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7 Effect of pyrolysis parameters on mechanical properties 8 of polymer-derived ceramics

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19 Polymer-derived ceramics (PDCs) which are fabricated through pyrolysis of preceramic
 20 polymers have attracted increasing attention due to their versatility in structure architec-
 21 ture design and property tailoring. Shaping at the polymer state using 3D printing allows
 22 the final ceramic products to exhibit arbitrary shapes and complex architectures that
 23 are otherwise impossible to achieve through traditional processing routes. The polymer-
 24 to-ceramic phase transition also provides additional space for mechanical property tai-
 25 loring. A multiscale computational model is developed to explore the phase transition
 26 mechanisms and their correlations with processing parameters and failure response. Cal-
 27 culations in this work concern PMHS/DVB preceramic polymers. Molecular dynamics
 28 (MD) simulations are carried out first to track the atomic structure evolution at differ-
 29 ent temperatures. Continuum-scale ceramic phase formation is calculated on the basis
 30 of the competition between gas generation and gas diffusion. The effect of processing
 31 parameters on mechanical properties of pyrolyzed PMHS/DVB is systematically studied.
 32 Conclusions from this study can provide direct guidance for fabricating PDC composites
 33 with tailored mechanical properties.

34 *Keywords:* Polymer-derived ceramics (PDCs); phase transition analysis; finite element
 35 simulation.

36 1. Introduction

37 Advanced ceramics represent a key enabling technology in aerospace, defense, power
 38 generation, and healthcare industries due to their superior properties, such as
 39 lightweight [Alizadeh-Osgouei *et al.*, 2018], high strength [Waku *et al.*, 1997], excel-
 40 lent thermal stability [Justin and Jankowiak, 2011] and high corrosion resistance
 41 [Wei *et al.*, 2005]. Traditional ceramic processing technique has very little control

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over material geometry and does not provide enough room for property tailoring [Gonzalez et al., 2018]. Discovery of polymer-derived ceramics (PDCs) in 1960 has enabled significant technological breakthroughs in ceramic science and technology [Colombo et al., 2009]. This fabrication approach, which converts preceramic polymers to ceramics through heat treatment under an inert or reacting atmosphere, opens up new opportunities for property tailoring through phase transition control [Gottardo et al., 2012; Soraru et al., 2019; Wan et al., 2004]. Recently, additive manufacturing technology has enabled fabrication of preceramic polymers with complex shapes and architectures [Eckel et al., 2016; Konstantinou et al., 2020]. Shaping at the polymer state not only avoids problems related to tool wear and brittle fracture upon finishing the ceramic component, but also provides new opportunities for geometric design which is of great importance in applications, such as customized biomedical implants, body armor, and energy storage devices, etc. Understanding the effect of key processing parameters on mechanical properties of PDCs requires in-depth understanding of the phase transition process. Experimental characterizations, e.g. thermogravimetric analysis (TGA) [Venkatachalam and Hourlier, 2019] and infrared spectroscopy [Gottardo et al., 2012], can track the mass loss associated with preceramic polymer decomposition during pyrolysis. However, these approaches alone cannot directly reveal the molecular structure evolution which is an important aspect of phase transition. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [Vry et al., 2020], which can provide detailed nano/micro structure characterization, are only available after sample pyrolysis. Computational models can address some of the underlying physics that cannot be directly captured during experiment. Molecular dynamics (MD) models have been employed to simulate the chemical reaction mechanisms and atomic structure change during pyrolysis [Lu et al., 2015; Ponomarev et al., 2019]. However, conclusions from MD simulations cannot be directly employed to guide the manufacturing process due to the large time and length scale gaps. Bernard et al. [2006] proposed a diffusion-controlled kinetic model which predicts polymer-to-ceramic phase transition at the structure level. Their prediction of polymer-to-ceramic conversion did not account for the temperature field evolution or the change of heat transfer behavior during the dynamic phase transition process. In fact, the current state phase composition will largely affect the heat transfer behavior and temperature field evolution that will ultimately determine the subsequent polymer decomposition and phase redistribution. This is because the thermal conductivity of ceramics is about ten times higher than that of polymers [Stabler et al., 2018]. The thermal conductivity of the entire material tends to increase when the polymer phase is gradually converted to the ceramic phase, leading to more intensified subsequent polymer decomposition. A computational model which finds the missing link between the atomic level structure evolution and macroscale phase composition map will promote in-depth understanding of the physics of phase transition process. Additionally, quantitative correlation of processing parameters with mechanical response

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of the pyrolyzed preceramic materials will provide a useful roadmap for fabricating PDCs/PDC composites with tailored properties and functionalities. Currently, few computational studies are available to find the systematic correlations, especially when intermediate polymer-ceramic phases are present.

