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Functionalized Cellulose Nanocrystal Sizing to Enhance Mechanical Properties of Glass Fiber–Reinforced Epoxy Laminates

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ABSTRACT

This study investigates the effects of chemically functionalized cellulose nanocrystal (CNC) coatings on glass fiber (GF)-epoxy laminate properties. Different types of modified CNCs, including sulfated, ion-exchanged with MePh_3P , silylated with (3-Aminopropyl)triethoxysilane, oxidized and oligomerized with tannic acid, and grafted with hexadecylamine, are slot die coated onto unidirectional GF fabrics prior to laminate fabrication. The CNC coatings are examined using scanning electron microscopy, Fourier transform infrared spectroscopy, and contact angle measurements to evaluate the functionalization, morphology, and changes to hydrophobicity. The effect of CNC coatings on interfacial adhesion is determined using single fiber fragmentation tests, and their effect on mechanical properties is characterized using flexural and interlaminar shear strength tests. It is found that the hexadecylamine grafted CNC coating strengthens the GF-matrix interface by up to 19%, and this enhancement provides additional improvement to the laminate flexural modulus and strength by 36% and 30%, respectively, in comparison to commercially sized (GF)-epoxy laminates with no added CNC. This work demonstrates the potential of using CNC in GF sizing, as well as the importance of CNC surface chemistries on enhancing GF-epoxy interfaces and composite performance.

1 | Introduction

Renewable and versatile cellulose nanomaterials (CNMs) have been used to enhance the mechanical performance of many different resin systems, including both thermoplastics such as polyethylene and polypropylene, and thermosets such as epoxies and polyesters [1–5]. Cellulose nanocrystals (CNCs) in particular, which are rod-like particles with high aspect ratio and stiffness produced following acid hydrolysis of cellulosic materials (e.g., woody plants), have been successfully used to reinforce not only polymer matrices but also composite interfaces in combination with glass fibers (GFs), carbon fibers, aramid fibers, and carbon nanotubes [4, 6–9]. The hydrophilicity of CNCs is

a frequent challenge for most applications involving dispersion in non-polar solvents and hydrophobic resins, necessitating the development of novel approaches to incorporate CNC and the pursuit of hydrophobic chemical modifications to the particles themselves.

Within GF reinforced epoxy composites, the addition of CNC powders to the resin matrix has often resulted in agglomeration, introducing flaws and defects that affect the composite performance [10]. Once dried, CNCs are difficult to redisperse as they form a strong hydrogen bond network that requires extensive mechanical treatment to break up, potentially damaging the particles in the process [1, 11]. These challenges

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Summary

- Hydrophobic modification of cellulose nanocrystals (CNCs) for polymer composite application.
- Scalable slot-die coating on a roll-to-roll to deposit CNCs onto glass fiber (GF) fabrics.
- CNC coating enhances interfacial adhesion between GF and epoxy.
- CNC-coated GF laminates have enhanced flexural and interlaminar properties.

can be addressed through chemical surface modification of CNC to improve their compatibility with hydrophobic media. Some successful methods for CNC modification, including surface esterification, silylation, alkyl-chain grafting, and ion exchanges, have yielded CNC particles with better in-matrix dispersibility due to increased hydrophobicity or reduced interparticle CNC–CNC interaction, which typically drives aggregation [9, 11–13].

Another solution which circumvents the dispersibility problem involves coating CNCs in their aqueous form onto fiber surfaces, using methods such as dip/immersion coating, spray coating, and slot die coating which deposit the particles on the fibers prior to resin infusion [7, 14–16]. To produce GF sizings (i.e., coatings) with CNC, low concentration aqueous CNC dispersions have also been emulsified with epoxies using surfactants and dispersants such as pluronic and poly-L-lysine prior to the deposition step [14, 15]. These methods rely on strengthening the GF–CNC–epoxy interactions at the interphase, rather than the formation of CNC networks throughout the polymer matrix to enhance composite performance [6, 17]. Furthermore, coating CNCs onto GFs requires a much lower overall CNC loading to achieve comparable enhancement compared to incorporating the particles into the matrix [6, 10].

Although the reinforcement CNCs provide at the GF-matrix interface relies heavily on the mechanical interlocking of epoxy chains onto the roughened surface of CNC-coated fibers, the chemical bonding of CNCs with the epoxy matrix and GFs can also play an important role [2, 17]. As typical GF sizings contain multiple components, including epoxies, lubricants, film formers, and silanes, all of which would not mix readily with aqueous CNC, the use of chemically modified CNCs in coatings could thus provide additional compatibility, interaction, and cross-linking to strengthen the GF-CNC-epoxy interphase [18]. The focus of this study is therefore to explore the use of functionalized CNCs as a pathway toward producing improved GF sizing with the combined advantages of mechanical interlocking and chemical bonding. To do so, different types of CNC dispersions—commercial sulfated, ion-exchanged, silylated, oxidized, and oligomerized with tannic acid (TA), and grafted with alkyl amine chains—are slot die coated onto unidirectional GF fabrics prior to the addition of epoxy resin. The resulting composites are characterized in terms of interfacial, flexural, and interlaminar properties to evaluate the influence of differing CNC surface chemistries on mechanical performance.

2 | Experimental

2.1 | Materials

Unidirectional E-glass (TG-13-U) fiber fabric from TEXONIC was used as-received, with the manufacturer's silane sizing intact, as the sizing protects fibers during processing, and its dissolution would introduce damage and surface defects [15, 19]. The fabric is woven with a warp/weft ratio of 99:1, with the weft yarn separating individual E-glass rovings. Commercially available never-dried CNC (CNC-CLF), batch NCV-100-NAL90 dispersion (6 wt% aqueous), treated with sulfate half ester, sodium counterion, was purchased from CelluForce Inc. This dispersion was diluted in DI water for further chemical functionalization. A CNC dispersion with methyl(triphenyl) phosphonium counterions (3 wt% aqueous) was additionally supplied from American University (Washington DC, USA), the production process for which can be found in [11]. TA, hexadecylamine (HDA), HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), (3-Aminopropyl)triethoxysilane (APTES), absolute ethanol (200-proof), NaOH solution (50% w/w), and acetic acid were obtained from Fisher Scientific. For composite production, a two-part system of 635 thin epoxy to 556 hardener was purchased from US Composites.

2.2 | Surface Modification of CNCs

Two types of surface-modified CNCs were produced. For both, the 6wt% CNC-CLF stock is first diluted and magnetically stirred using DI water to a 1 wt% concentration and sonicated in an ice water bath using a Qsonica 500 ultra sonicator for 5 min at a 60% amplitude, with a 5 s pulse and a 3 s off cycle.

