

# Hemp Nanosheet Reinforcement of a Hemp-Oil Vitrimer

A Proof-of-Concept Study of Mechanical, Thermal, Rheological, and Vitrimeric Performance

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| Work package | WP-HNS-01                                                                        |
| Document     | MLSS-ZILA-HNS-WP-001, Rev. v0.2 (red-team corrected; live-cited)                 |
| Programme    | Hempoxies multiscale composite platform                                          |
| Status       | Hypothesis / research protocol — forward-looking; no validated commercial claims |
| TRL          | Current 1–2   Target on completion 3–4                                           |

## Epistemic status

This is a forward-looking research protocol, not a report of completed work or a product claim. All hypotheses (H1–H6) are stated as testable propositions with explicit success *and* null/failure criteria. Prior-art and material-status statements are sourced to the live-verified references in §12; no performance figure attributed below to the proposed system has yet been measured.

## Contents

|   |                       |   |
|---|-----------------------|---|
| 1 | Background            | 2 |
| 2 | Objectives            | 3 |
| 3 | Scientific hypotheses | 3 |
| 4 | Experimental design   | 4 |
| 5 | Materials             | 4 |
| 6 | Sample preparation    | 4 |
| 7 | Characterization      | 5 |

|    |                         |   |
|----|-------------------------|---|
| 8  | Success criteria        | 5 |
| 9  | Failure / null criteria | 5 |
| 10 | Expected outcomes       | 6 |
| 11 | Future work             | 6 |
| 12 | References              | 6 |

## 1 Background

Nanostructured carbon fillers — graphene nanoplatelets, graphene oxide, carbon nanotubes, and nanocellulose — have repeatedly improved the mechanical, thermal, and multifunctional properties of thermosetting polymers, typically at low loadings where dispersion can be controlled. Whether a *hemp-derived* carbon nanosheet can deliver comparable reinforcement *inside a dynamic covalent (vitrimer) network* is the specific question this work package addresses.

This study investigates the effect of hemp nanosheets (HNS) dispersed within a hemp-oil-based bio-epoxy that exhibits reported vitrimer-type (dynamic covalent) chemistry, of the class developed by ZILA BioWorks. The aim is to establish a first systematic dataset describing the interaction between hemp-derived carbon nanosheets and a transesterification-type bond-exchange matrix.

### 1.1 Prior art and positioning

The novelty of this work is narrow and specific, and should not be over-stated. Three points of established prior art bound it:

- **Hemp carbon nanosheets already exist and are characterised.** Interconnected, partially graphitic carbon nanosheets (10–30 nm thick, specific surface area up to  $\sim 2287 \text{ m}^2 \text{ g}^{-1}$ , intrinsic electrical conductivity  $211\text{--}226 \text{ S m}^{-1}$ ) were produced from hemp bast fibre by Wang, Mitlin, and co-workers [1]. The *material* is therefore not new; its use as a dispersed reinforcement in a vitrimer is.
- **Hemp-derived carbon fillers in epoxy are documented.** Bartoli et al. pyrolysed waste hemp fibre to carbon and showed that, in a conventional epoxy, it raises the storage modulus and lifts electrical conductivity to the order of a few  $\text{mS m}^{-1}$  at high loading ( $\sim 10 \text{ wt\%}$ ) [2]. This is the nearest neighbour to the present work and the primary baseline to differentiate against.
- **Hemp-fibre / graphene-nanoplatelet epoxy nanocomposites have been reported** [3], confirming that 2D carbon reinforcement of hemp-bearing epoxy systems is an active area.

The genuinely open contribution here is the *intersection*: hemp-derived carbon nanosheets in a *vitrimer* matrix, with explicit measurement of how the filler couples to stress-relaxation and bond-exchange kinetics (H5). To our knowledge that coupling has not been reported, and it — not the nanosheet itself — is what the work package claims.

## 1.2 Matrix selection and sourcing feasibility

The intended matrix is a hemp-oil bio-epoxy with dynamic covalent character. The ZILA BioWorks resin (marketed as a hemp-seed-oil bio-epoxy, up to ~85% bio-based, described by the developer as using “vitrimer” dynamic-covalent chemistry that enables composite recyclability) is the motivating example [4].

### Material-status caveat (corrected)

ZILA’s resin is *not* an openly available commercial vitrimer. As of the most recent public reporting the company is at pilot stage, works only with selected manufacturing partners, and has historically outsourced its R&D and production to universities and national labs [4,5]. Earlier drafts of this protocol described it as a “commercial hemp-oil vitrimer matrix”; that over-stated both availability and the formal vitrimer classification (the public characterisation is “bio-epoxy with vitrimer-type chemistry”). The protocol is corrected accordingly and does not assume off-the-shelf procurement.

