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A nanostructured cellulose-based interphase layer to enhance the

mechanical performance of glass fibre-reinforced polymer composites

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Abstract

In this study, we report the effect of sizing glass fibres (GFs) with tetramethylpiperidine-1-oxyl (TEMPO)-mediated cellulose nanocrystals (t-CNC) to improve the interfacial mechanical performance of glass fibre reinforced polymer composites (GFRP). These nanoparticles are introduced at different concentrations to yield a coating of t-CNCs which are (1) sparsely deposited at low concentrations, and (2) uniformly self-assembled over the glass fibre at a higher concentration. The mechanical, morphological and interphase results show that self-assembled CNC coating around a fibre provides better strengthening than sparsely deposited a \sim 30% increase in the interlaminar shear strength (ILSS), 43% increase in flexural strength and 40% increase in flexural modulus of the GFRP composite. Strong nanoscale interactions

between the t-CNC and GF, coupled with the formation of a high modulus gradient interphase layer, contributed to the significant improvement in the mechanical performance of t-CNC/GFRP composites.

KEYWORDS: A. Cellulose; A. Nano-structures; B. Mechanical properties; D. Microstructural analysis; E. Vacuum infusion

1. INTRODUCTION

Fibre-reinforced polymer (FRP) composite materials exhibit high specific strength and stiffness, improved fatigue performance and corrosion resistance. They are increasingly being developed wherever lightweighting is critical, such as in aerospace, marine, defence and automotive structures [1-4]. Recently, glass fibre-reinforced polymer composites (GFRP) have received renewed interest owing to the various enhancements that can be achieved through interface and matrix modifications [3]. Most fibrous composites suffer from poor out-of-plane/through thickness (matrix-dominated) mechanical properties [5]. Inorganic glass fibres with their smooth surface may exhibit particularly poor adhesion with the surrounding matrix leading to fibre-matrix debonding [6]. Improvement of this interface is key to enhancing the mechanical properties of GFRP composites [7-8].

The recent interfacial technology landscape shows that the introduction of nanomaterials (i.e. clay, graphene, carbon nanotubes etc.) onto the fibre surface or into the matrix has attracted significant interest [2, 5, 9-11]. Both approaches potentially result in a significant improvement in the mechanical performance of FRP composites. From these studies, it is well established that the presence of dispersed functionalized nanomaterials, either in matrix or over the fibre surface, not only improve the interfacial adhesion but also alter the prevailing fracture mechanisms via crack bridging, crack deflection and crack arresting mechanisms [12-17].

The growing interest in bio-based cellulose nanocrystals (CNCs), as a reinforcement for polymers [18-19], stems from their attractive combination of physical and chemical properties such as high aspect ratio, high elastic modulus (100-150 GPa) and tensile strength (7-10 GPa), low density (1.56 g/cm³), crystalline structure and surface-rich chemistry [18,20]. To date, attempts have been made to mix CNCs with a range of thermoplastic or thermoset resins [19, 21]. Surprisingly, little attention has been paid towards CNC-enhanced FRP composites. Certain efforts to date have focused primarily on (1) CNC-modified epoxy-reinforced GFRP composites [22], (2) CNC-coated chopped glass fibre/epoxy composites [23-24] and (3) CNCcoating on single continuous carbon fibres to improve the CF/matrix interfacial adhesion [25]. Uribe et al. manufactured TEMPO-mediated cellulose nanofibrills (CNFs) coated plain-woven GF/CF fabric reinforced composites and realised a 54 % and 62 % enhancement in flexural strength, respectively [26-27]. On a fundamental level, CNF and CNC possess the same chemical structure, but ribbon like CNF contain amorphous cellulose and are not as highly crystalline as CNC (rigid rode-like shape) [28]. CNFs, because of their high aspect ratio (80-150), form a highly entangled morphology. However, CNCs due to their tiny size (small aspect ratios: 10-20) can readily be dispersed and self-assembled into multi-layered nanostructures with long-range orientation order with increasing concentration [29-32]. Recent research has shown that CNC self-assembled into hierarchical/bouligand type nanostructures, which resembles the hierarchical arrangement of nanofibrills in strong and tough natural biological architectures such as bone, ivory and crustacean shells [29, 30, 33].

