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ORIGINAL RESEARCH

Transparent tempo oxidized cellulose nanofibril (TOCNF) composites with increased toughness and thickness by lamination

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Abstract The favorable mechanical properties and performance of TEMPO-oxidized cellulose nanofibril (TOCNF) films has been limited by their brittleness and the incapability of obtaining thick enough materials for self-supported applications. In this study, lamination 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 (e.g., TOCNF, epoxy), the number of layers, and the overall total thickness of the laminate, on the tensile and flexural properties are investigated. Lamination was successful at increasing the toughness and thickness of TOCNF composites, resulting in an increased work of fracture that was associated with fracture retardation by crack digression in three-point bending specimens. The ultimate tensile strength and Young's modulus were higher for laminates with low volume fractions of epoxy although not statistically different than the neat TOCNF films, but decreased with increasing volume fraction of epoxy, and with increasing number of TOCNF layers.

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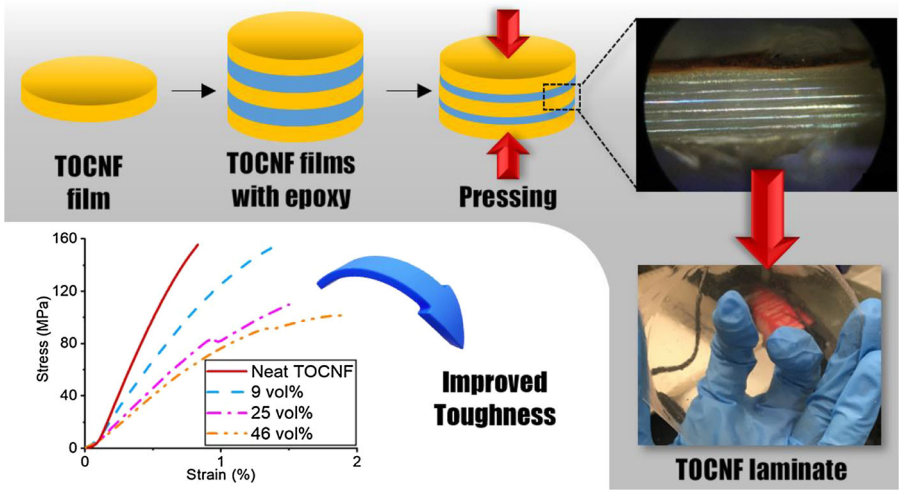
Graphic abstract



Keywords Cellulose nanofibers · Lamination · Composites · Failure mechanisms · Crack digression

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 nanofibrils (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 (Saito et al. 2009; Isogai et al. 2011; Fujisawa et al. 2011; Moon et al. 2011; Benítez et al. 2013; Zhao et al. 2017).

Films made of TEMPO-oxidized cellulose nanofibrils (TOCNFs) have excellent mechanical properties, with Young's Modulus around 6 to 14 GPa, ultimate tensile strength between 130 and 300 MPa and strain to failure within 2% and 10% (Saito et al. 2009; Isogai et al. 2011; Fujisawa et al. 2011; Moon et al. 2011; Benítez et al. 2013). 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 (< 2 wt%), 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 μm have been reported, values which are not thick enough for self-supported applications such as transparent protective cases and impact resistant windows (Iwamoto et al. 2007; Benítez et al. 2013; Zhao et al. 2017).

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 stiffness (Feng et al. 2000). 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 (Cook et al. 1964; Cepeda-Jiménez et al. 2008b).

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.

Materials and methods

Materials

A TOCNF suspension 1.1 wt% 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 (Renier and Rudie 2013). The TOCNFs have a carboxylate content of 0.44 mmol/g solids, and was measured following a titration procedure (Johan Foster et al. 2018). Room temperature cure transparent epoxy EpoxAcast 690^{TM} was bought from Smooth-On, Inc, Macungie, PA, USA to use as an adhesive interlayer for the laminates. 30.5 × 30.5 cm × 1.60 mm thick acrylic sheets were bought from McMaster-Carr, along with fiberglass sheets for tabs and 5-min Epoxy Gel from Devcon, both needed for the tensile testing specimens.

