In-situ 3D Visualization of Composite Microstructure During Polymer-to-Ceramic Conversion

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Abstract

One route for producing fiber-reinforced ceramic-matrix composites entails repeated impregnation and pyrolysis of a preceramic polymer in a fiber preform. The process relies crucially on the development of networks of contiguous cracks during

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pyrolysis, thereby allowing further impregnation to attain nearly-full densification. The present study employs in-situ x-ray computed tomography (XCT) to reveal in three dimensions the evolution of matrix structure during pyrolysis of a SiC-based preceramic polymer to 1200°C. Observations are used to guide the development of a taxonomy of crack geometries and crack structures and to identify the temporal sequence of their formation. A quantitative analysis is employed to characterize effects of local microstructural dimensions on the conditions required to form cracks of various types. Complementary measurements of gas evolution and mass loss of the preceramic polymer during pyrolysis as well as changes in mass density and Young’s modulus provide context for the physical changes revealed by XCT. The findings provide a foundation for future development of physics-based models to guide composite fabrication processes.

1 Introduction

Fiber-reinforced ceramic-matrix composites (CMCs) are on the verge of large-scale insertion in hot section components in gas turbine engines for civil aviation [1–4]. The materials of prime interest comprise SiC fibers with thin BN coatings and a matrix of SiC. The coatings produce weak fiber-matrix interfaces, which impart high toughness to the CMC by promoting deflection of matrix cracks into the interfaces and frictional pullout of broken fibers [1, 2, 4]. Relative to the superalloys they are replacing, SiC/SiC composites have only about one third the mass density and can survive sustained loading up to temperatures that are 100-200°C higher [2, 4]. In addition to anticipated increasing use in gas turbines, CMCs are slated for use in hypersonic jet engines, nuclear reactors, and
space vehicles [1–4].

Fabrication of fully dense and compositionally pure SiC matrices that can operate at their targeted use temperature (up to 1500°C) remains an outstanding challenge [4]. One route for producing SiC matrices involves the use of preceramic polymers which, after shaping, may be pyrolyzed at \(~1000\) to \(1600\)°C to produce polymer-derived ceramics (PDCs). PDC processing has gained significant interest recently for its potential in low-temperature manufacturing of complex-shaped components for a myriad of applications, including thermal protection systems, microelectromechanical systems, electronic device packaging, and porous burners [5, 6].

Preceramic polymers are used to produce CMCs through repeated polymer impregnation and pyrolysis (PIP) in fiber preforms [1, 3, 4, 7–10]. Due to mass loss from gas evolution and a significant increase in mass density during pyrolysis, large shrinkage strains ensue. When shrinkage is constrained – as it is within the confines of a continuous fiber array – it is accommodated at least in part by formation of pyrolysis cracks. Importantly, to ensure complete impregnation of the void spaces in subsequent process cycles, the conversion process must ideally yield a matrix structure comprising a contiguous network of pyrolysis cracks. In some variants of the process, the final pyrolysis treatment may be followed by either melt or chemical vapor infiltration to produce SiC or other refractory Si-based compounds within the remaining void spaces. Here again a contiguous network of ingress pathways must be present after the final pyrolysis treatment in order to attain nearly-full densification during subsequent processing steps.
X-ray computed tomography (XCT) has been used previously to non-destructively characterize the 3D microstructure of SiC-based CMCs [11, 12]. Recent advancements in XCT instrumentation have enabled in-situ four-dimensional (3D+time) imaging of materials under load in controlled environments at very high temperatures [1, 13]. The current study demonstrates the use of XCT to observe microstructure evolution in-situ during material processing at high temperatures.

The study focuses specifically on the evolution of composite microstructure during pyrolysis of a SiC-based preceramic polymer contained within a bed of unidirectionally aligned SiC fibers. Intricate details of the three-dimensional nature of crack structures (each consisting of multiple individual cracks) and their evolution are obtained by in-situ x-ray computed tomography (XCT) during heating up to 1200°C. Examinations of over 140 crack structures are used to guide the development of a unified taxonomy of crack geometries and crack structures and to identify the temporal sequence of their formation. Crucially, the 3D nature of the observations enables insights into crack structures that would otherwise not be possible through, for example, ex-situ observations of specimens from interrupted tests or by 2D imaging alone. Effects of temperature and local geometry on the formation of various crack types are characterized. This work represents the first step in understanding crack evolution during the conversion process and sets the foundation for development of physics-based models to guide future composite fabrication processes.
2 Materials and Methods

