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Quantification of Thermoset Composite Microstructures for Process Modeling

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Large scatter of bulk composite properties is linked to the process-induced microstructural variations during composite manufacturing. It is hypothesized that quantification and virtual reproduction of these process-induced variations in the composite microstructure can highlight the effect of processing conditions on the composite microstructure and on subsequent bulk composite properties allowing for the optimization of composite manufacturing process. To this end, a novel approach is presented in this study to quantify and virtually reproduce the process-induced variability in the composite microstructure. This study employs experimental techniques such as micro-CT image analysis and micro-Raman spectroscopy to quantify the process-induced variability in the fiber and the matrix, respectively. Statistical descriptors are developed to quantify the local variation in the fiber volume fraction of the composite microstructure. Micro-Raman spectroscopy coupled with confocal imaging is used to quantify the spatial variation in the matrix cure evolution. Finally, a finite element (FE) based computational process modeling approach is introduced to correlate the process-induced variability in the composite microstructure to the scatter in the bulk composite properties through virtual curing and testing analysis.

I. Introduction

Processing of Polymer Matrix Composites (PMCs) is a complex process during which the matrix material transitions from a liquid resin to a glassy solid through a chemical exothermic reaction defined as curing. Processing conditions, such as the cure temperature, time, and pressure, along with low thermal conductivities of the matrix material, impose spatially varying thermal histories, that influence the curing process and the subsequent property evolution in the composite during manufacturing [1]. Furthermore, thermo-mechanical constraints, introduced by irregular and off-axial fiber architecture, lead to residual stress generation and damage accumulation during curing, which results in in-situ matrix behavior. Our limited understanding of the evolution of this in-situ matrix behavior combined with the large scatter of the experimentally measured composite properties, result in inefficient structural designs and increase our reliance on testing for design and certification of composite parts.

The field of Integrated Computational Materials Engineering (ICME) increasingly recognizes such scatter of the measured properties to be linked to the process-induced variations in the composite microstructure [2]. Understanding the effect of curing on the composite microstructure and quantifying the resulting variability in the bulk composite properties will enable the optimization of the manufacturing process and improve composite designs to achieve better performance, lower the manufacturing cost and minimize energy consumption [3–5].

The objective of this research is to establish a correlation between the processing conditions, composite microstructures, and their bulk properties to reduce the scatter of the measured properties, improve composite design and optimize the manufacturing process. It is hypothesized that quantification of the process-induced variations in the fiber and the matrix, which constitute the composite microstructure, can highlight the influence of manufacturing on the composite microstructure. Finite element (FE) based process modeling analysis of virtually reconstructed composite laminates can then reproduce these process-induced variations, thus, correlating the processing conditions to the composite

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microstructure and the bulk composite properties [3]. The manuscript is organized as follows: the methodology to quantify and virtually reproduce the process-induced variability in the composite microstructure is presented in Section II, the results are discussed in Section III and main conclusions are drawn in Section IV.

II. Methodology

The approach to quantify and virtually reproduce the process-induced variability in the composite microstructure is schematically presented in Figure 1. Statistical descriptors, such as the local fiber volume fraction, are developed to quantify the process-induced variations in the fiber architecture. Micro-CT scans of several composite laminates, which are manufactured under different processing conditions, are analyzed with the developed statistical descriptors. Micro-Raman spectroscopy and confocal imaging setup are used to measure and map out the variation in the degree of cure in neat epoxy specimens. This technique is further explored to quantify the variation in the matrix curing during composite manufacturing. In order to correlate such variations in the composite microstructure to the scatter of the bulk properties and optimize the manufacturing process, a finite element (FE) based computational process modeling approach is proposed. Representative volume elements (RVEs) of composite laminates are virtually reconstructed in FE software Abaqus. A previously developed process model is used to virtually cure and test the RVEs. By virtually reproducing the experimentally observed process-induced variability in the composite microstructure, it is possible to understand the effect of the processing conditions on the subsequent state and mechanical response of the composite microstructures, therefore, establishing a processing-microstructure-property relationship.