In this current work, inspired by the unique assembling traits of CNC with increasing concentration, we investigate the effect of two distinct CNC sizing morphologies on the interfacial mechanical properties of FRP composites manufactured through vacuum-assisted resin transfer technology (VARTM). Here, we used tetramethylpiperidine-1-oxyl (TEMPO)

mediated CNC (t-CNC) which have plenty of surface active carboxyl and hydroxyl groups and exhibit a better colloidal stability due to strong electrostatic repulsion between COO⁻ groups, a prerequisite for uniform dispersion and any self-assembly to occur [31].

2. EXPERIMENTAL WORK

2.1. Materials and Methods

Plain-woven E-glass fabric reinforcements (RE50 P, density 2.50 g/cm3, modulus 69 GPa, tensile strength 2.4 GPa and fibre diameter 5.0-5.5µm) was supplied by Gurit (UK) Ltd. The dry glass fabric reinforcements were used without removing any industrial sizing. Infusion grade bi-component ultralow viscosity epoxy resin (IN2, η ~ 500 mPa.s, density ~ 1.12 g/cm³) and poly(oxypropylene) diamine (slow hardener AT30, η =10-20 mPa.s, density 1.10 g/cm³) was mixed and cured according to the supplier's recommendation (resin: hardener (100:30 by weight)), η ~ 200 mPa.s, density 1.12 g/cm³, pot life 90 min.). Resin and all consumable items were purchased from Easy Composites Ltd. U.K. TEMPO-mediated cellulose nanocrystals (t-CNC, surface charge: 1.0 mmol-COONa/g, density ~ 1.56 g/cm³) were supplied by Cellulose Lab, Canada, as suspensions (3.99 % solid content). The CNCs were characterized by AFM to give an average length of 220± 81 nm, and a height of 10±2 nm (Fig.1).

2.2. Preparation of t-CNC/GFRP composites

2.2.1. Sizing treatment: TEMPO-mediated CNCs (t-CNC), which were already dispersed in water (3.99% solid content), were diluted from the bulk concentration to 0.25% and 1.0% working stock concentrations. These two concentrations were selected after several trials to achieve sparsely deposited CNCs and uniformly coated self-assembled CNC nanostructures [35, 42]. The stock concentrations were sonicated for 1h (using Fisherbrand FB11006 at ultrasound power of 140% (equivalent to 56 kHz) to homogenize the dispersions for further

use. For the glass fabric coating, the dispersions were transferred to transparent petri-dishes of size 110mm x100 mm x15 mm. The glass fabric (100 mm \times 100 mm) was immersed in the CNC dispersion at two different concentrations (0.25 and 1.0 %), respectively, for 1 min to cover the large surface area of the fabric with uniform coating. Subsequently, coated fabrics were air dried at 60 °C overnight and then finally dried at 120°C for 24 hr using a standard oven. The control glass fabric plies were also exposed to the water immersion step to keep the processing history identical. The sized fabrics (named t-CNC025-GF and t-CNC1-GF were stored in a desiccator for further use. Digital images of the fabric and the coating process are provided in Fig. 1S.

2.2.2. t-CNC/GFRP composites: In order to prepare the t-CNC/GFRP composite laminates through vacuum-assisted resin transfer manufacturing (VARTM), 40 plies of t-CNC-coated glass fabric was stacked on top of each other and then sealed in a vacuum bag on an aluminium plate (thickness~ 10mm) coated with release agent. Fig.2 represents the complete process from fabric coating to GFRP composites preparation. The manufacture of the GFRP composites is described in the Supplementary Information document and our previous published work [22]. The average density (ρ) and fibre volume fraction (FVF) of the control GFRP and t-CNC/GFRP were estimated as 1.68±0.01 g/cm3 and 41.1±1.5 vol%, respectively. The fibre volume fraction (FVF) of the composite laminates were estimated by the density method according to equation $V_f = (\rho_c - \rho_m)/(\rho_f - \rho_m)$, where ρ_c , ρ_m and ρ_f are the density of the composite, matrix and fibre, respectively [34]. The density of the composites was measured using water displacement using a Sartorius weighing specific gravity kit as per ASTM standard D792 [23]. The composite panels were cut to the different sizes with a wet diamond saw (VITREX versatile pro 750).

