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Nano-engineered hierarchical natural fibre composites with localised cellulose nanocrystals and tailored interphase for improved mechanical properties

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ABSTRACT

Natural fibre composites have been utilised in many applications such as automotive and buildings, thanks to their high specific properties and environmentally friendly nature. However, the incompatibility between hydrophilic natural fibres and hydrophobic polymer resins remains a longstanding issue in natural fibre composites. Inspired by nature's hierarchical structures and tailored functionalities, a nano-engineered hierarchical natural fibre composite has been developed in this study, utilising cellulose nanocrystals (CNCs) as localised nano-reinforcements at flax surfaces in a flax/bio-epoxy system. A simple and versatile spray coating technique was used to deposit CNCs on unmodified flax fibres, without using any chemical solvents. With the increased surface roughness and hence improved epoxy wetting on nano-engineered flax surfaces (3 wt% CNC loading), mechanical properties of the hierarchical composites have been significantly improved, with a 60 % increase in interlaminar shear strength, indicating an enhanced interfacial load transfer between flax and epoxy, alongside improved flexural modulus (14 %) and strength (23 %). This green approach without using any chemicals provides a scalable and sustainable way to develop tailored interfaces for natural fibre composites with enhanced resin wetting and mechanical properties.

1. Introduction

With the increasing awareness of environmental sustainability over the last years, natural fibres have regained significant interests in various fields in automotive, sports equipment, and beyond. Their eco-friendly attributes of negative carbon dioxide emission during growth, low density, biodegradability, abundance, and mechanical properties make them ideal candidates in fibre reinforced composites [1,2]. Flax, for instance, stands out due to its widespread availability and relatively high specific properties, making it a popular choice in many engineering applications [3,4]. However, the inherent hydrophilic nature of natural fibres introduces persistent challenges, such as high moisture uptake and poor interfacial adhesion with hydrophobic resins. These issues inevitably posing significant challenges in utilising natural fibre reinforcements for wider applications [1,5].

To enhance resin wetting and interfacial load transfer in natural fibre composites, extensive efforts have been made over the years, utilising both physical and chemical methods to treat the natural fibre surfaces [6–8]. Le Moigne et al. treated the flax fibre with organosilane and achieved a 25 % increase in yield stress with 5 wt% of silane (to fibre weight) compared to the reference flax/PLA composites [9]. Van de Weyenberg et al. demonstrated that alkali treatment (4 % NaOH for 45 s) can increase flax fibre-epoxy matrix adhesion, with a 30 % increase in laminate transverse strength, while associated issues of residual alkali induced swelling and porosity have also been noticed [10]. Zhang et al. employed ozone treatment to eliminate the non-cellulosic components from the surface of flax fibre and achieved an increased surface roughness and friction coefficient on flax fibre, although at the cost of reduced strength and elongation of the fibres due to delignification and destruction of cellulose chains during the treatment [11]. Bozaci et al. enhanced flax fibres interfacial adhesion hence interfacial shear strength to HDPE and unsaturated polyester using argon and air atmospheric plasma treatment, attributed to the increased surface roughness [12]. However, it is worth noting that the high plasma power might decrease fabric strength, as evidenced by cracks and longitudinal grooves on fibre surfaces [12]. While these chemical or physical treatments have shown great potential in improving fibre/matrix interactions, they often compromise fibre integrity and raise environmental concerns due to

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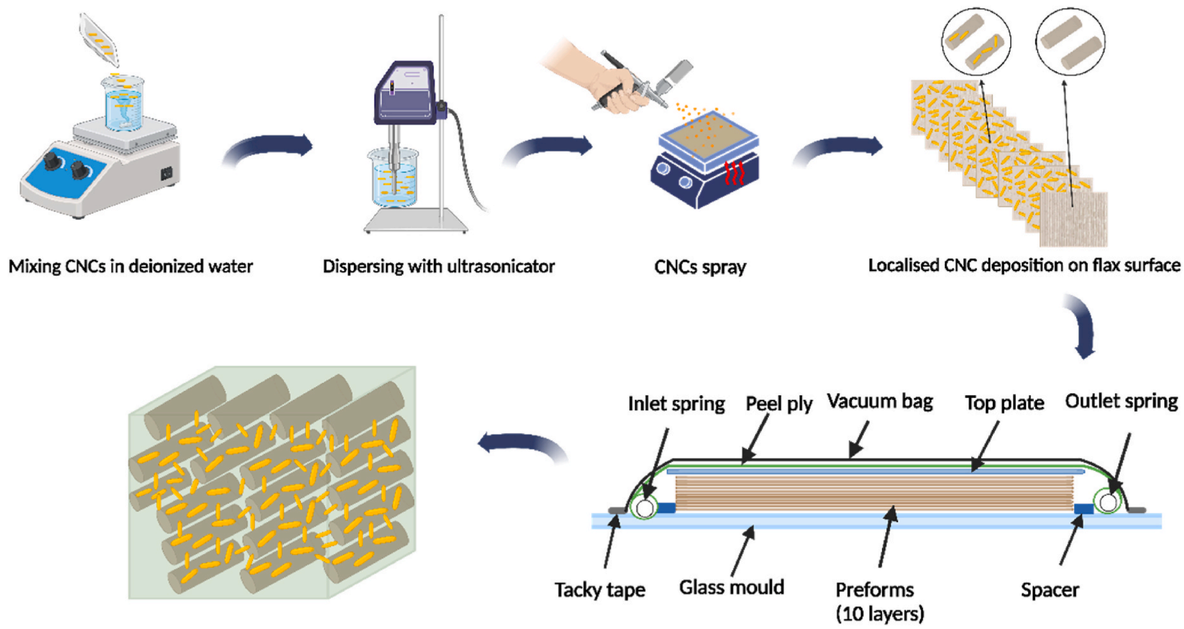