The procedure to quantify the process-induced variability in the fiber and matrix is described in detail in Section II.A. The virtual reconstruction procedure and process modeling of composite laminates in FE is detailed in Section II.B.

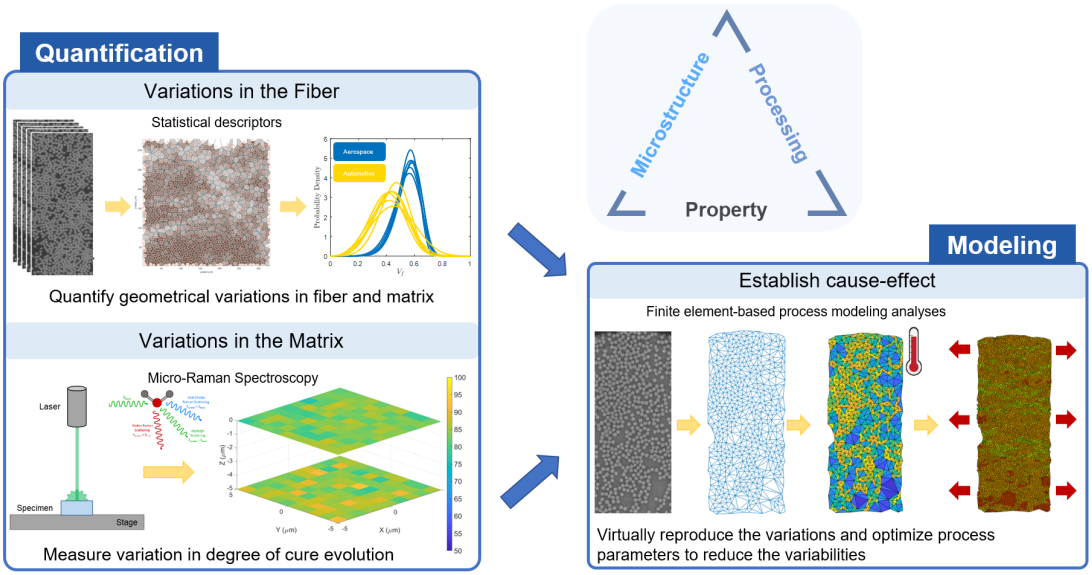


Fig. 1 Approach to quantify and virtually reproduce process-induced variability in composite laminates

A. Quantification of Process-induced Variability

The development of statistical descriptors, particularly the local fiber volume fraction v_f, to quantify the variability in the fiber architecture is discussed in Section II.A.1. The variability in the matrix curing is measured using micro-Raman spectroscopy, the procedure for which is described in Section II.A.2.

1. Variability in the Fiber Architecture

In order to quantify the process-induced variability in the fiber architecture, micro-CT image stacks of several composite laminates, which are manufactured under different processing conditions, are analyzed. A custom MATLAB program is developed to detect the fiber positions in each image stack (cross-section) and stitch them together to generate

a 3D volume of the laminate as shown in Figure 2. By fitting the corresponding fiber centers in each cross-section to a spline, the program can trace fiber paths in the 3D volume, which are representative of the process-induced variability, such as spatial distribution and entanglement in the fibers. Local metrics or statistical descriptors are developed, that can quantify such variability in the fiber architecture. Previous work by the authors have reported several statistical descriptors, such as the local fiber volume fraction, cluster formations, polar angle, etc, for quantification of such variability [3, 4, 6]. This study, in particular, focuses on the local fiber volume fraction v_f to quantify the variations in the fiber distribution and to virtually reconstruct composite laminates for process modeling.

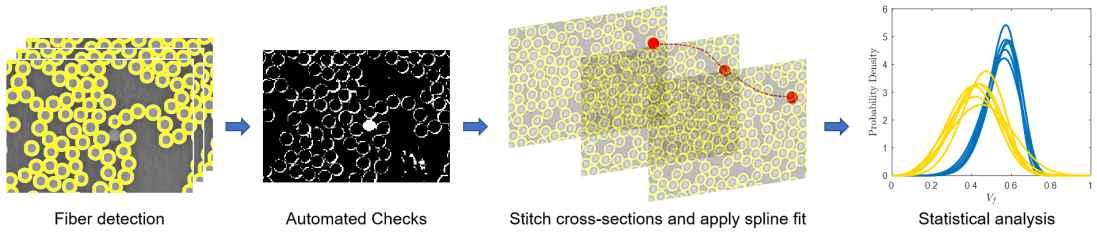


Fig. 2 Method for the analysis of the microstructure by finding the fibers within the image stack, linking fibers within images and generating statistical data based on fiber centerline paths.

