°C)     | $T_{m1}$ (°C)     | $T_{m2}$ (°C)     | $X_c$ (%)        |
|------------|---------|-------------------|-------------------|-------------------|-------------------|------------------|
| PLA        | -       | $55.12 \pm 0.52$  | $118.24 \pm 1.8$  | $149.46 \pm 0.25$ | -                 | $0.62 \pm 0.18$  |
|            | -       | $52.34 \pm 0.43$  | $103.92 \pm 1.22$ | $142.56 \pm 0.46$ | $150.88 \pm 0.20$ | $2.85 \pm 0.55$  |
|            | 1 CNF   | $51.94 \pm 0.58$  | $104.22 \pm 2.12$ | $142.60 \pm 0.72$ | $150.70 \pm 0.36$ | $2.94 \pm 0.65$  |
|            | 5 CNF   | $53.87 \pm 0.004$ | $109.64 \pm 0.20$ | $145.38 \pm 0.08$ | $151.70 \pm 0.15$ | $1.17 \pm 0.34$  |
|            | 1 fCNF  | $54.10 \pm 0.75$  | $113.19 \pm 2.05$ | $146.43 \pm 0.68$ | $151.89 \pm 0.15$ | $1.48 \pm 0.28$  |
|            | 5 fCNF  | $54.41 \pm 0.21$  | $113.58 \pm 0.22$ | $146.61 \pm 0.30$ | $151.59 \pm 0.10$ | $0.57 \pm 0.18$  |
|            | 1 wsCNF | $53.59 \pm 0.22$  | $111.6 \pm 2.40$  | $145.32 \pm 0.47$ | $151.62 \pm 0.14$ | $1.83 \pm 0.52$  |
|            | 5 wsCNF | $53.87 \pm 0.22$  | $113.30 \pm 0.09$ | $146.37 \pm 0.24$ | $151.67 \pm 0.10$ | $0.63 \pm 0.41$  |
|            | -       | $55.69 \pm 0.05$  | $105.57 \pm 0.32$ | $143.28 \pm 0.02$ | $151.09 \pm 0.01$ | $1.14 \pm 0.11$  |
|            | 1 CNF   | $50.82 \pm 0.25$  | $105.75 \pm 0.36$ | $142.73 \pm 0.32$ | $150.59 \pm 0.25$ | $1.948 \pm 0.36$ |
|            | 1 fCNF  | $51.62 \pm 0.24$  | $104.74 \pm 0.46$ | $142.98 \pm 0.32$ | $150.75 \pm 0.01$ | $0.45 \pm 0.10$  |
|            | 1 wsCNF | $51.91 \pm 0.16$  | $104.83 \pm 0.54$ | $143.11 \pm 0.09$ | $151.07 \pm 0.04$ | $0.76 \pm 0.07$  |
|            | -       | $50.56 \pm 1.38$  | $101.69 \pm 2.48$ | $140.99 \pm 1.95$ | $149.81 \pm 1.61$ | $0.68 \pm 0.25$  |
|            | 1 CNF   | $49.28 \pm 0.18$  | $99.59 \pm 0.56$  | $139.45 \pm 0.08$ | $148.7 \pm 0.12$  | $0.46 \pm 0.15$  |
|            | 1 fCNF  | $51.6 \pm 0.14$   | $101.95 \pm 0.07$ | $142.24 \pm 0.08$ | $150.91 \pm 0.14$ | $0.32 \pm 0.26$  |
|            | 1 wsCNF | $51.12 \pm 0.02$  | $100.27 \pm 0.03$ | $141.41 \pm 0.11$ | $150.44 \pm 0.15$ | $1.42 \pm 0.12$  |

