

HEMPOXIES 44 "GENESIS"

Pre-Experimental Scientific Proposal — Septenary (7-Level) Architecture

Targets: 1500 MPa Tensile Strength · 120 GPa Modulus · $\geq 85\%$ Bio-Based Content

SECTION 1

ABSTRACT

This proposal presents the pre-experimental design, formulation rationale, and experimental characterization plan for **Hempoxies 44 "Genesis"** — a novel high-performance bio-based structural composite governed by a proprietary *Septenary (7-Level) Architecture* (L0–L6). The composite matrix integrates a tri-network bio-vitrimer system comprising epoxidized hempseed oil (EHO, 25 wt%), hemp-derived furanic benzoxazine (HF-BX, 20 wt%), and sebacic acid hardener (17 wt%), reinforced with N,P-doped carbon quantum dots (CQDs, L0), hemp cellulose nanofibers (HCNFs, L3), hemp-derived defect-controlled nano-sheets (HDCNS Gen II, L4), and hemp interphase carbon filler (HICF, L5), combined with a primary load-bearing hybrid PAN carbon fiber / hemp bast fiber preform (L6, 40–50 vol%). The formulation targets ≥ 1500 MPa tensile strength, ≥ 120 GPa tensile modulus, > 1400 J/m² Mode-I fracture toughness (G_{IC}), and $\geq 85\%$ bio-based content by mass. All components are Canada-sourced. A full curing schedule (gelation at 80°C, advance cure at 120°C, post-cure at 180°C) and a comprehensive characterization standard operating procedure (SOP) are specified.

Keywords: *hemp composite; bio-vitrimer; benzoxazine; carbon quantum dots; septenary architecture; epoxidized hempseed oil; PAN carbon fiber; high-performance bio-composites; sustainable materials.*

DESIGN TARGETS

KEY PERFORMANCE INDICATORS

1500

MPa

TENSILE
STRENGTH

120 GPa

TENSILE
MODULUS

>1400

J/m²

G_{IC}
TOUGHNESS

≥85%

BIO-BASED
CONTENT

INTRODUCTION & SCIENTIFIC RATIONALE

Structural composites derived from bio-based matrices represent a critical frontier in sustainable materials science. Current high-performance composites — predominantly epoxy/PAN-CF systems — achieve excellent mechanical properties (tensile strengths of 1200–1800 MPa) but rely on petroleum-derived resins with a substantial environmental footprint. Bio-based thermosets, including epoxidized plant oils and polybenzoxazines derived from lignocellulosic precursors, have demonstrated promising mechanical properties but typically fall short of structural-grade benchmarks without hybridization strategies.

The **Hempoxies 44 "Genesis"** system addresses this gap through a hierarchical *Septenary Architecture* — a seven-level framework that controls mechanical performance at molecular (L0–L2), nanoscale (L3–L5), and mesoscale (L6) length scales simultaneously. The matrix forms a tri-network vitrimer: (i) an epoxy network from EHO ring-opening, (ii) a polybenzoxazine network from HF-BX polymerization, and (iii) a dynamic ester-exchange vitrimer network catalyzed by inherent tertiary amines in the benzoxazine structure, enabling recyclability without sacrificing crosslink density.

N,P-co-doped CQDs (L0/L2) serve dual roles as molecular chain-transfer agents that increase crosslink homogeneity and as synergistic flame retardants. At the nanoscale, HCNFs (L3) provide cellulosic reinforcement with aspect ratios >100 , while HDCNS Gen II (L4) bridge matrix and fiber interphases. The load-bearing phase (L6) employs hybrid PAN-CF (for modulus) / hemp bast fiber (for bio-content and toughness).

SEPTENARY (7-LEVEL) ARCHITECTURE

MASTER FORMULATION

wt%

Component	Role	(matrix basis)	Canadian Source
Epoxidized Hempseed Oil (EHO)	Epoxy resin component; bio-plasticizer	25%	Naturally Splendid Enterprises (BC); Hemptown Organics
Hemp-Furanic Benzoxazine (HF-BX)	Polybenzoxazine network precursor	20%	Custom synthesis from furfurylamine + hemp-phenol
Sebacic Acid	Bio-based dicarboxylic acid hardener	17%	Bioamber (Sarnia, ON); Croda Canada
N,P-Doped CQDs	Molecular modifier; flame retardant	1–2%	In-house synthesis
HCNFs (Hemp Cellulose Nanofibers)	Nano-reinforcement	3%	Alberta Innovates pilot facility; Canfor (BC)
HDCNS Gen II	Nano-sheet modulus enhancer	3%	In-house pyrolysis of hemp hurd
HICF	Interphase carbon filler	3%	In-house carbonization of hemp bast at 900°C
PAN Carbon Fiber (unidirectional)	Primary load-bearing reinforcement	40–50 vol%	Toray Composites Canada; SGL Carbon (Montreal)
Hemp Bast Fiber (woven)	Secondary bio-reinforcement; toughening	10–15 vol%	Prairie Hemp Council growers (SK/AB)