2.1 Composite design and fabrication

In-situ XCT was conducted during pyrolysis of a composite specimen made with state-of-the-art fibers and a preceramic polymer. The composite specimen was fabricated by first inserting nine tows (≈ 4500 fibers) of BN-coated Hi-Nicalon™ Type-S SiC fibers into a quartz tube with a 1.5\( \text{mm} \) inner diameter (VitroTubes™). The interstices between the fibers were filled with allylhydridopolycarbosilane (AHPCS) (SMP-10, Starfire® Systems), which yields SiC following pyrolysis above 850°C. Prior to impregnation, the AHPCS was mixed with 0.2 wt\% dicumyl peroxide (DP) initiator to promote subsequent curing. The preceramic polymer was introduced into the composite via pressure-assisted impregnation. First, the fiber-filled quartz tube and a cup of liquid AHPCS were placed into a vacuum chamber and the chamber was evacuated. The AHPCS was then poured over the tube, fully submerging the specimen in the liquid. Next, the chamber was brought back up to atmospheric pressure. The submerged specimen was then transferred to a pressure chamber and the chamber was pressurized to 275 \( kPa \) using compressed air. The entire chamber (with the specimen) was placed in an oven at 120°C for two hours, during which the AHPCS was lightly pre-cured.

2.2 In-situ x-ray computed tomography

XCT was performed at the hard X-ray beamline 8.3.2 at the Advanced Light Source at Lawrence Berkeley National Laboratory. The specimen was imaged inside a high-temperature testing rig [1, 13]. Heating was accomplished with a hexapole arrangement of
halogen lamps. The test specimen was mounted vertically in the testing rig in water-cooled grips. An inert environment was maintained by flowing argon through the chamber at a rate of 20\,g/h. The testing rig was mounted on a rotation stage, and supply lines for argon gas, cooling water, and lamp power were carefully arranged to ensure negligible rig vibration during rotation. Specimen temperatures during pyrolysis were obtained from offline calibration experiments with an identical specimen containing an embedded R-type platinum-rhodium thermocouple, positioned in the center of the hot zone inside of the testing rig. With a calibrated temperature vs. lamp power relationship, a lamp power vs. time program was generated and used to produce the desired heating cycle for the pyrolysis experiments performed in the beamline. Over the course of about 20 hours, the specimen was heated to 1200°C according to the temperature profile shown in Figure 1(A) (25°C to 250°C at 2°C/min, 250°C to 700°C at 1°C/min, 700°C to 930°C at 3°C/min, 930°C hold 70min, 930°C to 1090°C at 3°C/min, 1090°C hold 70min, 1090°C to 1200°C at 2°C/min, 1200°C hold 70min, cool at -5°C/min. This profile is similar to that recommended by Starfire® Systems [14]; slight differences are due to limitations in calibration precision and temperature control).

XCT images were collected continuously during the entire pyrolysis cycle, with each complete scan taking about 12 minutes. The reported scan temperatures are the averages of those at the beginning and at the end of each scan. Each scan consisted of 4096 radiographs of 40\,ms exposure time, over a 180° rotation. Filtered white light was used for illumination. The light was passed through a 6\,mm-thick aluminum filter to reduce the heat load on the scintillator. The specimen-to-detector distance was approximately 110\,mm.
Radiographs were collected with a pco.dimax camera. The field of view was approximately 2mm by 2mm by 2mm. The resulting 3D tomograms have a spatial resolution of 0.98µm per voxel edge, which is sufficient to resolve the SiC fibers (each approximately 13µm in diameter) and the pyrolysis cracks within the matrix.

Tomographic slices were reconstructed using a commercial reconstruction algorithm (Octopus v8; IIC UGent, Zwijnaarde). The data were analyzed manually using ImageJ (Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997-2016), and 3D visualizations were segmented manually and rendered in Avizo® version 9.2.0 (FEI Visualization Sciences Group). Crack initiation is characterized by the temperature at which the first signs of the crack are evident.

### 2.3 Characterization of polymer-to-ceramic conversion

During pyrolysis, AHPCS undergoes significant changes in physical, chemical, and mechanical properties [15–21]. The conversion process includes crosslinking between about 100 and 650°C, ceramization between about 850 and 1100°C, and crystallization between about 1150 and 1650°C (Starfire® Systems documentation [14] and [15–17]). The polymer-to-ceramic conversion is accompanied by gas evolution and associated mass loss, an increase in mass density and corresponding volume reduction, and an increase in stiffness.