In this paper, a multiscale computational model is developed to study the effect of key pyrolysis parameters on phase transition and mechanical properties of pyrolyzed PMHS/DVB samples. Gas generation during pyrolysis is captured through MD simulations. Continuum-scale phase transition is predicted based on the competition between gas generation and gas diffusion in Sec. 2.1. The constitutive law in the intermediate phase is developed on the basis of the microhardness testing results. The overall mechanical response of the PDC composites is predicted through tension simulation as presented in Sec. 2.2. The effect of heating rate, pyrolysis temperature and holding time on elastic modulus and tensile fracture behavior is systematically studied in Secs. 3.1 and 3.2, respectively. The developed model, which correlates key processing parameters with mechanical response, will reduce the time and cost in developing future PDCs with tailored mechanical properties.

2. Model Description

2.1. Multiscale modeling of phase transition

2.1.1. MD simulation on atomic structure evolution

A preceramic polymer system, in which polymethylhydrosiloxane (PMHS) is crosslinked by divinylbenzene (DVB), is modeled in this work. Polymer chains with molar mass of 1500g/mol are first constructed and randomly packed in the simulation box. DVB molecules are bonded to different polymer chains to create the network structure, which is imported to large-scale atomic/molecular massively parallel simulator (LAMMPS) to obtain system equilibrium [Ma et al., 2017b; Plimpton, 1995]. Parameters of reaction force field are selected based on the work of Kulkarni et al. [2013]. Constant temperature and pressure ensemble (NPT) are utilized with a time step of 0.1 fs. The pre-pyrolysis system is equilibrated at 300K as shown in Fig. 1(a). The pyrolysis process is simulated by considering a range of pyrolysis temperatures from 873K to 2500K with constant heating rate of 0.1 K/fs and time step of 0.2fs. The top surface of the simulation box is set to move freely along the vertical direction. At the height of three times of the initial box length, the temperature is set to 0.1K by Berendsen thermostat in order to trap the diffused gas molecules. Periodic boundary conditions are applied to the rest of the surfaces.

Chemical reactions during pyrolysis are elucidated in Fig. 1(b). At a pyrolysis temperature of 1500K, bond breakage occurs to form free radicals (e.g., $\cdot\text{CH}_3$) and atoms (e.g. H atoms). Gaseous products, such as H_2 and C , are generated due to the new bond formation. Mass loss occurs as the gaseous products are gradually released out of the system during pyrolysis. In the MD model, mass loss is counted as the overall mass of generated gaseous molecules. As indicated in Fig. 1(c), higher

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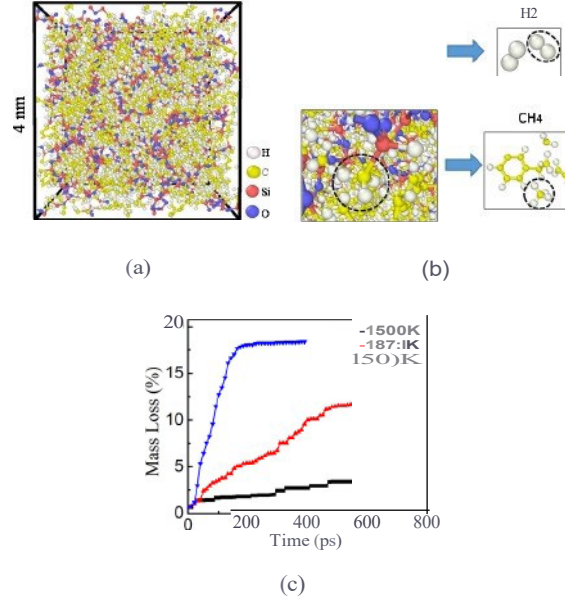


Fig. 1. (a) Equilibrated PMHS/DVB systems before pyrolysis; (b) atomic debonding and rebonding process at 1500 K during pyrolysis; and (c) mass loss at different pyrolysis temperatures.

pyrolysis temperature corresponds to higher amount of mass loss, which is consistent with the TGA [Li *et al.*, 2018a; You *et al.*, 2019]. Additionally, an earlier saturation of mass loss is reached at a higher pyrolysis temperature. It can be inferred that the time required for complete gas generation is 772ps under 1500K, 473ps under 1873K, and 180ps under 2500 K, respectively. Therefore, it is reasonable to consider that gas generation occurs instantly at the structure level. The total amount of mass loss only depends on the pyrolysis temperature. The generated gas density $\rho_{gas}(T)$ is calculated as

$$\rho_{gas}(T) = \frac{m_{gas}(T)}{V} = \frac{m_{loss}(T) \rho_{initial}}{V} \quad (1)$$

where $\rho_{initial} = 1.21 \text{ g/cc}$, $m_{gas}(T)$ is the mass of generated gas products at temperature T , $m_{initial}$ is the initial system mass, $\rho_{loss}(T)$ is the mass loss ratio which is extracted through the thermogravimetric (TGA) analysis from Li *et al.* [20186]. Here, the gas volume in Eq. (1) is assumed to be constant during the fast gas generation process due to the uniform gas molecule distribution in the system.

