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# Pyrolytic transformation of liquid precursors to shaped bulk ceramics

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## Abstract

The pyrolysis behavior of polysiloxane liquids in transformation to shaped ceramic bodies has been studied through liquid casting, crosslinking, and pyrolysis. The control of crosslinking temperatures with a second heating allows the self-demolding of crosslinked polysiloxanes from casting molds to form shaped polysiloxane bodies with good bonding quality. Pyrolysis of the polysiloxane bodies at various temperatures yields dense shaped SiOC materials changing in appearances from colorless transparent to dark brown to dark, corresponding to different degrees of pyrolysis. This indicates the homogeneous transformation of the polysiloxane network during organic-to-inorganic transformation. The bulk pyrolysis characteristics including bonding quality, microstructures, densities and shrinkage are studied in association with the effect of pyrolysis temperatures and precursor chemistries. The structural evolution of the polymeric network is analyzed by $^{29}$Si NMR, $^{13}$C NMR and FTIR spectroscopy. Through controlling the crosslinking and optimizing precursors, we have achieved net-shaped bulk SiOC material with a relatively large dimension.

*Keywords:* Polymer-derived ceramics; Silicon oxycarbide; Polysiloxanes

## 1. Introduction

Polymer-derived ceramics such as SiCN, SiBCN and SiOC have a low density, resist to high temperatures, and have tailored electrical conductivities, promising for applications in high technological areas.[1,2] The fabrication of shaped bulk polymer-derived ceramics (PDCs) is an important step towards their applications. Bulk PDCs of SiCN, SiBCN, SiC and SiOC ceramics are fabricated from their respective precursors along the powder compact route that involves crosslinking the precursor into an infusible solid, powdering the precursor, warm- or cold-pressing of the precursor powder and pyrolysis.[3–6] Nevertheless, a more attractive approach to bulk PDC is the direct pyrolysis of a liquid precursor as this will allow the simple cast of a precursor liquid hence one-step fabrication of net-shaped PDC monolithic by pyrolysis. Surprisingly, there has been less amount of published work on the fabrication of macroscopic bulk PDCs by the liquid cast process. Previous works involving the direct pyrolysis of a liquid precursor addresses mainly on the fabrication of small PDC parts or miniatures for MEMS applications (on the millimeter scale).[7,8] Other work relevant to the liquid transformation to PDCs is the sol–gel process that generally involves a solvent reaction, gelation, drying and pyrolysis. Many works report on the fabrication of SiOC ceramics along this process,[9–15] among which, a few work involves the fabrication of shaped SiOC bulk ceramics.[16,17] However, the sol–gel process generally involves a solvent, a slow gelation and a long time drying process, which makes it difficult to control the bonding qualities of the precursor bodies, apart from a lower efficiency.

In contrast, polymerized precursors are more appropriate for the bulk transformation to PDCs as the process does not involve a solvent, and the precursor can be more efficiently crosslinked (faster) and involves smaller weight loss and shrinkage in pyrolysis.[12] For the bulk transformation of a liquid precursor to PDCs, polysiloxanes should be an attractive precursor because they are commercially available in liquids with tailored physical and chemical states, less sensitive to air and moistures,[6] and thus can be processed in air facilitating large-scale productions.

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Many kinds of polysiloxanes have been pyrolyzed to SiOC ceramics including poly(hydridomethylsiloxane) ($[CH_3(H)SiO]_n$),[18–21] poly(methylpenylsiloxane) ($[CH_3(C_6H_5)SiO]_n$),[19] poly[(dimethylsiloxane)-co-(vinylmethylsiloxane)] ($[(CH_3)_2SiO]_n[CH_2{=}CH(CH_3)SiO]_m$)[2,19] and tetravinylcycletetrasiloxanes ($[(CH_3)(CH_2{=}CH)SiO]_4$)[14,17] and poly(methylsilsesquioxane) ($[CH_3SiO_{1.5}]_n$).[6,22] Most of work addresses on the pyrolysis behavior of the precursors and the characterization of structure of the resultant ceramics. Other work on the fabrication of shaped bulk SiOC ceramics from polysiloxanes adopts the powder compact process,[6,22] or the filler approach involving the addition of inert or active powders,[23] rather than direct liquid forming and pyrolysis.

This work provides the first systematic study on the bulk transformation of a precursor liquid into dense bulk ceramics, including the liquid casting behavior, crosslinking, demolding and bulk transformation to ceramics. A finding is that dense bulk SiOC ceramics can be intrinsically transformed from polysiloxanes through the controlled liquid casting, demolding and pyrolysis. The ceramics kept dense after pyrolysis at different temperatures. Microstructure observations show the formation of amorphous structures in the bulk materials at the different pyrolysis temperatures. The liquid casting and crosslinking process control the bonding quality of the shaped precursor body and that of the final SiOC ceramics. The bulk pyrolysis characteristics, including densities, shrinkage and bonding quality, the effects of pyrolysis temperatures, and the precursor chemistries are systematically studied. The evolution of atomic bonding configurations of the polymeric network is characterized by spectroscopes. Through optimizing the crosslinking conditions and the mixing ratio of the precursor components, we have achieved net-shaped bulk SiOC material with a relatively large dimension. These results should be valuable for the fabrication of polymer-derived ceramics with this attractive liquid casting process. Although this work uses polysiloxane liquid as the precursor, the result should have general implication to other liquid systems like polysilazanes.