The first modification follows the one-pot water-based method for grafting polymer chains onto CNC and cellulose nanofibrils (CNF) as outlined in [2] and [13]. HEPES (0.476 g) was added to 200 mL of 1 wt% CNC-CLF dispersion and stirred until dissolved, and NaOH was used to adjust the pH to 8.0. TA, 0.1 g, was added, and the mixture was magnetically stirred at 200 rpm at ambient conditions for 6 h, turning brown as the TA grafts onto CNC, forming CNC-TA. HDA, 4 g, is dissolved in 50 g of ethanol is then added to the CNC-TA suspension and allowed to react stirring for 3 h. The CNC-TA-HDA product is concentrated by centrifuging at 4000 rpm for 10 min and is washed three times with DI water and anhydrous ethanol. The recovered product was dried in a vacuum oven with desiccants at 80°C and then dispersed in anhydrous ethanol to the concentration of 1 wt% CNC-TA-HDA.

The second modification to produce silylated CNC using APTES is adapted from [20] and [21]. Hundred milliliters of water-ethanol 80/20 (v/v%) with 5 mL of APTES is adjusted to a pH of 4 using glacial acetic acid, after which 32 g of as received CNC-CLF is added to the solution. The mixture was magnetically stirred at ambient conditions for 2 h, after which it was centrifuged at 4000 rpm for 10 min and washed with DI water and absolute ethanol twice to concentrate CNC-APTES and remove excess APTES. A portion of the resulting CNC-APTES gel was dried in a vacuum oven with desiccants at 80°C to measure the concentration (3.5 wt% CNC-APTES);

the remainder of the gel was refrigerated for later use. To produce a coating dispersion, CNC-APTES is diluted to 1 wt% in DI water.

2.3 | Slot Die Coating of GF Fabric

Vacuum-assisted slot die coating on a roll-to-roll, as depicted in Figure 1a, is used to deposit CNC dispersions onto GF fabrics similar to the process described in [22]. The CNC coating formulations used in this study and their abbreviated sample names are summarized in Table 1. The GF fabric was cut into 10×10cm squares and taped onto a vacuum plate, connected to a Robinair 6CFM Vacuum Pump exerting a vacuum pressure of −8.8kPa at the plate inlet. The use of vacuum facilitates the coating penetration and distribution throughout the thickness of the GF fabric. The coating is pumped at a preset flow rate of 7 mL/min through a stainless-steel slot die head forming a coating bead through which the vacuum plate and fabric are carried at a web velocity of 5 mm/s. As a buildup of thicker CNC films on top of GF is undesirable, the combination of flow rate and velocity was chosen such to produce a minimally thin wet film without observed wetting failure and coating breakup [23].

All coated GF fabrics were dried in a vacuum oven at 80°C for 2 h and then stored in a sealed container at ambient conditions.

2.4 | Fabrication of CNC-Coated GF Fabric Composites

Hand lay-up and vacuum bagging only (VBO), as depicted in Figure 1b, was used to fabricate CNC-coated unidirectional GF-fabric laminates of 2-mm thickness. Six layers of GF fabric were brushed with epoxy resin, rolled, stacked unidirectionally, and allowed to gel at ambient conditions for 5 h. The formed laminate was then cured using VBO at 100°C for 1 h and 120°C for 2 h, and post-cured at ambient conditions for 24 h.

2.5 | Characterization Techniques

2.5.1 | Contact Angle Measurements

To evaluate the hydrophobicity of individual CNC dispersions, 1 wt% CNC films were dip coated onto glass slides and dried in a vacuum oven with desiccant at 80°C. Contact angle

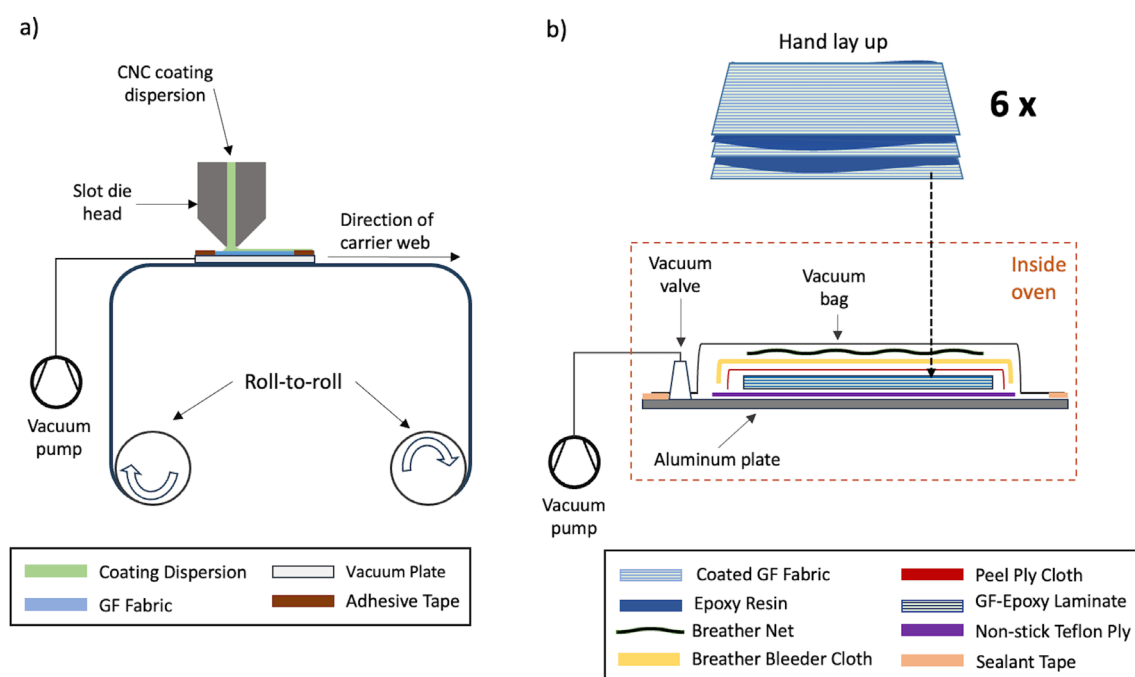


FIGURE 1 | Schematics of (a) slot die coating on a roll-to-roll with vacuum assist and (b) vacuum-bagging only fabrication process for curing GF-epoxy laminates.

TABLE 1 | CNC-coating formulations used in the study.