2.1.2. Finite element simulation of phase transition at the continuum level

Gaseous products, which are generated during pyrolysis, need to release out of the system so that the ceramic structure can be formed. Therefore, phase transition requires in-depth understanding of the interplay between gas generation and gas diffusion. At the structure level, a PDC sample during pyrolysis may include three

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phases: polymer phase (phase 1), ceramic phase (phase 2) and intermediate phase with partially decomposed polymers. Due to the huge discrepancy of thermal conductivity in each phase, a non-uniform temperature field is expected when different phases coexist. Gas diffusion is triggered as a result of the gas density gradient. Gas diffusion rate $\frac{\partial \psi}{\partial t}$, is calculated as

$$\frac{\partial \psi}{\partial t} = D_T \nabla^2 \psi(x, y, z, t). \quad (2)$$

where D_T is the diffusion coefficient from the work of Merkel et al. [2000]. At a given moment during pyrolysis, a selected volume of the sample is either under gas gain or gas loss. Ceramic formation requires $\frac{\partial \psi}{\partial t} < 0$ when gas loss is activated. The ceramic fraction f is defined as

$$f = \frac{\psi_{\text{Prelease}}}{\psi_{\text{Jmax}}}, \quad (3)$$

where ψ_{Prelease} is the current gas release density and ψ_{Jmax} is the maximum gas density that can be generated in a given unit volume. Calculation of f is carried out through a user subroutine UMATHT in ABAQUS. Details of the algorithm can be found in Ma and Li [2021]. In this study, phase transition analysis is conducted on eight cubic preceramic polymer samples with side dimension of 20 mm. Each sample is pyrolyzed according to the predefined heating rate, pyrolysis temperature and holding times as illustrated in Fig. 2 and summarized in Table 1. Figure 3 illustrates the phase composition evolution in the middle cross-section when a heating rate of 0.63K/s and a pyrolysis temperature of 1273K are considered. It is noted that no fully converted ceramic phase is observed at 1200s and 1360s. No pure preceramic polymer phase exists either. At 1540s, around 40% of the sample has been fully converted to ceramics. Complete ceramization of the entire sample is achieved at 2440s according to the simulation. The developed model, which simulates macroscale phase transition process by accounting for both heat transfer and gas diffusion kinetics, can explicitly resolve the real-time phase composition map in

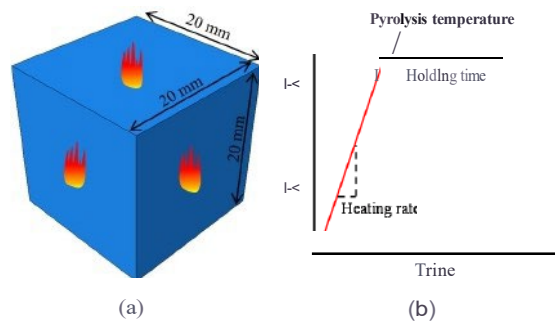


Fig. 2. (a) Scheme of the phase transition model and (b) characterization of key processing parameters.

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Table 1. List of samples employed in the phase transition simulations.

Sample number	Heating rate (K/s)	Pyrolysis temperature (K)	Holding time (s)
1	0.63	1273	1200
2	0.63	1273	1360
3	0.63	1273	1540
4	0.17	1273	1200
5	1.26	1273	1200
6	0.63	1273	1700
7	0.63	1473	1700
8	0.63	1673	1700

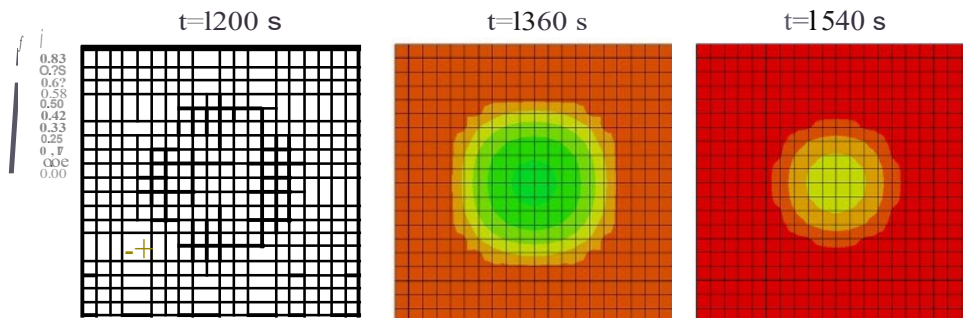


Fig. 3. Phase evolution in the middle cross section at different holding times with heating rate of 0.63 K/s and pyrolysis temperature of 1273 K.

any PDC sample configurations. The phase distribution information will serve as the input for mechanical response prediction in Sec. 2.2.

