TRANSPARENT TEMPO OXIDIZED CELLULOSE NANOFIBRIL (TOCNF) COMPOSITES WITH INCREASED TOUGHNESS AND THICKNESS BY LAMINATION

by

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ABSTRACT

TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) cellulose nanofibrils (TOCNF) are polysaccharide nanomaterials that are extracted mainly from wood, plants and other biomass sources. TOCNF suspensions of negatively charged fibrils can be cast to produce totally transparent films with exceptional mechanical properties. Nevertheless, the inherent brittleness and the high stresses generated within the films during drying processes, makes the production of thick materials difficult and reduce the potential usage of TOCNFs films in industrial applications.

Hence, in this study lamination of TOCNF films with room temperature curable epoxy was used to combat brittleness, increase thickness, and produce a more damage tolerant material. The effect of the volume fraction and layer thickness of both phases, the number of layers, and the overall total thickness of the laminate on the tensile and flexural properties were investigated. Lamination was successful at increasing the toughness and thickness of TOCNF composites, resulting in an increased work of fracture (WOF) that was associated with fracture retardation by crack digression. The ultimate tensile strength (UTS) and Young's modulus were higher for laminates with low volume fractions of epoxy, and with increasing number of TOCNF layers.

To further increase the mechanical properties of TOCNF materials, water-soluble polymers were screened as strengthening aids through solution casting. Polyvinyl alcohol (PVA) and poly(2-ethyl-2-oxazoline) (PEOX) were found as reinforcement agents for various types of cellulose nanofibrils (CNFs) films. Mechanical property increases of 99% in elastic modulus, 93% in UTS and 134% WOF were reported for TOCNF with 0.44 mmol/g carboxylate groups and 15 wt.% PVA. PEOX had a higher elastic modulus increase of 113% over PVA, yet lower UTS and WOF increases were found at 63% and 28%, respectively. Additionally, increases in UTS and elastic modulus were also seen in mechanically fibrillated CNF and TOCNFs with higher carboxylate contents (1.5 mmol/g). The toughening mechanism was attributed to the formation of strong hydrogen bonding between the CNFs and the hydrophilic polymers added. The presence of such mechanisms was indirectly confirmed by tensile testing, zeta potential and rheology.

Finally, an enhanced version of TOCNF laminates was fabricated using TOCNF films with PVA strengthening aid and four different epoxy formulations as interlayer. Flexural testing showed

a correlation between the presence of stronger layers in the laminate with a higher flexural strength, bending modulus, and WOF. Different modes of fracture within the laminates occurred based on epoxy type. A stiffer epoxy generated a reduced mechanical response and substantial intralayer damage. On the other hand, a more ductile epoxy increased the WOF of the laminates, inducing a higher delamination at the interface. The addition of a silane coupling agent (APTES) resulted in a higher compatibility between the TOCNF and epoxy. In general, laminates with stronger TOCNF layers (TOCNF + PVA) and increased adhesion (APTES), showed a flexural strength increase of 61%, a bending modulus increment of 80% and the same WOF when compared with the original laminates. Finally, impact testing of TOCNF materials was performed, the specific energy to rupture of laminates was comparable to those achieved by acrylic and borosilicate glass, while maintaining a higher or similar specific strength to glass. Laminates maintained good transparency and low haziness to the naked eye.

1. INTRODUCTION

1.1 Background and Motivation

Cellulose nanofibers (CNFs) can be harvested from different sources (e.g. trees, plants, bacteria, algae, and even waste biomass)¹⁻⁶. CNFs have high specific surface areas with fibrils that are composed of both crystalline and amorphous regions and are known for exhibiting high stiffness and strength while also being inherently sustainable, bio-renewable and, non-toxic ^{1,7}. Generally, two approaches are used to produced CNFs. The first one requires the fibrillation of cellulose slurries in a disc refiner or grinder. The resulted material has a white appearance and is constituted by larger and more aggregated fibrils. CNFs produced by purely mechanical methods are here called mCNF and have been largely studied in literature. Films produced with mCNF exhibit a semi-ductile behavior with strain ratios that can reach the 10% and an ultimate tensile strength (UTS) of 200MPa^{1,8,9}. A second approach for producing CNFs involves coupling the mechanical processes with a chemical oxidative process where the catalyst TEMPO (2,2,6,6 tetramethylpiperidine-1-oxyl radical) is used in conjunction with a primary oxidizer (a strong acid) to covert the primary hydroxyl groups on the surface of the fibrils to carboxylic acids ^{10–12}. The reaction is usually carried out in water and produces a more stable suspension of fibrils due to a decrease in the fibril-fibril interactions (i.e. increase dispersion). The resulted suspension of TEMPO CNF is better known in literature as TOCNF and it has been extensively used in the production of highly transparent films with excellent mechanical properties. Neat TOCNF and high percentage TOCNF composite films have been reported with an elastic modulus of up to 20 GPa and UTS of up to 300 MPa while sustaining a more brittle fracture than their counterpart (mCNF) ^{1,9,10,13–15}.

Even when TOCNF films exhibit promising mechanical properties (high strength and stiffness) other characteristics like their brittleness and the inability to make thick materials out of them have limited their applicability ¹³. The films are usually produced by casting TOCNF suspensions (usually less than 2wt% TOCNF) followed by the removal of water. During this procedure, the media is removed either by evaporation or filtration, causing high shrinkage stresses within the film. The conjunction of both the inheriting brittleness of TOCNF and the high stresses in the films leads to the fracture of thick films, limiting the thickness of films and high percentage

TOCNF composites to values around the 20-100um ^{9,16,17}. A possible solution to some of the scalability problems of TOCNF was first proposed by Liu et al (2014). In his work, a laminated system of TOCNF and different interlayers was proposed (i.e. polyvinyl butyral and polystyrene-poly(ethylene/butylenes)-polystyrene (SEBS)), the resulted laminates showed a substantial increase in the work of failure (WOF) and a slight strength increase when laminated with PVB ¹⁸.

The technique used by Liu et al (2014), has been extensively studied. In fact, an extraordinary example of the advantages of the technique can be found in laminated glass, where by laying up a brittle material such as glass with a softer interlayer like PVB, an improvement in toughness without comprising the transparency of glass was achieved ¹⁹. Lamination takes advantage of crack retardation mechanisms to enhance the toughness of materials. In general, the failure mechanism of laminate structures is linked to the production of new surfaces or cracks inside the structure that propagate fast causing fracture. When a new surface or crack is produced inside a laminate it will propagate rapidly, but if the crack finds a weak interface in its way it might be diverted along the interface direction, retarding fracture. Also, when this diversion occurs, new interfaces are created making even more difficult for a crack to propagate, magnifying the overall toughness ^{20–22}.

1.2 Research Objectives

The goal of this work is to further study lamination as a possible solution to make mechanically tougher and thicker TOCNF materials. With that intention in mind the following specific objectives have been proposed:

- Study how the volume fraction, the layer thickness of both phases, the number of layers, and the overall total thickness of the laminate impact the final mechanical properties of the laminate. Relate mechanical properties of the laminates to possible mechanisms of fracture retardation at play.
- Improve TOCNF films to reduce their brittleness and enhance the mechanical properties of the films. Investigate different water-soluble polymers and their role in possible enhancing mechanisms.
- Investigate the role of stronger TOCNF layers, softer and stiffer interlayers and an increased adhesion at the interface in the final properties of the laminates. Study impact

properties of neat TOCNF films and high percentage TOCNF composite films along with TOCNF laminates.

1.3 Overview of this Work

In this work laminates made of TOCNF and epoxy are studied with the goal of cutting out some of the roadblocks that impede the proper commercialization of TOCNF materials due to their lack of thickness and excessive brittleness. Chapter 1 describes the lamination of TOCNF layers with a room temperature curable epoxy. The effect of the volume fraction and layer thickness of both layers, the number of layers and overall thickness of the laminate on the tensile and bending properties are investigated. Crack digression along the weak interfaces is studied as one of the primary mechanisms for fracture retardation in the laminates. Chapter 2 describes the screening of several water-soluble polymers as reinforcing agents for CNF films. The polymers were added in small concentrations (from 5 wt% to 20 wt%) and polyvinyl alcohol (PVA) and poly(2-ethyl-2oxazoline) (PEOX) were found as reinforcement agents for cellulose nanofibrils (CNFs) films. The mechanical increases are described for different types of CNF and the toughening mechanisms attributed to the formation of strong hydrogen bonding between the CNFs and the hydrophilic polymers added is investigated and indirectly confirmed by tensile testing, zeta potential and rheology. Chapter 3 introduces the reinforced TOCNF layers described in Chapter 2 to the lay-up systems describe in Chapter 1. Additionally, four different epoxy formulations are studied as interlayers for the laminates. Additionally, a silane coupling agent (APTES) is added to increase the adhesion at the interface between the reinforced TOCNF layers and the epoxy interlayers. Mechanical properties are studied for the different laminate configurations and related to different modes of fracture within the laminates. Finally, the specific energy to rupture of laminates and neat TOCNF layers is measured and compared to other materials like borosilicate glass and acrylic.

2. TRANSPARENT TEMPO OXIDIZED CELLULOSE NANOFIBRIL (TOCNF) COMPOSITES WITH INCREASED TOUGHNESS AND THICKNESS BY LAMINATION

All lab-work in this chapter was performed by Endrina Forti. All analysis was performed by Endrina Forti with guidance by Dr. Jeffrey Youngblood. All writing was performed by Endrina Forti with guidance and editing by Dr. Robert Moon, Dr. Gregory Schueneman and Dr. Jeffrey Youngblood.

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2.1 Introduction

Cellulose nanomaterials are attractive due to their renewable and sustainable basis. These materials are mainly extracted from woody biomass but can be found in multiple organisms as well. Two well-known categories can be identified: cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs). Specifically, CNFs have large specific surface areas with fibrils composed by both crystalline and amorphous regions. CNFs can be produced either by mechanical grinding or by chemically aided methods. The latter generally involves the usage of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in conjunction with hypochlorite to convert the primary hydroxyl groups in the cellulose structure to carboxylic acids and aldehydes groups via catalytic oxidation. This reaction is carried out in water and the final product consist of negatively charged fibrils that, due to electrostatic repulsion, form a stable aqueous suspension, allowing further fibrillation. The fibrils prepared with this method are typically 3-4 nm in width and can be several microns long depending on the extraction source^{9,12,15,23}.

Films made of TEMPO-oxidized cellulose nanofibrils (TOCNFs) have excellent mechanical properties, with Young's Modulus around 6 to 14GPa, ultimate tensile strength between 130MPa to 300MPa and strain to failure within 2% and 10% ^{1,9,10,12,15,23}. Although TOCNF materials exhibit promising mechanical properties, other characteristics such as their inherent brittleness and the inability to make thick materials have limited their applicability. Neat TOCNF films are generally produced through solution casting of dilute suspensions (<2wt%), followed by the removal of water (or another medium). During casting, the dispersion is subjected

to evaporation or filtration that cause high shrinkage stresses within the films. The high stresses in conjunction with the inherent brittleness of TOCNFs lead to fast fracture of thick cast films, limiting the production of thicker materials. Consequently, neat TOCNF films and high percentage TOCNF composites with typical thickness around 25-100 μ m have been reported, values which are not thick enough for self-supported applications such as transparent protective cases and impact resistant windows ^{16,23}.

Here, lamination is introduced as a possible solution to make mechanically tougher and thicker TOCNF composite materials. A simple but reliable lamination technique involves the lamination of a plastically deformable material to a high strength/brittle one. This combination has been shown to produce high toughness materials as in the case of safety glass, where a high toughness material, such as polyvinyl butyral (PVB), is combined with glass to improve its toughness without compromising its high transparency and stiffness¹⁹. Lamination takes advantage of crack retardation mechanisms to enhance the toughness of materials. Two well-known mechanisms have been described in literature: crack digression, where cracks are diverted through a weak interface, and crack blunting, were sharp crack tips are blunted and decrease stress concentration. Generally, specimens with a higher volume fraction of the ductile phase display evidence of crack blunting. On the other hand, specimens with lower volume fractions and low adhesion at the interface presented crack digression as the main toughness mechanism. Hence, the volume fraction of both phases have a significant effect on the mechanical response of laminates ^{20,24}.

In the present study, lamination was used as a mechanism to increase the toughness, and thickness of TOCNF composites by laminating it with a more compliant interlayer such as epoxy. The effect of the volume fraction and layer thickness of both phases (e.g., TOCNFs, epoxy), the number of total layers, and the overall total thickness of the laminate, on the tensile and flexural properties are investigated. Finally, analyses of crack stopping mechanisms present in the laminates are discussed.

2.2 Materials and Methods

2.2.1 Materials

A TOCNF suspension 1.1wt% in water produced by USDA Forest-Service-Forest Products Laboratory (FPL), Madison, WI, USA. (Lot #2018-FPL-CNF-080), was purchased from the University of Maine ²⁵. The TOCNFs have a carboxylate content of 0.44 mmol/g solids and was measured following a titration procedure ²⁶. Room temperature cure transparent epoxy EpoxAcast 690TM was bought from Smooth-On, Inc, Macungie, PA, USA to use as an adhesive interlayer for the laminates. 30.5 x 30.5cm x 1.60mm thick acrylic sheets were bought from McMaster-Carr, along with fiberglass sheets for tabs and 5-minute Epoxy Gel from Devcon, both needed for the tensile testing specimens.

2.2.2 Fabrication of samples

TOCNF films

TOCNF suspensions in water were diluted with deionized water to 0.73wt% and cast into 100mm polystyrene Petri dishes as reported in previous studies ¹. With the objective of obtaining TOCNF films with different thicknesses, the following volumes of solutions were cast: 30ml, 45ml and 70ml. The cast solutions were placed in a humidity chamber with a fixed relative humidity of 50% at room temperature (~21 °C). Films were completely dry after 7 to 15 days with thicknesses of 20µm, 30µm and 40µm. When dry the TOCNF films were removed from the Petri dish by cutting the edges of the film and slowly detaching them with the help of tape. The TOCNF films had high transparency and low haze.

TOCNF - epoxy laminates

The fabrication method for the laminates was based on a standard hand-layup approach similar to what is used in sheet molding compounds ²⁷. In the first stage of the fabrication process, a room temperature cure epoxy (EpoxAcast[™] 690) was pre-mixed using a planetary centrifugal mixer (DAC 400.1 FVZ, FlackTek Inc., Landrum, SC, USA). The mixed resin was applied on top of a TOCNF film using a spatula. Then, a new TOCNF film was placed on top to get a sandwich structure composed of two TOCNF layers with epoxy resin interlayer. The process was then

repeated until the desired number of layers was reached. The assembly process is presented in Figure 2.1. To control the thickness of the laminates, an acrylic mold with interchangeable spacers of different thicknesses was used. The spacers controlled the overall laminate thickness. Additionally, by controlling the number of TOCNF films and their thickness, an average epoxy weight percentage was estimated. This mold assembly was pressed (Model 3856 Bench Top Laboratory Manual Press, Carver Inc, IN, USA) at 1 kPa for 5hr, after which laminates were removed from the mold. Final laminates were visually inspected, showing high transparency and low haze. Laminates were produced having 6 to 14 TOCNF layers, layer thickness of either 20µm, 30µm, and 40µm and volume fractions of epoxy ranging from 2% to 44%.



Figure 2.1 Schematics of TOCNF/epoxy laminate fabrication and final laminate

2.2.3 Tensile testing

TOCNFs

A laser cutter (Muse Hobby Laser Cutter, Full Spectrum Laser, Las Vegas, NV, USA) was used to obtain 1:5 scale dogbone-shaped specimens of 1mm width and 6.5mm of gauge length according to the ASTM D638 Standard Test Method for Tensile Properties of Plastics. Samples were tested in a dynamic mechanical analyzer (DMA) (Q850 TA instruments New Castle, DE, USA), with a rate-controlled mode fixed at a 0.1mm/min displacement rate. Specimens had an average thickness of $30 \pm 3\mu$ m. Samples were left in a low humidity chamber (15%RH) for three days at room temperature before testing. A minimum of 5 specimens were tested at room temperature (21°C) and 35%RH. Young's modulus was determined from the maximum slope of the stress-strain curve, ultimate tensile strength (UTS) was taken as the highest tensile stress on the stress-strain curve, while the work-of-failure (WOF) was calculated by integrating the area under the stress-strain curve.

Epoxy

EpoxAcast 690[™] epoxy was cast in 33mm x 33mm square polystyrene Petri dishes. Mirroring the TOCNF films, dogbone-shaped specimens were cut using the laser cutter according to ASTM D638. Specimens were then tested in tension in an MTS insight (MTS system Corp, Eden Prairie, MN, USA) with a 1000N load cell, and a 0.1mm/min displacement rate. At least 5 specimens were tested at room temperature (21°C) and 35%RH. Elastic modulus, UTS and WOF were calculated from the stress-strain curve as detailed in the previous section.