To keep the study executable independent of one supplier, the matrix is defined functionally rather than by brand:

- **Primary route:** ZILA hemp-oil bio-epoxy, subject to a material-transfer agreement or research partnership; classification as a true vitrimer to be confirmed in-house by stress-relaxation behaviour (§7.4), not assumed.
- **Fallback route:** an in-house or third-party transesterification vitrimer (e.g. an epoxy / fatty-acid network with a Zn or comparable transesterification catalyst), so that H1–H6 can be tested even if the ZILA material is unavailable. Hemp-oil content then becomes a desirable feature rather than a precondition.

## 2 Objectives

1. Evaluate the dispersion quality of hemp nanosheets in the vitrimer matrix.
2. Quantify changes in thermal and mechanical properties versus a neat-matrix control.
3. Determine effects on vitrimer stress-relaxation behaviour.
4. Measure the activation energy of bond-exchange reactions.
5. Assess potential multifunctional benefits, including electrical conductivity, with percolation explicitly in scope.
6. Establish a foundation for future hybrid Hempoxies formulations.

## 3 Scientific hypotheses

Each hypothesis is paired with its rejection condition in §9.

- H1** Hemp nanosheets increase the storage modulus ( $E'$ ) of the vitrimer matrix.
- H2** Hemp nanosheets increase the glass-transition temperature ( $T_g$ ).
- H3** Hemp nanosheets reduce creep deformation under load.
- H4** Hemp nanosheets increase fracture toughness.
- H5** Hemp nanosheets modify the activation energy ( $E_a$ ) of vitrimer bond-exchange reactions. (*Primary novel claim; direction not pre-specified — the filler may accelerate or retard exchange, and either is an informative result.*)

**H6** Hemp nanosheets raise electrical conductivity relative to the neat matrix. (*Exploratory: at the loadings studied, the system may approach but not cross the percolation threshold — see §7.5, §9.*)

## 4 Experimental design

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A single-factor design is used.

### 4.1 Independent variable

Hemp nanosheet loading: 0.00 wt% (control), 0.25, 0.50, 1.00, and 2.00 wt%.

#### Note on the loading range

This range is appropriate for detecting mechanical and  $T_g$  effects (H1–H4), which for 2D carbon fillers commonly optimise below  $\sim 1$  wt% before agglomeration dominates. It is, however, deliberately low for *conductivity*: the comparable hemp-carbon/epoxy baseline required  $\sim 10$  wt% to reach single-digit  $\text{mS m}^{-1}$  [2]. High-aspect-ratio nanosheets percolate at lower loadings than chopped fibre or particles, so a conductivity onset within this window is plausible but not assured. If percolation analysis (§7.5) indicates the threshold lies above 2 wt%, an extended high-loading arm (e.g. 3–10 wt%) should be added for H6 only.

### 4.2 Controlled variables

Resin formulation; catalyst concentration; cure schedule; sample geometry; mixing protocol; testing environment.

## 5 Materials

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- Hemp-oil bio-epoxy vitrimer resin — primary: ZILA BioWorks (subject to MTA/partnership, §1.2); fallback: in-house transesterification vitrimer.
- Hemp nanosheets (HNS), of the partially graphitic, hemp-bast-derived type [1].
- Mechanical stirrer; ultrasonic dispersion equipment; vacuum degassing system; standard mould geometries.

## 6 Sample preparation

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1. Dry hemp nanosheets under vacuum.
2. Pre-mix nanosheets into the vitrimer resin.
3. Apply ultrasonication to improve dispersion.
4. Degas the mixture under vacuum.
5. Cast specimens into standardised moulds.
6. Cure according to the matrix specification (manufacturer spec for the primary route; characterised in-house cure for the fallback).
7. Condition samples for 48 h before testing.

## 7 Characterization

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### 7.1 Morphology

Optical microscopy; SEM imaging; quantitative dispersion analysis (to correlate any property change with genuine dispersion rather than loading alone).

### 7.2 Thermal analysis

DSC, DMA, and TGA, yielding  $T_g$ , storage modulus ( $E'$ ), loss modulus ( $E''$ ), and damping factor ( $\tan \delta$ ).

### 7.3 Mechanical testing

Tensile, flexural, fracture-toughness, and hardness testing, yielding tensile strength, elastic modulus, elongation at break, and fracture energy. Replicates sufficient for statistical comparison against the control (target  $n \geq 5$  per condition).