## 2. Experimental

The polysiloxane precursors were polyhydrodimethylsiloxane (PHMS) (Me-$[MeHSiO_2\text{-}]_n$-Me, Zhejiang Shantai Factory for Organoslianes, Quzhou, China) and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcycletetrasiloxane (denoted as $D_4Vi$), ($[MeViSiO]_4$, purity 99.8 wt.%, Zhejiang Shanmen Co. Ltd. Ningbo, China), which were used in as-purchased form. The viscosity of PHMS and $D_4Vi$ is 95.80 and 30.80 mPa s, respectively, measured using a viscometer (Brookfield DV-Middleboro, USA). PHMS and $D_4Vi$ were filled in a 50 ml flask with different weight ratios ($R = [PHMS]/[D_4Vi]$) between 0.25 and 4.0, and mixed by magnetic stirring at room temperatures for 40 min. Platinum–divinyltetramethyldisiloxane complex ($Pt[(ViMe_2Si)_2O]$ $[ViMe_2SiOSiMe_2OH]$, [Pt]: 3000 ppm, Shenzhen Platimun Complexes Co. Ltd., Shenzhen, China) was added into the polysiloxanes at an amount of 1 wt.%, as a catalyst (Pt catalyst), mixed by magnetic stirring for another 40 min. The precursor mixture was filled in a mold and crosslinked by heating. Different size molds made of various materials were used for casting the precursors, including potassium carbonate glass (potash) beakers (∅23 mm × 30 mm), polyethylene tube (∅11 mm × 45 mm) and a Teflon cuvette (50 mm × 10 mm × 5 mm). The crosslinking was conducted by placing the precursor-filled mold into an oven, raising temperature at 3 °C/min to 25–80 °C, and heating for 0.5 h–2 days. The solidified polysiloxane was mechanically demolded from the mold and then placed in an alumina crucible for pyrolysis. The pyrolysis was conducted at a temperature between 400 and 1000 °C for 2 h in flowing argon with heating rate 2–5 °C/min.

Crosslinked and pyrolyzed products were analyzed using Fourier transformation infrared spectroscopy (FTIR) (FTS 6000, Bio-Rad Company, CA, US) using KBr pellets, and solid state nuclear magnetic resonance spectroscopy ($^{29}$Si NMR and $^{13}$C NMR, Infinty plus 300WB, Varian, USA, recorded at 4 and 12 kHz). Thermal gravimetric analysis (TGA) (Netzsch STA 449C, Germany) was conducted in Ar at heating rate 10 °C/min. Bulk densities of SiOC materials were measured from the weight and dimension of the sample. Microstructures were observed by scanning electronic microscopy (SEM, XL30ESEM, Phlilps, Eindhoven, Holland). Phase analysis was performed on X-ray diffractrometry (XRD, Rigaku D/max 2500 v/pc, Tokyo, Japan) using Cu Kα radiations. Elemental analyses were performed on N/O-Analyzer (Leco TC-436, USA) for [O] and a C-Analyzer (Leco C-200, USA) for [C].

## 3. Results and discussions

### 3.1. Crosslinking and solidification of the PHMS + $D_4Vi$ liquids

For the bulk transformation of polysiloxane precursors into SiOC, the precursor should be crosslinkable and enables to provide a high ceramics yield upon pyrolysis. In this regard, a polysiloxane containing crosslinking active groups is desired. Radovanovic et al. studied the pyrolysis behavior of polymethylsiloxane and tetravinylcycletetrasiloxane and the structures of the derived SiOC ceramics by spectral analysis.[18] The polysiloxanes are a low viscosity liquid and contain crosslinkable Si–H groups and vinyl groups. We have recently fabricated SiOC microparts and patterned microstructures via the mold transfer and direct imprint process using these precursor systems.[8] This precursor system is crosslinkable under controlled heating without volume changes and can provide a high ceramic yield (over 85 wt.%) after pyrolysis which are appropriate for the bulk transformation to SiOC ceramics.

Upon aging and/or heating, the PHMS + $D_4Vi$ liquids containing the Pt catalyst transform into a rubber-like substance and then to a rigid solid after crosslinking. The solidification behavior of the precursor liquids depends on the crosslinking temperature, aging and the mixing ratio of PHMS and $D_4Vi$ ($R = [PHMS]/[D_4Vi]$). Fig. 1 shows the variations of the solidification time with $R$ at the three different crosslinking temperatures (50, 60 and 80 °C). At room temperature (25 °C), the precursors with $R = 1.0$ solidify after aging for 3 days. The solidification becomes faster under heating, complete in 2 h at 50 °C

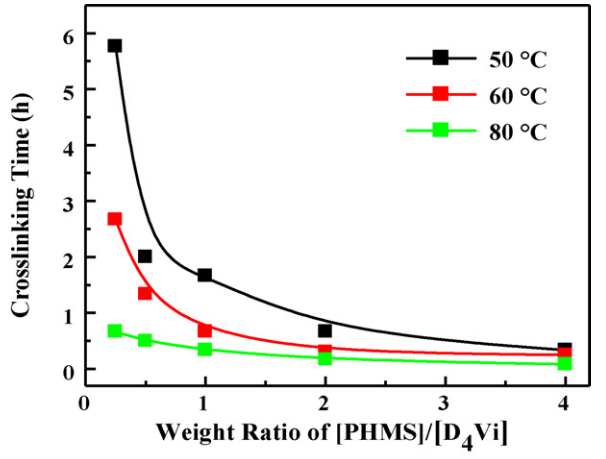
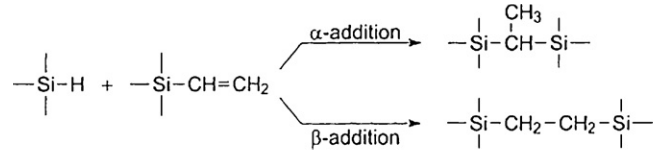


Fig. 1. The variations of times for crosslinking of the PHMS + $D_4$Vi liquids with the mixing ratio of the two components (*R* = [PHMS]/[$D_4$Vi]) at the three different temperatures.

and 0.5 h at 80 °C. With the variation of *R*, the solidification of the precursors become slower with the increasing amount of $D_4$Vi in the precursors ($R < 1$), whereas it becomes faster and tends to a similar time when *R* is between 2.0 and 4.0 at the different crosslinking temperatures. The accelerated crosslinking likely results from that the enhanced attacking of the linear PHMS molecules to the $D_4$Vi molecules with the increasing amount of PHMS in the precursor liquids.

