Improved Mechanical Properties of Polylactide Nanocomposites- Reinforced with Cellulose Nanofibrils through Interfacial Engineering via Amine-Functionalization

Yuan Lu¹, Mario Calderón Cueva², Edgar Lara-Curzio¹, Soydan Ozcan^{1*}

¹Materials Science and Technology Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Knoxville, TN. 37831

²Universidad San Francisco de Quito, Quito, Ecuador.

*Address correspondence to Dr. Soydan Ozcan

Email: ozcans@ornl.gov.

ABSTRACT

One of the main factors responsible for the mechanical and physical properties of nanocomposites is the effectiveness of the interfacial region to transfer loads and mechanical vibrations between the nano-reinforcements and the matrix. Surface functionalization has been the preferred approach to engineer the interfaces in polymer nanocomposites in order to maximize their potential in structural and functional applications. In this study, amine-functionalized cellulose nanofibrils (mCNF-G1) were synthesized via silylation of the hydroxyl groups on the CNF surface using 3-aminopropyltrimethoxysilane (APTMS). To further increase the amine density (mCNF-G2), dendritic polyamidoamine (PAMAM) was grafted onto mCNF-G1 by the Michael addition of methacrylate onto mCNF-G1, followed by the transamidation of the ester groups of methacrylate using ethylenediamine. Compared to native CNF-reinforced, poly(L-lactide) (PLLA) nanocomposites, amine-functionalized CNF exhibited significantly

improved dispersion and interfacial properties within the PLLA matrix due to the grafting of PLLA chains via aminolysis. It is also a more effective nucleating agent, with 15% mCNF-G1 leading to a crystallinity of 32.5%, compared to 0.1 and 8.7% for neat PLLA and native CNF-reinforced composites. We have demonstrated that APTMS-functionalized CNF (mCNF-G1) significantly improved the tensile strength compared to native CNF, with 10% mCNF-G1 being the most effective (i.e., >100% increase in tensile strength). However, we also found that excessive amines on the CNF surface (i.e., mCNF-G2) resulted in decreased tensile strength and modulus due to PLLA degradation via aminolysis. These results demonstrate the potential of optimized amine-functionalized CNF for future renewable material applications.

KEYWORDS: Polylactide, cellulose nanofibrils, silylation, PAMAM, aminolysis

1. INTRODUCTION

Over the last several decades, much attention has been paid to environmentally friendly or “green” nanocomposites as alternatives to heavy steel and petroleum-based materials due to the depletion of petroleum sources and environmental issues.(Fujisawa, Saito, Kimura, Iwata & Isogai, 2013; Goffin et al., 2011a; Raquez, Habibi, Murariu & Dubois, 2013) This category of materials is often prepared utilizing biodegradable polymers originating from renewable sources, which are then reinforced with various nanoparticles (e.g., carbon nanotubes, nanoclays, graphenes).(Brzezinski & Biela, 2014; Coleman, Khan & Gun'ko, 2006; Lee, Fasulo, Rodgers & Paul, 2005; Rafiee, Rafiee, Wang, Song, Yu & Koratkar, 2009; Ramanathan et al., 2008) Poly(L-lactide) (PLLA) is a polymer synthesized from lactic acid, a compound which can be derived from corn and potato starch.(Garlotta, 2001) Owing to low cost, good mechanical properties, and easy processing, PLLA represents the most attractive bio-based polymer as demonstrated by

its use in numerous applications including food packaging, water and milk bottles, degradable plastic bags, and automotive applications.(Auras, Harte & Selke, 2004; Jonoobi, Harun, Mathew & Oksman, 2010; Lunt, 1998)

To date, a considerable number of studies on PLLA composites reinforced with natural fibers/particles have been reported.(Ganster, Fink, Lau, Hussain & Lafdi, 2010; Iwatake, Nogi & Yano, 2008; Mathew, Oksman & Sain, 2006; Nakagaito, Fujimura, Sakai, Hama & Yano, 2009; Okubo, Fujii & Thostenson, 2009; Petersson, Kvien & Oksman, 2007; Quero et al., 2010; Sanchez-Garcia, Gimenez & Lagaron, 2008; Shanks, Hodzic & Ridderhof, 2006; Suryanegara, Nakagaito & Yano, 2009; Thunwall et al., 2008) Nanocellulose is particularly attractive as a reinforcing phase due to its exceptional strength (e.g., 2-6 GPa),(Saito, Kuramae, Wohlert, Berglund & Isogai, 2013) light weight, transparency, and excellent biocompatibility. The nanocellulose family consists of bacterial nanocellulose, plant-derived cellulose nanofibrils (CNF), and cellulose nanocrystals (CNC).(Czaja, Krystynowicz, Bielecki & Brown, 2006; Habibi, Lucia & Rojas, 2010; Lu, Tekinalp, Eberle, Peter, Naskar & Ozcan, 2014; Xu, Liu, Jiang, Zhu, Haagenson & Wiesenborn, 2013) Bacterial nanocellulose is produced by the *acetobacter xylinum* bacterium using a fermentation process. Compared to plant-derived nanocellulose, bacterial nanocellulose has greater purity, degree of polymerization, crystallinity, and mechanical stability.(Gatenholm & Klemm, 2010) Unfortunately, procedures for bacterial removal hinder industrial scale production. On the contrary, plant-derived CNF and CNC have already been produced on a large scale at affordable cost and thus are currently more suitable for commercial applications.(Paakko et al., 2007; Wagberg, Decher, Norgren, Lindstrom, Ankerfors & Axnas, 2008)