The changes were characterized in the following ways.

#### 2.3.1 Thermogravimetric analysis and mass spectrometry

Thermogravimetric analysis and mass spectrometry (TGMS) were performed on a neat specimen of AHPCS + 0.2wt% DP that had been pre-cured at 120°C for 2h in argon. The
tests were performed at NETZSCH Instruments North America, LLC (Burlington, MA) with a STA 449 *F1 Jupiter*® thermogravimetric analyzer with an Oxygen Trap System (OTS®) coupled to a QMS 403 *Aëolos*® quadrupole mass spectrometer. The tests were run under flowing argon with a heating rate of 1.4°C/min from room temperature to 1550°C. A constant heating rate was used to eliminate artifacts in the mass spectrometry data that would result from isothermal holds and changes in heating rate.

### 2.3.2 Mass density

Density measurements were performed at room temperature (21°C) on powders prepared from pellets of AHPCS + 0.2wt% DP. The pellets had been pre-cured in air at 120°C for 2h followed by interrupted pyrolysis treatments in argon to various temperatures (temperature profile: 25°C to 250°C at 2°C/min, 250°C to 650°C at 1°C/min, 650°C to 850°C at 3°C/min, 850°C hold 60min, 850°C to 1000°C at 3°C/min, 1000°C hold 60min, 1000°C to 1200°C at 3°C/min, 1200°C hold 60min, cool at -5°C/min, as recommended by Starfire® Systems [14]). The measurements reported for room temperature (21°C) are those of powders after pre-curing. The measurements reported for 375-1200°C are those of powders following pyrolysis to the designated temperature.

The density, $\rho$, was determined via mass measurements using an analytical scale and volume measurements using a Quantachrome Ultrapyc™ 1200e (Boynton Beach, Florida) pycnometer. The coefficients of variation of the measured densities at each temperature were $\leq 0.7\%$. The volumetric yield was estimated as $(m/m_0)/(\rho/\rho_0)$, where $m$ is mass, $m_0$ is initial mass at room temperature, and $\rho_0$ is density at room temperature.
2.3.3 Young’s modulus

The Young’s modulus of pellets of AHPCS + 0.2wt% DP were measured at room temperature (21°C) by nanoindentation. The pellets had been pre-cured in air at 120°C for 2h followed by interrupted pyrolysis treatments in argon to various temperatures (temperature profile: 25°C to 250°C at 2°C/min, 250°C to 650°C at 1°C/min, 650°C to 850°C at 3°C/min, 850°C hold 60min, 850°C to 1200°C at 2°C/min, 1200°C hold 60min, cool at -5°C/min, as recommended by Starfire® Systems [14]). The measurements reported for room temperature (21°C) are those of pellets after pre-curing. The measurements reported for 375-1200°C are those of pellets following pyrolysis to the designated temperature.

Nanoindentation was performed with a Hysitron TriboIndenter® using a Berkovich tip for indentation and fused quartz for tip-shape calibration. The Young’s modulus was calculated from the unloading curves following standard protocols [22]. The coefficients of variation of the measured moduli at each temperature were < 6%.

3 Results and discussion

3.1 Polymer-to-ceramic conversion

The evolution of physical, chemical, and mechanical properties for the polymer-to-ceramic conversion is summarized in Figures 1(B-F). The TGMS results show a 21.5% mass loss caused by liberation of hydrogen ($m/z = 2$), methane ($m/z = 16$), and silanes (silane, methylsilane, dimethylsilane, trimethylsilane, and tetramethylsilane, with $m/z = 29, 30, 31, 43, 44, 45, 58, 59, 73$). Furthermore, the combination of mass loss and density increase
(from about 1.0 to 2.5 g/cm³) results in a volumetric yield of 32% upon completion of pyrolysis. As a result of these changes, the Young’s modulus increases by over three orders of magnitude, from 0.0234 ± 0.0005 GPa after pre-curing to 153 ± 7 GPa after heating to 1200°C. Most of the changes occur over the temperature range of 200 to 800°C. These results provide context for the physical changes revealed by XCT images of the composite specimen.

