

The effect of nanocellulose coating on S2-glass and E-glass fabric composites

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Abstract

In this study, unidirectional E-glass and S2-glass fabrics are coated with cellulose nanocrystals (CNC), and the influence of the coating on the glass fiber (GF)-epoxy matrix interfacial properties and GF fabric-epoxy laminate tensile properties are investigated. The methodology and processing conditions for vacuum-assisted slot die coating of CNC dispersions onto GF fabrics are described. Scanning electron microscopy (SEM) and single fiber fragmentation test (SFFT) results determined that the addition of vacuum assist was crucial to producing uniform CNC coatings, preserving good fiber separation, and producing consistent interfaces for both E-glass and S2-glass composites. The deposition of CNC onto E-glass fabrics increased the fragment count following SFFT from 43 to 50, correlating with a fiber-matrix interfacial adhesion enhancement of 14 %, and resulted an increase in on-axis tensile strength, from 718 to 823 MPa, a total of 15%, for unidirectional E-glass/epoxy laminates.

Keywords

Cellulose nanocrystals, composite, glass fibers, polymer, slot-die coating

Introduction

Glass fiber (GF) reinforced polymer composites are versatile materials that can be tailored to meet various applications due to their engineered mechanical and thermal properties¹ and their corrosion or alkali resistance among other advantages. E-glass and S-glass are considered leading types for structural composite reinforcements, with E-glass being the most common, owing to its lower cost and earlier development.^{2,3} S-glass, or S2-glass, also called structural glass, outperforms typical borosilicate E-glass in tensile strength and is subject to higher cost.⁴

Commonly used in the automotive industry, the current challenge is to improve GF composite mechanical performance while reducing their weight, as even a 10% reduction in vehicle weight can improve fuel economy by 6%–8% while providing a 14% increase in driving range for electric vehicles.^{5,6} A demonstrated approach to lightweighting of GF composites is the enhancement of the GF-polymer interfacial interactions through the addition of nanomaterials, which can allow for the reduction of GF content, the main reinforcement and the heaviest component in the formulation. The use of cellulose nanomaterials as reinforcement has been shown to enhance the mechanical properties of E-glass/epoxy composites with as low as 1 wt % added as either filler in the matrix or sizing on the GF leading to an 8%–10% density decrease.^{7–10}

Cellulose nanomaterials are cellulose-based nanosized particles typically extracted from woody plant biomass, with particles produced by acid hydrolysis generally called cellulose nanocrystals (CNCs), having a spindle-like particle morphology.¹¹ Adding CNCs into the polymer matrices can result in the enhancement of the composite mechanical properties, although in excess the particles can create defects due to their propensity for self-aggregation.⁹ Depositing CNCs directly onto the fiber surface bypasses the difficulties with mixing CNCs into polymer resins and allows it to directly influence the fiber-polymer interface, improving the interfacial adhesion and strength.^{8,12–14} While prior studies have investigated the effect of CNC

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coatings on E-glass-epoxy interfaces, their use on S2-glass composites has been limited.

A novel method explored for depositing CNCs onto GF fabrics is slot die coating. A scalable and pre-metered process, the coating dispersion is pumped at a set flow rate through a fixed slot gap onto a moving substrate forming a thin liquid film.¹⁵ Prior trials utilizing slot die coating of CNCs onto E-glass rovings have resulted in poor coating distribution forming a caked film on the top and the sides of the fiber rovings while leaving the bottom minimally coated.¹⁰ This morphology suggests that while the capillary and slot die coating bead pressures were sufficient at driving the liquid through the fiber gaps, they were insufficient in ensuring homogeneity in the coating of GF through the thickness of the fiber roving.¹⁰ The technical challenge that this study addresses is how to coat/size individual GFs within a roving/fabric, (e.g., a porous media) throughout its thickness i.e., how to control the fluid penetration depth not just create a coating/barrier layer on a porous substrate, to produce a uniformly sized GF fabric.

In this work, the use of vacuum-assisted slot die coating to deposit CNCs onto both E-glass and S2-glass fabrics, and the subsequent effects of the coating on the fiber-matrix interface, composite quality, and tensile properties are investigated. The coating process is conducted on a roll-to-roll (R2R) manufacturing system integrated with the slot die and vacuum platform. The GF fabrics are characterized using scanning electron microscopy (SEM), optical microscopy, and Fourier transform infrared spectroscopy (FTIR). Unidirectional continuous GF fabric-epoxy composites are then fabricated, their quality is assessed using density and void content measurements, and single fiber fragmentation test (SFFT), and tensile tests are conducted to determine the effect of the coating methodology and composition on the fiber-matrix interfacial interactions and unidirectional laminate properties.

Materials and methods

Materials

The coating solution contains DGEBA low viscosity epoxy, Pluronic P123, and 3 wt% CNC functionalized with methyl (triphenyl) phosphonium with a density of 1.6 g/cc on

average, supplied from American University. Details of the CNC functionalization and material characteristics are given within,^{16–18} but a brief description is given here for completeness. Ion exchange was used to replace sodium cations of a starting sulfated CNC suspension produced by sulfuric acid hydrolysis, neutralized to sodium form, and having a 0.95% mass fraction of sulfur on a dry basis.¹⁸ The degree of ion exchange of sodium to phosphonium cations was approximately 80%. The resulting functionalized CNCs had an average diameter of 6 nm and length of 130 nm. The GF fabrics used are unidirectional S2-glass fabrics with an average reported density of 2.42 g/cc, and fiber diameter of 9 μm , and E-glass unidirectional fabric with an average reported density of 2.50 g/cc, and average fiber diameter of 18 μm . Both types of fiber are pre-sized and were placed uniaxially as warp yarn rovings and held together using fill yarn in Lowmelt Heatset coating in the perpendicular direction. The S2-glass fabric thickness is 0.28 mm, and the E-glass fabric thickness is 0.34 mm per specifications provided by suppliers. For composite production, DGEBA epoxy and amine hardener are used as a part of a 2:1 ratio, with a combined experimentally measured density of 1.1 g/cc. The materials used in the vacuum bagging only (VBO) process including the mold release film, peel ply, breather bleeder cloth, release bag, and mesh.

Coating solution preparation

The coating solutions were prepared following the procedure described in our prior work.¹² A primary coating solution composition of 5 wt% epoxy emulsion (4 wt% thin epoxy and 1 wt% PL123) and 1 wt% CNC, named 5EM1CNC, was chosen due to demonstrated superior performance and is used to determine an optimal set of slot die coating parameters.¹⁰ A formulation with increased CNC concentration, 5EM2CNC, containing 5 wt % epoxy-emulsion and 2 wt% CNC was also used in the study. Samples containing 5EM1CNC solution applied to the substrate in two passes are denoted as 5EM1CNC 2x. As-received GF fabrics with no added coating are denoted as AR. All sample names and their corresponding compositions along with glass fiber fabric types are reported in Table 1.

Table 1. Naming scheme for all coating formulations and fiber types.

Sample name	Fiber type	Emulsion content	CNC content	Coating passes
AR-S	S2-glass	N/A	N/A	0
5EM1CNC-S	S2-glass	5 wt%	1 wt%	1
5EM2CNC-S	S2-glass	5 wt%	2 wt%	1
5EM1CNC 2x-S	S2-glass	5 wt%	1 wt%	2
AR-E	E-glass	N/A	N/A	0
5EM1CNC-E	E-glass	5 wt%	1 wt%	1

Vacuum-assisted slot die coating of CNC dispersions onto fabric

For each experiment, a 10×10 cm square of GF fabric was taped down on a stainless-steel vacuum plate with the fibers oriented in the direction of flow, designated as the x -direction, and coated using a slot die on a R2R system, similar to that depicted in Figure 1. The vacuum plate was connected to a Robinair 6CFM Vacuum Pump and trials were conducted with and without the vacuum during the coating deposition. The vacuum pressure applied at the vacuum plate inlet was measured to be -8.8 kPa using a Dwyer-Omega HHP240 Digital Manometer. The solution was pumped from 20 mL, 22 mm diameter Norm-Ject syringes by a syringe pump through a slot die with a width of 100 mm and a slot gap (W) of 0.16 mm. The downwards flow of fluid penetration is designated as the $-z$ -direction. The coating gap (H) was maintained at 0.3 mm. The solution flow rate (Q) and the velocity of the polyethylene terephthalate (PET) carrier web (v) were varied to establish operating parameters at which the coating bead was stable. The GF fabric was completely coated without having any dry spots and dried in a vacuum oven at 60°C and -0.08 MPa for 2 h. For trials requiring multiple passes, the previously coated and dried fabric was turned over, reattached to the vacuum plate and all steps were repeated.

