

Multiscale cure process modeling of an advanced 3D-woven composite for thermal protection systems applications

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Abstract

As-manufactured woven polymer matrix composites often exhibit in-situ cracking due to residual stresses that arise from curing. NASA's Heatshield for Extreme Entry Environment Technology (HEEET) is a state-of-the-art 3D-woven composite thermal protection system featuring a highly porous phenolic matrix, blended fiber yarns, and a complex woven architecture. To predict residual stresses in HEEET due to curing, a bottom-up hierarchical multiscale cure process modeling framework was engineered. The modeling framework spanned three length scales: nanoscale, microscale, and mesoscale. A novel application of molecular dynamics was developed to generate microstructure models with characteristic cross-sections of the blended yarns. Cure- and temperature-dependent properties of the phenolic matrix were established to serve as homogenization inputs at the nano and microscales. Residual stresses predicted by virtual curing of HEEET at the mesoscale were compared quantitatively to simple, relatively low computational cost thermal cooldown simulations and qualitatively with micro-computed tomography imaging data.

Introduction

NASA's Heatshield for Extreme Entry Environment Technology (HEEET) is a 3D-woven composite that provides enhanced thermal insulation capabilities and improved stiffness and strength at a lower weight compared to previous generations of thermal protection systems (TPS) [1], [2], [3], [4], [5]. The composite includes inter-woven recession and insulation layers, each with distinct woven architectures, to tailor the material's performance during atmospheric entry conditions where ultra-high temperatures are present [4]. Extensive testing has demonstrated that HEEET is suitable for entry heating rates in the range of 1500 W/cm^2 to at least $6,000 \text{ W/cm}^2$ and pressures up to 6 atm, making it an ideal solution for atmospheric entry applications in future missions [1], [4], [6]. To enhance its ablative performance, HEEET features a phenolic matrix engineered with significant nano-porosity to and woven yarns containing a blend of carbon and phenolic fiber blends with respectively circular and non-uniformly oriented elliptical cross-sections to deliver both low thermal conductivity and strong mechanical behavior [7], [8]. However, as-manufactured HEEET has been shown to exhibit cracking within and between its woven yarns [7]. While recent studies have employed multiscale modeling techniques to better understand the thermomechanical performance of theoretically pristine as-manufactured HEEET [7], [8], [9], research directly targeting the curing process stage where these defects arise remains a gap in the existing literature. Real-time experimental observation and quantification of in-situ multiscale phenomena (e.g., material phase/property evolution at the nanoscale, interactions between fiber and matrix at the microscale) that drive the accumulation of defect-triggering and performance-affecting residual stress across length scales poses a substantial challenge. As such, multiscale physics-based process modeling frameworks are an essential tool for analyzing how intrinsic thermal-chemical-mechanical interactions propagate across length scales, ultimately driving in-situ residual stresses and the as-manufactured performance of complex composite materials [10], [11], [12]. In the case of HEEET, a robust process modeling framework should have the ability to account for multiscale interactions between the porous phenolic matrix, the blended yarns, and the woven architecture.

One solution to processing simulation is to employ a simple thermal cooldown type analysis, where the model temperature is brought from some elevated curing temperature down to room temperature to induce thermo-mechanical deformations and residual stress due to the mismatch in the coefficients of thermal expansion between the constituents in the composite [13]. However,

this neglects a key nonmechanical deformation occurring throughout processing, namely cure shrinkage [14], [15], [16], making it difficult to optimize cure cycle parameters (cure temperature, hold times, ramp rates) and predict progressive damage leading to in-situ cracking.

Comprehensive process modeling frameworks have shown that, when coupled with a robust set of material properties defined as functions of cure and temperature and a physics-based representation of the curing process, improved prediction of matrix-dominated properties such as transverse stiffness and strength of composite materials is possible [17]. Critical to achieving this are an extensive range of constituent matrix properties that are driven by the processing state [11], [17], [18], [19], [20], [21], [22]. However, obtaining an extensive set of state-dependent matrix material properties via experiment is challenging [20], [23], [24], and so computational methods such as molecular dynamics (MD) have been adopted to aid in the characterization process [18], [19], [20], [22].

Furthermore, when establishing numerical models of composites with complex architectures, the generation and meshing of quality geometries which explicitly and simultaneously capture individual constituents across multiple length scales in high resolution is extremely challenging and, in most cases, unrealistic. As such, concurrent and hierarchical homogenization strategies have been leveraged to perform multiscale numerical analysis of composites in finite element (FE) frameworks. Recent examples of concurrent process modeling frameworks include the research performed by Chen and Zhang [25], Wang et al. [26], and Zhi et al. [16]. The main downside to concurrency is that because multiple length scales are simulated simultaneously, even for simple material architectures, the problem size and complexity becomes extremely computationally expensive and requires trade-offs in terms of modeling fidelity and simulation time. Nagaraj and Maiaru [27] and Nagaraj et al. [28] recently applied the Carrera Unified Formulation [29] (CUF) higher-order FE formulation in a concurrent multiscale process modeling framework in an effort to establish more computationally efficient alternative to classical 3D FE. Despite the reported 10x simulation speed increase in their approach compared to 3D FE, this concurrent strategy remains hamstrung by the steep escalation in problem size as the composite architecture grows in complexity. Conversely, in a bottom-up, hierarchical multiscale modeling approach, behavior at each length scale is homogenized independently of the others starting with the lowest length scale of interest. Then, the outputs from the homogenization process at one length scale are passed to

the next length scale(s) up. The de-coupling of scales is advantageous because the problem size, and number, of each individual analysis is significantly smaller, and thus representative models can be of higher fidelity without the exponential increases in computational cost characteristic of the concurrent approach. Trofimov et al. [21], [30] established a hierarchical process model to study a 3D woven carbon fiber composite, where effective curing behavior was characterized and linked between the microscale, mesoscale, and macroscale through de-coupled FE analyses at each length scale. Specific to HEEET, thermomechanical performance accounting for both matrix porosity and the blended yarn microstructure, was studied in previous works using the NASA Multiscale Analysis Tool (NASMAT) [8], [9] and the Porous Microstructure Analysis (PuMA) software [31]. However, multiscale modeling of the curing process, whether through concurrent or hierarchical means, has yet to be explored for this material.

To overcome this shortcoming, this work aims to establish a bottom-up hierarchical strategy for multiscale process modeling of the HEEET insulation layer using the FE method. The study focuses on three key length scales: the nanoscale (inter-/intra-yarn porous phenolic matrix); microscale (blended yarns); and mesoscale (3D weave). Starting from the porous phenolic matrix, effective material behavior as a function of cure and temperature is established and passed up to one or more higher length scales for further homogenization via the proposed hierarchical strategy. Representative models for each of the relevant length scales are established based upon the multiscale architecture of HEEET. The strategy facilitates a virtual curing model of at the mesoscale which contains the previously characterized nano and microscale process-dependent material evolution. Residual stresses predicted by the mesoscale simulation are compared quantitatively to simple thermal cooldown simulations and qualitatively to micro-computed tomography (CT) scans of a sample of the as-manufactured HEEET insulation layer, completing the bottom-up hierarchical multiscale process modeling workflow.

The HEEET insulation layer constituents consist of a porous phenolic matrix SC-1008, a resole-type phenolic [32], [33], [34], [35], and blended AS4-carbon/phenolic fiber tows. Data regarding the composition of the composite was reported previously [7], [8], [9] with key details summarized here. The volume fractions of the porosity in the intra- and inter-yarn phenolic matrices were assumed to be 55.2% and 84.6%, respectively, consistent with a previous study [8]. The AS4-carbon fibers feature a circular cross-section, while the phenolic fibers exhibit an elliptical cross-

section. A micro-CT image [8] taken of a section of an individual tow showing the in-situ carbon fibers (white circles) and phenolic fibers (grey ellipses) is provided in Figure 1. The approximate geometry and volumetric contributions of the two constituents determined via the microscopy data are reproduced from [8] in Table 1. Figure 2 contains both raw and processed micro-CT images of a section of the bulk woven architecture. Note, each yarn in the weave is comprised of four twisted blended fiber tows.

Results

Size and mesh convergence of FE models

Elastic properties predicted for the nanoscale size and mesh convergence study were similar regardless of model size and mesh density. As a result, both the intra- and inter-yarn matrix RUC models utilized a cubic simulation domain length of 1.0 μm and a global mesh seed ratio of 0.075 in the subsequent state-dependent homogenization procedure at the nanoscale. At the microscale, elastic material behavior was confirmed to be transversely isotropic. Like the nanoscale, it was found that the global mesh seed ratio and RUC size also had a negligible effect on the elastic response. Thus, a blended yarn RUC containing 100 carbon fibers and a global mesh seed ratio of 0.20 was adopted for the state-dependent homogenization procedure at the microscale.

Numerical homogenization at the nanoscale and microscale

The suite of effective material properties as a function of temperature and cure state, characterized via the computational homogenization procedure for the intra- and inter-yarn porous matrix models and blended yarns, is provided in Figure 3 through Figure 5 and Figure 6, respectively. Data points shown in the figures are averages either for the full isotropic (porous matrix) or transversely isotropic (blended yarn) properties. For reference and comparison against the properties pertaining to the porous phenolic, the dense matrix properties are also included in Figure 3. The shear modulus of the porous matrix was assumed to follow the isotropic relationship $G = \frac{E}{2(1+\nu)}$ and thus results are not shown in Figure 3. The total chemical shrinkages estimated for each case are given in Table 2. For the blended yarns, shrinkage was small enough to be considered zero in the fiber-dominated axial direction and thus occurred only in the transverse directions.

For the porous matrix models, the progression of material properties mirrored those of the fully dense matrix. The elastic moduli, shear moduli, and coefficients of thermal expansion were tied to the degree of cure, temperature, and porosity. Poisson's ratio was a function of cure state and porosity only. Like with the porous matrix homogenization results, the progression of material properties in the blended yarn microstructure mirrored those of the fully dense matrix. Transversely, isotropic material behavior was confirmed for the yarns, independent of degree of cure and temperature. The elastic modulus, shear modulus, and coefficient of thermal expansion were tied to the degree of cure, temperature, and porosity. Poisson's ratio for the blended yarn demonstrated very minor sensitivity to temperature and thus was considered to be a function of cure state only. The lack of smoothness in the results for ν_{23} was ascribed to the matrix-dominated 23-plane and the very low matrix modulus at early cure stages and high temperatures.

The homogenization data suggests that porosity acts as a scale factor for the properties of the dense matrix. Elastic modulus, Poisson's ratio, and shear modulus all decreased significantly with increasing porosity. Conversely, CTE increased, albeit marginally. The total chemical shrinkage increased with porosity, which can be explained by the very small Poisson's ratio that was prescribed to the highly compressible porous "material" used in the RUC representations. Consequently, the material property models for the dense phenolic described were extended to include a term that scales the properties as a quadratic function of porosity. E.g., for a generic property ψ of the fully dense matrix

$$\psi^p(\phi, T) = (\kappa_1 v^p{}^2 + \kappa_2 v^p + \kappa_3) * \psi^d(\phi, T) \quad 1$$

where ψ^d and ψ^p are the values of the property for the fully dense and porous matrix, respectively, v^p is the porous volume fraction, and κ_i are dimensionless model parameters fit by a nonlinear least squares regression. Excellent agreement was found between the FE results and data fit using this approach as evidenced by Figure 3. The parameters κ_i fit for each material property are provided in Table 3.

In the case of the blended yarn RVE, fiber-dominated axial modulus and CTE (Figure 6) in the fiber direction had little to no variation as a function of the intra-yarn matrix temperature or cure state. As such, a simple rule of mixtures (ROM) approach was adopted for homogenizing the axial modulus, and a near-constant magnitude of 9.7×10^{-8} $^{-}/^{\circ}\text{C}$ both above and below T_g . The lack of smoothness in the results for ν_{23} was ascribed to the matrix-dominated 23-plane and the very low

matrix modulus at early cure stages and high temperatures. Data fits shown in Figure 6 for the various evolving effective properties were the outcome of a re-fit to the corresponding property models for the fully dense porous matrix. Specifically, the elastic and shear moduli were fit Equation 9, and the Poisson's ratio and CTE were fit to Equation 10. Refer to Table 4 and Table 5 for all updated model parameters as per the re-fitting procedure.