3.2 In-situ x-ray computed tomography

XCT images in Figures 2-5 show the progression of crack formation with increasing temperature. Figure 2 shows three 3D images of the same location at various stages of pyrolysis. The image after complete pyrolysis was taken at room temperature, after cooling from 1200°C. The cracks are the least absorbing features and are rendered transparent while the fibers, being most absorbing, are rendered light yellow. Meanwhile, as the matrix material converts from AHPCS to SiC, it becomes more highly absorbing (red to orange to yellow color scheme in Figure 2), nearly matching that of the fibers after complete pyrolysis. In the rendering of the CMC after complete pyrolysis (Figure 2(C)), the fibers bounding the crack planes can be seen behind the remaining cracked pieces of matrix material. The first cracks to form are evident at about 200°C. New cracks continue to form at temperatures as high as 700°C. Unsurprisingly, this temperature range corresponds to that of the most significant gas evolution, mass loss, and volume reduction. Throughout this process and at higher temperatures, the opening displacements of existing cracks progressively increase, a result of continued matrix evolution and constraints imposed by the fibers.
In the following discussion, crack geometries and crack evolution are discussed in the context of local matrix regions bounded by surrounding fibers. Because the fibers are nearly parallel with only gradual variations in their lateral spacing along the length of the composite, the size of the matrix region containing cracks is characterized by $\sqrt{A_n}$ where $A_n$ is the cross-sectional area of that region measured normal to the fiber direction.

The focus here is on regions in which impregnation of the preceramic polymer between fibers was complete. (Although occasional mesoscale defects such as bubbles and long (> 500 µm) longitudinal cracks were observed, the cracks around them are not considered here.) The results are based on exhaustive examinations and measurements of more than 140 crack structures.

3.3 Geometry, taxonomy and temporal sequence of pyrolysis cracks

Several prototypical crack types and evolution sequences are obtained. The first crack to form in a particular local matrix region is referred to as the primary crack. Other cracks can form in the same region as the matrix continues to evolve; these are referred to as secondary, tertiary, and quaternary cracks, dictated by the temporal sequence. The concatenation of connected cracks within a local matrix region at the completion of pyrolysis is referred to as a crack structure. Primary cracks are one of two broad types. The first comprises alternating (A) and wavy (W) cracks, collectively designated A/W (Figures 3(A), 4(A), and 6(A)). The cracks form rapidly (within a single XCT scan), and thus their temporal evolution is not directly observed. However, based on geometric analyses and reports of similar crack geometries in adhesive joints [23–25], we infer that both crack types initiate
from putative interfacial cracks and grow nominally parallel to the fibers.

Alternating cracks of similar geometry have been observed previously in adhesive joints and other layered structures and have been analyzed using established fracture mechanics principles [23, 24]. We thus infer that these cracks extend through a repeating process in which an interfacial crack propagates to a critical length, kinks into the matrix at a shallow angle, follows a curved trajectory across the local matrix region, and deflects at the fiber-matrix interface on the opposite side of this region to form another interfacial crack (Figure 3(A), Figure 6(A)). Because of the characteristic angles at which alternating cracks emanate from one interface and deflect into another, the direction of propagation can be readily inferred from crack shape (e.g. vertical red arrow in Figures 3(A)(i) and 6(A)). The 3D crack surfaces form an occasionally kinked ribbon with the edges of the ribbon cupped inward toward the matrix region (the cupped feature is not observed in 2D adhesive joint geometries [23, 24]).

Wavy cracks have also been observed previously in adhesive joints [25]. Because the wavy cracks observed here do not begin or end in the middle of local matrix regions, we infer that they initiate similarly from putative interfacial cracks. In contrast to alternating cracks, wavy cracks exhibit a smooth (nearly sinusoidal) shape (Figures 4(A), 6(A)). Occasionally they contact the bounding fibers tangentially at their peaks and troughs. The 3D crack surfaces form smooth wavy ribbons with inwardly-cupped edges (Figure 4(A)).

The nature of alternating and wavy cracks cannot be ascertained from 2D sections alone. For example, when viewed within some longitudinal sections, alternating cracks can ap-
pear to be wavy in nature (seemingly without the kinked features); in other sections, they
can appear to be periodically spaced cracks perpendicular to the fibers (Figure 3(A)(vii)).
Only 3D imaging provides conclusive evidence of their true geometry.