Fig. 1. A schematic illustration of CNC spray coating process to fabricate CNC/flax bio-epoxy hierarchical natural fibre composites with localised nano-modifications.

chemical usage.

With the evolvement of nanomaterials over last few years, many nanoparticles such as graphene nanoplatelets (GNPs) and carbon nanotubes (CNTs) have been integrated into flax fibre composites to improve the properties of the laminates [13–15]. Li et al. used carboxyl-functionalised CNTs to coat flax yarns through a soaking or spray-drying process, and achieved a 26 % increase in interfacial shear strength and 20 % in interlaminar shear strength with only 1 wt% CNTs [16]. These improvements were attributed to the formed hydrogen bonding between functionalised CNTs and flax fibres. Improved properties have also been observed by introducing GNPs in flax epoxy composites. Alipour et al. dispersed 0.5 wt% of GNPs in epoxy resin to make a GNP/flax/epoxy composite laminate, and obtained an increased modulus from 4.95 GPa to 5.9 GPa at a GNP loading of 0.5 wt% [17]. The potential of supercritical fluid infiltration with nanoparticles to modify natural fibre surfaces has been explored by Langhorst et al., presenting another approach to further enhance the mechanical properties of natural fibre composites [18].

More recently, natural nanomaterials, such as bacterial cellulose (BC), cellulose nanocrystals (CNCs), and cellulose nanofibrils (CNFs), have been explored and gained significant attentions due to their biocompatibility, biodegradability, and mechanical properties [19–23]. Researchers have examined the use of cellulose nanomaterials in natural fibre composites, to develop a multi-scale natural fibre composite. For instance, the adherence between matrix and natural fibres have been enhanced by modifying the fibre surfaces with nanosized bacterial cellulose, with an increased off-axis and parallel strength of 68 % and 44 %, respectively, observed in modified sisal/PLLA [24]. Lee et al. shown that the use of bacterial cellulose paper with a grammage of 60 g m^{-2} in epoxy nanocomposites can achieve a significantly improved Young's modulus of 7.1 GPa from 3.0 GPa of neat resin [25].

The commercialisation and increased availability of cellulose nanocrystals (CNCs) in recent years, have made hierarchical natural fibre composites closer to reality. Some promising achievements have been reported, although only a limited volume of literatures can be found to date. Doineau et al. absorbed CNC and xyloglucan (XG) onto short flax fibres and mixed with polypropylene and MAPP coupling agent to make a hierarchical composite, tuning flax fibre microstructures to improve its mechanical properties [26]. Both surface free energy and polar characteristics of flax fibres have been altered by the CNC/XG treatment, with a 21 % increase in work of rupture obtained in flax/CNC/XG/PP short fibre composites [26]. Han et al. demonstrated the potential of CNC in enhancing the mechanical properties of ramie fibres/biodegradable polybutylene succinate (PBS) composites [27]. By immersing the fibres in CNC solutions (up to 2 wt%), significantly enhanced properties were achieved with a CNC loading of 15 wt% to ramie fibres. Kumar et al. reported that the addition of 2 wt% CNC to a CNC/glass fibre epoxy system resulted in a 56 % increase in storage modulus, a 50 % increase in flexural modulus, and a 55 % increase in flexural strength [28]. Zhang et al. explored the use of electrophoretic deposition (EPD) to integrate CNCs into sisal fibres, creating a uniform and randomly oriented nanocellulose coating on the sisal fibres' surface [29]. This nanocoating layer, particularly with alkali-CNCs, demonstrated a synergistic effect of alkali treatment and CNC modification on sisal fibre. The alkali treatment facilitated the removal of hemicellulose, lignin, and impurities, enabling the CNCs to fill the resultant micro voids that were left between the nano-sized fibrils with an over 60 % increase in tensile modulus of sisal fibres and 30 % increase in interfacial shear strength.