Coating parameters for the 5EM1CNC solution were initially established by varying the solution flow rate at a set web velocity until a stable coating bead was produced. The coating experiments began with a low solution flow rate of $Q = 1$ mL/min at a web velocity of $v = 5$ mm/s, which was used in our prior slot die coating studies.¹⁰ Experiments conducted at these coating parameters, resulted in an unstable bead with coating breakage and incomplete fiber coverage. Thus, the coating flow rate was gradually increased until incomplete coating, as depicted on S2-glass in

Figure 2(a)), was no longer present but a complete coverage as shown in Figure 2(b) was achieved. Both S2-glass and E-glass fabrics required an increase in coating flow rate to produce complete coverage. A lower bound of a partial coating window combining Q and v parameters for S2-glass is shown in Figure 2(c), summarizing the combinations which resulted in broken and complete S2-glass fabric coating. Using a ratio of working values for Q and v , additional Q and v combinations were linearly extrapolated to increase the rate of operation. This method effectively yielded additional combinations that produced fully coated samples as reported in Table 2 for both S2-glass and E-glass fabrics. The same Q and v values were used to deposit the 5EM2CNC solution, i.e., solution with double the amount of CNC onto the S2-glass fabrics. For the purposes of this study, only the combinations of $Q = 3$ mL/min and $v = 5$ mm/s for S2-glass, and $Q = 5$ mL/min and $v = 5$ mm/s for E-glass fabrics are used.

Characterization of coated GF fabrics

A Nicolet iS5 FTIR with an iD7 ATR Diamond probe was used with a total of 32 scans per sample generating absorbance spectra between 397 and 4000 cm^{-1} with a 3.86 cm^{-1} step size. The coated and AR GF fabrics were examined using the Leica DVM6 Digital Microscope with a PlanAPO FOV 12.55 objective lens, and sputter coated with gold using Zeiss sputter-coater for characterization using a Phenom XL G2 SEM with accelerating voltage of 10 kV. Additionally, to determine the total coat weight deposited by the slot die coating process, the entire coated GF fabric is weighed before and after the coating and drying steps. Coating thickness on top of GF fabrics is measured from SEM images of fabric cross sections with ImageJ image processing software; an average of 20 measurements is reported.

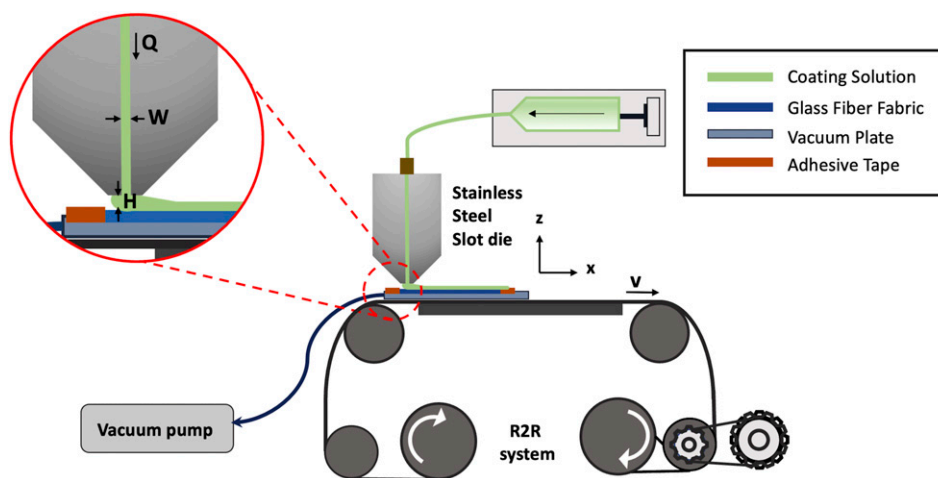


Figure 1. Schematic of slot die coating with vacuum assist on a roll-to-roll system.

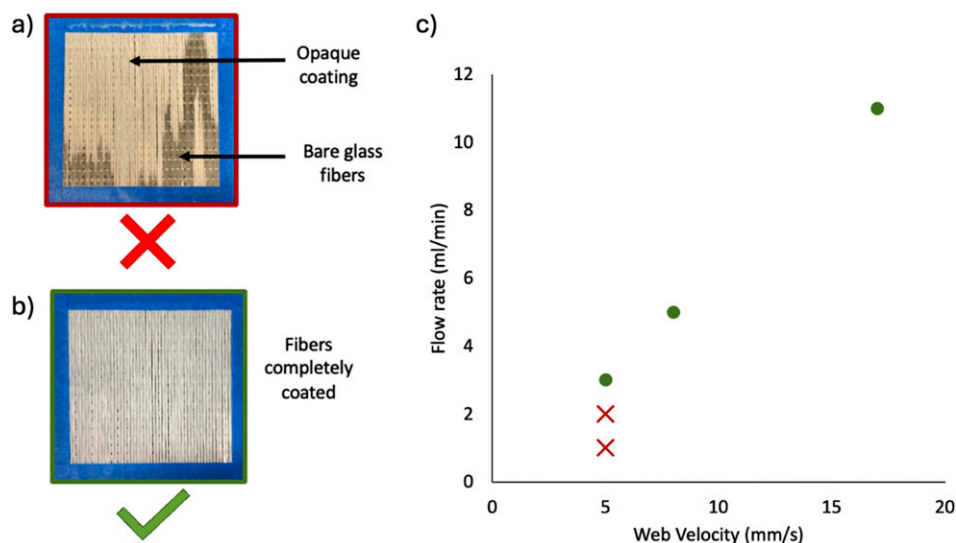


Figure 2. Representative images of S2-glass fiber fabric coated in SEMICNC at parameters (a) outside of operating limits and (b) within operating limits, along with (c) lower bound of coating window established for S2-glass fiber fabric.

Table 2. Operating parameters for fully coated S2-glass and E-glass fabrics.

GF fabric type	Solution flow rate (Q) (mL/min)	Web velocity (v) (mm/s)
S2-glass	3	5
S2-glass	5	8
S2-glass	11	17
E-glass	5	5
E-glass	11	11
E-glass	17	17

Fabrication and characterization of GF/epoxy laminates

Composites were produced using a hand lay-up process depicted in Figure 3(a)). Epoxy to hardener at a ratio of 2:1 was mixed and degassed for 15 min in a vacuum oven at -0.08 MPa. GF fabric layers were then brushed with the resin, stacked in 0° unidirectional orientation, rolled using a rolling pin, and pre-cured at room temperature for 5 h, allowing the epoxy resin to begin gelling prior to the application of heat. Due to the low viscosity of the resin, immediate curing using VBO would result in over-bleeding, high resin matrix loss, and poorly wetted areas creating voids.^{19,20} The composite was fully cured using a VBO process at a vacuum pressure of -28 in Hg, for 1 h at 100°C and then 2 h at 120°C , and then allowed to post-cure at room temperature for 24 h according to.²¹ The resulting laminate plate with dimensions of approximately $100 \times 100 \times 1$ mm was cut into coupons and tabbed with GF-epoxy tabs at the ends as shown in Figure 3(b)).

Single fiber fragmentation test

Single fiber fragmentation tests (SFFT) were performed to assess the influence of coatings on the fiber-matrix interfacial adhesion. For each sample, 10 coupons were fabricated by embedding a single fiber removed from fiber fabrics into an epoxy coupon with a gauge length of 2.5 cm, following the procedure outlined in prior studies.^{10,12} The coupon is tensile tested on an Instron 33R 4466 with a load cell of 500 N, shown in Figure 3(c)) at an extension rate of 1 mm/min. Throughout the test, the stress is transferred through the coupon to the embedded fiber, fragmenting it until saturation (maximum fragment number) is reached, whereupon the number of fragments produced and the fracture morphology is assessed using the DVM6 Digital Microscope with a PlanAPO FOV 12.55 objective lens with CXI lighting. Due to the non-universal methodologies used to calculate interfacial shear strength (IFSS) of polymer matrix composites, the number of fiber fragments, which correlates with IFSS, is used to compare the interfacial properties of tested composites instead.¹⁰

Characterization of composite properties

The tensile properties of composites were determined based on ASTM D3039 standards using an Instron 5982 with a 100 kN load cell, shown in Figure 3(d) equipped with an Epsilon ONE optical extensometer with laser-alignment and <0.5 μm resolution; the extension rate set to 1 mm/s. The following specimen geometry was used: width = 10 mm, thickness = 1 mm, and length = 100 mm to accommodate the overall smaller size of the composite plate. The specimen gauge length was 50 mm, and the modulus was calculated between strain values of 0.05 and 0.2%. The