Although both alternating and wavy cracks are observed, alternating cracks appear to be
more common; about 75% of 91 cracks analyzed in the alternating/wavy family show a
purely alternating geometry. However, alternating and wavy cracks are not always en-
tirely distinct from one another; one type can morph into the other as the crack grows.
For example, a crack can grow in an alternating fashion for some distance and then grow
further in a wavy fashion, and vice versa. Because of the similarities in their geometric
characteristics, the two crack types are grouped as one, alternating/wavy (A/W), in
subsequent discussion.

In the second category, primary cracks are, for the most part, nearly perpendicular to the
surrounding fibers. The edges of these cracks are bounded by a wall of nearly-touching
fibers (Figures 5(A,E) and 6(B)). These are named perimural (P) cracks. (The term stems
from the Greek root peri, meaning around, and the Latin root mur, meaning wall.)

Most perimural cracks appear to be preceded by and emanate from one end of a small
interfacial crack. The cracks kink into the matrix and grow predominantly perpendicular
to the fibers. Similarly to the A/W cracks, primary crack formation occurs rapidly (within
a single XCT scan). Figure 5(A) shows an example in which two parallel perimural cracks
were spawned by two ends of a single thin interfacial crack; a 2D section revealing the in-
terfacial crack is shown in Figure 7. Among 51 sets of perimural cracks examined, about
80% show clear evidence of originating at a fiber-matrix interface. Indeed, among the perimural cracks with evident interfacial cracks, each was connected to only one interfacial crack in the early stages after formation. From this observation we infer that the interfacial cracks precede and nucleate the perimural cracks, not vice versa. (Otherwise, if perimural cracks were to nucleate within the matrix and then kink into the interface, at least some of these cracks would be expected to kink at two or more locations.) This nucleation process is similar to that associated with alternating cracks. In some sense perimural cracks formed this way can be viewed as incipient alternating cracks that failed to grow past the first half-wavelength. It is important to note that, because of the localized nature of the putative interfacial cracks that spawn the (typically much larger) perimural cracks, 2D cross-sections (e.g. Figure 5(F-I)) rarely reveal the presence of the initiating crack, leading to the false conclusion that most perimural cracks nucleate homogeneously within the central regions of the matrix pockets.

Additional cracks often form within matrix regions containing primary cracks. Their geometry and temporal sequence depend on the primary crack type.

For alternating/wavy primary cracks, secondary and tertiary cracks may be of two types: (i) interfacial (I) cracks, which form and propagate along fibers still attached to the matrix; and (ii) cracks perpendicular to the fibers, bounded partially by fibers and partially by another crack surface (in this case, the alternating/wavy crack surface, and possibly an interfacial crack surface). The latter are referred to as semi-perimural (SP) cracks. Similarly to perimural cracks, semi-perimural cracks may also be spawned from putative interfacial cracks. The potential temporal sequences of these secondary and tertiary
cracks are summarized in Figure 6(C); examples are shown in Figure 3 (and corresponding Video 1), as well as Figures 4 and 6(A). Each crack type labeled in Figures 3-6 (e.g., P, A/W, and I) forms independently as a unique event, with purely interfacial (I) cracks distinct from the interfacial cracks included within the P and A/W crack geometries.

In addition to the preceding crack taxonomy based on temporal sequence (e.g., primary - quaternary), we define the final hierarchical order (FHO) as the number of unique crack types within a crack structure in a local matrix region after completion of pyrolysis. For example, the crack sequence in Figure 3 begins with a primary alternating crack followed by secondary semi-perimural cracks and tertiary interfacial cracks. The crack structure is characterized by its FHO (3) and the primary crack type, together denoted 3A/W. Figure 4, on the other hand, shows a primary wavy crack with secondary semi-perimural cracks in some segments and secondary interfacial cracks in others; these are W-SP and W-I cracks. Both are crack structures with FHO of 2 in the alternating/wavy family, abbreviated as 2A/W.

Following formation of perimural primary cracks, two types of secondary cracks may form: (i) straight longitudinal (L) cracks, oriented approximately parallel to the fibers, within the matrix between two perimural cracks (Figures 5(B,G) and 6(B)); and (ii) interfacial (I) cracks between the fibers and the remaining matrix. These may be followed by tertiary/quaternary interfacial (I) and semi-perimural (SP) cracks (Figure 5(B-D)). The semi-perimural cracks are bounded partially by the fibers and partially by a longitudinal crack and/or an interfacial crack. The potential temporal sequences are summarized in Figure 6(C); examples are shown in Figures 5 (and corresponding Video 2) and Figure
6(B). Final crack structures in the perimural family may be composed of perimural, longitudinal, semi-perimural, and interfacial cracks. For example, the crack structure in Figure 5 is a **P-L-SP-I** crack. This is a crack structure with a FHO of 4 in the perimural family, abbreviated as 4P.

