RAPID COMMUNICATION

New insight into SiOC atomic structure evolution during early stage of pyrolysis

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Abstract
This study focuses on the early stage of polymer-derived SiOC ceramic conversion. We demonstrate that the perceived SiOC phase separation is nonexistent. Instead, SiO_2 and free carbon clusters form first and then carbothermal reduction sets in to induce SiOC formation. Such fundamental understanding is supported by both synchrotron X-ray diffraction study and reactive force field simulation. This work for the first time unifies the understanding of atomic evolution process of polysiloxane-based polymer to ceramic conversion.

KEYWORDS
carbothermal reduction, polymer-derived ceramics, reactive force field (ReaxFF), SiOC, synchrotron X-ray diffraction

SiOC is an interesting polymer-derived material due to its simple synthesis process yet complex atomic structure after pyrolysis. As Si, O, and C have close atomic numbers and the resulting phases are either very small or amorphous or both, it is challenging to understand the atomic evolution during pyrolysis and the resulting phases and microstructures after pyrolysis, especially regarding the early stage of the pyrolysis at low temperatures. Because of atomic similarities, mixing of amorphous phases, and formation of small clusters of <5 nm, understanding of SiOC systems requires use of characterization techniques with high sensitivity and resolution. However, even high-resolution transmission electron microscopy (TEM) cannot distinguish amorphous phases of SiO_2, SiO_3C, SiO_2C_2, and $SiOC_3$ (SiO_xC_y) apart. Our 4D scanning TEM work attempted to distinguish the phase distribution of SiOC systems, but the information is for a specific pyrolyzed state.[1] On the theoretical side, we have developed a Gibbs energy minimization approach to calculate the percentages of different amorphous phases.[2–4] Still, the exact

thermodynamic process is unknown and the calculated phase amounts cannot be verified.

In the literature, it was proposed that SiOC glass undergoes phase separation during pyrolysis, forming SiO_2, and SiC (Equation 1), with the process starting at 1200°C.[5,6] At temperatures >1300°C, the precipitation of SiC nanocrystallites embedded in vitreous SiO_2 was identified by high-resolution TEM.[5] The claim for this chemical reaction mainly originated from the electron energy loss spectroscopy observation that Si–O bond feature became more pronounced at 1400°C.[5] Because the peak corresponding to the Si–O bond was not observed at 1000°C through X-ray diffraction (XRD) Rietveld refinement,[6] it was assumed that the Si–O bond feature at 1400°C represented a phase-separation process.

$$2SiOC \rightarrow SiO_2 \, (amorphous) + SiC \, (\beta) + C \qquad (1)$$
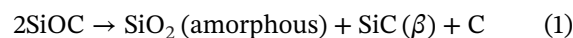
Others[7] and our group[2,3,8] also took this claim and assumed that the SiOC separation proceeded the

carbothermal reduction process. However, the interpretation of the mechanisms can be wrong even when phase characterization was properly carried out. For example, white Si−O−C(−H) particles were synthesized from a silicone resin precursor. Pyrolysis of the precursor particles in a hydrogen atmosphere allowed removal of excessive carbon.[9] If SiOC phase separation started at 1200°C, then SiC would have formed. In reality, this has not been observed until 1400°C.[9] Only amorphous SiO_2/SiOC halo was observed even though the study also cited SiOC phase separation from earlier work.[5,10]

In this study, high-energy XRD (HE-XRD) and reactive force field (ReaxFF) molecular dynamics (MD) simulations were used to understand the phase evolution and atomic interaction during the early stage of the SiOC pyrolysis. The work shed new light on the Si, O, and C bonding tendency and the SiO_xC_y phase change during the ceramic formation process.

Two polymer systems were studied. The first system contained 85 wt% polyvinylmethylsiloxane (PVMS, 41.86 wt% C in the repeating unit) + 15 wt% polyhydromethylsiloxane (PHMS, 20.00 wt% C in the repeating unit) and was simply labeled as PVMS. Both chemicals were from Gelest Inc. (Morrisville, PA, USA). The second system was polysiloxane SPR-684 Polyramic (59.55 wt% C in the repeating unit, Starfire Systems, Inc.) and was simply labeled as PSO. 2.1–2.4 wt% platinum−divinyltetramethyldisiloxane complex in xylene (Gelest Inc.) was diluted in toluene and used as a catalyst. Overall, the precursor carbon content was 38.58% for the PVMS system and 59.55% for the PSO system. The cross-linking was at 50°C for 12 h and then at 120°C for 12 h. Pyrolysis was conducted in a horizontal tube furnace (model No. 1730–12, CM Furnaces Inc.) at 1200 and 1500°C for 2 h, respectively, with the heating and cooling rates at 2°C/min in flowing Ar gas. The high-energy synchrotron XRD measurements were conducted at the 11-ID-B beamline at the Advanced Photon Source (APS, at the Argonne National Laboratory).