Although some progress have been seen in hierarchical natural fibre composites, challenges such as the use of organic solvents and relatively complex procedures often limit the wider adoption of nano-engineered green composites. It is of great necessity to develop an effective interfacial adhesion between hydrophilic fibre surfaces and hydrophobic polymer resins, with a universal and environmental friendly method to reveal the potential of these natural fibre composites.

In this study, a hierarchical natural fibre composite consisting of cellulose nanocrystals as nano-reinforcement in a flax/bio-epoxy composite has been developed, targeting the persistent challenges of fibre/resin wetting and interfacial load transfer in natural fibre composites. Localised nano-modifications on flax fibre surfaces have been achieved, via a green and simple spray coating method without using any chemical solvents. Systematic characterisation from interlaminar shear strength, flexural properties, and morphologies of the hierarchical natural fibre composites have been performed.

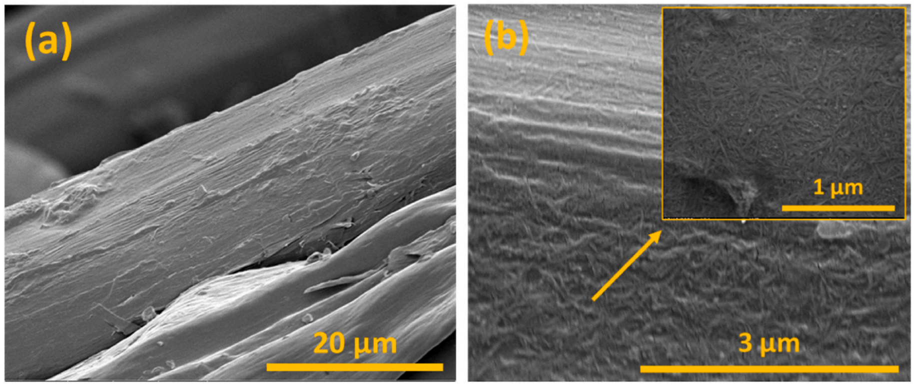

Fig. 2. SEM images of (a) neat flax, and (b) flax with spray coated 3 wt% CNC, showing an increased surface roughness with locally deposited CNCs.

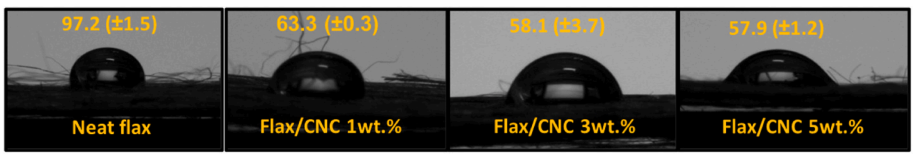

Fig. 3. Effect of CNC surface modification on epoxy wetting behaviour of flax preforms, with a clear reducing trend of contact angle between epoxy and CNC modified flax preforms, indicating an improved epoxy wettability after localised CNC deposition.

Table 1
Surface free energies of neat and CNCs modified flax fibres with polar and dispersive components exhibit a rise in total surface energy, showing the fibre surface's affinity for epoxy resin.

Samples	σ_S^D (mJ/m^2)	σ_S^P (mJ/m^2)	σ_S^{tot} (mJ/m^2)
Neat flax	11.35 ± 1.61	13.70 ± 1.04	25.05 ± 2.65
Flax/CNC 1 wt%	21.22 ± 3.36	14.39 ± 1.53	35.61 ± 4.88
Flax/CNC 3 wt%	27.56 ± 0.21	13.23 ± 0.73	40.79 ± 0.94
Flax/CNC 5 wt%	31.28 ± 3.75	12.84 ± 1.30	44.12 ± 5.05

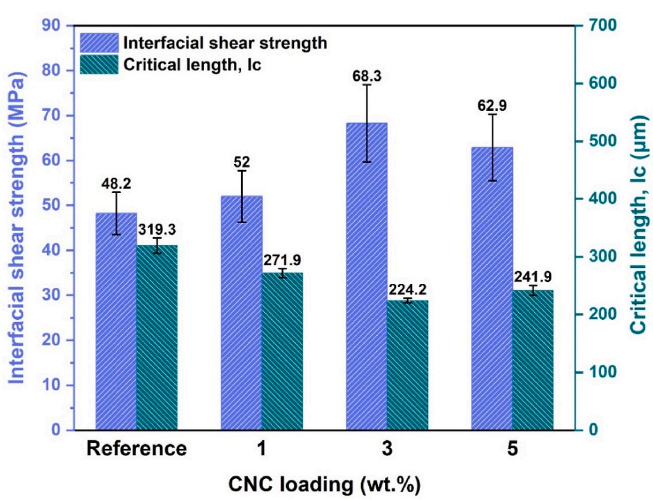

Fig. 4. Interfacial shear strength and calculated fibre critical length of reference and CNC-modified flax in bio-epoxy resins, showing an increasing trend of IFSS with CNC loading up to 3 wt%, alongside a decreased fibre critical length compared with reference specimens.