Similar to the tensile performance, the temperature sweeps as measured via DMA (Figure 7) demonstrate an increase in storage modulus in both the rubbery and glassy regimes with the incorporation of any filler into the PLA matrix; this stiffening effect is greatest for the flax-containing composites, as seen in Figure S2. While there is minimal variation in the storage modulus with temperature between the BSK- and wheat straw-containing composites and their hybrid counterparts, there is clearly a higher storage modulus at elevated temperatures for the flax composites over the flax hybrid composites. Additionally, there is a clear decrease in the  $T_g$  as measured from the onset of the storage modulus or peak of the  $\tan(\delta)$  curve seen in Figure 7b,e with the addition of any nanofiber into the flax composites, which is mimicked by a statistically significant 2–6 °C decrease in  $T_g$  as measured via DSC. While the wheat straw composites appear to have a similar behavior in Figure 7c, this is not found to be a statistically significant shift in  $T_g$ . Interestingly, this decrease in storage modulus and decrease in the  $T_g$  with hybridization in the flax

composites is accompanied by an increase in the damping properties as reported via the  $\tan(\delta)$ . In all cases, the addition of a filler decreases the damping properties of the final composite compared to neat PLA, with the flax hybrids showing enhanced damping properties over all other hybrid formulations. In BSK and wheat straw composites and their hybrid counterparts, there does not appear to be any statistically significant changes in DMA behavior. This enhanced flexural behavior of the flax composites at elevated temperatures also corresponds to higher HDT values, as reported in Figure S3a. In addition, the HDT of the BSK hybridized composites confirms enhanced thermomechanical performance, with a statistically significant 7% improvement in HDT for composites with lignocellulosic CNF as compared to hybrids with BSK-based CNF (cf. Figure S3b).

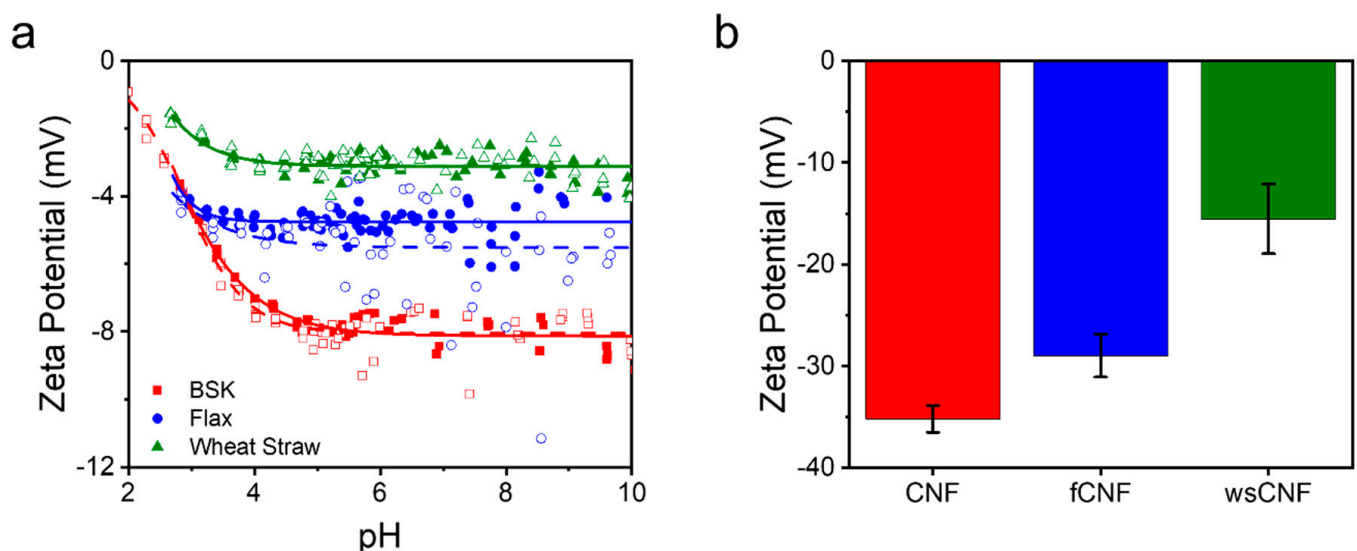


**Figure 7.** Temperature sweep results are shown for all hybrid composites where the macroscale fiber in each case is BSK (a,d), flax (b,e), and wheat straw (c,f).