TOCNF-epoxy laminates

Rectangular specimens (40mm x 4mm) were cut using the laser cutter (PLS6MW MW laser engraver, Universal Laser Systems, Scottsdale, AZ, USA), for each laminate. Rectangular fiberglass tabs (4mm wide and 10mm long) were glued to the tensile specimens using structural epoxy from DEVCO, according to ASTM D3093 Standard Test Method for Tensile Properties Matrix Composites. Samples were left in a low humidity chamber (15%RH) for three days at room temperature before testing. Five specimens were tested in the MTS Insight with a 1000N load cell and tensile grips, at room temperature (21°C) and 35%RH. A strain rate of 0.5mm/min was selected. Analyses of variance (ANOVA) were conducted to compare results, at a threshold level of 0.05. Young's modulus, UTS and WOF were calculated as detailed previously.

2.2.4 Digital Image Correlation (DIC)

The tensile testing via MTS was recorded using a Nikon D3200 camera, with a SWM VR ED Micro IF 1:1, with a lens diameter of 62mm. Strain was measured by tracking the motion of natural defect points within the laminates (e.g., dirt or tiny bubbles) during the initial and deformed stages. Results were analyzed with ImageJ open source software and the MTrackJ plugin. The

initial and deformed stages were correlated using the stress values obtained from the MTS. A minimum of 5 measurements were done for every data point.

2.2.5 Flexural testing

TOCNF-epoxy laminates

Rectangular specimens 40mm long and 4mm wide were cut using the laser cutter. Laminates were tested with a small 3-point bending fixture in DMA at a 0.1mm/min speed using a ratecontrolled mode at room temperature. A minimum of 5 specimens were tested for each data point. Analyses of variance (ANOVA) were conducted to compare results, at a threshold level of 0.05. Young's modulus, UTS and WOF were measured as detailed previously.

2.2.6 Polarized light microscopy

Side views of polished samples were obtained using a Carl Zeiss (Axio, Observer A1) inverted microscope in transmission mode. Images were taken between cross polarizers using 5X, 10X and 20X magnification objectives.

2.2.7 Adhesion testing

A lap shear experiment was designed and modified from the ASTM D3164-03(2017) Standard Test Method for Strength Properties of Adhesively Bonded Plastic Lap-Shear Sandwich Joints in Shear by Tension Loading. Metal sheets 9.40mm wide, 100mm long and 12mm thick were used. A 9.40mm wide by 100µm long TOCNF layer was cut using the laser cutter and glued to the surface of the metal sheets with structural epoxy. A second set of metal sheets with the same dimensions were covered with EpoxAcast 690TM resin and left to cure. Later, both surfaces were glued together with EpoxAcast 690TM. Once cured, a minimum of 5 specimens were tested in an MTS with a uniaxial tension configuration, using a strain rate of 1.27mm/min. After confirming delamination failure, the interfacial shear strength was calculated using the UTS and the overlapping area of adhesion.

2.2.8 UV-Vis Spectroscopy

Optical absorbance of neat TOCNF films, neat epoxy, and TOCNF-epoxy laminates were measured by UV-vis absorbance spectroscopy (UV–Vis spectrophotometer (Spectramax Plus 384, Molecular devices Corp., Sunnyvale, CA) in the wavelength range from 400 to 750nm with air as the background. Transmission data was normalized by the sample thickness for comparison purposes.

2.2.9 Scanning Electron Microscopy (SEM)

The side-view of post fractured laminate samples were imaged via a Phenom SEM (FEI Company, Hillsboro, OR, USA), so that the fracture zones could be imaged and then analyzed. Prior to SEM imaging, the surface was platinum coated for 30s using an Emitech, K550X Sputter coater (Quorum Technologies Ltd., East Sussex, UK).

2.3 Results and Discussion

2.3.1 Processing

Epoxy was chosen as interlayer for the laminates due to its generally high adhesion, commercial availability and use in composite materials ^{19,28,29}. To maintain the transparency of the TOCNF films within the laminates, a principal advantage of TOCNFs, only clear epoxies were considered for use in this study. Also, a room temperature curable resin was desired to avoid the exposure of TOCNFs to heat, which is a known oxidizer of TOCNF layers ³⁰. For this process, two commercially available resins were taken into consideration, EpoxAcast 690[™] from Smooth-on and Epoxy 561/588-1001 from US composites. Out of the two, EpoxAcast 690[™] was selected due to its good wettability with the TOCNFs, which translated into laminates with fewer visible defects. It is believed that some level of covalent bond was formed between the TOCNF and epoxy films.

A hand layup method of alternating TOCNF films and epoxy interlayers was used to fabricate the laminates as described in Materials and Methods section and shown in Figure 2.1. The thickness of TOCNF films was adjusted by controlling the volume of the cast solutions. Additionally, by drying within a 50% RH chamber, the lower water evaporation rate decreases the buildup of shrinking stresses that could cause cracks within the films. The maximum and minimum TOCNF film thicknesses achieved were limited by several factors including the inherent

brittleness of the material, ease of delamination from the Petri dishes and stress build-up during drying. The thinnest layers that could be produced were 20µm thick, while a maximum thickness of 40µm was selected to avoid fracture of the films.

The epoxy layer thickness was limited by its low viscosity. After the TOCNF films were stacked with epoxy as the interlayer and the laminate was compressed, excess epoxy was squeezed out of the laminate. The percentage of epoxy was lower for laminates with thicker TOCNF layers, going from 44% to 30% for laminates with a fixed number of TOCNF layers with thicknesses of 20µm and 40µm, respectively.

The laminate thickness is dictated by the thickness and number of TOCNF films used in its construction, allowing the opportunity to produce thicker TOCNF materials. For demonstration purposes laminates have been produced up to 1.5mm in thickness, by adhering sixty 20µm thick TOCNF films or forty-five 30µm thick TOCNF films (Figure 2.2). This laminate thickness is nearly 15 times larger than values found in literature for films of either neat TOCNFs or high TOCNF content composites, which are usually around 25-60µm ^{9,16,23}. It should be noted that it is possible to produce thicker laminates by either increasing the number of layers or the volume fraction of epoxy, indicating that the laminate thickness is not a limitation for the lay-up process used in this study.



Figure 2.2 Side view of a 1.5mm thick TOCNF-epoxy laminate, formed by adhering sixty 20um thick TOCNF films

Moreover, lamination of TOCNFs with epoxy was successful at maintaining a high level of transparency of the TOCNF laminate. Figure 2.3 shows characteristic plots of transmittance obtained by UV-vis spectroscopy, performed on neat TOCNF films (Figure 2.4, left), neat epoxy, a 10-layer TOCNF-epoxy laminate (Figure 2.4, right) and silica glass. The normalized results showed a similar transmittance of TOCNFs and epoxy, which are both lower by 5% when compared with silica glass. In general, both TOCNFs and epoxy have high overall transparency. For laminates the transparency is similar to neat TOCNFs and epoxy at long (red) wavelengths, however, there is an increasing loss of transparency for decreasing wavelengths, diverging from TOCNFs/epoxy at orange/yellow and becoming progressively worse through the blue range. A potential reason for this could be interfacial reflections between layers, destructive interferences, or some other process that induces yellowing. Regardless, the loss of transparency in the laminates is not noticeable by the naked eye.



Figure 2.3 Visible transmittance via UV-Vis spectroscopy of TOCNFs, epoxy, TOCNF-epoxy laminates and silica glass normalized by the thickness. Thickness was normalized using the epoxy thickness as reference (0.8mm).



Figure 2.4 Photographs show the transparency of TOCNF films (left) and a 10-layer TOCNFepoxy laminate (right)

2.3.2 Tensile Properties

The mechanical properties of laminates were evaluated via uniaxial tensile testing. Laminates were composed of 10 TOCNF/epoxy layers with volume fractions of epoxy ranging from 2% to 44%, and different TOCNF layer thicknesses of 20µm, 30µm and, 40µm. Mechanical properties (Table 2.1) of neat TOCNFs and epoxy films were measured for comparison purposes. No statistical difference between TOCNF films with different thicknesses of 20µm, 30µm and 40µm were found. Representative stress-strain plots are presented in Figure 2.5. The stress-strain curve for neat TOCNF films and all laminates produced, showed characteristics of brittle behavior. In contrast, the neat epoxy curve exhibit plastic deformation, which is representative of a ductile performance. Young's Modulus values obtained for TOCNF films are slightly higher than those found in literature ^{9,10,15,30,31}. It is believed that the TOCNFs used has an inherent higher modulus or that the extremely slow drying process (over two weeks) leaded to different (e.g. denser) networks. Regardless, multiple calibrated instruments agree on this data.

Table 2.1 Mechanical properties of neat 30 μ m TOCNFs and 0.8mm epoxy films. (+ -) range represent 1 standard deviation

Material	Young's Modulus (GPa)	Ultimate tensile strength (MPa)	Strain to failure (%)	Work of failure (MJ/m ³)
TOCNFs	22 ± 1	135 ± 16	1.0 ± 0.1	0.1 ± 0.4
Epoxy	2.3 ± 0.6	45 ± 1	11 ± 3	2.6 ± 0.7



Figure 2.5 Representative plots of TOCNFs, epoxy, and three 10-layer TOCNF- epoxy laminates, with 20µm TOCNF layer thickness and varying volume fractions of epoxy (44vol%, 27 vol%, 9 vol%)

Young's modulus:

Theoretical values of the Young's Modulus of TOCNF-epoxy laminates, E_L, were calculated using the Voigt model (iso-strain) and the Reuss model (iso-stress). Both of these models assume that every layer is perfectly bonded and Poisson ratios are neglected in the calculations ¹⁸. The differences in the strain rates and used to conduct the tensile testing for both the TOCNF-epoxy laminates and neat TOCNF and epoxy films were also neglected for the modulus prediction. The Voigt model or iso-strain model assumes every layer is subjected to the same amount of deformation and that a perfect load transfer occurs between layers. Equation 1 shows the model's expression where the Young's Modulus, E, is linearly related to the volume fraction, V, of the materials involved. The Voigt model defines the upper theoretical bound of the Young's Modulus as the laminate finds its maximum stiffness when a uniaxial stress is applied parallel to the layers ¹⁸.

$$E_{L} = E_{CNF}V_{CNF} + E_{Epoxy}V_{Epoxy}$$
(1)

In contrast, the Reuss model or the iso-stress model, defines the theoretical lower bound for Young's modulus as the laminate finds its minimum stiffness when a uniaxial stress is applied perpendicular to the layers. It assumes every layer is subjected to the same amount of stress, implying different deformation rates in the components of the laminate if the elastic properties of those are not the same ¹⁸.

$$\frac{1}{E_{L}} = \frac{V_{CNF}}{E_{CNF}} + \frac{V_{Epoxy}}{E_{Epoxy}}$$
(2)

The theoretical values of Young's modulus from both models were compared against experimental results (Figure 2.6), in which displacement was measured either from the load cell of the MTS testing machine, or from DIC. Experimental values measured by load cell displacement were low and close to the iso-stress model, this is unexpected as the testing and laminate layer configuration were such that uniaxial strain was applied parallel to the layers, and thus the results should have been more like the idealized Voigt model configuration. The lower Young's Modulus, could be indicative of an inefficient load transfer among the layers, especially as TOCNF layer thickness increases ³². Alternately, the results may be artificially underreported due to experimental artifacts such as grip slippage or underestimation of the grip compliance in the system, both of which would increase the apparent strain in the measurements ³³. Thus, to eliminate any possible experimental artifact, a new set of strain measurements were taken using DIC. Young's Modulus values obtained using DIC were closer to the iso-strain model, confirming that shear stresses at the interface of the layers were able to transmit the load efficiently to subsequent layers. This is an important factor since an adequate load transmission is critical for improving mechanical performance of laminated materials, governing failure modes and the overall strength of the laminate ^{34–37}. Results obtained also showed that the modulus decreases as the volume fraction of epoxy increases for all laminates tested.



Figure 2.6 Theoretical prediction of the Young's Modulus of TOCNF-epoxy laminates with the Reuss model (iso-stress) and the Voigt model (iso-strain) as function of the volume fraction of epoxy and TOCNF layer thickness (20 μm, 30 μm, 40μm), with results of Young's modulus of laminates obtained from the displacement of the MTS and DIC. Error bars represent 1 standard deviation

Ultimate tensile strength (UTS)

The ultimate tensile strength (UTS) of neat TOCNF films and laminates are shown in Figure 5 with a line indicating the rule-of mixtures predicted strength. Neat TOCNF films (in the 20-40 μ m thickness range) had a UTS of ~ 135MPa and has a wide distribution of values. Laminates with low volume fractions of epoxy (e.g., less than 22 vol %) were similar to those exhibited by neat TOCNF films, which is an indication of good bonding between layers. As the volume fraction of epoxy increased, in general, the UTS decreased. This is to be expected because the UTS of epoxy used in this study is lower than that of TOCNF films (See table 1) and typically mechanical properties are linearly related to a volume-weighted average of the phases present. Also, the effect of TOCNF layer thickness in the laminate was not statistically significant in the UTS properties. However, when compared to the strength predicted by the rule of mixtures of the components, the strengths achieved by laminates were increased, indicating the presence of strengthening mechanism in the laminate.



Figure 2.7 Ultimate tensile strength of 10-layer TOCNF-epoxy laminates, with different volume fractions of epoxy and different TOCNF layer thicknesses (20µm, 30µm and 40µm). Error bars represent 1 standard deviation

The failure of TOCNF laminates is related to the defect size within the TOCNF layers. Since the TOCNFs are stiffer than the epoxy (see Table 2.1), the load applied to the sample during tensile testing will result in higher stress in the TOCNF layers. Additionally, since the tensile load was applied parallel to the layers, the fracture of a single TOCNF layer in the laminate will dictate the failure of the entire structure. As a crack initiates within the first layer, there is a sudden reduction of the effective cross-sectional area over which the applied load acts. This increases the stress fields inside the laminate, decreasing the applied load necessary to propagate a crack and have it extend through epoxy interlayers and subsequent TOCNF layers, causing catastrophic fracture of the entire laminate ^{20,32}. This is evident in Figure 2.5, where the laminates show a stress-strain profile indicative of brittle materials. The nucleation of cracks within brittle materials is related to the presence of defects or voids, where the stress is amplified ³⁸. Since the defects are randomly sized and distributed in the TOCNF films, the mechanical response within individual films was highly varied (wide standard deviation in Figure 2.7 and table 1).

While the materials failed in a brittle fashion, the laminates were stronger than expected. The increased UTS in the laminates is indicative of a strengthening mechanism at play. While it is unclear what such mechanism is, it is possible that the epoxy layers suppress crack initiation. If cracks nucleate at the surface of the TOCNF layers, epoxy coating may prevent them from forming. Alternatively, cracks may initiate but the layering may isolate them and prevent the nucleated cracks from causing catastrophic failure until enough microcracks and defects have formed. Regardless, it is clear that lamination is a way to strengthen TOCNF materials.

Work of failure (WOF):

The work of failure (WOF) of neat TOCNF films and laminates are shown in Figure 6. Neat TOCNF films (in the 20–40µm thickness range) had a WOF of 0.1 MJ/m³ and has a wide distribution of values. Values of WOF of all laminates were higher than those measured for neat TOCNF films, but lower than for epoxy (2.7MJ/m³). Additionally, there is a general trend of increasing WOF as the volume fraction of epoxy in the laminate increases, which may be expected as the epoxy used in this study has a higher strain to failure and WOF than neat TOCNF films. When compared to the expected WOF based on a rule-of-mixtures, lamination significantly increased toughness in these materials, in some cases ending at the same WOF as epoxy, but at high TOCNF content with the concomitant increase in strength that it entails.



Figure 2.8 Work of failure of 10-layer TOCNF-epoxy laminates, with different volume fractions of epoxy and different TOCNF layer thicknesses (20µm, 30µm and 40µm). Error bars represent 1 standard deviation

The increase in the WOF can be related to the laminate structure, in which the layer structure is capable of dissipating energy and therefore, increases the work of failure of the specimens ^{21,22,39}. Additionally, the increase in the epoxy layer thickness (due to the increase in the volume fraction of epoxy) relates to the increase in the plastic zone that can be formed around the cracks. The increase in the plastic area directly translated in higher WOF values ^{40–42}. Like the behavior observed in UTS, WOF is clearly higher than that of the sum of the parts, indicating that a toughening mechanism is at play. As before, the exact mechanism is unclear, crack digression may be possible. Due to the catastrophic failure, obtaining clear photographic evidence of this is difficult, however in laminates this mechanism is common. While crack suppression and isolation as suspected in the UTS can increase WOF, the increase seen here likely has another mechanism at play as WOF is increased significantly more than UTS.

2.3.3 Flexural Properties

The mechanical properties of laminates were evaluated via three-point bending. Specimens were prepared from 10-layer TOCNF/epoxy laminates with volume fractions of epoxy ranging from 2% to 44% and TOCNF layers with different thicknesses ($20\mu m$, $30\mu m$, and $40\mu m$). Results are shown in Figure 2.9.