CNC ID	CNC functionality	Solvent	CNC content (wt%)
CNC-CLF	Sodium sulfate	DI water	1
CNC-MePh ₃ P	Methyl(triphenyl) phosphonium	DI water	1
CNC-TA	Tannic acid	DI water	1
CNC-TA-HDA	Tannic acid and hexadecylamine	Absolute ethanol	1
CNC-APTES	APTES	DI water	1

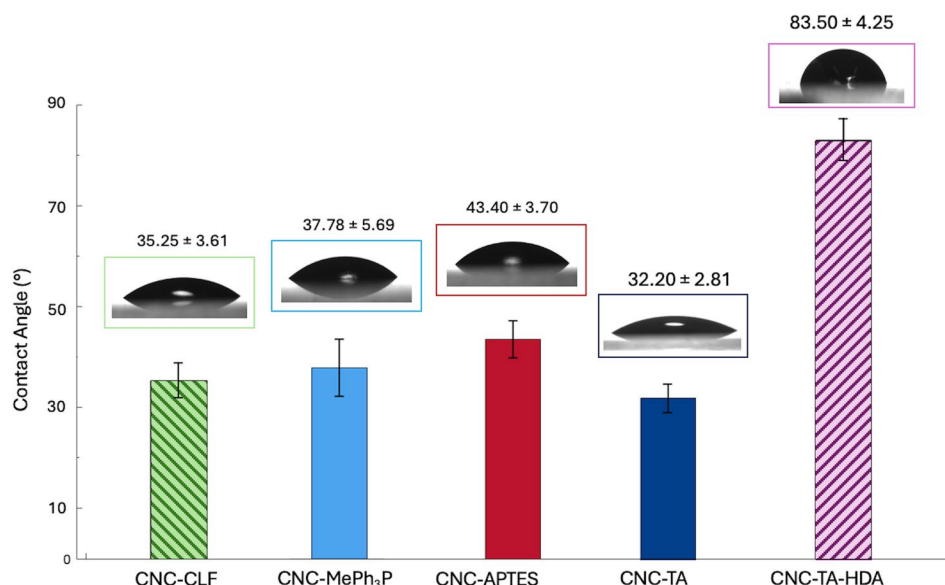


FIGURE 2 | Static contact angles of DI water on CNC films cast onto glass slides. Averages and standard deviation provided for eight measurements.

measurements were obtained with a Rame-Hart goniometer Model 250 with DROPimage Advanced software. Using the sessile droplet method, a droplet of DI water ($4\mu\text{L}$) was dispensed onto the CNC film, and static contact angles on the edges of the droplet were measured.

2.5.2 | Characterization of CNC Coating

All CNC coating dispersions, as listed in Table 1, are characterized using a Nicolet iS5 FTIR with an iD7 ATR Diamond probe with a total of 64 scans per sample generating absorbance spectra between 500 and 4000 cm^{-1} with a 3.86 cm^{-1} step size to confirm the successful grafting of functional groups. FTIR is used to confirm the successful deposition of all CNC coatings onto GF fabric as well. The coating morphology on GF fabrics and individual fibers was examined using a Phenom XL G2 SEM with an accelerating voltage of 10 kV .

2.5.3 | Single Fiber Fragmentation Test

To determine the influence of each CNC coating formulation on fiber-matrix interfacial adhesion, a single fiber fragmentation test (SFFT) was performed [24]. Single fibers removed from the GF fabric were embedded into epoxy coupons as described in [15]. The fully cured coupons were then tensile tested using an Instron Universal Testing Machine 33R 4466 with a load cell of 500 N at an extension rate of 1 mm/min . The stress is gradually transferred through the matrix and fiber-matrix interface, fragmenting the fiber inside until saturation is reached, after which the fragment lengths become shorter than the critical length, cannot reach their ultimate strength, and thus cannot be fractured further. The number of fragments, which correlates with interfacial shear strength (IFSS) is reported in lieu of strength calculations using the Kelly-Tyson model, which, while still commonly used, relies on assumptions inaccurate to GFRP behavior [15, 25]. A DVM6 Digital Microscope with a PlanAPO FOV 12.55 objective lens with CXI lighting is used to count the

number of fragments and to assess the photo elastic fracture patterns.

2.5.4 | Characterization of Composite Properties

The void content and density of GF laminates were measured using the water displacement technique following ASTM D2734. The laminates were subjected to flexural testing and short beam/interlaminar shear strength (ILSS) testing following ASTM 7264 and ASTM D2344, respectively. Both tests were carried out using an Instron Universal Testing machine (model: 68TM-30) with a 30-kN load cell, equipped with a 3-point-bend fixture. For flexural testing, the coupons were cut in the longitudinal direction and tested using a support span to thickness ratio of 32:1 at a crosshead rate of 1 mm/s . The short beam test coupons were tested using a support span of 4:1 and a crosshead rate of 1 mm/s . The cross sections of laminates were examined using a DVM6 Digital Microscope with a PlanAPO FOV 12.55 objective lens and a Phenom XL G2 SEM with an accelerating voltage of 10 kV .

3 | Results and Discussion

3.1 | Characterization of CNC Films and Coatings

3.1.1 | Contact Angle Measurements

All CNC dispersions, diluted to $1\text{ wt}\%$, as listed in Table 1, were coated onto glass slides and the contact angle formed by a sessile droplet of DI water was measured, as shown in Figure 2, providing insight into the successful modification and hydrophobization of CNCs. CNC-CLF films are hydrophilic, with low contact angles of 35° . The modified CNC-MePh₃P and CNC-TA films exhibited similarly low contact angles, although a slight increase to 37° for MePh₃P and a minor decrease to 32° for CNC-TA were noted, which may signify a minor increase and decrease in hydrophobicity, consistent with findings in prior studies [13]. Notable increases

