High-performance cellulose nanofibril-reinforced epoxy composites using directional freezing and flax hybridization

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1 Abstract

Substituting metal vehicle parts with their composite equivalents helps increase energy efficiency by reducing weight, an important strategy as powertrain and aerodynamic efficiency gains are being exhausted. However, traditional glass and carbon fibre-reinforced composites are expensive, energy-intensive to produce, and in the case of glass fibres, have a relatively high density. Here, we investigate the physical compatibility of cellulose nanofibrils (CNF), as improving chemical compatibility between CNF and epoxy does not eliminate the issues of CNF aggregation caused by drying. We successfully arranged CNFs along the fibre loading direction by a combination of directional freezing and freeze-drying, manifesting as improved in-plane resin flow during infusion. Next, flax fibres were mechanically bridged using a simple dip coating process, although the fracture toughness was lowered due to excessive CNF coating density. Our research shows that the correct CNF morphology and amount is equally important to chemical compatibility with the matrix and both approaches must be combined to achieve high mechanical properties. Our hybrid flax-CNF composites provide a pathway to strong, light, and tough composites while using a smaller amount of relatively expensive CNFs.

2 Introduction

Greater adoption of composite materials is an important strategy in vehicle lightweighting, as electrification continues to increase vehicle weight [1]. However, wider adoption of composite vehicle parts is hampered by the high cost and high embedded energy required to produce carbon fibre reinforced composite parts [2]. Glass fibres are a cheaper and less energy-intense reinforcement, but have a higher density and correspondingly lower lightweighting potential. [3]

Cellulose nanofibrils (CNFs) are a promising alternative to glass fibre reinforcements, combining relatively high stiffness and strength with low density and abundant source material. [4], [5] Unfortunately, the adoption of CNFs as a reinforcing fibre remain limited as their hydroxy-rich surface makes them highly hydrophilic, resulting in a weak fibre-matrix interface when mixed with non-polar resins [6]. In a previous paper, we have demonstrated that a water-based CNF hydrophobization reaction reduces the CNF hydrophilicity and improves the CNF-epoxy interface [4], [7]. However, the hydrophobized CNFs still aggregate after drying, which limits the maximum CNF content to 1 % w/w and causes the aggregates to behave as stress

concentrations that embrittle the final composite. Furthermore, the alignment of CNF in composites is difficult to control, which eliminates one advantage of using composite materials. Therefore, the unique morphology and drying behaviour of CNFs requires different fibre architectures compared to conventional fibres to achieve high stiffness, strength, and toughness, in addition to chemical compatibility.

In this work, we explore two fabrication methods for CNF-reinforced composites to tackle the twin issues of CNF aggregation during drying and alignment. First, we align modified and unmodified CNFs along the resin infusion and loading region using a directional freezing method described by Nissilä, [8]. Second, we use CNFs to mechanically bridge unidirectional (UD) flax fabric by a dip coating-drying process, exploiting the ability of CNFs to permanently bond to other cellulosic fibres during drying. [9] This allows us to use a small amount of the relatively expensive CNF to help improve the mode I fracture toughness (GI_c) of natural fibre composites, which is a weak point of ply-based composites while the flax fibres take the in-plane loads.

3 Experimental section

3.1 Materials

Mechanically fibrillated CNF produced from northern bleached softwood kraft pulp was obtained from Performance Biofilaments (Vancouver, Canada) as a 10 % w/w CNF-water paste. This paste was redispersed into 0.5 % and 0.25 % w/w CNF-water suspensions using a kitchen blender. Distilled water was used for all experiments.

UD flax fabric (ca. 100 g/m^2 dry)for hybrid composites was purchased from EcoTechnilin (Valliquerville, France). Composites were made using EPIKOTE RIMR 235 resin and RIMH 235 hardener (Hexion, Columbus, USA). For vacuum infusion, nylon vacuum bags (AeroFilm VB160, Easy Composites, Stoke-on-Trent, UK), tacky tape (AT-200Y, General Sealants Inc., La Habra, USA), release agent-coated peel ply (Fibre Glast 582, Brookville, USA), release film (WL5200B, Airtech, Huntington Beach, USA) and flow media (Fibre Glast 1405) were used.