Stoichiometric Note: EHO oxirane content $\approx 5.9\%$ (O.O.C.); sebacic acid provides $-\text{COOH}$ groups at 1.05:1 equiv. ratio to epoxy. HF-BX ring-opening is self-catalyzed by inherent tertiary amines above 120°C . No external catalyst required for vitrimer exchange ($T_v \approx 160^\circ\text{C}$).

SECTION 5

PRE-EXPERIMENTAL CURING PROTOCOL

- 1 Resin Blending (RT, 30 min):** Combine EHO, HF-BX, and sebacic acid in a 3-neck flask at 25°C . Disperse CQDs, HCNFs, HDCNS Gen II, and HICF via tip sonication (400 W, 30 min, ice bath, 20 kHz). Degas under vacuum (50 mbar, 15 min).
- 2 Preform Impregnation:** Hand lay-up or resin transfer molding (RTM) at 40°C . Stack sequence: $[0^\circ/90^\circ/\pm 45^\circ]_s$ — alternating PAN-CF UD and hemp bast woven layers. Apply 0.6 MPa consolidation pressure.
- 3 Gelation Stage — 80°C , 2 hrs:** Partial benzoxazine ring-opening initiates; EHO–sebacic acid esterification begins. Resin viscosity increases from $\sim 450 \text{ mPa}\cdot\text{s}$ to gel point. Monitor via in-mold fiber-optic dielectric analysis (DEA).
- 4 Advance Cure — 120°C , 2 hrs:** Epoxy-acid network reaches full conversion ($>95\%$ by DSC). Vitrimer dynamic ester bonds established. Polybenzoxazine network initiates ($T > 110^\circ\text{C}$ for HF-BX).
- 5 Post-Cure — 180°C , 1 hr:** Complete benzoxazine ring-opening; final network densification. Target $T_g \geq 175^\circ\text{C}$ (DMA, E'' peak). Ramp at $2^\circ\text{C}/\text{min}$.
- 6 Controlled Cooling:** Slow cool at $-2^\circ\text{C}/\text{min}$ to 60°C , then free-cool to RT. Prevents residual thermal stresses in PAN-CF layers.

SECTION 6

CHARACTERIZATION PLAN — SOP SUMMARY

Mechanical Testing

Test	Standard	Specimens
Tensile (0°)	ASTM D3039	n=5, 250×25×2 mm
Flexural (3-pt)	ASTM D7264	n=5, span/depth=32
Compressive (0°)	ASTM D6641	n=5
ILSS	ASTM D2344	n=5, short-beam
Mode-I G_{Ic}	ASTM D5528	n=6, pre-crack 50 mm
Impact (Charpy)	ISO 179	n=10, notched

Thermal & Spectroscopic

Test	Instrument	Conditions
DSC	TA Q2000	5°C/min, N ₂ , −40→300°C
DMA	TA Q800	3-pt bend, 1 Hz, 2°C/min
TGA	TA Q500	10°C/min, N ₂ /air
FTIR-ATR	Bruker Vertex 70	Ring- opening conversion
Raman	Renishaw inVia	CQD D/G ratio; HDCNS
SEM/EDX	FEI Quanta 250	Fracture surface analysis

SECTION 7

EXPECTED OUTCOMES

Property	Target	Typical Bio-Epoxy/Hemp	Conv. CFRP Baseline
Tensile Strength (MPa)	1500	320	1200
Tensile Modulus (GPa)	120	28	70
Flexural Strength (MPa)	1100	280	900
G _{IC} (J/m ²)	1400	350	800
T _g (°C)	175	95	150
Bio-Based Content (%)	85	100	0

SECTION 8

COMPLETE LATEX SOURCE CODE (IEEE/ELSEVIER)

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\documentclass[12pt, a4paper]{article}
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% _____
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% PACKAGES
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% _____
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\usepackage[utf8]{inputenc}
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\usepackage[T1]{fontenc}
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%  TITLE BLOCK
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\title{%
  \textbf{Hempoxies 44 ``Genesis'': Pre-Experimental Proposal
for a\\
  High-Performance Bio-Based Structural Composite\\
  via Septenary (7-Level) Architecture}
}

