Synthesis and characterization of carbon-enriched silicon oxycarbides

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Abstract

Polyhydridomethylsiloxane (PHMS) is a very practical and versatile source for a broad range of silicon oxycarbide (SiOC) and other silicon containing ceramic materials. PHMS modifications and crosslinking is conveniently achieved by dehydrocoupling and hydrosilylation reactions. The molecularly level mixed carbon content of the derived SiOC can be incrementally increased by reacting PHMS with 0–40 mol% of divinylbenzene (DVB) using 5 ppm of Pt catalyst relative to PHMS. With ceramic yields exceeding 80 wt.% and a dense microstructure, the derived carbon-enriched SiOCs exhibit significantly higher chemical stability compared with other high-carbon content polymer derived ceramics. Phase separation and nanocrystallinity are inhibited to at least 1200 °C for all the evaluated samples and the materials are completely amorphous. Very fine nanocomposite microstructures are obtained at 1450 °C, consisting of 5–10 nm graphite regions and amorphous SiOC domains with no significant porosity. Synthesis and microstructure characterization of the new carbon-enriched SiOC are discussed in comparison to the sole PHMS pyrolyzed product.
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Keywords: Nanocomposites; Microstructure; Precursors-organic; Chemical properties; Polymer-derived SiOC

1. Introduction

Silicon oxycarbides (SiOC, also known as black glass) derived from crosslinked organopolysiloxanes or processed by sol–gel techniques have been the subject of numerous research efforts and development of practical applications in the past 15 years.[1–18] In particular, they were investigated as precursors to composite matrices,[19,20] silicon carbide formed in situ via carbothermal reduction,[21–23] and ceramic foams[24–29] using polymer processing techniques. A renewed interest in these materials in the past few years has been observed because of their exceptional characteristics. They are predominantly amorphous up to 1300 °C and exhibit high-temperature creep and chemical resistance relative to silica. More recently, tailored SiOC-based compositions have demonstrated good oxidation resistance at temperatures above 1000 °C, provided that they possess a low level of excessive carbon content beyond the stoichiometric formula of $SiO_{2(1-x)}C_x$.

It is commonly understood, corroborated by experimental results, that an excessive level of carbon in polymer derived ceramics leads to lower thermal stability and inferior oxidation resistance.[20,30] Rationally, the presence of carbon domains should be more vulnerable to high-temperature oxidation. The excess of carbon is well known in the literature as "free" carbon (C_{free}). Consequently, much attention in developing SiOC applications has focused on minimizing the over-stoichiometric amount of carbon as expressed in the following equation: $SiO_{2(1-x)}C_x + yC_{free}$, where $x + y$ is the molar ratio of the carbon relative to the silicon content.

In a recent effort to develop a ceramic matrix composite (CMC) built on a combined method of preceramic polymer infiltration technology and reaction bonded silicon carbide (RBSC), a new type of precursor to SiOC was designed and synthesized. This precursor intentionally contained a significantly high molar fraction of "C_{free}". The carbon source was explicitly incorporated at the molecular level by catalyzed hydrosilylation reaction between polyhydridomethylsiloxane (PHMS) and divinyl benzene (DVB). The carbon-enriched polymer-derived SiOC was anticipated to strongly interact with molten silicon to form a silicon carbide matrix through a

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combination of carbothermal reduction and reaction-bonded silicon carbide:

$$SiO_mC_n + Si_l^* \rightarrow SiC + Si^*C + CO_2 \qquad (1)$$
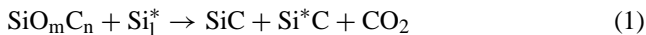
Si*: silicon derived from the infiltrated molten silicon.

Nevertheless, these new high-carbon-content SiOC materials demonstrate unexpectedly high thermal, chemical, and environmental stability, as well as remarkable microstructural stability at their amorphous stage (at least up to 1200 °C). Also, visual observation revealed that pyrolyzed pieces of bulk precursors remain intact even after heating to 1450 °C as a result of the additional carbon content, while bulk PHMS tends to shatter during the heating process. These physical and chemical observations, combined with the ease of introducing the carbon content in a controlled fashion, have prompted further investigation of the characteristics of this new type of precursor to carbon-enriched SiOC.