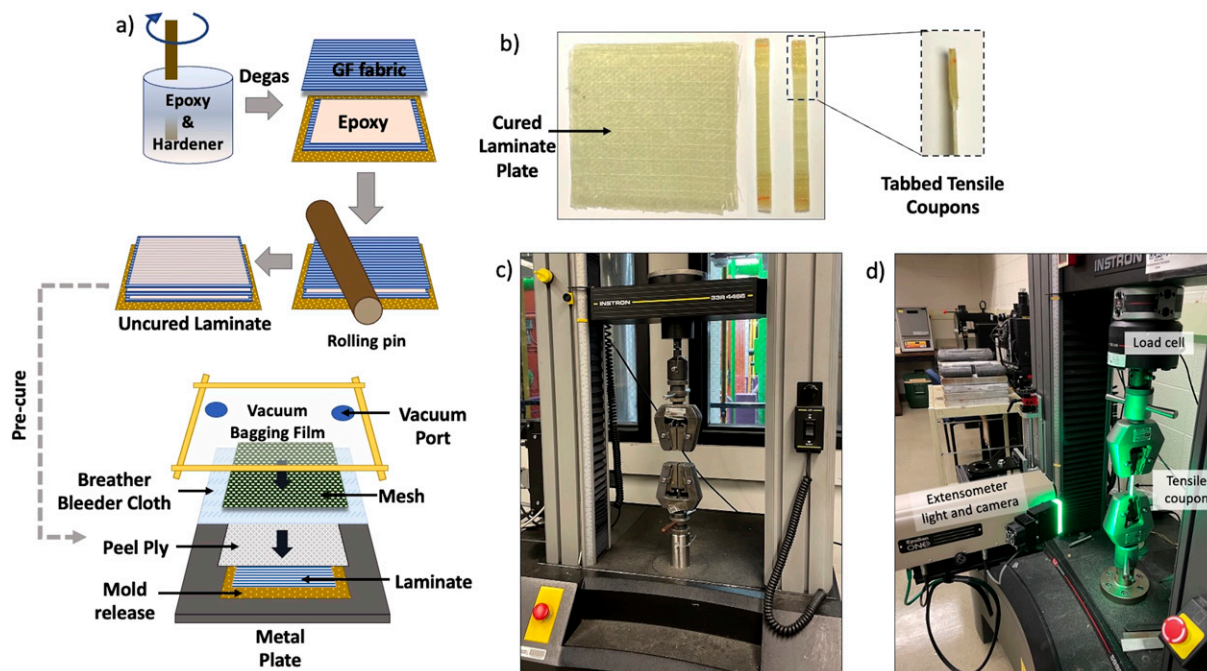


Figure 3. (a) Schematic of hand lay-up and VBO process for composite production and curing, (b) macro-view of the cured laminate plate and tabbed coupons, (c) the Instron 33R 4466 used for SFFT, and (d) Instron 5982 with extensometer used for tensile testing.

composite density and void content were measured and calculated respectively using water displacement tests, following the ASTM D792-20 and D2734-94 standards. Ten coupons were tested for each type of GF fabric and coating.

Results

Characterization of coated GF fabrics

GF fabric coating morphology. To determine the effect of drawdown vacuum on coating GF fabrics, trials were performed with and without its application. Vacuum assist slot die coating has generally been applied downstream or upstream of the application point to stabilize the coating bead^{22–24} whereas here it is used for driving fluid flow within porous GF fabric substrates. This novel approach of pairing drawdown vacuum with slot die coating has been successfully applied to the formation of filtration membranes, but its ability to redistribute coating fluid remains to be tested.²⁵

The coated fabrics were examined under SEM to assess the in-plane and through-plane coating uniformities, i.e., top and bottom, and through the thickness, respectively, to ensure consistent coating penetration. As all commercial GF both as-received (AR) S2-glass and E-glass fabrics are already sized, the sizing fully covers the fibers and the gaps between them, as shown in Figure 4(a) and (b). To better understand the effect of the CNC sizing on the fibers and avoid any synergistic effects, the as-received fibers should

be free of this sizing but removing it using such as hot acetone baths or burning it off will introduce and expose surface defects, leaving the fiber more susceptible to damage.^{12,26,27} The CNC-epoxy emulsion solution was therefore coated on top of the original fiber sizing, encapsulating the pre-existing contour and contamination completely.

In the absence of vacuum, slot die coating resulted in non-homogeneous coatings, similar to that reported in.¹⁰ At a $Q = 3$ mL/min and $v = 5$ mm/s for S2-glass and $Q = 5$ mL/min and $v = 5$ mm/s for E-glass, the fabrics appeared fully coated by the 5EM1CNC formulation, but the coating morphology on the top and bottom of the fabric differed noticeably. While the coating formed a solid film on the top of the fabric, as shown in Figure 4(c) and (d), for S2-glass and E-glass respectively; heavily obscuring the fiber separation and gaps, the individual fibers remained clearly separate and distinguishable on the bottom, as seen in Figure 4(e) and (f) for S2-glass and E-glass respectively, demonstrating the asymmetry of the coating distribution.

The addition of the vacuum pressure aided the existing flow and capillary pressure in driving and redistributing the solution around the fibers through the thickness of the fabric. As shown in Figure 4(g)–(j), the fibers on the top and bottom of the S2-glass and E-glass fabrics are coated with films of similar morphology; the caked appearance, observed in our previous study on the top, is no longer present, demonstrating the efficacy of using vacuum-assist to prevent barrier film formation on top of GF fabric.¹⁰ The

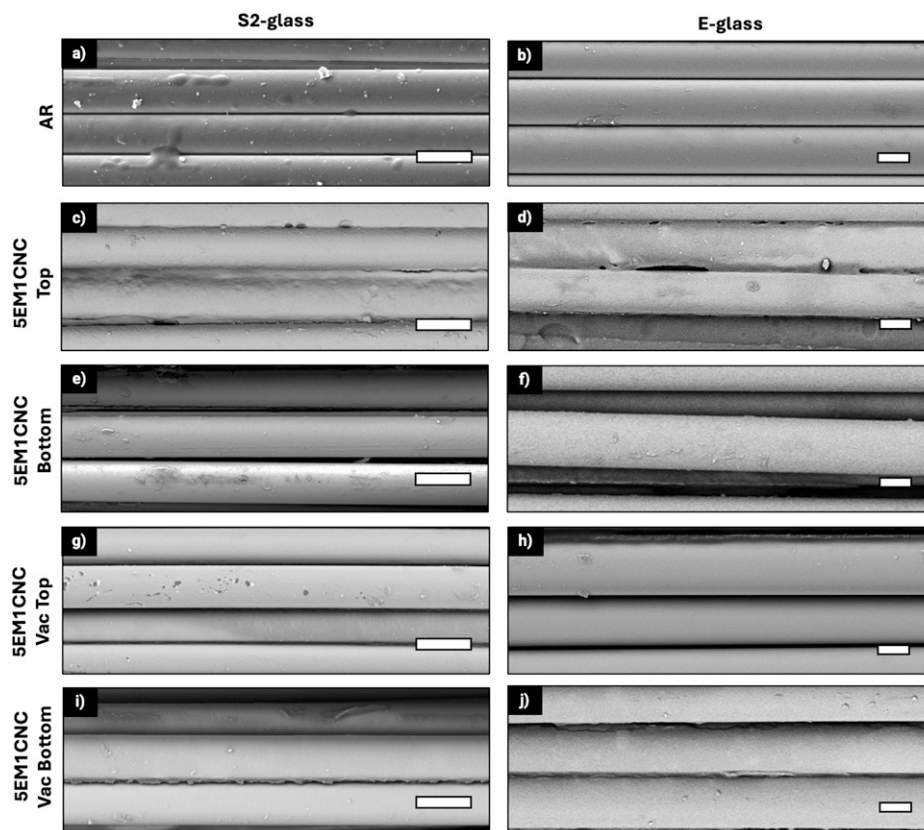


Figure 4. SEM Images of S2-glass (left) and E-glass (right) fiber fabrics (a–b) as- received, (c–f) top and bottoms surfaces coated with 5EM1CNC without vacuum, and (g–j) top and bottom surfaces coated in 5EM1CNC with vacuum. Scale bar represents 10 μm .

coating morphology change due to vacuum pressure can be further examined using cross sections of 5EM1CNC coated GF fabrics in Figure 5(a) and (c) for S2-glass, and Figure 5(b) and (d) for E-glass. For fabrics coated without vacuum, similar observations of excess caked coating on the top of the fabric are made. In contrast, fabrics coated with vacuum demonstrate much clearer fiber separation, and significantly less caking is observed. This finding was further reflected through coating thickness measurements on top of the GF fabric, as reported in Table 3, where the addition of vacuum was found to reduce the average coating thickness by 62 % for S2-glass fabrics and by 57% for E-glass fabrics. Since all measurements include the film thickness on top of individual fibers and in the gaps within the top fiber layer, high standard deviation remains across the measurements even with vacuum present.