Fabrication of samples

TOCNF films

TOCNF suspensions in water were diluted with deionized water to 0.73 wt% and cast into 100 mm polystyrene Petri dishes as reported in previous studies (Moon et al. 2011). With the objective of obtaining TOCNF films with different thicknesses, the following volumes of solutions were cast: 30 ml, 45 ml and 70 ml. 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 20 μm, 30 μm and 40 μm. 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 (Elkington et al. 2015). In the first stage of the fabrication process, a room temperature cure epoxy (EpoxAcast^{TM} 690) was premixed 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 the Figure SI1 (Supplemental Information). 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 5 h, 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 20 μm, 30 μm, and 40 μm and volume fractions of epoxy ranging from 2 to 44%.

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 1 mm width and 6.5 mm 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 0.1 mm/min displacement rate. Specimens had an average thickness of 30 ± 3 μm. Samples were left in a low humidity chamber (15% RH) for 3 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^{TM} epoxy was cast in 33 mm x 33 mm 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 1000 N load cell, and a 0.1 mm/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 (40 mm × 4 mm) were cut using the laser cutter (PLS6MW MW laser engraver, Universal Laser Systems, Scottsdale, AZ, USA), for each laminate. Rectangular fiberglass tabs (4 mm wide and 10 mm 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 3 days at room temperature before testing. Five specimens were tested in the MTS Insight with a 1000 N load cell and tensile grips, at room temperature (21 °C) and 35% RH. A strain rate of 0.5 mm/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.

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 62 mm. 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.

Flexural testing

TOCNF-epoxy laminates

Rectangular specimens 40 mm long and 4 mm wide were cut using the laser cutter. Laminates were tested with a small 3-point bending fixture in DMA at a 0.1 mm/min speed using a rate-controlled 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.

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 5×, 10× and 20× magnification objectives.

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 9.40 mm wide, 100 mm long and 12 mm thick were used. A 9.40 mm wide by 100 µm 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 690^{TM} resin and left to cure. Later, both surfaces were glued together with EpoxAcast 690^{TM}. Once cured, a minimum of 5 specimens were tested in an MTS with a uniaxial tension configuration, using a strain rate of 1.27 mm/min. After confirming delamination failure, the interfacial shear strength was calculated using the UTS and the overlapping area of adhesion.

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 750 nm with air as the background. Transmission data was normalized by the sample thickness for comparison purposes.

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 30 s using an Emitech, K550X Sputter coater (Quorum Technologies Ltd., East Sussex, UK).

Results and discussion

Processing

Epoxy was chosen as interlayer for the laminates due to its generally high adhesion, commercial availability and use in composite materials (Feng et al. 2000; Zhao et al. 2003; Kaw 2006). 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 (Isogai et al. 2011). For this process, two commercially available resins were taken into consideration, EpoxAcast 690^{TM} from Smooth-on and Epoxy 561/588-1001 from US composites. Out of the two, EpoxAcast 690^{TM} 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 SI1. 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 20 µm thick, while a maximum thickness of 40 µm 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 20 µm and 40 µm, 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 1.5 mm in thickness, by adhering sixty 20 µm thick TOCNF films or forty-five 30 µm thick TOCNF films (Figure SI2). 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 25–60 µm (Iwamoto et al. 2007; Benítez et al. 2013; Zhao et al. 2017). 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.

Moreover, lamination of TOCNFs with epoxy was successful at maintaining a high level of transparency of the TOCNF laminate. Figure 1 shows characteristic plots of transmittance obtained by UV–Vis spectroscopy, performed on neat TOCNF films (Fig. 2, left), neat epoxy, a 10-layer TOCNF-epoxy laminate (Fig. 2, 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