2. Experimental

2.1. Materials

The composites system in this study consists of unidirectional flax fabrics (EcoTechnilin, FLAXTAPE 110) with an aerial weight of 110 g/m^2 and cellulose nanocrystals (CNCs) supplied by CelluForce (NCV100-NASD90) in powder form. According to the supplier's datasheet, the CNCs have a particle length in the range of 1-50μm and diameter <150 nm. The bio-epoxy (IB2 Epoxy Infusion Bio Resin) and hardener (IB2 epoxy hardener) with a mixing ratio of 100:22 by weight were purchased from Easy Composites Ltd (UK).

2.2. Spray coating

Fig. 1 illustrates the main steps in spray coating processing. The spraying setup consists of an airbrush system from Iwata Performance (H4001 HP-CPLUS), connected with an Iwata studio series air compressor. Measured amounts of CNC were dispersed in water to achieve the final CNC loadings of 1, 3, and 5 wt% (to the total weight of composite laminates). The CNC/water suspension with a total volume of 75 ml was magnetically stirred for 30 min, followed by probe sonication of 1000 J/g energy at 20 % of maximum amplitude (2 s on and 2 s off). The air pressure during spray coating was set at 30 psi (2.07 bar), and the distance between the spraying nozzle and the prepreg layer was 10 cm. A heating stage with a fixed temperature of 100 °C was placed under the preforms (15 cm by 15 cm) to facilitate the water evaporation. A sprayed reference panel was fabricated by spraying the same amount of water without any CNC onto the preforms, to eliminate any effect of spraying water on the subsequent properties. All preforms were dried at 80 °C for 24 h before subsequent steps to avoid any water residuals. This temperature, which is lower than the typical oven-drying temperature of 105 °C for plant fibres [30,31], was chosen to avoid any significant decrease in fibre strength. A consistent fibre mass was detected following this period of drying.

2.3. Manufacturing of composite laminates

Vacuum-assisted resin infusion (VARI) was used to fabricate the flax/

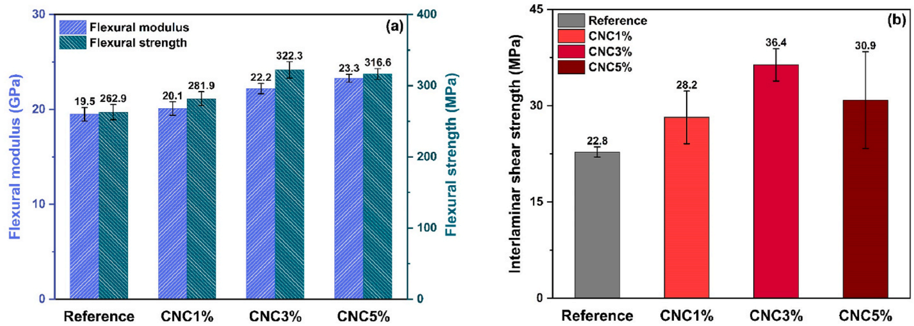

Fig. 5. (a) Flexural properties and (b) interlaminar shear strength of flax/epoxy and hierarchical CNC/flax/epoxy laminates, showing an increasing trend of flexural properties and interlaminar shear strength with increased amount of CNC deposited at the flax surface.

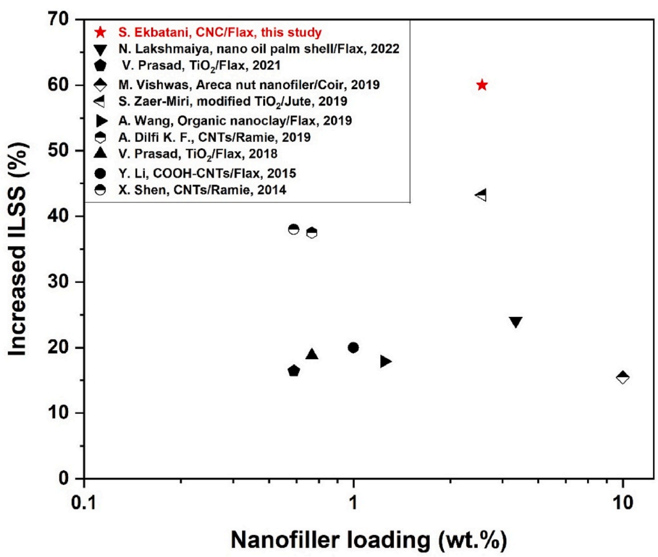

Fig. 6. A comparison plot of reported ILSS increment in natural fibre/epoxy composites by introducing various nanofillers from literature and this work.

Table 2
Glass transition temperatures (T_g) of nano-engineered composites by DMA.