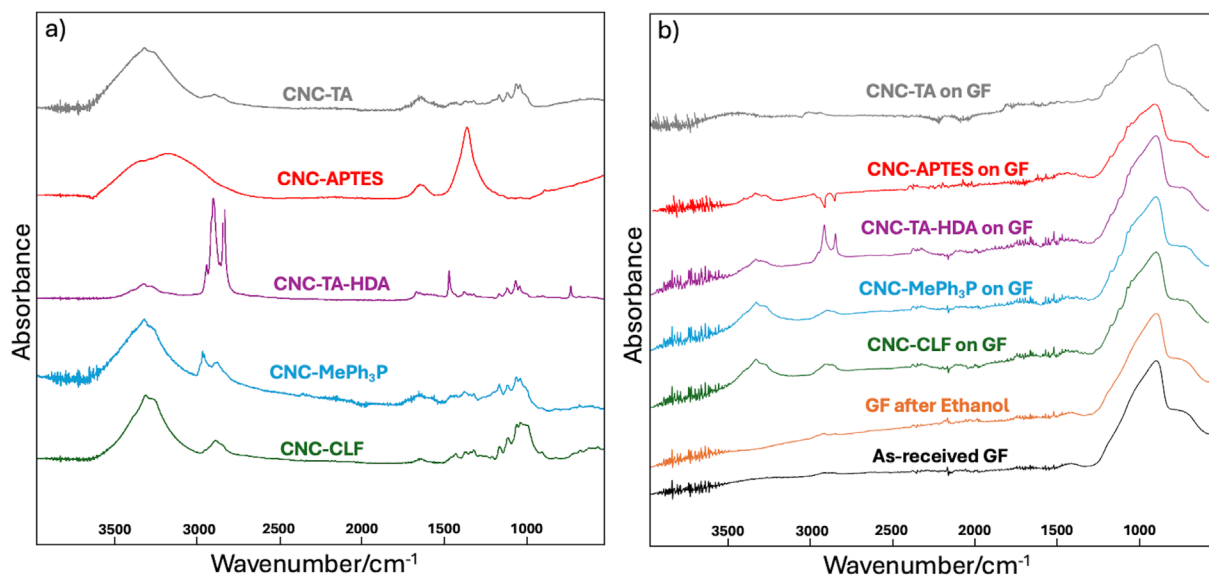


FIGURE 3 | FTIR spectra of (a) dried pure CNC product and (b) E-glass fabrics As-received and coated with the corresponding labeled CNC formulation. Additional spectra for E-glass coated in ethanol is included to assess the effect of non-polar solvent use.

in contact angles to 43° are noted for CNC-APTES, and an even larger one to 84° for CNC-TA-HDA, making it the most hydrophobic formulation, which corroborates its lack of dispersibility in DI water and requires the use of organic solvents to be redispersed.

3.1.2 | FTIR of CNC Coatings

To verify the functionalization of CNCs and the subsequent successful deposition onto GF fabric, FTIR spectra were collected of both pure dried CNC and CNC-coated GF fabrics as shown in Figure 3. All CNC samples exhibited functional groups typical to cellulose with prominent peaks around $3000\text{--}3500\text{cm}^{-1}$ corresponding to stretching vibrations of O—H on pyranose rings [13, 15]. On both pure CNC and coated GF, CNC-CLF, CNC-MePh₃P, and CNC-TA additionally show typical bands between 2800 and 2900cm^{-1} which can be assigned to the abundant C—H bonds in cellulose [1, 15]. The spectra for CNC-CLF and CNC-MePh₃P are nearly identical due to the low concentration of the MePh₃P group, which, whereas difficult to detect on FTIR, was previously distinguishable using X-ray photoelectron spectroscopy (XPS) [14]. The successful grafting of HDA on the CNC-TA-HDA sample can be confirmed from the prominent peak between 2800 and 2940cm^{-1} , corresponding to the CH₂ stretches of the C10 alkyl chain [13]. The silylation of CNC to produce CNC-APTES was confirmed by the appearance of clearer peaks at $1580\text{--}1690\text{cm}^{-1}$, typical of primary amines, and $1200\text{--}1440\text{cm}^{-1}$ typical of Si—C bonds [26, 27].

The spectra for coated GF fabrics all show prominent peaks around 1000cm^{-1} corresponding to the Si—O bond within the E-glass. All samples coated with 1 wt% CNC show a broad peak at $3000\text{--}3500\text{cm}^{-1}$ from the O—H bond in CNC confirming the successful coating deposition. An additional GF sample was produced, coated solely in pure anhydrous ethanol to investigate whether organic solvent use, which was necessary to disperse CNC-TA-HDA, would result in any stripping of manufacturer's silane sizing already present on the GFs. The spectra produced

for As-received and ethanol-coated GF fabric were identical, with both samples still showing minor broad peaks at 2900cm^{-1} which correspond to —CH₃ groups in typical silane sizings.

3.1.3 | SEM of CNC Coating on GF Fabric

To assess the coating morphology of the CNC coatings, representative SEM images were taken of the surface of GF fabrics as well as individual removed fibers. As shown in Figure 4a,b, the surface of as-received GF fabric shows darker spots and regions of pre-existing accumulated sizing or contaminants. For all CNC coating formulations, a thin film is coated right over the sizing layer, sometimes accumulating slightly between the fibers, introducing some thicker regions of the coating, particularly visible in Figure 4c,g for CNC-CLF and CNC-APTES, respectively.

The removal of single fibers, as required for SFFT, from the coated GF fabric introduces defects to the CNC coating as the brittle film tears during the process. The coating thickness and surface coverage on individual GFs is thus slightly varied, with lighter and darker regions visible on all CNC-CLF, CNC-MePh₃P, CNC-TA, CNC-APTES, and CNC-TA-HDA samples. Prior studies using slot die coating to deposit 1 wt% CNC dispersions onto GF rovings have described irregularities and pooling of the low viscosity coating; this issue has, however, been largely corrected through the introduction of vacuum assist to the coating process to remove and redistribute excess fluid [14]. Slightly jagged edges and larger sections of clinging CNC coating were still observed for the CNC-APTES sample, as seen in Figure 4h, suggesting a more uneven film was formed due to the possible cross-linking of APTES with itself as well as CNC, resulting in a greater likelihood of aggregation and a more brittle coating [26, 28]. Although greater irregularity and roughness provide a larger surface area for mechanical interlocking at the interface, agglomerated CNC can also introduce slippage at the interface and reduce stress-transfer efficiency [6].