To further test the ability to deposit high quality coatings with higher CNC content, S2-glass fabrics were coated in (i) 5EM2CNC solution i.e., solution that contains 2% CNC and (ii) double coated in 5EM1CNC, denoted as 5EM1CNC 2x, which is expected to double the amount of CNC, using the same coating parameters previously determined. As shown in Figure 6, despite the application of vacuum, at the tested processing conditions, the gaps between fibers of the

5EM2CNC and 5EM1CNC 2x coated fabrics are bridged by the dried coating with a more caked coverage due to the larger quantity of solids deposited. These features can become a hindrance in the case of laminated composites. While the coating serves to increase the interfacial adhesion between the fiber and polymer resin, its excessive presence can isolate the inner fibers within the fabric, decreasing the available interface area where fiber and matrix can interact, and introducing dry spots, voids, and defects where the resin cannot penetrate during the composite fabrication process.

The coat weights deposited by the slot die coating process with vacuum were measured for GF fabrics at their slowest operating parameters and reported in Table 4; these combinations are $Q = 3 \text{ mL/min}$ and $v = 5 \text{ mm/s}$ for S2-glass and $Q = 5 \text{ mL/min}$ and $v = 5 \text{ mm/s}$ for E-glass respectively. 5EM2CNC-S and 5EM1CNC 2x-S samples have the highest coat weights, further underscoring the issues with excess coating identified from SEM images. While the coat weights of 5EM1CNC-S and 5EM1CNC-E samples are lower, at 5.59 wt% for S2-glass and 3.79 wt% for E-glass, these values still exceed typical commercial sizing quantities which vary between 0.2 and 2 wt % of GF weight.²⁸ The overall higher coat weights of S2-glass samples can increase the incidence of defects and resin flow hindrances during composite manufacturing.

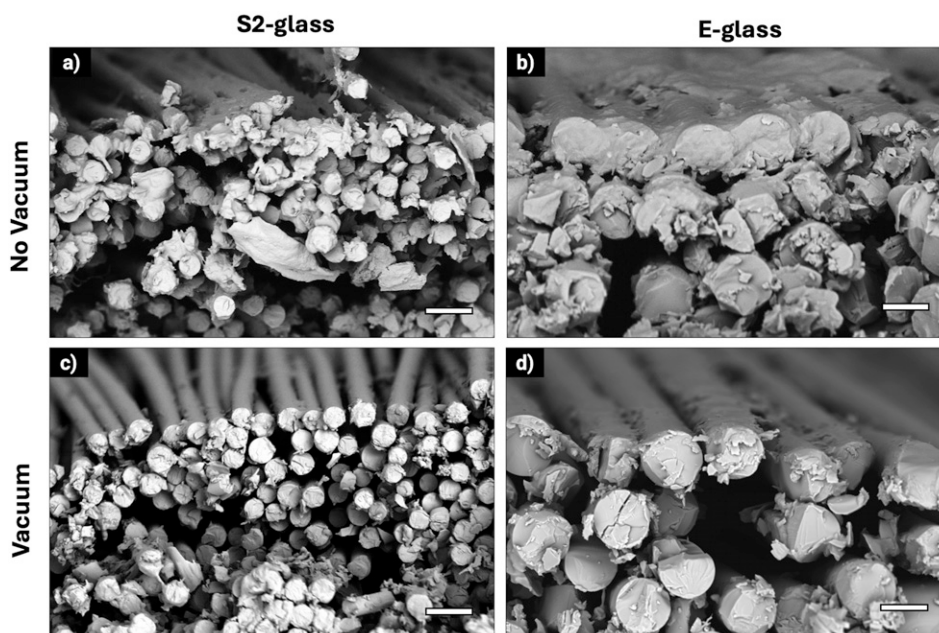


Figure 5. SEM cross sectional images of 5EM1CNC coating distribution on top of (a) S2-glass fabric coated without vacuum, (b) S2-glass fabric coated with vacuum, (c) E-glass fabric coated without vacuum, (d) E-glass fabric coated with vacuum. Scale bar represents 20 μm .

Table 3. Coating thickness on top of S2-glass and E-glass fiber fabrics. Averages and 1 standard deviation calculated for 20 measurements.

Sample	Coating thickness (μm)
5EM1CNC-S no vacuum	1.67 ± 1.45
5EM1CNC-S vacuum	0.64 ± 0.42
5EM1CNC-E no vacuum	1.49 ± 1.19
5EM1CNC-E vacuum	0.84 ± 0.61

Coating characterization by FTIR. To confirm the presence of individual coating components in the AR-S and AR-E, i.e., as-received S2-glass and E-glass samples, 5EM1CNC-S, 5EM1CNC-E, 5EM2CNC-S and 5EM1CNC2x-S, coated fabric samples were additionally analyzed using FTIR. The reported spectra in Figure 7(a) and (b), for S2-glass and E-glass samples respectively, show that both types of GF fabrics exhibited prominent peaks between 780 and 930 cm^{-1} , for Si-O stretching vibrations corresponding to the silica of both GFs.²⁹ Furthermore, an absorption peak visible at 500 cm^{-1} can be attributed to overlapping Si-O-Si and Al-O-Al bonds from SiO_2 and Al_2O_3 present in both S2-glass and E-glass.³⁰ However, the two types of GFs can be distinguished when AR-S and AR-E spectra are compared, with the AR-E exhibiting a peak at 1400 cm^{-1} due to the presence of additional oxides e.g. (boron oxide, calcium oxide etc.) which are not present in S2-glass.^{4,31}

The addition of epoxy-emulsion and CNC coating on GF fabrics produced a narrow peak at 1500 cm^{-1} corresponding

to C-H vibrations from nanocellulose.³² The broad peak at 2780 cm^{-1} is attributed to C-H aromatic stretching present in all coating components of epoxy, PL123 and CNC, while 3230 cm^{-1} peak is characteristic for O-H stretching of pyranose rings in CNC.^{12,32,33} The CNC functional methyl (triphenyl) phosphonium group could not be detected due to its relatively low concentration. This matches results in previous studies where GFs coated in functionalized and non-functionalized CNC dispersions produced identical spectra, showing the unique C-H stretching of the phenyl group ($\sim 750 \text{ cm}^{-1}$) could only be detected with difficulty for pure CNC films.¹²

Characterization of coated GF composites

Composite porosity. Unidirectional composites were produced for all AR-S, AR-E, 5EM1CNC-S, 5EM1CNC-E, 5EM2CNC-S and 5EM1CNC2x-S coated fabrics. Experimental density and void content were measured using water displacement tests following D792-20 and D2734-94 standard for all composites and reported in Table 5. Due to the higher density of E-glass (2.5 g/cm^3) compared to S2-glass (2.42 g/cm^3), the resulting AR-E and 5EM1CNC-E composites had higher density than the AR-S and 5EM1CNC-S samples. All samples had voids present, increasing with the amount of coating deposited, with the AR-S and AR-E samples coming lowest for each respective fabric at $4.90 \pm 0.72\%$ and $1.42 \pm 0.36\%$. 5EM1CNC-S and 5EM1CNC-E had void contents of $5.21 \pm 0.69\%$ and $2.68 \pm$

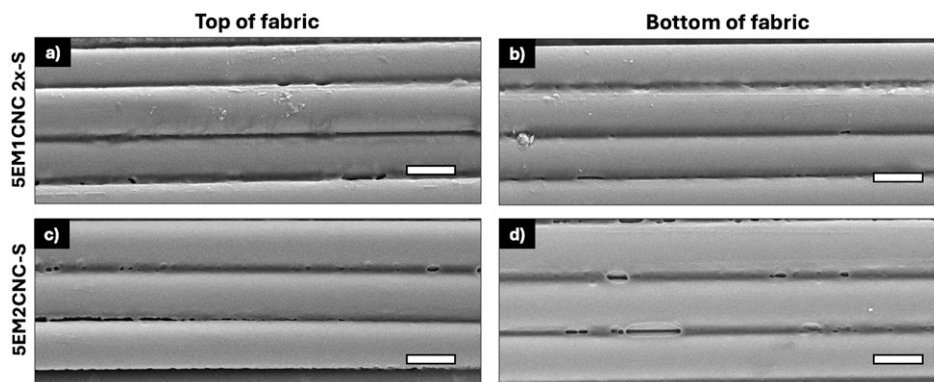


Figure 6. S2-glass fabric coated in (a–b) 5EM1CNC formulation in two passes, (c–d) coated in 5EM2CNC formulation in one pass. Scale bar represents 10 μm .

Table 4. Coat weight of GF fabrics coated with vacuum applied. Averages and 1 standard deviation calculated for 5 samples.