Figure 2.9 Mechanical properties of 10-layer TOCNF-epoxy laminates with different volume fractions of epoxy and different TOCNF layer thicknesses (20µm, 30µm and 40µm). (a) Bending modulus, (b) bending strength, and (c) work-of-failure. Error bars represent 1 standard deviation

In general, all mechanical properties decreased as the volume fraction of epoxy increased. This trend is expected for bending modulus and bending strength, as it can be assumed that the epoxy has lower flexural strength and stiffness than neat TOCNF films (bending strength 75MPa, flexural modulus: 2GPa). However, it should be taken into consideration that since all laminates have 10 TOCNF layers, the increase in epoxy vol% corresponds to an increase in the thickness of the epoxy layers, which may also influence the flexure properties ⁴³. Finally, there is also a trend of higher mechanical properties for thinner TOCNF layered laminates, however, this may be partially influenced by differences in the overall laminate thickness. It is important to notice that the usage of different TOCNF layer thicknesses to fabricate the laminates is inherently related to a change in overall laminate thickness for a fixed volume fraction of epoxy and same number of layers. In other words, two 10-layer laminates with the same volume fraction of epoxy (for example 10%) and with TOCNF layers that are either 20μm and 40μm thick will result in laminates having an overall thickness of 0.22mm and 0.45mm, respectively.

Effect of Number of Layers and Total Laminate Thickness

To study the effect of the number of layers and total laminate thickness on flexure properties, without the influence of changing epoxy vol%, two new sets of laminates were prepared in which the epoxy vol% was fixed at 7 vol%. A detailed composition of the laminates can be found in Table 2.2. In the first set, laminates were produced having an overall thickness of 0.25 mm; to achieve this, thinner TOCNF films were used for laminates with a higher number of layers (e.g., 40µm layer thickness for 6-layer laminate, 30µm layer thickness for 8-layer laminate, and 20µm layer thickness for 12-layer laminate). The results of the first set of laminates are presented as blue triangles in Figure 2.10, and clearly show a decrease in properties as the number of TOCNF layers increased. This is considered to result from the larger number of TOCNF-epoxy layer interfaces associated with increasing numbers of TOCNF layers within a laminate. Flexure testing is more sensitive to the effects of interfaces on the resulting mechanical properties. Since bending properties decreased with increasing number of interfaces, it can be assumed that the number of interfaces are a source of weakness within the laminate, leading to lower bending modulus, bending strength, and WOF ^{20,32}. It should also be noted that there may also be a layer thickness influence, in which both the TOCNFs and epoxy layers become thinner with increasing number of layers in the laminate. While it is true that thinner layers may be more compliant in flexure testing and may limit defect size as compared to thicker layers, there are also strain conditions that affect thinner layers more than thick ones ⁴⁴. The flexural properties (both bending modulus and bending

strength) of a laminate are a combined reflection of the single constituents' properties in tensile and bending. When subjected to a flexural stress, the deformation is related to the applied moment, and, for a constant curvature, the tensile and compression strains are associated to the distance of the layers to the neutral axis. For that reason, the strain in laminates varies linearly through the thickness, meaning that layers above the neutral line experience a compressive strain state, while layers placed bellow are in tension. If a comparison is made between two laminates of the same thickness but different layer thickness, thinner layers will need a smaller force to crack than thicker layers when the curvature of both laminates reaches the same value. This translates into a decrease in the flexural properties as the layers within the laminate become thinner ⁴⁵. Nevertheless, it is more probable that the defects associated with the TOCNF-epoxy interface are significantly larger and dominate the properties.

Table 2.2 Laminate configuration for investigating the role of laminate thickness on flexural properties

Different overall laminate thickness					
Average volume fraction of	TOCNF layer	Number of	Average total		
epoxy (%)	thickness (µm)	TOCNF layers	thickness (mm)		
		14	0.47 ± 0.02		
7 ± 2	30	10	0.340 ± 0.004		
		6	0.19 ± 0.01		
Same overall laminate thickness					
Average volume fraction of	TOCNF layer	Number of	Average total		
epoxy (%)	thickness (µm)	TOCNF layers	thickness (mm)		
	20	12			
7 ± 2	30	8	0.25 ± 0.01		
	40	6			

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Figure 2.10 Mechanical properties of laminates with the same and different overall thicknesses, and 7% volume fraction of epoxy. (a) Flexural strength, (b) Bending strength, (c) Work of failure. Error bars represent 1 standard deviation

In the second set of new laminates, the TOCNF layer thickness was fixed at 30 μ m, and laminates were produced having 6, 10, and 14 layers, which resulted in overall laminate thickness of 0.19 mm, 0.34 mm and 0.47 mm, respectively. The results of this second set of laminates are presented as orange squares, and clearly shows a decrease in properties as the number of TOCNF layers increase, which also corresponds to increasing laminate thickness. The mechanism for decreasing properties was likely a result of the increased number of TOCNF-epoxy layer interfaces as previously demonstrated and discussed. One other aspect that could influence properties was the overall laminate thickness, in which laminates with more layers were thicker. Flexural damage
has been reported to be extensive in thicker laminates ⁴⁶. For thin laminates, the damage is usually distributed across all the thickness, while in thicker laminates the damage is centered in the outer layers (that experience a greater amount of compression or tension). This damage is attributed to a lower bending stiffness in thin laminates, which results in a greater plasticity and ability to sustain damage. At the same time, thicker laminates are stiffer than thinner ones which leads to higher interlaminar stresses, decreasing mechanical properties ⁴⁶. Nevertheless, the effect of laminate thickness is likely not a dominant effect over the presence of a greater number of interfaces within the laminates.

Fracture Behavior of Laminates

Other variables affecting the flexural strength and WOF are associated with fracture events, more specifically, susceptibility of the brittle layer to cracking, the contribution of interface cracking and the ease of layer delamination ⁴⁷. Therefore, it is relevant to understand the propagation of cracks and their relation to the delamination behavior of laminates. For instance, when a crack is nucleated, one of the main properties that affect the propagation speed is the adhesion between the layers that constitute the structure. The general fracture behavior of homogenous brittle materials shows that, once a crack is created, it will propagate rapidly, straight through the specimen. However, if the crack finds a weak interface, such as the ones created between two materials in a laminate, the crack will be diverted along the interface direction, retarding crack growth. Also, when this diversion occurs, new interfaces are created, impeding the crack propagation which increases the overall toughness in laminated materials. However, promoting the crack deflection along interfaces by weakening the interface strength, may compromise the overall strength of the laminates. In this case, the crack will be able to deflect itself through the interlayer, but the cohesion of the laminate will be weak, affecting the overall strength of the structure ²⁰⁻²².

With the high level of importance of adhesion on the creation of new surfaces within a laminate, an adhesion coefficient has been developed to provide a criterion at which strength is not compromised but failure is retarded in laminates. There is an optimal scenario where the bond is sufficiently strong and capable of dissipating energy but weak enough to cause crack digression. A study have shown that if the interface adhesion is less than 0.20 times the cohesive strength of

the strong face of the interface, then a potentially good crack-stopping mechanism can be achieved ³⁹. For cracks with sharp tips such as the ones found in brittle materials, a ratio of 0.35 of the matrix strength was predicted for the interface to produce crack deflection, as shown in Equation 3 ⁴⁸;

$$\frac{\sigma_{\rm if}}{\sigma_{\rm mf}} < \frac{\sigma_{\rm xx}}{\sigma_{\rm yy}} \tag{3}$$

Where σ_{if} is the interface strength, σ_{mf} the strength of the bulk material and σ_{yy} and σ_{xx} are the normal stress acting on the interface and the stress acting perpendicular to the crack, respectively ^{48,49}.

The energy criterion for the crack deflection model (Equation 3) was applied to the TOCNF-laminates. Adhesion results obtained by performing a simple shear lap test of TOCNF-epoxy interfaces, measured an adhesion value of 4.0 ± 0.3 MPa. Using this value with the strength of TOCNF film of 135 MPa in Equation 3, a value of 0.03 is obtained, far less than the range of 0.2-0.35 that is desired. This suggest for TOCNF-epoxy laminates that crack digression is likely the dominant mechanism of crack retardation. One of the most compelling evidence of crack digression is the finding of signs of delamination as a crack progresses through the structure ²⁸. For this reason, a 10-layer laminate with 10vol% epoxy was analyzed under a microscope as soon as the first crack initiated during a three-point bending test, so that crack deflection and crack delamination could be observed (Figure 2.11). In the same fashion, the fracture morphology of specimens tested to failure in three-point bending with a different volume fraction of epoxy was analyzed and are presented in Figure 2.12. It is notable how the fracture is not smooth for any of the cases, instead, it follows a tortuous path, confirming the presence of crack deflection and delamination as a toughening mechanism in the laminates.



Figure 2.11 Optical micrograph of initial cracks in a 10-layer 20µm thick TOCNF- and 44vol% epoxy laminate during three-point bending. Crack propagation direction is from bottom of the image to the top



Figure 2.12 Optical micrograph of 30µm TOCNF/epoxy laminates after three-point bending: (a) 3%, (b) 12%, (c) 16%, (d) 27% and (e) 37% volume fraction of epoxy

Another indicative sign of crack digression is found on the mechanical response of laminates as they bend. To assess how the epoxy interlayer thickness affects crack digression, two 10-layer laminates with 40µm thick TOCNF layers, with either 1 vol % or 30 vol % epoxy were prepared. Both laminates were subjected to three-point bending. Characteristic stress-strain curves and microscopy of the samples are presented in Figure 2.13(a). Results show a reduction in the bending strength for the laminate with a 1 vol% epoxy, however, the WOF was almost doubled. These findings indicate that less epoxy for an interlayer increased the probability of delamination and favored crack digression (i.e. the decreased interface adhesion, increases toughness). This is in agreement with the published literature, where a low interfacial adhesion promotes delamination, increasing toughness, but decreasing the strength of the structure ^{19,20,50}. The low volume fraction of epoxy in the laminate may influence the extent of adhesion between the TOCNFs and the epoxy, it is considered here that it lowers this adhesion. At 1 vol.%, the insufficient epoxy to cover the whole surface (i.e. epoxy accumulated in depressions on the films that translates into zones with lower adhesion). The first stress drop detected on the stress-strain curved presented in Figure 2.13 (a) corresponds to the fracture of the first brittle layer. The crack is later arrested at the epoxy interface of the subsequent layer and a plateau region is then generated in the curve, which correlates to the plastic deformation of the remaining layers. When the energy required to nucleate a new crack is achieved, another drop shows in the curve. This behavior corresponds to the fracture of a new brittle layer, manifested as delamination in the laminate. The type of delamination observed in laminates with a lower volume fraction of epoxy (Figure 2.13 (b)), does not impart any damage to subsequent layers ahead of the crack. The creation of new surfaces diverges the crack across the interface of the delaminated layer and this is the main process that allows a higher extension of the plateau region in the curve, or in other words, increase the amount of energy the laminate can sustain before failure ²⁴.



Figure 2.13 Mechanical response and optical micrographs of two 10-layer TOCNF-epoxy laminates subjected to three-point bending (a) Stress-strain curves of 1 vol% of epoxy, and a 30 vol% of epoxy laminate, where the numbers for each plot represent their corresponding WOF. (b) Micrograph of a 1% volume fraction of epoxy sample. (c) Micrograph of a 30% volume fraction of epoxy laminate

There is evidence of structural damage in the individual TOCNF layers as illustrated in Figure 2.13 (b) and Figure 2.14. The damage is presented in the form of a parallel stacking of fibrils in the heavily packed cellulose structure. The 2D network of TOCNF fibrils have a heavy intra-laminar interaction, but the inter-laminar interaction is not as strong, which might produce the nucleation of new surfaces within the individual TOCNF layers and increase the work of failure in the TOCNF-epoxy laminates ¹.



Figure 2.14 SEM image of polished side surface of a 1% volume fraction of epoxy laminate. Evidence of internal structural damage inside TOCNF layers after being subjected to three-point bending

Compared with the 1 vol% epoxy laminate, the 30vol% epoxy sample has a different fracture behavior and mechanical response. The stress-strain plot indicates that once a crack was nucleated, it proceeded across the laminate fracturing several layers, reducing its bending strength. This is represented in the figure by a big step down to stress values close to zero. Later, there is another plateau region that correlates to the breakage of the remaining layers of the laminate. As a consequence of higher surface contact between the TOCNFs and the epoxy, laminates presented a better strength but a lower probability of diverting a crack, decreasing the WOF of the structure.

All things considered, there is a marked increase in the bending properties as a result of lamination. The introduction of a thin epoxy interlayer not only facilitates crack digression as a mechanism to increase toughness, but also creates an important mismatch of elastic properties in the structure, which results in a good crack stopping mechanism by itself. According to literature, the addition of thin layers of a soft material with a modulus 5 times lower than the elastic moduli of the strong layer within the laminate, has a marked impact on the driving force of the crack. In comparison with a homogenous material, the crack driving force grows with the crack length until the crack reaches the middle section of a soft layer. At this point, the driving force drops and starts increasing again. If the drop in the driving force is less than the crack growth resistance, then the crack will be arrested, and the material will gain toughness 51,52. For TOCNF-epoxy laminates, this modulus mismatch is well above 5 (e.g., 22/2.3 = 9.6).

2.4 Summary

Lamination of TOCNFs with clear epoxy by a wet layup method was used to create laminates of up to 1.5mm in thickness. The TOCNF laminates were highly transparent, with low haziness and had good mechanical properties.

Tensile testing of laminates showed that Young's modulus values fit well with the Voigt model. Modulus, UTS and WOF trends decrease as the volume fraction of epoxy increased. The scatter of the values was assumed to be associated with the presence of defects that acted like crack nucleators. Overall, an increase in the WOF and UTS was achieved and the values obtained were higher than those calculated by the rule of mixtures for almost all volume fractions of epoxy tested indicating that lamination strengthened and toughened the composites.

It was notable that flexural strength, bending modulus and flexural WOF of TOCNF-epoxy laminates decreased with increasing number of TOCNF layers within the laminate. It was considered that the TOCNF-epoxy interfaces dominated flexural mechanical properties. At the same time, it was found that laminates with 1 vol% epoxy resulted in a higher flexural WOF, but lower bending strength. Crack digression along the weak TOCNF-epoxy interfaces is thought to be the primary mechanism responsible for the increase in the apparent toughness of TOCNF-epoxy laminates in bending. Overall, lamination was shown to be able to both create thicker materials and lower the inherent brittleness of TOCNF composites.

3. MECHANICAL ENHANCEMENT OF CELLULOSE NANOFIBRIL (CNF) FILMS THROUGH THE ADDITION OF WATER-SOLUBLE POLYMERS

All lab work in this chapter was done by Endrina Forti with the following exceptions: tensile characterization, analysis and preparation of mCNF films performed by Sami el Awad. Tensile characterization of TOCNF films was performed by Endrina Forti with the assistance of Xin Ng. Finally, TEM images and analysis was performed by Whirang Cho and Dr. Douglas Fox. All writing was performed by Endrina Forti with guidance and editing from Dr. Gregory Schueneman, Dr. Robert Moon, Dr. Douglas Fox and Dr. Jeffrey Youngblood.

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3.1 Introduction

Cellulose nanofibers (CNF) are polysaccharide nanomaterials that can be harvested from numerous sources including wood, plants, and other biomass ^{1,7,30}. These materials are inherently sustainable, bio-renewable and non-toxic. Additionally, their uniform widths, high crystallinity, and large aspect ratios make them attractive reinforcing materials. Two approaches are generally used to isolate CNFs. The first one requires fibrillation of cellulosic slurries in a disc refiner or high-pressure homogenizer. The extracted CNF, sometimes called cellulose microfibrils (CMF), has a white appearance and is constituted by larger and more aggregated fibrils. Here we will refer to this as mCNF for mechanical CNF to distinguish this from the broader classification of CNF. Generally, mCNF films exhibit a semi-ductile behavior with strain ratios that can reach the 10% mark and UTS values around 200MPa^{1,8,9}. A chemically oxidative process can also be employed to isolate CNFs products which involve the use of oxidants such as 2,2,6,6 tetramethylpiperidine-1-oxyl radical (TEMPO) to produce a more stable suspension of fibrils (i.e., increased dispersion) and facilitate fibrillation. TEMPO-oxidized cellulose nanofibrils or TOCNFs are constituted by 2-3nm wide fibrils with reduced adhesion between them, generating transparent films with outstanding mechanical properties. TOCNF films have been reported with an elastic modulus of up to 20GPa and ultimate tensile strength (UTS) of up to 300MPa while sustaining a more brittle behavior than mCNF^{1,9–13,15,30}.

An important application of both types of CNFs has been found in their use as reinforcing agents in biodegradable polymers. The strategy often generates films or fibers with improved mechanical performance (> 30%) and environmentally friendliness ^{53–60}. Although the reported literature has been successful at processing more biofriendly nanocomposites, there is a lack of literature concerning the development of nanocomposites with higher CNF content (>20 wt.%). For instance, Kurihara et al. (2015) used poly(acrylamide) (PAM) to produce transparent films with higher mechanical properties when the polymer was added in the 10-25wt% range into TOCNF. Another example can be found in the work performed by Hakalahti et al. (2015) whereby adding polyvinyl alcohol (PVA) to TOCNF solutions, they produced films that were stable in wet conditions. However, a robust study of other polymers has yet to be investigated for reinforcement in high CNF content nanocomposites ^{31,61}.