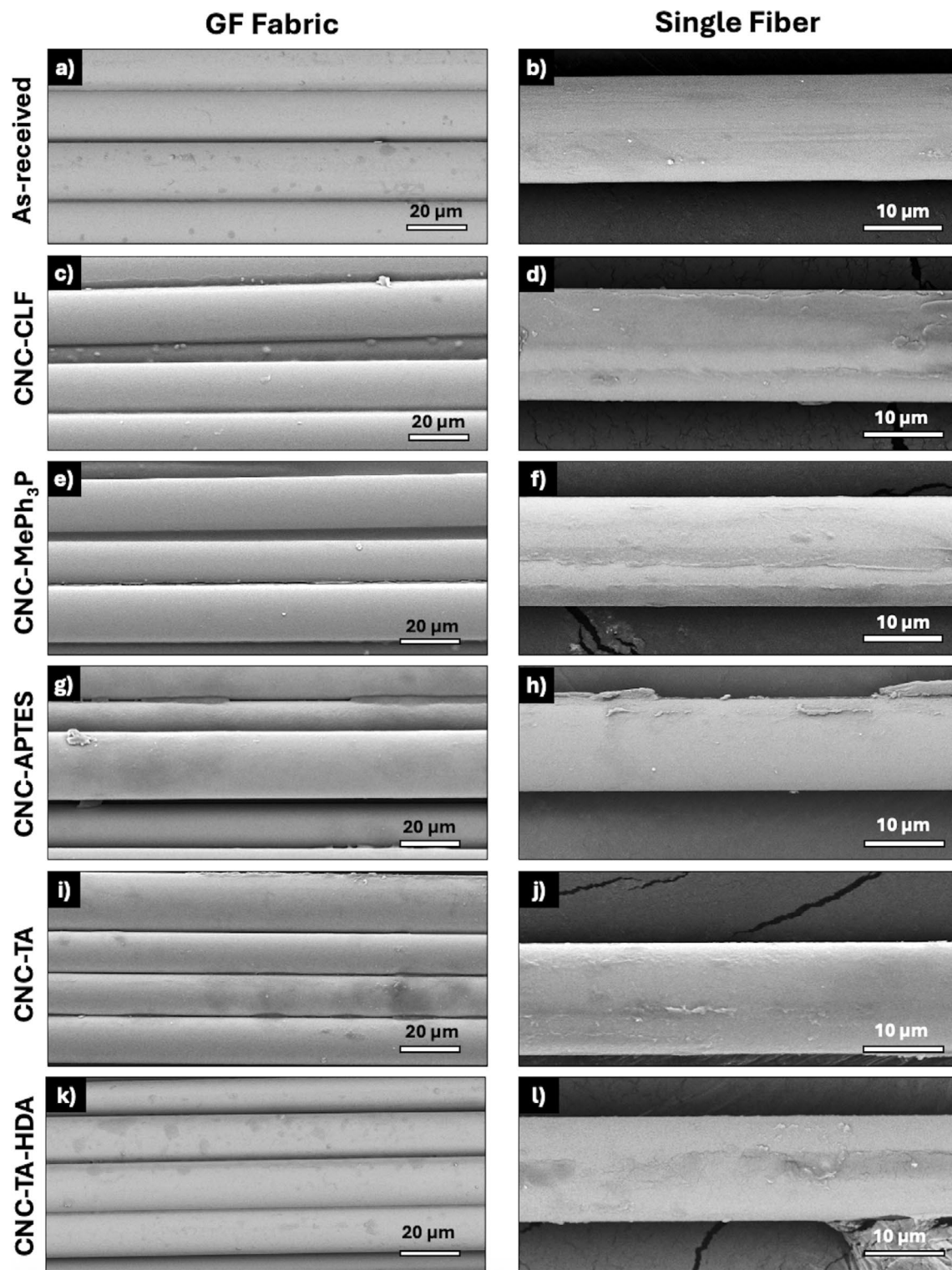


FIGURE 4 | Surface morphology of GF fabric and removed individual fibers for (a, b). As-received, coated in (c, d) CNC-CLF, (e, f) CNC-MePh₃P, (g, h) CNC-APTES, (i, j) CNC-TA, and (k, l) CNC-TDA-HDA.

3.2 | Characterization of Interfacial Properties

To compare the degree of interfacial adhesion provided by each type of CNC, the number of fragments following SFFT are counted and reported in Figure 5. Although the critical fragment length is typically used with the Kelly-Tyson model to

approximate IFSS, the lack of universal methods for determining GF fragment strength in combination with the model's elastic-plastic matrix assumptions, which epoxy does not adhere to, can result in poor approximations of real IFSS for the GF-epoxy systems; thus, the fragment count, which strongly correlates with the IFSS, is used for comparative purposes [15, 25].

The fragmentation increased with the addition of most CNC coatings, showing that CNC successfully reinforced the interface, resulting in better fiber-matrix adhesion. A single exception was the CNC-TA sample; this divergence could be attributed to the formulation being the only one that did not increase the CNC film hydrophobicity but, in fact, may have made it more hydrophilic. Samples CNC-MePh₃P and CNC-APTES, whereas functionalized to be more hydrophobic, did not outperform CNC-CLF. In the case of MePh₃P, the ion disrupts CNC-CNC interactions, which may have resulted in a brittle film more prone to damage, creating an inconsistent CNC coating and interface; additionally, the reduced interfacial energy of CNC-MePh₃P can also cause it to bond more poorly with the resin matrix [11]. Although the silane and amines attached to CNC-APTES

should promote further bonding to both the fiber surface and epoxy, the use of already silane-sized GFs in this instance may have negated some benefit provided by additional APTES, resulting in similar performance to that of the CNC-CLF coating [16]. Furthermore, irregularities resulting from APTES and CNC cross-linking prior to exposure to epoxy may have introduced further interfacial defects [26]. The sample coated in CNC-TA-HDA, the most hydrophobic formulation, performed the best, resulting in a 28% increase in fragmentation compared to As-received GF. For comparison, commercial CNC-CLF provided an increase of 15% in fragmentation compared with the As-received sample. Besides the hydrophobicity, this improvement could be attributed to the addition of long alkyl chains attached to CNC aiding the formation of network structures at the interphase, and the secondary amines allowing the particles to chemically bond with the epoxy matrix more effectively [29].

The examination of fiber fracture modes following SFFT can offer a qualitative assessment of the interfacial adhesion. For a strongly bonded interface in GF-epoxy systems, the load transfer to the fiber is sufficient to propagate the crack into the matrix, forming a combined double cone or vertical/disk shape; however, poor interfacial strength and adhesion is often represented by a pattern of debonding when the load transfer is no longer sufficient to initiate further fiber cracking and only friction between fiber and matrix occurs [6, 15, 30, 31]. As shown in Figure 6, all samples, including the As-received GF, exhibited mostly double-cone shaped or vertical/disk shaped cracks propagating into the surrounding matrix, signifying good adhesion between the underlying sizing, CNC, and epoxy. However, the samples with CNC-MePh₃P and CNC-TA, pictured in Figure 6c,e, also

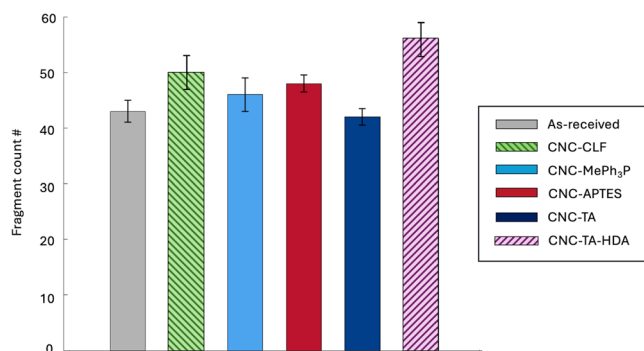


FIGURE 5 | SFFT fragment count for all formulations. The error bar represents 1 standard deviation. Cross-hatched bars represent samples that significantly outperformed the As-received sample for a confidence interval of 99%.