To further understand the siloxane-based polymer decomposition and interactions of the constituting Si, O, and C species, a ReaxFF energy potential[11,12] in conjunction with LAMMPS[13] was used to simulate the polymer to ceramic conversion. ReaxFF is fundamentally an MD simulation method. It originated from simulations of the initial oxidation process of an SiC surface exposed to O_2 and H_2O molecules and is an atomically detailed reactive MD method that naturally models the breaking and forming of bonds. The approach describes Si–Si, Si–O, Si–H, Si–C–O, and Si–O–H bond interactions. It can also simulate C–C bond formation.[11,12,14,15] In this study, the polymer chains were allowed to relax using NPT for 80 000 timesteps at 0.2 fs per timestep. To mimic the formation of gas during the pyrolysis, a new method of gas deletion was
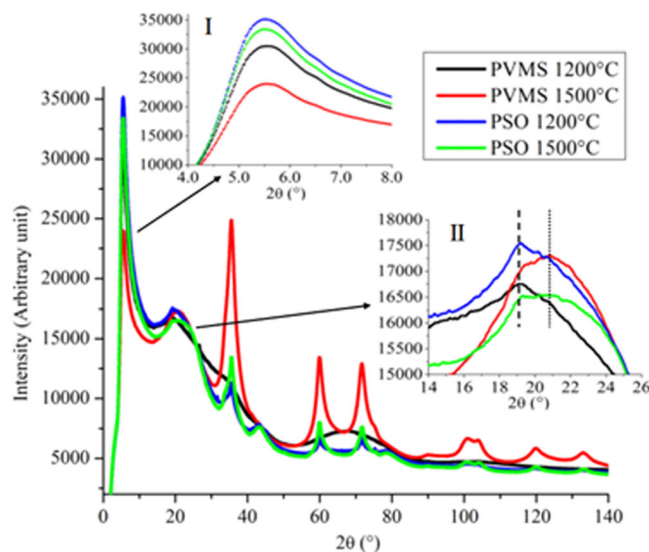

FIGURE 1 High-energy X-ray diffraction (HE-XRD) data from synchrotron X-ray study. The inset I shows the orthorhombic SiO_2 peak at ~5.5°; the inset II shows the amorphous SiO_4/SiO_3C/SiO_2C_2/$SiOC_3$ halo at 18°–23°.

created in Python to remove specific molecules consisting of CH_4, C_2H_2, C_2H_4, C_2H_6, C_6H_6, CO_2, CO, CH_2O, H_2O, O_2, and H_2. The specific molecules were determined based on the yield data from our experimental work,[16–19,8,20–23] which correlates well with many of the molecules deleted in studies by Kroll and Gao.[11,24] The time between deletions was 5 ps. The types of molecules deleted were kept consistent throughout the entirety of the simulation.

Figure 1 shows the HE-XRD data from synchrotron X-ray study. For the first time, we identified that during the SiOC pyrolysis, both amorphous SiO_2 and crystalline SiO_2 (more specifically tridymite, which is orthorhombic) form. The peak centering at 44.4° is indexed as graphitic C (JCPDS Card No. 00-075-1621). The diffraction peaks at 35.7°, 60.1°, and 71.9° correspond to the (111), (220), and (311) crystalline planes of the β-SiC phase (JCPDS Card No. 01-073-1665). In the conventional XRD characterization, only amorphous SiO_2 with a halo at 22°–23° is detected.[17,2] This is because HE-XRD can detect diffraction peaks at small 2θ angles (such as <10°). If the phase separation reaction (Equation 1) is true, then C-rich systems should less likely lead to SiO_2 formation. However, Figure 1 shows that the result is opposite. For both C-rich SiOC systems of PVMS and PSO, even at 1200°C, crystalline SiO_2 (tridymite, orthorhombic) is observed. The crystalline phase formation for SiO_2 means that the SiO_2 domain size is large enough for crystallization to occur. For the first time, based on the persistent and distinct peak of orthorhombic SiO_2, it shows that crystalline SiO_2 forms before detection of crystalline SiC. This is consistent with the absence of SiC peaks for the PVMS and PSO