### 7.4 Vitrimers performance

Stress-relaxation experiments fit the single-exponential form

$$\varepsilon(t) = \varepsilon_0 \exp(-t/\tau), \quad (1)$$

with relaxation times  $\tau$  obtained at multiple temperatures. An Arrhenius construction

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (2)$$

( $\tau$  relaxation time,  $E_a$  activation energy,  $R$  gas constant,  $T$  absolute temperature) yields  $E_a$  for the neat matrix and each loading. This step also *confirms* the matrix is vitrimers (associative, Arrhenius-type relaxation) rather than assuming it.

### 7.5 Electrical properties

Volume and surface conductivity across all loadings, with explicit percolation-threshold analysis (power-law fit of conductivity versus filler fraction above onset). The neat matrix is measured as the insulating baseline.

## 8 Success criteria

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Support for H1–H6 would include: increased  $E'$ , increased  $T_g$ , reduced creep, increased fracture toughness, and a statistically resolvable change in  $E_a$  (in either direction), each relative to control. For H6, evidence is either a measurable conductivity increase *or* a well-characterised percolation curve that locates the threshold, even if it lies above the studied range.

## 9 Failure / null criteria

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- H1–H4 are rejected if the corresponding property is statistically unchanged, or if agglomeration causes net mechanical degradation.
- H5 is rejected if  $E_a$  and relaxation behaviour are statistically indistinguishable from the control.

- H3 is additionally informative if stress-relaxation *deteriorates* (faster creep), which would itself be a reportable filler effect.
- For H6, a null is *not* treated as study failure: if conductivity does not rise within 0–2 wt%, the expected interpretation is that the percolation threshold lies above the range (\$7.5), motivating the extended high-loading arm rather than a negative conclusion about the material.

## 10 Expected outcomes

By analogy with graphene and carbon-nanoplatelet systems, moderate loadings (0.5–1.0 wt%) are expected to give the best balance of mechanical reinforcement and processability for H1–H4. Conductivity behaviour (H6) is genuinely uncertain at these loadings and is treated as exploratory. The study will establish whether hemp nanosheets are a viable bio-derived nanoreinforcement for future Hempoxies multiscale architectures — and, equally usefully, will bound where they are *not*.

## 11 Future work

On successful validation: (1) hemp nanosheets + PAN carbon fibre; (2) hemp nanosheets + hemp carbon fibre; (3) hemp nanosheets + hemp biochar; (4) fully hierarchical Hempoxies architectures; (5) multifunctional structural energy-storage composites (a natural extension given the supercapacitor pedigree of hemp nanosheets [1]).

## 12 References

1. Wang, H.; Xu, Z.; Kohandehghan, A.; Li, Z.; Cui, K.; Tan, X.; Stephenson, T. J.; King'ondo, C. K.; Holt, C. M. B.; Olsen, B. C.; Tak, J. K.; Harfield, D.; Anyia, A. O.; Mitlin, D. "Interconnected Carbon Nanosheets Derived from Hemp for Ultrafast Supercapacitors with High Energy." *ACS Nano* **2013**, 7(6), 5131–5141. DOI: 10.1021/nn400731g.
2. Bartoli, M. et al. "Mechanical, electrical, thermal and tribological behavior of epoxy resin composites reinforced with waste hemp-derived carbon fibers." *Journal of Materials Science* **2022**. DOI: 10.1007/s10853-022-07550-9.
3. Erklığ, A. et al. "Investigation of Mechanical and Impact Properties of Hemp Fiber Reinforced Epoxy-Based Nanocomposites." *Polymer Composites* **2025**. DOI: 10.1002/pc.30135.
4. ZILA BioWorks — technology and development-stage description (hemp-seed-oil bio-epoxy; vitrimer-type dynamic-covalent chemistry; pilot stage). zilabioworks.com (accessed 17 June 2026).
5. "Renton company finalist in \$3M global business competition for its bio-epoxy resins." *425 Business*, Nov. 2025 — corroborates ZILA's pilot stage, Hempoxy Resin branding, and outsourced/bootstrap R&D model.

*Live-verified citations; no fabricated sources or unmeasured performance figures attributed to the proposed system. Corrections in this revision: ZILA material re-described as pilot-stage bio-epoxy with vitrimer-type chemistry (not a commercial vitrimer); novelty narrowed to the hemp-nanosheet / vitrimer intersection with prior art cited; H6 reframed as exploratory with percolation explicit; sourcing fallback added.*