The local fiber volume fraction is a local statistical descriptor, defined as the ratio of a fiber's cross-sectional area and the area between fiber under consideration and its neighboring fibers. Delaunay triangulation technique is used to discretize each cross-section of the laminate and compute the local fiber volume fraction of each triangle [7]. Statistical analysis are performed to quantify the variation in the local fiber volume fraction distribution in terms of the mean volume fraction and its variance (standard deviation). Micro-CT images of automotive grade composite laminates, manufactured using Vacuum Assisted Resin Transfer Molding (VARTM), are analyzed in this study. Furthermore, Delaunay triangulation is used for virtual reconstruction of the scans in an FE framework, the procedure for which is discussed in Section II.B.

2. Variability in the Matrix Cure Evolution

The process-induced variability in the matrix curing is measured with micro-Raman spectroscopy (Horiba Multiline Raman Spectrometer equipped with a 532 nm laser). This technique measures the unique vibrational modes of molecules associated with each functional group in an epoxy to provide a structural fingerprint of the material. During curing, specific functional groups which participate in the reaction evolve therefore, altering the vibrational modes of the associated molecules. Such alterations, referred to as Raman shift, are detected by the Raman spectrometer. By monitoring the Raman shift associated with a specific bond during curing, the degree of cure ϕ can be determined.

To measure the degree of cure, epoxy specimens are prepared at room temperature and allowed to cure at an isothermal temperature of 80^{o}C. Point-wise Raman spectra are collected for uncured and fully cured epoxy specimen using a confocal Raman imaging setup. The point-wise Raman spectra are then analyzed to determined the degree of cure ϕ and to reconstruct a 3D distribution map of ϕ throughout the volume of the epoxy specimen. The process-induced spatial variation in the degree of cure is then quantified from the 3D maps.

B. Virtual Reconstruction and Process Modeling

In order to establish the processing-microstructure-property correlation, it is critical to not only quantify the process-induced variations in the composite microstructure i.e. the fiber and the matrix, but also reproduce them in FE. This will allow the prediction of residual stresses in the composite microstructure, the resulting in-situ matrix behavior and the subsequent mechanical response of the microstructure, all of which are significantly affected by the processing conditions. RVEs, based on the local fiber volume fraction statistical descriptor, are generated in FE software Abaqus as illustrated in Figure 3. Triangular cells, that are generated using Delaunay triangulation technique, are imported into Abaqus via Python scripts. Each cell has a volume fraction v_f associated with it, which is used to compute and assign homogenized material properties of the composite for process modeling analysis. The RVEs are meshed with C3D6T elements (six node triangular prism elements with temperature degrees of freedom) [8]. Flat boundary conditions (FBCs) are applied to allow the RVE to expand or contract due to temperature change, and to contract due to cure

shrinkage during curing.