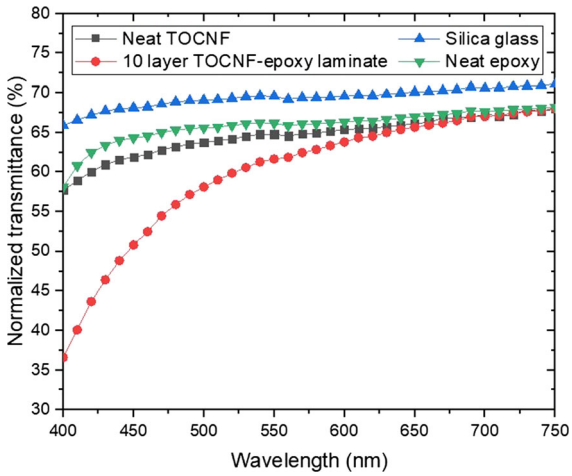


Fig. 1 Visible transmittance via UV–Vis spectroscopy of TOCNFs, epoxy, TOCNF-epoxy laminates and silica glass normalized by the thickness. Thickness was normalized using the epoxy thickness as reference (0.8 mm)

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.

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 20 µm, 30 µm and, 40 µm. Mechanical properties (Table 1) of neat TOCNFs and epoxy films were measured for comparison purposes. No statistical difference between TOCNF films with different thicknesses of 20 µm, 30 µm and 40 µm were found. Representative stress–strain plots are presented in Fig. 3. 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 (Isogai et al. 2011; Fujisawa et al. 2011; Fukuzumi et al. 2013; Benítez et al. 2013; Kurihara and Isogai 2014). It is believed that the TOCNFs used has an inherent higher modulus or that the extremely slow drying process (over 2 weeks) led to different (e.g. denser) networks. Regardless, multiple calibrated instruments agree on this data.

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 (Liu 2014). 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

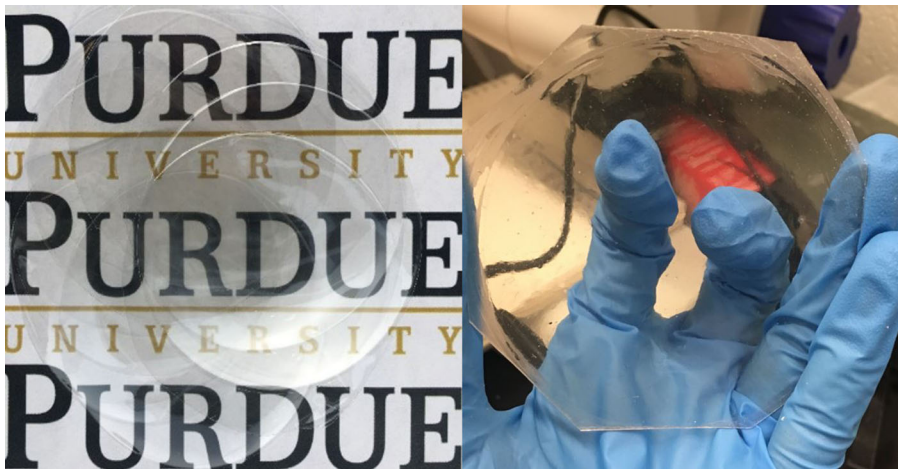


Fig. 2 Photographs show the transparency of TOCNF films (left) and a 10-layer TOCNF-epoxy laminate (right)

Table 1 Mechanical properties of neat 30 μm TOCNFs and 0.8 mm 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

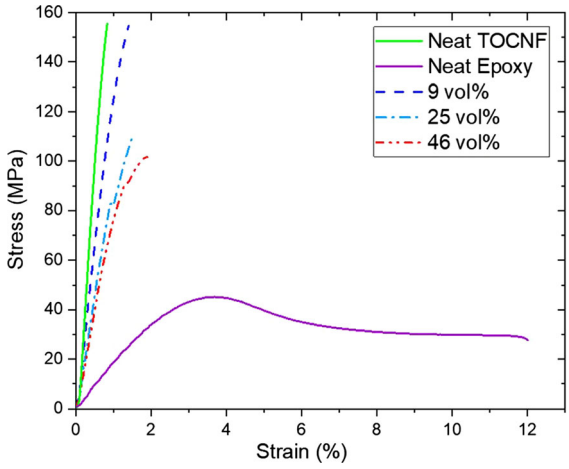


Fig. 3 Representative plots of TOCNFs, epoxy, and three 10-layer TOCNF-epoxy laminates, with 20 μm TOCNF layer thickness and varying volume fractions of epoxy (44 vol%, 27 vol%, 9 vol%)

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 (Liu 2014).

$$E_L = E_{CNF}V_{CNF} + E_{Epoxy}V_{Epoxy} \quad (1)$$

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 (Liu 2014).