2.2. Mechanical property prediction of pyrolyzed PDC composites

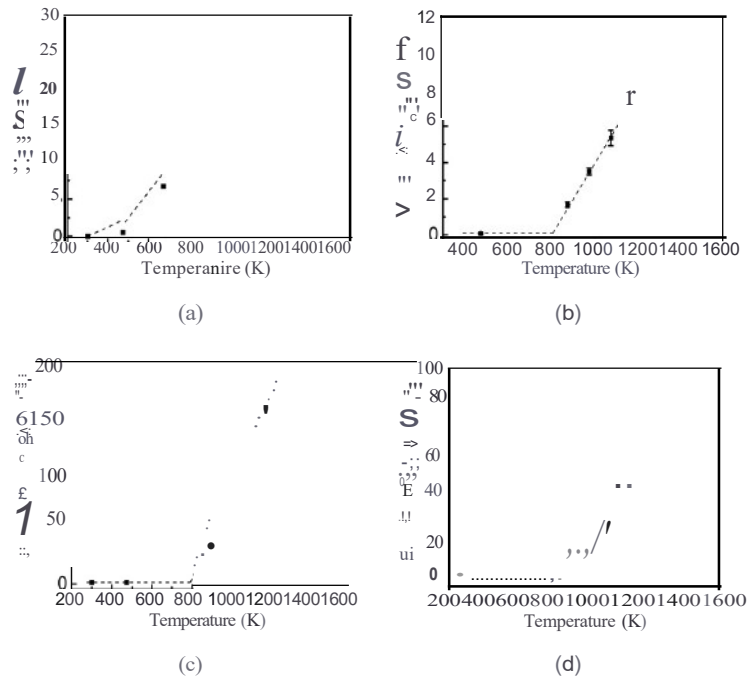
2.2.1. Constitutive modeling

Different constitutive laws are assigned to the sample based on the phase distribution as illustrated in Fig. 3. In the region where $f = 0$ (Region P), the material is pure preceramic polymer and follows the constitutive relationship that is determined through experiment [Kim *et al.*, 2011]. In the region where $f = 1$ (Region C), the material has been fully converted to the ceramic phase. It follows the isotropic linear elastic constitutive relation with Young's modulus $E_c = 101$ GPa and Poisson's ratio $\nu_c = 0.11$. In this work, the intermediate phase ($0 < f < 1$) is divided into five regions as illustrated in Table 2. According to the discussion in Sec. 2.1, f primarily depends on the pyrolysis temperature T . In order to find the mathematical model of $f(T)$ in the intermediate phase, we prepared a set of PMHS/DVB samples with a mean thickness of 0.615 mm. These samples were pyrolyzed at 873 K, 973 K, 1027 K, 1173 K and 1273 K in a muffle furnace, respectively. The mass loss ratio T_{Joss} is fitted as a function of temperature T as shown in Fig. 4(a). It is noted that T_{Joss} starts to saturate around 30.3% when $T > 1273$ K. Below this temperature

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Table 2. Region division criterion.

Region name	Ceramic fraction f
Region P	$f=0$
Region 1	$0 \leq f \leq 20\%$
Region 2	$20\% \leq f \leq 40\%$
Region 3	$40\% \leq f \leq 60\%$
Region 4	$60\% \leq f \leq 80\%$
Region 5	$80\% \leq f \leq 100\%$
Region C	$f = 100\%$

Fig. 4. Relationship of pyrolysis temperature with (a) mass loss ratio, (b) Vickers hardness, (c) ultimate strength and (d) elastic modulus (Kim *et al.*, 2011; Soran *et al.*, 2019).

1 threshold, a bilinear mass loss-temperature relationship is found as

$$T_{\text{loss}}(T) = \begin{cases} 1.28 \times 10^{-41} T - 0.0384, & T \leq 473 \text{ K}, \\ 3.51 \times 10^{-41} T - 0.1438, & 473 \text{ K} < T \leq 1273 \text{ K}. \end{cases} \quad (4)$$

2 According to Eqs. (1) and (3), the ceramic volume fraction f is formulated as

$$f(T) = \begin{cases} 4.22 \times 10^{-41} T - 0.1267, & T \leq 473 \text{ K}, \\ 1.16 \times 10^{-37} T - 0.4746, & 473 \text{ K} < T \leq 1273 \text{ K}. \end{cases} \quad (5)$$

