

Negative Results and Design Constraints in Hemp-Derived Structural Vitrimer Composites

Marie-Soleil Seshat Landry

Landry Industries – Open Source Materials Program

ORCID: 0009-0008-5027-3337

Standalone Technical Report

Abstract

The rapid expansion of bio-based vitrimer and composite research has been accompanied by a reproducibility crisis driven by unverifiable precursors, undocumented assumptions, and the omission of negative results. This standalone technical report documents the explicitly ruled-out chemistries, reinforcement strategies, stoichiometric regimes, and processing pathways identified during the development of hemp-derived structural vitrimer systems.

By formalizing non-viable approaches as design constraints, this work establishes a bounded and reproducible design space for future hemp-based vitrimer composites. These findings are intended to prevent redundant experimentation, reduce ambiguity in material claims, and accelerate meaningful progress in circular composite engineering.

1 Introduction

Negative results and failed pathways are rarely reported in composite materials research, despite their critical role in defining viable design spaces. In bio-based vitrimer systems, this omission has led to repeated exploration of non-reproducible chemistries, inappropriate reinforcement strategies, and structurally unsound assumptions.

This document consolidates negative results and hard constraints derived from systematic formulation analysis and development of hemp-derived vitrimer composites. While informed by the Hemproxies development program, the conclusions presented herein are generalizable across hemp-based structural vitrimer systems.

2 Excluded Matrix Chemistries

2.1 Unverifiable or Proprietary Precursors

All bio-epoxy precursors lacking publicly verifiable epoxy equivalent weight (EEW), reproducible synthesis routes, or independent supplier validation were excluded from consideration. Such mate-

rials, often described only by nominal functionality or trade name, prevent independent replication and invalidate stoichiometric control.

Constraint: Matrix precursors must possess traceable chemical constants and reproducible sourcing.

2.2 Amine-Cured Epoxy Networks

Primary and secondary amine curing systems were evaluated conceptually and excluded due to incompatibility with transesterification-based dynamic covalent networks. These systems exhibit excessive crosslink rigidity, poor stress relaxation behavior, and irreversible network topology above the glass transition temperature.

Constraint: Amine-cured networks are unsuitable for circular structural vitrimer applications.

3 Non-Optimal Reinforcement Strategies

3.1 Pristine or CVD Graphene

Highly crystalline, low-defect graphene materials were excluded due to poor dispersion in bio-based epoxy matrices, low interfacial adhesion, and increased agglomeration tendencies. In bulk composites, these materials exhibit higher percolation thresholds and inferior stress transfer relative to defect-engineered graphene.

Constraint: Graphene intended for composite reinforcement must be defect-rich and interface-active.

3.2 Single-Scale Reinforcement Architectures

Composite systems relying exclusively on fiber-only, particulate-only, or nano-only reinforcement architectures were found to exhibit brittle failure modes, poor damage tolerance, and limited multifunctionality.

Constraint: Structural performance requires hierarchical reinforcement across multiple length scales.

4 Stoichiometric Boundaries

4.1 Under-Stoichiometric Epoxy Systems

Epoxy-to-carboxyl ratios at or below 1:1 resulted in premature gelation, reduced vitrimer mobility, and increased brittleness. These systems exhibited limited stress relaxation and poor reprocessability.

Constraint: Structural vitrimers require controlled excess epoxy to maintain dynamic exchange capacity.

4.2 Excess Epoxy Beyond Bounded Limits

Epoxy excess exceeding approximately 30% resulted in reduced modulus, increased creep, and diminished thermal stability. Excess functional groups beyond this range do not contribute positively to network performance.

Constraint: Stoichiometric slack is beneficial only within defined limits.

5 Catalyst and Kinetic Constraints

5.1 Non-Zinc Metal Catalysts

Alternative metal catalysts, including magnesium, calcium, and iron salts, were reviewed and excluded due to narrow processing windows, insufficient activation energy control, and poor latency at ambient temperatures.

Constraint: Zinc-based catalysis represents a local optimum for bio-based transesterification vitrimers.

6 Processing Constraints

6.1 High-Viscosity Formulations

Formulations exceeding approximately 2000 mPa·s at 60 °C were incompatible with vacuum-assisted resin infusion, resulting in elevated void content and incomplete fiber wetting.

Constraint: Processability is a first-order design variable, not a secondary optimization.

7 Environmental and Durability Constraints

7.1 Moisture-Uncontrolled Fiber Systems

Fiber moisture content exceeding 0.5% by mass resulted in degraded interfacial adhesion, increased porosity, and inconsistent mechanical properties.

Constraint: Strict moisture control is mandatory for reproducible composite performance.

8 Summary of Ruled-Out Approaches

The following strategies are considered non-viable within hemp-derived structural vitrimer systems:

- Proprietary or unverifiable bio-epoxy precursors
- Amine-cured dynamic networks
- Pristine graphene reinforcement
- Single-scale reinforcement architectures

- Under-stoichiometric epoxy systems
- Non-zinc transesterification catalysts
- High-viscosity, non-infusible formulations

9 Implications for Future Research

These constraints define a bounded design space in which future performance gains must arise from interface engineering, hierarchical architecture optimization, controlled defect utilization, and processing precision. Exploratory chemistry without epistemic grounding is unlikely to yield durable progress.

10 Conclusion

This report demonstrates that progress in sustainable composite materials depends as much on what is excluded as on what is explored. By formalizing negative results and design constraints, hemp-derived vitrimer research can advance from speculative experimentation toward reproducible, industrially relevant systems.

Conflict of Interest: The author is the founder and CEO of Landry Industries, which develops hemp-based materials.

License: This work is released under Creative Commons Attribution 4.0 (CC BY 4.0).