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

The theoretical values of Young's modulus from both models were compared against experimental results (Fig. 4), 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, which is unexpected as the testing and laminate layer configuration were such that uniaxial strain was

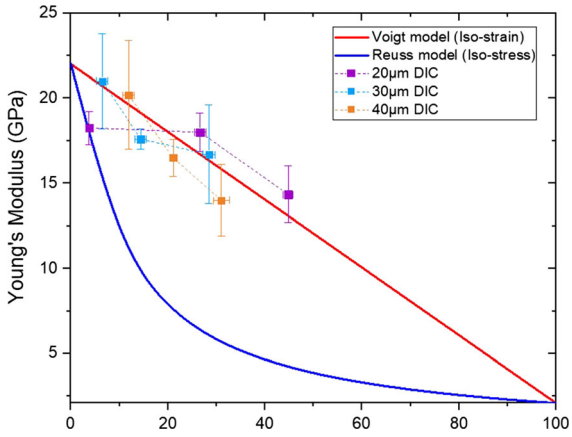


Fig. 4 Theoretical prediction of the Young's Modulus of TOCNF-epoxy laminates with the Reuss model (iso-stress) and the Voigt model (iso-strain) as function of the volume fraction of epoxy and TOCNF layer thickness (20 μm, 30 μm, 40 μm), with results of Young's modulus of laminates obtained from DIC. Error bars represent 1 standard deviation

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 (Phillipps et al. 1994). 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 (Hervy et al. 2017). 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 (A comparison between Young's modulus obtained from the displacement of the MTS and DIC can be found in FigSI3 in supplemental information), 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 (Herakovich 1981; Kant and Swaminathan 2000; Shokrieh and Akbari 2012; Viet et al. 2018). Results obtained also showed that the modulus decreases as the volume fraction of epoxy increases for all laminates tested.

Ultimate tensile strength (UTS)

The ultimate tensile strength (UTS) of neat TOCNF films and laminates are shown in Fig. 5 with a line indicating the rule-of mixtures predicted strength. Neat TOCNF films (in the 20–40 μm thickness range) had a UTS of ∼ 135 MPa 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.

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 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

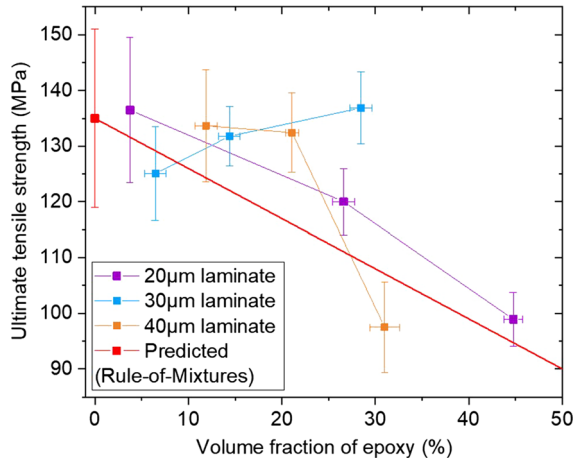


Fig. 5 Ultimate tensile strength of 10-layer TOCNF-epoxy laminates, with different volume fractions of epoxy and different TOCNF layer thicknesses (20 μm, 30 μm and 40 μm). Error bars represent 1 standard deviation

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 (Cook et al. 1964; Phillipps et al. 1994). This is evident in Fig. 3, 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 (Lee et al. 1996). 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 Fig. 5 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 Fig. 6. Neat TOCNF films (in the 20–40 μm thickness range) had a WOF of 0.1 MJ/m^3 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 (2.7 MJ/m^3). 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