Samples	Reference	CNC 1 wt%	CNC 3 wt%	CNC 5 wt%
T_g (°C)	74.7 (±0.4)	77.6 (±0.6)	79.5 (±0.5)	81.1 (±0.1)

bio-epoxy composite laminates. 10 plies of unidirectional flax fabrics were placed in the mould for each panel, while 9 out of 10 plies were spray coated with a desired amount of CNC for nano-engineered panels. The panels were 150 mm × 150 mm in size, with a thickness of 2 mm for all laminates. The laminates were cured at room temperature for 16 h followed by a post-curing at 80 °C for 8 h. Detailed panel specifications can be found in Table S1 in the Supplementary Information.

2.4. Optical microscopy

An optical microscope (VWR TR300) coupled with a 4× magnification lens was used to measure the diameter of single flax fibres. Flax fibres were mounted on a glass slide and measured at random intervals along their length to achieve a valid average diameter. The average fragment length of the single fibre after mechanical testing was measured and averaged from ten specimens in each formulation.

2.5. Scanning electron microscopy

Scanning electron microscope (SEM) (FEI Inspect-F, Netherlands) was used to examine the morphology of the fracture surfaces of the composites after the flexural tests. The samples were cryo-fractured after three-point bending test, and gold sputter with a 6 nm coating before the imaging with an accelerating voltage of 5 kV.

2.6. Contact angle

Wettability characteristics of both unmodified and CNC-coated flax fibres at varying CNC concentrations were measured using a drop shape analyser (DSA100, KRÜSS GmbH, Germany). All measurements were conducted at room temperature. The contact angle of each droplet was measured after a duration of 5 s upon deposition, with 10 repeats for each sample.

2.7. Mechanical properties

An Instron 5566 universal testing machine equipped with a load cell of 1 kN has been used to measure the mechanical properties of the laminates. Flexural properties of the flax/epoxy composites were measured by three-point bending test in accordance with ASTM D790, with sample dimensions of 50 mm × 12.7 mm × 2 mm and a span-to-depth ratio at 16:1. Interlaminar shear strength (ILSS) was measured in accordance with ASTM D2344, with a crosshead speed of 1 mm/min and span-to-depth of 4. Six samples with dimensions of 12 mm × 4 mm × 2 mm were tested for the average values.

Tensile properties of individual flax fibres were determined using an Instron 3342 universal testing frame. Individual technical fibre was mounted on a paper frame then with both ends clamped within the grips before the test. Tensile tests were conducted at a crosshead rate of 0.2 mm/min with a 10 N load cell at room temperature, adhering to ASTM D3379. Single fibre fragmentation test (SFFT) was performed on both untreated and CNC-coated flax technical fibre embedded in the bio-epoxy resin, with an Instron 5566 universal testing frame and a 1 kN load cell at a crosshead speed of 0.2 mm/min. Fibre diameter was measured via optical microscopy before each test for accurate assessment and subsequent calculation. Ten repeats were made for each sample.

2.8. Thermomechanical properties

Thermomechanical properties of the laminates were characterised by dynamic mechanical analysis (DMA, TA Instruments Q800) in three-point bending mode. The laminates were cut into 58 mm × 12.8 mm × 2 mm and measured with a temperature sweep ranging from room temperature to 150 °C at a rate of 5 °C/min, 1 Hz frequency, and 1 % strain, with 3 repeats for each sample.