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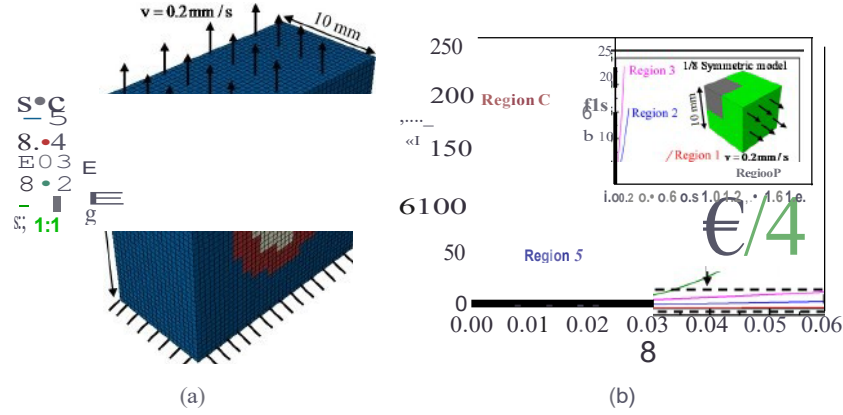


Fig. 5. (a) Sample configuration used in simple tension simulation. Phase composition is extracted at 1360s with pyrolysis temperature of 1273 K and heating rate of 0.63K/s and (b) constitutive relations in different regions.

The ultimate strength σ_{TS} is predicted according to

$$\sigma_{TS}(T) = H_v(T)/\text{Const}, \quad (6)$$

where hardness H_v is measured by applying a 1.96N indentation load on each pyrolyzed sample for 15s using the Wilson Tukon microhardness tester. $\text{Const} = 21.4$ is reported by the existing literature [Voza, 2021; Zhang *et al.*, 2011]. According to Figs. 4(b) and 4(c), three linear segments are found from the experiment. The stress-strain relationship of each intermediate region before reaching the ultimate strength is determined from the uniaxial compression simulation as shown in Fig. 5(b). Only 1/8 of the sample is modeled due to symmetry and computational efficiency. The Poisson's ratio of intermediate region i ($i = 1, 2, 3, 5$) is estimated according to $\nu_i = \nu_{\text{five}} + (1 - \nu_i)\nu_p$, where $\nu_e = 0.11$ and $\nu_p = 0.48$ are the Poisson's ratio of pure ceramics (Region C) and preceramic polymers (Region P), respectively. J_i is the averaged ceramic fraction in region i . Figure 5(b) illustrates the stress-strain curve of each region in Table 2. The constitutive relationship is imported to ABAQUS for material property assignment.

2.2.2. Prediction of the effective elastic modulus E

As shown in Fig. 5(a), the top surface of the PDC composite sample is subject to a velocity boundary with $V = 0.2 \text{ mm/s}$, while its bottom surface is fixed. According to the region decomposition criterion in Table 2, region 3, region 4 and region 5 coexist in the sample. The interface between each region can be explicitly delineated as illustrated in Fig. 5(a). The constitutive law of each region is defined according to Sec. 2.2.1. The effective elastic modulus E of the entire PDC composite sample is evaluated through simple tension simulation. This approach is applied to other PDC composite samples that are pyrolyzed under different pyrolysis parameters. The

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computationally predicted effective elastic modulus is compared with the analytical solution using the Mori-Tanaka (MT) model [Fisher and Brinson, 2006; Lee, 2018; Thorvaldsen, 2015]. In the MT model, the effective stiffness tensor C is formulated as

$$C = A_0 \left[\left(1 - \sum_{i=1}^7 v_i \right) C_{\text{polymer}} + \sum_{i=1}^7 v_i C_i A_i^{\text{dil}} \right], \quad (7)$$

where C_{polymer} is the polymer stiffness tensor; v_i and C_i are the volume fraction and stiffness tensor of region i ; A_0 and A_i^{dil} are the strain concentration factors following the following expressions as

$$A_0 = \left[\left(1 - \sum_{i=1}^7 v_i \right) I + \sum_{i=1}^7 v_i A_i^{\text{dil}} \right]^{-1}, \quad \text{and} \quad (8)$$

$$A_i^{\text{dil}} = [I + S_i C_{\text{polymer}}^{-1} (C_i - C_{\text{polymer}})]^{-1}. \quad (9)$$

Here, I and S_i are the identity tensor and the Eshelby tensor of region i , respectively. In this study, only diagonal elements of the Eshelby tensors are considered due to the uniaxial loading condition. The diagonal elements can be calculated according to

$$S_{\text{diagonal}} = \frac{7-5\nu p}{15(1-\nu p)}. \quad (10)$$

The diagonal value along the C tensor is extracted as the effective elastic modulus. Predictions of the effective elastic modulus from both simple tension simulation and MT method under different pyrolysis conditions are discussed in Sec. 3.1.