2. Experimental procedures

2.1. General procedures and synthesis

Polyhydridomethylsiloxane was purchased first from United Chemical Technologies, USA, and later on from Gelest, USA. Activated molecular sieve beads were added to dry the liquid polymer from residual water. 1,3,5,7-Tetramethyl-1,3,5,7-tetravinyl-cyclotetrasiloxane 95% and 2.1–2.4% platinum-divinyltetramethyldisiloxane complex in xylene was purchased from Gelest and diluted further in xylene to provide a solution containing 5.89×10^{-2} wt.% of catalyst. Divinylbenzene (technical 80%, mixed isomers) was purchased from Sigma-Aldrich and used as received.

2.2. Crosslinking (curing) of PHMS

A mixture of PHMS (20.0 g) and Vinylmethyltetracyclomer (1.0 g; 5 wt.%) was prepared without any additional solvent. An amount of 0.17 g of 5.89×10^{-2} wt.% solution of Pt catalyst in xylene was added to the mixture (5 ppm relative to PHMS). The low-viscosity mixture was placed in a glass dish forming a 3 mm thick layer, and it was covered to eliminate excessive incorporation of oxygen via a side reaction of dehydrocoupling with moisture.

The cast solution was allowed to stand overnight at RT until complete gelation was observed. (*Note*: the reactivity is very sensitive to temperature, thus the curing time can vary between one hour to overnight depending on the actual room temperature.) The curing can be accelerated at 40 °C. The cured material is a hard and brittle rubbery material with very high level of transparency. After room-temperature curing, the specimens were heated gradually to 120 °C in dry air and kept at this temperature overnight for completion of curing. The cured material was broken to pieces with convenient size for the pyrolysis step.

2.3. Reaction and curing of PHMS with divinylbenzene

The platinum catalyst (always 5 ppm relative to PHMS) and various quantities of divinylbenzene were first mixed together and then added to the polymer. Amounts of 20, 40, 60, and 85 wt.% of divinylbenzene relative to the polymer were used to prepare a series of carbon-enriched SiOC products. The rest of the procedure was carried out as described above for PHMS itself. After RT gelation, all the cured products are hard rubbery materials with increased level of ductility as the level of divinylbenzene increases. The materials are glassy and highly transparent in their nature. They were cut with a sharp knife to about 2 cm × 2 cm squares before pyrolysis.

2.4. Pyrolysis of cured PHMS-based polymers

The various cured polymers are pyrolyzed under argon in a Lindberg tube furnace, equipped with alumina tube. The standard heating rate was 5 °C/min to reach the desired temperature and was kept at that temperature for 1 hour before cooling down.

2.5. Characterization

Elemental analyses of C, H, and Si were performed by Galbraith Laboratories, Knoxville, TN, USA. Elemental O analysis was performed by ATI Wah Chang, Albany, OR, USA. Thermal Gravimetric Analysis was performed by TA Instruments' TGA2050 under an argon atmosphere.

Microstructural characterization of powder samples was performed by SEM using (1) a LEO 435 instrument and (2) a FEI Quanta600 instrument operating at 30 keV. Prior to imaging, the samples were gold-coated to avoid charging under the electron beam. In addition, TEM was employed using a FEI CM200STEM microscope operating at 200 keV. Here, TEM-foils were prepared employing standard ceramographic techniques, which involve cutting, grinding, dimpling and Ar-ion thinning to perforation. To minimize charging during TEM imaging, the samples were lightly coated with carbon. Local chemical analysis was performed with a PGT EDX system with a thin-window Si detector.

3. Results and Discussion

3.1. Synthesis and curing of precursors

The synthesis of the precursors, as illustrated in Scheme 1, is based on grafting and crosslinking polyhydridomethylsiloxane (PHMS) with divinylbenzene (DVB) using a hydrosilylation reaction in the presence of a very efficient platinum catalyst. Only 5 ppm (relative to PHMS) of 1,3-divinyltetramethyldisiloxane platinum complex is added to the low-viscosity liquid mixture. No additional solvent is necessary, with the exception of the small amount of xylene added for diluting the catalyst solution prior to its blending.
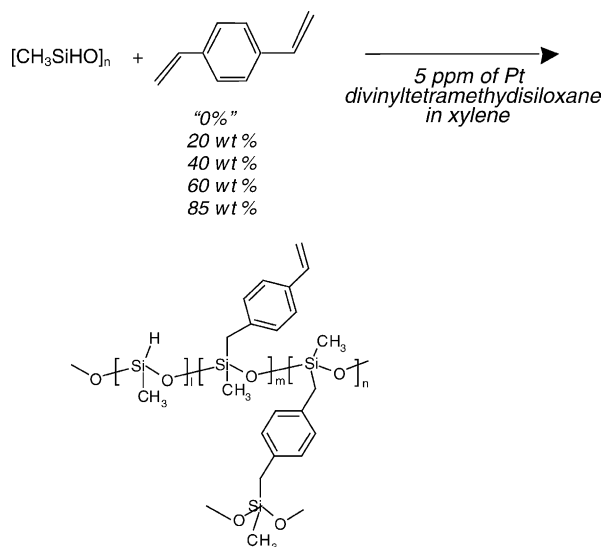
Scheme 1. Synthesis of high-yield precursors to high-carbon-content SiOC.