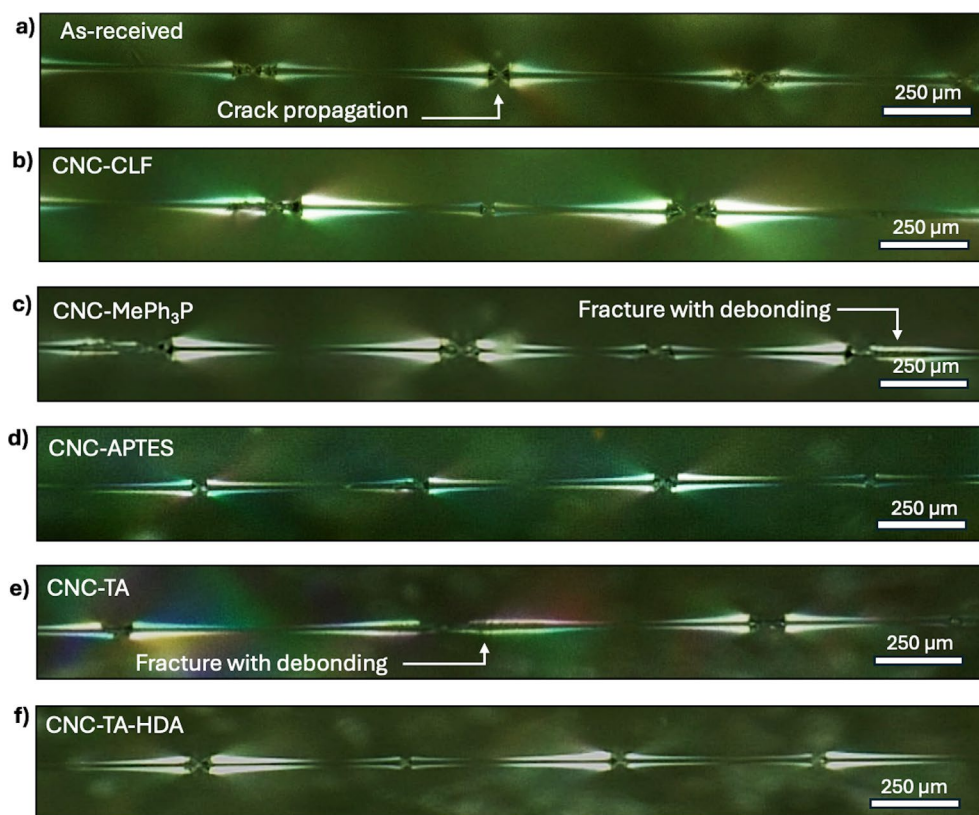


FIGURE 6 | Optical micrographs of fractured GF in epoxy following SFFT for (a) As received, (b) CNC-CLF, (c) CNC-MePh₃P, (d) CNC-APTES, (e) CNC-TA, and (f) CNC-TA-HDA formulations.

showed areas of frictional debonding surrounding several fractures, signifying inconsistent interfacial adhesion, supporting the observed underperformance compared with the CNC-CLF formulation.

To evaluate whether the improvements to fragmentation are statistically significant, the Tukey–Kramer method or Tukey's HSD test were performed to compare the fragmentation of all formulations and also provide pairwise comparisons between individual samples. For a confidence interval of 99%, only CNC-CLF and CNC-TA-HDA were found to have statistically significant improvement in fragmentation when compared with the As-received GFs. The CNC-TA-HDA sample was also found to be significantly different from CNC-CLF ($p=0.01$), demonstrating that the functionalization using HDA improves the CNCs' ability to enhance interfacial strength. As the two best performing formulations, CNC-CLF and CNC-TA-HDA coated GF fabrics were used to fabricate unidirectional laminates and their effect on mechanical properties are evaluated.

Even though the present commercial sizing is formulated to bond well to epoxy matrices, as evident by the low incidence of frictional debonding following SFFT, the addition of CNC was able to further improve on the GF-matrix interfacial adhesion. Although prior studies testing the IFSS of GF-CNC-epoxy

showed that the deposition of CNC onto silane-sized GFs produced more consistent enhancement when pre-dispersed with epoxy-emulsions and surfactants, the functionalized CNC in this study produced significant enhancement when deposited without additional compatibilizers, allowing for the formulation of simpler coatings with fewer components [14, 15]. For GF-fabric laminates, the application of sizing formulations with higher solids content would additionally be undesirable as thicker coatings could cause the formation of caked films on top of GF bundles, resulting in poorer resin infiltration [14].

3.3 | Mechanical Properties of Composites

Unidirectional laminates were fabricated using GF fabrics and epoxy, and the effect of CNC-CLF and CNC-TA-HDA coatings on the composite's flexural and interlaminar properties is evaluated and reported in Figure 7. The flexural modulus and strength were found to increase following the addition of both CNC-CLF and CNC-TA-HDA coatings. The largest improvement came from CNC-TA-HDA, with an increase of 36% in modulus and 30% in strength compared with the As-received laminate. The hydrophobized CNC-TA-HDA also outperformed the commercial CNC-CLF by 9% in modulus and 19% in strength, continuing the trend observed from SFFT, showing

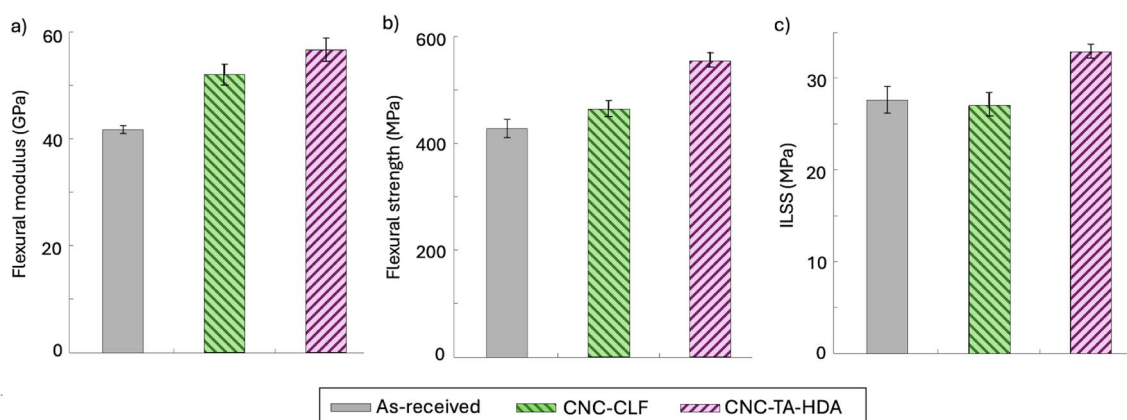


FIGURE 7 | Comparison of (a) flexural modulus, (b) flexural strength, and (c) interlaminar shear strength of As-received, CNC-CLF, and CNC-TA-HDA-coated GF fabric laminates. Error bar represents 1 standard deviation.