Mesoscale process modeling of the HEEET insulation layer

The maximum principal and normal (S11/S22/S33) residual stress fields in the isotropic inter-yarn porous phenolic matrix (yarns removed) predicted from the full process modeling simulation case are shown in Figure 7. Figure 8 shows the maximum principal and normal residual stress fields in the blended yarns (matrix removed), where stress components are instead with respect to the individual local yarn orientations. A quarter section cut of the model was made to aid in visualization of the stress field within the weave and between the yarns. Because consistent trends in terms of the spatial gradients of stress were observed for all three process simulation cases, with key differences being in their minimum/maximum magnitudes, contours of the residual stress fields from the simple cooldown processing simulation cases are not shown. Commentary on the stress fields resulting from the simple cooldown cases compared to full process modeling are in the following discussion. For qualitative comparison with the simulation results, Figure 9 contains micro-CT imaging of the HEEET insulation layer taken along the warp and fill directions [7].

In the inter-yarn porous matrix (Figure 7), the maximum principal stress peaked at ~28 MPa for the full process modeling simulation case. Stresses peaks were greatest in the fill (11) and warp (22) directions, which were approximately 21 MPa and 18 MPa, respectively. While results of the simple thermal cooldown cases yielded similar trends, stress peaks were overpredicted by the CD-RT case and underpredicted by the CD-VT case when compared to full process modeling. For CD-RT, this corresponded to ~8% for maximum principal stress and ~8%, ~7%, and ~3% for fill, warp, and through-thickness (33) direction stresses, respectively. A significantly higher relative error was observed in the CD-VT, where underpredictions with respect to full process modeling ranged from ~22-25%. From a qualitative perspective, there were noticeably greater stress concentrations in tight pockets of matrix between overlapping warp/fill yarns which agree with the locations of visible cracking observed in the sample micro-CT imaging (Figure 9).

The S11 normal component of stress in the blended yarns (Figure 8) was, as expected for the direction corresponding to the yarn fibers' longitudinal axes, the component of stress with the greatest magnitude for the yarns in all cases both in tension and compression. Consequently, S11 stresses had a nominally higher magnitude compared to the transverse components S22 and S33 in tension. For the full process modeling, CD-RT, and CD-VT simulation cases, maximum values of S11 predicted at the end of processing were approximately 179 MPa, 156 MPa, and 138 MPa in tension and -297 MPa, -272 MPa, and -219 MPa in compression, respectively. Here, there was a discrepancy of almost 13% in tension and 10% in compression between the full process model and CD-RT cases. Compared with the CD-VT case, the relative error rose to approximately 23% in tension and 26% in compression. Differences between the CD-RT and full process model cases were less significant in the transverse components of stress, where instead resulted in slight CD-RT overprediction of at worst 2%. Meanwhile, the CD-VT case continued to result in a significant underprediction of residual stresses compared to full process modeling, here by up to 25%. Maximum principal stress peaks also deviated significantly between the three cases, with the ~211 MPa shown for full process modeling being ~11% and ~22% greater than what was predicted respectively by CD-RT and CD-VT simulations. While the predicted values of residual stress in the yarns was unrealistically large due to the lack of a means for stress relaxation in the model (e.g., via progressive damage), their local concentrations were indicative of the significant damage shown in and around the overlapping and undulating yarns in the micro-CT imaging (Figure 9).

Plots of the evolution of volume-averaged residual stresses as a function of processing time in the inter-yarn porous matrix and one of the blended yarns for the full process modeling simulation case are provided in Figure 10. In Figure 11, the results of the thermal cooldown simulations are overlaid on those of the full process modeling simulation from the start of its cooldown phase. In these figures and the following discussion, $\sigma^{(1)}$ refers to the maximum principal stress, and σ_{ii} refers to the normal stress component ii . Finally, Figure 12 shows the relative error for the end-of-cure volume-averaged residual stress state between the two simple thermal cooldown and full process model simulation cases.

The residual stress evolution in the inter-yarn porous matrix and the blended yarns for all components shown in the plots was highly nonlinear. Gelation occurred around 10,000 seconds of processing time when the stress began to first rise due to thermal expansion effects. After reaching

an initial peak while approaching the curing temperature of 250°C, the stress began to drop due to the competing effect of chemical shrinkage and decreasing CTE with increasing degree of cure. Once fully cured, no further shrinkage occurred, and the stress leveled out for the remainder of the hold period at the curing temperature. Finally, the stress began to greatly increase during the final cooldown to room temperature. The volume-averaged maximum principal stress and all normal components of stress were tensile in the inter-yarn phenolic matrix. This held true for the blended yarns except for σ_{11} , which was compressive.

When comparing the final states of residual stress predicted by the full process model with the simple thermal cooldown simulation cases, the CD-RT case had good agreement with the process model. This can be confirmed by Figure 12, where the relative error at the end of cure between the CT-RT case and full process modeling was at overall larger in the blended yarns relative to the phenolic matrix, peaking at ~6% (σ_{22}) and ~5% (σ_{33}), respectively. While it was previously discussed that large discrepancies were observed in the maximum stress peaks between the two models, the local maximums were smeared out for the volume-averaged stresses. In line with what was expected from the contours of the residual stress fields, the CD-VT case consistently produced significant underpredictions relative to the full process modeling case. In this simple thermal cooldown simulation case, the end-of-cure relative error for the residual stresses ranged from ~20-30% in both the phenolic and the blended yarns. In isolation, from Figure 11 and Figure 12 it may appear that the simple thermal cooldown approach is sufficient for predicting process-induced residual stresses in the HEEET insulation layer. However, when taking into consideration the full stress history predicted in the process modeling simulation shown in Figure 10, it is evident that simple thermal cooldown-type analyses miss complex non-negligible thermal-chemical-mechanical interactions occurring throughout the entire processing cycle. Critically, the residual stresses accumulated in the constituent materials at intermediate points in the curing process due to these interactions may lead to the initiation of damage, which would otherwise not be captured by a simple cooldown processing simulation. Should progressive damage be included in the multiscale analysis, more pronounced differences between the simple thermal cooldown and full process modeling approaches owing to stress redistribution resulting from any damage accumulated during cure would be expected.

Notably, the predictions made from the full process model provide enable insight into what parameters in the cure cycle can be modified for reduction in the woven composite during processing. For example, while a stress-relaxation term is not present in the current modeling framework, it is clear from Figure 10 that there are non-negligible stresses generated during the initial ramp up to the final curing/hold temperature. Assuming hold time is not an absolute constraint in the curing protocol, extending the hold time at curing temperature could lead to stress relaxation in a real-world environment. Furthermore, ramp rate, curing temperatures, and number of intermediate holds could be tailored such that thermal expansion of the matrix post-gelation (can sustain load) during ramp-up is limited.

Discussion

In this research, a hierarchical approach was established and employed to perform multiscale process modeling of the HEEET 3D woven composite insulation layer. The material architecture was broken down into three distinct length scales: 1) nanoscale (porous phenolic matrix), 2) microscale (blended yarns), 3) mesoscale (3D weave). Nanoscale models adopted RUC representations. At the microscale, a novel approach that leveraged the LAMMPS MD simulation tool was deployed to generate RUCs of the blended yarns containing random dispersions of circular carbon fibers and elliptical phenolic fibers of non-uniform orientations. Material properties of the dense phenolic matrix were implemented into the process model as generic functions of cure and temperature. A numerical homogenization approach was adopted to obtain effective properties as a function of processing state at the nanoscale and microscale. Nanoscale results showed the effective properties of the porous matrix models were essentially scaled from the dense matrix by a quadratic function of the porosity. Models for effective properties at the microscale were established by fitting the data to the dense phenolic property models established previously. These effective properties became inputs for the process modeling at the mesoscale. Process modeling at the mesoscale resulted in good qualitative agreement between locations of stress concentrations in the FE model at the end of cure and locations of intra- and inter-yarn cracking found in micro-CT imaging of the HEEET insulation layer. Comparisons between full process modeling and simple thermal cooldown simulation cases at the mesoscale showed large discrepancies between the predicted peak residual stresses at the end of processing, especially in the blended yarns. Volume-averaged stress predictions from a simple thermal cooldown approach

with constant room temperature properties agreed well with the final residual stresses predicted by full process modeling. A simple cooldown case with temperature-dependent properties consistently underpredicted stresses relative to full process modeling results. Crucially, the full process model results demonstrated that the stress history during processing is highly nonlinear due to the complex thermal-chemical-mechanical evolution of the constituents. These features were unable to be properly captured in the simple thermal cooldown simulations.

In future work, a comprehensive experimental/modeling study on the state-dependent properties of the matrix is required to improve the inputs to the model, including characterization of failure properties (e.g., tensile strength). Generation of more statistically realistic geometries to represent the porous matrix, and analysis on various microstructure features (e.g., elliptical fiber orientation) and how they compare to the micro-CT imaging data will be advantageous to building a higher-fidelity representation of the multiscale structure. Furthermore, by incorporating progressive damage modeling into the hierarchical processing framework, a more accurate prediction of the residual stress evolution and cracking mechanisms could be performed. Future work will aim to integrate these capabilities into the process model to enable progressive damage modeling of HEEET during cure simulations. This advancement can then be used to inform models investigating how processing influences as-manufactured performance of HEEET or other complex, 3D woven composite systems.

Methods

Governing equations for process modeling

The process model employed in this study features a governing thermal-chemical-mechanical model to describe the constituent materials' curing behavior across length scales. Mechanical behavior was described via an instantaneous linear elastic constitutive law:

$$\begin{aligned}\sigma_{ij}(t) &= C_{ijkl}(t)\varepsilon_{kl}^{mech}(t) \\ \varepsilon_{kl}^{mech}(t) &= \varepsilon_{kl}^{tot}(t) - \left(\varepsilon_{kl}^{th}(t) + \varepsilon_{kl}^{ch}(t) \right) \delta_{kl}\end{aligned}\tag{2}$$

where

$$\varepsilon_{ij}^{th}(t) = \alpha_{ij}(t)\Delta T, \quad i = j\tag{3}$$

and

$$\varepsilon_{ij}^{sh}(t) = \begin{cases} 0, & \phi < \phi_{gel} \\ \beta_{ij}\Delta\phi, & \phi \geq \phi_{gel} \end{cases}, \quad i = j \quad 4$$

In the above equations, stress σ , strain ε , material stiffness C , and coefficient of thermal expansion α terms are a function of time t to account for the instantaneous state of the curing material, e.g. degree of cure ϕ and temperature T . δ_{kl} is the Kronecker delta. The mechanical (mech) strains are decomposed into the total (ε^{tot}), thermal (ε^{th}), and chemical shrinkage (ε^{sh}) strains. Post gelation shrinkage strains ε^{sh} are assumed to be a linear function of the cure state as shown experimentally for both epoxy and phenolic resins [17], [36], modeled by the linear coefficient of chemical shrinkage term β .

The thermal behavior of the material was modeled using the transient heat equation:

$$\rho c_p \frac{\partial T}{\partial t} = -\lambda \cdot \nabla^2 T + S^{exo} \quad 5$$

Here, density ρ , specific heat capacity c_p , and thermal conductivity λ were assumed to be constant material parameters. The source term S^{exo} accounts for exothermic heat generated due to the curing reaction [34], [37], [38], which is a function of the curing rate $\frac{d\phi}{dt}$, total heat of reaction H^{tot} , mass density ρ^m , and constituent volume fraction v^m of the matrix material [39].

$$S^{exo} = v^m \rho^m H^{tot} \frac{d\phi}{dt} \quad 6$$

Finally, the evolution of cure was modeled using a phenomenological kinetic equation experimentally characterized previously by Nam and Seferis for the SC-1008 phenolic [34], where an Arrhenius constant k described the temperature-dependence on the cure rate:

$$\frac{d\phi}{dt} = k(1 - \phi)^n \quad 7$$

$$k = Z \exp\left(-\frac{E_a}{RT}\right) \quad 8$$

Constant model parameters are activation energy E_a , pre-exponential factor Z , dimensionless constant n , and universal gas constant R .