samples pyrolyzed at 1200°C. Such results would not support the SiOC phase separation theory. The orthorhombic SiO_2, after all, is simply the well-known tridymite phase, which forms from 870 to 1470°C and has been well accepted. In addition, the C-rich PSO system shows a higher crystalline SiO_2 peak than the less C-rich PVMS system. Even though more C is present, it still demonstrates preferential formation of SiO_2 (likely orthorhombic and amorphous SiO_2, depending on the cluster size) in the overall SiOC system. This again refutes the SiOC phase separation theory.

As stated earlier, the PSO sample has more C, yet the orthorhombic tridymite peak is the highest. The 5° peak was also observed in the more Si-rich cage-like precursors.[25] For different siloxane-based polymers, Si–O bond is intrinsically present on the polymer backbone. During the polysiloxane decomposition, active radicals are generated at low pyrolysis temperatures. With the radical formation, the Si–O bonds on the polymer chains have higher affinity than the Si–C bonds on the side groups. The active Si–O bonds can easily regroup and form SiO_2 clusters. When free C is present, the overall stoichiometry indicates SiOC. However, if C does not diffuse into the SiO_2 cluster structure, SiO_2 continues its growth process and forms tridymite SiO_2.

The 18°–23° halo is consistent with the result from conventional XRD, which designates them as amorphous SiO_2/SiOC tetrahedrals. The slight right shift of this halo for both the PVMS and PSO samples after 1500°C pyrolysis (in comparison with the 1200°C pyrolysis halos) indicates that the C-rich systems have induced C diffusion into the amorphous SiO_2 structure, leading to more C-rich SiOC tetrahedrals with the consumption of orthorhombic SiO_2. With continuous C diffusion into the SiOC tetrahedrals, SiC_4 also forms, manifested by the cubic SiC peaks at 1200°C for the PSO sample (the blue curve). Thus, the presumed two-step process of SiC formation during the SiOC pyrolysis, SiOC phase separation, and carbothermal reduction is just one integrated process of SiO_2 and C carbothermal reduction. Equation (1) is a hypothetical process that does not exist.

We also believe that the C species from the polymer side groups is directly responsible for the formation of free C. This is because the C from the polymer side groups is the only C source in the pyrolyzed SiOC systems. Considering the highly C-rich nature, as we have reported earlier,[2,18,26] most of the C species should be in an amorphous state. The C peak detected at 44.4° for the pyrolyzed PSO system should be from the limited amount of graphitic C.[2] In fact, the presence of the graphitic C peak for the PSO system yet the absence of the graphitic C peak for the PVMS system at 1200°C reflect the C-rich nature of the PSO precursor. Regardless, the diffusion of the C species into SiO_2 should be mostly from the amorphous C because the crystalline C amount is limited.

Interestingly, both 1500°C pyrolyzed samples show weaker orthorhombic SiO_2 peaks compared to the 1200°C pyrolyzed samples (inset I in Figure 1). This means that orthorhombic SiO_2 is consumed with the formation of cubic SiC through carbothermal reduction. C presence and then diffusion can further hinder SiO_2 crystalline phase formation. This also explains why the amorphous SiO_2 phase is resistant to crystallization. More importantly, the 18°–23° halo, with its right shifting center, demonstrating C diffusion into the SiO_2 network (inset II in Figure 1). The specific halo center is determined by the relative amounts of SiO_4/SiO_3C/SiO_2C_2/$SiOC_3$ tetrahedrals. Although it is impossible to differentiate SiO_4/SiO_3C/SiO_2C_2/$SiOC_3$ species, the slight right shift of the halos indicates the formation of more Si–C bonds and consumption of the Si–O bonds, such as from SiO_4 and SiO_3C species. It should also be noted that the PVMS sample still has no graphitic C formation, and the graphitic C peak for the PSO sample after 1500°C pyrolysis remains almost the same as that for the 1200°C pyrolyzed sample. Such limited graphitic C formation at high pyrolysis temperatures again indicates that C is being consumed by Si–O carbothermal reduction, without much chance for its crystalline phase growth.