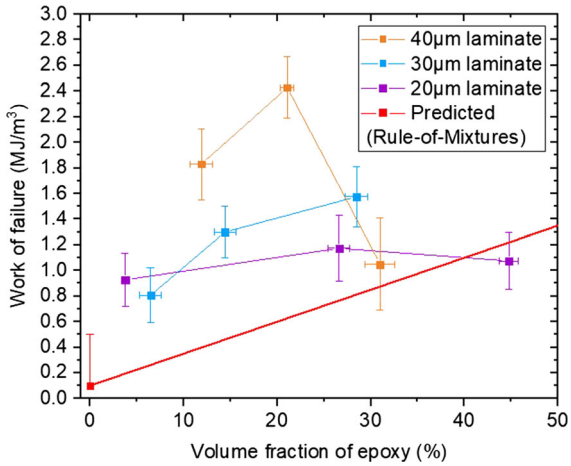


Fig. 6 Work of failure of 10-layer TOCNF-epoxy laminates, with different volume fractions of epoxy and different TOCNF layer thicknesses (20 μm, 30 μm and 40 μm). Error bars represent 1 standard deviation

epoxy, but at high TOCNF content with the concomitant increase in strength that it entails.

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 (Kendall 1975; Clegg et al. 1990; Chellappa and Jang 1996). 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 (Lee et al. 2004; Yeon et al. 2019; Manterola et al. 2019). 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.

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 µm, 30 µm, and 40 µm). Results are shown in Fig. 7.

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 75 MPa, 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 (Stoll et al. 2019). 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 20 µm and 40 µm thick will result in laminates having an overall thickness of 0.22 mm and 0.45 mm, 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 SI1 in supplemental information. 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., 40 µm layer thickness for 6-layer laminate, 30 µm layer thickness for 8-layer laminate, and 20 µm layer thickness for 12-layer laminate). The results of the first set of laminates are presented as blue triangles in Fig. 8, 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