Hierarchical modeling approach

In bottom-up hierarchical multiscale modeling schemes, material behavior at lower length scales is passed up to one or more higher lengths scales in the form of effective material properties,

obtained using a homogenization technique, in a de-coupled fashion. Thus, length scales are linked by the effective material behavior obtained at lower length scales that are used as inputs. For the multiscale process modeling analysis of the HEEET insulation layer performed in this work, three length scales were examined, each described with a representative FE model. They were:

1. **Nanoscale:** Intra- and inter-yarn phenolic matrix
2. **Microscale:** Blended carbon/phenolic yarn microstructure
3. **Mesoscale:** HEEET insulation layer 3D weave

During cure, because the matrix evolves as a function of state and is one constituent within the composite, it can be asserted that the bulk composite evolves as a function of state in tandem with the matrix. Considering this, a hierarchical process model necessitates the transfer of effective composite properties as a function of cure and temperature across length scales to facilitate simulation of composite curing behavior at higher scales. Meaning, for all state-dependent properties for the dense phenolic matrix, an analogous set of effective state-dependent properties must be established for each length scale being studied in a simulation. For the dense matrix, state-dependent properties considered in this study were the elastic modulus E , Poisson's ratio ν , coefficient of thermal expansion α , and post-gelation chemical shrinkage ε_{pg}^{sh} . When homogenized with additional constituents (e.g., porosity, fibers) and assuming orthotropic material behavior, the analogous state-dependent effective properties were the elastic moduli E_{ii} , Poisson's ratios ν_{ij} , shear moduli G_{ij} , coefficients of thermal expansion α_{ii} , and the linear coefficients of chemical shrinkage β_{ii} .

In summary, numerical homogenization was performed at the nanoscale and microscale levels, and process modeling was performed at the mesoscale. Effective, state-dependent material properties of the porous matrix at the nanoscale were utilized in both the microscale (intra-yarn matrix) homogenization and mesoscale process modeling simulations (inter-yarn matrix). Likewise, effective properties of the blended yarns at the microscale were also utilized in the mesoscale process modeling simulations, completing the hierarchical transfer of material behavior up the length scales. A schematic of the hierarchical processing modeling pipeline for HEEET is outlined in Figure 13.

The commercial FE solver Abaqus Standard was used for all analyses performed in this work. The process modeling governing equations presented above, which defined the thermal-chemical-mechanical behavior of the constituent materials at all length scales in the simulations, were integrated with Abaqus via user subroutines UMAT and UMATHT. Note, damage of the constituent materials was not considered for this iteration of the hierarchical model. Representative FE models, state-dependent properties of the phenolic matrix, the numerical homogenization procedure, and process modeling of the HEEET insulation layer are discussed in detail in the following sections.

Representative finite element (FE) models

From the micro-CT imaging data and constituent materials described above, three length scales were identified to be included in the hierarchical process modeling framework developed for this work. They were, in order from lowest to highest length scale: nanoscale (porous matrix), microscale (blended yarns), and mesoscale (3D weave). The models generated to represent each in the FE analyses are discussed below.

Nanoscale

Idealized repeating unit cell (RUC) representations, where a single spherical pore was centered inside of a cubic simulation domain, were used to model the intra- and inter-yarn porous phenolic matrix (see Figure 14). Due to the lack of publicly available data regarding the approximate pore size of porous SC-1008 used in HEEET, a range of values within the measurements by Sha et al. [40] (~ 0.25 to ~ 6.0 μm) for several porous phenolic resins were adopted in this study to evaluate the effect of pore size on the elastic response of the matrix, if any. Therefore, in generating the RUCs, the pore size was varied as a function of the simulation domain size, which ranged from 0.25 to 2.0 μm , to maintain constant pore volume fractions equal to the reported intra- and inter-yarn phenolic matrix porosities. The size study was also combined with a mesh convergence study, where the global mesh seed size (termed the “mesh seed ratio”) was varied from 12.5% down to 2.5% of the domain length.

Abaqus CAE was used to generate and mesh the RUCs with quadratic tetrahedral coupled temperature-displacement (C3D20T) elements. Periodic boundary conditions (PBCs) were enforced for all directions in all analyses. To simplify generation of a periodic mesh, the spherical pore centered in the simulation domain was explicitly modeled as a highly compressible material

with near-zero Young's modulus (for numerical stability) as opposed to an empty space/void. This approach is common when performing computational micromechanics due to ease of implementation and is consistent with previous modeling efforts [41], [42]. An exploratory simulation at the highest porosity (inter-yarn matrix) where the pore was omitted (i.e., modeled as a spherical hole instead of a distinct material) confirmed that this modeling assumption did not significantly impact the predicted elastic properties ($<1\%$).

It was also assumed that of the two porosities, the inter-yarn scenario would be the most sensitive to size and mesh topology. This was because the near-zero stiffness elements, which were greatest in the inter-yarn porous phenolic models, were expected to impact stress transfer during mechanical loading. Thus, for both the size and mesh convergence studies, results of the inter-yarn matrix RUC were considered to hold true for the intra-yarn counterpart. Six mechanical loading conditions discussed in the numerical homogenization section below were used to carry out the size/mesh study and judge convergence.

Microscale

At the microscale, multiple RUCs of the blended yarns were modeled consisting of random dispersions of circular carbon fibers and elliptical phenolic fibers in increasing numbers. While solutions exist for generating microstructure RUCs containing fibers with circular cross-sections [43], [44], tools for generating microstructure realizations with randomly oriented elliptic fibers characteristic of the HEEET yarns are yet to be established in the literature. To address this, a novel application of the LAMMPS [45] MD simulation software using Gay-Berne particle interactions [46] was used to generate the microstructures characteristic of the blended yarns. Note that this workflow required that LAMMPS be built with ASPHERE and GRANULAR packages.

A flowchart of the MD simulation steps for creating a single RUC realization are shown in Figure 15 and are described in detail as follows. The model microstructure size was first calculated based upon a user-defined value for the total number of carbon fibers desired in the model. Through knowledge of the constituent fiber volume fractions, the number of phenolic fibers and thus the domain size of the RUC was back calculated. Note that this was an approximation because "partial" fibers required to achieve the exact constituent volume fractions could not be created using this method. After computing the microstructure geometric parameters, a Lennard-Jones unit system was set, and a 2D periodic simulation box was created that was much larger than what was

required to satisfy the target fiber volume fraction of the microstructure. Following this, circular and elliptical particles with radii prescribed as per the carbon and phenolic geometries were randomly placed within the simulation box without permitting overlap. A random velocity was applied to each of the particles, and temperature equilibration was run using the npt/asphere fix. Essential to this procedure was the interactions between the circular and elliptical particles, which were described using a Gay-Berne pairing style [46]. After thermal equilibration, dynamics were run, and the simulation box was slowly deformed until the target fiber volume fraction and thus domain size calculated previously had been achieved using the nve/asphere and deform fixes, respectively. Finally, energy minimization was run, and the overlapping of particles was queried. If any overlap was found, or if the target volume fraction was not achieved, the realization was discarded, and another attempt was made. Once an acceptable particle dispersion that met the input microstructure parameters had been achieved, the coordinates and orientation (quaternion) of the particles were written to a file. This information was used to guide the construction of the 3D microstructure RUC geometries within Abaqus CAE. The MD simulation to FE model pipeline was tied together and automated using Python. Note that only the constituent fiber volume fractions were verified to be consistent with the experimental observations; analysis of statistical features in the generated RVEs such as orientations of the ellipses and local fiber clustering [47] with respect to the micro-CT imaging data were not considered and remain a subject of future research efforts.

To evaluate the impact of RUC size on the elastic response of the blended microstructures, RUCs containing 50, 75, 100, and 150 carbon fibers corresponding to 8, 11, 15, and 23 phenolic fibers were generated using the simulation strategy outlined above. Based on the volume fractions and dimensions of the blended fibers, the model with 50 carbon and 8 phenolic fibers was selected to ensure the effect of the randomly oriented and distributed phenolic fibers was sufficiently captured while remaining relatively small to keep its computational cost low. The larger microstructures were selected to verify that there was no significant difference in response when used in simulations compared to the smallest, most computationally efficient model. See Figure 16 for an example realization generated for each microstructure size. In total, 20 realizations per RUC size were analyzed to assess any variability driven by the randomized nature of the microstructures. All RVEs were meshed with 3D linear coupled temperature-displacement (C3D8RT) elements. PBCs were enforced for all directions in the analyses. A mesh convergence study was performed

prior to the size effect study to first establish the optimum mesh density for computational efficiency. As with the nanoscale mesh study, a global mesh seed ratio was used. For the microscale, this metric was a function of the carbon fiber radius and varied from 20% down to 10%. Mechanical and thermal material properties of the fibers used in the blended yarn RUCs, which were assumed to be constant with respect to cure and temperature in all analyses, are provided in Table 6 [8], [9], [35], [48]. E , ν , G , α , k , c_p , and ρ refer to the elastic modulus, Poisson's ratio, shear modulus, coefficient of thermal expansion (CTE), thermal conductivity, specific heat capacity, and mass density, respectively.

Mesoscale

A simplified periodic unit cell representation of the HEEET insulation layer, dimensioned at 5.08 mm (fill direction) by 5.08 mm (warp direction) by 1.717 mm (thickness), was constructed for previous research by Izquierdo et al. [31] using the open-source software package TexGen [49], [50], [51]. As shown in Figure 17, the unit cell was discretized with a voxel mesh containing a total of 330,000 C3D8RT elements. PBCs were enforced on all faces. The yarns were provided with local material orientations along their paths, where the 11-direction followed the longitudinal axis of a yarn, and the 22- and 33-directions followed the two orthogonal transverse axes of a yarn.

Models for state-dependent matrix material properties

The evolution of properties during processing that are captured in the C , ε^{th} , and ε^{ch} terms described in the governing equations defined previously requires a robust set of cure and temperature dependent matrix material property inputs. However, extensive experimental data for the material properties of SC-1008 as a function of cure and temperature state was absent in the literature, and characterization was outside the scope of this research. As such, to describe the evolution of the phenolic properties during cure within the computational framework, a combination of approaches was exploited. These included leveraging MD simulations of SC-1008 performed by Monk et al. [32], [52], properties reported for the fully cured phenolic, and engineering assumptions based upon the behavior of other curing polymeric resins. Note that all properties detailed in the following subsections are for the fully dense phenolic matrix, i.e., zero porosity. Furthermore, thermal properties of the matrix as a function of state were not gathered as a part of this research and were instead assumed to be the constant values listed in Table 7 [3], [8], [35].

Cure kinetics

The kinetic model adopted for this study to describe the cure evolution of is shown in Equations 7 and 8. Values of the kinetic model parameters used in these equations are provided in Table 8. The total heat of the curing reaction H_{tot} , used to model the curing reaction exotherm per Equation 6, was reported by Nam and Seferis for the SC-1008 phenolic to be 233.4 J/g [34]. Note that the gel point ϕ_{gel} of SC-1008 was previously reported as approximately 0.57 [34]. Figure 18 provides a plot of the degree of cure evolution as a function of time for the phenolic matrix undergoing a representative cure cycle.

Elastic modulus

The elastic modulus of the phenolic was modeled using the MD data provided by Monk et al. [32]. Predictions made with MD tend to overpredict the elastic properties of polymers as a consequence of relying on extremely small simulation timescales in what is known as the strain rate effect [18], [53]. To mitigate the effect of strain rate which was evident in the dataset (e.g., non-zero elastic modulus at low degrees of crosslinking), a MD to experimental strain rate mapping methodology presented by Patil et al. [20] was employed. In their approach, the “experimental” elastic modulus $E(\phi, T)$ is computed by scaling the MD-reported modulus E_{MD} as a function of the strain rate $\dot{\epsilon}$, degree of cure ϕ , and temperature T . The model used to define the matrix modulus evolution behavior of the phenolic was:

$$\begin{aligned}\tau &= 1 - \frac{T(K)}{T^{ref}} \\ \frac{E(\phi, T)}{E_{MD}(\phi, T)} &= f_\alpha(\alpha) * f_\phi(\phi) * f_\tau(\tau, \phi) \\ f_\alpha(\alpha) &= \alpha_a \ln\left(\frac{\dot{\epsilon}_{exp}}{\dot{\epsilon}_{MD}}\right) \alpha_b \\ f_\phi(\phi) &= 1 - \left[1 + \exp\left(1 + \frac{\phi - \phi_0}{\phi_\sigma}\right)\right]^{-1} \\ f_\tau(\tau, \phi) &= \left\{1 - \left[1 + \exp\left(1 + \frac{\tau - \tau_0(\phi)}{\tau_\sigma}\right)\right]^{-1}\right\} \tau_* \\ \tau_0(\phi) &= \tau_0^a \phi + \tau_0^b \\ \tau_*(\tau) &= \tau_*^a * \tau^{(\tau_*^b)}\end{aligned}\tag{9}$$

For an in-depth discussion of the model, its derivation, and the various phenomenological parameters, refer to Patil et al. [20]. Important to note here is the dimensionless normalized temperature τ which describes the current temperature of the matrix measured in kelvins $T(K)$ relative to a reference value T^{ref} . This was chosen to be the glass transition temperature T_g of the fully cured matrix (~ 533 K [32]). Experimental $\dot{\epsilon}_{exp}$ and MD $\dot{\epsilon}_{MD}$ strain rates were respectively equal to 10^{-3} sec $^{-1}$ and 10^8 sec $^{-1}$. The values of the phenomenological parameters used in the equations above are summarized in Table 9. Sample curves for the elastic modulus of the fully dense phenolic matrix as a function of ϕ and T modeled per Equation 9 are shown in Figure 19.