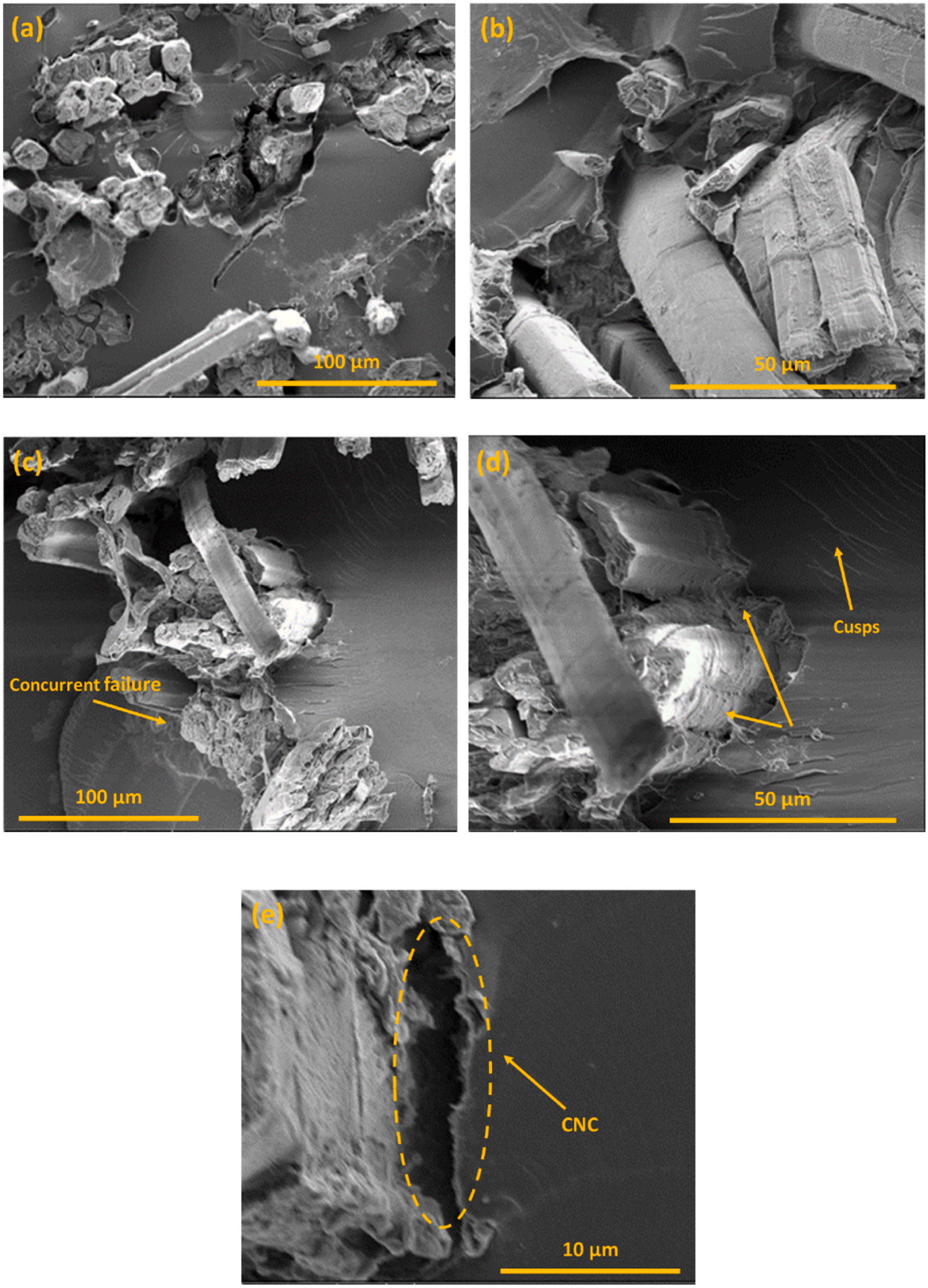

Fig. 7. SEM images of fracture surfaces of: (a–b) reference flax/epoxy laminates showing evidence of fibre pull-out alongside a smooth fracture surface; (c–e) 3 wt% CNC/flax/epoxy specimens, showing clear evidence of enhanced fibre-matrix bonding with CNC bridging and exposed at the interface with some traces of plastic deformation and cusps.

2.9. Zeta potential measurements

Zetasizer (Malvern Mastersizer 2000) was used to measure zeta potentials of the CNC/water suspensions. The given values are the average of six measurements for each CNC loading, with details of surface characteristics of CNC solutions in Table S2 in SI.

3. Result and discussion

3.1. Morphologies of nano-engineered flax fibres

The morphology of both neat and nano-engineered flax fibres have been examined by the scanning electron microscope. Fig. 2a reveals a relatively smooth fibre surface of neat flax fibres, showcasing their inherent fibrous structure along their length. In contrast, Fig. 2b shows a relatively uniform layer of spray coated CNC on the fibre surface, without any obvious agglomerates, indicating an effective CNC deposition through spray coating. Compared with reference flax fibres, a clearly increased surface roughness can be observed in CNC/flax specimens, attributable to the large surface area of CNC. The hydrophilic nature of both flax and CNC have facilitated the surface modification process, leading to a homogenous coverage of nanofillers on flax fibres. The enhanced surface roughness and uniform CNC coverage suggest potential improvements in the interfacial bonding between the fibres and the matrix, without explicitly altering the original attributes of the fibres.

3.2. Wetting properties

As mentioned earlier, the surface compatibility between natural fibres and polymer matrices such as epoxy resins is one of the long-standing issues in natural fibre composites. To achieve an efficient load transfer between epoxy resin and reinforcing fibres, an adequate wetting of the resin on the fibre surface is of great necessity.

Fig. 3 shows the wetting behaviours of epoxy resin on flax preforms, with contact angles measured for specimens ranging from neat flax to flax modified with CNC at different loadings. As expected, a relatively poor wetting was found in reference specimen, with a contact angle of 97.2° due to the hydrophilic nature of flax surface and the hydrophobicity of the epoxy resin. No obvious change was noted for specimen tested with pure water sprayed (see Fig. S1 in SI).

The introduction of CNC via spray coating significantly improved the epoxy wetting, as evidenced by a substantial reduction in contact angle compared to reference specimens (Fig. 3). With only 1 wt% of CNC coated on flax, an improved wetting with more than 30 % decrease in contact angle values (from 97.2° to 63.3°) have been achieved. A further reduced contact angle of only 58.1° (a 40 % reduction) was successfully achieved at a CNC loading of 3 wt%, indicating a clear improvement in epoxy wettability after CNC surface modifications. Since both CNC and flax are hydrophilic, this significantly improved epoxy wetting can be attributed to the increased surface roughness due to the relatively large surface areas of CNC nanofillers.