FTIR spectra of the polysiloxanes crosslinked at 50 and 80 °C show the disappearance of vinyl absorptions (3061 and 1595 $cm^{-1}$) and a reduced intensity of the Si–H absorption (2100 $cm^{-1}$), as comparing to those of the starting precursor (Fig. 2). These spectral changes indicate the occurrence of hydrosilylation between the vinyl group in $D_4$Vi and the Si–H group in PHMS. The hydrosilylation is represented by Scheme 1 (Ref. 2) which may involve α-addition and/or β-addition (Scheme 1). $^{13}C$ NMR spectrum of the 80 °C–2 h crosslinked polysiloxane shows the origination of a chemical shift peak for $CH_2$ at 8.9 ppm,[24] as seen from Fig. 3, which is due to the formation of Si–$CH_2$–$CH_2$–Si bonds in the products, but without CH peaks. This indicates that the crosslinking occurred mainly via the β-addition. The β-addition links the PHMS and $D_4$Vi molecules into a polysiloxane network, which accounts for the solidification of the polysiloxane liquids. The hydrosilylation of PHMS and $D_4$Vi does not involve a by-product, and weight and volume changes, which is desired for the bulk transformation of the polysiloxane into ceramics via liquid cast process.



Scheme 1. The mechanism of hydrosilylation reactions.

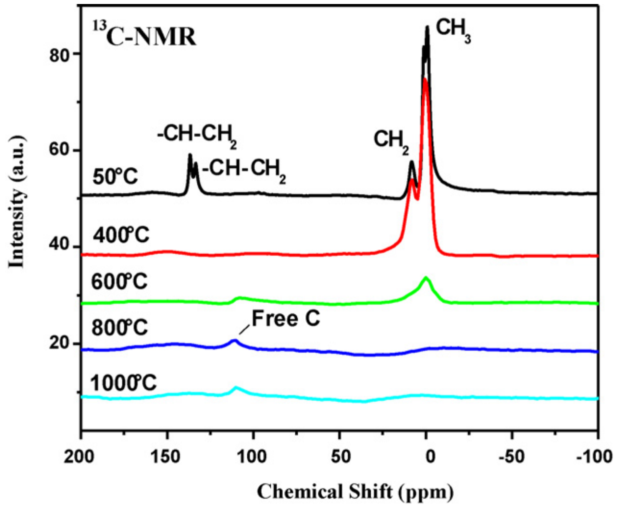


Fig. 3. Solid state $^{13}C$ NMR spectra of SiOC materials pyrolyzed from the crosslinked PHMS + $D_4$Vi polysiloxane body at the different pyrolysis temperatures. Crosslinking condition: 50 °C–2 h.

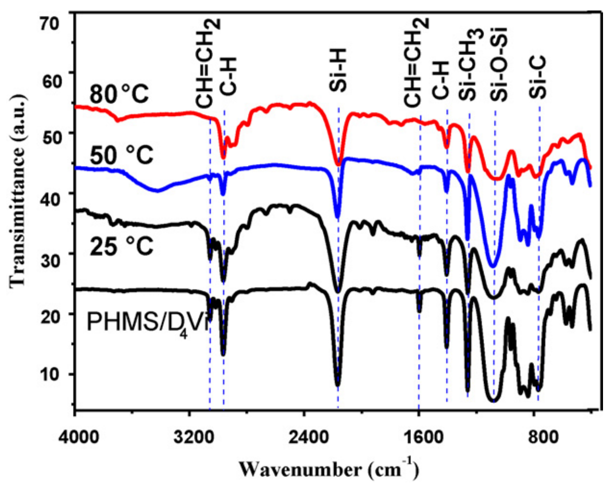


Fig. 2. FTIR spectra of the PHMS + $D_4$Vi precursor ($R = 1.0$) and the polysiloxane bodies crosslinked at room temperature (25 °C) for 6 days, 50 °C for 6 h and at 80 °C for 6 h.

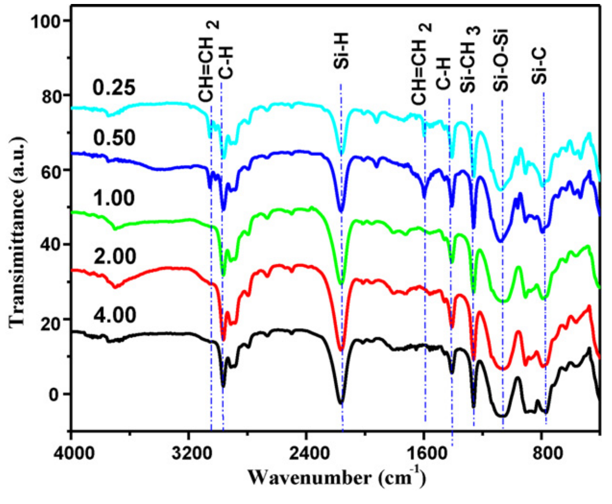


Fig. 4. FTIR spectra of the polysiloxane solids crosslinked at 50 °C–2 h from the PHMS + $D_4$Vi precursor with different weight ratio *R* = [PHMS]/[$D_4$Vi]: 0.25, 0.5, 1.0, 2.0 and 4.0.