3. CHARACTERIZATION

The size, shape, sizing and fractured morphology of t-CNC and t-CNC/GFRP composites was analysed by AFM (Asylum, Cypher E5) and SEM (JEOL: JSM 6500 F). The surface roughness and quantitative measurement of binding forces (please see supplementary information for detail) between t-CNC and GFs were examined by AFM in tapping and contact mode. In AFM, AM-FM (amplitude-frequency modulation) viscoelastic mapping mode was used to capture the local interface modulus transition at the fibre/matrix interface for GFRP and t-CNC/GFRP composites. In this mode, cantilever frequency/amplitude respond sensitively to the changes in the sample properties during scanning. A high cantilever frequency/small dissipation (small amplitude decrease) response means higher stiffness/modulus [35,36]. For the contact stiffness measurement, we used an AC 160 TSA probe with cantilever spring constant 38.5 N/m accurately calibrated with GetReal[™] software. All the samples were uniformly polished to minimise the surface topographic effects on imaging and interphase measurement [37]. A related adhesion parameter, the shear strength between GF and t-CNC was also determined using the energy dissipated (E_{Diss}) under the force-displacement curve during delamination (please see supplementary information for detail). Similar methods and procedures of deriving lateral forces and shear strength between nanoparticles and the fibre surface using AFM has been previously reported by Lahiji et al. and Pugno et al. [38-39]. The fracture between t-CNC and GF occurs most likely in mixed-mode, rather than in pure-shear. The fracture behaviour is strongly dependent on the flatness of the surface as well as the shape and size of the CNC particles. An uneven surface can cause the AFM probe to twist which in turn can influence the delamination behaviour. A pure-shear-based relationship between shear modulus and shear strength/strain (Ga $\sim \tau/\gamma$) is assumed in the calculation described above. These uncertainties can influence the obtained shear strength results. By calibrating the cantilever prior to the measurement (zeroing the deflection and lateral signal) and adapting a high displacement speed

with the AFM probe along the GF surface, we hope to have reduced any deviating effects to an extent where pure-shear fracture is approximated.

The flexural and interlaminar shear strength (ILSS) tests were performed according to ASTM D790 and ASTM D2344 at a testing rate of 1mm/min. The flexural tests were performed using a universal testing machine (Zwick/Roell Z100). Flexural modulus was calculated from each stress-strain curves between 0.05 and 0.25% strain. The interlaminar shear strength (ILSS) of the laminates was conducted using a Lloyd (Model: LS5) testing machine at a test speed of 1 mm/min. Five specimens were tested for each composition. Dynamic mechanical thermal analysis (DMTA) was performed in dual cantilever mode using a Tritec 2000 DMA, manufactured by Triton Technology, Ltd. (UK). Samples were subjected to a sinusoidal strain of 0.05% with a heating rate of 3°C/min at a constant frequency of 1Hz. The interactions between t-CNC-GF and t-CNC-epoxy were characterized by a Perkin Elmer Spectrum 100 FTIR spectrometer. X-ray diffraction (XRD) of t-CNCs modified GF was carried out using a PANalytical X-ray diffractometer (Model: X' pert Pro) at a step size of 0.020° in the 2θ range of 5–65°. A First Tech Angstroms FTA125 Goniometer- Contact Angle & Surface Tension Machine measured the wettability characteristics of GF and t-CNC modified GF.

4. RESULTS AND DISCUSSION

To gain a comprehensive understanding of the surface characteristics of t-CNC sized GF, we first investigated the sizing morphology, surface roughness, wettability and adhesion forces between t-CNC and GF. Fig.3 presents the surface morphology of the control and t-CNCs sized GFs. As can be seen from Fig. 3a, the control GF presents a smooth and neat surface, but t-CNC sized GFs show a significantly distinct surface morphology. At low concentration, the t-CNC025-GF surface (Fig. 3b&c) reveals the presence of the sparsely deposited needle like t-

CNCs. More interestingly, at high concentration (t-CNC1-GF, Fig. 3(d-f)), the fibre surface looks completely encased with a strongly adhered coating of self-assembled t-CNCs. Wrapping of the fibre surface by functional nanoparticles (having surface active groups such as COO-, OH etc) has been reported to be highly beneficial for enhancing the interfacial properties between epoxy and fibre [5,8,13,25]. Uniformly deposited nanoparticles, having a high specific surface area, can act as effective anchors to boost surface roughness and wettability, further leading to strong mechanical interlocking between the GFs and resin matrix. To another end, the surface of the t-CNC1-GF displays several unique features, such as convex hills, encompassing sharp preferentially oriented needle-like CNC protruding ends (upright and perpendicular to the fibre surface, as indicated by the white arrows in Fig. 3d&e). These types of distinct sharp features play a favourable role in enhancing the surface roughness and provide large surface area for interfacial interactions [11-12, 25]. The sharp protruding ends extend into the epoxy to build a strong mechano-chemical locking system [10]. In the supplementary information provided, we present SEM images (Fig.2S) of the cross section view of drop casted CNC films from 1.0% dispersion, which shows periodically arranged layers of self-assembled nanostructures of CNCs. The spindle like shape morphology and the repulsive electrostatic forces (arising because of the high surface charge density) between uniformly dispersed CNCs promotes the formation of liquid crystalline phases which finally gives rise to self-assembles nanostructures with parallel packing of CNCs in each layer (as shown by the white circle in Fig.3e and supplementary Fig. 3S). However, the concentration, aspect ratio, surface charge density and drying process play a significant role in controlling and tuning the self-assembly process. In addition, these hierarchical ordered nanostructures, deposited over fibres, could provide several toughening mechanisms that hinder the catastrophic macroscopic propagation of cracks [29-30, 33]. Further, XRD and FTIR studies confirmed the deposition and chemical interactions between CNCs and GF (FTIR and XRD results and discussion are presented in the