### 3.4 Initiation temperatures and characteristic length scales

With a view toward future development of a mechanistic framework to describe the spatial and temporal evolution of pyrolysis cracks, we present measurements and preliminary analyses on the effects of the size of matrix regions, characterized by $\sqrt{A_r}$, on: (i) the temperatures at which *primary* cracks initiate, $T_{p}^{i}$; (ii) the FHO; and (iii) the characteristic spacings, $L_c$, associated with the two types of primary cracks – the half-wavelength, $\lambda/2$, for alternating/wavy cracks and the longitudinal spacing, $l_P$, between perimural cracks.

A process flow diagram depicting the steps followed to make these measurements is illustrated in Figure 7*. In the first step, primary cracks were identified and categorized by crack type (P, A, or W) by scrolling through longitudinal image stacks taken at a variety of temperatures (Figure 7(A)). For example, the primary cracks in Figure 7(A) (same as those in Figures 5(A,F)) are identified as perimural because they are predominantly perpendicular to fibers. Each emanates from one end of an interfacial crack. The interfacial crack is identified by two key features: (1) the curved trajectory of the perimural cracks near the interface, and (2) the large opening displacement of the interfacial crack after

*Although all data in the current study were collected manually, the resulting database may be used in the future to inform machine learning algorithms to automate measurements of a similar nature. Data are available upon request.
complete pyrolysis (Figure 7(C)). Next, the crack initiation temperature is determined by examining image stacks taken at progressively lower temperatures until the primary crack is no longer visible (Figure 7(B)). In the third step, the FHO is determined by examining the same region in the image stack after complete pyrolysis (Figure 7(C)). For example, in Figure 7(C), longitudinal, semi-perimural, and interfacial cracks are identified (in addition to the primary perimural crack). Thus, the FHO for this crack structure is 4. Purely interfacial cracks are identified as those that do not kink into the matrix to form perimural, semi-perimural or alternating cracks. Such cracks can only be identified when their opening displacements are large enough to differentiate them from the fiber-matrix interface. Thus, crack initiation temperatures reported for purely interfacial cracks are only approximate. Additionally, not every interfacial crack in the local matrix regions is shown in Figures 3, 4, 5, and 7; only the minimum number of such cracks needed to determine the FHO are presented. Finally, crack areas, \( A_n \), and characteristic spacings, \( L_c \), were measured, as described below and illustrated in Figures 3-5.

For alternating cracks, \( \lambda/2 \) was measured from the start of the fiber-matrix interface crack through the end of the trans-matrix crack that kinked from the interface (Figure 3(A)(i,vi)). The cross-sectional area normal to the fibers, \( A_n \), corresponds to the area traversed by the trans-matrix crack (Figure 3(A)(ii-v)). For wavy cracks, \( \lambda/2 \) was measured from the peak to the adjacent trough of the crack path (Figure 4(A)). Here, \( A_n \) corresponds to the area traversed by the sinusoidal crack between the peak and adjacent trough. For alternating/wavy cracks, the average cross-sectional area was measured for each half-wavelength; 530 segments from 91 distinct cracks were analyzed.
Areas of perimural cracks were measured in the way illustrated in Figure 5(E). Often, multiple perimural cracks formed nearly simultaneously, i.e. within the same XCT scan, in the same local matrix region. Their longitudinal spacings, $l_p$, were measured only at this point in the pyrolysis cycle. (Additional perimural cracks can form between the initial cracks at higher temperatures and thus the reported crack spacings do not necessarily represent the spacings after the completion of pyrolysis.) 51 regions containing perimural cracks were analyzed.

The results are summarized in Figures 8 and 9. The results in Figure 8(A) show that the initiation temperatures for both types of primary cracks decrease as $\sqrt{A_n}$ increases. This trend is consistent with other cracking phenomena in thin films and sandwich layers, wherein the driving forces for cracking generally increase with the local dimensions of the cracking phase [25, 26]. Figure 8(A) also shows that for primary cracks that initiate at temperatures below approximately 350°C, alternating/wavy cracks tend to form in smaller matrix regions than perimural cracks. As noted earlier, most perimural cracks initiate at the fiber-matrix interface and then kink into the matrix, akin to the first half-wavelength of alternating cracks. These results suggest that continued growth of such cracks into alternating cracks (rather than termination as perimural cracks) is more favorable in smaller channels.