The total surface free energy (σ_L^{tot}) and polar and dispersive components σ_S^P and σ_S^D (mJ/m^2) of both neat and nano-engineered flax fibres were derived from contact angle measurements using deionized water and ethylene glycol (EG), based on the Owens, Wendt, Rabel, and Kaelble (OWRK) equation [32], Eq. (1), where θ denotes the contact angle between liquid droplet and fibre surface in radians.

$$\frac{\sigma_L^{tot}(\cos\theta+1)}{\left(2\sqrt{\sigma_L^D}\right)}=\left(\sqrt{\sigma_S^P}\right)\frac{\sqrt{\sigma_L^P}}{\sqrt{\sigma_L^D}}+\sqrt{\sigma_S^D} \quad (1)$$

The polar and dispersive surface tensions of the testing liquids, σ_S^P and σ_S^D (mJ/m^2), are shown in Table 1, alongside the total surface free energy of each specimen. An increased surface free energy from 25.05 mJ/m^2 of neat flax to 40.79 mJ/m^2 of 3 wt% CNC/Flax specimens was observed, confirming the effect of nanofillers on the surface free energy and polarity of the fibres which are in agreement with literature [33–35]. It is acknowledged that CNCs exhibit mainly dispersive properties because of their highly crystalline nature [26]. This attribute could account for the enhanced dispersive characteristics of flax fibres that have been coated with CNCs. The introduction of CNCs may also change the topographic feature of the flax fibres, while the polar characteristics of CNCs may have a preferred interaction with flax surface, leading to a more dispersive characteristics exposed. Consequently, the polar component slightly decreases, and the dispersive component is increased. As a result, the total surface energy of the fibre surface, when modified with a higher percentage of CNC nanoparticles, generally increases. In addition, as the sprayed water swells the flax fibres (Table S3 in SI), the enlarged surface porosity during the spray process may facilitate the penetration the nanoscale CNCs into the flax fibre structure, achieving a mechanical interlocking with increased surface roughness [16,36].

3.3. Single fibre composites

Mechanical properties of single flax fibres (technical fibres), with diameters ranging from 30 to 90 μm, were assessed through single fibre tensile test, as well as single fragmentation tests to evaluate their interfacial shear strength (IFSS). As expected, no changes in single fibre tensile modulus after the CNC modification (see Fig. S2 in SI), while a clear improvement was observed from the IFSS results after embedding the fibre in epoxy resin. As shown in Fig. 4, with 1 wt% of CNC deposited on flax surfaces, IFSS in CNC/Flax/epoxy specimens increased from 48.2 MPa to 52 MPa. When the CNC loading increased to 3 wt%, more than 40 % increase in IFSS, alongside a reduced fibre critical length to 224.2 μm from 319.3 μm, was obtained. This decreased fibre critical length indicates an enhanced adhesion and stress transfer, which can be attributed to the homogenous coverage and swell-induced interlocked CNC nanoparticles, acting as a bridge to facilitate the load transfer between resin and flax fibres. With increased CNC loadings to 5 wt%, no further increasing trend in IFSS was observed, suggesting a saturation of current system with CNC coverage on flax surfaces.

These improvements are in good agreement with literature on using nanocellulose in natural fibre composites. Marion Pommet et al. developed a hierarchical natural fibre composite with nano-scale bacterial cellulose, and obtained a significantly enhanced interfacial bonding (46 %) and IFSS (21 %) [37]. Hajlane et al. demonstrated that small CNC addition (0.1–0.4 wt%) can enhance bonding between regenerated cellulose fibres and epoxy [38]. Asadi et al. reported a 69 % increase in IFSS via single fibre fragmentation tests with 1 wt% CNC-coated glass fibre, indicating enhanced stress distribution at the fibre-epoxy interface by the introduction of CNC [39]. Li et al. observed improved stiffness and bonding in flax yarns with 1.0 wt% CNTs, attributing this to the mechanical interlocking facilitated by CNTs, which generate a bridging effect to enhance fibre/matrix adhesion [16]. These studies highlight the effectiveness of nanoscale modifications in enhancing the interfacial characteristics and overall performance of natural fibre composites. It is worth noting that although IFSS is typically measured via single fibre fragmentation test (SFFT) and pull-out tests, comparing results across different methods, particularly in variable natural fibre systems like flax, could be challenging. Such variability highlights the need for careful interpretation of IFSS data. In this work, similar fibre diameters were used while a repetition of 10 fibres per CNC loading was performed, to provide a relatively consistent comparison within the current system and hence to evaluate the effect of CNC modification on single fibre properties. Detailed calculations can be found in SI.