As previously noted, it is unclear as to what driving factor causes the increased mechanical performance with the incorporation of non-wood CNF, and it could be attributable to a number of factors including hydrophobicity, morphology, or the chemical composition of the individual constituents. As seen in Table S1 and noted in the previous literature [24], BSK contains only cellulose and hemicellulose while the flax and wheat straw additionally contain lignin at a 15.3% and 24.8% concentration, respectively. In this case, an assumption is being made that since the nanofiber suspension production is purely mechanical and does not involve any chemical treatments, the cellulose, hemicellulose, and lignin content is unchanged between the macroscale fiber and the nanofiber state. It is reasonable to assume that increases in lignin content, and corresponding hydrophobicity, should result in better reinforcement within the composites due to favorable filler/matrix adhesion with the inherently hydrophobic PLA matrix; to that end, the fiber composition and hydrophobicity must be considered in tandem.

Figure 8a reports the zeta potential measurements performed on the macroscale fibers. BSK demonstrates the highest absolute zeta potential, and the wheat straw demonstrates the lowest, indicating lower stability of the aqueous wheat straw suspension. Some replicate points for the same pH describe noisy or discontinuous streaming potential vs. pressure

drop curves and appear as outliers from the sigmoidal trend lines; this behavior is attributed to fibers flexing within the porous plug and disturbing the electrolyte flow profile. This flexing behavior was most noticeable for the flax samples. All three macroscale fibers are seen to be hydrophilic in nature, as expected, and demonstrate isoelectric points (IEP) below pH 3, implying acidic characteristics. Furthermore, the sample duplicates show particularly good agreement for the plateau values of their sigmoidal trend lines. At high pH values, usually greater than pH 8 or 9, zeta potential curves will typically plateau. It is commonly observed that hydrophobic surfaces have, perhaps paradoxically, stronger negative charge at high pH values. Some hydrophobic surfaces have zeta potential plateau values as high as or exceeding  $-70$  mV in magnitude. The mechanism for this behavior is perhaps best explained by the phenomenon of negatively charged hydroxide ions displacing water molecules at hydrophobic interfaces [55]. Theoretical work has found that hydroxide ion adsorption is favorable compared to positively charged hydronium ion adsorption due to differences in ionic structure and spatial charge distribution [56]. These observations have been correlated with contact angle measurements in the literature [57]. The general trend of increasingly negative zeta potentials correlating to increasing hydrophobicity is valid if the starting material is a chemically inert substrate, such as polypropylene or perfluorinated polymers [55]. However, given the abundant presence of functional groups in the molecular structure of cellulose, it is theorized that the negative charge is a result of deprotonated functional groups on the fiber surface rather than adsorbed hydroxyl ions. Such acidic functional groups generally promote hydrogen bonding with water, rendering the surface more hydrophilic. As such, the BSK can be considered the most hydrophilic macroscale fiber in this study, while wheat straw is the least hydrophilic with the variation in zeta potential being relatively small among the three fibers. The fact that all three macroscale fibers perform similarly from a tensile property perspective is likely attributable to the similarity in hydrophobicity of the macroscale fibers and therefore comparable interfacial adhesion with the PLA matrix.



**Figure 8.** Zeta potential measurements are reported as measured for the macroscale fiber with 1 mM KCl electrolyte as a function of pH (a) and the nanofiber suspension (b). Solid and open symbols for (a) represent two separate replicate measurements of different samplings; trend lines are least-squares-fitted sigmoidal functions.

The trend in hydrophilicity aligns nicely between the zeta potential of the macroscale fiber (Figure 8a) and the corresponding nanofiber suspensions (Figure 8b). The presence of lignin and other noncellulosic moieties in the wsCNF (24.8%) and fCNF (15.3%) should