FTIR spectra show there remains strong Si–H absorption bands in the polysiloxanes crosslinked at different temperatures and with $R = 0.25$–$4.0$ (Fig. 4), and the vinyl absorption bands for the polysiloxane with $R = 0.25$–$0.5$. For the polysiloxane with $R = 1.0$–$4.0$, the vinyl absorptions disappear from the FTIR spectra (Fig. 4), but the $^{13}$C NMR spectrum shows the existence of the vinyl group signals for the crosslinked precursor with $R = 1.0$, as seen from the chemical shift peaks at 137 ppm due to $CH{=}CH_2$ and at 134 ppm due to $CH{=}CH_2$ (Ref. 24) (Fig. 3). These spectral characteristics indicate an incomplete crosslinking of PHMS and $D_4Vi$, which appears independent of the crosslinking temperature and the fraction of the two components in the precursors, which is likely due to a spatial effect. These active groups (Si–H and vinyl groups) crosslink further upon pyrolysis at higher temperatures, and contribute to the ceramic bonding of polysiloxane during the transformation to SiOC ceramics.

### *3.2. Casting of the polysiloxane liquids, shaping and demolding*

The precursor liquids of PHMS + $D_4Vi$ were cast in molds and placed in an oven at a temperature for crosslinking to solidification. The control of crosslinking temperatures is necessary for ensuring the formation of a dense and crack-free polysiloxane body. At a crosslinking temperature of 80 °C, the precursors crosslinked too fast, resulting in foaming of the precursors in the mold. When the crosslinking temperature was 50 °C, the precursor did not foam and formed a dense, transparent and crack-free polysiloxane body in the mold.

In general, the solidified polysiloxane body is stick to the mold walls which makes it difficult to directly demold, especially at a lower crosslinking temperature. A Teflon mold has a weaker adhesion of the precursor part and the mold walls because of its lower surface energy which allows easier demold-

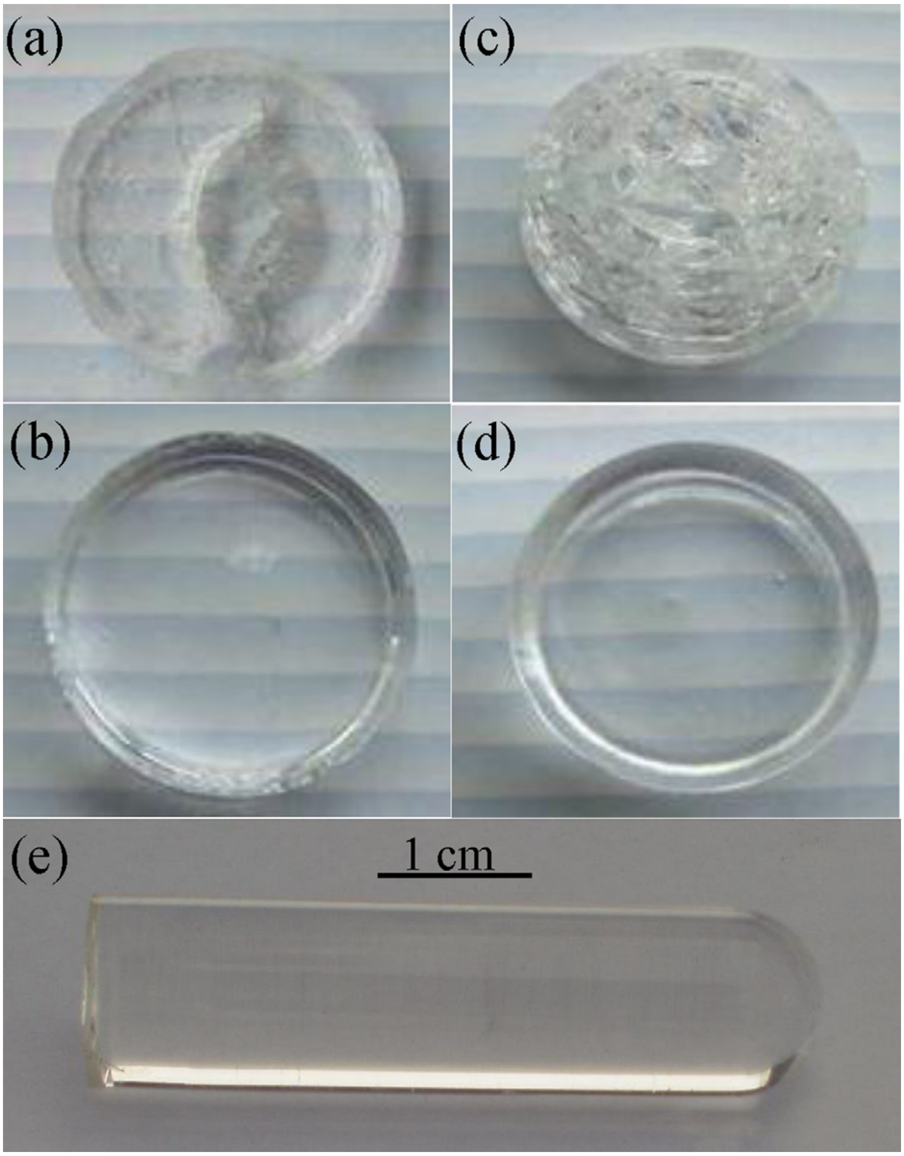


Fig. 5. Photographs of shaped PHMS + $D_4Vi$ bodies with $R = 1.0$ under different crosslinking conditions: 25 °C–72 h (a), 50 °C–6 h (b), 80 °C–2 h (c), 50 °C–6 h/80 °C–2 h (d) and a solid column (e) with dimension of ∅11 mm × 40 mm obtained under the condition as (d).