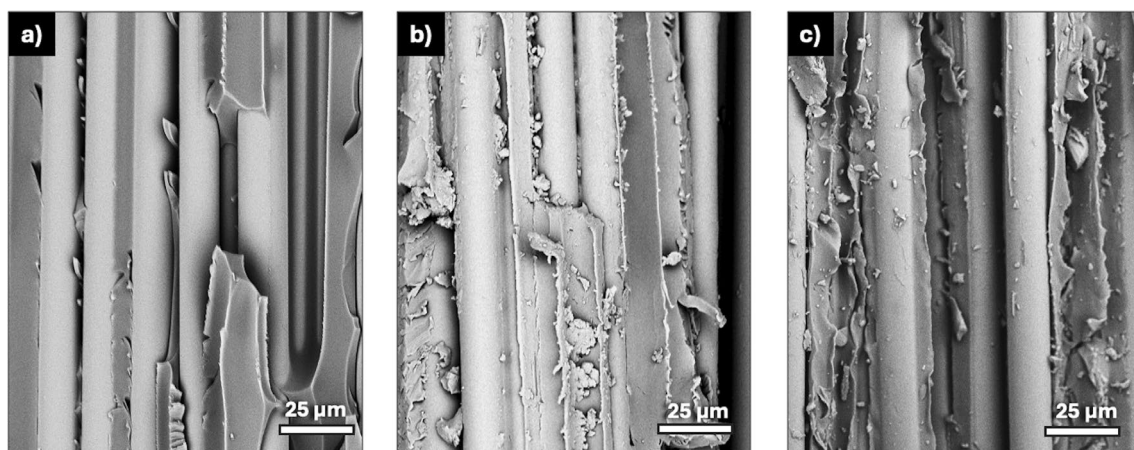


FIGURE 8 | Fracture surfaces from flexural testing of (a) As-received, (b) CNC-CLF, and (c) CNC-TA-HDA laminates.

that the modification resulted in a CNC coating that was more compatible with the GF-epoxy system. For both CNC formulations, the chemical bonding of CNC with epoxy likely contributed additional reinforcement, as the hydroxyl and secondary amine groups in CNC-CLF and CNC-TA-HDA can participate in cross-linking reactions with epoxy, forming stronger interphases [2, 17].

Although longitudinal properties of unidirectional laminates in theory exhibit low sensitivity to interfacial adhesion, prior studies have indicated that the addition of CNCs may result in an extended distinct GF-CNC-epoxy interphase with a higher modulus from the surrounding matrix, often forming a gradient-like zone allowing for more efficient stress transfer resulting in enhanced on-axis properties [7, 8, 17, 24]. These improvements are attributed to the CNC reducing the incidences of stress concentration and mitigating the large modulus contrast between stiff GF and soft epoxy matrix [8, 17, 24]. Molecular dynamics simulations of GF-epoxy interphases have likewise reported interfacial thickening following the addition of silane and CNC coatings onto GF surfaces, improving the energy absorption and strength of composites [32, 33]. Deposited individually, silane facilitates GF-matrix bonding through covalent bonds, and CNC

is shown to improve interfacial adhesion via hydrogen bonding and mechanical interlocking at the interphase [32, 33]. When both are coated onto GF surfaces, CNC can become embedded in the silane coating from interpenetration, resulting in a thicker interphase region with stronger shear resistance; this synergistic effect further improves the IFSS and alters the local failure mode from adhesive to cohesive [32].

The enhanced adhesion and interfacial bonding between GF-matrix can also be corroborated by examining the fracture surfaces of laminates following flexural testing, as shown in Figure 8. Although the fracture of the As-received sample, in Figure 8a, shows clean and smooth debonding dominating the surface, the laminates produced using CNC-coated GF fabrics, in Figure 8b,c, exhibit much rougher fracture surfaces with more matrix residue stuck to GFs, suggesting that the GF-matrix interface has been altered. These results reflect the findings of prior studies incorporating both CNC into the epoxy matrix and at the GF surfaces [6, 10, 17].

Short beam strength tests were conducted to measure the apparent ILSS between As-received, CNC-CLF, and CNC-TA-HDA samples, as reported in Figure 7c. The 3-point-bend loading of the test often induces complex local stresses resulting in mixed-mode failures within the composites; thus, the calculated strength, which is approximated directly from maximum load, may not produce true ILSS values [34, 35]. However, for simple geometries such as unidirectional laminate plies used in this study, the test can still provide approximate values for comparative purposes.

Consistent with IFSS and flexural performance, laminates fabricated using CNC-TA-HDA coated GF fabric produced the highest apparent ILSS, outperforming the As-received

TABLE 2 | Void content and density of GF-epoxy laminates.

Laminate sample	Void content (%)	Density (g/cm ³)
As-received	2.82% ± 0.73%	1.89 ± 0.01
CNC-CLF	4.06% ± 2.13%	1.90 ± 0.03
CNC-TA-HDA	2.50% ± 1.77%	1.91 ± 0.02

Note: The average is reported for eight samples with 1 standard deviation.