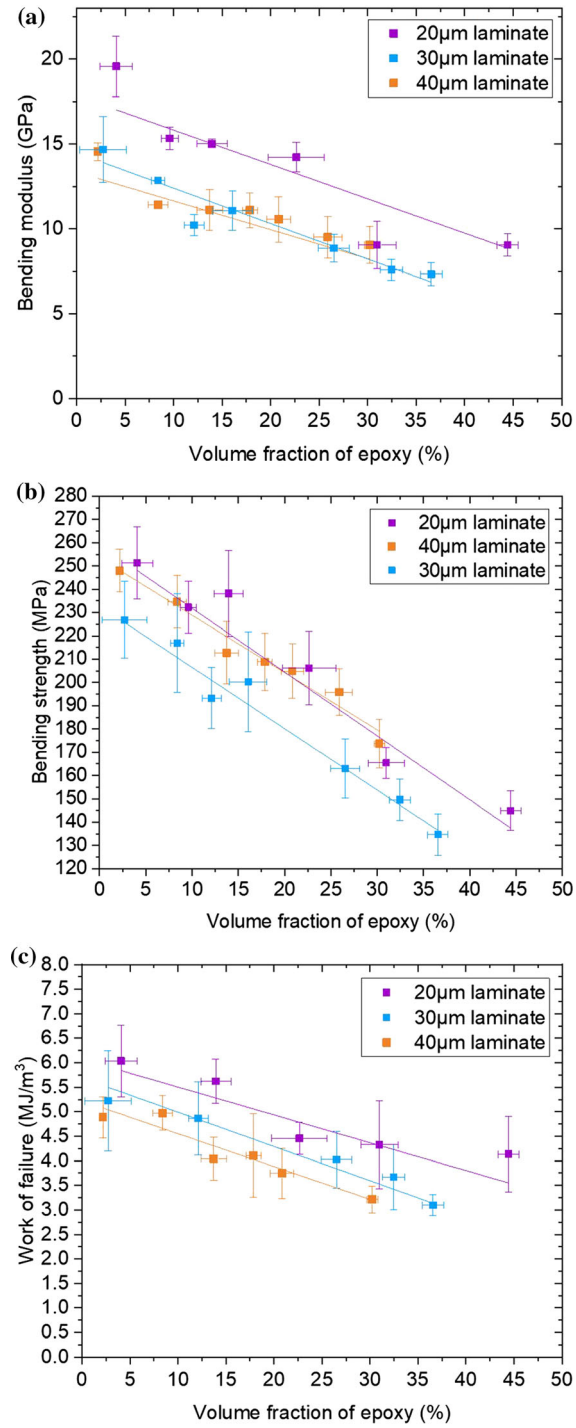


Fig. 7 Mechanical properties of 10-layer TOCNF-epoxy laminates with different volume fractions of epoxy and different TOCNF layer thicknesses (20 µm, 30 µm and 40 µm). **a** Bending modulus, **b** bending strength, and **c** work-of-failure. Error bars represent 1 standard deviation

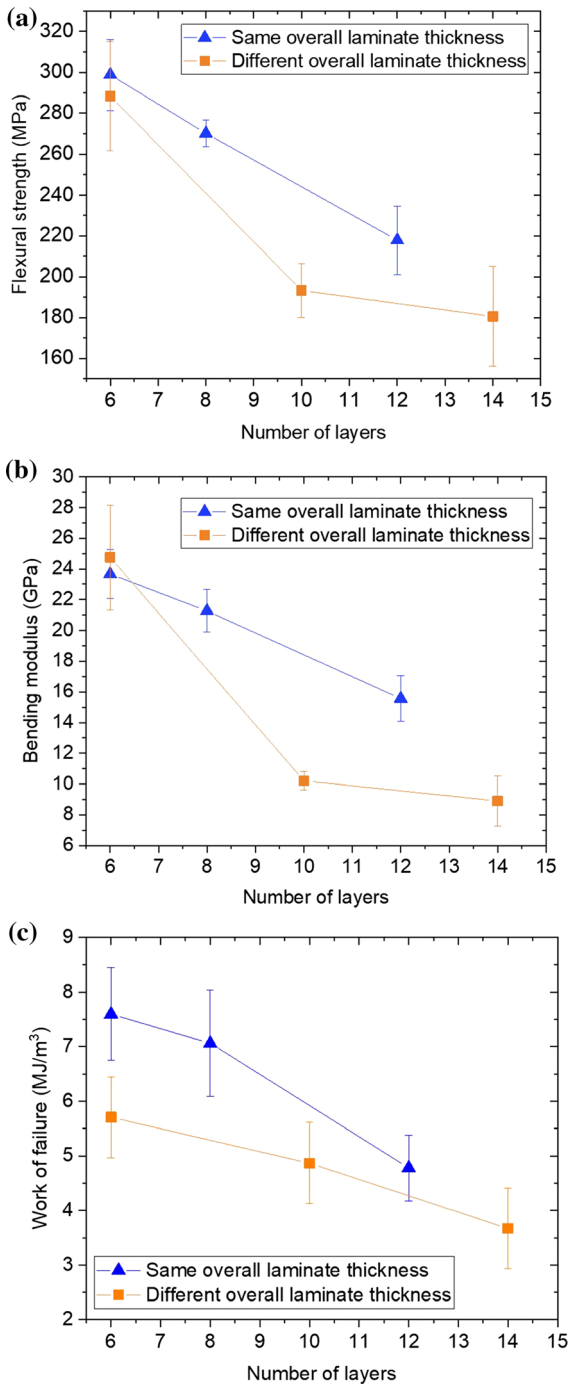


Fig. 8 Mechanical properties of laminates with the same and different overall thicknesses, and 7% volume fraction of epoxy. **a** Flexural strength, **b** Bending strength, **c** Work of failure. Error bars represent 1 standard deviation

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 (Cook et al. 1964; Phillipps et al. 1994). 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 (Yokozeki et al. 2008). 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 stress 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 (Wu et al. 2017). Nevertheless, it is more probable that the defects associated with the TOCNF-epoxy interface are significantly larger and dominate the properties.

In the second set of new laminates, the TOCNF layer thickness was fixed at 30 µm, 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 in Fig. 8, 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 (Caminero et al. 2019). 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 (Caminero et al. 2019). 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 (Cepeda-Jiménez et al. 2008a).