Fig. 1. TGA plots of the various PHMS formulations.

Typically, the formulation is converted overnight at room temperature into a rubbery material with various degrees of brittleness. To guarantee the maximum level of crosslinking, the polymers were further heated at 120 °C for 24 h in dry air. The evolved rubbery materials were completely dense and transparent. The degree of brittleness of the cured material is reduced as the amount of DVB increases. This reduced brittleness is interestingly manifested also at various pyrolysis and high-temperature heat treatment stages of the carbon-rich material.

The "0%" DVB material is PHMS crosslinked by 5 wt.% of tetramethyl-tetravinyl-cyclotetrasiloxane. In previous studies the PHMS has been found to be a very versatile polymer for both ceramic[31–33] and polymeric[34,35] applications by employing extremely effective catalytic reactions of hydrosilylation (with Pt complexes) and/or dehydrocoupling (with homogeneously dissolved $Ru_3(CO)_{12}$).[36] The combination of these reactions allows the formation of many functional polymers and the manipulation of PHMS to fit the processing requirements of a given application. Most of the combination reactions are performed in a "one pot reaction", and in many cases the reaction solution is used "as is" for further processing.

3.2. Precursor pyrolysis

Highly cured materials have been obtained by employing the hydrosilylation reaction alone, without intentional incorporation of additional oxygen into the cured precursor. Therefore, the overall level of oxygen remains very similar in all the pyrolyzed SiOCs. The DVB serves all together as (a) reactive cosolvent, (b) carbon content enhancer, and (c) crosslinking agent. The crosslinking reactivity is very efficient, resulting in very high ceramic yields (over 80%) for the series of materials when pyrolyzed in argon, as shown from the thermal gravimetric analysis (TGA) profiles (Fig. 1). The pyrolysis
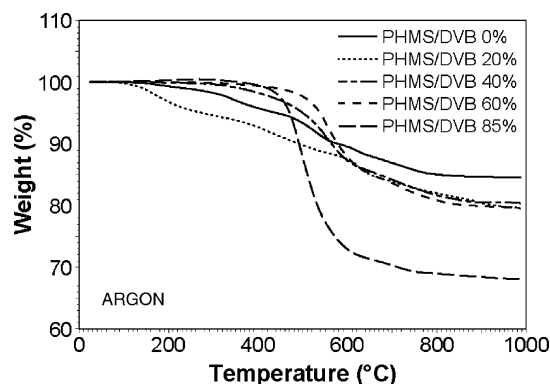
in the discussed set of experiments was carried out under argon, using heating rates of 5 °C and 10 °C/min with a dwell time of 1 h at the maximum heating temperature. No interim-temperature hold periods were used.

Fig. 1 indicates that the ceramic yields decrease only when the DVB added exceeds 60 wt.% of PHMS. It means that up to 60 wt.%, the reacted DVB predominantly bonds to two silicon atoms and serves as a crosslinking unit. Further increase of the reagent (i.e., the 85 wt.% addition) results in a significant molar fraction of DVB as either pendant groups or self-polymerized that are hydrosilylated to the polymer backbone through a single vinyl site, and this fraction is no longer serving as crosslinking units. Notice that the 85 wt.% DVB material remains thermally stable at its polymeric stage up to 500 °C without any weight loss. This remarkable thermal stability for a thermoset polymer reveals the potential of using these hybrid materials for applications in which the temperature exceeds 400 °C.