\author{%
  [Principal Investigator Name]\textsuperscript{1,*} \and
  [Co-Investigator Name]\textsuperscript{1}\\[0.5em]
  \normalsize\textsuperscript{1}Department of Materials Science
and Engineering,\\
  [Institution Name], Canada\\[0.3em]
  \normalsize\textsuperscript{*}Corresponding author:
  \href{mailto:pi@institution.ca}{pi@institution.ca}
}

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\date{April 2026}

\begin{document}

\maketitle

\linenumbers

% _____

% ABSTRACT

% _____

\begin{abstract}

This proposal presents the pre-experimental design, formulation rationale, and

characterization plan for \textbf{Hempoxies 44 ``Genesis''} – a novel

high-performance bio-based structural composite governed by a proprietary

\textit{Septenary (7-Level) Architecture} (L0--L6). The composite matrix

integrates a tri-network bio-vitrimer comprising epoxidized hempseed oil

(EHO, 25\,wt\%), hemp-furanic benzoxazine (HF-BX, 20\,wt\%), and sebacic

acid (17\,wt\%), reinforced with N{,}P-doped carbon quantum dots (CQDs),

hemp cellulose nanofibers (HCNFs, 3\,wt\%), hemp-derived defect-controlled

nano-sheets (HDCNS Gen\,II, 3\,wt\%), and hemp interphase carbon filler

(HICF, 3\,wt\%), combined with a primary hybrid PAN carbon fiber / hemp bast

fiber preform (40--50\,vol\%). Design targets are: tensile strength

$\geq$ \, \SI{1500}{\mega\pascal}, tensile modulus

$\geq$ \, \SI{120}{\giga\pascal},

Mode-I fracture toughness $G_{Ic} >$ \, \SI{1400}

{\joule\per\square\metre},

and bio-based content $\geq$ \, 85\,wt\%. All components are Canada-sourced.