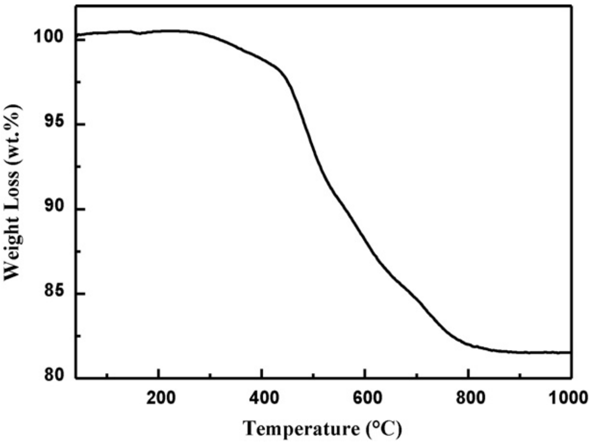


Fig. 6. Thermal gravity analysis (TGA) of a PHMS + $D_4$Vi solid with $R = 1.0$ crosslinked at 50 °C–6 h.

ing as comparing to the glass mold. Fig. 5 compares the shaped and demolded polysiloxane bodies by crosslinking at different temperatures. The room temperature crosslinked precursor was not rigid enough, causing cracking of the specimen during mechanical demolding (Fig. 5a). The specimen crosslinked at 50 °C–6 h was damaged at edges during demolding because of the adhesion of the crosslinked polysiloxane to the mold walls (Fig. 5b). In contrast, extensive cracks were observed for the 80 °C crosslinked polysiloxane during crosslinking because of the crosslinking too fast (Fig. 5c). We found that the applying of a post-heating to the crosslinked polysiloxane solid in molds allows a spontaneous separation of the polysiloxane solid from the mold wall. Fig. 5d shows a good quality polysiloxane body obtained by crosslinking at 50 °C for 6 h followed by heating at 80 °C for 2 h. The second heating leads to slight expansion of the precursor part in the mold that breaks the interface bonding of the precursor solid and the mold walls. The controlling crosslinking and demolding process allows the obtaining of large-size polysiloxane part with good bonding quality as the one demonstrated in Fig. 5e.

### 3.3. *Bulk pyrolysis of the shaped polysiloxanes at different temperatures*

The general pyrolysis behavior of polysiloxane was analyzed by TGA. Fig. 6 shows a TGA curve for a polysiloxane solid crosslinked at 50 °C–6 h from room temperatures to 1000 °C in Ar. The major weight loss occurs between 400 and 800 °C, which corresponds to the stage of organic-to-inorganic transformation. The total weight loss by 1000 °C is 17.9 wt.%, corresponds to a ceramic yield of 82.1 wt.%.

Bulk pyrolysis was conducted with the shaped polysiloxane bodies in an argon flow at different temperatures between 400 and 1000 °C with a 200 °C interval. Crack-free bulk bodies in appearances of a light yellow transparent, brown translucent and dark, were obtained from the different pyrolysis temperatures (Fig. 7). The linear shrinkage of the polysiloxane solids is 1.1, 7.5 and 20% at 400, 600 and 800 °C, respectively. SEM observations of the fractural surfaces of the different temperature pyrolyzed materials show they are dense, free of pores and cracks (Fig. 8). The formation of crack-free bodies at the different temperatures indicates that the homogeneous evolution of the polysiloxane network in the process of organic-to-inorganic transformation. The density and shrinkage of the SiOC materials obtained at the different temperatures are listed in Table 1.

Fig. 9 shows the bulk SiOC ceramics with different sizes and shapes obtained from PHMS + $D_4$Vi at $R = 1.0$ by pyrolysis at 1000 °C for 2 h. The largest SiOC ceramic body we have obtained has the size of ∅9 mm × 31 mm, which is significantly larger than those obtained before from the sol–gel process.[16,17] The ceramics kept the shapes of the polysiloxane solid, despite the occurrence of a large linear shrinkage of 22% from the pyrolysis. SEM images show both the surface and the fractural surface of the ceramics are dense, free of pores and cracks (Fig. 10). The ceramic yield from the bulk pyrolysis at 1000 °C is 81.4 wt.%, which is close to that of 82.1 wt.% from the TGA analysis. X-ray diffraction checked the SiOC ceramics being amorphous. Elemental analyses gives the compositions of the SiOC ceramics being [Si]:49.43 wt.%, [C]:23.73 wt.% and [O]:26.84 wt.%, corresponding to a formula $SiO_{0.95}C_{1.12}$.

### 3.4. *Structural evolutions of the polysiloxane networks in bulk pyrolysis*

The structures of the SiOC materials obtained from different pyrolysis temperatures and the evolution of the polysiloxane network at different stages of bulk pyrolysis are studied using FTIR and NMR spectroscopy.

At 400 °C, the $^{29}$Si NMR spectrum of the pyrolyzed material (Fig. 11) shows a reduced intensity of the $CHSiO_2$ peak (−37.6 ppm, Ref. 25 and 26), and the $^{13}$C NMR spectrum (Fig. 3)

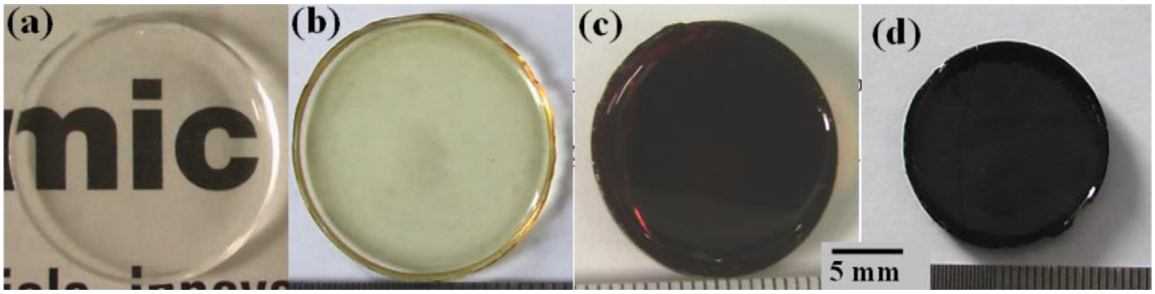


Fig. 7. Photographs of SiOC materials pyrolyzed from a shaped polysiloxane solid (a) at different temperatures: (b) 400 °C, (c) 600 °C and (d) 800 °C. PHMS + $D_4$Vi: $R = 1$, crosslinking condition: 50 °C–6 h.