Although CNF and CNC have shown great potential as mechanical reinforcing fillers, the large amount of hydrophilic hydroxyl groups on the surface leads to poor compatibility with hydrophobic polymer matrices (e.g., poor dispersion and interfacial adhesion with polymer), which has become the greatest obstacle to reaching their theoretical potential.(Fujisawa, Saito, Kimura, Iwata & Isogai, 2013; Habibi, Lucia & Rojas, 2010) As a result, surface modification of native CNF/CNC has attracted much attention recently as a method to improve interfacial properties within the polymer matrix. Surface hydroxyl groups are often reacted with other compounds via silylation, esterification, and polymer grafting.(Berlitz, Molina-Boisseau, Nishiyama & Heux, 2009; Blaker, Lee, Li, Menner & Bismarck, 2009; Bulota & Hughes, 2012; Cao, Habibi & Lucia, 2009; de Menezes, Siqueira, Curvelo & Dufresne, 2009; Goffin et al., 2011a, b; Lacerda, Barros-Timmons, Freire, Silvestre & Neto, 2013; Lin & Dufresne, 2013; Sassi & Chanzy, 1995; Xhanari, Syverud & Stenius, 2011; Yuan, Nishiyama, Wada & Kuga, 2006) As an example of a nanocellulose-reinforced PLLA composite, Fujisawa et al. reported the preparation of PEG-grafted cellulose nanofibrils for PLA composites. Cellulose nanofibrils were treated by (2,2,6,6-Tetramethylpiperidin-1-yl)oxy (TEMPO) oxidation to yield carboxylic acid groups, which then formed ionic bonds with primary amine-functionalized poly(ethyleneglycol) (PEG) chains.(Fujisawa, Saito, Kimura, Iwata & Isogai, 2013) Dispersion of PEG-grafted cellulose nanofibrils (i.e., 1% loading) led to an increase of Young's modulus, tensile strength, and work of fracture of nanocomposites by 40, 26, and 52%, respectively, compared to neat PLLA films. However, no data were presented regarding films with unmodified cellulose nanofibrils. As such, it is not conclusive that improvements in mechanical properties can be completely attributed to surface modification.(Goffin et al., 2011a) Another approach to improve compatibility with the PLLA matrix is to graft PLLA chains onto the surface of nanocellulose.

Ring opening polymerization of L-lactide initiated by hydroxyl groups on the CNC surface was performed in toluene utilizing tin(II) ethylhexanoate as the catalyst.(Goffin et al., 2011a) The PLLA coating limited the degradation of CNCs during extrusion. Despite improved thermal stability, limited reinforcing effects were observed below the glass transition temperature (T_g) due to a plasticization effect of the grafted PLA chains.(Goffin et al., 2011a) Collectively, enhancing the tensile strength of PLLA through nanocellulose still needs further improvement, necessitating the design of new surface chemistry and a better understanding of its effects on interfacial bonding mechanisms.

Herein, we report the preparation of amine-functionalized CNF (mCNF) with controlled amine content on the surface via the silylation of surface hydroxyl groups and grafting of dendritic polyamidoamine (PAMAM). Aminolysis of PLLA during mixing with mCNF allows for the grafting of PLLA chains and formation of amide linkages between mCNF and the PLLA matrix. This results in improved dispersion and interfacial adhesion within the PLLA matrix when compared to native CNFs, consequently contributing to significantly enhanced tensile strength.

2. EXPERIMENTAL

2.1 Materials. Cellulose nanofibrils (CNF) suspension was kindly provided by U.S. Department of Agriculture-Forest Product Laboratory. Poly(L-lactide) (PLLA) 6202D was purchased from Nature Works LLC (Minnetonka, MN). 3-aminopropyltrimethoxysilane (APTMS), methyl acrylate (MA), and ethylenediamine (EDA) were purchased from the Aldrich Chemical Company (Milwaukee, WI). Common laboratory salts and solvents were purchased from Fisher Scientific (Pittsburgh, PA). Unless noted otherwise, all materials were used as received without further purification.

2.2 Synthesis of amine-functionalized CNF generation 1 (mCNF-G1). To enable surface modification, CNFs were precipitated using acetone, collected by centrifugation, and redispersed in acetone by sonication. This centrifugation-redispersion cycle was repeated three times for the solvent exchange process. The resulting CNFs were then solvent exchanged from acetone to toluene following the same protocol. The CNF suspension in toluene was kept at room temperature for further modification. For the synthesis of mCNF-G1, aliquot of APTMS (0.5 mL) was added to the CNF (250 mg) suspension in toluene (25 mL). The mixture was refluxed at 85 °C under stirring for 24 h. The resulting mCNF-G1 was collected by centrifugation, washed with acetone three times to remove the unbound silanes, and dried under vacuum at room temperature to evaporate the residual solvent.

2.3 Synthesis of amine-functionalized CNF generation 2 (mCNF-G2). A dendritic polyamidoamine (PAMAM) structure was anchored onto the surface of CNF to yield mCNF-G2. mCNF-G1 (500 mg) and methacrylate (MA) (5 mL) were mixed in methanol (30 mL) and stirred at room temperature for 3 d. The MA-modified CNF (mCNF-G1.5) was collected by centrifugation, washed three times in ethanol, and dried under vacuum at room temperature.

mCNF-G1.5 (600 mg) was then re-suspended in 50 mL methanol followed by the addition of ethylenediamine (EDA) (10 mL). The mixture was stirred at room temperature for 3 d prior to collection by centrifugation. The precipitates were washed three times in ethanol and dried under vacuum at room temperature. The resulting CNF modified with dendritic PAMAM is referred to as mCNF-G2.

2.4 Preparation of PLLA/native CNF and modified CNF nanocomposites. Poly(L-lactide) was dissolved in chloroform (20 mL) with a concentration of 50 mg/mL, followed by the

addition of native CNF with various weight ratios to PLLA. The mixture was sonicated for 1 min to disperse the native CNF. The chloroform solution was then cast onto a glass substrate and dried at room temperature for 24 h and under vacuum at 40 °C for 24 h to form PLLA/CNF films. These films were then hot pressed at 175 °C for 3 min and cooled to room temperature at a rate of 10 °C/min to obtain the final nanocomposite films. The PLLA/mCNF films were prepared in a similar manner except that the PLLA/mCNF solution in chloroform was stirred at room temperature for 16 h to allow for the aminolysis of PLLA prior to film casting.

2.5 Characterization of the PLLA/CNF nanocomposite films. Scanning electron micrographs were recorded with a Hitachi S-4800 scanning electron microscope (Pleasanton, CA) to characterize the distribution of the CNFs within the PLLA matrices and the interfacial properties.

X-ray photoelectron spectroscopy (XPS) analysis of the CNFs was carried out with a Thermo Scientific K-Alpha X-ray photoelectron spectrometer equipped with a conventional electron energy analyzer. The latter was operated in the fixed transmission mode at constant pass energy of 200 eV for the survey spectra and 50 eV for the core level spectra. A monochromatic Al K α source (1486.6 eV) operated at 420 W (14 kV; 30 mA) was used as incident radiation. Photo-emitted electrons were collected at a take-off angle of 90° from the sample and the pressure was about 10⁻⁷ Pa. The spectrometer energy scale was calibrated with respect to Ag 3d5/2, Au 4f7/2, and Cu 2p3/2 core level peaks, set with binding energies of 368.3, 84.0, and 932.7 eV, respectively. For elemental quantification, the accuracy of the analysis was considered to be $\pm 1\%$.