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\end{abstract}
```

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\textbf{Keywords:} hemp composite; bio-vitrimer;  
polybenzoxazine; carbon quantum  
dots; septenary architecture; epoxidized hempseed oil; high-  
performance  
bio-composites; sustainable materials
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% _____  
% 1. INTRODUCTION  
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```
\section{Introduction}
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\label{sec:intro}
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Structural composites derived from petroleum-derived epoxy matrices and polyacrylonitrile-based carbon fibers (PAN-CF) dominate aerospace, automotive, and infrastructure applications, delivering tensile strengths of 1200--1800\,MPa and moduli of 70--120\,GPa~\cite{ref:hull2019}. However, their ecological footprint – stemming from non-renewable resin synthesis and energy-intensive carbon fiber production – motivates the development of bio-derived alternatives that retain structural-grade performance~\cite{ref:astrue2018}.

Bio-based thermoset matrices – including epoxidized plant oils, polybenzoxazines derived from lignocellulosic precursors, and dynamic covalent adaptable networks (vitrimers) – have individually demonstrated encouraging properties but consistently fall short of structural benchmarks without hierarchical

reinforcement strategies~\cite{ref:liu2023, ref:lotfi2020}.

\textbf{Hempoxies 44 ``Genesis''} addresses this performance gap through

a \textit{Septenary Architecture}: a seven-level hierarchical framework that

simultaneously controls mechanical performance at molecular (L0--L2),

nanoscale (L3--L5), and mesoscale (L6) length scales. The matrix forms a

\textit{tri-network vitrimer}: (i) an epoxy network from EHO ring-opening,

(ii) a polybenzoxazine network from HF-BX self-polymerization, and

(iii) dynamic ester-exchange vitrimer bonds catalyzed by inherent tertiary

amines in the benzoxazine repeat unit~\cite{ref:zhao2021}.

N,P-co-doped CQDs (L0/L2) act as molecular chain-transfer agents that

homogenize crosslink density and provide synergistic flame retardancy –

a strategy validated by Wang et al.\ (2024) for epoxy systems~\cite{ref:wang2024}.

At the nanoscale, HCNFs (L3) form a percolating cellulosic network

(aspect ratio >100), while HDCNS Gen\,II (L4) bridge matrix and

fiber interphases via defect-controlled π -stacking. The load-bearing

phase (L6) hybridizes PAN-CF (high modulus) with hemp bast fiber (bio-content and toughening contribution), consistent with recent literature

on damage-tolerant bioepoxy/hemp systems~\cite{ref:dunne2024}.

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% 2. SEPTENARY ARCHITECTURE

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\section{Septenary (7-Level) Architecture}

\label{sec:arch}

Table~\ref{tab:arch} summarises the seven hierarchical levels of the

Hempoxies 44 system.

\begin{table}[H]

\centering

\caption{Septenary Architecture – Component Summary}

\label{tab:arch}

\small

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\toprule

Level & Component & Length Scale & Primary Function & wt\,\%

\\

\midrule

L0 & N,P-Doped CQDs & 1--10\,nm & Molecular crosslink homogenization; flame retardancy & 1--2 \%

L1 & Tri-Network Bio-Vitrimer & Molecular/bulk & Primary matrix; dynamic covalent network; high T_g & ~ 62 \%

L2 & CQD Surface Modifiers & 1--50\,nm & Interfacial coupling at fiber/matrix interphase & (in L0)

\\

L3 & HCNFs & 5--20\,nm ϕ & Nano-toughening; percolating cellulosic network & 3 \%

L4 & HDCNS Gen\,II & 100--500\,nm & Modulus amplification; crack deflection & 3 \%

L5 & HICF & 0.5--5\, μ m & Interphase modulus bridging; adhesion & 3 \%

L6 & Hybrid PAN-CF/Hemp Bast & μ m--mm & Primary load-bearing reinforcement & 40--50\,vol\% \%

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\end{tabular}
\end{table}

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% 3. MASTER FORMULATION
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\section{Master Formulation}
\label{sec:form}

\subsection{Matrix Resin System}
The bio-vitrimer matrix (Table~\ref{tab:form}) is formulated as follows:

\begin{equation}
\label{eq:stoich}
n_{\text{COOH}} : n_{\text{oxirane}} = 1.05 : 1
\quad \rightarrow \quad
w_{\text{sebacic}} = \frac{M_{\text{sebacic}}}{2} \cdot \text{EEW}_{\text{EHO}} \times 1.05
\end{equation}

where  $\text{EEW}_{\text{EHO}}$  is the epoxy equivalent weight of the epoxidized hempseed oil ( $\approx 340$  g/mol for OOC  $\approx 5.9$  wt%).

\begin{table}[H]
\centering
\caption{Hempoxies 44 ``Genesis'' Master Formulation}
\label{tab:form}
\small
\begin{tabular}{llrrl}
\toprule
Component & Role & wt\,\% & vol\,\% & Canadian Supplier \\
\midrule
Epoxidized Hempseed Oil (EHO) & Epoxy component; bio-  
plasticizer & 25 & 24 & Naturally Splendid (BC)
\end{tabular}

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Hemp-Furanic Benzoxazine (HF-BX) & Polybenzoxazine precursor & 20 & 19 & Custom synthesis \\	
Sebacic Acid	& Dicarboxylic acid hardener; vitrimer & 17 & 16 & Bioamber, Sarnia ON \\
N,P-Doped CQDs	& Molecular modifier; FR agent & 1--2 & 1 & In-house synthesis \\
HCNFs	& Nano-reinforcement & 3 & 3 & Alberta Innovates pilot \\
HDCNS Gen\,II	& Nano-sheet modulus enhancer & 3 & 3 & In-house (hemp hurd pyrolysis) \\
HICF	& Interphase carbon filler & 3 & 3 & In-house (hemp bast, 900\,\textdegree C) \\
PAN-CF (UD prepreg)	& Primary load-bearing & -- & 40--45 & Toray Canada / SGL Mtl \\
Hemp Bast Fiber (woven)	& Bio-reinforcement; toughening & -- & 10--15 & Prairie Hemp Council (SK) \\
\bottomrule	
\end{tabular}	
\end{table}	

\subsection{Stoichiometric Rationale}

Sebacic acid (dodecanedioic homologue; $M = 202.25$ g/mol) provides two -COOH groups per molecule for epoxy ring-opening at the primary alcohol of EHO. The slight excess (1.05 equiv.) ensures complete epoxy conversion while providing free -OH groups that participate in ester-exchange vitrimer reactions at $T > T_v \approx 160^\circ\text{C}$. HF-BX undergoes self-polymerization without hardener above 110°C , catalyzed by released primary amines – no external catalyst is required.

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\section{Pre-Experimental Procedure}
\label{sec:proc}

\subsection{Step 1 – Component Preparation}
\begin{enumerate}
  \item Dry HCNFs at  $80^{\circ}\text{C}$  for 24 h under vacuum
    ( $50\text{ mbar}$ ) to remove physisorbed water.
  \item Synthesize N,P-CQDs via solvothermal method: citric acid
    (1 g) + hexachlorotriphosphonitrile (0.5 g) in DMF (20 mL), autoclave at  $200^{\circ}\text{C}$ ,
    12 h.
    Purify by dialysis (MWCO 1 kDa). Target diameter: 3–7 nm.
  \item Prepare HDCNS Gen II: pyrolyze hemp hurd at
     $600^{\circ}\text{C}$  ( $N_2$ , 2 h),
    activate with KOH (1:3 mass ratio) at  $800^{\circ}\text{C}$ .
    Target B.E.T. surface area
     $>400\text{ m}^2/\text{g}$ .
  \item Prepare HICF: carbonize hemp bast fiber at
     $900^{\circ}\text{C}$  in inert atmosphere.
    Mill to  $D_{50} \approx 2\text{ }\mu\text{m}$ .
\end{enumerate}

\subsection{Step 2 – Resin Blending}
\begin{enumerate}
  \item Combine EHO + HF-BX + sebacic acid in a 3-neck round-
    bottom
    flask under  $N_2$  at  $25^{\circ}\text{C}$ .
  \item Add CQDs, HCNFs, HDCNS, Gen II, HICF sequentially.
  \item Disperse via tip sonication (400 W, 20 kHz, 30 min,
    ice bath).
  \item Degas under vacuum ( $50\text{ mbar}$ ) for 15 min.
  \item Measure viscosity (Brookfield DV-II+): target
     $<600\text{ mPa}\cdot\text{s}$ .
\end{enumerate}