Poisson's ratio

No literature data was found for Poisson's ratio of SC-1008 as a function of cure and/or temperature. As shown for other polymeric resin systems [17], [54], [55], the evolution of Poisson's ratio is a function of ϕ that tends to follow a sigmoidal shape. These studies did not report any observations as to the influence of temperature on Poisson's ratio; thus, for the fully dense phenolic matrix, this property was modeled as a sigmoidal function of cure state and assumed to be independent of temperature. To formulate the model, it was first assumed that the phenolic initially acted as a near-incompressible fluid when uncured, i.e., $\nu^0 \approx 0.48$. The Poisson's ratio of fully cured SC-1008 was assumed to be temperature-independent with $\nu^1 \approx 0.37$ as reported for phenolic resins by others [56], [57]. The resulting model for Poisson's ratio as a function of cure state was therefore established by

$$\nu(\phi) = \frac{\kappa_1}{1 + \exp(\kappa_3 * [\phi - \kappa_4])} + \kappa_2 \quad 10$$

where κ_1 through κ_4 are model parameters fit through a non-linear least squares regression. The values of these parameters are provided in Table 10. The curve for Poisson's ratio of the fully dense phenolic matrix as a function of ϕ modeled per Equation 10 is shown in Figure 20.

Coefficient of thermal expansion (CTE)

The evolution of the coefficient of thermal expansion of SC-1008 at temperatures both below and above the glass transition temperature T_g was also characterized through MD by Monk et al. [32].

As with Poisson's ratio, the state-dependent CTE was fit to a sigmoidal function through a non-linear least squares regression.

$$\alpha(\phi) = \frac{\kappa_1}{1 + \exp(\kappa_3 * [\phi - \kappa_4])} + \kappa_2 \quad 11$$

The data fitting procedure was repeated twice, once each for values reported at temperatures above and below T_g . Resulting values for parameters κ_1 through κ_4 are reported in Table 11. Curves for CTE of the fully dense phenolic matrix as a function of ϕ both below and above T_g modeled per Equation 11 are shown in Figure 21.

Glass transition temperature

The glass transition temperature T_g as a function of crosslinking degree D was characterized through MD and fit to a DiBenedetto model by Monk et al. [32]:

$$\frac{\ln(T_g(D)) - \ln(T_g^0)}{\ln(T_g^\infty) - \ln(T_g^0)} = \frac{\lambda D}{1 - (1 - \lambda)D} \quad 12$$

Here, T_g , T_g^0 , T_g^∞ are the current, uncured matrix, and fully cured matrix glass transition temperatures, respectively, and λ is model parameter equal to 0.422. However, much like with the elastic modulus, it was observed that temperature cooling rate effects resulted in overestimation of T_g . Therefore, a scaling factor which varies as a function of cure state was implemented to knock down the MD-predicted T_g to be more in-line with those values extracted from experiment [32], [58]. The resulting function to describe the scaled glass transition temperature used in the process model for SC-1008 was thus

$$T_g(D) = (\kappa_1 D + \kappa_2) * T_g^{MD}(D) \quad 13$$

$$\frac{D}{D_{max}} = \frac{\phi}{\phi_{max}}$$

where $\kappa_1 = 0.2488$, $\kappa_2 = 0.5249$, and T_g^{MD} is the glass transition temperature modeled by Equation 13. To map between ϕ and D , it was assumed that the two state variables describing the phenolic chemical evolution were proportional to each other. Hence, $\frac{D}{D_{max}} = \frac{\phi}{\phi_{max}}$, where D_{max} is the maximum degree of crosslinking of the phenolic achieved in the MD simulations, approximately 0.85, and ϕ_{max} is the maximum degree of cure equal to 1.0. The curve for T_g of the fully dense phenolic matrix as a function of ϕ modeled per Equation 13 is shown in Figure 22.

Chemical shrinkage

Experimentally characterized values for the post-gelation chemical shrinkage of the SC-1008 phenolic matrix were not found in previous publications. As a stand-in, the post-gelation shrinkage values provided by Guo et al.[36] for a resole-type phenolic matrix, measured as $\varepsilon_{pg}^{sh} = -0.01163$, were used. This value was used to compute the shrinkage strain coefficient β by

$$\beta = \frac{\varepsilon_{pg}^{sh}}{(1 - \phi_{gel})} \quad 14$$

Numerical homogenization

By coupling the computational micromechanics technique, the process model, and the comprehensive suite of state-dependent dense phenolic material properties, effective properties at the nanoscale and microscale as a function of state were derived. Eight loading conditions were applied to representative FE models to fully characterize the effective elastic moduli E_{ii} , shear moduli G_{ij} , Poisson's ratios ν_{ij} , coefficients of thermal expansion α_{ii} , and coefficients of chemical shrinkage β_{ii} at each length scale. Innovative to the typical computational micromechanics approach was the use of the process model to virtually “freeze” the degree of cure and temperature of the modeled material(s) during a loading analysis to capture the instantaneous state-dependent response. Thus, by repeating the eight loading conditions across an array of material cure and temperature states, a mapping of the evolution of effective properties as a function of the processing conditions at each length was constructed. Numerical homogenization of effective thermal properties, such as thermal conductivity k_{ii} , using the strategy described here was not within the scope of this study and was instead reserved as a topic of future research efforts.

Six of the eight load types were mechanical: three tensile loads applied along the normal directions (11/22/33) and three pure shear loads (12/13/23). Displacement boundary conditions were imposed to deform the models accordingly. Room temperature (20°C), the matrix maximum cure temperature (250°C), an intermediate (135°C) temperature, and a range of degrees of cure from 0.1 to 1.0 were selected for the mechanical loading conditions to be repeated over. For each mechanical load analysis, the thermal and shrinkage strains were forced to be zero.

Another load type was a temperature ramp, where the FE models were subjected to a unit change in temperature and permitted to deform volumetrically. Two temperatures were selected for

repeating this load type: one above and one below the respective maximum and minimum T_g of the phenolic akin to the model for the dense matrix CTE shown previously. As with the mechanical loads, a range of degrees of cure from 0.1 to 1.0 were chosen for the repeat analyses. For each temperature ramp analysis, the shrinkage strains were forced to be zero.

The final load type was an isothermal temperature hold, where the model was permitted to cure from gelation onward and shrink volumetrically. Because the matrix shrinkage was dependent on the cure state only, and because the evolution of shrinkage was assumed to be a linear function of cure state, only a single analysis of this type was required. The isothermal hold analysis type was unique in that the cure state was allowed to evolve to induce chemical shrinkage; however, as with the other cases, the material properties were held constant for the duration of the analysis. In this case, thermal strains were forced to be zero.

In all cases, PBCs were enforced. The cure and temperature states that the loading conditions were repeated over are detailed in Table 12. In total, for each length scale model subject to the homogenization procedure described above, 96 simulations were performed to obtain effective properties as a function of the processing state.

Once an individual load case was run and completed, the volume-averaged stresses $\bar{\sigma}$ and strains $\bar{\varepsilon}$ of the entire FE model were extracted in the global coordinate system and used to compute the effective properties at the current discrete temperature/cure state:

$$\begin{aligned}\bar{\sigma} &= \frac{1}{V} \int_V \sigma * dV \\ \bar{\varepsilon} &= \frac{1}{V} \int_V \varepsilon * dV\end{aligned}\tag{15}$$

Here, V is the volume of the FE element model and σ , ε , and dV are respectively the integration point stresses, strains, and volumes. The effective properties that were characterized following the individual loading conditions are outlined in Table 13, which were computed by taking the slope of the volume-averaged stress vs. strain, transverse vs. axial strain, strain vs. temperature, and strain vs. degree of cure curves:

$$E_{ii} = \frac{\bar{\sigma}_{ii}}{\bar{\varepsilon}_{ii}}\tag{16}$$

$$G_{ij} = \frac{\bar{\sigma}_{ij}}{\bar{\varepsilon}_{ij}}$$

$$\nu_{ij} = -\frac{\bar{\varepsilon}_{jj}}{\bar{\varepsilon}_{ii}}$$

$$\alpha_{ii} = \frac{\bar{\varepsilon}_{ii}}{\Delta T}$$

$$\beta_{ii} = \frac{\bar{\varepsilon}_{pg,ii}^{sh}}{(1 - \phi_{gel})}$$

In the above, $\bar{\varepsilon}_{pg,ii}^{sh}$ is the volume-averaged total post-gelation chemical shrinkage in principal direction ii . The effective elastic properties determined for each discrete processing state ϕ and T through the procedure outlined above could then be used to construct the homogenized evolving stiffness tensor C_{ijkl} during process modeling at higher length scales (Equation 2). In the process model, for convenience and generalization to orthotropic material behavior, the compliance tensor S_{ijkl} was calculated first, then inverted to arrive at the stiffness as a function of the current processing state:

$$C_{ijkl}(t) = S_{ijkl}(t)^{-1} = \begin{bmatrix} \frac{1}{E_{11}(\phi, T)} & -\frac{\nu_{12}(\phi, T)}{E_{11}(\phi, T)} & -\frac{\nu_{13}(\phi, T)}{E_{11}(\phi, T)} & 0 & 0 & 0 \\ -\frac{\nu_{12}(\phi, T)}{E_{11}(\phi, T)} & \frac{1}{E_{22}(\phi, T)} & -\frac{\nu_{23}(\phi, T)}{E_{22}(\phi, T)} & 0 & 0 & 0 \\ -\frac{\nu_{13}(\phi, T)}{E_{11}(\phi, T)} & -\frac{\nu_{23}(\phi, T)}{E_{22}(\phi, T)} & \frac{1}{E_{33}(\phi, T)} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2G_{12}(\phi, T)} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2G_{13}(\phi, T)} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2G_{23}(\phi, T)} \end{bmatrix}^{-1}$$

Mesoscale process modeling of the HEEET insulation layer

As shown in the pipeline for hierarchical process modeling (Figure 13), outputs from numerical homogenization analyses at the nanoscale and the microscale became inputs for processing simulations of the HEEET insulation layer unit cell at the mesoscale. Specifically, these were effective state-dependent material properties for the inter-yarn porous matrix and the blended yarns analogous to the material property models for the dense phenolic matrix provided above. Effective thermal conductivity, specific heat capacity, and mass density of the inter-yarn porous phenolic matrix and blended yarns were assumed to be constant with respect to degree of cure and

temperature in accordance with the same assumption made previously for the fully dense matrix. Their values for use in the mesoscale processing simulations were computed from the assumed thermal properties [3], [8], [35] and experimentally characterized volume fractions of the constituents using rule of mixtures [59], [60], [61], see Table 14.

The thermal-chemical-mechanical evolution of HEEET undergoing a representative full cure cycle was simulated using the governing equations for process modeling defined earlier and outputs of the numerical homogenization methodology proposed in this Chapter, completing the hierarchical multiscale pipeline. To illustrate the merits of the process modeling framework versus classical approaches, two additional analyses were carried out that simulated a simple thermal cooldown from curing temperature to room temperature. In one simple cooldown case, it was assumed that material properties of the intra-yarn porous phenolic matrix and blended yarns were constant values for the fully cured materials at room temperature, i.e., $\phi = 1.0$ and $T = 20^\circ\text{C}$. In the other, material properties of the intra-yarn porous matrix and blended yarns were instead permitted to vary with temperature as per the material property models derived during the numerical homogenization procedure performed here. For simplicity, the room temperature and variable temperature simple cooldown simulation cases shall respectively be referred to as the CD-RT and CD-VT cases in the following sections.

A definitive reference cure cycle for SC-1008 phenolic was not found in literature, so a representative thermal profile used for the curing protocol in the full process modeling case was assumed to be:

1. Ramp from room temperature (20°C) to curing temperature (250°C) at $1^\circ\text{C}/\text{min}$
2. Hold at 250°C for two hours
3. Ramp from 250°C to 20°C at $1^\circ\text{C}/\text{min}$.

For the CD-RT and CD-VT simulation cases, the temperature was ramped from 250°C to 20°C at $1^\circ\text{C}/\text{min}$ to match the cooldown stage of the full process modeling simulation. The thermal profiles were directly prescribed to the exterior faces/nodes of the HEEET insulation layer FE model as boundary conditions in a coupled temperature-displacement analysis step to induce virtual processing, see Figure 23.