Infrared absorption spectra of native and modified CNFs were obtained using a Thermo Nicolet Nexus 670 FTIR spectrometer with a Diamond attenuated total reflectance (ATR) attachment

with a spectral resolution of 4 cm⁻¹. The native and modified CNF powders were subjected to measurement under ambient condition.

Gel permeation chromatography (GPC) was carried out using a GPC system consists of a Waters model 510 pump, a Rheodyne model 7725(i) manual injector with a 200 µl loop, and a Knauer Smartline model 2300 RI detector. The columns were calibrated with a set of PS standards with chloroform as the mobile phase.

Differential scanning calorimetry (DSC) measurements were performed using a TA DSC Q2000 from 20 to 200 °C, with cooling and heating rates of 10 °C/min. The degree of crystallization (X_c) was derived from equation 1, where ΔH_m and ΔH_c are the melting and crystallization enthalpies of the nanocomposite films, respectively. ΔH_{100} and w are the melting enthalpy for 100% crystalline PLLA and weight percentage of the PLLA, respectively. The ΔH_{100} value used for the calculation was 93 J/g.¹

$$X_c = \frac{\Delta H_m - \Delta H_c}{w\Delta H_{100}} \times 100\% \quad \text{Equation 1}$$

Tensile tests of the nanocomposite films were performed on a customized micro testing system consisting of a high torque NEMA 23 stepper motor with optical encoders, an 11.1 N load cell, a custom slider linear air bearing. A labview virtual instrument was used for data acquisition and control. The entire system was mounted onto an air table to reduce mechanical vibrations. Load was transferred to the test specimens by adhesively bonding them with Loctite 406 instant adhesive onto a pair of stainless steel mounds. The unsupported length between the grips was defined as the initial gauge section. Five specimens were tested to provide the average and standard deviation.

3. Results and discussion

Nanocellulose materials (e.g., CNF and cellulose nanocrystals (CNC)) have been utilized to reinforce PLLA as green composites, due to their biocompatibility and great mechanical properties (e.g., tensile strength of 2-6 GPa).(Fujisawa, Saito, Kimura, Iwata & Isogai, 2013; Goffin et al., 2011a; Jonoobi, Harun, Mathew & Oksman, 2010) To improve the interfacial properties, poly(ethylene glycol) (PEG)(Fujisawa, Saito, Kimura, Iwata & Isogai, 2013) and PLLA(Goffin et al., 2011a) were anchored to the surface of nanocellulose materials. These surface modifications have resulted in enhanced compatibility with non-polar solvents and PLLA. However, only limited increases in tensile strength were observed which may be attributed to insufficient interfacial adhesion. In this regard, we predict that amine-functionalized CNFs will lead to the grafting of PLLA brushes via aminolysis, (Zhu, Gao, Liu, He & Shen, 2004) thus resulting in strong adhesive interaction with the PLLA matrix and a significant increase in mechanical properties. In addition, compared to the grafting of PLLA via the ring opening of lactide on the CNF surface, it is a more convenient approach to create covalent bonding at the interface. To determine the efficacy of approach, amine-functionalized CNFs were synthesized with controllable amine density on the surface of CNFs to prepare PLLA/CNF nanocomposites with enhanced mechanical strength and stiffness.

3.1 Synthesis of amine-functionalized CNFs (mCNFs). A number of strategies have been reported to functionalize the hydroxyl groups on the surface of CNFs, including silylation,(Blaker, Lee, Li, Menner & Bismarck, 2009; Xhanari, Syverud, Chinga-Carrasco, Paso & Stenius, 2011) acetylation,(Berlitz, Molina-Boisseau, Nishiyama & Heux, 2009; de Menezes, Siqueira, Curvelo & Dufresne, 2009; Sassi & Chanzy, 1995; Sebe, Ham-Pichavant & Pecastaings, 2013) and polymer grafting.(Cao, Habibi & Lucia, 2009; Lin & Dufresne, 2013;

Ljungberg, Bonini, Bortolussi, Boisson, Heux & Cavaille, 2005; Lonnberg, Fogelstrom, Zhou, Hult, Berglund & Malmstrom, 2011) Among these techniques, silylation is a convenient approach to modify the surface with a wide range of functional groups due to the commercial availability of structurally diverse silanes. In this study, we adapted this strategy to modify the hydroxyl groups on the surface of CNF. Cellulose nanofibrils suspension in the reaction medium (i.e., toluene) was prepared using a solvent exchange process. 3-aminopropyltrimethoxysilane (APTMS) was then anchored to the CNF surface to impart the amine moieties (Figure 1a). The reaction temperature (i.e., 85 °C) was chosen to minimize the loss of APTMS which exhibits a boiling point of ~90 °C. To demonstrate the grafting of APTMS, XPS was performed to characterize the surface property of the mCNF-G1 (Table 1). As shown in Table 1, the atomic percentage for nitrogen on the surface of APTMS-modified CNF (mCNF-G1) is determined to be 6.0% while native CNF showed no amine groups. Of note, the theoretical nitrogen atomic percentage is 6.6% assuming that each silane reacts with three hydroxyl groups (Figure 1) and no carboxylic acid groups are present on the CNF surface. Despite the inaccuracy of the theoretical value (caused by the assumptions), it enables us to estimate the yield of APTMS-modified units in mCNF-G1 by the ratio of experimental and theoretical atomic percentage. Inspection of the XPS results for mCNF-G1 revealed that ~90% of the units on CNF surface were functionalized by APTMS.

Given that carboxylic acid (1.24 mmol/g) groups are present on the CNF surface, it has been reported that amines may be adsorbed on the surface in a polar solvent like water via ionic bonding. The bonding is so strong that the amine compounds are still adsorbed on the surface after extensive wash. (Fujisawa, Saito, Kimura, Iwata & Isogai, 2013) However, no ionic bonding is expected in non-polar solvent (e.g., toluene) because both species are not protonated

or deprotonated. Negligible adsorption may thus be expected after extensive washing. To confirm this hypothesis, CNF was suspended in toluene and APTMS at room temperature for 16 h. The resulting CNF was washed with acetone three times prior to drying in the oven at room temperature. The nitrogen atomic percentage was determined to be ~0% by XPS (Figure S1). This result confirms that the APTMS was covalently attached to the mCNF-G1 surface.