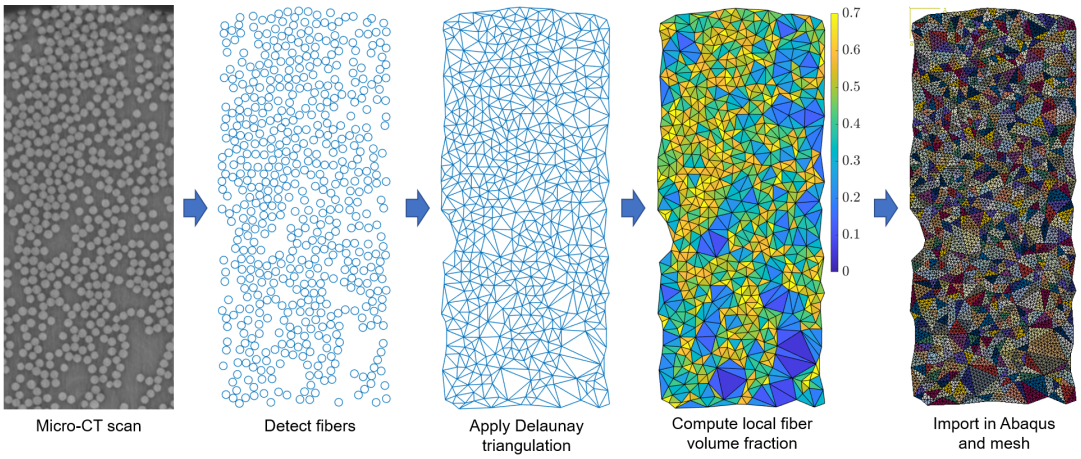


Fig. 3 Procedure to generate a homogenized FE model from a micro-CT scan.

Process modeling analysis of the generated RVEs are carried out with the implicit solver Abaqus/STANDARD, supplemented by user-written subroutines UMATHT and UMAT [9]. The process model employs a phenomenological kinetic model to compute the degree of cure ϕ for a given cure profile. The evolution of the homogenized thermo-mechanical material properties of the composite as a function of ϕ is modeled based on the previous work by the authors [3]. An instantaneous linear elastic model is used to define residual stress generation in the homogenized RVE during curing [10].

III. Results and Discussion

A. Quantification of Process-induced Variability

The process-induced variability in the fiber and the matrix are quantified as per the procedure highlighted in the previous section. The results from the quantification study are discussed in Section III.A.1 and Section III.A.2, respectively.

1. Variability in the Fiber Architecture

The variability in the local fiber volume fraction is quantified with the help of statistical descriptors. Micro-CT scans of automotive grade composite laminate are analyzed to determine the variation in the local fiber volume fraction for each cross-section. One such cross-section of the laminate along with the fiber volume fraction distribution is shown in Figure 4. The laminate manifests a global mean fiber volume fraction $v_f = 0.45 \pm 0.11$. Three different sections of the scan (highlighted in yellow) are individually analyzed for virtual reconstruction and their local fiber volume fraction distribution is shown in Figure 4 (inset). The laminate exhibits a large scatter in the local fiber volume fraction, which is evident from the distribution functions in Figure 4. This can be attributed to the processing conditions under which the laminate is manufactured. Low-pressure VARTM allows relative fiber movement during infusion and subsequent curing, which alters the fiber architecture. Such variations in the fiber can lead to entanglement, which results in stress concentration and premature failure during manufacturing and subsequent loading. By quantifying such variability in the fiber architecture, it is possible to highlight critical aspects of the manufacturing process that influence the fiber architecture and in turn, affect the bulk composite properties.

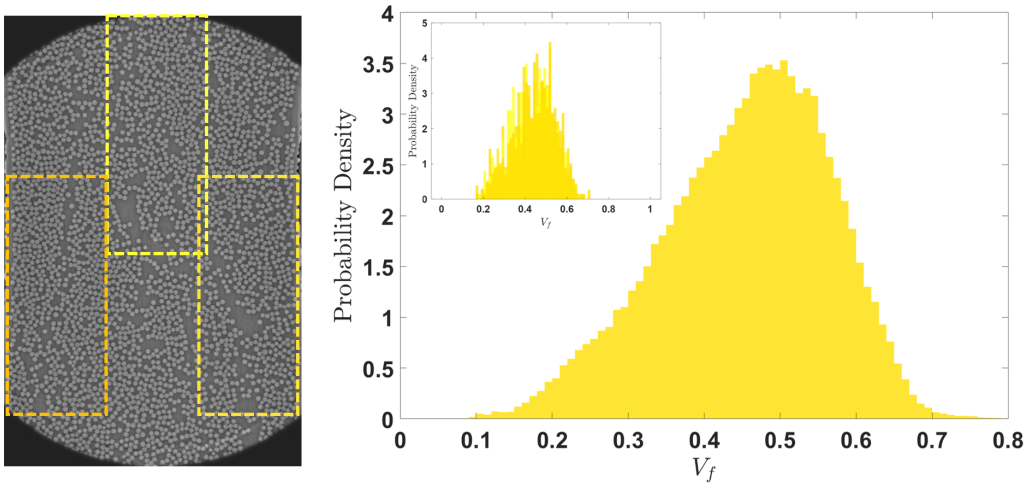


Fig. 4 A micro-CT image of an automotive scan and its local fiber volume fraction distribution. Inset shows the variation in the local fiber volume fraction distribution for three different sections highlighted in yellow.