3. Results and Discussion

3.1. Effect of pyrolysis parameters on the effective elastic modulus E

Three sets of studies are carried out to evaluate the effect of holding time, heating rate and pyrolysis temperature on the effective elastic modulus of PDC composites. In the first set of this study, sample 1 to sample 3 are employed by considering different holding times of 1200 s, 1360 s and 1700 s under the constant heating rate of 0.63 K/s and pyrolysis temperature of 1273 K. The effective elastic modulus E is calculated according to the MT model, and the simple tension finite element model. The finite element predictions consider two scenarios: one scenario with each phase following idealized linear elastic constitutive law, and another scenario with each phase following the real constitutive law as shown in Fig. 5(b). It is noted from Fig. 7(a) that the number of co-existing phases decrease with the holding time. At 1200 s, there are 2.4% of phase 2, 10.3% of phase 3, 60.4% of phase 4 and 26.9% of phase 5, respectively. When the holding time increases to 1360 s, phase 2 disappears. The remaining phase 3, phase 4 and phase 5 are redistributed with the ratio of 2.7%, 9.7% and 87.6% instead. When the holding time increases to 1700 s,

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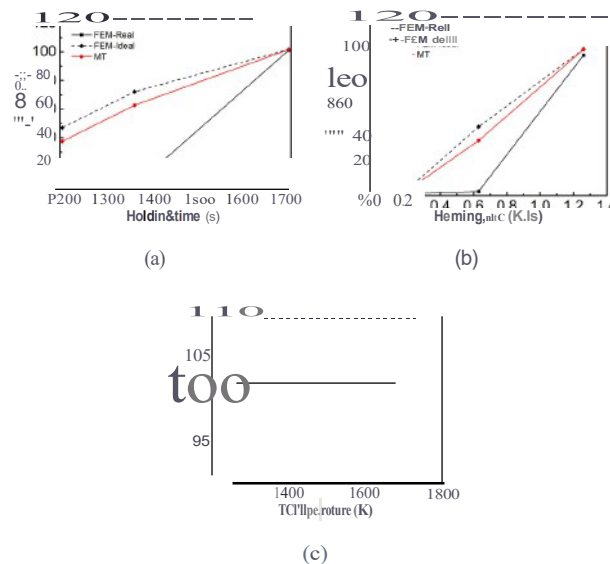


Fig. 6. Comparison of effective elastic modulus predicted from simple tension finite element simulation and MT approach under different (a) holding time, (b) heating rate and (c) pyrolysis temperature. The finite element predictions consider both idealized and realistic phase constitutive relationship.

only two phases exist; more percentage of the sample has been converted to ceramic phase while the rest of 1% stays in phase 5. As indicated in Fig. 6(a), the MT prediction is very close to the idealized FEM prediction, especially at a longer holding time. However, the FEM prediction that employs the constitutive laws yields a much lower effective elastic modulus. This is because the MT model can only deal with two-phase linear elastic composite in a dilute situation. For multi-phase composites with different shapes or alignments of reinforcements, the MT solution becomes less accurate due to the violation of diagonal symmetry, internal-consistency and dilute requirements [Ferrari, 1991; Li, 1999]. Additionally, the MT model does not consider the non-linear constitutive behaviors in PDC composites. Therefore, both the MT solution and the idealized FEM prediction would overestimate the effective elastic modulus in PDC composites, especially when the sample has more than two phases with low ceramic fraction phases being dominant. In two-phase composites with pure ceramics as the dominant phase, the three E predictions are reasonably close to each other according to Figs. 6(a) and 6(b).

It should be noted that the effective elastic modulus becomes independent of temperature when $T > 1273\text{K}$ as shown in Fig. 6(c). This is because under the heating rate of 0.63K/s , the sample can almost achieve full ceramization under pyrolysis temperature of 1273K for 1700s . Further increase of pyrolysis temperature does not affect the ceramization process, leading to negligible change of elastic modulus as indicated in Fig. 7(c). This conclusion is consistent with the TGA

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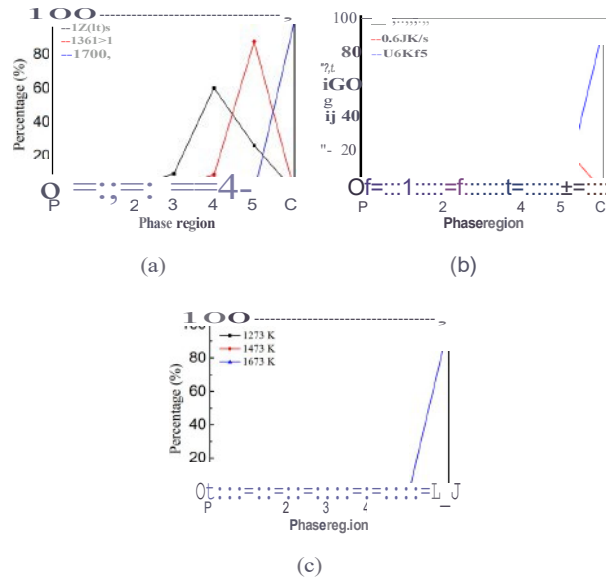


Fig. 7. Comparison of phase distribution under different (a) holding times, (b) heating rates and (c) pyrolysis temperatures.

analysis as the mass loss and ceramic yield remain unchanged once the temperature exceeds a certain threshold [Ma *et al.*, 2017a].