The HE-XRD data only show the final pyrolyzed state and the overall phase/crystallinity information. There is no experimental method available to examine atomic structural evolution at a local scale, especially in the early stage of the pyrolysis when the decomposed polymer converts into amorphous ceramics. ReaxFF simulation can provide insight into the atomic evolution process below 1200°C pyrolysis temperatures. It can also provide local domain/cluster separation process. More excitingly, it can provide quantitative bond fraction data for each polymer precursor system and fill the understanding void that cannot be resolved by experimental work.

Figure 2 shows the atomic structure evolution during pyrolysis for the two SiOC systems at 1800 K simulation temperature (~1200°C experimental temperature). Even though the hydrogen content is high in atomic percent, the weight content is only ~1%. In this study, the hydrogen species is removed from the images for display clarity. Figure 2A–C is for the PVMS derived system. Figure 2D–F is for the PSO-derived system. With these two systems, C effect on phase evolution can be observed. At the initial stage of the pyrolysis, the overall atomic structures are homogeneous; Si and O atoms form fractal structures (Figure 2A,D). There are more and larger Si–O rich fractal structures for the PVMS system. These fractal structures resemble the initial polymer chain backbones and manifest themselves as long-strand, zigzag clusters. This is more so for the C-rich PSO system. In-between the
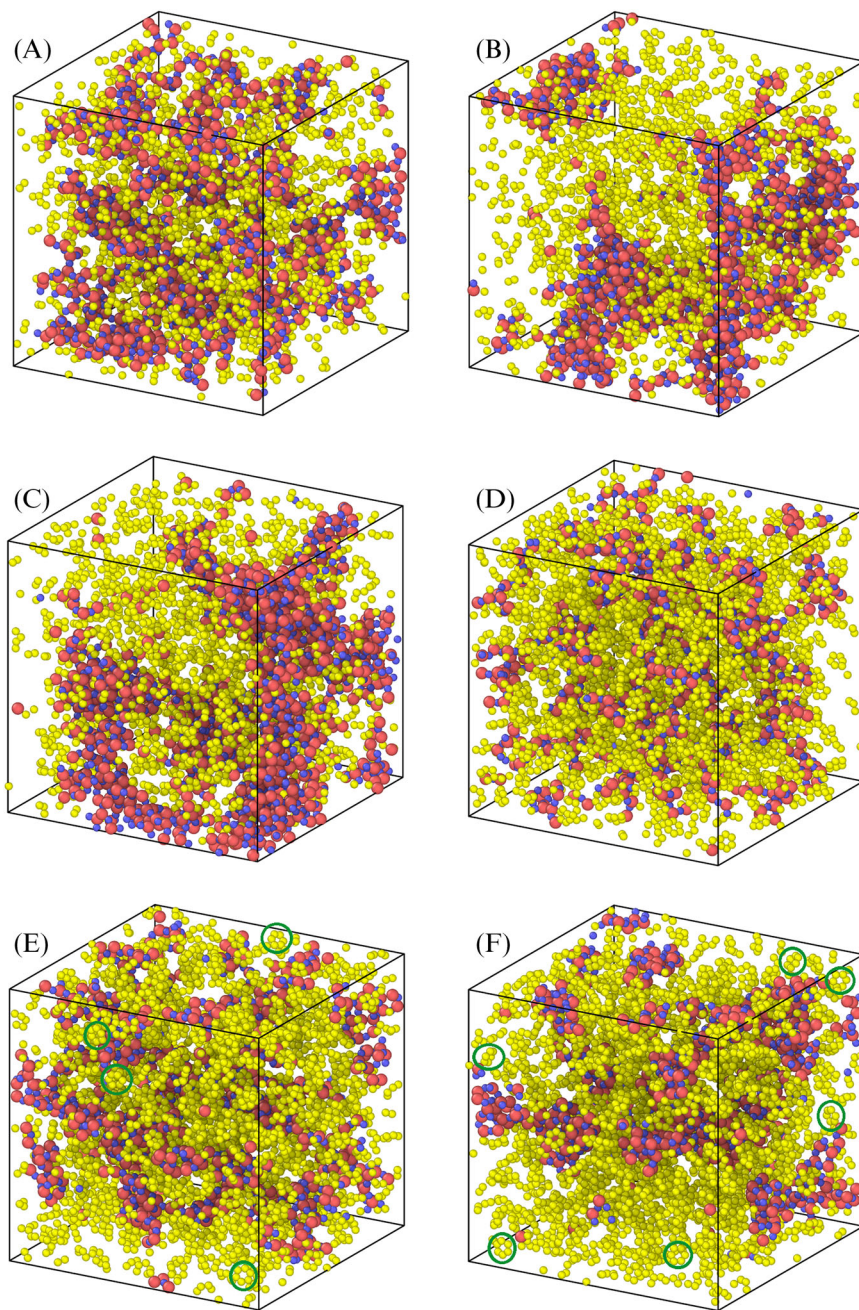
FIGURE 2 Simulated microstructures of polyvinylmethylsiloxane (PVMS) and PSO: (A) PVMS system reaching 1800 K, (B) PVMS system holding at 1800 K for 0.5 ns, (C) PVMS system holding at 1800 K for 1 ns, (D) PSO system reaching 1800 K, (E) PSO system holding at 1800 K for 0.5 ns, (F) PSO system holding at 1800 K for 1 ns, and (G) bond change with simulation time. In all the images, the color scheme is as follows: Si-red, O-blue, C-yellow.
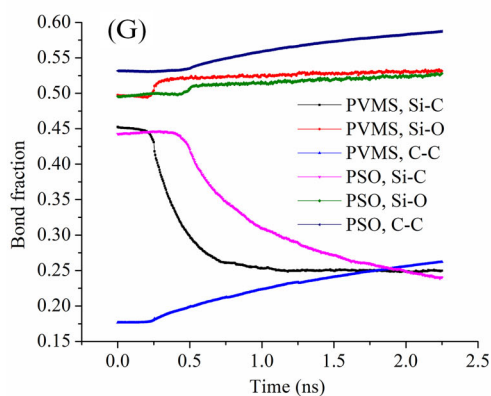
fractal structures are C atoms, which are believed to cleave from the polymer chains and become free C, intimately mixed with the Si−O rich regions. The amount of C is also proportional to its interpenetration in-between the Si−O rich structures. The more Si−O rich system (PVMS) shows more SiO_2 clustering and thus large SiO_2 domain sizes; for the less Si−O rich system (PSO), C regions are more prevalent (Figure 2D). In addition, rings with six carbon atoms (indicated by green circles) are seen for the C-rich PSO system, indicating the formation of graphitic C away from the Si−O rich clusters. Overall, SiO_2 and C coexistence indicate the atomic structure evolution after the polymer decomposition.