3.2 Methods

3.2.1 Combined infusion-compression moulding process

CNF-flax hybrids were made by a combination of vacuum infusion and compression moulding process. First, the preform (i.e. flax or CNF cryogel) was fully infused using a normal vacuum infusion process and flow mesh. Next, the inlet tube was clamped, the vacuum pot was vented to the atmosphere, the vacuum bag peeled back slowly, and the flow mesh was carefully removed. Then, the vacuum bag was reattached to the mould and the resin inlet tube is also connected to the vacuum pot using a tee fitting. This ensures that excess resin can escape through both hoses during the pressing stage. Vacuum is slowly re-applied to ensure the bag above the preform is smooth. The wetted-out preform is then pressed for 60 min with a Wabash MPI Genesis press (Wabash, USA) at 70 °C and 8 kN compaction force. Machined aluminium shims placed around the preform maintain the composite thickness (3.5 mm for CNF cryogel composites; 3.1 mm for CNF-flax hybrids). CNF cryogel composites were fabricated only with a normal vacuum infusion process. All composites were post-cured at 70 °C for 15 h.

3.2.2 Directional freeze-drying of CNF

Directionally-frozen CNFs were made using a procedure adapted from Nissilä et al.[8] We fabricated directional freeze-drying moulds using a 6.3 mm-thick aluminium cold plate, a 3D-printed 2-piece rectangular mould, and cork seals. Next, we filled the mould cavity up to the brim with 0.5 % w/w CNF suspension, placed the mould in an insulating box, and poured liquid nitrogen until the aluminium cold plate was fully immersed (ca. 7-10 mm deep). The liquid nitrogen level was maintained at this level for ca. 180 min, and excess CNF suspension was continuously removed to avoid spilling as the ice level rises. After ice rises to the brim, the mould was disassembled and the CNF "ice cube" was freeze-dried at > 5 Pa and <-100 °C collector temperature for 72 h using a Labconco FreeZone 4.5 freeze drier (Kansas City, USA). The dried cryogel was removed carefully by hand to avoid cracking and used as the preform in a standard vacuum infusion procedure.

3.2.3 Coating flax fabric with CNF

Flax fabric was coated using a procedure adapted from Goyo-Brito et al. [10] UD flax fabric was cut into 18 170 mm × 210 mm sheets and dried at 80 °C overnight. Next, we poured ca. 80 g of 0.25 % w/w CNF suspension into a tray lined with a large plastic bag and placed one flax sheet onto the CNF. The flax sheet is pressed by hand until CNF suspension flows through the fibre gaps. Then, 80 g of CNF suspension is poured on top of the wet flax, another flax sheet is stacked on top and pressed again. After stacking the ninth layer, a 25 µm-thick release film (insert) was placed 80 mm from the preform edge to serve as a crack. The soak-stack process was repeated until all 18 plies were stacked. The preform was removed by sliding a metal plate under the plastic bag and lifting the plate to avoid misaligning the fibres, then placed on a glass plate, dewatered with a rolling pin, and dried overnight at 80 °C. The CNF-flax preform is then weighed, infused and pressed as previously described. Plain flax composites were stacked similarly, but water was used instead of CNF suspension. The CNF coating density on flax was determined by comparing uncoated dry weight to coated dry weight.

3.2.4 Mode I fracture toughness testing

Fracture toughness tests were done following ASTM D5528 [11]. Samples were cut from flax-CNF plates into 20 mm × 3.1 mm × 180 mm strips using an Altendorf F30 table saw (Minden, Germany) with a Kanefusa Sash Pro 691-D207-405 blade (Ohguchi, Japan). The insert end of the sample was trimmed to achieve 76 mm insert length. Aluminium piano hinges were bonded onto the test strips with Scotch-Weld DP420 adhesive (3M, Minnesota, USA). All samples were loaded at 2 mm/min until the crack extends 30 mm beyond the initial insert depth in the pre-cracked stage and unloaded at 10 mm/min, using an Instron 3342 universal tester (Norwood, USA); and the crack position tracked using a video camera with a 1:1.4 close-up lens (M.Zuiko 60 mm Macro, OM System, Tokyo, Japan).

4 Results and discussion

4.1 Directionally-frozen CNF composites

We successfully freeze-dried CNF suspensions into oriented cryogel using the mould seen in Figure 1 (a, b). The finished cryogel maintained the shape of the mould (Figure 1 (c)), with very fine, longitudinally oriented pores (< 1 mm; Figure 1 (d, e)). In contrast, CNFs slowly frozen in a regular freezer and regular ice cube trays created large, vertically oriented pores (Figure 1 (f-h)),

as the top surface of the mould was exposed to the cold air. These pores are also significantly smaller than the large CNF flakes visible in our previous paper. [4] During directional freezing, the solidification front rose gradually (Figure 2) with no height difference between the edge and centre of the mould (data not shown), indicating that heat transfer occurred mostly along the vertical direction. The directional appearance extends the entire length of the cryogel (180 mm), which is significantly longer than 100 mm [8] previously demonstrated.