3.2. Effect of pyrolysis parameters on fracture behaviors

According to the discussion in Sec. 3.1, increase of holding time, heating rate and pyrolysis temperature before the threshold can lead to improved stiffness. In this section, effect of each processing parameter on the tensile fracture behavior is investigated. Figure 8(a) shows the stress-strain evolution during tensile deformation at various holding times when the heating rate of 0.63K/s and pyrolysis temperature of 1273 K are applied. At the holding time of 1200 s, the sample exhibits the most ductile behavior as its stress does not quickly drop to zero after reaching the peak. Instead, the sample can continue carrying load with additional stretch. As shown in Fig. 9(a), cracks start to initiate at the interface between phase 4 and phase 5 near the four sample corners. This is because a higher stress level is induced in phases with high ceramic fraction under the same amount deformation according to Fig. 5(b). Additionally, stress singularity that develops at the interface due to property mismatch promotes crack formation. Afterwards, the initiated cracks quickly propagate to phase 5, leading to an immediate stress drop from 19.18 MPa to 11.51 MPa. It is noticed that further crack propagation tends to be along the interface at 0° plane which is perpendicular to the loading direction. The material is still able to regain strength as the emerged cracks are successfully bridged by the uncracked ligaments in phases 2, 3 and 4. Upon additional tension loading, new cracks are initiated in

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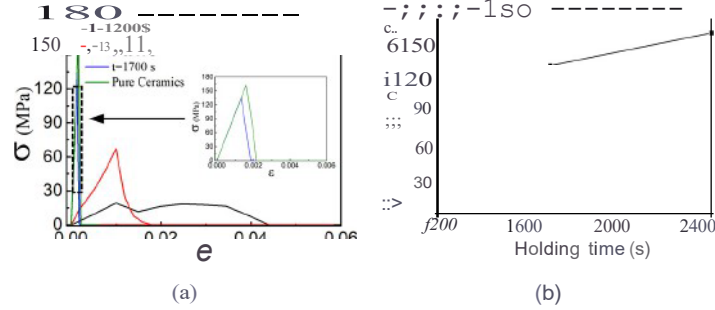


Fig. 8. (a) Stress-strain relationship and (b) ultimate strength of pyrolyzed samples under different holding times at temperature of 1273K and heating rate of 0.63K/s.

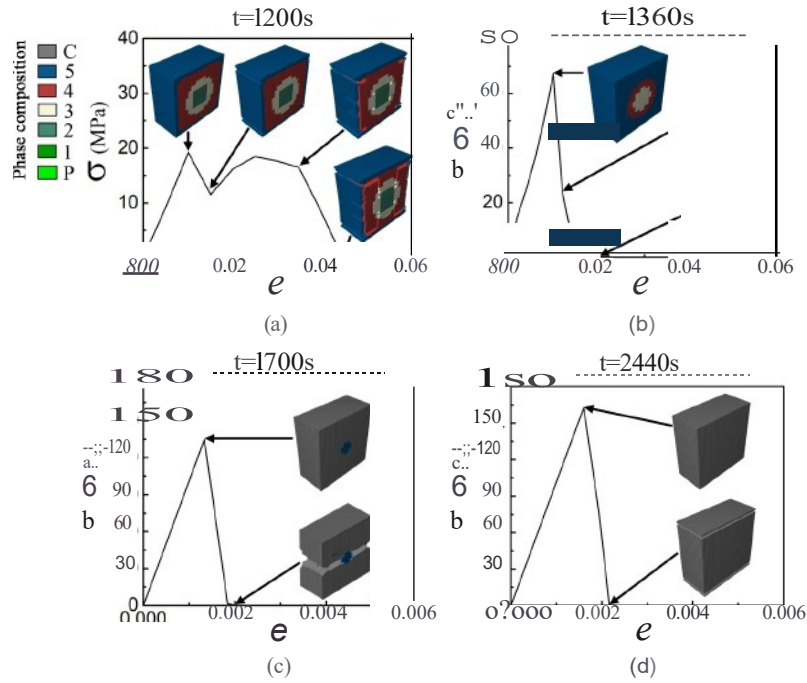


Fig. 9. Stress-strain curves with representative crack evolution snapshots at holding times of (a) 1200s, (b) 1360s, (c) 1700s and (d) 2440s, respectively. Heating rate is kept at 0.63K/s with pyrolysis temperature of 1273K.