2. Variability in the Matrix Cure Evolution

The variability in the matrix cure evolution is measured using micro-Raman spectroscopy. The point-wise Raman spectra of a 20 μm x 20 μm section of a fully cured epoxy specimen is presented in Figure 5. The band at 1255 cm^{-1} corresponds to the vibrations of the epoxide functional group, the peak intensity of which decreases as the free epoxide groups are consumed with the progression of cure. Meanwhile, the intensities of the Raman bands at 1112 cm^{-1}, 1186 cm^{-1} and 1607 cm^{-1}, which correspond to the backbone chain vibrations in the epoxy, remain unchanged. For this study, the strongest Raman band at 1607 cm^{-1} is selected as an internal reference peak, while the band at 1255 cm^{-1} is used to quantify the degree of cure ϕ. A custom MATLAB script is developed to isolate the target peaks (1255 cm^{-1} and 1607 cm^{-1}) from the remainder of the spectra. The area integrals of the deconvoluted peaks are determined and used to estimate the degree of cure ϕ using Equations 1 and 2.

$$\left(A^0_{1255}\right)_{\mathrm{r}} = \frac{A^0_{1255}}{A^0_{1607}} \qquad \left(A^t_{1255}\right)_{\mathrm{r}} = \frac{A^t_{1255}}{A^t_{1607}} \tag{1}$$

$$\phi = 1 - \frac{\left(A^t_{1255}\right)_{\mathrm{r}}}{\left(A^0_{1255}\right)_{\mathrm{r}}} \tag{2}$$

where A^0_{1255} and A^t_{1255} are the areas under the Raman peaks at 1255 cm^{-1} at the beginning of the cure and at a given time t, respectively; A^0_{1607} and A^t_{1607} are the areas under the Raman peaks at 1607 cm^{-1} at the beginning of the cure and at a given time t, respectively; $\left(A^0_{1255}\right)_{\mathrm{r}}$ and $\left(A^t_{1255}\right)_{\mathrm{r}}$ are normalized relative area under the peak at 1255 cm^{-1} at the beginning of the cure and at a given time t, respectively.

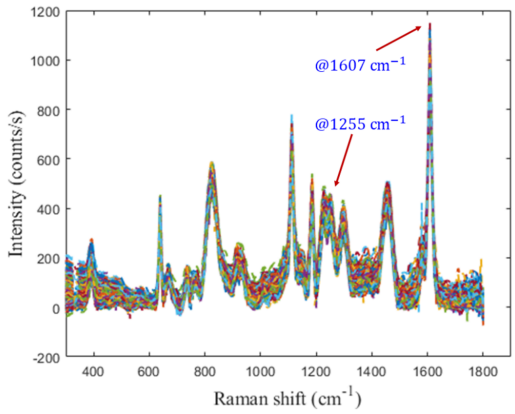


Fig. 5 Point-wise Raman spectra of a fully cured test specimen showing the reference peak (1607 cm^{-1}) and the peak of interest (1255 $^{-1}$).

The point-wise Raman spectra of uncured and fully cured epoxy specimen are analyzed using the procedure mentioned above. The degree of cure is computed for each point in the Raman spectra to generate a 3D distribution map. One such 3D map of the degree of cure distribution in a fully cured test specimen is presented in Figure 6. The in-plane variation in the degree of cure is calculated as $\phi^{\mathrm{I}}_{\mathrm{avg}} = 93.1 \pm 1.3$ % for the top surface and $\phi^{\mathrm{II}}_{\mathrm{avg}} = 93.0 \pm 1.06$ % for the subsurface at a depth of 6μm. This clearly shows the effectiveness of the micro-Raman confocal imaging technique to accurately capture the process-induced variations in the matrix curing. By correlating the spatial variation in ϕ to the manufacturing processing conditions, it is possible to highlight key microstructural attributes that influence the curing and property evolution of the matrix material. One such microstructural attribute, that affects the matrix curing and contributes to process-induced variability, is the presence of reinforcements, such as fibers. Discrete and real-time Raman spectroscopy of epoxy specimens with fibers will allow direct "visualization" of the localized cure evolution and chemical characteristics that originate as a consequence of the presence of fibers and due to the manufacturing process. A qualitative comparison of the measured variability with the FE predictions will then correlate the microstructural variations in the composite to the manufacturing process and the resulting in-situ matrix behavior.