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 (Cook et al. 1964; Kendall 1975; Chellappa and Jang 1996).

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 (Kendall 1975). 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 Eq. (3) (Gupta et al. 1993);

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

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 (Gupta et al. 1993; Huang et al. 2015).

The energy criterion for the crack deflection model (Eq. 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 $\pm$ 0.3 MPa. Using this value with the strength of TOCNF film of 135 MPa in Eq. (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 (Zhao et al. 2003). For this reason, a 10-layer laminate with 10 vol% 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 (Fig. 9). 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 Fig. 10. 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.

Another indicative sign of crack digression is found on the mechanical response of laminates as they bend.

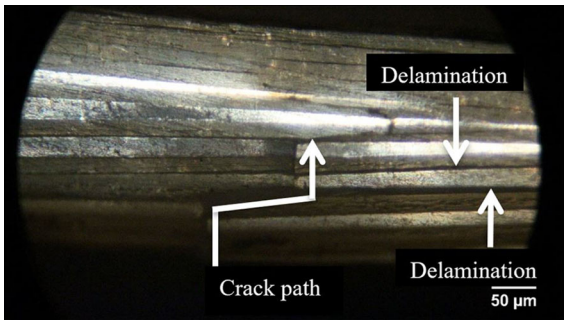


Fig. 9 Optical micrograph of initial cracks in a 10-layer 20 µm thick TOCNF- and 44 vol% epoxy laminate during three-point bending. Crack propagation direction is from bottom of the image to the top

epoxy were prepared. Both laminates were subjected to three-point bending. Characteristic stress–strain curves and microscopy of the samples are presented in Fig. 11a. 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 (Cook et al.

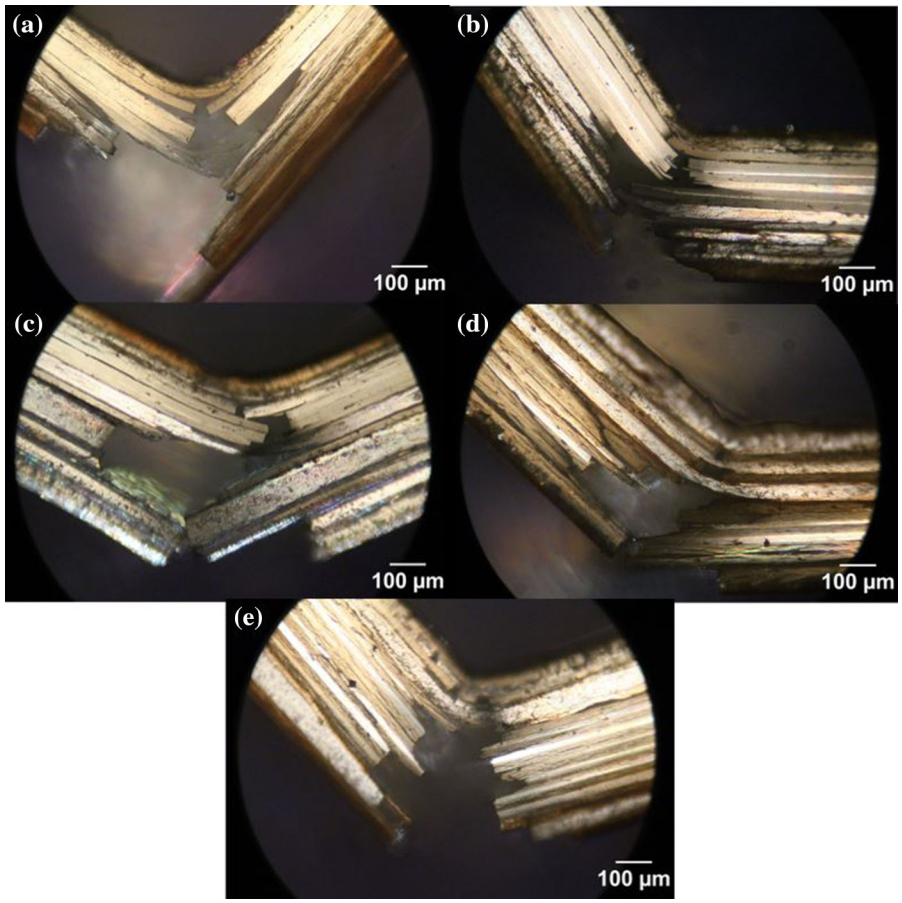


Fig. 10 Optical micrograph of 30 µm TOCNF/epoxy laminates after three-point bending: **a** 3%, **b** 12%, **c** 16%, **d** 27% and **e** 37% volume fraction of epoxy