To address this knowledge gap, we utilized solution casting as a simple yet reliable method to process nanocomposite films of CNF containing small concentrations (5 to 20 wt.%) of a variety of water-soluble polymers to investigate whether they can act as mechanical property enhancing additives. The addition of PVA and poly(2-ethyl-2-oxazoline) (PEOX) generated remarkable improvements in the UTS and Young's modulus of TOCNF films while maintaining their transparency. Therefore, special attention was dedicated to assessing the effects of varying the molecular weight, hydrolysis degree and concentration of these polymers in the TOCNF mechanical properties. To elucidate the nature of the polymer interactions, zeta potential, and capillary rheology analysis were performed. Finally, to prove the efficacy of the method with different CNF types, the same concentrations of PVA and PEOX were added to mCNF solutions, where a significant increase in the mechanical properties and similar trends were observed. The outstanding mechanical increases achieved open a wide window for potential application of these films in future light-weighted and high-performance renewable materials.

3.2 Materials and Methods

3.2.1 Materials

Two different TOCNF suspensions produced by USDA Forest-Service-Forest Products Laboratory (FPL), Madison, WI, USA and purchased from the University of Maine were used. TOCNF (lot #2019-FPL-CNF-139) was prepared using sodium chlorite at pH 7 with a carboxylic content of 0.44mmol/g¹¹. TOCNF (lot #2018-FPL-CNF-129) was prepared using the sodium hypochlorite method at pH 10 and had a carboxylic content of 1.5mmol/g¹². Both materials will be denominated c-TOCNF and h-TOCNF respectively to avoid confusion during the discussion. Additionally, a mCNF slurry with a solid concentration of 3 wt.% was also purchased from the same vendor (lot CNF, Batch #103). Additionally, several water-soluble polymers were obtained from different vendors and can be seen in Table 1.

Polymer	Abbreviation	Manufacturer	Lot number (#)	Molecular weight (g/mol)	Hydrolyzation (%)
Poly(vinyl alcohol)	PVA 85-124 99%H	Sigma- Aldrich	MKBS2768V	85,000- 124,000	99
Poly(vinyl alcohol)	PVA 146- 186 99%H	Sigma- Aldrich	MKCC7856	146,000- 186,000	99
Poly(vinyl alcohol)	PVA 146- 186 87- 89%H	Sigma- Aldrich	MKBX9187V	146,000- 186,000	87-89
Poly(2-ethyl-2- oxazoline)	PEOX 50	Sigma- Aldrich	04629JJ	50,000	-
Poly(2-ethyl-2- oxazoline)	PEOX 200	Sigma- Aldrich	MKCC1604	200,000	-
Poly(2-ethyl-2- oxazoline)	PEOX 500	Sigma- Aldrich	MKBX0709V	500,000	-
Poly(acrylamid e-co-acrylic acid)	PAMA	Sigma- Aldrich	02312LE	5,000,000	-
Poly(2- hydroxymethyl methacrylate)	РНЕМА	Sigma- Aldrich	12801TC	300,000	-
Methyl 2- hydroxyethyl cellulose	MHEC	Sigma- Aldrich	MKBX7592V	130	-
Poly(ethylene oxide)	PEO	Sigma- Aldrich	05010KH	1,000,000	-
Polyvinylpyrro lidone	PVP	Fluka Analytical	BCBF3274V	360,000	-

Table 3.1 Water-soluble polymers purchased from different suppliers along with molecularweight and hydrolyzation (%)

3.2.2 Fabrication of nanocomposite films

TOCNF suspensions in water were diluted with deionized water to 0.53wt%. Water-soluble polymers were added in concentrations ranging from 5-20 wt.% (dry weight relative to TOCNF). The mix was stirred at different temperatures to promote the dissolution of the polymers in water. The solutions were later cast into 90 mm polystyrene Petri dishes as reported in previous studies ¹. To obtain films with approximately the same thicknesses, 50 ml of the solution was cast. The cast solutions were placed in a humidity chamber with a fixed relative humidity of 50% at room temperature (~21 °C). Films were completely dry after 7 days with an average thickness of 30 μ m ± 2. After drying, the films were removed from the Petri dish by cutting the edges of the film with a razor blade and slowly detaching them with the help of tape.

In the case of mCNF films, water-soluble polymers were first diluted in deionized water with mild heating (90 °C) and mechanical stirring. Once dissolved, the polymeric solutions were added to a 3 wt.% mCNF suspension in water and mixed using a planetary centrifugal mixer (DAC 400.1 FVZ, FlackTek Inc., Landrum, SC, USA) at 2500rpm for a total time of 2 minutes. The mixture was then cast into 90 mm Petri dishes and dried in a fixed relative humidity of 50% at room temperature (~21 °C). The films were completely dry after 7 days and were detached with the help of tape and scissors. Table 3.2 shows a detailed composition of the samples prepared for mCNF, c-TOCNF, and h-TOCNF.

Polymer		Weight			
rorymer		percentage (%)		6)	
Matrix	Water-soluble polymer	5	10	15	20
	PVA 85-124 99%H	\checkmark	\checkmark	\checkmark	\checkmark
	PVA 146-186 99%H	\checkmark	\checkmark	\checkmark	\checkmark
	PVA 146-186 87- 89%H	✓	\checkmark	✓	✓
	PEOX 50	\checkmark	\checkmark	\checkmark	-
^c TOCNE	PEOX 200	\checkmark	\checkmark	\checkmark	-
C-TOCINI	PEOX 500	\checkmark	\checkmark	\checkmark	-
	PAMA	-	\checkmark	-	-
	PHEMA	-	\checkmark	-	-
	MHEC	-	\checkmark	-	-
	PEO	-	\checkmark	-	-
	PVP	-	\checkmark	-	-
h-TOCNF	PVA 146-186 99%H	\checkmark	\checkmark	\checkmark	-
	PEOX 200	\checkmark	\checkmark	\checkmark	-
mCNF	PVA 146-186 99%H	-	\checkmark	\checkmark	-
	PEOX 200	-	\checkmark	\checkmark	-

Table 3.2 Composition of films produced

3.2.3 Tensile testing

A laser cutter (Muse Hobby Laser Cutter, Full Spectrum Laser, Las Vegas, NV, USA) was used to obtain 1:5 scale dogbone-shaped specimens of ~0.8mm width and ~6.5mm of gauge length according to the ASTM D638 Standard Test Method for Tensile Properties of Plastics. Samples were tested in a dynamic mechanical analyzer (DMA) (Q850 TA instruments New Castle, DE, USA), using the rate-controlled stress ramp mode fixed at a 1 N/min displacement rate. TOCNF specimens had an average thickness of $40 \pm 3 \mu$ m while mCNF specimens had an average thickness of $74 \pm 5 \mu$ m. Samples were conditioned in a low humidity chamber (25% RH) for three days at room temperature before testing. A minimum of 5 specimens were tested at room temperature (24 °C) and 35% RH. Young's modulus was determined from the maximum slope of the stress-strain curve, ultimate tensile strength (UTS) was taken as the highest tensile stress on the stress-strain curve, while the work-of-failure (WOF) was calculated by integrating the area under the stress-strain curve. Analyses of variance (ANOVA) were conducted to compare results, at a threshold level of 0.05.

3.2.4 Transmission Electron Microscopy (TEM)

A 0.0005 – 0.001 wt% TOCNF solution was dropped onto a Formvar/Carbon or silicon monoxide coated 200 mesh Cu grid. After 4 min, the excess liquid was wicked using an ashless Whatman filter paper. The grids were then stained with 2 % uranyl acetate ethanolic solution for 4 min and dried before imaging. Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100 Plus with an accelerating voltage at 200 kV. Images were taken at x50,000 magnification with a resolution of 0.255 nm/pixel. The image size was calibrated using a calibration diffraction grating replica. Fiber widths were measured using a custom ImageJ macro⁶².

3.2.5 Zeta potential

Solutions (Table 3.2) were diluted to 0.1wt% solids using deionized water. At least 5 measurements of each sample were obtained using a Zetasizer Nano Series (Malvern Instruments, MA, USA) in z-potential mode at room temperature (24°C). Analyses of variance (ANOVA) were conducted to compare results, at a threshold level of 0.05.

3.2.6 UV-Vis Spectroscopy

Optical absorbance was measured by UV-Vis spectroscopy (UV–Vis spectrophotometer Spectramax Plus 384, Molecular devices Corp., Sunnyvale, CA) in the wavelength range from 400 to 750nm with air as the background. Transmission data was normalized by the sample thickness for comparison purposes.

3.2.7 Rheometry

The shear rheological behavior of solutions was analyzed using a Bohlin Gemini HR nano Rheometer (Malvern Instruments, MA, USA) with a 40 mm serrated parallel plate configuration with a 1 mm gap to avoid wall depletion effects. An ABS vapor-trap device with a wet sponge was used to minimize moisture loss of the samples during testing ⁶³. A pre shear of 1000 s⁻¹ was applied to all the samples for 30 seconds. The experiment was set to run a shear stress ramp of 40 logarithmic increment steps from a min shear rate of 0.1 s⁻¹ to 500 s⁻¹. All tests were run at room temperature (25 °C).

3.3 Results and Discussion

3.3.1 Processing

Water-soluble polymers were chosen due to their ease of dispersion in water CNF solutions, leading to maximized interactions between fibrils and polymeric chains. Solution casting was chosen as it is a simple and reliable method to process CNF films with high dispersion. In the case of TOCNFs, the solutions were diluted and easily mixed using a stirrer plate and low temperatures. In all cases, the temperature was kept below 90 °C for less than two hours to achieve the total dissolution of the polymers in the TOCNF solution. All films were left to dry inside a humidity chamber with a controlled relative humidity of 50% and detached after 7 days for further inspection. Self-standing composite films produced were flat, highly transparent with no appreciated haziness and smooth surfaces (Figure 3.1). Furthermore, films were glossy and flexible as shown in Figure 3.1 (c). Characteristic plots of transmittance obtained by UV-Vis is shown in Figure 3.2. Overall, both the TOCNF and composite films showed a small decrease in transparency when compared with silica glass. The normalized transmittance shows a 10% lower transmittance of neat TOCNF films in the blue range when compared with silica glass. The difference is reduced at long (red) wavelengths reaching a difference of less than 2% at the 700nm wavelength. TOCNF + PVA composites' behavior showed a similar trend to neat TOCNF, with a slight decrease in transparency through all the regions. In contrast, PEOX composites showed a better transmittance than neat TOCNF in the blue regions, maintaining transparency throughout the spectrum. While TOCNF has been known to have a slight yellow/brown color explaining the small loss in transparency that is magnified in the blue region, it is not clear why composites differ as both PVA and PEOX have extremely high transparency in this region. However, differences may be related to small variations in dispersion of the TOCNF upon adding the polymers. Regardless, the loss of transparency is not noticeable to the naked eye.



Figure 3.1 Photograph show the transparency of composite films. (a) TOCNF + 15wt% PVA composites. (b) TOCNF + 15wt% PEOX composite. (c) TOCNF + 15wt% PVA showing the glossiness and flexibility of films.



Figure 3.2 Visible transmittance via UV-Vis spectroscopy of neat TOCNF, TOCNF composites and silica glass. Thickness was normalized using the silica glass thickness as reference (0.9mm)

3.3.2 Mechanical Properties

Water-soluble polymers

A wide range of polymers were added to c-TOCNF at an initial concentration of 10 wt%. Films produced were tested in tension until failure in a DMA. The mechanical response can be observed in Table 3.3.

Samples	Ultimate tensile strength (MPa)	Young's Modulus (GPa)	Work of failure (MJ/m ³)	Strain to failure (mm/mm)
Neat c-TOCNF	163 ± 16	13 ± 2	1.6 ± 0.3	2.0 ± 0.4
c-TOCNF + 10 wt% PAMA	184 ± 25	16 ± 1	2.3 ± 0.6	2.1 ± 0.3
c-TOCNF + 10 wt% PHEMA	183 ± 19	16 ± 1	2.3 ± 0.5	2.2 ± 0.3
c-TOCNF + 10 wt% PVP	189 ± 12	15 ± 1	2.6 ± 0.5	2.3 ± 0.3
c-TOCNF + 10 wt% MHEC	191 ± 15	11 ± 1	3.4 ± 0.5	3.1 ± 0.2
c-TOCNF + 10 wt% PEO	189 ± 17	11 ± 2	2.4 ± 0.6	2.5 ± 0.4
c-TOCNF + 10 wt% PVA 85-124 99% RH	302 ± 10	25 ± 1	3.8 ± 0.7	2.1 ± 0.3
c-TOCNF + 10wt% PEOX 500	267 ± 18	28 ± 1	2.1 ± 0.4	2.1 ± 0.1

Table 3.3 Tensile response of TOCNF films with 10wt% addition of water-soluble polymers

Most of the water-soluble composite films achieved increased mechanical properties when compared with neat c-TOCNF films. The increment in some of the properties constitutes in itself an indirect indication of the binding capabilities of water-soluble polymers with TOCNF fibrils. In fact, such an increase has previously been reported in literature. In the work performed by Kurihara et al. (2015) poly(acrylamide) (PAM) was mixed into TOCNF solutions, achieving a mechanical increase in the films when added in the compositions ranging from 10 to 25wt%. The effect was attributed to the filling or covering of the boundary of the TOCNF domains by PAM³¹. An explanation for this reinforcement was schematized by Kurihara et al (2015) based in previous findings reported by Saito et al. (2011). According to the authors, TOCNF in solution forms randomly distributed elements with self-aligned and nematic-ordered structures inside small domains or clusters. Once dry, TOCNF films exhibit an oriented strand board (OSB) structure as can be seen in Figure 3.3 (a). When polymers such as PAM are added in small concentrations, they aggregate in the boundary regions of the domains (Figure 3.3(b)). This aggregation serves as a bridge between domains, increasing the mechanical properties of the material. If the concentration of polymer keeps increasing and surpasses a critical value, TOCNF fibrils do not form self-aligned elements, and instead, get distributed in a polymeric matrix, decreasing the mechanical properties of the films ^{14,31}.



Figure 3.3 Schematic of TOCNF domains. (a) Neat TOCNF. (b) TOCNF composites. Taken and modified from ³¹

In this study, PAMA, a polymer with a similar structure was studied. Nevertheless, the mechanical increases achieved by the inclusion of the polymer were not substantial when compared with values reported by Kurihara et al (2015). Similarly, other polymers exhibited similar mechanical increases, such is the case of PHEMA and PVP, two water-soluble polymers

that are usually used in the biomedical industry. Other water-soluble polymers tested, and highlighted in blue in Table 3.3, showed an increased UTS and WOF while the elastic modulus remained within the range of neat c-TOCNF. Such was the case of PEO and MHEC. The hydrogen bonding formation of both polymers is well described in the literature ^{64,65}. Nevertheless, the small increases in UTS and WOF seem to indicate that those interactions may not be responsible for the increased toughness of the films.

Out of all water-soluble polymers tested, PVA 85-124 99%H and PEOX 500 presented exceptional mechanical increases in the films. Tensile testing results indicated an increase of 85% and 63% respectively for UTS. Young's modulus was enhanced by 92% in the case of PVA and 115% with the addition of PEOX. Finally, the WOF of the films showed more than 100% increase, while retaining the same strain to failure when compared to neat c-TOCNF films. Therefore, special attention was given to the interaction between CNF and these polymers.

c-TOCNF + PVA and PEOX

PVA is one of the highest volume semicrystalline, nontoxic, water-soluble polymers produced in the world ⁵³. PVA is used in a wide range of applications like adhesives, packaging materials, films and medical products ⁵⁴. Many applications of PVA takes advantage of the hydroxyl groups in its chemical structure (Figure 3.4(a)), that are responsible for the binding interactions of PVA with a high number of polymers. Usually, the degree of solubility and some physical properties of PVA can be controlled by varying the molecular weight and degree of hydrolysis of the PVA ⁶⁶. Likewise, PEOX is a low cytotoxicity polymer with good light stability and re-solubility. The PEOX structure contains a substituted amide group (Figure 3.4 (b)), that polymerizes by cationic ring-opening polymerization ⁶⁷. PEOX is suspected to form hydrogenbonded complexes with polymers containing proton donating groups ⁶⁸.



Figure 3.4 Chemical structure for (a) PVA and (b) PEOX

To further understand the mechanical increase achieved by the addition of PVA and PEOX to the c-TOCNF matrix, two different PVAs were selected with different molecular weights and hydrolysis degrees. In like manner, two molecular weighs for PEOX were selected. Further information about the specific molecular weight and hydrolysis of the PVAs and PEOX can be found in Table 3.1 on the materials and methods section. Overall, the tensile stress-strain behavior of these six different polymers were studied in a wide range of compositions ranging from 0 to 20 wt% in TOCNF. Figure 3.5 shows characteristic curves for the neat c-TOCNF, PVA and PEOX. Overall, PVA showed a higher elongation (>50%), in which case the polymer can yield and plastically deform until failure. Contrarily, PEOX behaved in a brittle manner, failing before reaching the yield point. To simplify this discussion, and due to the different mechanical behavior of both polymers, TOCNF – PVA and TOCNF - PEOX nanocomposites response will be discussed separately in the following sections.



Figure 3.5 Representative plots of neat c-TOCNF, PEOX 200, and PVA 146-186 99%H (solid lines). Additionally, plots of c-TOCNF + 15wt% of PVA 146-86 99%H and c-TOCNF + 15wt% of PEOX 200

c-TOCNFs + PVA nanocomposites

The response of the nanocomposite films containing PVA at different concentrations can be seen in Figure 3.6 and in Table 3.4. All trends showed a significant statistical difference according to the variance analysis performed. All the properties measured showed a marked plateau at 15 wt% that continue through 20 wt%. At concentrations higher than 20 wt%, a further decrease of the mechanical properties of the films can be expected, and therefore, higher concentrations of polymer were not considered in this study.