3.3. Characterization of polymer-derived ceramics

Fig. 2 illustrates a remarkable linear relationship between the fractional addition of DVB and the final carbon content of the SiOC. The molar ratio of O:Si remains almost constant (values are near 1:1) throughout the entire series of DVB variations. This steady ratio indicates that the occurrence of either the dehydrocoupling[36] or oxidation reactions during the curing step (performed in air) was negligible in this set of experiments.

The density of the derived SiOCs is reduced with the increased level of C_{free} as shown in Fig. 3. However, the density increases for each of the varied levels of C_{free} when the maximum heating temperature is increased. The increased density must be associated with rearrangement at the molecular and nanoscale level, since the very low surface area (less than 1 m²/g) and early nanostructure analysis reveal that these materials do not contain nanoporosity and remain predominantly amorphous up to at least 1200 °C, for both the base PHMS-derived material and the material derived from PHMS with 60 wt.% DVB, as shown in the corresponding high-resolution TEM images given in Fig. 4.
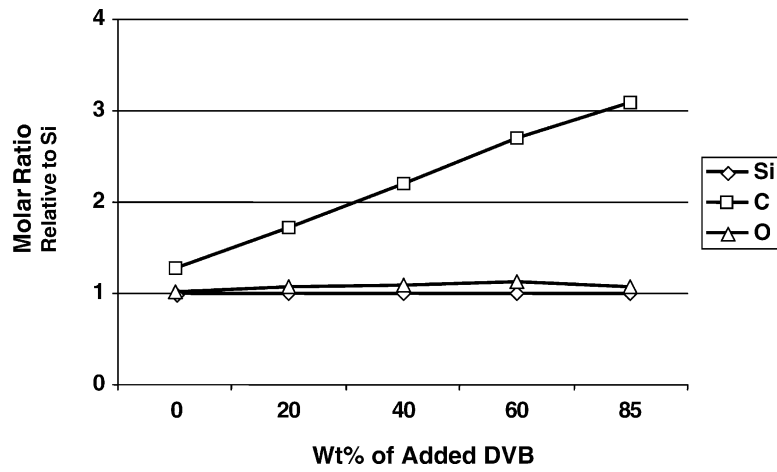
Fig. 2. Linear relationship between the wt.% of added DVB and the final carbon content of SiOC.
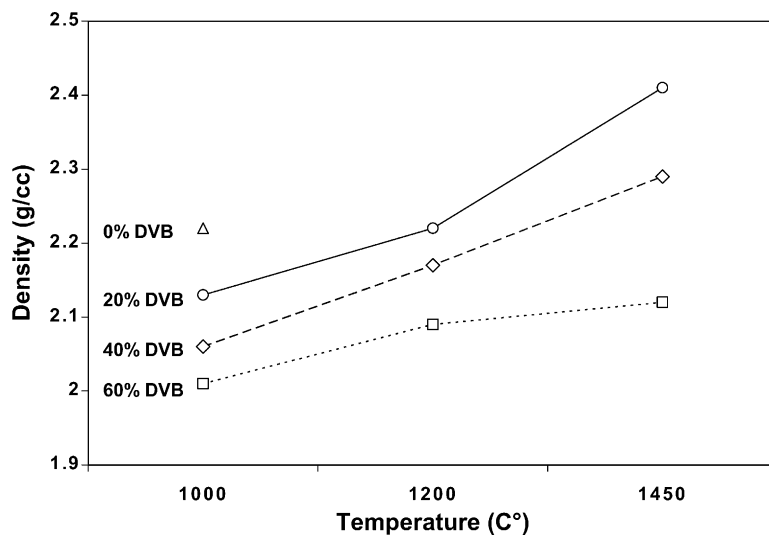