To assess how the epoxy interlayer thickness affects crack digression, two 10-layer laminates with 40 µm thick TOCNF layers, with either 1 vol% or 30 vol%

1964; Feng et al. 2000; Wang et al. 2012). The low volume fraction of epoxy in the laminate may influence the extent of adhesion between the TOCNFs

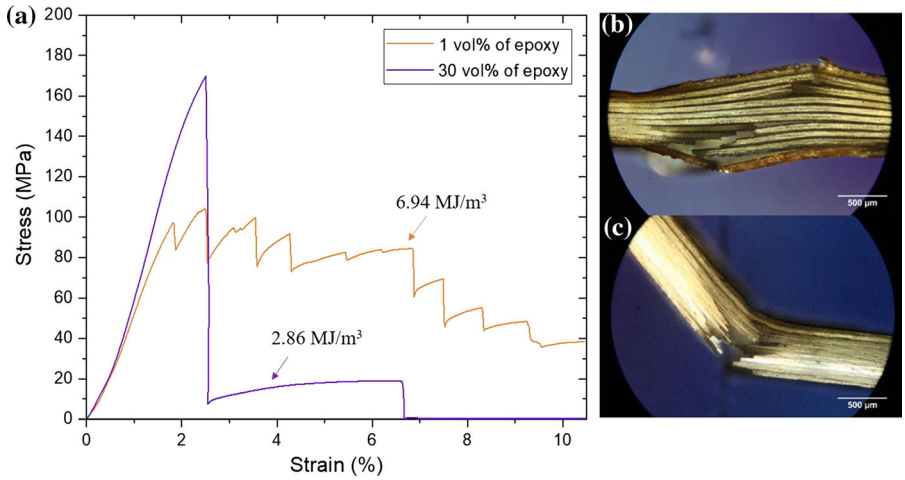


Fig. 11 Mechanical response and optical micrographs of two 10-layer TOCNF-epoxy laminates subjected to three-point bending **a** Stress–strain curves of 1 vol% of epoxy, and a 30 vol% of epoxy laminate, where the numbers for each plot represent their corresponding WOF. **b** Micrograph of a 1% volume fraction of epoxy sample. **c** Micrograph of a 30% volume fraction of epoxy laminate

and the epoxy, it is considered here that it lowers this adhesion. At 1 vol%, there is 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 Fig. 11a 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 (Fig. 11b), 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 (Cepeda-Jiménez et al. 2008b).

There is evidence of structural damage in the individual TOCNF layers as illustrated in Fig. 11b and Figure SI4 (supplemental information). 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 (Moon et al. 2011).

Compared with the 1 vol% epoxy laminate, the 30 vol% 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 (Fratzl et al. 2007; Kolednik et al. 2011). For TOCNF-epoxy laminates, this modulus mismatch is well above 5 (e.g., 22/2.3 = 9.6).

Conclusions

Lamination of TOCNFs with clear epoxy by a wet layup method was used to create laminates of up to 1.5 mm 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.

Supporting information

The following files are available free of charge:

- A Schematic of the TOCNF/laminate fabrication (PDF).
- Side view of 1.5 mm thick TOCNF-epoxy laminate (PDF).
- Theorical prediction of Young's Modulus with results obtained from displacement of the MTS and DIC.
- A table of the laminate configuration for investigating the role of laminate thickness on flexural properties (PDF)
- A SEM figure of the polished side surface of a 1% volume fraction of epoxy laminate (PDF)

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Author contributions The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Compliance with ethical standards

Conflict of interest The author declares no competing financial interest.

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