The crack initiation temperatures in Figure 8(A) are further sorted according to the FHO of the terminal crack structures and re-plotted in Figure 8(B) for $A/W$ cracks and in Figure 8(C) for $P$ cracks. (Information about initiation temperatures of secondary, tertiary and quaternary cracks is not contained in these figures.) The largest matrix regions typically
crack first (at the lowest temperatures) and contain crack structures with higher FHO following complete pyrolysis, e.g. 4P cracks, represented by orange diamonds in Figure 8(C). Conversely, the smallest regions are last to crack and contain crack structures with lower FHO following complete pyrolysis, e.g. 1P cracks, represented by purple circles in Figure 8(C). We find that, for both families of primary crack, the crack initiation temperatures progressively decrease while the FHO increases with increasing $\sqrt{A_n}$. This trend is also consistent with cracking phenomena in thin films, wherein the driving forces for additional cracking between existing cracks increase with further increase of the loading and with the local dimensions of the cracking phase [25].

The characteristic spacings associated with the two types of primary cracks – $\lambda/2$ for alternating/wavy cracks and $l_p$ for perimural cracks – follow similar scalings with $\sqrt{A_n}$ (Figure 9). Notably, $(\lambda/2)/\sqrt{A_n} = 2.2 \pm 0.7$ for alternating/wavy cracks and $l_p/\sqrt{A_n} = 2.1 \pm 1.0$ for perimural cracks ($\pm$ are standard deviations). In sandwich structures, the ratios of the characteristic length scales to film thickness for both alternating cracks and tunneling cracks have been shown to depend on film thickness, the elastic moduli of the film and substrate, and the misfit strain, among other factors [24, 26]. Here we find that, despite significant changes in the Young’s modulus of the matrix and the misfit strain, $L_c/\sqrt{A_n}$ appears to be essentially constant, independent of $T_i^p$ and $\sqrt{A_n}$ for both alternating/wavy and perimural cracks.
4 Conclusions and outlook

In-situ x-ray computed tomography has been used to ascertain the nature of crack structures and their evolution during pyrolysis of a SiC-based preceramic polymer contained within a unidirectional fiber bed. Importantly, the true character of these cracks can only be definitively identified with 3D imaging; 2D images can readily lead to false impressions of crack nucleation locations and of crack geometry and topology. Examinations of a large number of such cracks have guided the development of a unified taxonomy of crack geometries and crack structures and revealed the temporal sequences of their formation. Primary cracks appear to nucleate almost exclusively from putative interfacial flaws and evolve in one of two ways: either through the formation of alternating/wavy cracks or perimural cracks. The observations further suggest that the primary crack types and their formation are not entirely distinct; perimural cracks appear to form analogously to the first half-wavelength of alternating cracks. As pyrolysis continues, secondary, tertiary and quaternary cracks also form.

The primary crack initiation temperature decreases and the final hierarchical order increases with increasing size of the local matrix region. For primary cracks that initiate below approximately 350°C, alternating cracks form in preference to perimural cracks within the smaller channels. Furthermore, the characteristic crack spacings – longitudinal spacing between perimural cracks and half-wavelengths of alternating/wavy cracks – are approximately proportional to the size of the regions in which these cracks are contained.
The findings reported here provide a framework for describing crack networks that result from a single impregnation and pyrolysis cycle and that, in practice, will ultimately need to be re-impregnated. Simple imbibition models using the crack geometries identified here may streamline the optimization of subsequent impregnation cycles or be used to identify optimal target shrinkage crack geometries. Furthermore, the present observations provide a foundation for development of a mechanics framework to describe pyrolysis cracking within fiber beds. These findings may simplify efforts to optimize and tailor crack formation, perhaps via altering the pyrolysis thermal cycle or more precisely tailoring the fiber packing characteristics.

Development of a mechanics framework will require measurements of additional inputs, including the driving forces for cracking (e.g. local shrinkage strains) as well as changes in matrix toughness and interfacial properties over the course of pyrolysis. Furthermore, descriptors of crack topology (e.g. connectivity) and channel dimensions may provide insights into the limits of densification that can be attained with this processing route.