Sample	Coat weight (wt%)
5EM1CNC-S	5.59 ± 0.11
5EM2CNC-S	6.59 ± 0.60
5EM1CNC 2x-S	10.05 ± 0.78
5EM1CNC-E	3.79 ± 0.01

0.79% which are consistent with acceptable void fraction for GF composites in industry.^{34,35} The increase in porosity was stark for samples 5EM2CNC-S and 5EM1CNC 2x-S, at greater than 14%, demonstrating the detrimental effect of excess amounts of CNC coating deposited. Despite the higher void content, the composite density for 5EM2CNC and 5EM1CNC 2x increased due to the increased fiber wt% within the composite due to poor resin impregnation, and greater CNC content which has higher density (1.6 g/cm^3) than the epoxy matrix (1.2 g/cm^3).

Examining the composite surface, shown in Figure 8, the samples show progressive yellowing with increasing CNC content. This type of discoloration has been attributed to the exposure of cellulose to elevated temperatures which occurred during curing at 100°C and higher.³⁶ While the S2-glass fiber fabric is made of woven rovings, as shown in Figure 8(a), the VBO and resin infiltration process compresses the fabric layers and spreads the rovings out to produce a uniform distribution with little distinction between individual rovings, as seen in Figure 8(b). Following the deposition of CNC however, it is apparent that the coating has led to tighter GF packing within individual rovings, reducing their original width whilst widening the gaps between them, as seen in Figure 8(c), (e) and (g). The GFs bundle together when wetted by the coating solution and remain so following drying, held together by the dried coating. While the AR-S and 5EM1CNC-S samples, shown in Figure 8(b) and (d), spread out to form a uniform laminate, the forces exerted during the VBO process could not

overcome the GF bundling within 5EM2CNC-S and 5EM1CNC2x-S samples, allowing the individual rovings within the coated fabric to retain their distinct shape, resisting resin infiltration and distribution, and giving rise to voids and defects within.

Composite performance. To determine the effect of CNC coatings on unidirectional GF-epoxy composite properties, only formulations which produced composites with low void content were selected for further characterization. The poor quality (i.e. high incidence of voids and non-uniform resin wetting) of laminates made from 5EM2CNC-S and 5EM1CNC 2x-S formulations would significantly confound or negate the influence of CNCs on the fiber-matrix interface. Thus, for S2-glass fabrics, interfacial characterization using SFFT was only carried out on AR-S and 5EM1CNC-S to determine both the influence of the coating formulation and the effect of vacuum-assist during slot die coating on interfacial properties. For E-glass fabrics, the performance of AR-E and 5EM1CNC-E coated with vacuum is compared.

In a typical SFFT, the Kelly-Tyson (K-T) model is used to explicitly calculate the interfacial shear strength (IFSS) of the fiber-matrix system as a function of the experimentally measured critical fragment length and its corresponding fiber strength.³⁷ However, the K-T model, which relies on the assumption of constant shear stress across the fiber-matrix interface, offers poor approximations between the critical length and IFSS for GFs within epoxy matrices since the polymer does not conform to the elastic-perfectly-plastic matrix criteria, but instead exhibits increased load carrying capability after the onset of yield.^{12,37,38} While the model is still widely used for comparative studies to predict interfacial properties within polymer matrix composites, the calculated IFSS can diverge from experimental results and varies widely due to the lack of a single accepted method of determining the fiber strength at its critical length.^{12,38} As such, the fragment count which directly correlates with

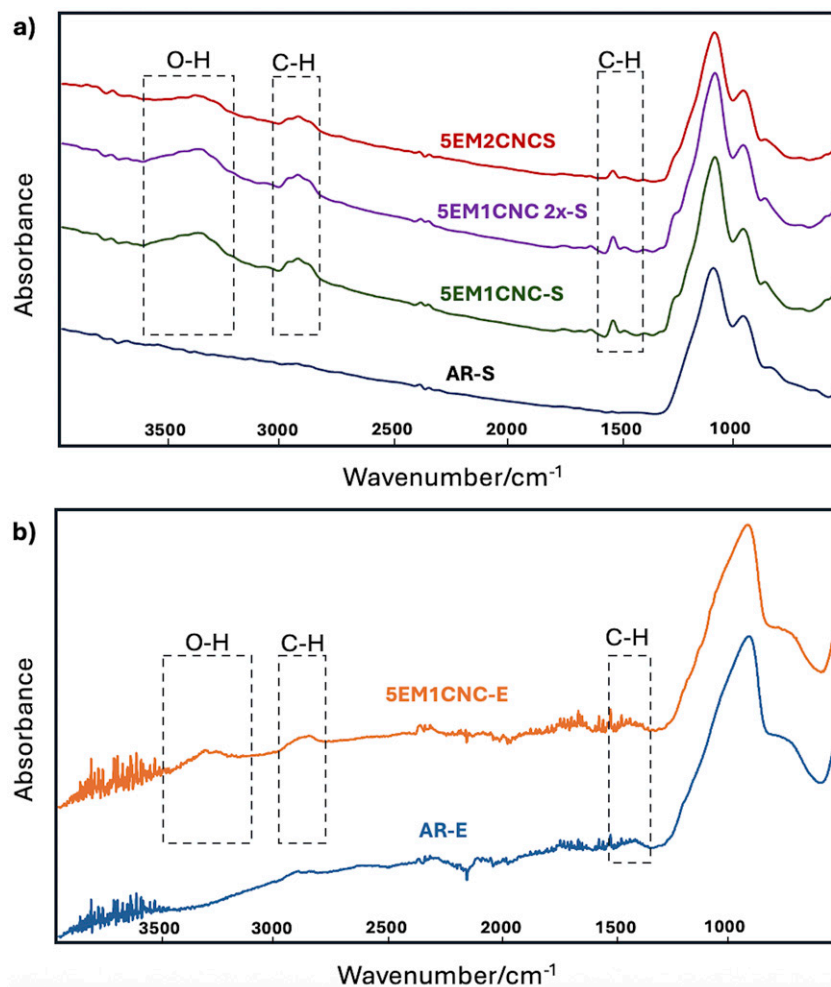


Figure 7. FTIR spectra for (a) S2-glass samples and (b) E-glass samples labeled with corresponding coating formulations.

Table 5. Composite density and void content for all tested formulations. Averages and 1 standard deviation calculated for 5 samples.

Sample	Density (g/cc)	Void content (%)
AR-S	1.85 ± 0.01	4.90 ± 0.72
5EM1CNC-S	1.83 ± 0.01	5.21 ± 0.69
5EM2CNC-S	1.90 ± 0.01	14.25 ± 0.58
5EM1CNC 2x-S	1.88 ± 0.00	14.34 ± 0.29
AR-E	1.95 ± 0.01	1.42 ± 0.36
5EM1CNC-E	1.87 ± 0.01	2.68 ± 0.79

fragment length and the IFSS is reported in [Figure 9\(a\) and \(b\)](#) for S2-glass and E-glass respectively.

For S2-glass composites, SFFT was only performed on AR-S and the 5EM1CNC-S formulation. Comparing the average fragment count and data sets between samples, no statistically significant difference in average fragmentation was found following the addition of 5EM1CNC coating. However, the addition of vacuum to the slot die coating

process proved impactful on the fragmentation behavior. The fragment count of 5EM1CNC-S sample coated without vacuum showed significant spread and a high standard deviation of 10.2, signifying an inconsistent interface between samples, which can be attributed to the observed uneven morphology and non-uniform quantity of coating between individual fibers throughout the fabric. The 5EM1CNC-S sample coated with vacuum showed more consistent fragmentation between fibers, with a standard deviation of only 4.8, underscoring the observed improved coating uniformity and distribution throughout the fabric. Unlike S2-glass, E-glass samples, 5EM1CNC-E coated with vacuum demonstrated better adhesion and thus higher fragment count when compared to AR-E, increasing from 43 to 50, a total of 14%, with statistical significance found for a confidence interval of $p = 0.05$ for a two-tailed t -test. This finding is consistent with results from prior work demonstrating the favorable effect of the 5EM1CNC formulation on the interfacial shear strength of fibers in E-glass rovings.^{10,12}