Data Availability

The data that supports the findings of this study are available within the article. Any additional data apart from what is provided within the manuscript can be supplied upon reasonable request.

Code Availability

The underlying code for this study is not publicly available but may be made available to qualified researchers on reasonable request from the corresponding author.

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Author Contributions

MNO: Investigation, Methodology, Software, Formal analysis, Writing- Original draft preparation, Data curation. TMR: Investigation, Methodology, Writing- Reviewing and Editing. MM: Conceptualization, Software, Writing- Reviewing and Editing, Project administration, Funding acquisition, Investigation, Supervision.

Competing Interests

The authors declare no competing interests.

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Figures

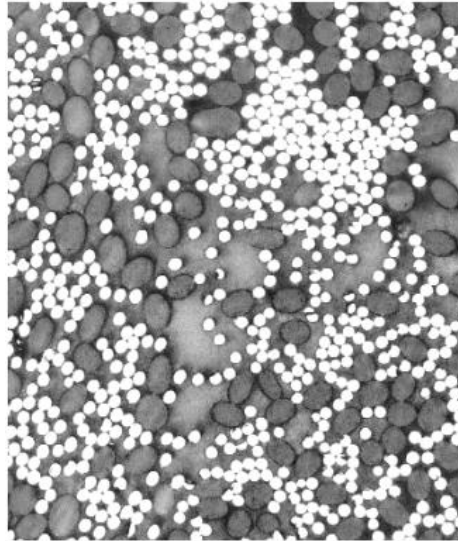


Figure 1. Micro-CT image for an area within a blended fiber yarn showing the in-situ carbon fibers (white circles) and phenolic fibers (grey ellipses).

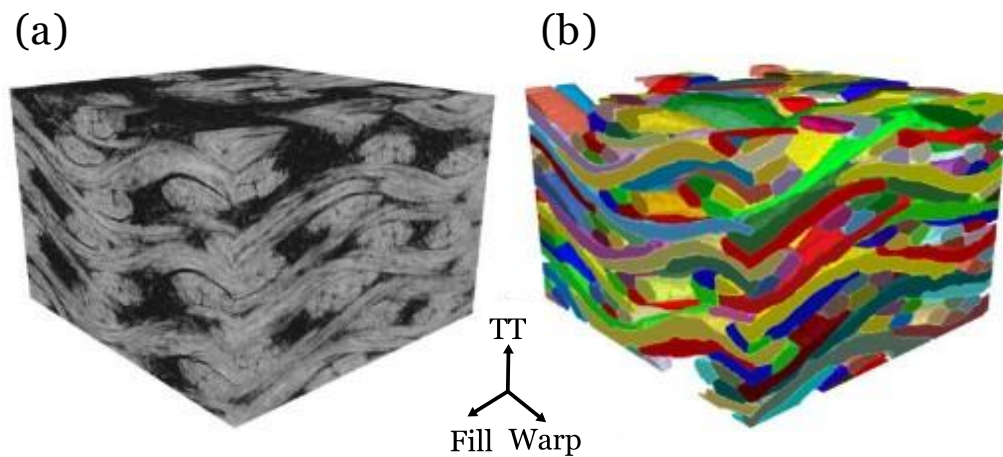


Figure 2. Micro-CT data from a sample of the HEEET insulation layer. The (a) raw and (b) processed (matrix hidden) images show the fill, warp, and through-thickness (TT) directions of the sample.

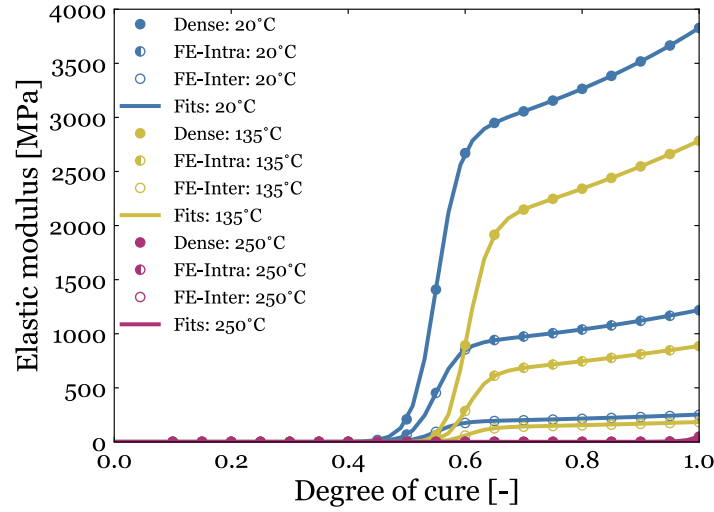


Figure 3. Evolution of the effective elastic modulus for the intra- (half-filled circles) and inter-yarn (empty circles) porous phenolic matrix models characterized through numerical homogenization (FE) and fit to phenomenological models (Fits). The evolution of the fully dense matrix properties (filled circles) are also shown for reference.

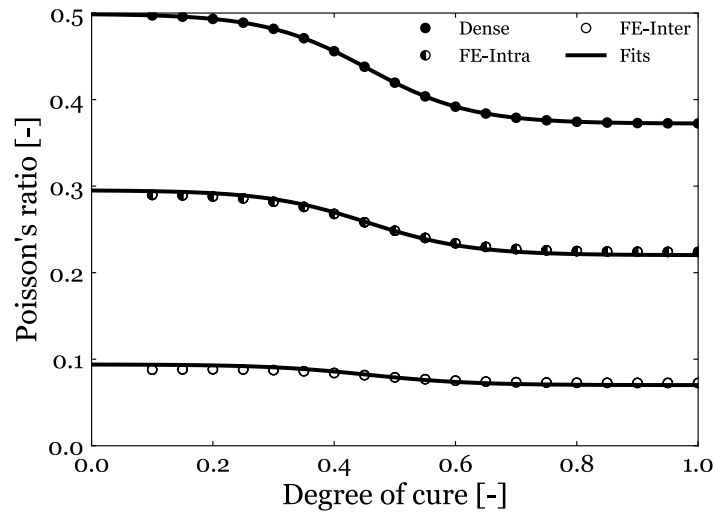


Figure 4. Evolution of the effective Poisson's ratio for the intra- (half-filled circles) and inter-yarn (empty circles) porous phenolic matrix models characterized through numerical homogenization (FE) and fit to phenomenological models (Fits). The evolution of the fully dense matrix properties (filled circles) are also shown for reference.

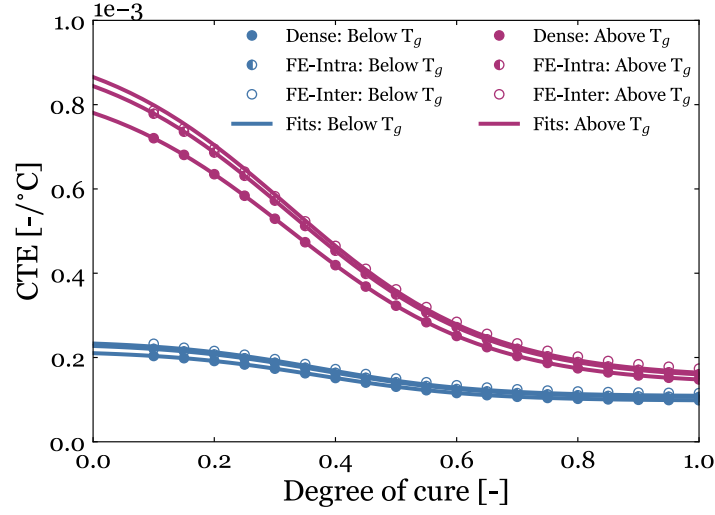


Figure 5. Evolution of the effective CTE for the intra- (half-filled circles) and inter-yarn (empty circles) porous phenolic matrix models characterized through numerical homogenization (FE) and fit to phenomenological models (Fits). The evolution of the fully dense matrix properties (filled circles) are also shown for reference.

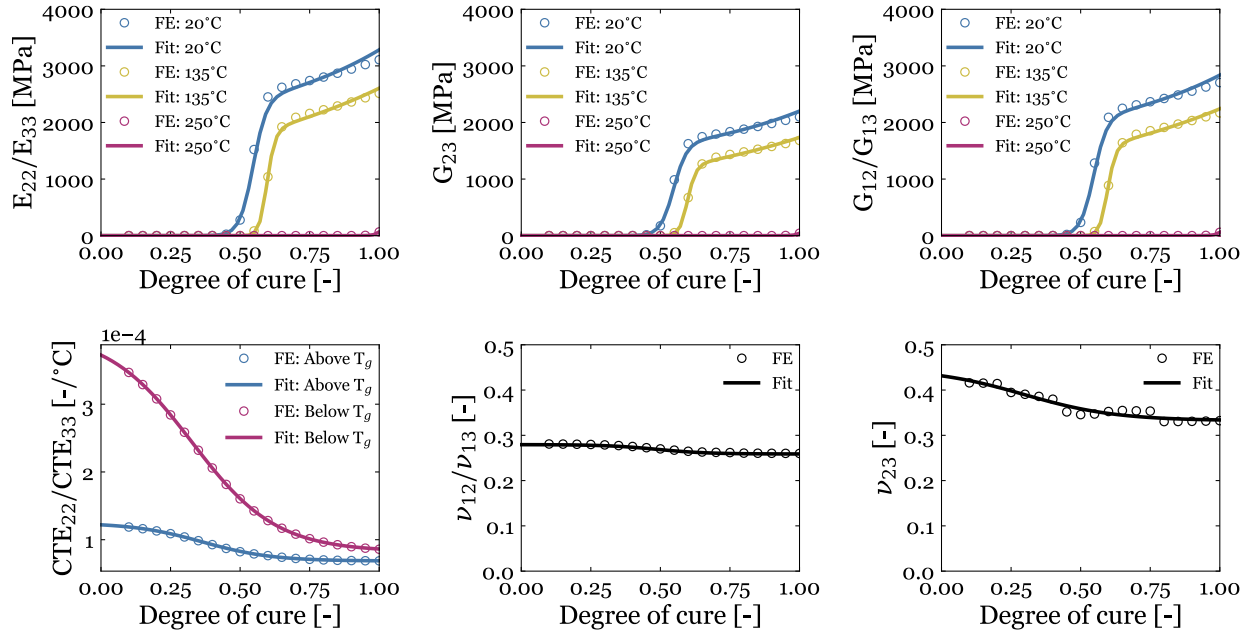


Figure 6. Evolution of the effective properties for the blended yarn models characterized through numerical homogenization (FE) and fits to phenomenological models.

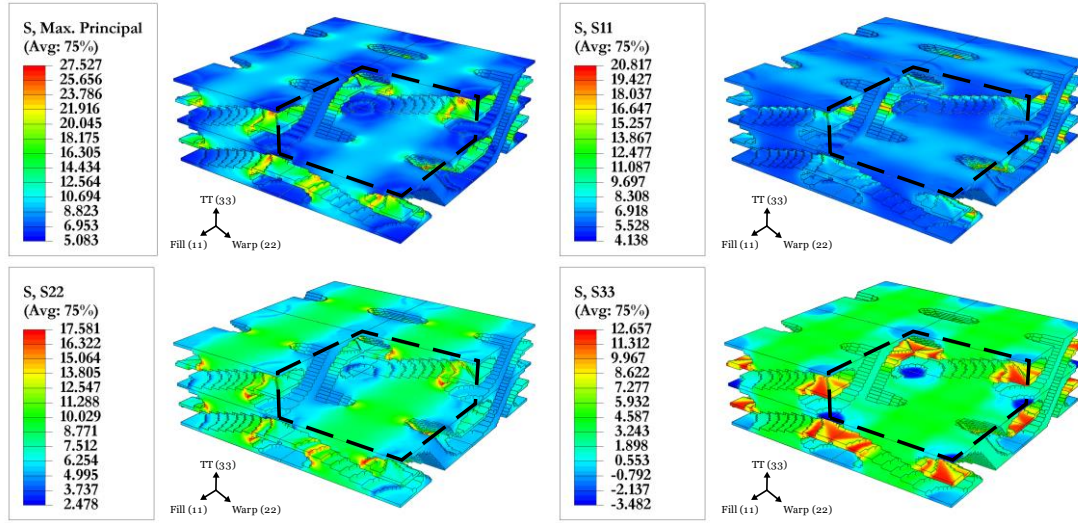


Figure 7. Maximum principal and normal residual stress fields in the inter-yarn porous phenolic matrix (yarns removed) with respect to the global orientation at the end of the full process modeling simulation of the HEEET unit cell mesoscale model. The volume outlined with dotted lines was hidden to provide a view within the 3D weave.