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Figure 1: Characterization of polymer-to-ceramic conversion. (A) Temperature profile for pyrolysis experiment performed in-situ in the beamline. (B) Changes in mass density of the preceramic polymer alone. (C) Mass spectrometry results labeled with \( m/z \) values. Also shown are changes in (D) mass, (E) volumetric yield, and (F) Young’s modulus. (Error bars in (F) are standard deviations.) Curves in (B,E,F) are hyperbolic tangent fits to the experimental data.
Figure 2: Three-dimensional volume renderings of a select region of the composite during pyrolysis. Images obtained (A) at 332°C, (B) at 519°C, and (C) after complete pyrolysis.
Figure 3: Evolution of a crack structure in the alternating family. (A)(i),(B)(i),(C)(i) Three-dimensional renderings of a crack structure with FHO of 3. In these renderings, fibers are semi-transparent blue, pyrolysis cracks are shown on a red-yellow scale that indicates initiation temperature, and matrix material is transparent. Each crack is labeled with its geometric type and its initiation temperature. Vertical red arrow in (A)(i) indicates the crack growth direction. (A)(ii-iv) Transverse (2D) views of the alternating crack at three points along the crack trajectory shortly after formation. Red arrows indicate the crack front. (A)(v) Transverse view showing the area spanned by the alternating crack in (A)(ii-iv). (A)(vi), (B)(ii), (C)(ii) Longitudinal 2D sections of raw XCT images taken from the same location in the 3D image stacks showing crack evolution during pyrolysis. (A)(vii) A longitudinal 2D section of the alternating crack, viewed in a plane orthogonal to that in
(A)(vi). Corresponding Video 1 is a three-dimensional rotating volume rendering, illustrating the temporal sequence of cracking.
Figure 4: Evolution of a crack structure in the wavy family. (A-B) Three-dimensional XCT renderings with complementary longitudinal sections of raw XCT images. The crack structure has a FHO of 2. Labels and color schemes are the same as those in Figure 3.
Figure 5: Evolution of a crack structure in the perimural family. (A-D) Three-dimensional renderings of a crack structure with FHO of 4. Labels and color schemes are the same as those in Figure 3. (E) Transverse 2D section of raw XCT image (indicated by red plane in (A)) showing the area spanned by the perimural crack. (F-I) Longitudinal sections (indicated by the gray plane in (A)) showing cracks at the temperatures corresponding to images in (A) through (D). Corresponding Video 2 is a three-dimensional rotating volume rendering, illustrating the temporal sequence of cracking.
Figure 6: Temporal evolution of pyrolysis crack structures. (A) Evolution of crack structures in the alternating/wavy family. Shown here are the evolution of crack structures with FHO of 3: alternating and wavy primary cracks followed by secondary semi-perimural and tertiary interfacial cracks. (B) Evolution of a crack structure in the perimural family. Shown here is the evolution of a crack structure with FHO of 4: primary perimural cracks followed by a secondary longitudinal crack, tertiary semi-perimural cracks, and a quaternary interfacial crack. (C) Crack evolution tree illustrating potential temporal sequences.
Measurements: process flow diagram
(example crack structure from Fig. 5)

A. Identify primary cracks and determine crack type (P, A, W)

B. Determine initiation temperature of primary crack, $T_p$

C. Determine final hierarchical order (FHO) by identifying L, SP, and I cracks in images taken after complete pyrolysis

D. Measure $A_n$ and $L_c$ as illustrated in Figs. 3-5

Figure 7: Process flow diagram for crack identification and measurements. Sample images are from cracks rendered in Figure 5. Colored lines on XCT images indicate intersectionality of perpendicular planes in the 3D image data.
Figure 8: Relationships between crack areas and primary crack initiation temperatures.
(A) All data, for alternating/wavy cracks (open purple circles, purple line) and for per-
imural cracks (closed orange triangles, orange line). Lines are logarithmic fits. (B-C) Data in (A) separated by primary crack type and FHO (purple circles represent FHO=1, green triangles represent FHO=2, blue squares represent FHO=3, orange diamonds represent FHO=4). Semi-transparent boxes indicate boundaries of first and third quartiles in $T_p$ and $\sqrt{A_n}$ for each data cluster. Solid lines indicate the full range of $T_p$ and $\sqrt{A_n}$, and intersect at the median of each data cluster.
Figure 9: Characteristic length scales of pyrolysis cracks. (A) Half-wavelength of alternating/wavy cracks and (B) longitudinal spacing of initial perimural cracks. Color scale indicates primary crack initiation temperature.