Supplementary Information document). Furthermore, contact angle and AFM measurements of t-CNC-GF confirmed the decreased in epoxy contact angle and significant increase in surface roughness. For t-CNC sized GF, the epoxy contact angle reduced to $66.01^{\circ}\pm1.5$ (t-CNC025-GF) and $49^{\circ}\pm3.5$ (t-CNC1-GF) from $74^{\circ}\pm2.1$ for the control GF. Here, it seems that the large quantity of the surface-active functional carboxyl (C=O) and hydroxyl groups present on t-CNCs increased surface energy, which improved the wettability and thus increased the fibre-epoxy interfacial adhesion. The surface roughness (R_a) increased from 50 ± 4.0 nm (control GF) to 79 ± 6.5 nm (t-CNC025-GF) and 195 ± 11.5 nm (t-CNC1-GF), respectively. The significant increase in surface roughness for t-CNC1-GF is quite evident, owing to the presence of the sharp features of uniformly coated self-assembled CNC nanostructures (Fig.4c) [10, 25]. This increased roughness plays a favourable role in enhancing the mechanical interlocking between the fabric and epoxy matrix, and wettability of the fabric.

Apart from studying the qualitative interactions between t-CNC and GF using FTIR, we quantitatively measured the molecular binding affinity between the t-CNC and GF. As shown in Fig.5b, at a normal force of 0.5 V, the cellulose nanocrystals remain bound to the fibre surface, but at the normal force of 1.0 V (Fig.5c), it was possible to detach/relocate the CNC along fibre surface. Figure 5d indicates that the probe travels along the GF surface with an almost constant lateral force until a rapid increase in resistive force is recorded upon reaching the CNC. The interfacial adhesion force (delamination force) between the glass fibre surface and the t-CNC was measured as 25 ± 1.2 nN (please see supplementary information for detailed calculations). A previous study by Lahiji et al. reported adhesion forces between CNCs (-OH functionality) and mica surface (having –OH surface groups) of around 10 nN [40]. However, in our case, higher values reveal that surface functionality of t-CNC (COO⁻ carboxylate group) and support surfaces can alter the adhesion forces.

The shear strength, τ ,between GF and t-CNC, was calculated for the normal force of 1.0 V (Figure 5d), using the energy dissipated (E_{Diss}) under the force-displacement curve during delamination of the t-CNC from the GF (Fig.5d). The shear strength under applied pressure was calculated as 179±14 MPa (please see supplementary information for detailed calculations). Similarly, Mahmood et al. observed a shear strength of 130 MPa between graphene oxide (GO) and glass fibre [13, 39].

After having gained insight into the CNC's sizing morphology, wettability characteristics, surface roughness as well as qualitative and quantitative interactions between t-CNC and GF surfaces, we infused an ultra-low viscosity epoxy resin through a layup of t-CNC-sized GF to prepare t-CNC/GFRP composite laminates. The composite specimens were examined to assess the interphase microstructure, interfacial mechanical properties and the prevailing fracture mechanism. Fig.6 shows a schematic representation of the quantitative nanomechancial interface mapping of the polished cross-section of GFRP and t-CNC/GFRP composites. In particular, we used non-invasive and high-resolution amplitude and frequency modulation (AM-FM) mapping that eventually provides an insight into modulus transition across fibre-matrix interfaces. In AM-FM mode, the AFM tracks both dissipation (amplitude) and frequency, which corresponds, to the relative modulus of the phases. In other words, a higher amplitude/frequency of the tip means a higher relative modulus, and vice versa.