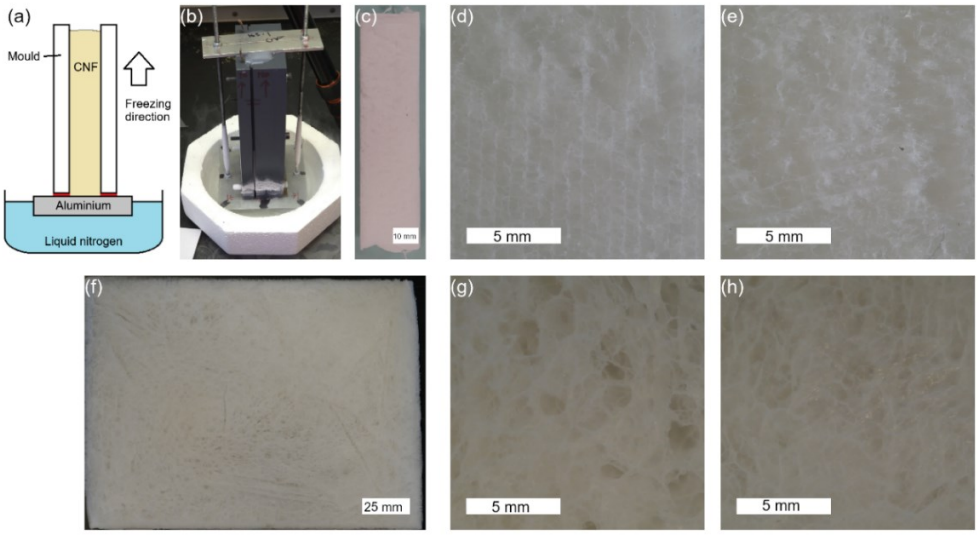

Figure 1: Schematic (a) and actual setup (b) of directional freezing mould, directionally-frozen cryogel seen from the top (c, d), and end (e); slow-frozen cryogels from top (f, g), and end (h)

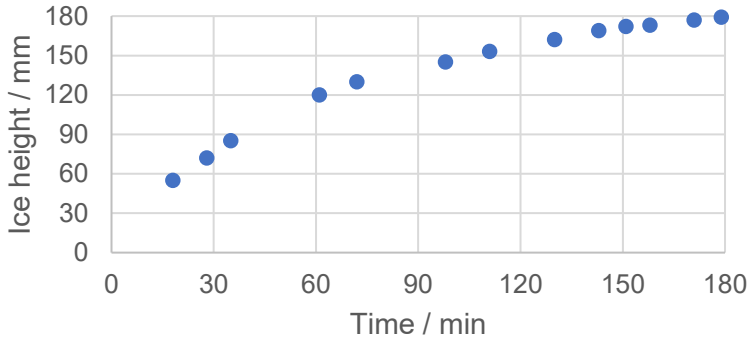

Figure 2: Height of solidification front during directional freezing

Further evidence for directional pore orientation can be seen during the resin infusion process: the resin flow front advances left-to-right in directionally-frozen CNF (Figure 3 (a-c)), while resin flow mostly occurs in the out-of-plane direction for slow-frozen CNFs. This means the

CNFs will be aligned along the loading direction (i.e. long axis), as opposed to perpendicular pores in the slow-frozen cryogel.