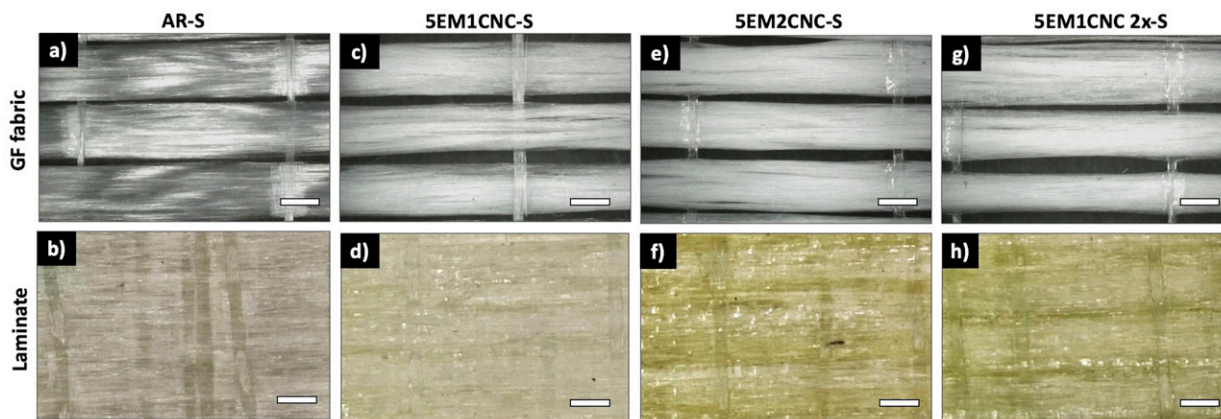


Figure 8. Optical microscopy images of S2-glass fabric (top) and the top surface of their corresponding epoxy laminates containing (bottom): (a–b) AR-S, (c–d) 5EM1CNC-S, (e–f) 5EM2CNC-S and (g–h) 5EM1CNC 2x-S. The scale bar represents 125 μm .

The examination of fracture modes of GFs within the SFFT coupons can additionally allow for a qualitative assessment of interfacial adhesion. For SFFT, the typical fragmentation modes are represented by (i) disk-shaped, and (ii) double cone-shaped, (iii) frictional debonding patterns, as depicted in Figure 10(a).^{8,10,39} For GF-epoxy systems, concurrent disk and cone shaped cracks represent moderate to strong interfacial adhesion with resultant surrounding matrix deformation following fracturing, whereas debonding signifies poor interfacial interaction and sliding friction between the fiber and matrix.¹⁰ Reflecting the lack of improvement in fragmentation, the fracture morphology of AR-S and 5EM1CNC-S, shown in Figure 10(b) and (c) is primarily dominated by frictional debonding, showing poor adhesion between the fiber, matrix, and the CNC coating. In contrast, the samples AR-E and 5EM1CNC-E, as seen in Figure 10(d) and (e), show a greater incidence of disk and cone-shaped cracks, signifying stronger interfacial adhesion and material system compatibility.

As 5EM1CNC-E demonstrated improved interfacial properties compared to the AR-E sample, longitudinal tensile testing was performed to determine the impact of the coating on the composite modulus and tensile strength. As shown in Figure 9(c) and (d), the addition 5EM1CNC sizing on E-glass fibers produced insignificant improvement on tensile modulus of 5%, increasing from 41.5 to 43.5 GPa, yet a statistically significant increase in tensile strength from 718 to 823 MPa for a total of 15% ($p < 0.001$). Comparing the stress and strain curves of three representative AR-E and 5EM1CNC-E samples, shown in Figure 9(e), and their respective fractured tensile coupons, shown in Figure 11 (a) and (c), it can be seen that the CNC coating has altered the laminate tensile failure. The AR-E composite breaks progressively at sporadic stressed locations, which can also be seen from the stress-strain curve's multiple dips before cumulative failure. In contrast, the 5EM1CNC-E's stronger interfaces can transfer stress more effectively within the

coupon, allowing for a higher sustained load, resulting in a much more dramatic failure with “brush-like” splitting of fiber and matrix.⁴⁰ Also reflected in the longitudinal view of tensile fractures in Figure 11(b) and (e), 5EM1CNC-E shows a rougher fracture surface with more matrix adhered to GFs than AR-E, reflecting the stronger fiber-matrix adhesion. Similar observations can be made from the perpendicular view of fracture surfaces in Figure 11 (c) and (f) as well, with AR-E showing much cleaner separation between GF and matrix while 5EM1CNC-E shows much more matrix residue on GF surfaces. These results demonstrate that while altering the fiber-matrix interface often results in a longitudinal modulus that is insensitive to change, improvements of longitudinal tensile strength can still be achieved due to changes in composite failure modes.⁴⁰

While the addition of CNCs at the fiber-matrix interface is meant to produce enhanced adhesion through both mechanical interlocking of polymer chains with CNC particles and chemical bonding of additional hydroxyl groups,⁸ the lack of observed improvement on S2-glass composites could be due to the proprietary sizing present on AR-S being incompatible with the CNCs or the epoxy system. While most commercial sizings are made primarily of film formers and silane coupling agents, their often-complex recipe also contains many additives, lubricants, and surfactants, frequently surpassing 10 or more total components with poorly understood interactions, and their compatibility with CNCs is challenging to confirm.^{41,42} To make CNC coatings that bond with the S2-glass-epoxy interface, surface energy measurements, evaluation of wetting behavior, adhesion, and appropriate CNC chemical functionalization may be necessary to produce a reinforcement compatible with the system. Furthermore, coating the 5EM1CNC formulation on top of preexisting sizing could result in suboptimal and excessive coating

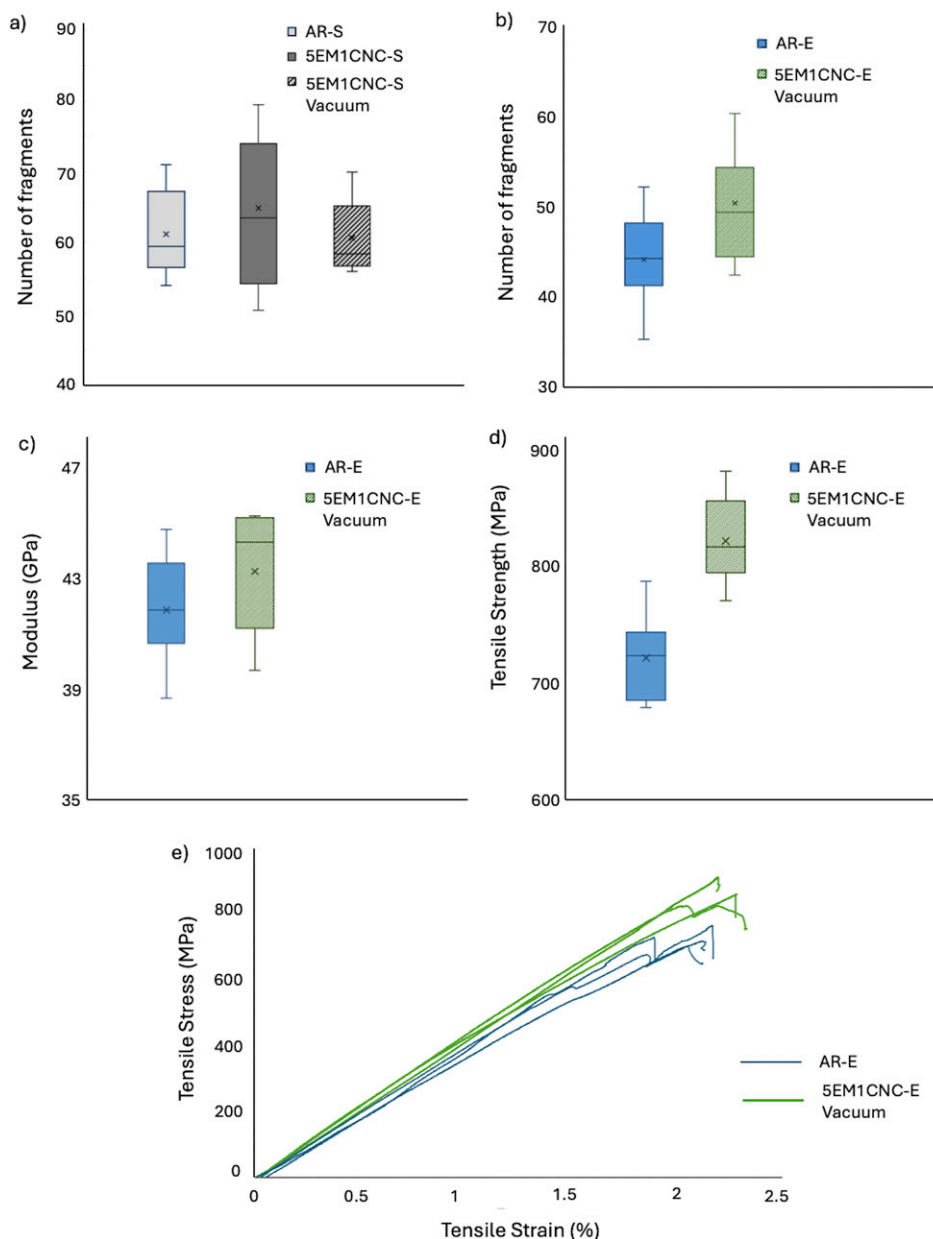


Figure 9. SFFT results for AR and 5EM1CNC coated (a) S2-glass comparing the effect of vacuum on fragment count, (b) E-glass demonstrating the effect of coating on fragment count. Tensile properties of E-glass-epoxy composite: (c) modulus, and (d) strength and (f) representative stress strain curves of 5EM1CNC-E and AR-E samples.

thickness, reducing the fiber-matrix interactions and subsequent interfacial adhesion, an issue that becomes more prominent on S2-glass than E-glass samples due to their relatively higher deposited coat weight.⁴³ While not presented in this study, it is likely that using interfacial modification to improve longitudinal tensile properties may be yet more challenging for the higher performing S2-glass fiber composites as their inherently higher modulus and strength may render any effects from CNC coatings even less apparent.