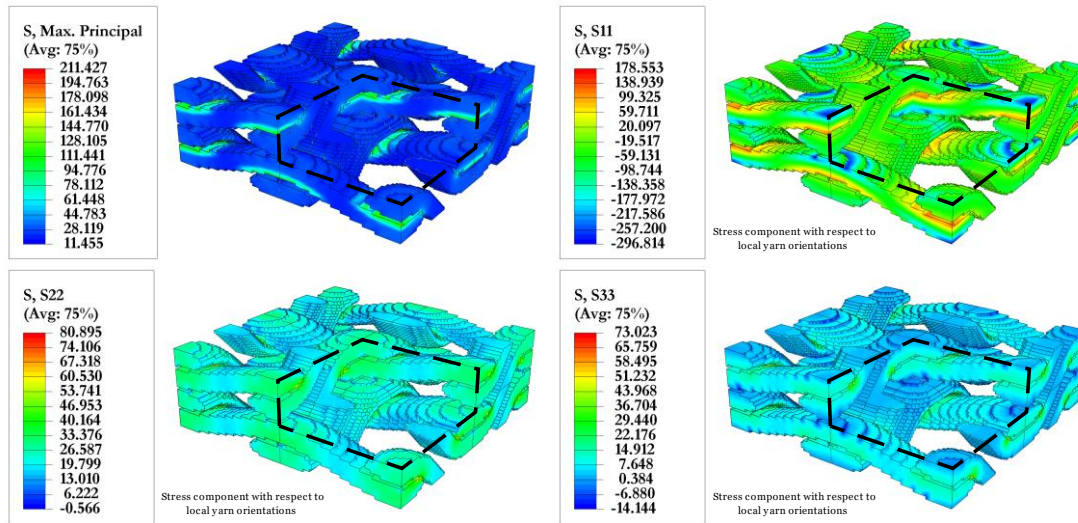


Figure 8. Maximum principal and normal residual stress fields in the blended yarns (matrix removed) with respect to the local yarn orientations at the end of the full process modeling simulation of the HEEET unit cell mesoscale model. The volume outlined with dotted lines was hidden to provide a view within the 3D weave.

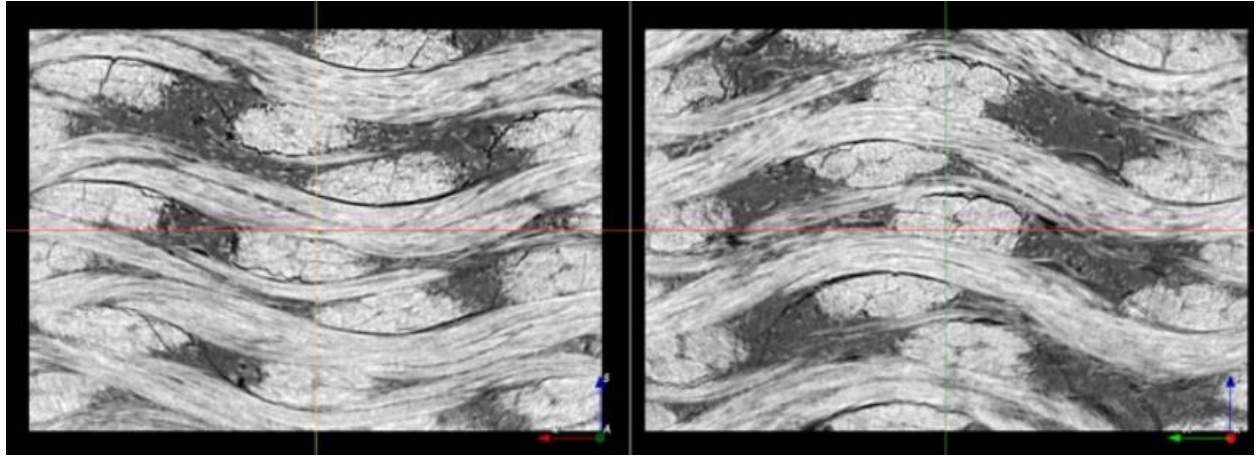


Figure 9. Micro-CT images of the cracks in the HEET insulation layer shown in the plane of the (left) fill direction and (right) warp direction [7].

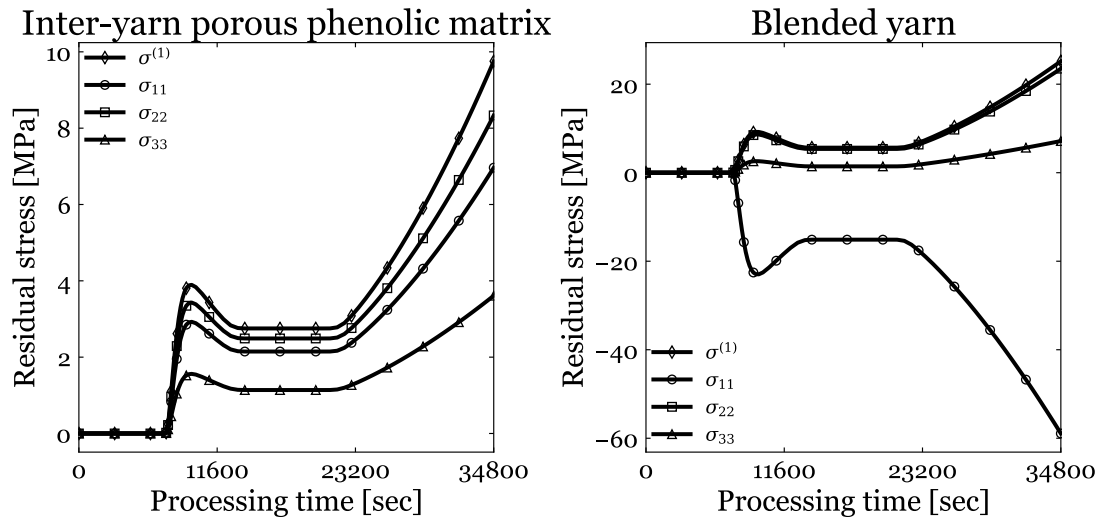


Figure 10. Evolution of the volume-averaged residual stresses in the inter-yarn porous phenolic matrix and blended yarns as a function of time for the full process modeling simulation of HEET. Stress components are with respect to the global coordinates for the inter-yarn matrix, and with respect to the local yarn orientations for the blended yarn.

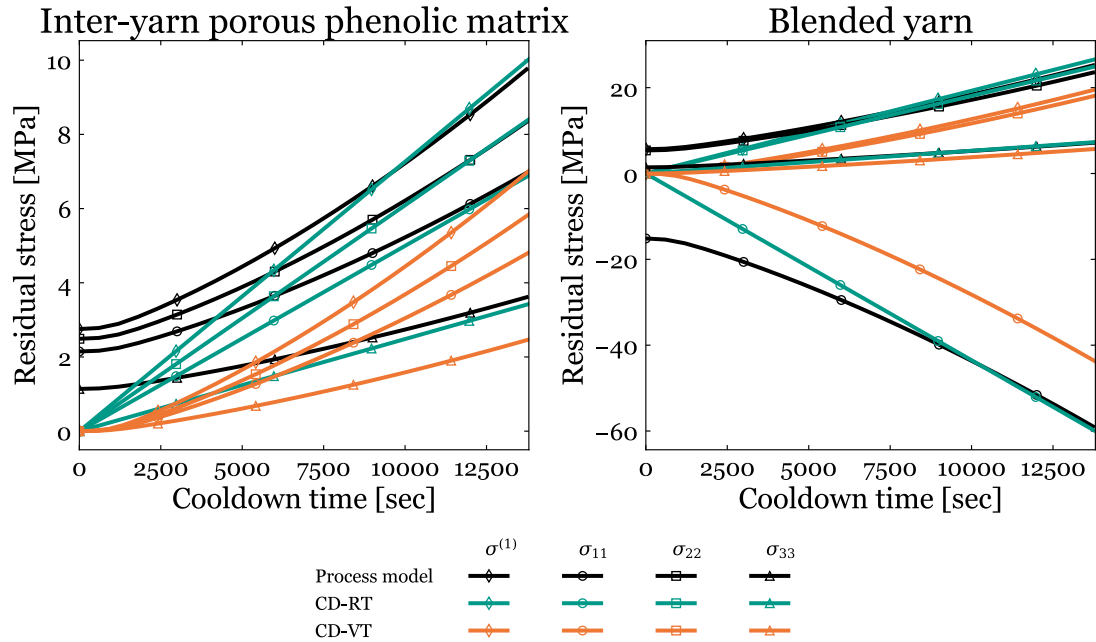


Figure 11. Residual stresses predicted by the simple thermal cooldown simulations overlaid on those from full process modeling from the start of its cooldown phase. Stress components are with respect to the global coordinates for the inter-yarn matrix, and with respect to the local yarn orientations for the blended yarn.

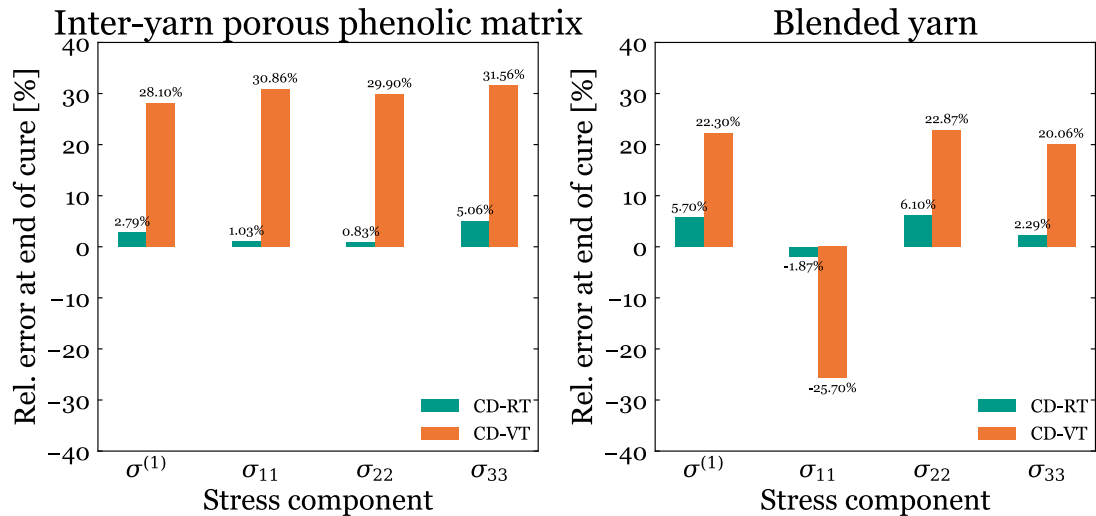


Figure 12. Relative error for the volume-averaged residual stress state at end-of-cure predicted by the simple thermal cooldown simulations compared to full process modeling. Stress components are with respect to the global coordinates for the inter-yarn matrix, and with respect to the local yarn orientations for the blended yarn.

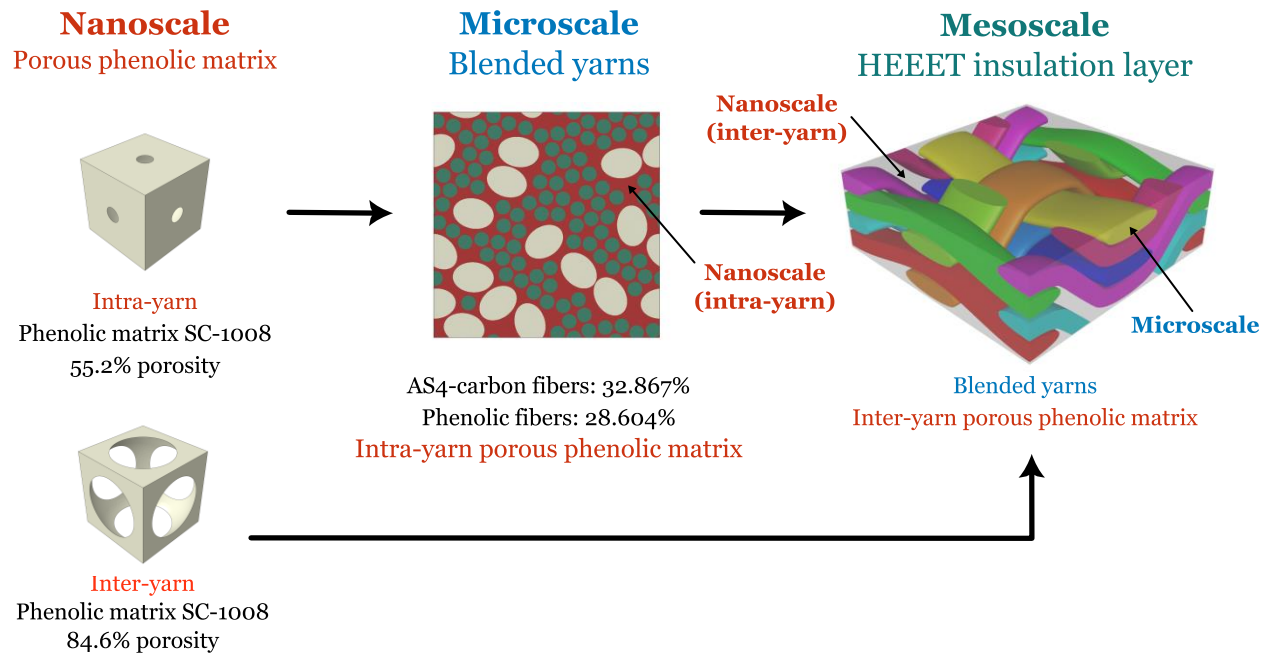


Figure 13. Hierarchical process modeling pipeline for the HEEET insulation layer.