From Fig.7a, it is quite clear that the interface line profile of GFRP is very steep without any obvious transition zone (regular interface) which represents a large property mismatch that possibly leading to a high stress concentration at the matrix-fibre interface [14]. This sharp interface also indicates the limited interfacial crosslinking between the fibre and epoxy. In contrast, the t-CNC/GFRP line profile provides evidence of the formation of an enhanced interphase with a gradient modulus. These gradient modulus interphases mitigate the large

modulus contrast between stiff fibres and compliant soft matrix, which have been reported to have a big impact in terms of reducing stress concentrations [15-16]. These gradient features exist in biological materials, i.e. between bone, cartilage and muscles to reduce stress concentration for better durability [15,30]. GFRP and t-CNC025/GFRP (Fig.7b) composites show an interphase thickness of ~49 nm and ~137.7 nm, respectively but for the t-CNC1/GFRP (Fig.7c) composite, the interphase thickness reaches ~ 307 nm. For t-CNC025/GFRP, the modulus shows a gradual increase from matrix to fibre, which demonstrates the formation of a CNC dispersed epoxy nanocomposite interfacial layer. Interestingly, for t-CNC1/GFRP, a new distinct intermediate modulus platform (ladder type) is observed at the interface between the fibre and matrix, which can be related to increased crosslink density due to the strong chemical interactions between a large number of active (-COO⁻ and-OH) groups of the self-assembled CNC coating and epoxy matrix [15, 22,24,27]. More recently, experimental studies have demonstrated that the engineered gradient modulus interphases, of a few hundred nanometres thickness, act as a stress transfer medium (buffer) and load can be transferred from matrix to the fibre more uniformly [15,17].

To evaluate the effect of CNC sizing and gradient modulus interphases on the flexural strength and modulus of the t-CNC/GFRP composites, we performed flexural tests. Fig. 8a shows the representative curves for flexural testing. It is clear that t-CNC sized GF exhibits a significant increase in flexural performance of t-CNC/GFRP composites. The flexural strength of t-CNC025/GFRP and t-CNC1/GFRP increased from 431 ± 10 MPa to 517 ± 35 MPa and 617 ± 25 MPa, respectively. The flexural modulus increased from 13.7 GPa to 15.1 GPa and 19.3GPa for t-CNC025GFRP and t-CNC1/GFRP, respectively. Notably, t-CNC1/GFRP composites showed significant improvement in flexural strength (43%) compared to that of control GFRP. This increase in flexural strength can be attributed to (1) stronger interfacial

bonding between t-CNC-GF and epoxy (as shown in SEM morphological studies discussed later) and (2) arresting of the interlaminar and intralaminar micro cracks by the gradient interphase layer between fibre and matrix. Simulation work by Romanov et al. demonstrated that thick gradient interphases reduce the stress concentration and play a major role in arresting the direct crack propagation from matrix to fibre interface [14]. The gradient interphases comprising self-assembled CNC nanostructures possibly deflect the major matrix cracks propagating towards fibres and deviate them away from the fibre surface to the interphase region [15]. In addition, stresses in the matrix confined within the nanoparticles coating decrease to lower levels in comparison to the stresses in the epoxy rich zones. Uniform nanoparticle coating tends to constrain the deformation of the matrix inside the nanocomposite layer (epoxy impregnated CNC coating layer) around the fibres to reduce the stresses [14]. However, in the case of t-CNC025/GFRP composites, flexural strength increase is solely attributed to strengthened interfacial interactions, since sparsely deposited t-CNC is not optimal for activation of micro-scale mechanisms such as damage diffusion, crack pinning and crack deflection. Similarly, for t-CNC1/GFRP we observed a significant increase in flexural modulus (40%), which can be attributed to the formation of a distinct intermediate modulus interphase, which might act as additional rigid reinforcement [16]. Several studies have recently established that the formation of a high modulus interfacial layer significantly enhances the overall modulus of the composites [23, 41, 42-44]. This significant increase in the modulus is consistent with previous findings on nanomaterials-enhanced multiscale FRP composites. Asadi et. al. investigated the CNC/short GF/epoxy composites and observed 44% increase in the flexural modulus at 0.9 wt% CNC [23]. Zhang et. al. reported a 54% increase in the flexural modulus for 0.5 wt.% carboxyl-functionalized carbon nanotubes-sized CFRP composites [44]. Paterson et al. observed a 68% increase in flexural modulus of the CFRP composites at 2.0 wt.% of aramid nanofibers [45]. In another work, Ma et. al. realised 78% increase in the flexural