3.4. Mechanical properties of flax/bio-epoxy composite laminates

Building on the promising outcomes observed in single fibre composites, the mechanical performance of nano-engineered natural fibre composite laminates have been examined in this section. As shown in Fig. 5a, with the increased amount of CNC introduced, an increasing trend can be found for both flexural modulus and strength, reaching 22.2 GPa and 322.3 MPa with a CNC loading of 3 wt%, respectively, translating to an increase of 14 % in modulus and 23 % in strength. At the highest CNC loading in this study, a further increased modulus of 23.3 GPa was observed while the strength started to reduce slightly. These results confirm the effective load transfer hence the mechanical performance of the laminates from localised CNCs in the hierarchical natural fibre composites.

A significant improvement in the interlaminar shear strength (ILSS) can be seen in Fig. 5b, reaching 36.4 MPa in 3 wt% CNC-modified laminates with an increase of nearly 60 % from the reference laminates. This enhancement can be attributed to the locally deposited CNCs at interfacial regions, which not only increased surface roughness but also facilitated interfacial mechanical interlocking between the flax and matrix. Fig. 6 provides a summary of literature on using various nanofillers to enhance the interlaminar shear strength in natural fibre composites [16,40–47]. Although no functionalisation on the CNCs or any chemical solvents was involved in this study, a clearly enhanced ILSS outperforming literature values in natural fibre composites was successfully achieved, highlighting the potential of nanofillers such as CNC to improve the mechanical properties of composite laminates.

The effect of CNCs on thermomechanical properties of flax/bio-epoxy laminates has been examined by DMA. As shown in Table .2, a slight increasing trend can be found with increased amount of CNC in the composites, with the Tg reaching 81.1 °C at 5 wt% of CNC. It is expected that the enhanced interfacial properties of CNC/flax/bio-epoxy could reduce the mobility of the polymer chains upon loading, leading to a slightly increased Tg of the composites. Both the mechanical and thermomechanical improvements promise an attractive path forward for the development of all cellulose based nano-engineered natural fibre composites.

3.5. Fractography of flax/bio-epoxy laminates

The fractography of both flax/epoxy and CNC/flax/epoxy laminates was examined and analysed. SEM images of the cryo-fracture surfaces after three-point bending tests highlight the impact of CNC on the fracture process of the hierarchical natural fibre composites. In the reference laminate, the fracture surface showed no obvious signs of plastic deformation, with the fibres exposed to a relatively smooth surface, as shown in Fig. 7a and b. Evidence of fibre pull-out with a clean fibre surface was observed, indicating a relatively weak interface. This lack of deformation aligns with the presence of fibre-directional cracks, highlighting clear potential to improve the interfacial adhesion. In contrast, the 3 wt% CNC/flax/epoxy laminates, as shown in Fig. 7c to e, have shown a different fractography. An improved bonding between flax fibres and epoxy can be observed, with clear evidence of CNC at the interfacial regions bridging the gaps. These observations are believed to contribute to the enhanced load transfer between matrix and fibres hence the mechanical performance of the laminates, as observed in previous results sections to confirm the effective reinforcement of localised CNC in flax composites [26,28].

4. Conclusion

A hierarchical nano-engineered natural fibre composite, integrating cellulose nanocrystals (CNC) into flax/bio-epoxy laminate, has been successfully developed through a simple and solvent-free spray coating process. Localised nano-modification has been achieved, with homogeneous CNC deposition on flax fibre surfaces. The long-standing issue of surface incompatibility between hydrophilic natural fibres and hydrophobic epoxy resins have been addressed, with a significantly enhanced epoxy wetting on nano-engineered flax surfaces with a contact angle of only 58.1° at a CNC loading of 3 wt%, a 40 % reduction compared to neat flax (97.2°). The interfacial shear strength has been improved with a reduced fibre critical length calculated from the nano-modified flax/bio-epoxy single fibre composites.

The mechanical properties of the flax/CNC/bio-epoxy laminates have been systematically characterised, revealing improvements in both flexural and interlaminar shear properties. A 60 % increase in interlaminar shear strength from 22.7 MPa to 36.4 MPa, and a 14 % increase in flexural modulus from 19.5 GPa to 22.3 GPa, were achieved at a CNC loading of 3 wt%. Morphological analysis confirmed an enhanced load transfer at the fibre/matrix interphase by the locally deposited CNC reinforcement.

This green approach of simple spray coating CNC onto natural fibre preforms, without involving any chemicals, provides a scalable and sustainable way to tailor the fibre/matrix interfaces. This approach significantly enhanced the resin wetting hence the mechanical performance of natural fibre composites, paving a promising way for the advancement of natural fibre composites.

CRediT authorship contribution statement

Shahed Ekbatani: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Yushen Wang:** Methodology, Investigation, Formal analysis. **Shanshan Huo:** Methodology, Investigation. **Dimitrios Papageorgiou:** Writing – review & editing, Supervision. **Han Zhang:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compscitech.2024.110719.

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