Figure 3.6 Tensile mechanical properties of c-TOCNF and PVA nanocomposites. (a) Young's modulus, (b) Ultimate Tensile Strength and (c) Work to failure

	Weight percentage relative to TOCNF (wt%)					
Polymer	0	5	10	15	20	
Chlorite TOCNF	13 ± 2	-	-	-	-	
PVA 146-186 87-89%H	-	15 ± 2	15 ± 1	22 ± 2	24 ± 2	
PVA 146-186 99%H	-	24 ± 1	21 ± 3	26 ± 1	25.8 ± 0.9	
PVA 85-124 99%H	-	23 ± 2	25 ± 1	26 ± 2	26 ± 2	
PEOX 500	-	22 ± 3	25 ± 3	25 ± 2	-	
PEOX 200	-	27 ± 2	28 ± 1	28 ± 3	-	
PEOX 50	-	21 + 4	25 ± 1	25 ± 2	-	
UTS (MPa)						
Chlorite TOCNF	163 ± 16	-	-	-	-	
PVA 146-186 87-89%H	-	183 ± 9	189 ± 12	241 ± 10	$231\ \pm 5$	
PVA 146-186 99%H	-	258 ± 10	229 ± 23	313 ± 13	310 ± 10	
PVA 85-124 99%H	-	273 ± 13	302 ± 10	296 ± 21	293 ± 18	
PEOX 500	-	260 ± 32	$267\ \pm 18$	$274\ \pm 18$	-	
PEOX 200	-	260 ± 15	261 ± 16	267 ± 22	-	
PEOX 50	-	210 ± 11	201 ± 8	221 ± 19	-	
WOF (MJ/m ³)						
Chlorite TOCNF	1.6 ± 0.3	-	-	-	-	
PVA 146-186 87-89%H	-	2.2 ± 0.4	2.6 ± 0.5	3.1 ± 0.5	1.6 ± 0.3	
PVA 146-186 99%H	-	2.7 ± 0.1	2.1 ± 0.7	3.7 ± 0.3	3.5 ± 0.3	
PVA 85-124 99%H	-	3.2 ± 0.4	3.8 ± 0.7	3.3 ± 0.3	3.6 ± 0.8	
PEOX 500	-	2.5 ± 0.6	2.8 ± 0.3	2.5 ± 0.6	-	
PEOX 200	-	2.3 ± 0.3	2.1 ± 0.4	2.0 ± 0.6	-	
PEOX 50	-	1.6 ± 0.3	1.1 ± 0.2	2.0 ± 0.6	-	

Table 3.4 Tension properties of c-TOCNF and PVA and PEOX nanocomposites Young's Modulus (GPa)

Young's modulus response can be seen in Figure 3.6 (a). The hydrolysis degree of PVA has a marked effect on the mechanical properties reported. For instance, nanocomposite films with higher molecular weight (M_w): 146,000–186,000 but lower hydrolysis 87-88 %H, had lower elastic modulus in comparison with the same M_w, but higher hydrolysis 99%H, specially at higher fractions of PVA. This is expected since the tensile modulus of PVA tends to increase as the degree of hydrolysis increases. A good explanation for this behavior derives from the higher number of hydroxyl groups present in the chain, creating a higher amount of strong hydrogen bonds ⁶⁶. It can be assumed then, that increasing the number of hydroxyl groups in the molecule could translate

into a higher number of interactions between c-TOCNFs and PVA, leading to a stiffer material. In the case of the elastic modulus, a higher molecular weight did not make a substantial difference.

Figure 3.6 (b) shows results of UTS, where some variability on the results can be seen and it is attributed to the brittle behavior of TOCNF films, where defects are randomly sized and distributed in the matrix. The presence of defects in the films produces an amplification of the stress, leading to failure ¹³. In the same manner discussed before, there is a marked increase in the mechanical properties related to the hydrolysis of the polymers, which could relate to the presence of a higher number of hydrogen bonds. An interesting behavior can be observed where a higher molecular weight gives a higher UTS. It can be assumed then that the larger number H-bonding groups found in a longer chain could increase the total interaction between polymer and fibrils, reinforcing the material ⁶⁹.

There is also an apparent increase in the WOF (toughness) of nanocomposite films by the addition of PVA (Figure 3.6 (c)). This is expected behavior due to the UTS increase in the films. For materials that fail in a brittle fashion, strength and toughness tend to correlate as a higher peak stress simply increases area under the curve at a constant strain to failure. The toughness increase was indistinguishable between the different PVA contents. Overall, the addition of pseudoplastic polymers increased the ability of the films to stretch without failing prematurely, reinforcing the films and increasing their stiffness in the elastic region. Increases achieved at 15 wt% loading were higher for the PVA 146-186 99% H with increments of 93% of the UTS, 99% of Young's modulus, and 137% of the WOF. Strong hydrogen bond formation in the nanocomposite films is suspected to have a large influence on the mechanical increase obtained and will be discussed in further sections of this chapter.

c-TOCNFs + PEOX nanocomposites

In the same fashion, the tensile response of nanocomposite films with PEOX is shown in Figure 3.7 and in Table 3.4. In contrast with PVA nanocomposites, the mechanical response seems to start a plateau after the addition of 5wt%. After the plateau region, the mechanical response could be expected to decrease. Therefore, compositions higher than 15wt% were not tested.



Figure 3.7 Tension properties of c-TOCNF and PEOX nanocomposites. (a) Young's modulus, (b) Ultimate Tensile Strength and (c) Work of failure

Similar to the addition of the PVA, the addition of PEOX generated a notable increase in the mechanical properties of c-TOCNF. Interestingly, while the brittle response of PEOX is drastically different from the ductile response of PVA (Figure 3.5), both polymers seem to reinforce c-TOCNF nanocomposites in a similar manner. As shown in Figure 3.7 (a) the elastic response of nanocomposites increased rapidly after 5wt% loading, reaching a peak at 5wt% and surpassing the values obtained by the addition of PVA (30GPa in comparison to 26GPa). Addition of PEOX 200 delivered higher modulus than the PEOX 500 and PEOX 50, while the last two showed a no significant difference as dictated by the ANOVA test performed. The reason for this behavior is currently unknown.

In comparison with the UTS response obtained by the addition of 15 wt% PVA 146-186 99% H (314 \pm 13 MPa), the addition of PEOXs generated a slightly lower strength as shown in

Figure 3.7 (b). In this case, the differences in strength of PEOX 500 and PEOX 200 were not significantly different from each other, while the addition of PEOX 50 generated at much smaller UTS for all weight percentages tested. While there are many possible reasons for the underperformance of PEOX 50, it is important to note that tensile properties of neat PEOX 50 could not be performed due to the brittle behavior of the samples as they failed prematurely before testing. Hence a simple rule-of-mixtures approach would indicate that PEOX 50 would have a lower strength.

Finally, WOF results can be observed in Figure 3.7(c). While no statistical difference could be observed between points of the same PEOX, there were differences between the different PEOX molecular weights. It seems that even when the mechanical response of neat PEOX is brittle, the addition of the polymer generates a small increase in the WOF response as expected from the increased UTS.

CNFs response to the addition of PVA and PEOX

To determine if the large mechanical property enhancement was conserved across CNF type, PVA 146-186 99%H and PEOX 200 was studied with different types of CNF. Two different TOCNF (h-TOCNF and c-TOCNF) and a purely mechanical CNF (mCNF) were used and nanocomposite films with different concentrations of the polymers were fabricated and tested in a DMA under tension.

The c-TOCNF, which was utilized previously in this work until now, was first developed by Saito et al. (2007). In their studies, they introduced catalytic oxidation of CNF with TEMPO and sodium chlorite at neutral conditions (pH 7) with the resulting fibrils having an average width of 5 nm and at least 2 μ m in length. Overall, an oxidation of 1.5mmol/g was achieved, which correlates to the oxidation of 15% of the primary hydroxyl group in the cellulose and with no aldehyde groups present ¹¹. Different from c-TOCNF, h-TOCNF was developed and the first study in a work done by Saito et al. (2009), where instead of using sodium chlorite, the method involved the usage of sodium hypochlorite under basic conditions (pH 10), which usually generates a higher amount of carboxylate groups in the TOCNF, achieving values of 0.78mmol/g ¹². In this study, morphological information of the TOCNF fibrils was obtained via TEM (Figure 3.8). An average value of (10.1 ± 5.6) nm was measured for c-TOCNF fibrils, while h-TOCNF had an average thickness of (13.3 ± 4.6) nm. Overall, no statistical difference was found between the widths of the different fibrils. Hence, the main difference between the TOCNFs studied here relies in the number of carboxylate groups present in the cellulose structure with h-TOCNF having a high value (1.5 mmol/g) and c-TOCNF having a lower value (0.44 mmol/g). A third CNF that was purely mechanically derived, containing little to no carboxylate was also included in the study. mCNF is directly derived from the high-speed fibrillation of cellulosic slurries. It is composed of larger and more aggregated fibrils, as a consequence of strong hydrogen bonds between fibrils (Figure 3.9).



Figure 3.8 TEM pictures showing TOCNF fibril morphology. c-TOCNF, scale bar 100 nm (left), h-TOCNF, scale bar 200nm (right)



Figure 3.9 Optical picture of mCNF fibril morphology, scale bar 1 mm.

For each type of CNF, different weigh percentages ranging from 0 to 15wt% of polymer were added to determine the optimal concentration needed to maximize mechanical properties. In the case of c-TOCNF, the optimal concentration was found approximately 15wt%, while for h-TOCNF was 10wt%. Plots of tensile properties for h-TOCNF can be found in Figure 3.10. For mCNF, both pictures of the mCNF nanocomposites and their mechanical properties in tension can be found in Figure 3.11 and Figure 3.12 respectively. According to the data gathered, 10wt% was selected as the optimal concentration at which mechanical properties were higher for the mCNF nanocomposites. Figure 3.13 shows a comparison between the best-performing films (i.e. optimal concentration for each CNF) along with the percentage increase achieved when compared to the neat CNF films. Figure 3.14 shows characteristic plots for the neat polymers along with the increased mechanical properties for the films.



Figure 3.10 Tension properties of h-TOCNF and PVA/PEOX nanocomposites. (a) Young's modulus, (b) Ultimate tensile strength and (c) Work to failure



Figure 3.11 Tension properties of mCNF and PVA/PEOX nanocomposites. (a) Young's modulus, (b) Ultimate tensile strength and (c) Work to failure



Figure 3.12 Photograph of a mCNF film with 15wt% PVA 146-186 99%H (left), mCNF and 15wt% PEOX 200 (right)



Figure 3.13 Mechanical response of different CNFs (c-TOCNF, h-TOCNF, mCNF) with different weight percentages of PVA and PEOX. (a) Young's Modulus, (b) Ultimate tensile strength (MPa) and (c) Work of failure.



Figure 3.14 Representative stress-strain plots of neat and optimized PVA and PEO 200 composite c-TOCNF, h-TOCNF and mCNF films

As can be seen in Figure 3.13, mechanical reinforcement was achieved for all the CNFs. Although there were some distinctive differences between them. The most significant were that the greatest percentage increase was obtained by the addition of 15wt% of water-soluble polymers (Either PVA 146-186 99%H or PEOX 200) to c-TOCNF and the mCNF had lowest mechanical properties.

It is important to highlight that the introduction of carboxylate groups in the nanofibrils surface has a big impact on the stability and mechanical properties of the films produced. In the work done by Saito et al. (2009), by decreasing the number of carboxylate groups, a higher UTS was achieved (312 MPa instead of 222 MPa) while maintaining the same Young's modulus ¹². According to the same author, the presence of carboxylate groups plays a role in the individualization of fibrils while producing stable dispersions (high electrostatic repulsions) ¹¹. In this work, the neat mechanical properties of c-TOCNF and h-TOCNF can be found in Table 3.5.

Overall, the mechanical performance of c-TOCNF (carboxylate content 0.44 mmol/g) was higher for UTS but lower for Young's modulus when compared with neat h-TOCNF films (carboxylate content 1.5mmol/g). When polymer reinforcement was added, a larger mechanical reinforcement was achieved for c-TOCNF composites than for h-TOCNF. While the exact mechanism of reinforcement remains unknown, the authors consider that some interactions can be established between TOCNFs and PVA/ PEOX and that such relationships can be related to the carboxylate content of the TOCNF materials used. In general, by decreasing the number of carboxylate groups on the surface (i.e. c-TOCNF – 0.44mmol/g) more hydroxyl groups in the fibril are available and ready to interact with molecules in the PVA/ PEOX forming hydrogen bonding interactions (Figure 3.15) that can potentially increase the mechanical response of films. In contrast, a higher carboxylic content (i.e. h-TOCNF 1.5mmol/g) would reduce the potential binding sites, resulting in a smaller percentual increase in the tensile properties.



Figure 3.15 Schematic of the proposed hydrogen bonding formation between different TOCNF and PVA.

Polymer	UTS (MPa)	Young's Modulus (GPa)	WOF (MJ/m ³)
c-TOCNF	163 ± 16	13 ± 2	1.6 ± 0.3
h-TOCNF	151 ± 11	20 ± 1	0.9 ± 0.2
mCNF	145 ± 14	12 ± 2	1.7 ± 0.9
PVA 85-124 99%H	76 ± 10	4.3 ± 0.6	32 ± 10
PVA 146-186 99%H	81 ± 10	6.0 ± 0.5	32 ± 10
PVA 146-186 87-89%H	66 ± 27	6.1 ± 0.3	5.9 ± 1.9
PEOX 50	-	-	-
PEOX 200	44 ± 4	3.7 ± 0.4	3.5 ± 0.6
PEOX 500	42.6 ± 0.7	3.5 ± 0.2	3.6 ± 0.1

Table 3.5 Mechanical properties of neat CNFs and water-soluble polymers (PVA and PEOX)

Following the same logic, mCNFs that have a more branched and an inherently agglomerated morphology did not see the same level of increase when compared to TOCNFs. The agglomerated and branched networks allow for lower fibril-to-polymer interactions and lower overall properties as well as the non-transparency of the nanocomposite when compared to TOCNFs. That said, there was still an increase in Young's modulus by 63% and 68% with the addition of PVA 146-186 99%H and PEOX 200 respectively (Figure 3.13a) when compared to the neat mCNF. Additionally, the UTS increased by 35% and 22% with the addition of PVA 146-186 99%H and PEOX 200 respectively (Figure 3.13a) when compared to the neat mCNF films, it seems that there was no change in the WOF when PVA 146-186 99%H was added, yet there appears to be a decrease when PEOX 200 was added. The plausible decrease in WOF could originate from the fact that PEOX made the relatively flexible mCNF structure brittle.

Interestingly, a higher percentage (15wt%) of the polymer was needed to reach the highest properties for c-TOCNF when compared with other CNFs (10wt%). Likely, the additional number of hydroxyl groups on the c-TOCNF surface required an extra amount of polymer to fully bond (i.e. more hydrogen bonds equal better mechanical properties).

3.3.3 Zeta potential

Because direct chemical analysis such as FT-IR proved too difficult due to the overlapping of some of the most important peaks, zeta potential (and rheology measurement) was performed to determine any interactions of PVA and PEOX with the CNFs via colloidal stability. Processes such as adsorption can alter the charge state and stability of nanoparticles in solution, thereby indicating whether polymers are attached ⁷⁰. The zeta potential of neat c-TOCNF and PVA/PEOX nanocomposites can be seen in Figure 3.16. All trends showed a statistically different behavior according to the analysis of variance performed. Neat c-TOCNF was chosen as a reference point due to the high mechanical property increase achieved. In the plots, neat c-TOCNF shows a negative value of zeta potential, a clear indicator of the negative electrostatic repulsion achieved by the presence of carboxylic groups on the CNF's surface ^{11,12,71}. The addition of different PVAs at different concentrations generated less negative zeta potential values of the solutions even at low PVA content (5%) and tailing upwards (less negative) at high content. The response obtained for c-TOCNF plus PEOX nanocomposites is also shown in Figure 3.16 (right). The trends, although different, likewise show a significantly less negative charge at modest polymer addition (5%). However, at higher concentrations of PEOX, a peak in the trend forms, and the zeta potential becomes more negative with further addition of polymer.

The observed reduction in negative charge correlates with a significant shielding effect of the PVA and PEOX on the electronegative surface of fibrils. It is the assumption of the authors, that this indicates adsorption of polymer onto the CNF, even at low contents (5%), which suggests that this interaction may be important for mechanical reinforcement. While there is a reduction of electrostatic repulsion by the addition of PVA and PEOX that could translate into a higher aggregation of fibrils, the amount is small so is unlikely to be deleterious to mechanical properties. However, adsorption of polymer may allow drying to higher degrees before drying induced aggregation takes place due to steric effects stabilizing the fibrils, thus increasing density and/or decreasing defect size. Alternatively, the polymers may be bridging CNF fibrils leading to reinforcement, or some combination of these factors. Regardless, it is likely that the interaction indicated by zeta potential is in some way leading to the increased mechanical properties.