While prior studies, such as,⁸ have reported similar findings by demonstrating a favorable impact of CNC coatings on the tensile strength of chopped E-glass fiber composites, replicating such improvement in unidirectional continuous fiber laminates is a promising step forward, as it demonstrates the ability of CNCs to influence the on-axis tensile properties through the fiber-matrix interface even when the applied load is carried predominantly by the long GFs. Such enhancements create potential for more versatile applications of CNC-E-glass/epoxy composites where

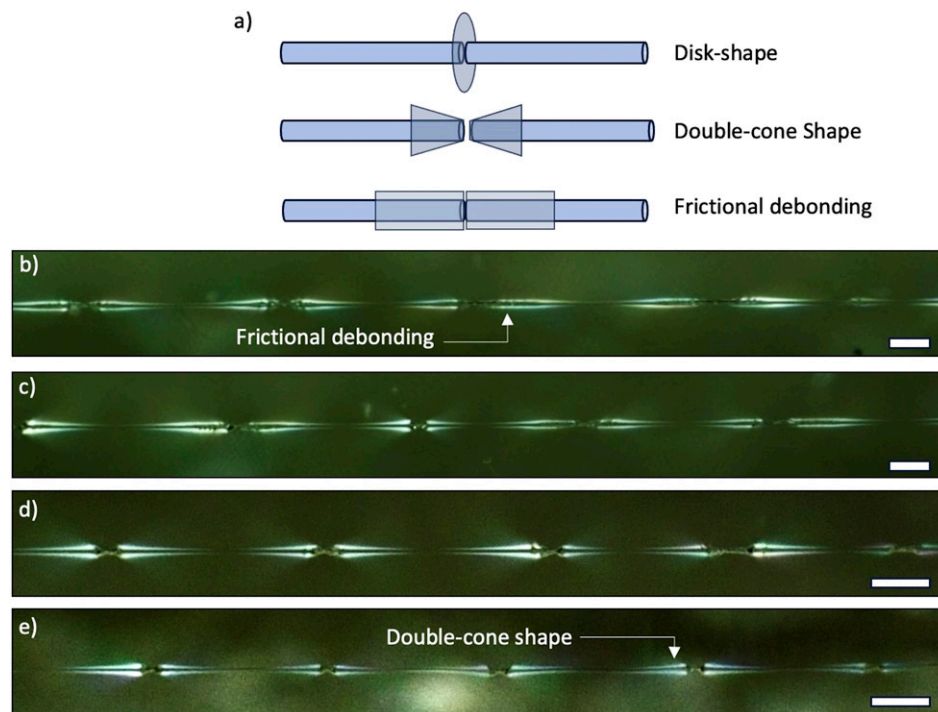


Figure 10. (a) Typical fracture modes, and optical micrographs of fractures following SFFT for (b) AR-S, (c) 5EM1CNC-S, (d) AR-E, and (e) 5EM1CNC-E. Scale bar represents 100 μm .

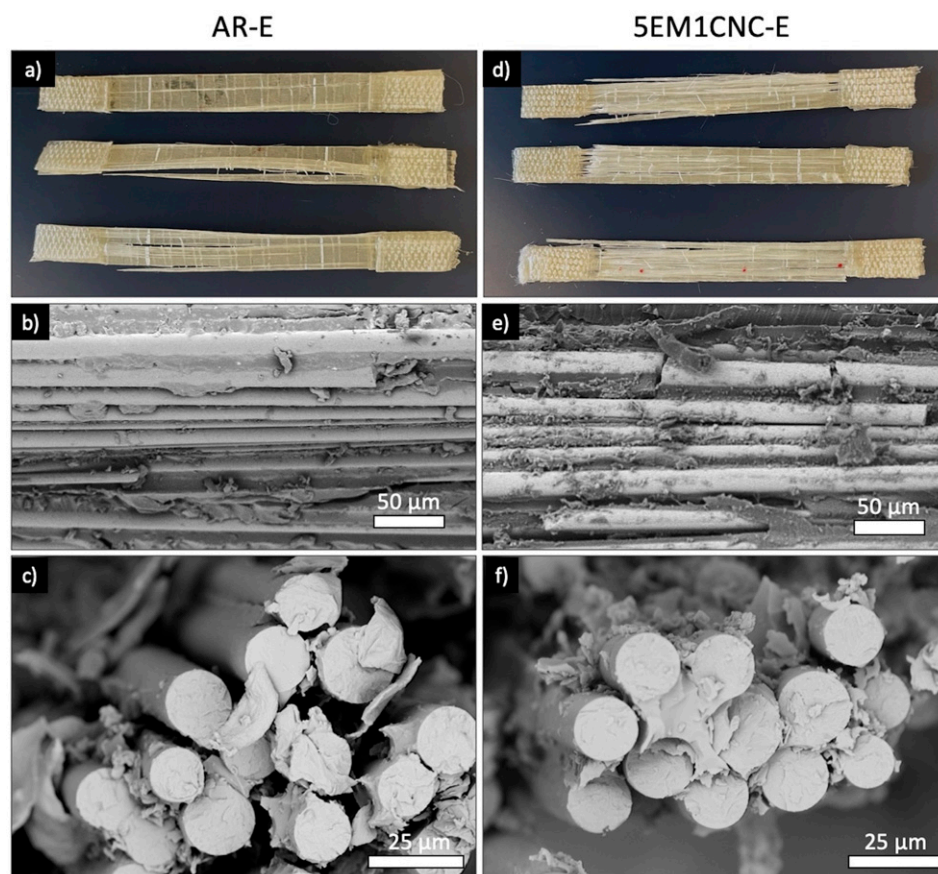


Figure 11. Failed tensile coupons and SEM images of tensile fracture surfaces of (a–c) AR-E, and (d–f) 5EM1CNC-E laminate. The coupons have a full-scale length of 100 mm.

greater control of fiber length and orientation is needed, while retaining the maximum load carrying capacity of E-glass fibers within the composites.

Conclusions

In this study, the viability of using vacuum-assisted slot die coating to fully coat unidirectional S2-glass and E-glass fabrics was demonstrated. A range of coating parameters were determined to ensure stable and complete wetting of the substrate at different rates of production. Challenges concerning coating inhomogeneity were remedied, and the limitations surrounding coating quality and resulting laminate quality were assessed.

The application of vacuum during the slot die coating process was found to assist existing flow field and capillary pressures in driving fluid through the GF gaps to produce uniform thin CNC coatings around individual GFs, preventing caking and excess fluid collection at the top fiber fabric surface. SEM analysis of fabric fracture cross sections further demonstrated that the coating solution penetrates through the entire depth of the fabric with consistent distribution. Furthermore, the film thickness deposited on S2-glass and E-glass fabrics was reduced by 62% and 57% respectively. However, the use of formulations with higher CNC content on S2-glass fabrics resulted in excess coating, leading to worse fiber separation which hinders resin flow, and air evacuation during composite formation increasing the void content to 14%. Using the VBO process, quality E-glass and S2-glass fiber laminates with low incidence of voids and defects were achieved for samples coated with 5EM1CNC formulation.

Characterization of the interfacial adhesion using SFFT found that the use of vacuum assist with slot die coating produced more consistent fragmentation for S2-glass fibers coated with 5EM1CNC formulation, underscoring the importance of the applied vacuum during slot die coating on producing uniform coating morphology and resulting fiber-matrix interface. However, an overall improvement to interfacial adhesion and fragmentation between S2-glass and epoxy was not achieved due to material system incompatibility. The addition of 5EM1CNC coatings on E-glass fabrics produced enhanced interfacial adhesion between the fiber and matrix, allowing for more effective stress transfer within the composite, and increased longitudinal tensile strength by 15% for unidirectional E-glass-epoxy laminates.