modulus of 1.0 wt.% graphene-sized CFRP composites [46]. As is evident in Fig. 3e, the GF is totally encased in a self-assembled coating of highly stiff and strong CNCs (Tensile strength ~ 10 GPa and Young's modulus ~ 150 GPa) which when impregnated with ultralow viscosity epoxy formed a high modulus layer around the fibre surface (as confirmed by AFM, Figure 7d and supplementary Fig.4S). It is postulated that the strong chemical interactions between surface active (-COOH and -OH) groups of self-assembled CNC coating and epoxy matrix resulted in this highly cross-linked thick interphase around the glass fibres that contributed to this considerable increase in flexural modulus [41]. However, t-CNC025/GFRP composites exhibit a relatively low increase in flexural modulus (only 10%) which explains limited CNC-CNC stress transfer capability of sparsely deposited CNC. Furthermore, we conducted interlaminar shear strength (ILSS) measurements to evaluate the strength of the interface between fibre and matrix. Short span specimens were used to induce a high shear stress at the mid-plane, to ensure interfacial delamination preceded any other failure mechanism [47]. The ILSS increased from 35.1±1.9 MPa for the control GFRP to 38.1±1.5 MPa and 45.6±1.2 for t-CNC025/ GFRP and t-CNC1/GFRP 'respectively. As shown in Fig. 8b-c, t-CNC0.25-GFRP shows an increase of 8.5 % of ILSS compared to that of the control GFRP. This is due to the dispersed CNCs in the interfacial region of the t-CNC025/GFRP composite, which increased the surface roughness and provided intimate molecular contact and stronger interfacial mechanical interlocking between the t-CNC-GF and matrix. In addition, the oxygen-based functional groups of the t-CNC enhance the interfacial adhesion between CNC modified GF and epoxy by establishing the hydrogen and covalent bonding sites during curing process [12,26-27]. However, for t-CNC1/GFRP, the ILSS increase shows a significant jump by 30% compared to that of the control GFRP. Here it is expected that apart from the significant increase in interfacial strength as described above, the formation of a distinct intermediate modulus interphase increased the resistance to crack propagation in the intra-ply regions and

between the ply layers (0° and 90°), thus improving the delamination resistance. The increase in the flexural and interlaminar shear strength (ILSS) is indicative of an increased resistance to crack propagation and delamination.

To this end, we have compared the effectiveness of CNCs against silane-based optimized sizing (Table 1S: supplementary information). We believe that a direct comparison is sometimes challenging as the experimental conditions, fibre composition, curing agent, and epoxy types are different, which directly influences the interlaminar shear strength. However, CNCs show a comparative improvement in ILSS.

In order to further understand the interfacial interactions and then effect on the viscoelastic behaviour of t-CNC/GFRP composites over a broad temperature range, we performed dynamic mechanical thermal analysis (DMTA). Fig.8d displays the variation of storage modulus (E') for the GFRP and t-CNC/GFRP composites. The presence of CNCs in the interfacial region between GF and matrix increased E' from 19.3 GPa to 21.4 GPa (by 10%) and 25.2 GPa (by 28%) in the glassy region and from 2.4 to 3.1 GPa (by 29%) and 6 GPa (by 150 %) in the rubbery region (at 120°C) for t-CNC025/GFRP and t-CNC1/GFRP composites, respectively. These finding indicates that inherent the high modulus of CNCs, enhanced interfacial interactions and stiffness of constituent's the interfaces enable efficient stress transfer and improved energy storage mechanism at the interphase. Notably, for t-CNC1/GFRP, we observed a distinct shift in the onset of modulus drop corresponding to glass/rubber transition, which indicates an increased stability of stiffness at higher temperatures. This shift provides compelling evidence of the formation of a highly cross-linked network around fibres through strong hydrogen bonding and mechanical interlocking between CNC coated GF and epoxy matrix, which increased the volume fraction of the rigid phase and thus resulted in a better

stability and increase in storage modulus at higher temperature [15, 26-27]. However, t-CNC025/GFRP composites do not show any shift in glass-rubber transition, which implies that sparsely deposited nanoscale CNCs exhibit limited effect on confinement of the epoxy chains.