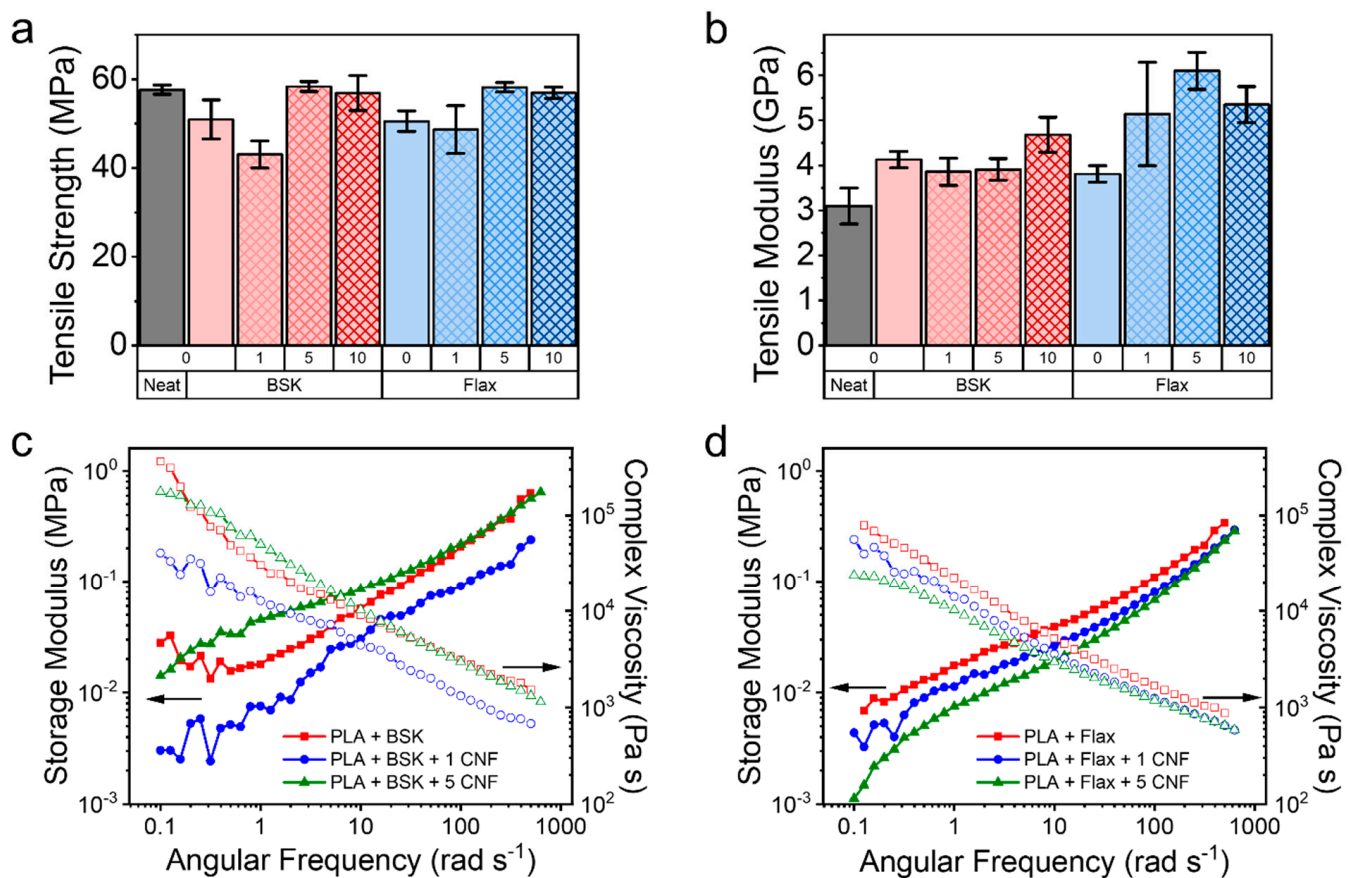
make them more hydrophobic than their CNF counterpart sourced from BSK, which is confirmed via DLS, whereby the degree of hydrophobicity trends with lignin concentration and the spread of the zeta potential values is greater, as also reflected in the literature [58]. Interestingly, the images of CNF suspensions in Figure 1 show water separating from the fCNF as evidenced by the lighter color liquid around the edges, indicating its lowered affinity for water compared to CNF [58]. This separation with water is also seen in the wsCNF suspensions but is harder to notice visually due to the lighter color of the wheat straw fiber. It is theorized that the increased hydrophobicity of the fCNF and wsCNF compared to CNF contributes to their higher tensile performance when hybridized with the macroscale fibers. However, regardless of composition, it is also worth considering the morphology and degree of fibrillation across the CNF suspensions. The previous literature has shown the higher propensity of the fCNF and wsCNF to fibrillate; for example, when mechanically fibrillated at a gross energy of ~8000 kW.h/MT, the BSK reaches ~80% fines content where both the fCNF and wsCNF reach 100% fines content at the same gross energy [24]. Amini et al. has also clearly shown that increasing the fines content increases the mechanical properties of CNF [58]. While lignocellulosic CNF tends to have a lower mechanical performance compared to CNF at comparable fines levels, the fCNF and wsCNF used here were fibrillated to a higher degree (~100% fines) using the supermasscolloider compared to the CNF produced on a pilot scale (90% fines) [58]. The lignocellulosic CNF samples may have possessed a slightly higher aspect ratio and surface area than the BSK-based pulp, which, along with their increased hydrophobicity, could contribute to their higher mechanical performance [24].