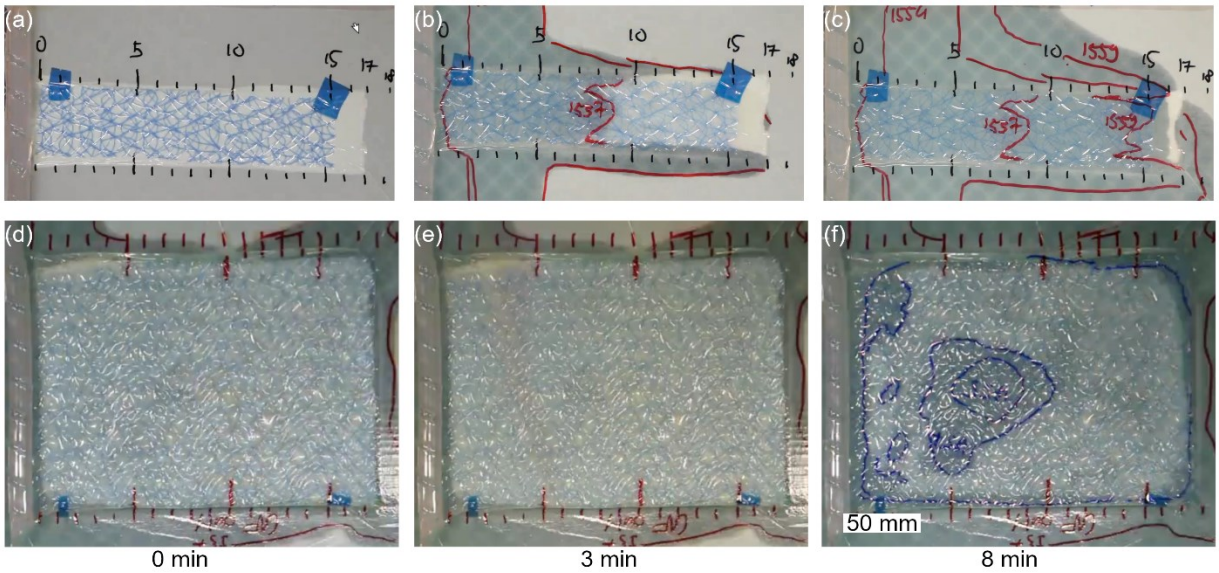

Figure 3: Infusion behaviour at 0, 3, and 8 minutes for directionally-frozen CNF (a-c), compared to randomly frozen CNF (d-f). All images have the same scale.

Although directional freezing significantly improves in-plane resin flow, the preform permeability is still too low to permit infusion without flow mesh and the epoxy resin only wets out 30 % of the cryogel, likely due to the tiny size of the cryogel pores. The rigid flow mesh must be removed as the mesh indents the finished composite, concentrating stress and causing premature failure during tensile testing. Therefore, we will use the infusion-compression moulding process to create our tensile test samples.

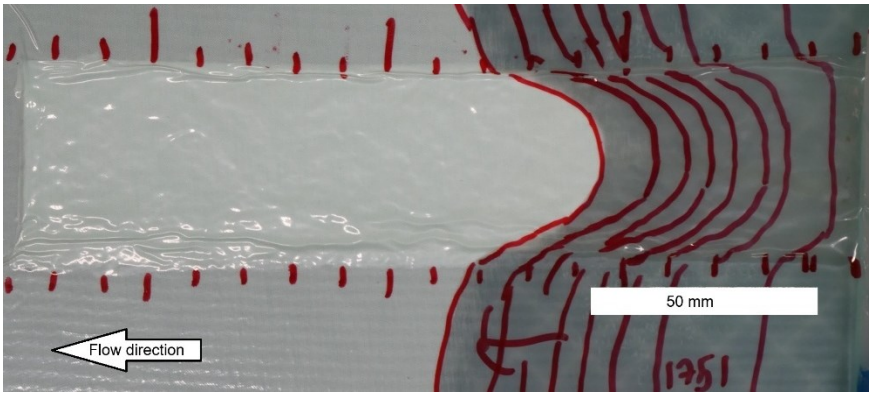

Figure 4: Directionally-frozen CNF infusion progress after 60 min without flow mesh

4.2 Fracture toughness of hybrid flax-CNF composites

Soaking flax fabric in 0.25 % CNF suspensions deposited ca. 0.4 % v/v of CNF onto the CNF surface. CNF-coated flax does not bend under its own mass as the CNFs successfully bridge the flax fibres, unlike uncoated flax fabric (Figure 5 (a,b)). The relatively dense CNF coating does not significantly affect the permeability of the preform (data not shown).