To correlate the interfacial mechanical properties with prevailing fracture mechanisms, we performed SEM imaging of the fractured surfaces of GFRP and t-CNC/GFRP composites. Fig.9 shows pulled-out fibres with a smooth surface indicating poor interfacial bonding. In contrast, for sparsely deposited t-CNC025/ GFRP composites, fragments of fractured epoxy can be observed on the fibre surface, which indicates partial improvement in the interfacial bonding between fibre and epoxy matrix (Fig.9b). Interestingly, for uniformly coated t-CNC1/GFRP composites, the interface between fibres and matrix remains intact even after failure (Fig. 9c-d). The fully epoxy encapsulated fibres as well as shearing and smearing of the matrix are evidence of stronger interfacial bonding between t-CNC-GF and epoxy matrix. Judging from the difference in interfacial fracture morphology it appears that a complete coverage of the fibre surface with CNCs leads to an efficient interphase design [12, 46]. To further gain an insight into, the role of CNC, on the interfacial bonding at the fibre-matrix interface, we performed SEM on off-axis fibres to the loading direction (Fig.10). For control GFRP composites, the epoxy was completely detached from the fibre surface, which indicates that fibre-matrix debonding is a major dominant failure mechanism. For t-CNC025/GFRP composites, the failure surface reveals the presence of a tightly bonded thin layer of epoxy partially covering the fibre surface. A closer view provides a clear indication that sparsely deposited t-CNC in the interfacial region act as potential anchoring sites to provide better mechanical interlocking between the fibre and epoxy. The carboxyl (-COO-), hydroxyl (-OH) and -C-O-C groups of t-CNC-sized glass fibre strongly interacted with epoxide groups of the epoxy via hydrogen and covalent linkage, increasing the wettability between GF and epoxy

resin. The strong chemical interactions between the carboxyl/or hydroxyl groups of the CNC nanoparticles and epoxy have already been confirmed by FTIR studies in literature [11, 20, 26, 48]. In our, previous work on CNC modified epoxy reinforced GFRP composites, FTIR studies revealed strong covalent bonding interactions between CNC and epoxy matrix [22]. Because of these interactions, the localized reinforcement of matrix around fibres generated a gradual change of the modulus across the interface that ensured better stress transfer, which is beneficial for improving the mechanical properties.

In contrast to t-CNC025/ GFRP, the interfacial morphology for t-CNC1/ GFRP is remarkably different. Fig.10d shows a very coarse interface failure having a thick layer of epoxy impregnated CNCs layer tightly clammed over the fibre surface. The presence of this highly localized enhanced modulus layer (comprising epoxy infiltrated self-assembled CNC layer) surrounding the fibre surface leads to the formation of distinct intermediate modulus platform (as shown in AFM Fig.7c). The morphology of preferentially oriented CNC layers in the composite (Fig.10d: indicated by black dotted circle and orientation by the arrow) exactly matches the preferentially oriented self-assembled CNC layer morphology in the CNCs films (supplementary information, Fig. 3S: SEM of cross section of CNC films), which indicates that during resin infiltration, the CNC sizing remains stable around the fibres. As suggested by other researchers, these intermediate platforms not only supress the diffusion of damage by arresting the cracks propagating directly towards the fibre surface but also act as stress transfer medium to facilitates the load transfer from matrix to fibres uniformly [15]. In Fig. 11, the fully encapsulated fibre surface with the dense and thick layer implies excellent wetting of selfassembled layered network of t-CNC sized GF with epoxy matrix. The presence of dendritic type networks of cracks contained within the interphase layer indicates that the cracks were continued in the matrix rich zone and fracture did not proceed towards the fibre surface,

because of the formation of the tough intermediate modulus interphase (thickness ~ 310 nm, similar to measure by AFM) between GF and epoxy matrix. Fig.12 shows a schematic representation of the difference in the interfacial fracture mechanism of GFRP and CNC enhanced GFRP composites. As shown in Fig. 12a, due to a weak interface/or in absence of a gradient interface, the crack can easily propagate through the interface and the epoxy easily detach from the fibre surface. As indicated by Fig.12 b&c, the formation of intermediate modulus interphase layer shifts the stress concentration and cracks away from fibre-matrix interface to the matrix rich phase, which indicates improved interfacial strength and stress distribution across the fibre-matrix interface. The effect of CNC sizing is also discernible from the interlaminar regions after interlaminar shear strength (ILSS) testing (Fig.13). The control GFRP composites display smooth and clear interfacial cleavage, but t-CNC1/GFRP fracture surfaces exhibit extensive interlaminar matrix deformation and the matrix became ragged indicating that interfacial debonding at the fibre/matrix interface was impended. The cleavage of fibre into numerous fragments and presence of clearly observable strongly bonded epoxy impregnated t-CNC film over GF suggests that multi-layered sized GFRP composite has a tougher and stronger interface between fibre-matrix. Interestingly, high magnification images, reflects scratch patterns (as indicated by the black arrow in Fig. 13e&f), peeling and breaking of the interfacial CNC layer, which suggest high fracture energy absorption and strong resistance of CNC sizing layer to crack propagation towards the fibres this explains why t-CNC1/ GFRP composites exhibit high flexural and interlaminar shear strength compared to t-CNC025/GFRP and control GFRP. Overall, from AFM and SEM imaging, it can be concluded that the increase of surface roughness, specific surface area, resin wettability and presence of active oxygen-based functional groups over t-CNC sized GF, together, play a crucial role towards bridging the epoxy and glass fibres in the composites.