### 3.3. Increasing CNF Content and Scale-Up

The impact of increasing the CNF inclusion was tested on samples produced with 1, 5, and 10 wt.% BSK-based CNF on BSK and flax fiber in PLA at 20 wt.% overall fiber loading. Samples were compounded on a small scale and compression-molded to produce samples for tensile testing, the results of which are shown in Figure 9a,b. While adding 1 wt.% of BSK-based CNF with respect to the loading of BSK or flax, the tensile strength decreased slightly or was not affected. Increasing the CNF loading to 5 or 10 wt.%, however, increased the tensile strength of both PLA/BSK and PLA/flax, yielding strength values close to that of neat PLA. For example, the flax-based composites saw a 3.7% decrease and 15.1% increase in tensile strength with the inclusion of 1 wt.% or 5 wt.% BSK-CNF, respectively. Increasing the CNF loading had little effect on the modulus of the PLA/BSK samples, with 1 and 5 wt.% samples yielding modulus values similar to that of PLA with neat BSK and 10 wt.% CNF sample demonstrating a slight increase in modulus. The flax samples, however, showed a significant improvement in modulus upon addition of CNF at various loadings. For example, the flax-based composites saw a 34.9% and 60.1% increase in tensile modulus with the inclusion of 1 wt.% or 5 wt.% BSK-CNF, respectively. This trend is also seen in the literature, where Jonobi et al. previously reported a 12.8% increase in tensile strength and no statistically significant change in tensile modulus for PLA composites with increases in CNF concentration from 1 wt.% to 5 wt.% [30]. Considering the tensile data in Figure 9a,b, a 5 wt.% loading of CNF on BSK and flax was selected for scale-up, as increasing CNF content from 1 to 5 wt.% had a positive effect on most of the tensile properties, but increasing further to 10 wt.% yielded diminishing returns.