Figure 1. Schematic illustration of the synthesis of amine-functionalized CNFs (i.e., a) mCNF-G1, b) mCNF-G1.5, c) mCNF-G2) and d) the formation of amide linkage between PLLA matrix and the amine-modified CNFs.

Table 1. Atomic percentage of nitrogen on the surface of cellulose nanofibrils by X-ray photoelectron spectroscopy.

Nitrogen content (%)	CNF	mCNF-G1	mCNF-G1.5	mCNF-G2
	0	6.0±0.2	3.3±0.3	15±3.0

As mentioned in the previous section, the objective of modifying the CNF surface with amines is to create covalent linkages between the PLLA matrix and the amine-modified CNFs. As such, the amount of amine groups is expected to greatly impact the interfacial properties of the resulting nanocomposites. We next sought to further increase the amine density on the CNF surface, which allows us to study how the amine density affects the properties of the nanocomposites. A dendritic polyamidoamine (PAMAM) was successfully grafted onto the surface of mCNF-G1 (Figure 1b and 1c). PAMAM dendrimers were the first complete dendrimer family to be synthesized, characterized and commercialized. Tomalia first synthesized PAMAM dendrimers in 1980's.(Tomalia et al., 1985) These dendrimers have a tree-like structure with primary amines on the periphery and surface groups which amplify exponentially at each generation.(Lu, Slomberg, Shah & Schoenfisch, 2013) Divergent synthesis of PAMAM dendrimers is accomplished by alternating between the Michael addition of amino-terminated surfaces onto methacrylate (MA) and the transamidation reaction of ester groups. In this study, this strategy was adapted to increase the amine density on surface of CNF. The amine groups on mCNF-G1 were reacted with MA via Michael addition, resulting in the formation of mCNF-G1.5 (Figure 1b). The atomic percentage of nitrogen decreased to 3.5% due to the addition of two MA molecules onto each amine. The carbonyl groups from the MA molecules have also been observed in the XPS C1s spectrum as shown in Figure 2. Compared with mCNF-G1, a distinct signal at 289 eV (which is characteristic of carbonyl groups) can be seen, indicating the successful addition of MA groups onto the CNF surface.

258 mCNF-G2 was synthesized by the transamidation of the ester groups on mCNF-G1.5 using
 259 ethylenediamine (EDA). Excessive EDA was used to minimize crosslinking between ester
 260 groups. (Tomalia et al., 1985) The resulting mCNF-G2 exhibited a nitrogen atomic percentage of
 261 15%, attributable to the high amine content of EDA. This increase in nitrogen content is
 262 accompanied by a decreased intensity of carbonyl groups in the XPS C1s spectrum compared
 263 with mCNF-G1.5, a result of the conjugation of EDA molecules onto the surface. The surface
 264 functional groups have also been confirmed by FT-IR spectroscopy (Figure 3). Distinct signal
 265 corresponding to primary amine and carbonyl groups were easily identified at 1620 (N-H
 266 bending) and 1780 cm^{-1} (C=O stretching vibration) for mCNF-G1 and mCNF-G1.5, respectively.
 267 The grafting of EDA to the mCNF-G2 was indicated by the increased intensity of 2883 cm^{-1} peak
 268 for alkane C-H stretching vibration.

269

Figure 2. The X-ray photoelectron spectroscopy (XPS) C1s spectrum of A) CNF, B) mCNF-G1, C) mCNF-G1.5, and D) mCNF-G2 showing the increase in carbonyl groups (289.3 eV) of mCNF-G1.5, and decrease in mCNF-G2 which is an indication of successful addition of MA and EDA groups, respectively. Binding energy assignment: 284 eV (C-Si), 284.6 (C-C), 286 (C-N), 286.5 (C-O), 287.9 (O-C-O), 289.3 (C=O).

Figure 3. FT-IR spectra of A) native CNF, B) mCNF-G1, C) mCNF-G1.5, and D) mCNF-G2.

3.2 Effect of amine-modification on the properties of CNF/PLLA. Nanocomposite films with a CNF content ranging from 5 to 15% were prepared by solution casting followed by compression molding. The resulting films exhibit a thickness of ~60 μm . To provide detailed information on the dispersion of unmodified CNF and interfacial properties, scanning electron

microscopy was utilized to characterize the fractured surface of native CNF and mCNF-G1-reinforced PLLA films (Figure 4).

Figure 4. Scanning electron microscopy images of the fracture surface of A) and C) PLLA/CNF films containing 10% CNF, and B) and D) PLLA/mCNF-G1 containing 10% mCNF-G1. Insets are the digital image of the composite films of 10 mm in width. Scale bar: 50 μm for A, B, and C; 500 nm for D. The arrow in A points at the aggregates of native CNF within the PLLA film.

mCNF-G1 showed significantly improved dispersion as indicated by the absence of large aggregates (Figure 4 B, D) and a uniform brownish tint throughout the film (Inset). Of note, the light brownish color of the CNFs was caused by thermal decoloration during compression molding at 175 °C. As expected, native CNF showed poor dispersibility into the PLLA matrix due to its incompatibility with hydrophobic polymers (Figure 4 A, C). As shown in the digital images of the films (insets in Figure 4), large aggregates (i.e., the light brown particulates) of

native CNF are present within the PLLA matrix. The aggregates of native CNF present in the film are $> 100\ \mu\text{m}$ in diameter and have similar thickness to the composite films (Figure 4A). As shown in Figure 4C, a cavity can be seen due to the pull-out of CNF aggregates, indicative of poor interfacial adhesion. In contrast, for mCNF-G1-reinforced films, no such aggregation was observed. The mCNF-G1 showed uniform dispersion within the PLLA matrix as shown in Figure 4D, indicating improved compatibility with PLLA. Of note, the round features seen in Figure 4D correspond to the cross-sections of mCNF-G1. We hypothesize that the improved compatibility is a result of the grafting of PLLA brushes onto mCNF-G1 via aminolysis (Figure 1d), resulting in better dispersion and interfacial adhesion. To confirm the grafting of PLLA brushes, XPS was performed to characterize the surface groups on mCNF-G1. mCNF-G1 grafted with PLLA was isolated from the composite film by dissolving it in chloroform. The fiber was extensively washed with chloroform prior to characterization.

Figure 5. The X-ray photoelectron spectroscopy (XPS) C1s spectrum of mCNF-G1, and PLLA grafted mCNF-G1 (G1-PLLA).