1 phase 5 near the sample center and along the interface between phase 3 and phase
 2 4. The material completely loses its load bearing capacity when the new interfa-
 3 cial cracks coalesce with the existing cracks. When the holding time is increased to
 4 1360s and 1700s, no corner cracks are observed as the interface location is further
 5 away from the corner as indicated in Figs. 9(b) and 9(c). Damages start to initiate
 6 at the interface located at the center of the sample and quickly propagate along the
 7 0° plane. When the sample is fully converted to ceramics at 2440 s in Fig. 9(d),

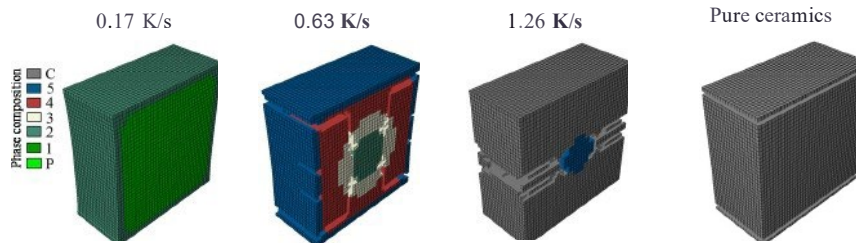
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Fig. 10. Phase composition and damage distribution at various heating rates. Holding time is 1200s and pyrolysis temperature is 1273K.

fracture surfaces are perpendicular to the loading direction and are very close to the top and bottom planes due to the boundary constraints [Cordero *et al.*, 2014; Zhang *et al.*, 2018].

It is worth mentioning that, when multiple intermediate phases co-exist, damages are prone to initiate at the interface near the sample surface. Crack bridging is primarily achieved through intermediate phases with low strength. Therefore, both high strength and high ductility are difficult to achieve simultaneously under uniform heating. Similar crack patterns are observed in samples that are subject to varying heating rates. As shown in Fig. 10, no crack is observed at the heat rate of 0.17K/s when the holding time and pyrolysis temperature are kept at 1200s and 1273K. Only phase 1 and phase 2 exist in the sample. This type of composition can effectively mitigate the load without causing any damage. When heating rate increases to 0.63K/s, four intermediate phases co-exist in the sample. This phase composition yields a more complex fracture pattern due to the coalesce of interfacial cracks between phase 4-phase 5 and phase 2-phase 3. When the heating rate is further increased to 1.26K/s, the majority of the sample has been converted to pure ceramics. Its crack pattern is very similar to the case in Fig. 9(c). This indicates that a single intermediate phase, especially a high ceramic fraction phase, is not as effective as multiple intermediate phases in crack bridging. Pyrolysis temperature has the same impact on material strength and fracture behaviors when the heating rate and holding time are fixed.

It can be concluded from the above study that pyrolysis of preceramic polymers in a closed furnace cannot yield PDC composites with high strength, high ductility and high toughness at the same time. This is due to the inherent phase evolution under uniform heating. A fundamental avenue to achieve flexible property tailoring, especially controlled phase composition generation, would require gradient heating with precise temperature control capability. Laser pyrolysis is a potential way to generate predefined phase composition. Our future work will explore the effect of varying the processing parameters, such as laser powers, scanning speeds, and focus vs. defocus on PDC phase distribution and mechanical response. The computational work developed here provides a useful tool to predict the phase composition map in any PDC samples under arbitrary heating/cooling histories.

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4. Summary

A multiscale computational model is developed to find the relationship among pyrolysis condition, phase transition and mechanical tensile response of PDC composites. The macroscale phase distribution is determined from the interplay between gas generation and gas diffusion. This model allows phase composition distribution to be explicitly extracted from arbitrary processing routes. The phase composition map serves as the input for finite element analysis. It is found that the MT model can only predict the effective elastic modulus in two-phase PDC composites under dilute situation. Property predictions in multi-phase or non-dilute two-phase PDC composites require advanced constitutive modeling in the intermediate phases. In this work, the constitutive law of each intermediate phase is determined through both experiment and simple tension simulation. It is found that the phase composition has a significant impact on the stiffness and strength of PDC composites. Microcracks tend to initiate at the interface between intermediate phases, especially those with ceramic fraction greater than 60%. Although intermediate phases with low ceramic fraction (<40%) can avoid microcrack formation, they cannot promote material strengthening due to their own low strengths. It is found that the optimized phase composition that can effectively bridge cracks without sacrificing strength cannot be achieved through uniform heating in a closed furnace. A more advanced pyrolysis design is required for achieving PDC composites with both high strength and toughness.

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