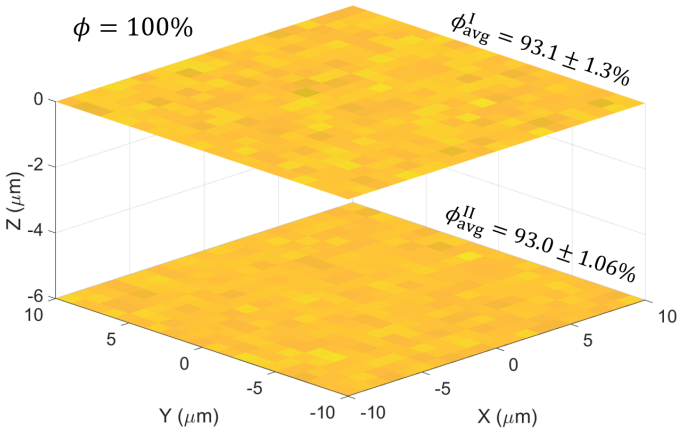
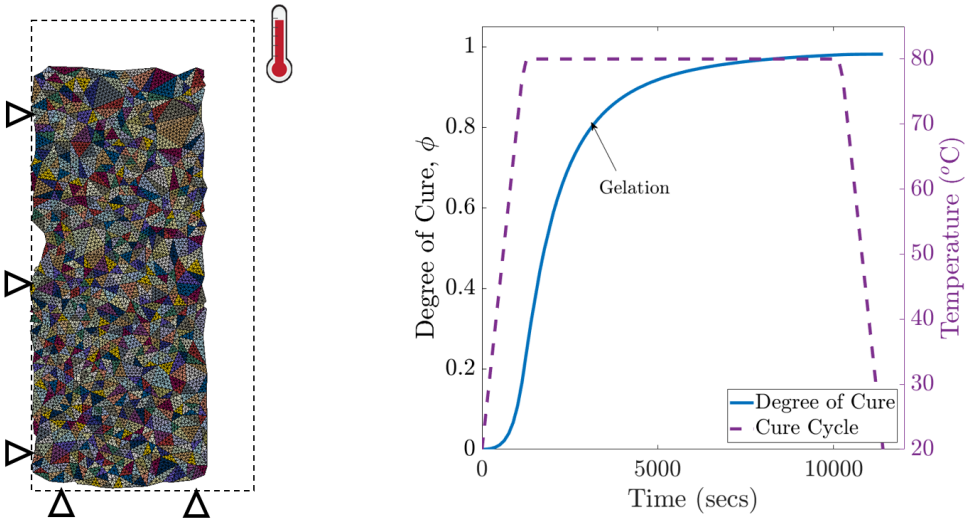


Fig. 6 3D map showing the variation in the degree of cure for a fully cured specimen generated using micro-Raman confocal imaging technique.

B. Virtual Reconstruction and Process Modeling

Composite microstructures containing approximately 600 fibers are homogenized based on the local fiber volume fraction descriptor and imported into Abaqus for process modeling analysis. Three different RVEs are virtually cured by applying FBC and subjecting them to the cure cycle shown in Figure 7. The resulting residual stress generation in each RVE is shown in Figure 8. It is evident that the local variation in the fiber volume fraction drastically alters the internal stress state of the composite, therefore, affecting the in-situ matrix behavior. By refining the model parameters and the applied boundary conditions, it is be possible to accurately reproduce the process-induced variations in the composite. Further comparison of the model predictions with the micro-Raman mapping will provide insight into the effect of microstructural variability on the composite response. With this approach, several statistically equivalent RVEs of composite laminates, manufactured under different processing conditions, can be analyzed and a processing-microstructure-property relation can be established.