As shown in Figure 5, the peaks at 287.5 and 289.5 eV correspond to the C-O and C=O ester bonds on PLLA, respectively. Collectively, we can conclude that the amide bond linkage can be formed between the amine-modified CNF and the PLLA matrix within nanocomposite films. Since the grafting of PLLA onto the amine-modified CNF is through the aminolysis of PLLA, the grafting is expected to be accompanied with a decreased molecular weight of the PLLA matrix. Gel permeation chromatography was thus performed to confirm this hypothesis. As shown in Table 2, the molecular weight of the PLLA matrix decreased with the concentration of mCNF-G1. This result along with the XPS analysis confirms the grafting of PLLA brushes onto the CNF surface.

Table 2. Molecular weight of the poly(L-lactide) for different composite films

Sample	CNF content (%)	M _n	M _w	PDI
PLLA		90700	139430	1.54
PLLA/CNF	5	85730	133140	1.55
	10	87570	134200	1.53
	15	94370	137970	1.46
PLLA/mCNF-G1	5	72960	109210	1.50
	10	70740	124490	1.76
	15	53050	98470	1.86
PLLA/mCNF-G2	10	39150	67710	1.73

Nano-sized additions have been demonstrated to influence the thermal properties of polymer matrices. To investigate how native CNF and APTMS-modification affects the crystallinity (X_c) and glass transition temperature (T_g) of resulting composites, differential scanning calorimetry (DSC) was conducted for nanocomposite films with different fillers and concentration levels. Table 3 shows the crystallization enthalpy, melting enthalpy, and crystallinity of the PLLA and nanocomposite films obtained by DSC analysis (Figure 6). The neat PLLA film exhibited a lower crystallinity (i.e., 0.1%). The crystallinity of PLLA increased by adding both native CNF and mCNF-G1 due to the nucleating property of the fillers, as previously

demonstrated.(Fujisawa, Saito, Kimura, Iwata & Isogai, 2013) Compared to unmodified CNF, mCNF-G1 leads to a significantly greater crystallinity increase at the same concentration level. For example, 15% mCNF-G1 resulted in a crystallinity of 32.5% compared to 8.7% for 15% CNF. Of note, the increase in crystallinity was also reported in a previous report by Goffin et al.(Goffin et al., 2011a) This is likely caused by the improved dispersion of mCNF-G1 within the PLLA matrix, which renders a larger interfacial surface for nucleation.

Table 3. Thermal properties of CNF and mCNF-G1/PLLA nanocomposites

Sample	CNF content (%)	T _g (°C)	T _m (°C)	ΔH _c (J/g) ^a	ΔH _m (J/g) ^b	X _c (%) ^c
PLLA		55.6	166.1	30.4	30.5	0.1
PLLA/CNF	5	51.7	166.0	26.4	29.7	3.7
	10	50.9	167.3	22.2	29.5	8.7
	15	54.3	166.0	15.5	23.9	10.6
PLLA/mCNF-G1	5	51.2	167.2	17.4	31.0	15.4
	10	50.5	166.5	9.4	30.1	24.7
	15	48.1	166.3	3.1	28.8	32.5

^aCrystallization enthalpy of PLLA component, ^bMelting enthalpy of PLLA component,

^cCrystallinity of PLLA component

Additionally, as shown in Figure 6, T_g decreases with additions of both CNF and mCNF-G1, corroborating previously reported results.(Fujisawa, Saito, Kimura, Iwata & Isogai, 2013) It is well known that in particle-filled polymers, a non-wetting interaction and the free volume readily incorporated by particles can decrease T_g.(Ash, Siegel & Schadler, 2004; Merkel et al., 2002) which may explain the T_g decrease caused by unmodified CNF. For the mCNF-G1, which contains PLLA brushes on the surface, variation in interfacial properties determines the effect on T_g. According to the report by Bansal et al. on polystyrene-grafted silica particles/polystyrene composites,(Bansal, Yang, Li, Benicewicz, Kumar & Schadler, 2006) when the grafted brushes have a molecular weight higher than that of the matrix, wetting is observed and an increase in T_g of the nanocomposite is noted. For a system where the molecular weight of the brushes is lower than that of the matrix, dewetting is observed and the T_g decreases with increasing filler content. Given that the PLLA brushes on the mCNF-G1 were grafted via aminolysis degradation, the

molecular weight is expected to be lower than that of the PLLA matrix. Therefore, a dewetting phenomenon may occur at the interface, leading to a decreased T_g . Of note, the T_g for all the composites in this study is comparable to that of PLLA and thus exerts minimal limitations to the application of PLLA-based materials. In addition, these composites exhibited similar thermal stability at temperatures below 100 °C. The addition of CNF or mCNF-G1 improves the thermal stability above 300 °C (Figure S3).

360 Figure 6. DSC curve of PLLA, A) CNF- and B) mCNF-G1-reinforced PLLA nanocomposite
361 films with different CNF contents obtained from the first heating run at 10 °C/min.

362

363 The mechanical properties of the nanocomposite films were investigated by tensile testing.

364 Figure 7 and S2 show the tensile strength and Young's modulus of these materials. Overall, the

365 unmodified CNF only led to a slight increase (~20%) in tensile strength and Young's modulus,

366 probably due to increased crystallinity. On the other hand, over 100% increase in tensile strength

367

368 Figure 7. Mechanical properties of nanocomposite films with different contents of CNF and
 369 mCNF: A) tensile strength, B) Young's modulus

370

371 was observed for the PLLA/mCNF-G1 film with a 10% concentration of nanofibrils. This
 372 significant enhancement in tensile strength is likely the result of greater crystallinity and the

improved dispersion/interfacial properties of mCNF-G1 within the matrix, as well as amide bond crosslinking with PLLA. These results demonstrate that amine-functionalization of the CNF surface is effective at improving compatibility with the PLLA matrix and enhancing the mechanical properties of the resulting nanocomposites.

3.3 Effects of the mCNF-G1 content on the mechanical properties. Nanocomposite films were prepared with various mCNF-G1 contents (i.e., 5, 10, and 15%) to investigate the influence of filler concentration level on mechanical strength. As shown in Figure 7, films with 10% mCNF-G1 exhibited the greatest tensile strength, despite the fact that 15% mCNF-G1 resulted in greater crystallinity. Given that overconcentration of nanoparticles can cause greater particle aggregation, we hypothesize that the weakening effect is attributed to increased mCNF-G1 aggregation within the matrix, which was confirmed by SEM images (Figure 8). Although the nanocomposite films from mCNF-G1 do not contain large aggregates like the native CNF, agglomeration was still observed. As shown in Figure 8, the arrows point to aggregates of mCNF-G1, the number of which increases with volume concentration. Of note, no pull-out was observed along the stretching direction (Figure 8D), indicating a strong interfacial adhesion between the fiber and the PLLA matrix. However, the interfacial adhesion between fibers within the aggregates is expected to be much weaker due to an insufficient PLLA binding effect. These aggregates are thus defects with weak adhesion within the PLLA matrix. As such, increased defects in the nanocomposite films with 15% mCNF-G1 contributed to the lower tensile strength of the films.