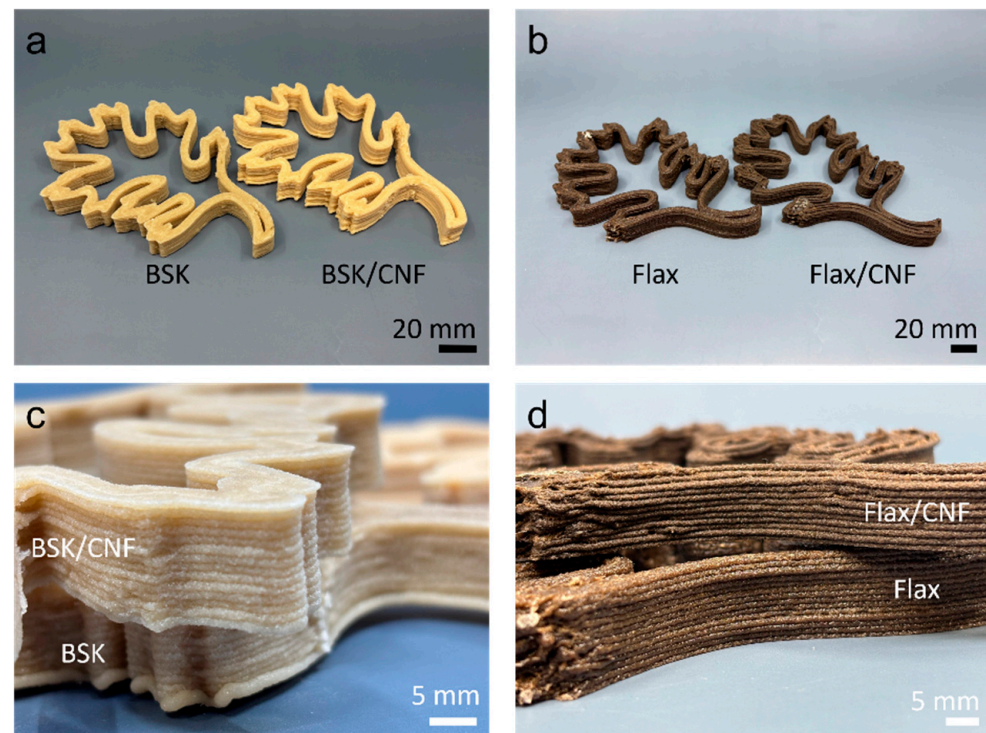
Frequency sweeps were performed on each of the PLA/BSK and PLA/flax materials at 180 °C to determine the impact of CNF addition on the material's flow behavior, shown in Figure 9c,d. Each sample exhibited shear thinning across the frequency range tested. The addition of CNF to the BSK composites demonstrated no clear trend for its complex viscosity or storage modulus behavior when the CNF is at either 1 or 5 wt.% with respect

to the macrofiber weight. In contrast, the flax composites demonstrated a decrease in both complex viscosity and storage modulus with increasing CNF addition across the frequency range tested.



**Figure 9.** (a,b) Tensile properties are shown for the BSK and flax composites with BSK-based CNF of varying concentrations. (c,d) Frequency sweeps collected via melt rheology are shown for the hybrid composites with (c) BSK and (d) flax composites produced with varying concentrations of CNF.

Four different batches of composites were then produced via twin-screw extrusion: PLA/BSK, PLA/BSK/CNF, PLA/flax, and PLA/flax/CNF, in which BSK-based CNF was at a concentration of 5 wt.% with respect to the macroscale fiber. The scaled composite materials were additively manufactured into leaves, as seen in Figure 10, to confirm their processability on medium-to-large-scale additive manufacturing using fused granulate fabrication (FGF). All materials were processed at the same conditions and yielded high-quality surfaces, shown in Figure 10c. The hybrid BSK composite is lighter in color compared to the BSK composite, with very little color change observed between the flax and flax hybrid composite, likely due to the inherently dark color making visual changes difficult to detect. However, there does appear to be a sheen to the printed flax composite, which is not seen in flax hybrid composite, which requires further study. Unlike desktop filament printers, there are few material options for medium-to-large-scale printers, which use highly filled, often-high-aspect-ratio fiber composite feedstocks to prevent warping and promote shape retention on the large scale. Typical feedstocks for these processes are 20 wt.% WF/PLA [15] or 20 wt.% carbon fiber/acrylonitrile butadiene styrene (CF/ABS) [59]. The ability to manufacture these hybrid composites at scale and then produce parts with the feedstocks at high geometric fidelity demonstrates their potential as future industrial feedstocks for FGF.



**Figure 10.** Images show the scaled and additively manufactured parts made from the composites containing both the macroscale fiber and the hybrid filler for (a) BSK and (b) flax. An image also shows (c) the high fidelity of the printed leaves for the BSK-containing composites as well as (d) the difference in sheen for the flax-containing composites.