(a) Flat Boundary Conditions

(b) Applied cure cycle and the degree of cure evolution

Fig. 7 Schematic of (a) the flat boundary conditions (FBC) and (b) the cure cycle used for virtual curing analysis of homogenized composite RVEs.

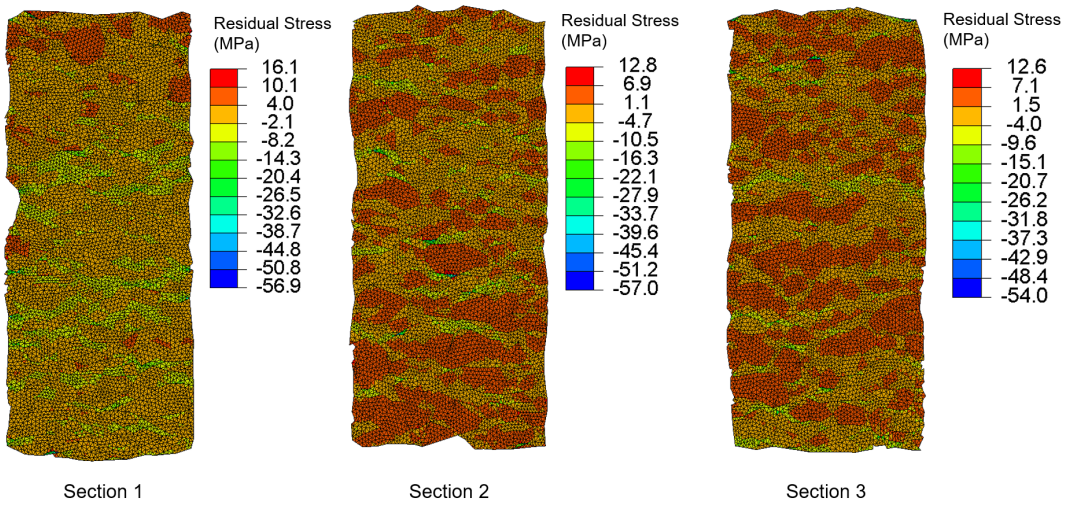


Fig. 8 Residual stress generation in three different RVEs at the end of the virtual cure analysis.

IV. Conclusions

This study presents a comprehensive methodology to quantify and reproduce the process-induced variability in composite laminates, which result in large scatter of the measured bulk properties. The local fiber volume fraction statistical descriptor is effectively used to quantify the process-induced variability in the fiber architecture. Micro-Raman spectroscopy and confocal imaging setup are effective tools used to detect the local variations in the matrix material during curing thus, highlighting key microstructural attributes that influence matrix curing and property evolution to provide a direct quantification of the localized properties and chemical characteristics resulting from the manufacturing process. A process modeling framework is developed to virtually reproduce the experimentally quantified variability in the composite laminates. The local fiber volume fraction statistical descriptor is successfully implemented to homogenize large composite RVEs, which are virtually cured in Abaqus to predict the process-induced stress state and in-situ matrix behavior.

Incorporating additional statistical descriptors will allow quantification of 3D variation in the composite laminates, such as cluster formation and fiber entanglement. Statistical analysis of a wide variety of composite laminates, manufactured under different processing conditions, will highlight critical aspects of manufacturing that influence the fiber architecture. Similarly, discrete and real-time micro-Raman spectroscopy of neat epoxy and fiber reinforced laminates will allow quantification of the process-induced variability in the matrix curing, which directly affects the residual stress generation and in-situ matrix behavior. Process modeling of statistically equivalent RVEs can predict the process-induced stress state and therefore, provide a direct comparison with the experimentally measured composite behavior. Integrated analyses of this nature, which rely on experiments and accurate physics-based modeling, can correlate the processing conditions with the variability in the composite microstructure and quantify the effect of such variability on the global scatter of the bulk properties, aiding in the optimization of the composite manufacturing process.

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