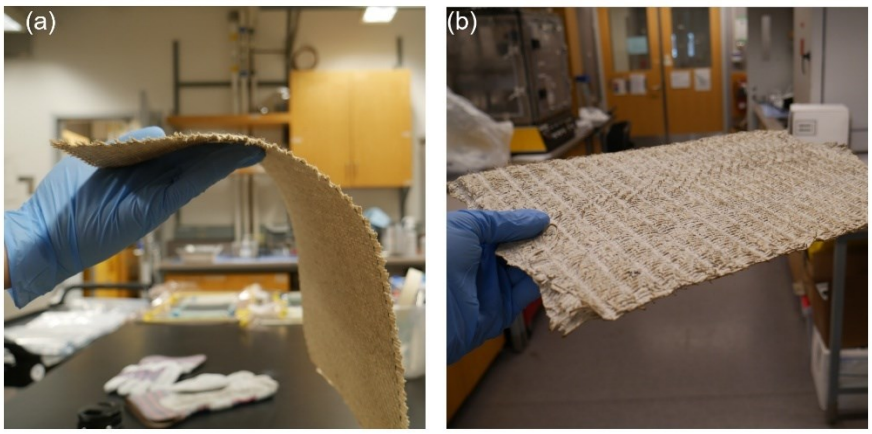

Figure 5: Uncoated flax (a) and CNF-coated flax (b) showing increased ply rigidity

However, the fracture toughness of flax-CNF hybrid composites is significantly lower than those of plain flax composites (Table 1), with a non-pre-cracked (NPC) fracture toughness of 0.26 kJ/m^2, 46 % lower than that of plain flax; and pre-cracked (PC) fracture toughness was also 38 % lower than flax.

Table 1: Mode I fracture toughness values for flax-CNF and flax, with n=4 for each composite

Composite	**% v/v**		**GI_C / kJ/m^2**	
	Flax	**CNF**	**NPC**	**PC**
Flax-CNF	43.6	0.4	0.26 ± 0.06	0.45 ± 0.08
Flax	40	0	0.40 ± 0.04	0.72 ± 0.06

Furthermore, a large scatter in the critical force and position of both NPC and PC flax-CNF composites is seen in Figure 6 (a, b), compared to those of plain flax (Figure 6 (c, d)). In post-mortem images of flax-CNF strips (Figure 7 (a), arrow) we observed a fuzzy white surface that is smooth to the touch, with few torn flax fibres (b), and CNF-rich zones (c, circle). A partially delaminated layer from the ply above is visible (b; c, arrow) caused by CNF-rich zones and is visible in the extension-force curve as sudden drops in force. Similar reductions in fracture toughness was observed in carbon fibre-CNF epoxy composites at 0.5 % w/w [12], and 0.2 % w/w CNF [13], with Zhu noting that CNF-rich zones form above 0.1 % w/w CNF [13]; these papers place the optimal CNF concentration to be < 0.1 % w/w of CNF deposited onto the surface. In contrast, the flax-only fracture surface is much rougher (a) with many torn flax fibres (b), showing that interlaminar opening stress was strong enough to tear the flax fibres. Therefore, we predict that 0.4 % v/v CNF coating is excessively thick, creating CNF-rich zones that become shortcuts for crack propagation.

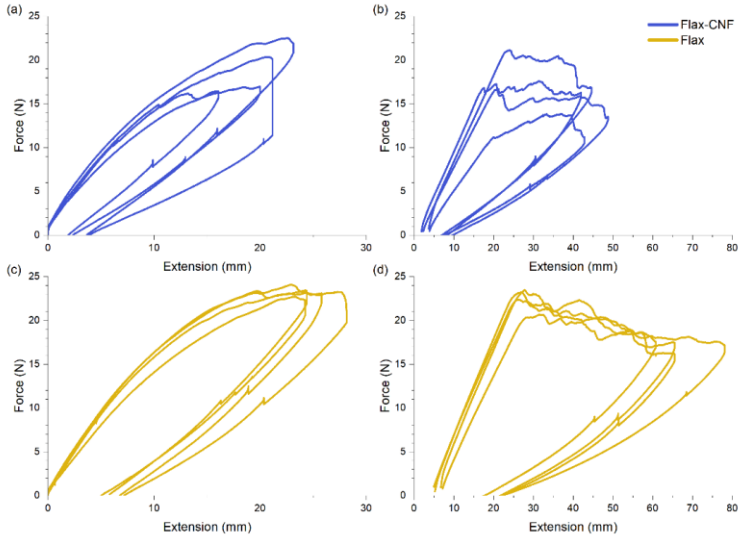

Figure 6: Extension-force curves for NPC flax-CNF (a), PC flax-CNF (b), NPC flax (c), and PC flax (d), with n=4