Figure 3.16 Zeta potential (mV) measurements of neat c-TOCNF and c-TOCNF composite solutions were fixed at 0.1wt%. PVA (left) PEOX (right)

3.3.4 Rheology

Rheology was also performed to elucidate clues to the fibril-polymer chain interactions. Figure 3.17 compares TOCNF suspensions held at a constant TOCNF concentration of 0.53wt% (to match initial concentration of casting solutions) with and without an extra 15wt% polymer added. c-TOCNF was again chosen due to the higher mechanical increase achieved by the incorporation of water-soluble polymers. Logically, when polymer is added to TOCNF solution, if each material is acting independently, then the composite fluid would have a higher viscosity than pure TOCNF. However, if a strong screening interaction occurs, fibrillar interaction in the fluid decreases, and the viscosity may be lower. Hence this is a method to determine if any interactions between polymer and TOCNF are having an effect on polymer chain motion, as opposed to simply happening. Pure polymer solutions for comparison are given to help identify transitions, although concentrations were 5 wt% and 15 wt% for PVA 146-186 99% H and PEOX 200, respectively to keep the viscosity in scale.



Figure 3.17 Rheology data for neat TOCNF, neat PVA 146-186 99%H, and neat PEOX 200 shown as triangular dots and composite fluids in circular dots. All TOCNF specimens are at constant 0.53 wt% TOCNF with any polymer added at 15 wt% to this.

The resultant curve for neat TOCNF (Figure 3.17 purple triangles) shows characteristics of shear-thinning behavior, as observed in other TOCNF suspensions ^{72–75}. In the work performed by Lundahl et al (2018) polarized imaging confirmed that the shear behavior at rates $<100 \text{ s}^{-1}$ are caused by wall depletion, whereas at higher shear rates (i.e. $>100\text{ s}^{-1}$) alignment of the fibrils takes place, lowering the viscosity of the solutions ⁷⁶. Figure 3.17 (blue triangles) depicts the rheological behavior of a neat PVA solution with a 5wt% solids concentration. As mentioned before, PVA is known to form intra an inter chain hydrogen bonding, an effect that increases with the increment in the degree of hydrolysis. Strong PVA-PVA interactions in water, are a plausible explanation for the high viscosity and shear thinning behavior of the solution as describe elsewhere ⁷⁷. PEOX characteristic behavior is shown in Figure 3.17 (red triangles). While the structure is known to participate in the formation of hydrogen bonds with other polymers ^{67,68}, literature concerning rheological properties is scarce. The plot shown highlights a marked decrease in the viscosity of the solution when shear is applied at small rates, potentially related to the destruction of PEOX-water structures. Interestedly, at higher shear rates >1 s⁻¹, all structures are destroyed, and the solution becomes Newtonian.

In the case of TOCNF where PVA/PEOX was added, the same characteristic shear thinning behavior as neat TOCNF was seen. This behavior is expected since TOCNF fibrils have high surface areas and are present in higher concentrations, which allow for strong fibril interactions (hydrogen bonds, entanglements), governing the rheological properties of the solutions. This is confirmed by the behavior of the neat TOCNF and the composite solutions at high shear rates, where all the curves tended to the same viscosity values, which confirms the governing behavior of TOCNF over the presence of small amounts of water-soluble polymers ⁷⁶. Most importantly, the viscosity decreases when small concentrations of PVA were added to the TOCNF solutions at low shear rates as shown in Figure 3.17 (blue dots). This is a clear indication of the TOCNF-PVA interactions in water. It is widely accepted in the literature that the interaction between TOCNF fibrils in suspension facilitates the creation of network structures by the creation of hydrogen bonds between fibrils ⁷⁸. The decreased viscosity achieved by the introduction of PVA also seems to indicate a reduced fibril-fibril interaction due to enhanced dispersion, giving an indirect indication of possible hydrogen bonding formation between fibrils and PVA that translates into a reduced viscosity explained by the reduction of fibril structures, allowing a better flow under shear and a decreased viscosity for shear rates <100s⁻¹. Practically, this lowered viscosity would allow a higher concentration before the gel-point during drying and reduced residual stress in the films, along with likely, smaller aggregates upon drying.".

The case of TOCNF + PEOX is shown in Figure 3.17 (red dots), where there is an increased viscosity measured for all ranges of shear until 100s⁻¹ where all trends unify and show similar values of viscosity. While this may indicate less or no interaction between TOCNF and polymer at this concentration, the likelihood of a higher number of interactions happening at higher concentrations (i.e. when films are drying) is still possible. Regardless, as both PVA and PEOX show uniquely high mechanical property increases and similar zeta potential changes, it is likely that some sort of interaction occurs, even if not rheologically determinable.

3.4 Summary

A wide range of water-soluble polymers were evaluated to enhance the mechanical properties of CNF. The two best performing candidates, PVA and PEOX, were selected for further testing due to the mechanical property increase achieved by the addition of 10wt% to a TOCNF

matrix. Different concentrations (up to 20wt%) of such polymers in combination with different molecular weighs and hydrolysis degrees were tested. Higher molecular weight generally led to increased properties, although hydrolysis level was the dominant factor in PVA, with higher hydrolysis leading to increased properties. Due to the observed improvement in the mechanical performance of TOCNFs, other CNFs were tested with the two best performing polymers, PVA 146-186 99% H and PEOX 200. An increase of 113% in the modulus, 93% in the UTS, and 134% in the WOF were achieved by c-TOCNFs; 48% in modulus, 93% in UTS, and 98% in WOF for h-TOCNF; and 68% in modulus, 35% in UTS, and a decrease in WOF due to embrittlement in mCNF were observed. Overall, PVA seemed to perform better than PEOX.

The increased mechanical response was attributed to the creation of hydrogen bonds between the CNF fibrils and the hydrophilic polymers added. Zeta potential and rheometry were used as an indirect verification of the creation of such bonds. Zeta potential showed an increase in charge (less negative) for both PVA and PEOX and rheometry showed a decrease in viscosity of TOCNF solution when a small amount of PVA is added indicating that polymer adsorption and screening is likely happening. Overall, the work showed that adding a small amount of polymer can successfully increase mechanical properties across different types of CNF, thereby providing a method to tune properties of this interesting class of materials.
4. OPTIMIZED MECHANICAL AND IMPACT PERFORMANCE OF HIGH STRENGTH TEMPO OXIDIZED CELLULOSE NANOFIBRIL (TOCNF)-EPOXY LAMINATES

All lab work in this chapter was done by Endrina Forti with the following exception: DSC characterization and analysis performed by Daniela Betancourt. All writing was performed by Endrina Forti with guidance and editing from Dr. Gregory Schueneman, Dr. Robert Moon, and Dr. Jeffrey Youngblood.

4.1 Introduction

TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-oxidized cellulose nanofibrils (TOCNF) are polysaccharide nanomaterials that are extracted mainly from wood, plants and other biomass sources ^{1,7,30}. These materials have attracted attention due to their sustainable and bio-renewable nature and are usually produced by chemically aided methods, where the catalyst TEMPO is used in conjunction with a primary oxidizer (usually hypochlorite or chlorite) to covert the primary hydroxyl groups on the surface of the fibrils to carboxylic acids. The reaction, which is usually carry out in water, helps loosen the bonds between cellulose such that mechanical action can produce a suspension of negatively charged fibrils that are several microns long and around 2-3 nm wide. Neat TOCNF suspensions and high percentage TOCNF mixtures can be cast to produce totally transparent films with exceptional mechanical properties, with Young's modulus up to 20 GPa and ultimate tensile strength (UTS) of around 300 MPa ^{1,7,9,10,12,13,30,79}. Even when films show high strength and stiffness, their brittleness and the high residual stresses generated within the films during drying, makes the production of thick materials difficult and reduce the potential for industrial applications ¹³.

In a previous publication, a potential solution to TOCNF scalability problems was introduced. Layup structures of TOCNF were prepared with improved mechanical properties both in bending and tension, creating thicker TOCNF materials while decreasing the inherent brittleness of TOCNF. The effect of the volume fraction of epoxy and layer thickness on such structures was determined. In summary, the highest mechanical properties were found when the volume fraction of the strong layer (TOCNF) was maximized around the 90% volume fraction, minimizing the presence of the epoxy interlayer to a 10% volume fraction. More importantly, crack digression

was found to be an active mechanism of fracture retardation, increasing the toughness of some of the laminates. Even so, it was found that a weak interface adhesion led to substantial delamination, translating in a decrease of mechanical properties when the number of layers was increased ¹³. The research helped clear a path to the creation of stronger and tougher TOCNF laminates. It was demonstrated that by increasing the ratio between the adhesion at the interface and the cohesive strength of TOCNF layers, the crack digression mechanisms that retarded fracture while increasing the integrity of the laminates (less delamination) could be optimized. However, the effects of stronger TOCNF layers and the impact of interlayers with different mechanical properties was not addressed. Furthermore, the impact fracture behavior of laminates was still unknown.

In this study, lamination is used to investigate the role of stronger TOCNF layers, softer and stiffer interlayers, and a higher adhesion at the interface on the final properties of the layup structures. With that purpose, 4 different epoxy formulations are studied as well as a strong TOCNF + PVA composite film. The different epoxy systems are characterized and the relationship between the glass transition temperature (T_g) and storage modulus of the interlayer are studied in relationship to the mechanical properties of the final laminates. Additionally, a silane coupling agent is studied and the relationship between a stronger interface and bending, tensile, and fracture properties, are investigated. Furthermore, different fracture behaviors are associated to crack digression and interlaminar delamination within the TOCNF layers as shown by secondary electron microscopy analysis and the ratio of adhesion at the interface and the cohesive strength of the TOCNF layers. Finally, impact testing was performed on these laminates and on TOCNF films for the first time in literature. The results suggested that TOCNF laminates and films showed an energy to rupture and specific strength similar to borosilicate glass and acrylics. Moreover, laminates were highly transparent and showed low haziness to the naked eye.

4.2 Materials and Methods

4.2.1 Materials.

A TOCNF suspension of 1.1 wt.% with a carboxylic content of (1.5mmol/g) was produced by USDA Forest-Service Products Laboratory (FPL), Madison, WI, USA and purchased from the University of Maine (lot #2018-FPL-CNF-129) ¹². Poly(vinyl alcohol) (PVA) with a molecular weight of 146,000 – 186,000 g/mol and hydrolyzation percentage of 99% was bought from Sigma-Aldrich Corp, St. Louis, MO, USA.

Room temperature epoxy EpoxAcast 690TM was bought from Smooth-On, Inc, Macungie, PA, USA. Two different hardeners were used: 5-Amino- 1,3,3-trimethylcyclohexanemethyl-amine (Lot #BCCB7259), mixture of cis and trans and O,O'-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol, better known as Jeffamine® ED-2003, Mw: 1900 (Lot #BCCB1323) and were purchased from Sigma Aldrich. A silane coupling agent, (3-Aminopropyl) triethoxysilane (APTES) 99% (Lot #MKCL4964) was also purchased from Sigma-Aldrich.

Different films were bought from McMaster including acrylonitrile butadiene styrene (ABS), low density polyethylene (LDPE), cellulose acetate, acrylic, polystyrene, aluminum, and borosilicate glass of different thicknesses.

4.2.2 Fabrication of Samples

TOCNF nanocomposites and films were fabricated by diluting TOCNF suspensions with deionized water to 0.53 wt%. PVA was added in a concentration of 10 wt.% (dry weight relative to TOCNF). The mix was stirred at 85°C for 2 h to promote the dissolution of the polymers in water. 40 g of the solutions were later cast into 90 mm polystyrene Petri dishes as reported in previous studies¹. The cast solutions were placed in a humidity chamber with a fixed relative humidity of 50 % at room temperature (~21 °C). Films were completely dry after 7 days with an average thickness of $26 \pm 2 \mu m$. After drying, the films were removed from the Petri dish by cutting along the edges with a razor blade and detaching them with tape.

Laminates were fabricated following a layup method described elsewhere by the author ¹³. Lay-up structures were produced having 10 TOCNF layers and different epoxy interlayers with a fixed average volume fraction of epoxy of 17 ± 3 . The description of each epoxy formulation can be found in table 1.

Epoxy formulation	Epoxy resin	Hardener A	Hardener B	Resin: Hardener A: Hardener B
A	EpoxAcast 690 TM Part A	EpoxAcast 690 ^{тм} Part B	-	100: 30: 0
В	EpoxAcast 690 ^{тм} Part A	5- Amino 1,3,3- trimethylcyclohex anemethy- amine	-	100: 30: 0
С	EpoxAcast 690 ^{тм} Part A	EpoxAcast 690 ^{тм} Part B	O,O'-Bis(2- aminopropyl) polypropylene glycol- block-polyethylene glycol-block- polypropylene glycol Mw:1900	100: 25: 5
D	EpoxAcast 690 ^{тм} Part A	EpoxAcast 690 ^{тм} Part B	O,O'-Bis(2- aminopropyl) polypropylene glycol- block-polyethylene glycol-block- polypropylene glycol Mw: 1900	100: 20: 10

Table 4.1 Epoxy formulations. Ratios respective to epoxy resin.

An adhesion promoter (APTES), used in literature to increase the compatibility between cellulose nanofibrils (CNF) and epoxy systems, was used on some of the laminates fabricated ⁸⁰. In this case, TOCNF + PVA composite films were subjected to high humidity (90 %RH) for 20 mins. After delamination, each layer was submerged in APTES for 2 mins, rinsed with ethanol and introduced to a 110 °C oven for 5 mins. Lamination with epoxy would follow as described previously elsewhere ¹³.

4.2.3 Epoxy Characterization

Tensile characterization of epoxy was done by casting dogbone-shaped specimens in a silicone mold. Specimens were tested in tension using an MTS insight (MTS system Corp, Eden Prairie, MN, USA) with a 1000 N load cell and a 0.5 mm/min displacement rate. Specimens were left under low humidity chamber (25 %RH) for three days at room temperature. At least 5

specimens were tested at room temperature (24 °C) and 35 % RH. Young's modulus was determined from the maximum slope of the stress-strain curve, UTS was taken as the highest point of stress before fracture and the work of failure (WOF) was calculated by integrating the area under stress-strain curve.

Dynamic Mechanical Analysis (DMA) of epoxy specimen were done by casting the different epoxy formulations into rectangular silicone molds of 37 mm x 7 mm and an average thickness of 1.5 ± 0.2 mm. Specimens were tested on a Q850 TA instruments DMA (New Castle, DE, USA), using a single cantilever clamp. Specimens were subjected to an oscillation temperature ramp from 0 °C to 80 °C at a 5 °C/min rate, with an amplitude of 15 µm and a frequency of 1.0 Hz. Elastic modulus (E') was taken at room temperature (24 °C). T_g was reported from the E' onset, tan delta peak and the storage modulus (E'') peak. Unpaired two-sample student t-tests were conducted to compare results with a threshold level set to 0.05.

Thermal characterization was performed using a differential scanning calorimetry (DSC) analyzer (Q2000 TA instruments, New Castle, DE, USA). A heating rate of 5 °C/min rate was applied to the samples over a -25 °C to 100 °C temperature range in a nitrogen environment. Midpoint T_g 's were calculated after the heating ramp.

4.2.4 Laminates Characterization

Tensile testing of neat TOCNF and TOCNF + PVA composites were conducted by cutting 1:5 scale dogbone-shaped specimens using a laser cutter (Muse Hobby Laser Cutter, Full Spectrum Laser, Las Vegas, NV, USA) to obtain 1:5 scale dogbone-shaped specimens of ~0.8mm width and ~6.5mm of gauge length according to the ASTM D638 Standard Test Method for Tensile Properties of Plastics. Samples were tested in a DMA using the rate-controlled stress ramp mode fixed at a 1 N/min displacement rate. TOCNF films and composites had an average thickness of $26 \pm 2 \mu m$. Samples were conditioned in a low humidity chamber (25% RH) for three days at room temperature before testing. A minimum of 5 specimens were tested at room temperature (24 °C) and 35% RH. Unpaired two-sample student t-tests were conducted to compare results with a threshold level set to 0.05.

Laminates were tested in tension by cutting 40 mm x 4 mm rectangular shapes using a laser cutter. Fiberglass tabs were glued to the specimens using a fast cured epoxy according to the ASTM D3093 Standard Test Method for Tensile Properties Matrix Composites as described elsewhere ¹³. Five specimens were tested on an MTS with a 1000 N load cell and a 0.5 mm/min rate. Unpaired two-sample student t-tests were conducted to compare results with a threshold level set to 0.05.

3-point bending of the laminates was performed on a DMA by cutting 40 mm x 3 mm rectangular shapes on a laser cutter. A small flexural clamp was used at a 0.1 mm/min speed using a rate-controlled mode at room temperature (24 °C) and 35% RH. 5 specimens were tested for each data point and t-tests were performed at 0.05 threshold to compare results.

Impact toughness measurements were performed on multiple polymeric films and TOCNF laminates following the ASTM D472 Standard Test Method for Total Energy Impact of Plastic Films by Dart Drop. A dart with a mass of 957g was used. A minimum of 3 samples were tested per data point.