Fig. 3. Density of SiOC as a function of carbon content and temperature.
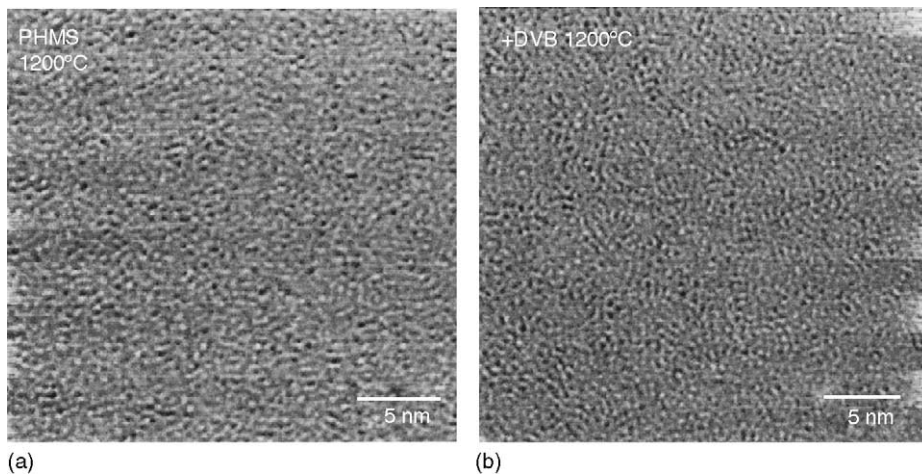

Fig. 4. HRTEM images of (a) PHMS and (b) PHMS + 60 wt.% DVB, pyrolyzed and annealed at 1200 °C.
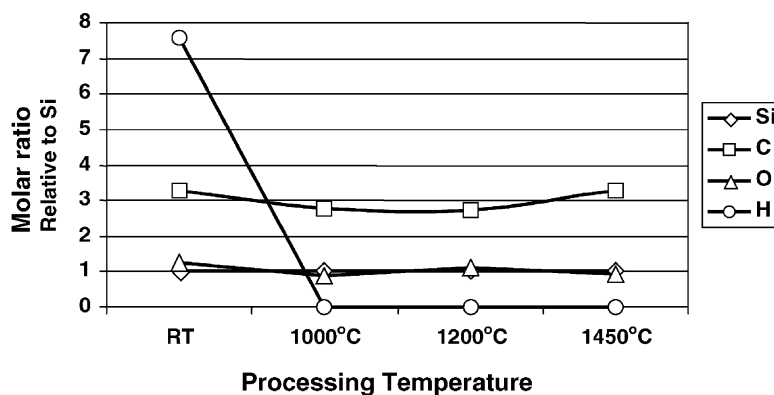
Fig. 5. Retention of SiOC atomic composition of PHMS–60 wt.% DVB as a function of temperature.

Previous research efforts to synthesize SiOCs with high carbon content have been performed to achieve efficient carbothermal reduction[23] or prove their lack of stability in an oxidative environment.[30] Nevertheless, the PHMS–DVB-derived materials demonstrate remarkable composition stability even when heated up to 1450 °C for short periods, suggesting that the carbothermal reduction is drastically inhibited in spite of the favorable molecular blending of the carbon and oxycarbide domains. As illustrated in Fig. 5, there is no significant change in the Si:O:C ratio of SiOC derived from 60 wt.% DVB between the materials developed at 1000 and 1450 °C, indicating that no major release of CO associated with the carbothermal reduction has occurred. Carbothermal reduction including the formation of crystalline SiC, is observed only after prolonged heating at 1450 °C.

Fig. 6 reveals a comparison of the pure PHMS material and the sample with additional 60 wt.% DVB upon heat treatment at 1450 °C. Note that the graphitic carbon is clearly visible in the DVB-containing sample (embedded in an otherwise amorphous matrix), while in the pure PHMS material only a rather small fraction of phase-separated graphitic domains was observed. It is worth mentioning that this material was also found to be predominantly amorphous even after annealing at 1450 °C.

The original plan for developing these high-carbon-content SiOC hybrids was their "reactive" use in RBSC composites. However, their reactivity with molten silicon was found to be limited to a reactive zone of only 1–2 μm in depth, even in the case of the 60 wt.% DVB product, as shown in Fig. 7. The micrograph shows the formation of SiC only in close proximity to the molten silicon (light color). An interface zone between the formed SiC and the amorphous SiOC is also observed (lighter color than the SiC zone), but has not been characterized in detail.