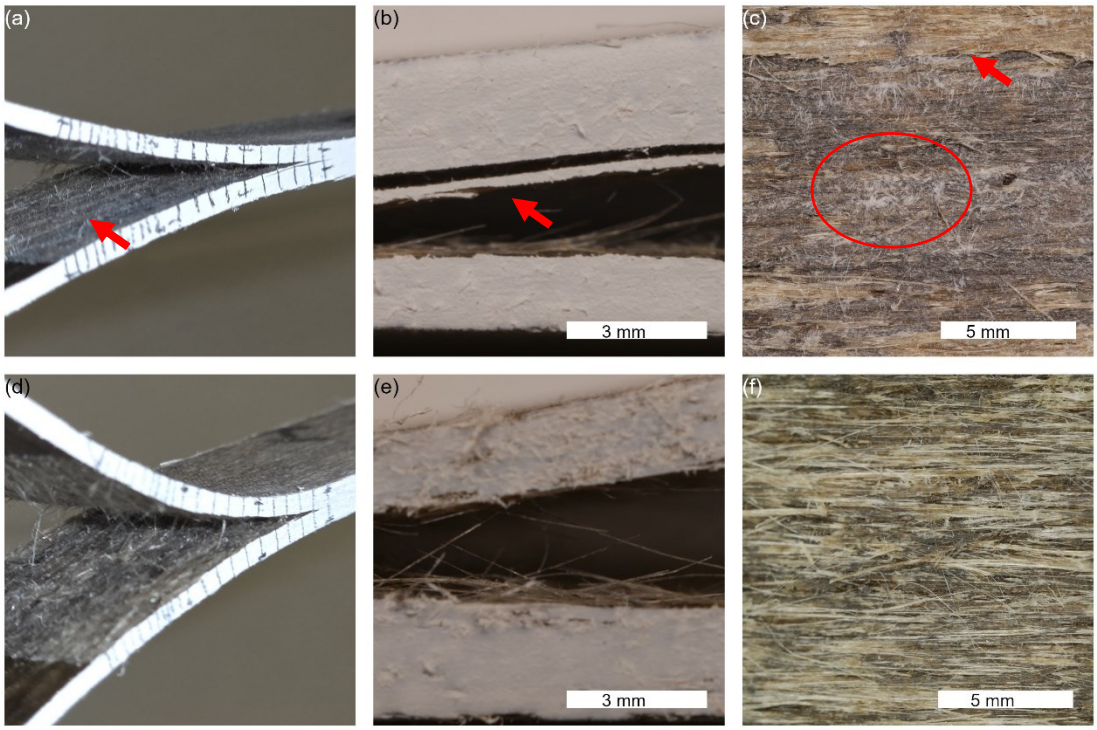

Figure 7: Test strip appearance at end-of-test, crack side view, and crack surface top view of flax-CNF (a-c) and flax (d-f) composites

5 Conclusions and next steps

In this paper, we explored two strategies to make CNF-reinforced composites: directionally-frozen CNF cryogels as a primary reinforcement; and CNFs a secondary fibre to mechanically bridge flax fibres and improve their fracture toughness. CNFs were successfully aligned along

the infusion and loading directions, with greater resin permeability compared to slow-frozen CNF cryogels. However, the preform permeability remains low and full preform wet-out requires flow mesh. We will use the combined infusion-compression moulding process to fabricate the CNF cryogel composites, allowing us to create smooth and defect-free tensile test coupons. The fracture behaviour of CNF-reinforced composites will be investigated with a combination of digital image correlation and scanning electron microscope analysis of the fracture surface.

Next, we used the ability of CNFs to permanently bond onto natural fibres when dried to bridge the inter- and intra-laminar region of UD flax fabrics, successfully creating stiff, "monolithic" flax-CNF preforms that can hold up their own weight. The large amount of CNFs coated formed CNF-rich zones that behave as stress concentrations and reduce the fracture toughness of flax-CNF hybrid composites, shifting the opening failure mode from flax fibre breakage to CNF layer tearing, reducing both NPC and PC fracture toughness values when compared to unmodified flax. We will determine the optimal CNF-flax coating density by measuring flax-CNF fracture toughness at lower CNF concentrations and observing changes in the interlaminar fracture behaviour.

Finally, we will repeat the previous experiments with our hydrophobized CNFs to determine whether the physical structure of CNF reinforcements have a synergy with the improved CNF-epoxy compatibility after hydrophobization. These experiments will clarify the relative importance of physical and chemical compatibility for composite performance and hopefully demonstrate a practical pathway for mass adoption of CNF-reinforced epoxy matrix composites.

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