A lap shear experiment was designed to test the adhesion at the interface between neat TOCNF films, TOCNF + PVA composites, the adhesion promoter (APTES) and the EpoxAcast 690TM (Epoxy A). The shear lap was modified from the ASTM D3164-03(2017) Standard Test Method for Strength Properties of Adhesively Bonded Plastic Lap-Shear Sandwich Joints in Shear by Tension Loading. Rectangular metal sheets (7 mm x 40 mm) x 10 mm thick were used. The films were glued into the surface of the metal using a fast-cured structural epoxy. A secondary sheet was covered with the polymer and left to cure at least 2 days. Finally, both surfaces were glued together with the same epoxy. At least 5 specimens were tested in an MTS in tension at a 1.27 mm/min rate. Failure at the interface was inspected visually and the interfacial shear strength was calculated in based of the calculated UTS and the area of bonding. Unpaired two-sample student t-tests were conducted to compare results with a threshold level set to 0.5.

Visual inspection of the laminates was performed before and after fracture. Polarized light microscopy was obtained of the side view of the laminates, by using a Carl Zeiss (Axio, Observer A1) inverted microscope in transmission mode. Polarizers were used and 10x and 20x objectives.

Additionally, scanning electron microscopy (SEM) were taken of the side views of fracture specimens. A Phenom SEM (FEI Company, Hillsboro, OR, USA) was used for this purpose. Samples were coated with platinum for about 45 s inside an Emitech, K550X Sputter coater (Quorum Technologies Ltd., East Sussex, UK).

Finally, optical absorbance (UV-Vis spectroscopy Spectramax Plus 384, Molecular devices Corp., Sunnyvale, CA) of neat TOCNF, TOCNF + PVA composites and laminated samples were measured and compared against borosilicate glass. A wavelength of 400 mm to 750 mm range was used with air as a background. Data was normalized by the sample thickness for comparison purposes.

4.3 **Results and discussion**

4.3.1 Processing remarks

A hand lay-up method was used to fabricate the different sets of laminates following a procedure described in detail in a previous publication¹³. A total of four epoxy formulations (described in the materials and methods section) with different mechanical properties were used as interlayers for the laminates. All samples maintained the transparency and low haziness of the original TOCNF layers as shown in Figure 4.1, although a few bubbles and dirt specks are visible.



Figure 4.1. Picture of a 10-layer TOCNF + PVA + APTES and epoxy A laminate, showing high transparency and low haziness.

In order to account for the transparency of the laminates, UV-Vis measurements were performed in air and compared against borosilicate glass (Figure 4.2). Results showed differences in the behavior of the three laminates. TOCNF + PVA laminates with epoxy A as interlayer seemed to have a diminished transparency (~6 %) when compared with other laminates. The results also indicated that adding a silane coupling agent (APTES) seem to reduce this effect, making the TOCNF + PVA + APTES laminates comparable with the original laminate (Neat TOCNF laminate), therefore increasing its transparency. The decreased transparency of TOCNF + PVA laminates can find an explanation in the reflection between layers or destructive interferences. The increased adhesion, or better wettability of the epoxy when APTES was applied could have reduced the reflection, making for better interfaces and increasing the transparency. In general, the APTES and the neat TOCNF + PVA laminate showed a decrease of around 6% when compared to borosilicate glass while the TOCNF + PVA laminate showed around 17% difference. Even when the loss in transparency, laminates show great transparency and low haziness to the naked eye.



Figure 4.2 Visible transmittance via UV-Vis spectroscopy of TOCNF laminates, and borosilicate glass. Thickness was normalized using the borosilicate glass as reference (0.9mm)

4.3.2 Flexural properties

The mechanical properties of the laminates were evaluated via bending on a DMA. All the laminates tested were comprised of 10 layers of neat TOCNF or TOCNF + PVA composite films and different epoxy interlayers. The volume fraction of epoxy was fixed at 17 ± 3 % out of the total laminate to isolate the effect of the interlayer in the mechanical properties of the laminate. Results showing the different laminates tested are presented in Figure 4.3. Information about the different epoxy formulations can be found on Table 4.1.



Figure 4.3. Flexural properties of 10-layer TOCNF and TOCNF + PVA laminates. (a) Flexural strength (MPa). (b) bending modulus (GPa) and (c) Work of failure (MJ/m³). The first square (from smallest to biggest) highlights the influence of stronger TOCNF layers, the second, the influence of different epoxies, the biggest, highlights the effect of an increased adhesion.
Numbers represent the increase when compared to the reference sample (Neat TOCNF – Epoxy A / red column), = means no statistical difference between the samples.

The percentage change of each laminate in relationship to the neat TOCNF - epoxy A laminate (red bar) is expressed in the charts. Each laminate system will be analyzed by isolating the effect of different components during the discussion, progressing from the smaller demarked square on the plot (Figure 4.3) to the biggest one.

4.3.3 Influence of TOCNF layers

The first square (smallest) correlates to the increase achieved by replacing neat TOCNF films with a TOCNF + PVA composite film. In a previous study performed by Forti et al. (2021),

the introduction of PVA at a low level of 10wt% (relative to the dry weight of TOCNF) as a reinforcing agent in hypochlorite TOCNF films was described. The mechanical increases achieved in tension were reported to be around the 48% in Young's modulus, 93% in UTS and 165% in WOF when compared with the neat TOCNF⁷⁹. The results shown in Figure 4.3 show increases of flexural strength of 29%, bending modulus of 50% and WOF of 25% when the same layers were introduced in the laminate. The increased tensile properties of TOCNF + PVA layers did not translate into the same proportion of increase in bended laminates, which is expected. While TOCNF + PVA films are the main component in the laminated samples, they do not constitute 100% of it. Only 80% volume fraction will follow the behavior of the TOCNF composite while the remaining is expected to follow the performance of the epoxy interlayer. This notion is well understood and described by the rule of mixtures of laminated materials in tension. Additionally, there is not a straight relationship between tension and bending properties of inhomogeneous materials. This conception lies in the fact that most materials do not exhibit the same moduli in tension as in compression. When a laminated material is bent, some of the layers will strain and others will constrain, making the comparison between tension and bending properties difficult ⁸¹. Hence, since the bending behavior of TOCNF + PVA films is difficult to account for (not enough thickness) and the relationship between the rule of mixtures of tensile and bending of materials is not direct, it is difficult to predict the magnitude of increases that should have been achieved by replacing the neat TOCNF layers with the stronger TOCNF + PVA composite films. Nevertheless, when accounting for the generation of extra interlaminar stresses generated by the mismatch between the mechanical properties of TOCNF and epoxy, it is safe to say that an increase of ~25% across diverse mechanical properties when a 17 vol% of epoxy is introduced is a good indication of the role of the stronger composite in the bending behavior of the laminates. To get an additional understanding of the differences between the two laminates, SEM pictures were taken after bending and are presented in Figure 4.4.



Figure 4.4. SEM images of the fracture behavior of 10-layer TOCNF film laminates. (a) Neat TOCNF – Epoxy A laminate, red arrows showing interfacial delamination events, (b) TOCNF + PVA – Epoxy A laminate, arrows showing intralayer damage within the layers.

The fracture behavior of the two set of laminates (neat TOCNF and TOCNF + PVA) show some relevant differences, especially when looking closer into the behavior of TOCNF+PVA layers. To better highlight such differences a scheme is presented in Figure 4.4. In general, laminates with neat TOCNF layers showed wide-spread interfacial delamination, which is understood as the debonding of the TOCNF film from the interface (epoxy). In contrast, TOCNF + PVA films induced a secondary type of crack retardation mechanism known in literature as interlayer delamination (called here "intralayer damage" to avoid confusion). In general, a single TOCNF film, when dried, is constituted of a stack of many individual layers (1 μ m or less in thickness), and it is between these layers that the intralayer damage occurs. In failure, the nucleation of cracks within the single TOCNF films is the result of the combined effect of:

- 1. The random in-plane orientation of the fibrils
- 2. The stronger intralaminar fibrils interactions compared to the weaker interlaminar bonding.

Consequently, intralayer damage takes advantage of the weaker interlaminar interactions, nucleating new surfaces in between the stack of layers within a single TOCNF film. The nucleation of such surfaces is an important energy dissipation mechanism of fracture retardation that increases the toughness of laminates, and will be discussed extensively during this study ¹.

4.3.4 Influence of epoxy formulation

Usually, lay-up structures are constituted by strong or stiff materials that are laminated with a very ductile interlayer to maximize properties. The ductile interlayers are usually in a lower volume percentage when compared to the strong material. Even so, a ductile interlayer plays a significant role in increased work of fracture due to the introduction of different mechanisms for fracture retardation ^{20,24}.

In this study, different epoxy systems were analyzed to further investigate the impact of ductile vs stiff epoxy layers in the mechanical properties of the laminates. For the different epoxy systems formulated, Figure 4.5 shows the T_g as measured by DMA and DSC analysis, while Figure 4.6 shows the storage modulus as measured by DMA.



Figure 4.5. Glass transition temperature of different epoxy formulations as taken from DMA and DSC.



Figure 4.6. Storage modulus of different epoxy formulations as taken from the DMA.

In general, the glass transition temperature in polymers is related to medium to long range motion of the polymer chain, therefore, it is defined as a function of chain stiffness/length and it is inversely proportional to the free volume in the polymeric network 82,83 . In this study, the T_g of the different epoxy systems was measured thought DMA and DSC. Dynamic measurements were performed with a single cantilever clamp at a fixed frequency and amplitude. The Tg was taken from the onset of the storage modulus, the peak of the loss modulus and the tan delta as the materials were deformed in a sinusoidal deformation. Each of these measurements is related to a specific set of events within the polymeric chains. The onset of E' occurs at the lower temperature when compared with the loss modulus peak and the tan delta. This temperature is usually understood as the onset of the decrease in mechanical properties in polymers, which is why it is relevant from a mechanical properties standpoint. The loss modulus peak is extensively related to molecular processes and it denotes the molecular movements happening at the medium and long range in the polymeric chain. Finally, tan delta occurs at the highest temperature as it is defined as the middle point between the rubbery and glassy state of the polymer ^{83,84}. DSC measurements were also conducted on all the samples, and T_g was reported as the middle point of the slope during a heat cycle ⁸⁵. Overall, all measurements showed a higher Tg for the epoxy B when compared with A. Furthermore, epoxy C and D had a lower Tg, where epoxy C showed higher transition temperatures than epoxy D. It is important to highlight that Tg values are reported from different techniques only for comparison purposes. It is the assumption of the authors that the $T_{\rm g}$ measured

from the onset of E, has a higher importance in the mechanical properties of the laminates, influencing the modes of fracture in the specimens (i.e. before T_g fracture behavior is independent of temperature)⁸⁶.

It is expected that by replacing the hardener of the initial epoxy formulation (epoxy A), described by the manufacturer as "Polyoxypropylenediamine" for one such as 5- Amino 1,3,3- trimethylcyclohexanemethy- amine (Figure 4.7) will result in an increased stiffness of the crosslinked structure, translating in a higher T_g and storage modulus but also in some brittleness in the resin. On the other hand, a longer and more ductile hardener such as O,O'-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Figure 4.8) with a relatively high molecular weight (i.e. M_w : 1900 g/mol) will introduce more space between crosslinks in the resin, making it more flexible and susceptible to movement at lower temperatures (therefore the lower T_g and storage modulus). This is true for epoxies C and D, where the original hardener of the epoxy was mixed with the high molecular weight hardener in two different proportions, resulting in lower values of T_g and moduli when compared with epoxy A.



Figure 4.7 Molecular structure of 5- Amino 1,3,3-trimethylcyclohexanemethy- amine. Introduced to formulation B.



Figure 4.8 Molecular structure for hardener O,O'-Bis(2-aminopropyl) polypropylene glycolblock-polyethylene glycol-block-polypropylene glycol used on formulation C and D.

Figure 4.3 shows the influence of such resins on the laminate properties, where the second square highlights the results. Overall, the introduction of a stiffer resin (epoxy B), decreased the mechanical properties of the laminate, reversing the 29% flexural strength increase achieved by the introduction of stronger TOCNF + PVA layers. Furthermore, Young's modulus and WOF showed no statistical difference when compared against TOCNF + PVA – epoxy A laminate. Considering epoxy C, a somewhat more ductile interlayer (20% decrease in elastic modulus when compared to epoxy A), there is no statistical difference with regards to formulation A with the TOCNF + PVA laminate for modulus, flexural strength or WOF. However, a continued increase in the epoxy ductility (e.g., lower T_g and elastic modulus) by using epoxy D, translated into a degradation of the strength, a large reduction of the bending modulus but an increase in the WOF of the laminate. Thus, as the epoxy interlayer ductility increased (e.g., stiffness decreased) there seems to be a threshold before which the epoxy makes little difference, but beyond which it reduces stiffness and strength, and increases WOF.

When examining the fracture behavior of the laminates in Figure 4.9 it is evident that different modes of fracture are being introduced depending on interlayer stiffness. Overall, the trend seems to highlight an intralayer damage within the TOCNF + PVA layers when introducing a stiffer interlayer (epoxy B), that changes into an interfacial delamination when a softer interlayer is in place (epoxy D). This behavior might be triggered by the difference in modulus between the strong layers (TOCNF + PVA) and the epoxy. When this difference is higher, as in the case of epoxy D that is more ductile, the amount of interfacial shear stress between the two materials can lead to increased delamination at the surface between the two (i.e. interfacial delamination). As this difference is reduced (by introducing stiffer epoxies) the shear stresses at the interface are reduced and the intralayer damage within TOCNF layers is more evident. Nevertheless, it seems like resins with a set of properties between the two extremes performed best. In this particular case, epoxy A and epoxy C behaved better in terms of increased flexural strength, moduli and WOF in the laminates. Figure 4.9 (c) shows the fracture of TOCNF + PVA laminate with epoxy C, where extensive delamination and intralayer damage can be appreciated. Therefore, the increased mechanical properties might be attributed to a combined effect of the two different fracture retardation mechanisms at play. As such, having a soft enough epoxy to promote interlayer

delamination, but stiff/strong enough to allow intralayer damage to balance the stresses of the two modes seems ideal.



Figure 4.9 SEM images of the fracture behavior of 10 layer TOCNF film laminates with different epoxy formulations as interlayers. Images are presented in order of stiffness a > b > c > d. (a) TOCNF + PVA – Epoxy B (b) TOCNF + PVA – Epoxy A. (c) TOCNF + PVA – Epoxy C.(c) TOCNF + PVA – Epoxy D.

4.3.5 Influence of a silane coupling agent

In a previous work by Forti et al (2020) the adhesion at the interface of TOCNF + epoxy A laminates was measured and found to be lower than desired when compared to the cohesive strength of neat TOCNF layers¹³, suggesting a potential mechanism for improvement. By increasing interfacial adhesion between TOCNF and epoxy, the laminates could improve their performance in mechanical loading, while also sustaining beneficial crack stop mechanisms such as crack digression.

To study how the level of adhesion at the interface between TOCNF and epoxy affects the mechanical properties of laminates, a silane coupling agent was added to a TOCNF + PVA – epoxy A system. The reasoning behind this can be found in literature, where silane coupling agents have been used to increase the compatibility of CNFs with different materials. In general, silane coupling agents serve as a bridge between two substrates, introducing ionic or covalent bonds between them and increasing their overall adhesion⁸⁷. In the specific case of CNFs and epoxy, APTES, a silane coupling agent with an amine active group that can easily react with epoxy, phenolics and polyesters has been previously studied⁸⁸. For example, Yeo et al. (2017) modified CNF fibrils with APTES to achieve a 1.5 - 2.2 times higher mechanical properties of the epoxy reinforced with the modified APTES⁸⁰. Therefore, APTES was introduced in this study as an adhesion promoter.

To demonstrate the effect of APTES on adhesion, a contact angle study was completed on TOCNF+PVA films that were clear of visible defects. Figure 4.10 shows the change in the contact angle after applying APTES to TOCNF+PVA films. Overall, TOCNF + PVA films exhibit a static contact angle of $70 \pm 3^{\circ}$ that was increased to $100 \pm 5^{\circ}$ after treatment with APTES, which is in line with previous APTES modification studies. Lu et al. (2008) achieved a change in the water contact angle of CNF from 15° to 90° without imparting any changes in the crystalline structure of CNF. In general, CNFs are rich in hydroxyl groups (OH) making them hydrophilic in nature ⁸⁹. While it can be expected that TOCNF may be somewhat different than CNFs due to the conversion of some of the OH groups to COONa, it will still retain a similar hydrophilic behavior thanks to the large amount of unconverted OH groups on the surface. Further, while many expect the amine surface to of APTES to be relatively hydrophilic, APTES tends to interact with hydrogen bonding groups underneath (such as alcohol or silanol) and push the propyl segment towards the top, giving a relatively hydrophobic surface (please refer to Figure 4.11 for the molecular structure of APTES) ⁹⁰.



Figure 4.10 Static contact angle photographs of water droplets in different substrates. (a). TOCNF + PVA (b) TOCNF + PVA + APTES



Figure 4.11 Molecular structure for APTES (3-Aminopropyl)triethoxysilane

Overall, a higher adhesion at the interface was achieved by the introduction of APTES as can be seen in the lap shear results exhibit on Table 4.2, where for both neat TOCNF and TOCNF composite films with epoxy A the results did not show a statistical difference. In contrast, when APTES was added, the peak stress increased by 47% while the strain before failure increased by 86%. This confirms the authors hypothesis that by achieving a surface treatment on the films through a hydrolysis-condensation reaction, a bridge between TOCNF and epoxy was achieved (Figure 4.12) resulting in a higher adhesion as shown by the data presented.