Finally, preliminary oxidation studies have revealed that even at the high carbon content of the PHMS plus 60 wt.% DVB, the materials are significantly resistant to oxidation in ambient air at 1000 °C (Fig. 8). This observation differs from results obtained with other sol–gel-derived SiOCs possessing similar levels of carbon; these materials suffer from severe oxidation even at temperatures as low as 700 °C.[30] The unexpected oxidation resistance of the new materials is currently under study in comparison with low-carbon sol–gel-derived SiOCs.[37]
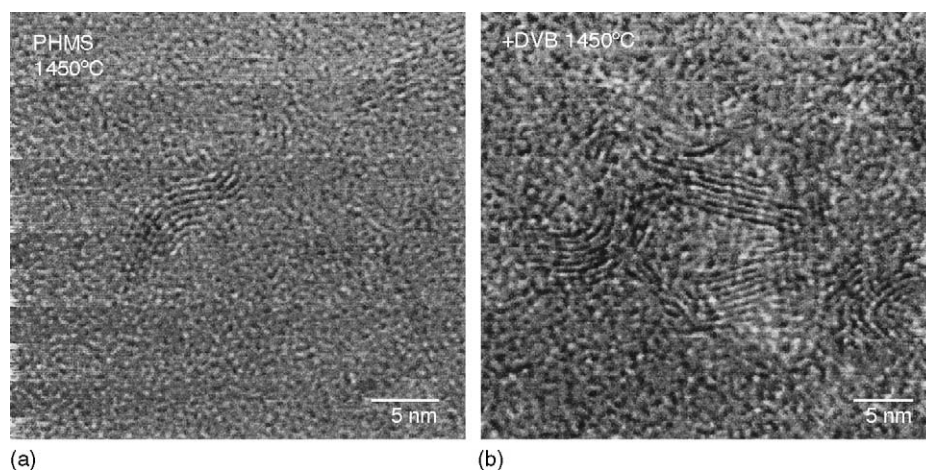

Fig. 6. HRTEM images of (a) PHMS and (b) PHMS + 60 wt.% DVB, both annealed at 1450 °C. Note the regions of graphitic carbon embedded in the amorphous SiOC matrix; no porosity was observed.
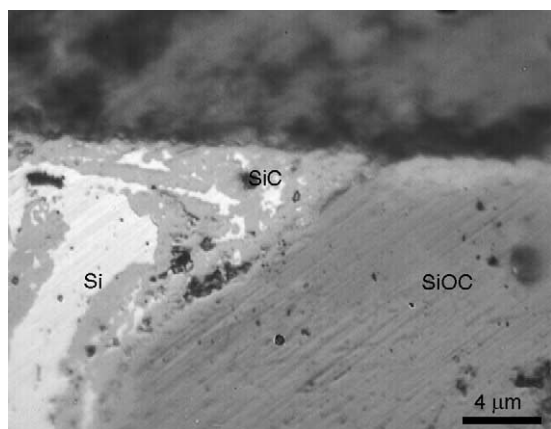
Fig. 7. Reactive and nonreactive zones developed at the interface of molten Si and PHMS–60 wt.% DVB.
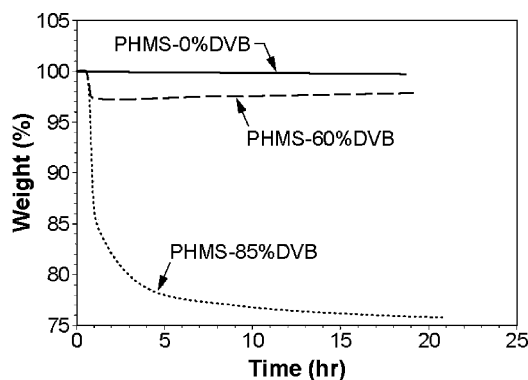

Fig. 8. Isothermal oxidation of PHMS–DVB in moist air at 1000 °C.

4. Conclusions

A versatile approach to using low viscosity PHMS as a commercially available feed stock to a broad range of silicon containing ceramics or polymeric materials has been developed by utilizing very efficient hydrosilylation and dehydrocoupling reactions homogeneously catalyzed by Ru and Pt complexes. A systematic method to form carbon-enriched SiOC has been explored and demonstrated via the reaction of PHMS with DVB. The molecular distribution of the carbon precursor provides very homogeneous and amorphous SiOC materials that convert to nanocomposites, consisting of nanosized graphitic domains and a still amorphous SiOC matrix, even at temperatures exceeding 1200 °C. In contrast to other reports about the destabilization of SiOCs and other polymer-derived ceramics in the presence of excessive amount of "free" carbon, the carbon-enriched SiOC materials described in this article are thermally durable and more chemically stable at high temperatures than anticipated. Both the amorphous and the evolved nanocrystalline stages of these materials are currently a subject for further exploration of properties and performance as well as for establishing better understanding of the role of "free" carbon in polymer-derived ceramics.

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