In summary, vacuum assisted slot die coating has been shown as an effective method for depositing CNC dispersions onto GF fabrics, providing an important step in developing a scalable manufacturing process for high volume of CNC-GF reinforced composite production. Furthermore, the deposition of low concentration CNC formulations enhanced the interfacial interactions and the tensile strength of E-glass fabric/epoxy laminates, demonstrating the capability of CNC sizing in influencing the

on-axis properties of continuous GF reinforced composites. The simplicity and scalability of the process and parameters could be further adapted to size other types of reinforcing fibers and provide enhancement to more fiber-reinforced polymer composite systems.

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Data Availability Statement

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

References

1. Stickel J and Nagarajan M. Glass fiber-reinforced composites: from formulation to application. *Int J Appl Glass Sci* 2012; 3: 122–136.
2. Sathishkumar T, Satheeshkumar S and Naveen J. Glass fiber-reinforced polymer composites – a review. *J Reinforc Plast Compos* 2014; 33: 1258–1275.
3. Kutz M. *Mechanical engineers' handbook, volume 1: materials and engineering mechanics*. John Wiley & Sons, 2015.
4. Mallick P. *Fiber-reinforced composites: materials, manufacturing, and design*. CRC Press, 2007.
5. Joost WJ. Reducing vehicle weight and improving U.S. Energy efficiency using integrated computational materials engineering. *JOM* 2012; 64: 1032–1038.
6. Robinson AL, Taub AI and Keoleian GA. Fuel efficiency drives the auto industry to reduce vehicle weight. *MRS Bull* 2019; 44: 920–923.
7. DiLoreto E, Haque E, Berman A, et al. Freeze dried cellulose nanocrystal reinforced unsaturated polyester composites: challenges and potential. *Cellulose* 2019; 26: 4391–4403.
8. Asadi A, Miller M, Moon RJ, et al. Improving the interfacial and mechanical properties of short glass fiber/epoxy

- composites by coating the glass fibers with cellulose nanocrystals. *Express Polym Lett* 2016; 10: 587–597.
9. Asadi A, Miller M, Singh AV, et al. Lightweight sheet molding compound (SMC) composites containing cellulose nanocrystals. *Compos Struct* 2017; 160: 211–219.
 10. Haque E, Shariatnia S, Jeong T-J, et al. Scalable coating methods for enhancing glass fiber–epoxy interactions with cellulose nanocrystals. *Cellulose* 2021; 28: 4685–4700.
 11. Moon RJ, Martini A, Nairn J, et al. Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem Soc Rev* 2011; 40: 3941–3994.
 12. Goswami J, Haque E, Fox DM, et al. The effect of cellulose nanocrystal coatings on the glass fiber–epoxy interphase. *Materials* 2019; 12: 1951.
 13. Zhao FM and Takeda N. Effect of interfacial adhesion and statistical fiber strength on tensile strength of unidirectional glass fiber/epoxy composites. Part I: experiment results. *Compos Appl Sci Manuf* 2000; 31: 1203–1214.
 14. Fallahi H, Kaynan O and Asadi A. Insights into the effect of fiber–matrix interphase physicochemical–mechanical properties on delamination resistance and fracture toughness of hybrid composites. *Compos Appl Sci Manuf* 2023; 166: 107390.
 15. Ding X, Liu J and Harris TAL. A review of the operating limits in slot die coating processes. *AIChE J* 2016; 62: 2508–2524.
 16. Fox DM, Rodriguez RS, Devilbiss MN, et al. Simultaneously tailoring surface energies and thermal stabilities of cellulose nanocrystals using ion exchange: effects on polymer composite properties for transportation, infrastructure, and renewable energy applications. *ACS Appl Mater Interfaces* 2016; 8: 27270–27281.
 17. Roy D, Kotula AP, Natarajan B, et al. Effect of cellulose nanocrystals on crystallization kinetics of polycaprolactone as probed by Rheo-Raman. *Polymer* 2018; 153: 70–77.
 18. Reid MS, Villalobos M and Cranston ED. Benchmarking cellulose nanocrystals: from the laboratory to industrial production. *Langmuir* 2017; 33: 1583–1598.
 19. Valenza A and Fiore V. Influence of resin viscosity and vacuum level on mechanical performance of sandwich structures manufactured by vacuum bagging. *Adv Polym Technol* 2010; 29: 20–30.
 20. Stringer LG. Optimization of the wet lay-up/vacuum bag process for the fabrication of carbon fibre epoxy composites with high fibre fraction and low void content. *Composites* 1989; 20: 441–452.
 21. Yu S, Yang Y and Colton JS. Improved composite open-hole compression strength and trade-off with manufacturability controlled by stacking sequence effect and non-standard ply angles. *Compos B Eng* 2022; 228: 109410.
 22. Brown ODMG; Inventors. Die coating method and apparatus. 1995.
 23. Tanwar J, Vinjamur M and Scriven LE. Design principles of integrated vacuum slot arrangement. *AIChE J* 2007; 53: 572–578.
 24. Beguin AE. Method of coating strip material. 1954.
 25. Esfahani AR, Ma C, Flewellen UA, et al. Scalable aqueous-phase fabrication of reduced graphene oxide nanofiltration membranes by an integrated roll-to-roll (R2R) process. *J Membr Sci* 2023; 678: 121669.
 26. Thomason JL. Glass fibre sizing: a review. *Compos Appl Sci Manuf* 2019; 127: 105619.
 27. Petersen HN, Kusano Y, Brøndsted P, et al. The influence of removing sizing on strength and stiffness of conventional and high modulus E-glass fibres. *IOP Conf Ser Mater Sci Eng* 2016; 139: 012040.
 28. Wu HF, Dwight DW and Huff NT. Effects of silane coupling agents on the interphase and performance of glass-fiber-reinforced polymer composites. *Compos Sci Technol* 1997; 57: 975–983.
 29. Bonon A, Weck M, Bonfante E, et al. Physicochemical characterization of three fiber-reinforced epoxide-based composites for dental applications. *Mater Sci Eng C* 2016; 69: 905–913.
 30. Liu J, Jiang M, Wang Y, et al. Tensile behaviors of ECR-glass and high strength glass fibers after NaOH treatment. *Ceram Int* 2013; 39: 9173–9178.
 31. Xu B, Long J, Xu G, et al. Facile fabrication of super-hydrophobic and superoleophilic glass-fiber fabric for water-in-oil emulsion separation. *Textil Res J* 2019; 89: 2674–2681.
 32. Azhary T, Kusmono WMW, Wildan MW, et al. Mechanical, morphological, and thermal characteristics of epoxy/glass fiber/cellulose nanofiber hybrid composites. *Polym Test* 2022; 110: 107560.
 33. Tesfaye B, Wogaso D and Mulugeta E. Synthesis of crystalline nanocellulose and its effect on the mechanical properties of E-glass fiber/epoxy composite for prosthetic shank applications. *J Compos Mater* 2023; 57: 1667–1681.
 34. Hyde A, He J, Cui X, et al. Effects of microvoids on strength of unidirectional fiber-reinforced composite materials. *Compos B Eng* 2020; 187: 107844.
 35. Wei J, Sun L, Gao X, et al. Microstructures failure analysis of fiber reinforced composites with various void types. *J Mater Sci* 2023; 58: 230–246.
 36. Jung K, Ji Y, Jeong T-J, et al. Roll-to-Roll, dual-layer slot die coating of chitin and cellulose oxygen barrier films for renewable packaging. *ACS Appl Mater Interfaces* 2022; 14: 44922–44932.
 37. Kelly A and Tyson WR. Tensile properties of fibre-reinforced metals: copper/tungsten and copper/molybdenum. *J Mech Phys Solid* 1965; 13: 329–350.
 38. Holmes G, Peterson R, Hunston D, et al. The effect of nonlinear viscoelasticity on interfacial shear strength measurements. In: *Time dependent and nonlinear effects in polymers and composites*. ASTM International, 2000, p. 0.
 39. Mullin JV and Mazzio VF. The effects of matrix and interface modification on local fractures of carbon fibers in epoxy. *J Mech Phys Solid* 1972; 20: 391–394.
 40. Drzal LT and Madhukar M. Fibre-matrix adhesion and its relationship to composite mechanical properties. *J Mater Sci* 1993; 28: 569–610.
 41. Demina NM. Current compositions for processing high-strength high-modulus continuous glass fiber (review). *Fibre Chem* 2016; 48: 118–124.(Review).
 42. Thomason JL. Sizing chemistry of glass fibers. In: Li H (ed). *Fiberglass Science and Technology: Chemistry, Characterization, Processing, Modeling, Application, and Sustainability*. Cham: Springer International Publishing, 2021, pp. 259–321.
 43. Frey M and Brunner AJ. Assessing glass-fiber modification developments by comparison of glass-fiber epoxy composites with reference materials: some thoughts on relevance. *Proc Inst Mech Eng Part L* 2017; 231: 49–54.