Table 1
Bulk densities, yields and linear shrinkage of SiOC materials pyrolyzed at different temperatures.

| | 50 °C | 400 °C | 600 °C | 800 °C | 1000 °C |
|---|---|---|---|---|---|
| Yield (wt.%) | 100 | 98.9 | 88.2 | 82.0 | 81.4 |
| Linear shrinkage (%) | 0 | 1.1 | 7.5 | 20.0 | 22.0 |
| Density (g/cm$^3$) | 1.07 | 1.09 | 1.15 | 1.97 | 2.10 |

shows the disappearance of the vinyl group (133.8–137.1 ppm, Ref. 24), as comparing to those of the as-crosslinked precursor. These spectral changes suggest a further crosslinking of the Si–H bond and the vinyl group in the crosslinked body at the elevated temperature. The heating around this temperature causes the thermal adjustment of the polysiloxane network making these active groups interacted. A small weight loss of 5 wt.% was observed between 280 and 400 °C from the TGA curve. This small weight loss may associate to the thermal adjustment of the polymeric network that caused the escaping of some uncrosslinked species from the polysiloxane network. The $^{29}$Si NMR spectrum indicates that the 400 °C pyrolyzed material con-

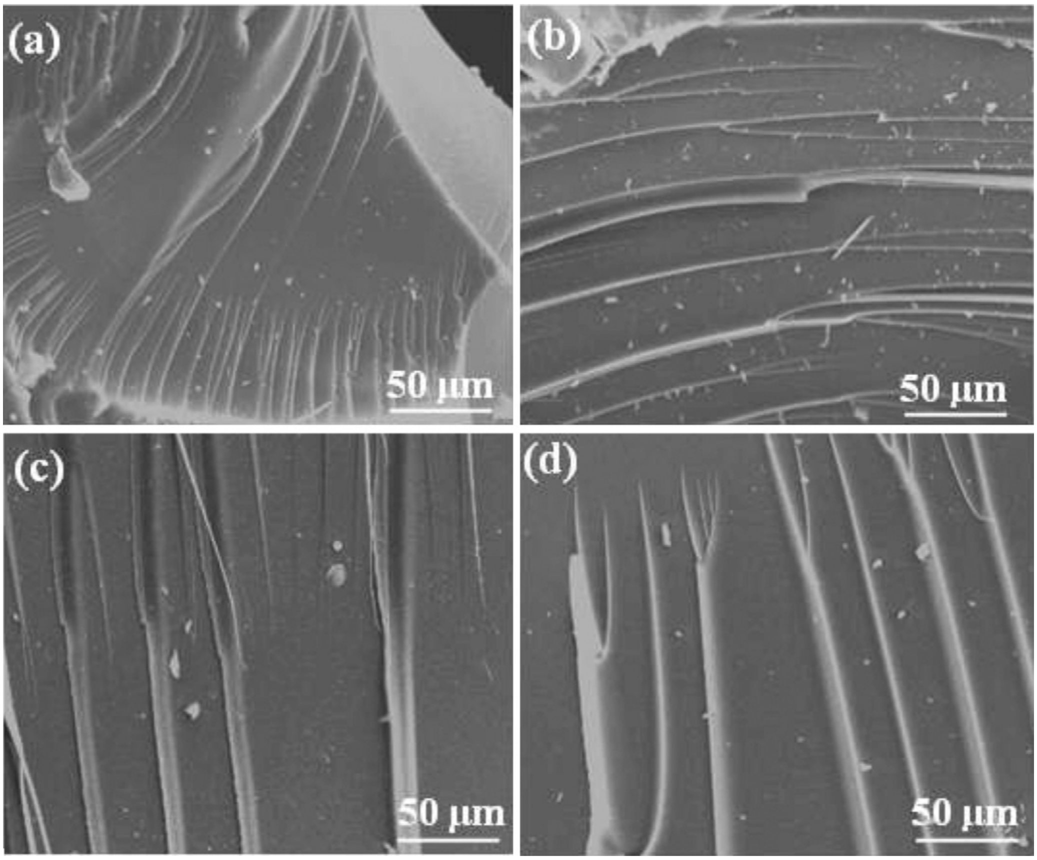


Fig. 8. SEM images of the fractured surfaces of bulk SiOC materials pyrolyzed at different temperatures: (a) 400 °C, (b) 600 °C, (c) 800 °C, and (d) 1000 °C.

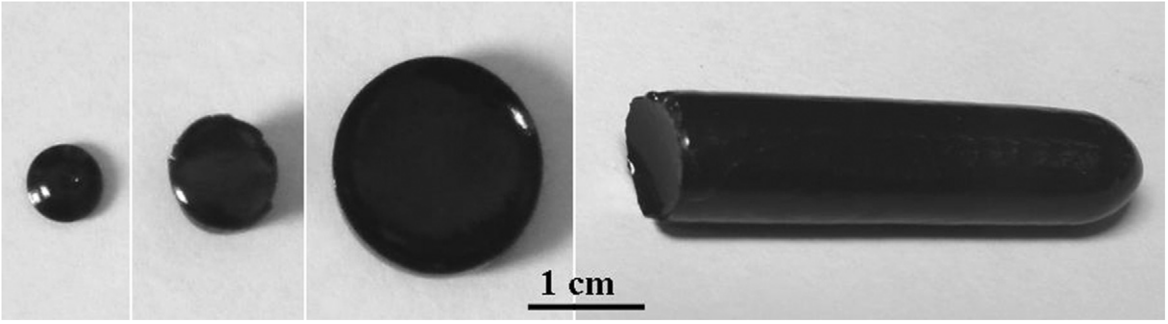


Fig. 9. SiOC ceramics with different size and shapes obtained from PHMS + D$_4$Vi by pyrolysis at 1000 °C (dimensions from left to right: ∅5 mm × 3 mm, ∅7 mm × 3 mm, ∅13 mm × 5 mm and ∅9 mm × 31 mm).