```

\subsection{Step 3 – Preform Lay-Up}

Stack sequence: $[0^\circ/90^\circ/\pm 45^\circ]_s$
alternating

PAN-CF (UD) and hemp bast (woven, 2×2 twill).

Consolidation:

RTM at 40°C , injection pressure 0.4 MPa ,
fiber volume fraction target: $45\pm 2\%$.

\subsection{Step 4 – Curing Cycle}

\begin{enumerate}

\item \textbf{Gelation:} 80°C , 2 h.

Partial benzoxazine ring-opening; EHO--sebacic
esterification

initiates. Monitor via DEA (dielectric analysis).

\item \textbf{Advance Cure:} 120°C , 2 h.

Epoxy--acid network $>95\%$ conversion (DSC).

Polybenzoxazine network initiates.

\item \textbf{Post-Cure:} 180°C , 1 h
(ramp: 2°C/min). Complete benzoxazine
ring-opening; final $T_g \geq 175^\circ\text{C}$.

\item \textbf{Cool-Down:} -2°C/min to
 60°C , then free-cool to RT.

\end{enumerate}

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% 5. CHARACTERIZATION SOP

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\section{Characterization Plan}

\label{sec:char}

\subsection{Mechanical Testing}

All mechanical tests performed at $23 \pm 2^\circ\text{C}$,
 $50 \pm 5\%$ RH, crosshead speed 1 mm/min unless stated.

\begin{table}[H]

\centering

\caption{Mechanical Characterization SOP}

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\label{tab:mech}
\small
\begin{tabular}{llll}
\toprule
Test & Standard & Specimen & $n$ \\
\midrule
Tensile (0\textdegree) & & ASTM D3039 & & \\
250\texttimes 25\texttimes 2\text{,mm} & 5 \\
Flexural (3-pt bend) & & ASTM D7264 & Span/depth = \\
32:1 & & 5 \\
Compression (0\textdegree, CLC) & ASTM D6641 & Combined \\
loading & & 5 \\
ILSS (short-beam) & & ASTM D2344 & Span/depth = \\
5:1 & & 5 \\
Mode-I $G_{Ic}$ (DCB) & & ASTM D5528 & Pre-crack \\
50\text{,mm} & & 6 \\
Charpy impact (notched) & & ISO 179-1 & & \\
80\texttimes 10\texttimes 4\text{,mm} & 10 \\
\bottomrule
\end{tabular}
\end{table}

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\subsection{Thermal Analysis}

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\begin{itemize}

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\item \textbf{DSC:} TA Q2000; 5\textdegree C/min;
N\textsubscript{2};
$-40$ to 300\textdegree C; cure kinetics + $T_g$.

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\item \textbf{DMA:} TA Q800; 3-point bend; 1\text{,Hz};
2\textdegree C/min;

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$T_g$ from $E'$ peak.

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\item \textbf{TGA:} TA Q500; 10\textdegree C/min;
N\textsubscript{2} then air; onset degradation
temperature.

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\end{itemize}

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\subsection{Spectroscopic Characterization}

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\begin{itemize}

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\item \textbf{FTIR-ATR:} Bruker Vertex 70; 4000-

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