With the pyrolysis time increase, the SiO_2 clusters grow and become less connected for both systems (Figure 2B,E). As a result, C separates the Si−O rich clusters. The less C-rich PVMS system has larger size SiO_2 clusters, consistent with its more Si-rich nature. From Figure 2A to B or from 2C to D, the atomic structure evolution simply demonstrates an aggregation/growth of Si−O rich and C-rich clusters; there is no indication of SiOC phase separation as initially there is no SiOC formation, except for some intermixing of Si−O rich fractals and C atoms. With further pyrolysis, the C domains and the SiO_2 clusters also grow larger. As the C phase is continuous, its size is related to the SiO_2 cluster separation distance. Overall, SiO_2 formation after the polymer chain disintegration can clearly be observed. C forms through the separation of the C-containing side groups from the polymer backbones. Even though the morphologies of these species are poorly defined and may even be intertwined, there is no presence of intermediate species SiOC.

With further pyrolysis (Figure 2C,F), the SiO_2 and C phases become more developed. Some C diffuses into the Si−O rich domains and leads to the carbothermal reduction of Si−O regions. For both parts (E) and (F) of Figure 2, abundant six-C rings can be observed (outlined by the green circles), indicating graphitic C formation due to the C-rich nature of the PSO precursor. Thanks to the amorphous state and thus higher mobility of the free C species, it starts to diffuse into the porous SiO_2 structure. Even though the SiO_2 structures are covalently bonded, rigid, and thus not mobile, the open structure of SiO_2 can accept the diffusing C species, especially considering the small C atom size.