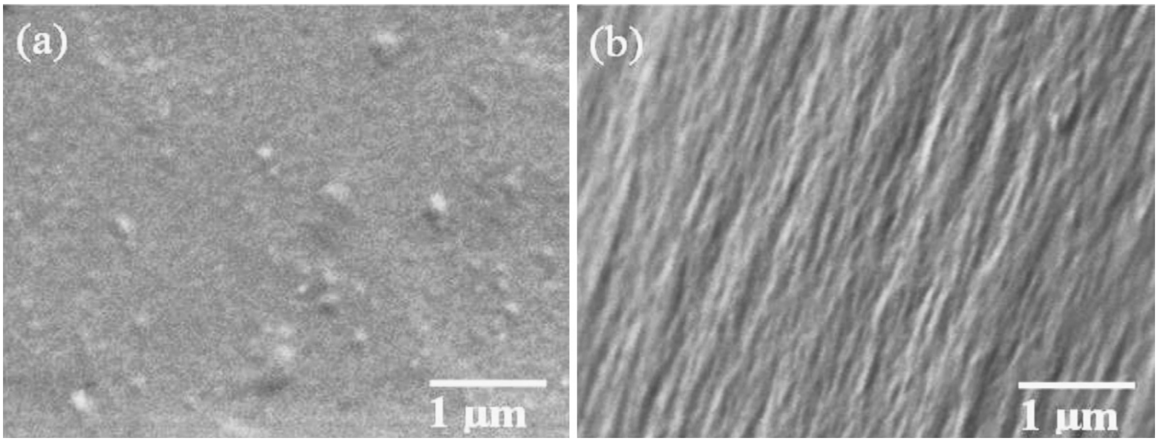


Fig. 10. SEM micrographs of surface and fracture of SiOC ceramics obtained by pyrolysis at 1000 °C.

sists of mainly $CHSiO_2$ and $C_2SiO_2$ units in the polysiloxane network.

At 600 °C, the amount of Si–H and $Si–CH_3$ in the pyrolyzed materials was reduced, as seen from the FTIR spectrum (Fig. 12). The $^{13}C$ NMR spectrum shows the reduction of the $CH_2$ and CH units (−5 to 25 ppm[26]). These spectral changes indicate the occurrence of reactions between the Si–H groups and the $Si–CH_3$ groups. The major reactions should be:

$$\text{Si–H} + \text{Si–CH}_3 \rightarrow \text{Si–CH}_2\text{–Si} + \text{H}_2\uparrow, \quad (1)$$

$$\text{Si–CH}_2\text{–Si} + \text{Si–CH}_3 \rightarrow \text{Si–C(Si)H–Si} + \text{CH}_4\uparrow, \quad (2)$$

and

$$\text{Si–C(Si)H–Si} + \text{Si–CH}_3 \rightarrow \text{(Si)}_3\text{–C–Si} + \text{CH}_4\uparrow\,. \quad (3)$$

These reactions gradually deplete the C–H bonds and produce Si–C bonds which are generally observed in the pyrolysis of a polysiloxane around this temperature.[27,28] The formation of the $Si–CH_2–Si$ intermediate unit is seen from the small absorption at 1380 $cm^{-1}$ in the FTIR spectrum, as found by Singh and Pantano from the pyrolysis of sol–gel derived siloxanes.[27] Moreover, the $^{29}Si$ NMR spectrum shows the reduction of $CHSiO_2$ (−37.6 ppm), and the formation of $C_2SiO_2$, due to the pyrolytic reactions. The formation of the $CSiO_3$ (−65.7 ppm) and $C_3SiO$ (6.1 ppm) units[25] are due to the transformation: $2C_2SiO_2 \rightarrow C_3SiO + CSiO_3$ (Ref. 18). The $^{13}C$ NMR spectrum shows the starting precipitation of free-carbon in the products from the origination of a small peak around 137 ppm.[25] This accounts for the brown color of the ceramic obtained at 600 °C. Despite the significant bonding changes and the precipitation of carbon, the polysiloxane network kept entire and transformed into an inorganic network.

At 800 °C, most organic groups are eliminated as seen from the FTIR and $^{13}C$ NMR spectra (Fig. 3) with only trace amount of Si–H and $Si–CH_3$ left in the products. The TGA curve shows the weight loss is nearly complete by 800 °C. The $^{29}Si$ NMR spectrum indicates the reduction of the $CSiO_3$ units and enhanced formation of $SiO_4$ units (−101.5 ppm) comparing to those in the 600 °C products. These changes were due to the transformation: $C_2SiO_2 + CSiO_3 \rightarrow C_3SiO + SiO_4$.[18] The $^{29}Si$ NMR spectrum indicates that the 800 °C products consist of mainly $C_2SiO_2$, $CSiO_3$ and $SiO_4$ along with free-carbon. The bonding units in

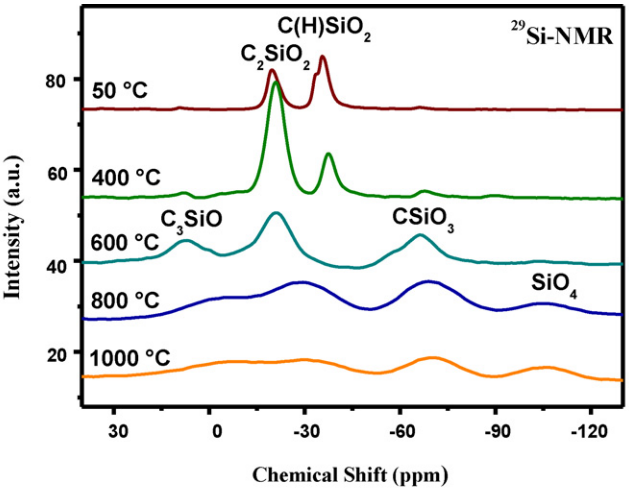


Fig. 11. Solid state $^{29}Si$ NMR spectra of SiOC materials pyrolyzed from PHMS + $D_4Vi$ ($R$ = 1.0) at the different temperatures.