5. CONCLUSION

This study has successfully demonstrated that improvement in the strength of a glass fibre/matrix interface may be achieved by promoting a gradient interphase around fibres containing sparsely deposited or a self-assembled coating of CNCs around the GFs. The sizing with cellulose nanocrystals (t-CNC: having surface-active carboxyl and hydroxyl groups) increased the surface roughness and GF wettability characteristics leading to enhanced interfacial mechanical performance. The qualitative and lateral force nano-mechanical mapping investigations of t-CNC modified GF (t-CNC-GF) confirmed the strong interfacial interactions and robustness of the sizing. The novel nano-mechanical mapping showed the formation of a high modulus interphase that lead to improved mechanical properties of t-CNC/GFRP composites. Mechanical and morphological results confirmed that a stronger interfacial bond between the GFs and the epoxy matrix was achieved for the fibres sized with uniformly self-assembled t-CNCs compared to the sparsely deposited t-CNC and un-sized GFs. Mechanical testing results confirmed that self-assembled CNC-coated GF reinforced composites (t-CNC/GFRP) yielded a ~30% increase in interlaminar shear strength (ILSS), a 43% increase in flexural strength, and a 40% increase in flexural modulus compared to the control GFRP composites. The remarkable high shear strength between t-CNC and GF (179±14 MPa which is 3.7 times higher than that of the interlaminar shear strength of the t-CNC/GFRP composites (45.6±1.2 MPa) confirms the SEM observations that failure of the t-CNC/GFRP composite happens preferably at the epoxy/t-CNC interface, rather than at the t-CNC/GF interface. This demonstrated the effectiveness of the t-CNC sizing for the GFRP composites.

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CONFLICT OF INTEREST

The authors declare no competing financial interest

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Fig. 1. Atomic force microscopic image of CNCs (a) phase image (b) height profile and (c) β helix-chemical structure of TEMPO-cellulose nanocrystals (t-CNCs).



Fig. 2. Schematic representation from coating to GFRP composites fabrication process.



Fig.3. SEM images of glass fabric (a) without sizing (b&c) sized with sparsely deposited t-CNCs (t-CNC025-GF) and (d&e&f) with self-assembled coating of t-CNCs (t-CNC1-GF).



Fig.4. Surface properties of the GF: epoxy contact angle and corresponding surface roughness of GF (a) without sizing (b) t-CNC025-GF and(c) t-CNC1-GF.



Fig.5. (a) AFM image of t-CNC sized fabric, (b&c) lateral force nanomechanical mapping experiment in which the AFM tip is moved at different normal forces (expressed in Voltage) over the fibre surface to determine the adhesive forces between the fibre and CNCs and (d) plot of lateral force vs displacement for image (c) which shows the relocation of the CNC at normal force of 1.0 V.



Figure 6: Working principle design of AM-FM for interphase measurement



Fig. 7. (a-c) AFM images of the polished cross-section of composites in AM-FM mode and corresponding section analysis of the interphase (a) control GFRP (b) t-CNC025/GFRP and

(c) t-CNC1/GFRP composites.



Fig.8. Mechanical properties of GFRP and t-CNC/GFRP composites (a) Flexural (b&c) interlaminar shear strength (d) storage modulus vs temperature.



Fig.9. SEM images of the flexural fractured surface of (a) control GFRP (b) t-CNC025/GFRP (c-d) t-CNC1/GFRP composites. Image (d) is a magnified version of (c)



Fig. 10. SEM images of the flexural fractured surface of (a) control GFRP (b-c) t-CNC025/GFRP (d) t-CNC1/GFRP composites. Image (c) is a magnified version of (b)



Fig.11. SEM images of the fractured surface of (a) control GFRP (b-d) t-CNC1/GFRP composites.







Fig. 13. Interlaminar shear strength testing fractured surface images for (a) control GFRP and (b-f) t-CNC1/GFRP composites.