The atomic bond ratio change with time for the PVMS and PSO systems also demonstrates the cluster evolution process. In this work, the Si−Si, Si−O, and Si−C bonds were normalized to the total number of Si-containing bonds, and the C−C bond was normalized to the total number of carbon-containing bonds. As shown in Figure 2G, the Si−C bonds decrease significantly with the pyrolysis time, with the PVMS system having more and earlier Si−C loss,

which is a manifestation of the C-containing side group breaking and separation from the Si−O polymer backbone. The difference between the two polymer precursor systems indicates that it is easier to decompose the PVMS polymer system. This event is drastic initially and then stabilizes with the pyrolysis time increase. In the end, the Si−C bond loss continues further for the PSO system. Increase in pyrolysis time at such a low pyrolysis temperature will not lead to new Si−C covalent bond formation to replace the Si−O bonds (carbothermal reduction). The slight increase in the Si−O bonds for both precursor systems is related to Si−O rich cluster formation and C-containing gas release. The C−C bond increase with the simulation time indicates the C cluster growth. The striking difference in the C−C bond fraction reflects the C amount in the two systems. The lower amount of C−C in the PVMS system can be directly seen in Figure 2A−C, which shows no sign of graphitic C. The above bond changes indicate that during the polymer decomposition and free C formation, the Si−O rich clusters and free C regions simply stay mixed. With the pyrolysis temperature increase, they, respectively, grow with limited C diffusion into the SiO_2 clusters in the form of carbothermal reduction.

C diffusion into the SiO_2 clusters is more prevalent at higher pyrolysis temperatures, as shown in Figure 3 for the microstructures at 2100 K simulation temperature (~1500°C experimental temperature) at 1 ns holding condition. At the C region and SiO_2 cluster interface, C atoms diffuse into the open SiO_2 clusters and reside in the interstitial voids of the Si−O atomic structure. There is a much smaller amount of Si−O rich clusters in the C-rich region. For the less C-rich PVMS system, C atoms diffuse into the SiO_2 clusters individually. For the more C-rich PSO system, C atoms stay as small clusters in the SiO_2 cluster. This gradually converts SiO_2 into SiOC with a wide range of stoichiometry. The C distribution is nonuniform, indicating the diffusion direction of C from high C content region to low C content region (as indicated by the large green ovals). Contrary to the assumption that SiOC phase separates into SiO_2, C diffuses into the SiO_2 structure, reduces O dominance, converts SiO_2 into SiOC, and eventually changes SiOC into SiC with CO release. This is the well-recognized carbothermal reduction. For the entire process, there is no SiOC phase separation. This is feasible because of the presence of free C and its diffusion into the open-structured SiO_2.

This study demonstrates for the first time that there is no SiOC phase separation during SiOC ceramic conversion from siloxane-based polymers. Both HE-XRD and ReaxFF simulation results are presented. Contrary to the general claim of SiOC formation and then phase separation, Si−O chains preferentially form Si−O clusters along with free C. These two types of clusters separately grow.
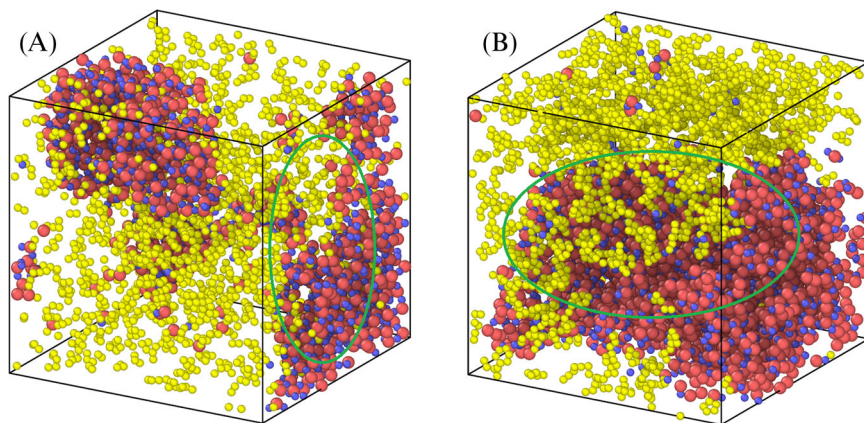
FIGURE 3 C diffusion into Si–O rich region at 2100 K simulation temperature at 1 ns holding for: (A) polyvinylmethylsiloxane (PVMS) precursor, (B) PSO precursor. In both images, the color scheme is as follows: Si-red, O-blue, C-yellow.

During high-temperature pyrolysis (such as at ≥1200°C pyrolysis temperature), C diffuses into SiO_2 open structures under the mechanism of carbothermal reduction. With longer pyrolysis time and especially higher pyrolysis temperature, this leads to more Si–C bonds and formation of intermediates SiOC, and eventually SiC.

CONFLICTS OF INTEREST
The authors declare that they have no known competing conflicts of interest or personal relationships that could have appeared to influence the work reported in this paper.

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