Figure 8. Scanning electron microscopy images of the fracture surface of mCNF-G1 reinforced PLLA nanocomposite films with A) 5%, B) 10%, and C) 15% fillers and D) a magnified image of the aggregates. Scale bar: 20 μm for A, B, and C; 3 μm for D. Arrows point at the aggregates.

3.4 Effect of amine density on tensile strength. Since aminolysis of PLLA is the key for amine-functionalized CNFs to reinforce PLLA, we next sought to investigate the effect of amine density on the mechanical properties of the nanocomposite films. mCNF-G2 with a dendritic PAMAM structure was synthesized and added to PLLA films (Figure 1). Nanocomposite films with 10% dopants were prepared due to the fact that 10% concentration of both native CNF and mCNF-G1 exhibited greater tensile strength compared to 5 and 15% (Figure 9).

Figure 9. Stress-strain curves for PLLA, PLLA/10% mCNF-G1, and PLLA/10% mCNF-G2 nanocomposite films.

As shown in Figure 9, increased amine density (i.e., mCNF-G2) resulted in decreased tensile strength (33.3 ± 5.0 MPa) and Young's modulus (1.2 ± 0.2 GPa) compared to mCNF-G1, which is probably the result of degradation of the PLLA matrix by aminolysis. The larger amount of amines on the mCNF-G2 surface was expected to decrease the molecular weight of the PLLA matrix more significantly, via the chain scission induced by aminolysis. These results demonstrate that the amine-modified CNFs have both positive and negative effects on the reinforcement of PLLA. Aminolysis resulted in the PLLA grafting and crosslinking with the matrix, which is accompanied by the degradation of the PLLA matrix. Excessive amines could compromise the mechanical properties of the nanocomposite. Indeed, as shown in Table 2, the molecular weight of PLLA matrix for film with 10% mCNF-G2 is significantly lower compared

to that with 10% mCNF-G1. Collectively, we conclude that 10% mCNF-G1 is the most suitable to reinforce PLLA amongst the formulations tested in this study.

4. Conclusion

With the motivation of developing renewable composites, much research has been focused on the use of nanocellulose to reinforce PLLA. Strategies to improve the interfacial properties of hydrophilic nanocellulose with hydrophobic PLLA include acetylation and polymer grafting. This study focuses on the synthesis of amine-functionalized CNF with tunable amine content and its use as a reinforcing filler for PLLA. The aminolysis of PLLA by the amine-functionalized CNF allows for the grafting of PLLA chains onto the fiber, thus improving the compatibility of the CNFs with the matrix, as indicated by better filler dispersion, interfacial adhesion, and greater tensile strength. However, excessive amines on the CNFs can compromise the mechanical properties of the nanocomposite films due to the degradation of PLLA via aminolysis. Based on the results shown in this study, 10% APTMS-modified CNF (mCNF-G1) resulted in the greatest reinforcing effect (i.e., >100% increase in tensile strength compared to neat PLLA). This study has demonstrated that introducing amine-functionalized CNFs is a simple and effective technique to improve the dispersion of CNF within PLLA and the mechanical properties of resulting composites.

5. Acknowledgement

The authors thank Rich R. Lowden for his assistance in the preparation of the experimental system for tensile testing. The authors gratefully acknowledge the generous assistance and valuable advice of Dr. Harry Meyer on XPS analysis. Thanks to the USDA Forest Service Forest Products Laboratory for providing cellulose nanomaterials as well as information on the

properties of cellulosic nanomaterials. This research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. This article has been authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the US Department of Energy. The US government retains and the publisher, by accepting the article for publication, acknowledges that the US government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US government purposes.

6. References

- Ash, B. J., Siegel, R. W., & Schadler, L. S. (2004). Glass-transition temperature behavior of alumina/PMMA nanocomposites. *Journal of Polymer Science, Part B: Polymer Physics*, 42(23), 4371-4383.
- Auras, R., Harte, B., & Selke, S. (2004). An overview of polylactides as packaging materials. *Macromolecular Bioscience*, 4(9), 835-864.
- Bansal, A., Yang, H. C., Li, C. Z., Benicewicz, R. C., Kumar, S. K., & Schadler, L. S. (2006). Controlling the thermomechanical properties of polymer nanocomposites by tailoring the polymer-particle interface. *Journal of Polymer Science Part B-Polymer Physics*, 44(20), 2944-2950.
- Berlitz, S., Molina-Boisseau, S., Nishiyama, Y., & Heux, L. (2009). Gas-Phase Surface Esterification of Cellulose Microfibrils and Whiskers. *Biomacromolecules*, 10(8), 2144-2151.
- Blaker, J. J., Lee, K. Y., Li, X. X., Menner, A., & Bismarck, A. (2009). Renewable nanocomposite polymer foams synthesized from Pickering emulsion templates. *Green Chemistry*, 11(9), 1321-1326.
- Brzezinski, M., & Biela, T. (2014). Polylactide nanocomposites with functionalized carbon nanotubes and their stereocomplexes: A focused review. *Materials Letters*, 121, 244-250.
- Bulota, M., & Hughes, M. (2012). Toughening mechanisms in poly(lactic) acid reinforced with TEMPO-oxidized cellulose. *Journal of Materials Science*, 47(14), 5517-5523.
- Cao, X. D., Habibi, Y., & Lucia, L. A. (2009). One-pot polymerization, surface grafting, and processing of waterborne polyurethane-cellulose nanocrystal nanocomposites. *Journal of Materials Chemistry*, 19(38), 7137-7145.
- Coleman, J. N., Khan, U., & Gun'ko, Y. K. (2006). Mechanical reinforcement of polymers using carbon nanotubes. *Advanced Materials*, 18(6), 689-706.
- Czaja, W., Krystynowicz, A., Bielecki, S., & Brown, R. M. (2006). Microbial cellulose - the natural power to heal wounds. *Biomaterials*, 27(2), 145-151.
- de Menezes, A. J., Siqueira, G., Curvelo, A. A. S., & Dufresne, A. (2009). Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites. *Polymer*, 50(19), 4552-4563.