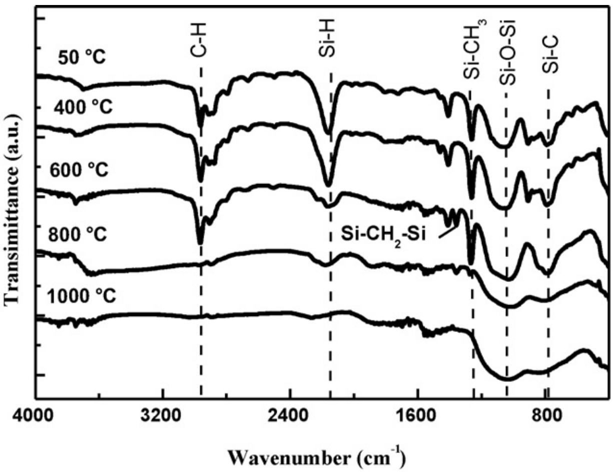


Fig. 12. FTIR spectra of the SiOC materials from PHMS + $D_4Vi$ ($R$ = 1.0) pyrolyzed at the different temperatures.

Table 2
Ceramic yields, densities, compositions and bonding qualities of SiOC ceramics from PHMS + $D_4$Vi with the mixing ratios of the two components.

| Sample no. | Mass ratio [PHMS]/[$D_4$Vi] | Mole ratio [PHMS]/[$D_4$Vi] | Ceramic yield (wt.%) | Density (g/cm$^3$) | Chemical composition | Bonding qualities of SiOC ceramics |
|---|---|---|---|---|---|---|
| 1 | 0.25 | 0.34 | 77.6 | – | – | Cracked |
| 2 | 0.5 | 0.67 | 78.8 | 1.97 | $SiO_{0.9}C_{1.4}$ | Bulk |
| 3 | 1.0 | 1.34 | 81.4 | 2.10 | $SiO_{1.0}C_{1.1}$ | Bulk |
| 4 | 2.0 | 2.68 | 79.2 | 1.82 | $SiO_{0.9}C_{1.0}$ | Bulk |
| 5 | 4.0 | 5.36 | 74.8 | – | – | Cracked |

the 1000 °C product are similar to those in the 800 °C products without distinct difference from the $^{29}$Si NMR spectrum.

### *3.5. The effects of the mixing ratio of PHMS and $D_4$Vi on the bulk pyrolysis behaviors*

The effects of the mixing ratio of PHMS and $D_4$Vi on the bulk transformation of the precursors to SiOC ceramics are studied, including bonding quality, yields and densities of the resultant ceramics, with the results summarized in Table 2. The mixing ratio of PHMS and $D_4$Vi ($R$) affects the bonding quality of the SiOC ceramics. Crack-free SiOC ceramics were formed when $R$ was in the range of 0.5 to 2.0 while the ceramics became cracked at the low or higher $R$ value ($R = 0.25$ and 4.0). This may suggest that an excess of Si–H or vinyl groups in the precursor produces larger stresses in the polymeric network during pyrolysis. With $R$ between 0.25 and 4.0, the ceramic yield is in the range of 74.8–81.4 wt.%, with the highest ceramic yield of 81.4 wt.% attaining at $R = 1.0$. The ceramic yield shows decreasing with $R$ deviating from the unit value indicating that the extra component has not been effectively incorporated into the polymeric network. From Table 2, it appears that the bulk density of SiOC ceramics increases with the ceramic yield. The highest ceramic yield also provides a better bonding quality of bulk SiOC ceramics.

The compositions of the SiOC ceramics formed from the different $R$ values were analyzed by chemical analysis as listed in Table 2. The ceramic composition can be summarized as $SiO_{0.9–1.0}C_{1.0–1.4}$, with $R$ in the range of 0.5–2.0. The amount of free-carbon in the ceramics for $R = 2.0$, 1.0 and 0.5 is calculated to be 14, 53 and 60 wt.%, respectively assuming Si bonds to C in SiC and to O in $SiO_2$. The amount of free-carbon increases with the fraction of $D_4$Vi in the precursor because it has the carbon-rich vinyl group in the precursor molecule. This suggests that it is possible to turn the compositions of the bulk SiOC ceramics by varying the ratios of the two components in the precursors.

## 4. Conclusions

Shaped bulk SiOC materials are fabricated through liquid cast, crosslinking and pyrolysis from a polysiloxane liquid consisting of polyhydromethylsiloxanes (PHMS) and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcycletetrasiloxane ($D_4$Vi). The controls of the crosslinking temperature and the ratio of the two components are necessary for ensuring the obtaining of a crack-free polysiloxane body. The pyrolysis of the shaped precursor body at different temperatures provide bulk SiOC materials with structures changing from organic-to-inorganic. Significant ceramic bonding changes occur between 600 and 800 °C accompanied by the precipitation of free-carbon. Despite these structural changes, the polysiloxane network kept entire and transforms to SiOC ceramics, as shown by the formation of dense bulk specimens at the different pyrolysis temperatures. Moreover, the mixing ratio of PHMS and $D_4$Vi have a large effect on the bulk pyrolysis behavior including shrinkage, yields, densities and bonding qualities of the resultant SiOC ceramics. Through the controlled crosslinking and forming, shaped bulk SiOC ceramics with a relative larger dimension are obtained after pyrolysis. The fabrication of macroscopic objects of shaped SiOC ceramics through the liquid cast process should contribute to the development of polymer-derived ceramics and their structural and functional applications.

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