#### 4. Conclusions

While the value of CNFs as a reinforcement tool in polymer composites is well reported in the literature, it is also understood that incorporating them into composites while retaining their nanoscale structure is often a costly and energy-intensive process. Herein, macroscale natural fibers are utilized as carriers to incorporate nanofiber suspensions into PLA composites via co-drying of the two reinforcements. In addition to trialing three macroscale fibers (i.e., BSK, flax, and wheat straw), three nanofiber suspensions sourced from the three fibers were also trialed. It was found that while the cellulosic BSK macroscale fiber produced composites with the highest performing mechanical properties (7.7% and 13.1% increases in Young's modulus over flax and wheat straw), the lignocellulosic nanofibers outperformed their cellulosic counterpart. For example, the hybrid wheat straw/wsCNF composite demonstrated a 15.0% and 20.6% improvement in both tensile strength and Young's modulus, respectively, over wheat straw alone. To combine the optimal reinforcement of the BSK macroscale fiber with the lignocellulosic nanofiber, it should be noted that a PLA/BSK/wsCNF composite yielded a 43.2% increase in tensile strength over the purely cellulosic hybrid composite. For the hybrid fibers where BSK-based CNF was incorporated, the optimal CNF loading was found to be 5 wt.% with diminishing returns in both tensile strength and modulus experienced at higher CNF loadings. Zeta potential measurements of both the macroscale fiber and the nanofiber suspensions confirm that the lignin content corresponds to a higher hydrophobicity, which is likely leading to favorable interactions with the hydrophobic PLA matrix. In addition, the higher propensity of the lignocellulosic fibers for fibrillation likely results in higher fines content, which is known to lead to higher mechanical performance. Finally, four composite formulations were manufactured at larger scales via twin-screw extrusion and were demonstrated to be compatible with additive manufacturing processes for high-fidelity part production.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app16136517/s1>, Table S1: Biomass compositional analysis is reported for the three natural fibers utilized in this study, as also reported in previous literature; Figure S1: Tensile properties are shown for all hybrid composites where the nanofiber concentration is varied up to 5 wt.% on the macroscale fiber; Figure S2: Temperature sweeps are reported for the macroscale fibers incorporated into the PLA matrix at a 20 wt.% loading; Figure S3: Heat deflection temperature (HDT) temperatures are shown for the composites with only macroscale fibers (a) and for the hybrid composites (b).

**Author Contributions:** A.M.H.—conceptualization, investigation, methodology, formal analysis, writing—original draft, writing—review & editing; K.C.—conceptualization, investigation, methodology, formal analysis, writing—original draft, writing—review & editing; C.M.C.—investigation, writing—original draft; K.B.R.—investigation, formal analysis, writing—original draft, writing—review & editing; M.E.L.—investigation; H.T.—funding acquisition, supervision, writing—review & editing; S.O.—funding acquisition, supervision. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, Advanced Materials and Manufacturing Office under CPS Agreement 35863. This research was supported by the U.S. Department of Energy (DOE), Advanced Manufacturing Office and used resources at the Manufacturing Demonstration Facility at Oak Ridge National Laboratory, a User Facility of DOE's Office of Energy Efficiency and Renewable Energy. This manuscript has been authored by UT-Battelle, LLC under contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

**Data Availability Statement:** The raw data supporting the conclusions of this article will be made available by the authors on request.

**Acknowledgments:** This research was supported by the U.S. Department of Energy (DOE), Advanced Manufacturing Office, and used resources at the Manufacturing Demonstration Facility at Oak Ridge National Laboratory, a User Facility of DOE's Office of Energy Efficiency and Renewable Energy. This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>, Accessed on 16 June 2026). Microscopy studies were completed at the Center for Nanophase Materials Sciences, a DOE Office of Science User Facility. The authors would like to thank Jacob Ragland and Scott Frasca from MiniFIBERS, Inc., for fruitful discussions and for providing the flax fiber as well as Daniel Webb from ORNL for assistance in compounding. The authors would also like to thank Colleen Walker and Donna Johnson from the University of Maine's Process Development Center for their fruitful discussions and for providing the CNF suspensions used throughout this study. The authors would also like to thank Sanjita Wasti for her help with SEM.

**Conflicts of Interest:** Author Keith B. Rodenhausen is employed by Company Anton Paar. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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