477 Fujisawa, S., Saito, T., Kimura, S., Iwata, T., & Isogai, A. (2013). Surface Engineering of Ultrafine Cellulose
 478 Nanofibrils toward Polymer Nanocomposite Materials. *Biomacromolecules*, 14(5), 1541-1546.
 479 Ganster, J., Fink, H.-P., Lau, A., Hussain, F., & Lafdi, K. eds. (2010). *PLA-based bio-and nanocomposites*.
 480 Boca Raton, Florida: Taylor & Francis Group.
 481 Garlotta, D. (2001). A literature review of poly(lactic acid). *Journal of Polymers and the Environment*,
 482 9(2), 63-84.
 483 Gatenholm, P., & Klemm, D. (2010). Bacterial Nanocellulose as a Renewable Material for Biomedical
 484 Applications. *MRS Bulletin*, 35(3), 208-213.
 485 Goffin, A. L., Raquez, J. M., Duquesne, E., Siqueira, G., Habibi, Y., Dufresne, A., & Dubois, P. (2011a).
 486 From Interfacial Ring-Opening Polymerization to Melt Processing of Cellulose Nanowhisker-Filled
 487 Polylactide-Based Nanocomposites. *Biomacromolecules*, 12(7), 2456-2465.
 488 Goffin, A. L., Raquez, J. M., Duquesne, E., Siqueira, G., Habibi, Y., Dufresne, A., & Dubois, P. (2011b).
 489 Poly(epsilon-caprolactone) based nanocomposites reinforced by surface-grafted cellulose nanowhiskers
 490 via extrusion processing: Morphology, rheology, and thermo-mechanical properties. *Polymer*, 52(7),
 491 1532-1538.
 492 Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose Nanocrystals: Chemistry, Self-Assembly, and
 493 Applications. *Chemical Reviews*, 110(6), 3479-3500.
 494 Iwatake, A., Nogi, M., & Yano, H. (2008). Cellulose nanofiber-reinforced polylactic acid. *Composites
 495 Science and Technology*, 68(9), 2103-2106.
 496 Jonoobi, M., Harun, J., Mathew, A. P., & Oksman, K. (2010). Mechanical properties of cellulose nanofiber
 497 (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Composites Science and
 498 Technology*, 70(12), 1742-1747.
 499 Lacerda, P. S. S., Barros-Timmons, A. M. M. V., Freire, C. S. R., Silvestre, A. J. D., & Neto, C. P. (2013).
 500 Nanostructured Composites Obtained by ATRP Sleeving of Bacterial Cellulose Nanofibers with Acrylate
 501 Polymers. *Biomacromolecules*, 14(6), 2063-2073.
 502 Lee, H. S., Fasulo, P. D., Rodgers, W. R., & Paul, D. R. (2005). TPO based nanocomposites. Part 1.
 503 Morphology and mechanical properties. *Polymer*, 46(25), 11673-11689.
 504 Lin, N., & Dufresne, A. (2013). Physical and/or Chemical Compatibilization of Extruded Cellulose
 505 Nanocrystal Reinforced Polystyrene Nanocomposites. *Macromolecules*, 46(14), 5570-5583.
 506 Ljungberg, N., Bonini, C., Bortolussi, F., Boisson, C., Heux, L., & Cavaille, J. Y. (2005). New nanocomposite
 507 materials reinforced with cellulose whiskers in atactic polypropylene: Effect of surface and dispersion
 508 characteristics. *Biomacromolecules*, 6(5), 2732-2739.
 509 Lonnberg, H., Fogelstrom, L., Zhou, Q., Hult, A., Berglund, L., & Malmstrom, E. (2011). Investigation of
 510 the graft length impact on the interfacial toughness in a cellulose/poly(epsilon-caprolactone) bilayer
 511 laminate. *Composites Science and Technology*, 71(1), 9-12.
 512 Lu, Y., Slomberg, D. L., Shah, A., & Schoenfisch, M. H. (2013). Nitric Oxide-Releasing Amphiphilic
 513 Poly(amidoamine) (PAMAM) Dendrimers as Antibacterial Agents. *Biomacromolecules*, 14(10), 3589-
 514 3598.
 515 Lu, Y., Tekinalp, H. L., Eberle, C. C., Peter, W., Naskar, A. K., & Ozcan, S. (2014). Nanocellulose in polymer
 516 composites and biomedical applications. *Tappi Journal*, 13(6), 47-54.
 517 Lunt, J. (1998). Large-scale production, properties and commercial applications of polylactic acid
 518 polymers. *Polymer Degradation and Stability*, 59(1-3), 145-152.
 519 Mathew, A. P., Oksman, K., & Sain, M. (2006). The effect of morphology and chemical characteristics of
 520 cellulose reinforcements on the crystallinity of polylactic acid. *Journal of Applied Polymer Science*,
 521 101(1), 300-310.
 522 Merkel, T. C., Freeman, B. D., Spontak, R. J., He, Z., Pinnau, I., Meakin, P., & Hill, A. J. (2002).
 523 Ultraparpermeable, reverse-selective nanocomposite membranes. *Science*, 296(5567), 519-522.