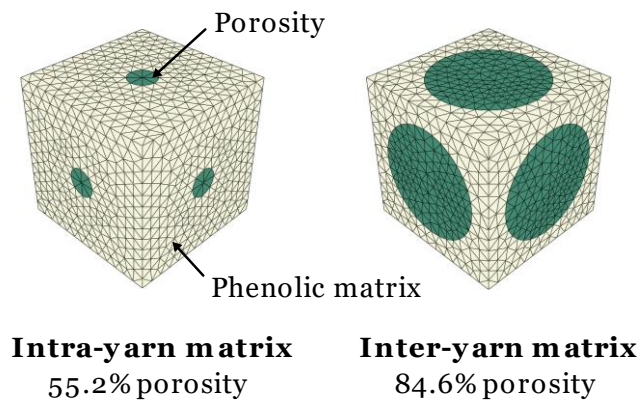


Figure 14. RUC model representations of the porous intra- and inter-yarn phenolic matrix.

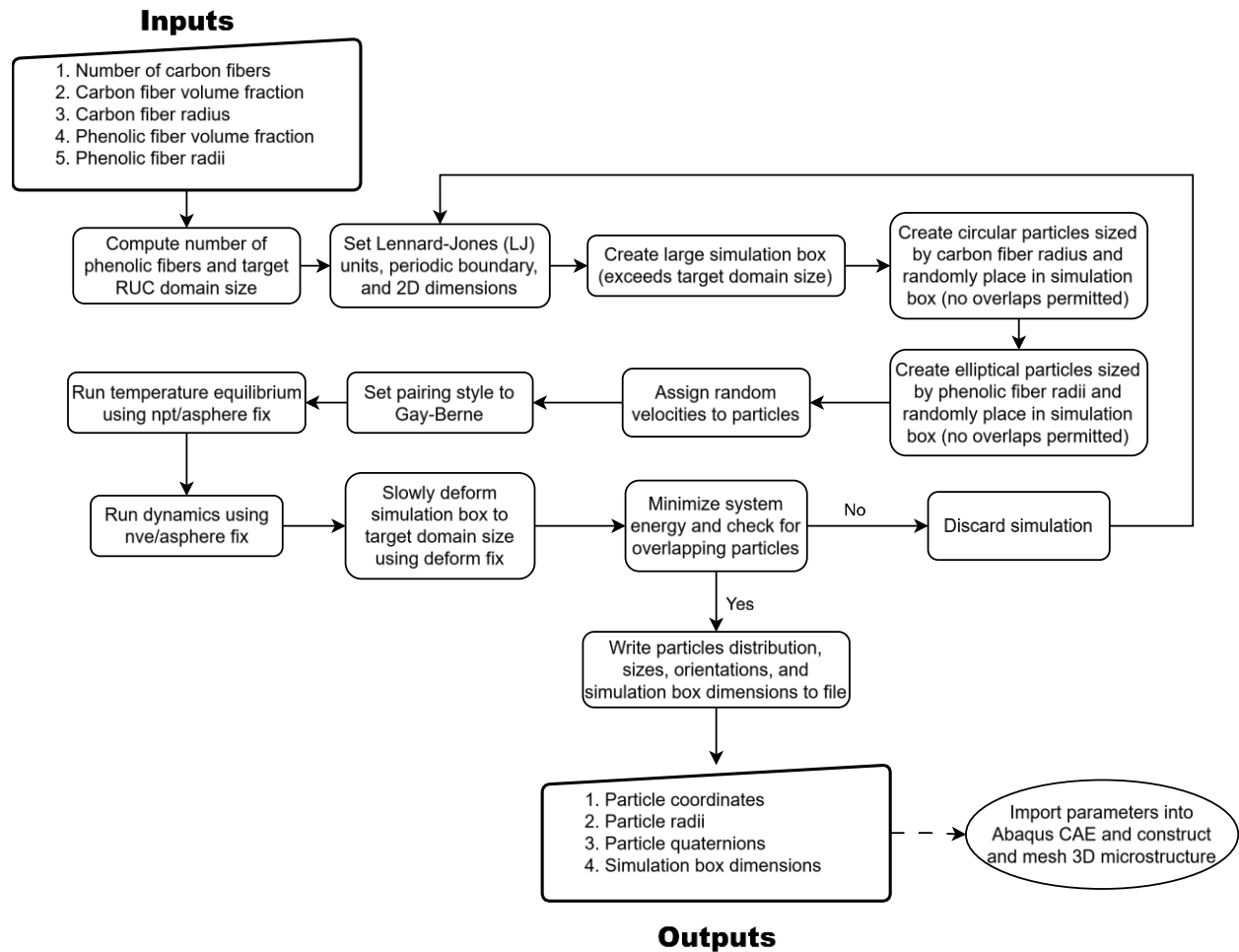


Figure 15. Flowchart detailing the MD simulation steps for creating a single RUC realization of the blended yarn microstructure.

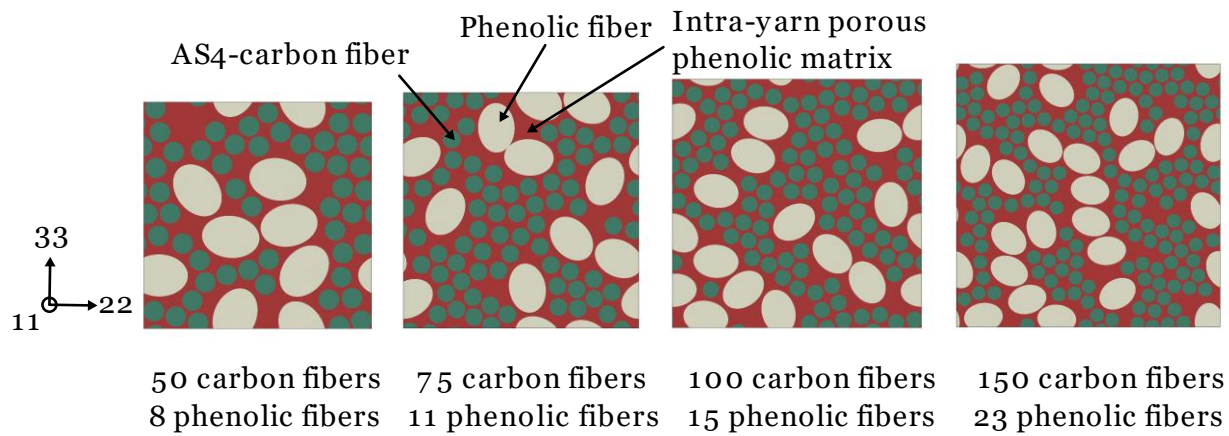


Figure 16. Example periodic RVE realizations of the HEET blended yarn microstructure containing 50, 75, 100, and 150 carbon fibers.

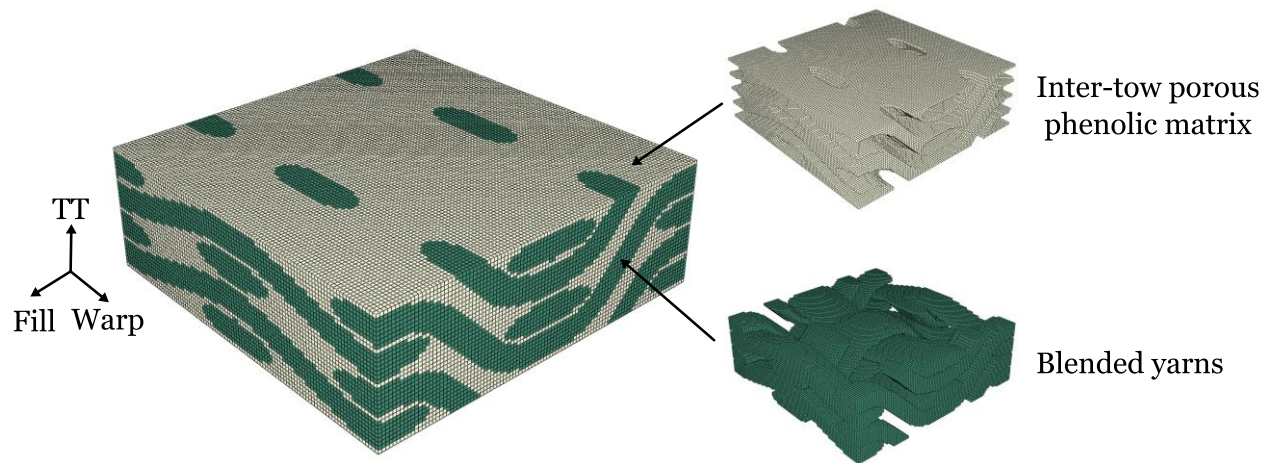


Figure 17. Periodic FE voxel model of the HEET insulation layer containing 330,000 C3D8RT elements.

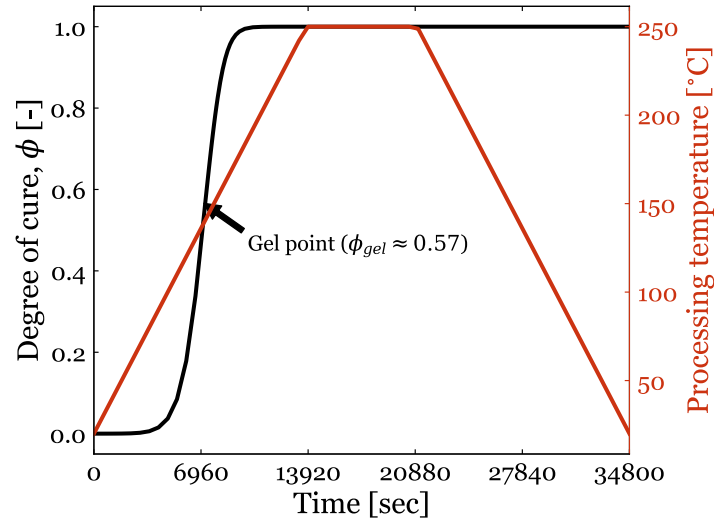


Figure 18. Evolution of the degree of cure as a function of time and processing temperature using the kinetic model provided by Equations 7 and 8 for the phenolic matrix.

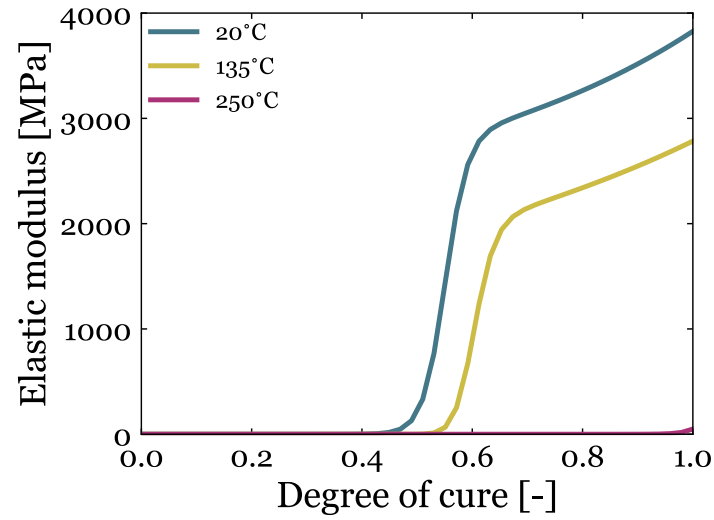


Figure 19. Evolution of the elastic modulus as a function of degree of cure and temperature using the model described by Equation 9 for the fully dense phenolic matrix.