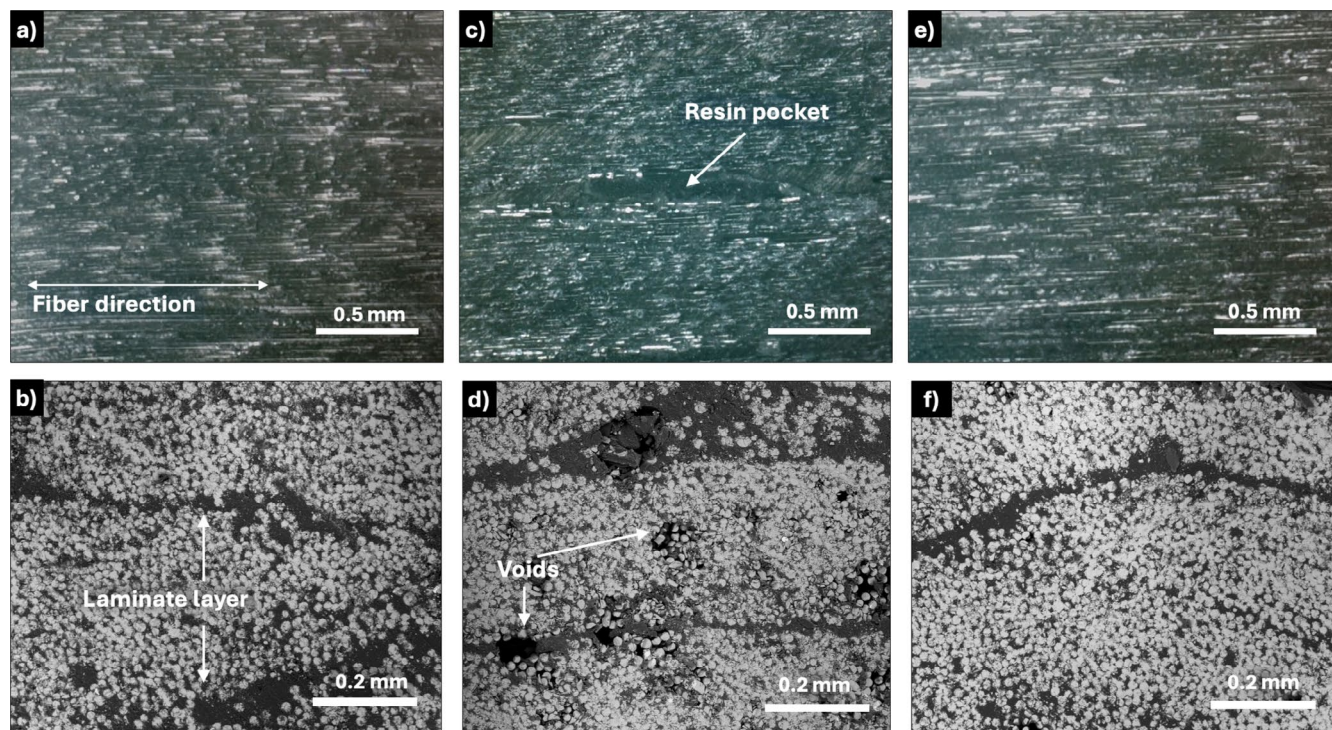


FIGURE 9 | Representative optical microscopy and SEM images of unpolished longitudinal and transverse cross sections of laminates (a, b) As-received, (c, d) CNC-CLF, and (e, f) CNC-TA-HDA.

sample by 19%. However, the use of CNC-CLF did not result in any improvement to the apparent ILSS of the laminates, despite enhancing the IFSS and flexural performance. This discrepancy may be explained by a higher porosity and interlaminar defects present in the CNC-CLF sample, as the more hydrophilic CNC coating may have caused wetting issues and inconsistencies with resin distribution during hand lay-up and vacuum-bagging, giving rise to “meso-void” formation between the individual GF fabric tows and laminate layers [36]. As reported in Table 2, the void content of CNC-CLF is not only higher but also has a higher standard deviation, signifying larger inconsistencies in porosity throughout the laminate. Optical microscopy and SEM were used to examine the cut surfaces of 5 short beam coupons. Although As-received (Figure 9a,b) and CNC-TA-HDA (Figure 9e,f) have relatively consistent fiber and matrix distribution with thin layers of resin delineating the separate rovings within individual laminate layers, the CNC-CLF laminate, shown in Figure 9c,d, shows a presence of larger resin-rich pockets and voids between and within the GF fabric layers, reflecting the higher void content and lack of uniformity. For a matrix and interphase-dominated mechanical property such as ILSS, these resin pockets and interlaminar voids prove to be a significant drawback as even a minimal increase in void % has been shown to cause a decline in the overall composite performance, creating areas of interlaminar stress concentration and negating the benefits provided by the enhanced interfacial bonding provided by CNC [36].

4 | Conclusions

In this study, different types of functionalized CNCs were coated onto GFs, and their influence on the GF-epoxy matrix interface and laminate properties was evaluated. The hydrophobicity of CNCs was found to influence interfacial adhesion, as the most hydrophobic modification (CNC-TA-HDA) produced the largest increase in fragmentation of 28% as compared with As-received GF following SFFT, whereas lowering CNC hydrophobicity (CNC-TA) resulted in a worse performance. The Tukey's HSD test ($p < 0.01$) additionally confirmed that the CNC-TA-HDA coating produced increased fragmentation significantly higher than not only the As-received GF but also all other CNC coatings. It was also found that increased hydrophobicity, on its own, however, did not improve the capability of CNCs to reinforce interfaces as samples. For example, CNC-MePh₃P did not increase interfacial adhesion compared with CNC-CLF, suggesting that the surface chemistry and the specific functionalities of the CNC, allowing the particles to chemically bond with the GF or matrix, also play an important role.

The addition of CNC-CLF coating also improved the flexural properties of the laminate, providing an increase of 25% in modulus and 9% in strength, demonstrating that the use of commercial CNC can enhance laminate performance. However, the greatest improvement was achieved with the CNC-TA-HDA formulation, which enhanced both the flexural and interlaminar properties of composites, resulting in an increase of 36% and 30% in flexural modulus and strength, and 19% in apparent ILSS compared with as-received GF. These improvements can likely be attributed to higher CNC hydrophobicity and

compatibility with epoxy resin and more consistent resin wetting [37]. Furthermore, the grafted long HDA chains provide additional entanglement and secondary amines to enhance bonding with the epoxy matrix.

These results indicate that coating chemically functionalized CNC onto silane-sized GFs is a promising method to significantly improve the interfacial GF-matrix bonding, outperforming regular silane sizing on GFs on its own, and providing greater enhancement compared with commercial sulfated CNCs, taking advantage of the synergistic effect of mechanical interlocking and chemical bonding at the interphase. This work provides a path toward formulating novel and improved sizings containing renewable nanoparticles as an alternative or addition to silane-based sizings. As all mechanical tests are conducted at ambient temperatures, further work is required to evaluate the effect of processing conditions, and the influence of CNC coatings and their functionalization on the thermal properties of laminates. Additionally, as all formulations are deposited using one set of identical coating parameters and the same dispersion concentrations, more experimental work as well as modeling may help optimize the coating parameters and provide a more complete procedure for sizing GFs using functionalized CNC.

Author Contributions

Kim Anh Pham: investigation, writing – original draft, validation, methodology, writing – review and editing, formal analysis, visualization. **Tequila A. L. Harris:** writing – review and editing, supervision, resources, conceptualization, funding acquisition, methodology. **Robert J. Moon:** writing – review and editing, supervision, resources. **Kyriaki Kalaitzidou:** conceptualization, writing – review and editing, supervision, resources, funding acquisition, methodology, project administration.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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