524 Nakagaito, A. N., Fujimura, A., Sakai, T., Hama, Y., & Yano, H. (2009). Production of microfibrillated
 525 cellulose (MFC)-reinforced polylactic acid (PLA) nanocomposites from sheets obtained by a
 526 papermaking-like process. *Composites Science and Technology*, 69(7), 1293-1297.
 527 Okubo, K., Fujii, T., & Thostenson, E. T. (2009). Multi-scale hybrid biocomposite: Processing and
 528 mechanical characterization of bamboo fiber reinforced PLA with microfibrillated cellulose. *Composites*
 529 *Part a-Applied Science and Manufacturing*, 40(4), 469-475.
 530 Paakko, M., Ankerfors, M., Kosonen, H., Nykanen, A., Ahola, S., Osterberg, M., Ruokolainen, J., Laine, J.,
 531 Larsson, P. T., Ikkala, O., & Lindstrom, T. (2007). Enzymatic hydrolysis combined with mechanical
 532 shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels.
 533 *Biomacromolecules*, 8(6), 1934-1941.
 534 Petersson, L., Kvien, I., & Oksman, K. (2007). Structure and thermal properties of poly(lactic
 535 acid)/cellulose whiskers nanocomposite materials. *Composites Science and Technology*, 67(11-12), 2535-
 536 2544.
 537 Quero, F., Nogi, M., Yano, H., Abdulsalami, K., Holmes, S. M., Sakakini, B. H., & Eichhorn, S. J. (2010).
 538 Optimization of the Mechanical Performance of Bacterial Cellulose/Poly(L-lactic) Acid Composites. *Acs*
 539 *Applied Materials & Interfaces*, 2(1), 321-330.
 540 Rafiee, M. A., Rafiee, J., Wang, Z., Song, H. H., Yu, Z. Z., & Koratkar, N. (2009). Enhanced Mechanical
 541 Properties of Nanocomposites at Low Graphene Content. *ACS Nano*, 3(12), 3884-3890.
 542 Ramanathan, T., Abdala, A. A., Stankovich, S., Dikin, D. A., Herrera-Alonso, M., Piner, R. D., Adamson, D.
 543 H., Schniepp, H. C., Chen, X., Ruoff, R. S., Nguyen, S. T., Aksay, I. A., Prud'homme, R. K., & Brinson, L. C.
 544 (2008). Functionalized graphene sheets for polymer nanocomposites. *Nature Nanotechnology*, 3(6), 327-
 545 331.
 546 Raquez, J. M., Habibi, Y., Murariu, M., & Dubois, P. (2013). Polylactide (PLA)-based nanocomposites.
 547 *Progress in Polymer Science*, 38(10-11), 1504-1542.
 548 Saito, T., Kuramae, R., Wohler, J., Berglund, L. A., & Isogai, A. (2013). An Ultrastrong Nanofibrillar
 549 Biomaterial: The Strength of Single Cellulose Nanofibrils Revealed via Sonication-Induced
 550 Fragmentation. *Biomacromolecules*, 14(1), 248-253.
 551 Sanchez-Garcia, M. D., Gimenez, E., & Lagaron, J. M. (2008). Morphology and barrier properties of
 552 solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. *Carbohydrate*
 553 *Polymers*, 71(2), 235-244.
 554 Sassi, J. F., & Chanzy, H. (1995). Ultrastructural Aspects of the Acetylation of Cellulose. *Cellulose*, 2(2),
 555 111-127.
 556 Sebe, G., Ham-Pichavant, F., & Pecastaings, G. (2013). Dispersibility and Emulsion-Stabilizing Effect of
 557 Cellulose Nanowhiskers Esterified by Vinyl Acetate and Vinyl Cinnamate. *Biomacromolecules*, 14(8),
 558 2937-2944.
 559 Shanks, R. A., Hodzic, A., & Ridderhof, D. (2006). Composites of poly(lactic acid) with flax fibers modified
 560 by interstitial polymerization. *Journal of Applied Polymer Science*, 101(6), 3620-3629.
 561 Suryanegara, L., Nakagaito, A. N., & Yano, H. (2009). The effect of crystallization of PLA on the thermal
 562 and mechanical properties of microfibrillated cellulose-reinforced PLA composites. *Composites Science*
 563 *and Technology*, 69(7-8), 1187-1192.
 564 Thunwall, M., Boldizar, A., Rigdahl, M., Banke, K., Lindstrom, T., Tufvesson, H., & Hogman, S. (2008).
 565 Processing and properties of mineral-interfaced cellulose fibre composites. *Journal of Applied Polymer*
 566 *Science*, 107(2), 918-929.
 567 Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, S., Roeck, J., Ryder, J., & Smith, P.
 568 (1985). A New Class of Polymers - Starburst-Dendritic Macromolecules. *Polymer Journal*, 17(1), 117-132.
 569 Wagberg, L., Decher, G., Norgren, M., Lindstrom, T., Ankerfors, M., & Axnas, K. (2008). The build-up of
 570 polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes. *Langmuir*, 24(3),
 571 784-795.

Xhanari, K., Syverud, K., Chinga-Carrasco, G., Paso, K., & Stenius, P. (2011). Structure of nanofibrillated cellulose layers at the o/w interface. *Journal of Colloid and Interface Science*, 356(1), 58-62.

Xhanari, K., Syverud, K., & Stenius, P. (2011). Emulsions Stabilized by Microfibrillated Cellulose: The Effect of Hydrophobization, Concentration and O/W Ratio. *Journal of Dispersion Science and Technology*, 32(3), 447-452.

Xu, X. Z., Liu, F., Jiang, L., Zhu, J. Y., Haagensohn, D., & Wiesenborn, D. P. (2013). Cellulose Nanocrystals vs. Cellulose Nanofibrils: A Comparative Study on Their Microstructures and Effects as Polymer Reinforcing Agents. *Acs Applied Materials & Interfaces*, 5(8), 2999-3009.

Yuan, H. H., Nishiyama, Y., Wada, M., & Kuga, S. (2006). Surface acylation of cellulose whiskers by drying aqueous emulsion. *Biomacromolecules*, 7(3), 696-700.

Zhu, Y. B., Gao, C. Y., Liu, X. Y., He, T., & Shen, J. C. (2004). Immobilization of biomacromolecules onto aminolyzed poly(L-lactic acid) toward acceleration of endothelium regeneration. *Tissue Engineering*, 10(1-2), 53-61.

Supporting Information

Improved Mechanical Properties of Polylactide Nanocomposites-
Reinforced with Cellulose Nanofibrils through Interfacial Engineering
via Amine-Functionalization

Yuan Lu¹, Mario Caledrón Cueva², Edgar Lara-Curzio¹, Soydan Ozcan^{1*}

¹Materials Science and Technology Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Knoxville, TN. 37831

²Universidad San Francisco de Quito, Quito, Ecuador.

*Address correspondence to Dr. Soydan Ozcan

Email: ozcans@ornl.gov.

X-ray photoelectron spectroscopy (XPS) analysis of APTMS absorbed cellulose nanofibrils.

To investigate whether significant amount of APTMS was absorbed on the surface of CNF in toluene, APTMS was suspended in CNF solution and stirred at room temperature for 16 h.

Extensive washing was employed to remove absorbed APTMS. Based on the XPS spectrum, we can conclude that there is no detectable amines on the surface indicating minimal absorption of APTMS on the CNF surface.

Figure S1. The X-ray photoelectron spectroscopy (XPS) A) survey and B) N1s spectrum of CNF mixed with APTMS after washing.

Figure S2. Stress-Strain curves for native CNF and mCNF-G1 reinforced PLLA.