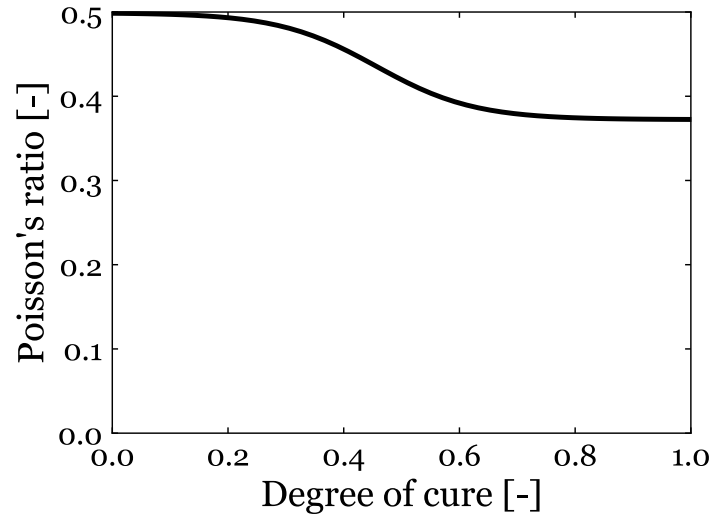


Figure 20. Evolution of Poisson's ratio as a function of degree of cure using the model described by Equation 10 for the fully dense phenolic matrix.

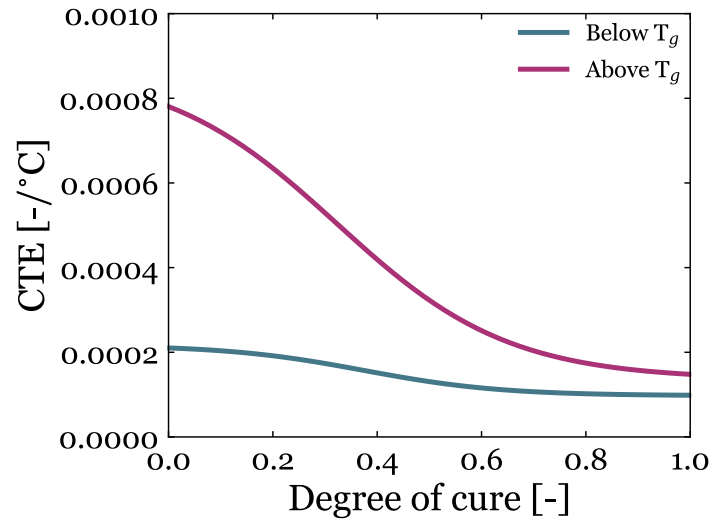


Figure 21. Evolution of CTE as a function of degree of cure above and below the glass transition temperature T_g using the model described by Equation 11 for the fully dense phenolic matrix.

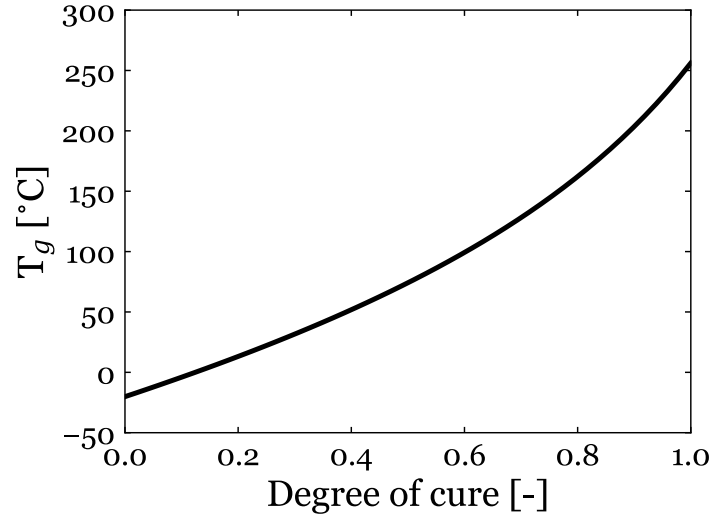


Figure 22. Evolution of T_g as a function of degree of cure using the model described by Equation 13 for the fully dense phenolic matrix.

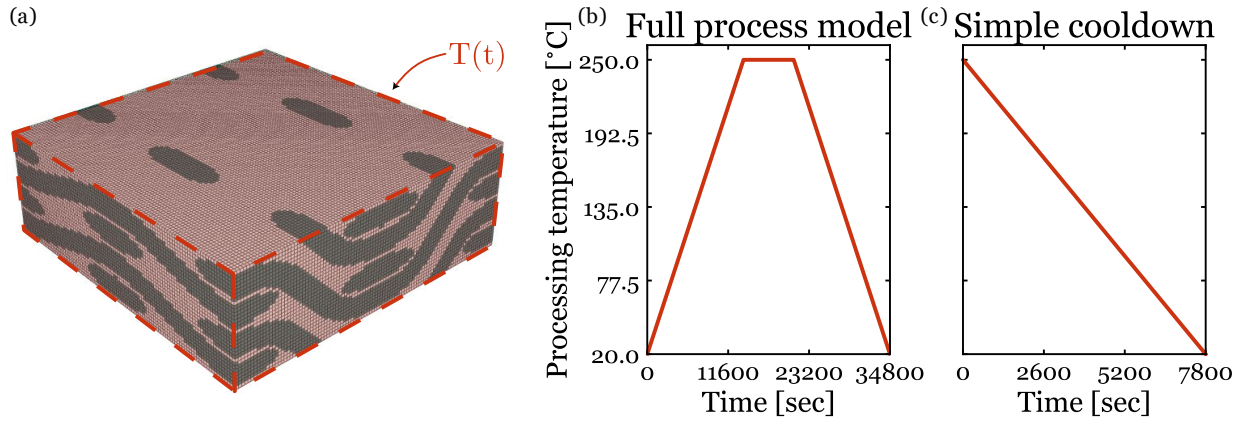


Figure 23. Thermal profile boundary conditions prescribed to the mesoscale model of the HEET insulation layer. (a) Temperature was prescribed as a function of time t to the mesoscale model to perform (b) full process modeling and (c) simple thermal cooldown curing simulations.

Tables

Table 1. Constituent distribution in HEEET blended yarns extracted from microscopy data [8].

Constituent	Minor diameter	Major diameter	Volume fraction
AS4-carbon fibers	6.8 μm	6.8 μm	0.329%
Phenolic fibers	14 μm	19 μm	0.286%
Intra-yarn porous phenolic matrix	--	--	0.321%
Cracks	--	--	0.064%

Table 2. Total post-gelation chemical shrinkage of the intra-yarn matrix, inter-yarn matrix, and blended yarns characterized from the numerical homogenization procedure.

Description	Total chemical shrinkage
Fully dense matrix	1.169%
Intra-tow matrix	2.807%
Inter-tow matrix	2.781%
Blended yarn (axial)	~0%
Blended yarn (transverse)	1.282%

Table 3. Model fit parameters for properties as a function of porosity.

κ index	1	2	3
Elastic modulus	0.444	-1.480	1.0
Poisson's ratio	-0.747	-0.327	1.0
CTE	-0.0640	0.183	1.0

Table 4. Model parameters fit to Equation 9 to model the effective elastic and shear moduli of the blended yarns as a function of cure and temperature.

Transverse elastic moduli and shear moduli			
Parameter	E_{22}/E_{33}	G_{12}/G_{13}	G_{23}
α_a	0.012949	0.016408	-0.0064496
α_b	0.98521	0.98683	0.68043
ϕ_0	0.57	0.57	0.57
ϕ_σ	0.024217	0.023971	0.023621
τ_0^a	0.006.9361	0.0072058	0.0071781
τ_0^b	-0.47772	-0.47673	-0.47690
τ_σ	0.52468	0.52442	0.52493
τ_*^a	1.1702	1.1773	0.60467
τ_*^b	0.16678	0.17370	0.17718

Table 5. Model parameters fit to Equation 10-11 to model the effective transverse CTE (above and below T_g) and Poisson's ratio of the blended yarns as a function of cure.

Transverse CTE and Poisson's ratio				
Parameter	α_{22}/α_{33} (Below T_g)	α_{22}/α_{33} (Above T_g)	ν_{12}/ν_{13}	ν_{23}
κ_1	-5.6299×10^{-5}	3.2383×10^{-4}	-0.020700	0.11565
κ_2	1.2486×10^{-4}	8.2512×10^{-5}	0.27945	0.33236
κ_3	-7.9991	6.5874	-1.0897	6.0392
κ_4	0.36506	0.32614	0.48668	0.29656

Table 6. Constant material properties of the constituent fibers used in the blended yarn models.

Property	AS4-carbon fiber	Phenolic fiber
E_{11}	231000 MPa	3500 MPa
E_{22}/E_{33}	15000 MPa	3500 MPa
ν_{12}/ν_{13}	0.21	0.35
ν_{23}	0.30	0.35
$G_{12/13}$	15800 MPa	15800 MPa
α_{11}	-5×10^{-7} -/°C	4.5×10^{-5} -/°C
α_{22}/α_{33}	1.5×10^{-5} -/°C	4.5×10^{-5} -/°C
k_{11}	6.8 W/m-K	0.25 W/m-K
k_{22}/k_{33}	2.5 W/m-K	0.25 W/m-K
c_p	1.13 J/g-K	1.5 J/g-K
ρ	1.79 g/cm ³	1.22 g/cm ³

Table 7. Assumed constant isotropic thermal properties of the dense phenolic matrix.

Property	Value
k	0.25 W/m-K
c_p	1.5 J/g-K
ρ	1.22 g/cm ³

Table 8. Parameters for the kinetic model describing the cure evolution of the phenolic matrix.

Parameter	E_a	Z	n
Value	96.1 kJ/mol	$10^{10.96}$ min ⁻¹	1.37

Table 9. Optimized phenomenological parameters for modeling the phenolic elastic modulus.

Parameter	α_a	α_b	ϕ_0	ϕ_σ	τ_0^a	τ_0^b	τ_σ	τ_*^a	τ_*^b
Value	0.0147	1.0849	0.57	0.02	-0.4712	0.5268	0.009	1.4	0.3

Table 10. Phenomenological parameters for modeling the phenolic Poisson's ratio fit by a non-linear least squares regression.

κ index	1	2	3	4
Value	0.12687	0.37225	11.812	0.45603

Table 11. Optimized phenomenological parameters for modeling the phenolic CTE.

κ index	1	2	3	4
Value (below T_g)	-1.19×10^{-4}	2.17×10^{-4}	-7.58	3.74×10^{-1}
Value (above T_g)	7.35×10^{-4}	1.36×10^{-4}	6.083	3.23×10^{-1}

Table 12. Cure and temperature states associated with the loading analysis type used in the FE homogenization procedure.

Loading analysis type	Cure state(s)	Temperature state(s)
Mechanical (tensile/pure shear)	0.1, 0.15, ..., 0.95, 1.0	20°C, 135°C, 250°C
Temperature ramp	0.1, 0.15, ..., 0.95, 1.0	Below T_g^{min} , above T_g^{max}
Isothermal hold	$\phi_{gel} = 0.57$	N/A

Table 13. Summary of the loading analyses used in the FE homogenization procedures corresponding to the characterized effective material properties as a function of state for process modeling

Loading analysis type	Loading direction	Property characterized
Mechanical: Tension	11	$E_{11}, \nu_{12}, \nu_{13}$
Mechanical: Tension	22	E_{22}, ν_{23}
Mechanical: Tension	33	E_{33}
Mechanical: Shear	12	G_{12}
Mechanical: Shear	13	G_{13}
Mechanical: Shear	23	G_{23}
Temperature ramp	Volumetric	$\alpha_{11}, \alpha_{22}, \alpha_{33}$
Isothermal hold	Volumetric	$\beta_{11}, \beta_{22}, \beta_{33}$

Table 14. Effective thermal material properties of the inter-yarn porous phenolic matrix and blended yarns used in the mesoscale processing simulations.

Property	Inter-yarn porous phenolic matrix	Blended yarns
k_{11}	0.060 W/m-K	2.35 W/m-K
k_{22}/k_{33}	0.060 W/m-K	0.23 W/m-K
c_p	1.5 J/g-K	1.31 J/g-K
ρ	0.19 g/cm ³	1.15 g/cm ³