Figure 4.12 Schematic of the surface modification achieved of TOCNF with APTES

Table 4.2 Lap shear results on different TOCNF and TOCNF + PVA composites and adhesion promoters.

Material A	Material B	Adhesion Promoter	Peak Stress (MPa)	Peak Strain (mm/mm)	Failure
TOCNF	Epoxy A	-	3.6 ± 0.5	0.008 ± 0.001	Interface
TOCNF + 10wt% PVA	Epoxy A	-	3.8 ± 0.9	0.008 ± 0.005	Interface
TOCNF + 10wt% PVA	Epoxy A	APTES	5.6 ± 0.4	0.015 ± 0.005	Interface

The measurement of the adhesion at the interface is important to understand crack digression mechanisms on the laminates. Overall, the adhesion between the interfaces of a laminate is vital and defines the behavior of nucleated cracks and their relation to the delamination behavior of laminates. In general, one of the main attributes that affects the propagation speed of a crack in a laminated material is the adhesion at the interface. To name an example, in homogenous brittle materials, once a crack is initiated, it will propagate through the material rapidly causing fracture. One can then infer that if the adhesion between the two interfaces in a laminate is sufficiently high, once a crack is nucleated, it might go through all the layers without perceiving the presence of an interface. In the opposite case (i.e. if the adhesion between the two is weak), the crack might diverge along the interface, increasing the overall toughness of the laminate, but causing early delamination and compromising the overall strength. However, there is an ideal scenario where

the adhesion is weak enough to provoke the diversion of a crack but strong enough not to weaken the specimen. This case for purely brittle materials has been defined in literature by a ratio, if the interface adhesion in a laminate is less than 0.35 times the cohesive strength of the strong material in the laminate, then cracks can be diverted but the laminate will retain some of its inheriting strength ^{13,20–22}.

In the particular case of neat TOCNF laminates, it was shown in a previous publication that this value was around 0.03, suggesting there was room for potential improvements¹³. Table 4.3 shows the same ratio calculated for different configurations of TOCNF composites with regards to epoxy A. To calculate such ratios, tensile testing of neat TOCNF and TOCNF + PVA films was performed via DMA. For the specific case of TOCNF + PVA + APTES films, the same value of UTS of the TOCNF + PVA composite film was assumed, since APTES does not disrupt the structure of the TOCNF layers ⁸⁹.

Table 4.3 UTS properties of Neat TOCNF and TOCNF + PVA films. TOCNF + PVA + APTES films are assumed to have the same UTS as TOCNF + PVA layers. Adhesion – Cohesive strength ratio for different TOCNF configurations. Adhesion measured in relation to Epoxy A.

Films	UTS (MPa)	Adhesion (MPa)	Ratio Adhesion / UTS (MPa/MPa)
Neat TOCNF	151 ± 11	3.6 ± 0.5	0.024
TOCNF + PVA	256 ± 12	3.8 ± 0.9	0.015
TOCNF + PVA + APTES	256 ± 12	5.6 ± 0.4	0.022

As can be seen in Table 4.3 the original ratio of 0.024 was reduced to 0.015 when TOCNF + PVA layers were incorporated to laminated specimens. This is due to the higher cohesive strength achieved by adding PVA to TOCNF layers. Without an adhesion promoter, the adhesion at the interface remained the same and the ratio was reduced. To further investigate how this ratio affected the mechanical properties of the laminates, a set of 3 different laminates were prepared and measured in tension. Results are presented in Figure 4.13.



Figure 4.13. Tensile testing of different laminates. Blue and red lines represent the iso-strain rule of mixtures of TOCNF + PVA – Epoxy A and Neat TOCNF – Epoxy A laminates

Tensile testing results show a different tendency for laminates with TOCNF + PVA composite films versus those made with neat TOCNF layers. Overall, laminates with TOCNF +PVA composites performed better due to the larger strength of the individual layers. Nonetheless, it seems like without an adhesion promoter such as APTES (open blue triangle marker) the UTS values in tension are not reaching the idealized performance predicted by the rule of mixtures. This behavior may be due to the increased difference in performance between TOCNF + PVA layers and epoxy A. When the difference in mechanical properties grows larger, the mismatch in Young's modulus between the strong layers and the epoxy produces an increased shear stress when the material is stretched in tension ^{34,35}. It is believed by the authors that the high shear stresses generated by the mismatch of mechanical properties, in addition to the decreased adhesion ratio in the interface, generates extensive delamination and an improper transmission of the load between the layers. When APTES was added (close blue triangle case) an increased adhesion was achieved, resulting in an improved tensile strength of the laminate, that is closer to the expected values (dictated by the rule of mixtures).

Finally, the flexural properties of the APTES laminates were measured and compared to the Neat TOCNF and TOCNF + PVA laminates. Results are shown in Figure 4.3 and are

highlighted by the biggest square in the plots. Data shows an increase of 25% in the flexural strength, 30% in bending modulus and a reduction of 25% in WOF properties attributed to the increased interfacial adhesion (taken from the straight comparison between TOCNF + PVA laminates with epoxy A interlayers). When compared to the original non-PVA laminate (red bar in the plots), an increase of 80% in flexural strength, 61% in bending modulus and approximately the same WOF was obtained, showing that both improved TOCNF strong phase and adhesion can lead to large increases in properties. Nonetheless, even when a much higher mechanical performance was achieved, the adhesion ratio of the samples is still low. Therefore, there may be still room for improvement, in fact, it is believed by the authors that achieving a higher adhesion between the TOCNF + PVA composites and the epoxy is crucial to decrease the delamination behavior of laminates while increasing the its overall performance.

4.3.6 Impact rupture energy

Both 3-point bending, and tensile testing involves the deformation of specimens to the point of fracture while increasing the load applied. While both techniques offer a wide range of information about the overall mechanical response of a specimen, they do not predict the fracture behavior of specimens under a moderate or high velocity blunt impact. Systems where a strong material is laminated with a ductile material have been shown to produce high toughness materials when the conditions are appropriate (i.e. an adequate combination of moduli, good adhesion, appropriate interlayer thickness and sufficient number of layers). A good example of this combination can be found in ballistic glass (glass with polyvinyl butyral or other polymers as interlayer⁹¹), where the match of the right properties produce a material capable of resisting impacts at high velocity ⁹². This type of study, necessary to predict the toughness capabilities of our system has not been done before on TOCNF materials and it is important to fully understand the behavior of the laminates under a wider range of conditions. Some of the most popular impact studies include techniques like Charpy and Izod where the material is notched and subjected to a high strain-rate impact. In this study, a free-falling dart test was used as it is a common impact test performed on thin films that are usually targeted for packaging applications, a field of interest for the cellulose community. The method is highly sensitive to thickness, making it hard to derive straight relationships between the energy to rupture and the thickness of different materials. Further, a complete rupture of the films is necessary to make the calculations possible, which limits

the spectrum of materials that can be tested. Hence, only films with similar thicknesses were tested as a comparison point for cellulose materials (both films and laminates).

A set of three different laminates were prepared and subjected to drop dart testing along with other common materials. 10-layer neat TOCNF – epoxy A, TOCNF + PVA – epoxy A, and TOCNF + PVA + APTES – Epoxy A were selected for the testing to analyze how different TOCNF composites and adhesion promoters could change the response of the laminates. Other common polymers within similar thicknesses and toughness such as ABS, known as an engineering polymer with excellent toughness ⁹³, LDPE, a common polymer used in the film industry due to its cheap price and great toughness ⁹⁴, cellulose acetate, used in a wide range of products including films for packaging applications ⁹⁵, acrylic (PMMA), known as a good alternative to replace glass ⁹⁶, high impact polystyrene (HIPS) ⁹⁷, aluminum and borosilicate glass ⁹⁸, extensively used in industry due to its higher resistance to thermal shock were tested. Results are presented in Figure 4.14 where the energy to rupture was divided thickness as rupture energy scales by the volume deformed and normalized by density to plot against the tensile specific strength of each material in an "Ashby" style plot to compare the materials.



Figure 4.14. Plot shows specific energy to rupture divided by thickness (t) against the specific strength of various materials, including ABS, LDPE, Cellulose acetate, Acrylic, PS, Aluminum, Borosilicate Glass, Neat TOCNF and TOCNF + PVA films and 3 different 10 layers TOCNF or TOCNF + PVA laminates. Blue bubble are ductile polymers (low specific strength but high specific energy to rupture), purple bubble somewhat brittle materials (low specific strength and energy to rupture), red bubble indicates high specific strength but low specific energy to rupture.

Results show a highlighted area for each group of materials studied. The blue bubble represents ductile polymers with an overall low specific strength but high specific rupture energy. ABS exhibited the highest specific energy to rupture, as expected as it is an engineering polymer, composed by acrylonitrile and butadiene (a synthetic rubber), which allows for a good chemical and thermal stability while also sustaining high toughness ⁹³. Acrylic in the other hand, showed a low specific rupture energy but higher specific strength, which is not uncommon due to its amorphous nature ⁹⁶. In comparison, laminates showed a similar toughness to acrylic, with a much higher specific strength. Finally, borosilicate glass and TOCNF and its laminates are shown in the low specific energy / high specific strength area of the plot (red bubble). While glass was expected to behave in a brittle manner (low toughness) the glass tested here was thin (i.e. characteristic strength goes up as size goes down) which explains the higher toughness exhibited ⁹⁹.

Single TOCNF films need some elaboration as this is the first report to date of falling dart impact testing of these materials. Neat TOCNF films showed strength to failure similar to borosilicate glass with a higher specific energy to rupture. The composite films (TOCNF + PVA) showed a higher specific strength but a reduced energy to rupture when compared to Neat TOCNF films. Overall, impact testing shows that TOCNF has great potential as a high strength transparent or structural material as when a small amount of PVA enhancer is added it can achieve similar specific impact energy to rupture to acrylic and aluminum, but almost 3 times and 7 times higher specific strength of each, respectively.

Neat TOCNF laminates performed similarly to its respective unlaminated single films and to borosilicate glass. As the TOCNF laminate is much higher in strength than typical polymers but still fails in a brittle manner, this is expected. While TOCNF + PVA -epoxy A laminate shows lower strength than the single film, its impact performance seems to be increased with lamination, indicating toughening mechanisms attributed to the interfaces Regardless, TOCNF + PVA -epoxy A performed better in terms of energy of rupture than either the glass or neat TOCNF laminate. In comparison, the laminate with an increased adhesion (APTES laminate) underperformed, reaching the same level than the original laminate (Neat TOCNF laminate) while showing a higher specific strength. This might find a good explanation in the crack digression mechanism exhibited by all the laminates. As discussed previously, the ratio between the interface adhesion and the cohesive strength of the material dictates the degree of crack digression that a system will experienced upon fracture. The lower this value is, the higher the crack digression in the system, leading to delamination but also a great degree of energy absorption as the crack deflects to an unfavorable direction, prolongating its path across the laminate, resulting in higher toughness ¹⁹. Therefore, the results shown in Figure 4.14 are in agreement with the ratios calculated in Table 4.3 where the TOCNF + PVA laminate shows the smaller adhesion/strength ratio (0.015), translating into a higher toughness. This was also corroborated by the three-point bending results, where this laminate showed the higher WOF just as both neat TOCNF and APTES laminates showed the same value of WOF, adhesion ratio, and energy to rupture. Overall, while the laminates fracture in a brittle way when compared to ductile polymers (ABS, LDPE and acetate), the specific impact rupture energy of the laminates is similar or higher than that of other transparent structural

materials such as glass and acrylic, yet with a significantly higher specific strength allowing for the potential of weight savings by using less material to accomplish a similar function.

4.4 Summary

Transparent TOCNF-epoxy laminates were fabricated and tested to determine how the strong layer properties, epoxy interlayer properties and strength of adhesion between the strong layer and the epoxy interface affected the overall laminate mechanical properties. 3-point bending results showed a strong relationship between the presence of stronger layers (TOCNF + PVA) with a higher flexural strength, bending modulus and WOF. Overall, a stiffer epoxy generated a diminished UTS and flexural modulus and substantial intralayer damage. On the other hand, a more ductile epoxy increased the WOF of the laminates, inducing a higher delamination at the interfaces. The delamination mechanism was attributed to the strong mismatch between the properties of TOCNF + PVA composites and the epoxy. Results highlighted a better mechanical performance when laminates were fabricated with an intermediate, i.e. not too stiff or too ductile interlayer, and were able to exhibit both delamination at the interface and intralayer damage as a fracture behavior mechanism. The addition of a silane coupling agent (APTES) to the TOCNF – PVA laminates increased the adhesion at the interface, resulting in a higher UTS when tested in tension and a reduced energy to rupture associated with the reduction of crack digression mechanisms in the system. In general, laminates with strong TOCNF layers (TOCNF + PVA) and APTES, increased the flexural strength (+61%) and bending modulus (80%) while retaining the same WOF. Finally, for the first time, impact testing of TOCNF was performed. The specific impact rupture energy of the laminates was comparable to or slightly higher to those achieved by acrylic polymers and borosilicate glass while maintaining a similar or higher specific strength to glass. Additionally, laminates showed an excellent transparency and low haziness to the naked eye.

5. CONCLUSIONS AND FUTURE WORK

This work studied lamination with a room temperature epoxy as a potential solution to solve some of the scalability problems of TOCNF. Lamination was successful at increasing the thickness of TOCNF materials and reduce the brittleness of the films while maintaining their inherent transparency. The highest mechanical properties were found when the volume fraction of epoxy was reduced to 10%. Additionally, crack digression was described as one of the primary mechanisms for fracture retardation in the laminates. It was found that a weak interfacial adhesion led to substantial delamination, which increased the toughness of the laminates at the expense of the integrity of the structure (i.e. a decrease in the UTS and Young's modulus). The research helped clear the path to the creation of enhanced laminates that could potentially compete in industry. A first approach to the fabrication of better laminates was the incorporation of stronger TOCNF layers. A screening of several water-soluble polymers found that both PVA and PEOX were good candidates to increase the mechanical properties of the films as their presence in the films facilitated the creation of numerous hydrogen bonding between the fibrils and the polymers. Such a mechanism of reinforcement was indirectly confirmed by zeta potential and rheology. When stronger TOCNF layers were introduced to the laminates, an increased mechanical response was obtained, and substantial intralayer damage was reported. Furthermore, a set of four different epoxy systems were introduced in the laminates and their mechanical response was characterized. It was found that an optimal mechanical response of the laminates could be substantiated by the introduction of an interlayer with an intermediate set of properties which could allow for intralayer damage and interfacial delamination to take place as retardation mechanisms. Finally, a silane coupling agent was introduced to decrease the delamination that was suspected to be the culprit of the high toughness but decreased integrity of the laminates. The enhanced laminates showed good transparency, and the specific energy to rupture of the systems was comparable to or slightly higher to those achieved by common materials such as acrylic and borosilicate glass.

Even though the enhancing mechanisms presented were successful, there is still a path ahead for the creation of more competitive laminates. For instance, an industrially scalable method to produce TOCNF films is still needed. Processes like roll to roll or extrusion followed by calendaring should be explored as feasible methods to shorten the drying times of TOCNF films and achieve continuous production of the material with a high control of the thickness and the transparency of the films. Furthermore, controlling the interlayer thickness is crucial to achieving repeatable mechanical responses across the laminates. The usage of a room temperature curing epoxy was proven to offer advantages in the manufacturing of the laminates (i.e. reducing the yellowing of TOCNF films) but achieving the same thickness of interlayer across the laminates was difficult to control. Spacers were tried but ended up acting as defects, debilitating the structure of the laminates. For that reason, finding films with a set thickness to laminate TOCNF is crucial to achieving even higher mechanical responses. Furthermore, being able to introduce such films into a scalable industrial process of lamination would be ideal.

It is clear that the introduction of a new set of interlayer materials can lead to the creation of some other roadblocks. For instance, it was proven that the adhesion between TOCNF and epoxy was not ideal even after the introduction of a silane coupling agent to the interface. This means that extensive delamination was still taking place within the laminates, debilitating the structure. Being able to control the ratio of cohesive strength/adhesion at the interface is vital to maximizing the mechanical properties of the laminates. A couple of options are suggested. Increasing the compatibility between TOCNF and epoxy through the treatment of TOCNF layers with different silane coupling agents ^{80,87}, an isocyanate pretreatment of the TOCNF layers for epoxy co-reaction ¹⁰⁰, or the hydrophobization of the TOCNF layers ¹⁰¹. Alternatively, the cohesive strength of TOCNF layers could be decreased to achieve a higher ratio. A good option to achieve a decrease in UTS would be the introduction of MHEC to the TOCNF films. This polymer introduced a higher strain to failure than others when it was added in low percentages to TOCNF films as can be seen in Chapter 3. Even when the suggested option would translate into the decrease in the mechanical properties of the laminates, it could open the door for other possible applications, where a higher ductility and strain to failure along with the renewable capabilities of TOCNF could be useful (i.e. packaging applications instead of structural).

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