Preparation of hybrid polymer as a near-stoichiometric SiC precursor by blending of polycarbosilane and polymethysilane

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A hybrid polymer as a near-stoichiometric SiC precursor was prepared by simply blending polycarbosilane (PCS) as a carbon-rich SiC precursor and polyborazine-modified polymethylsilane (M-PMS) as a silicon-rich SiC precursor at an optimized ratio of 0.25 : 1.00 (PCS : M-PMS) by weight. The hybrid precursor showed a very high ceramic yield of 82 wt.% and higher molecular weight than that obtained using a single precursor. The excellent processibility of the hybrid precursor was proven by dry-spinning it into green fibers. Based on XRD, ^{13}C MAS-NMR and ^{29}Si MAS-NMR measurements, the SiC ceramic derived from the hybrid precursor at 1400 °C showed no excess Si and little residual carbon, and a chemical composition of 98.08 wt.% SiC and 1.92 wt.% SiO_2 by SEM-EDX analysis.

Introduction

Routes for preceramic polymers to prepare SiC-based fibers, coatings and bulk materials have been the subject of intensive research over the past two decades in application areas, such as aerospace, weapons system, electronic and photoelectronic devices.[1,2] However, to date most polymer-derived SiC is non-stoichiometric, i.e. has excess of Si or C, which is harmful to the high temperature properties of materials. For example, Yajima polycarbosilane (PCS), a precursor of commercial SiC fiber, is converted into SiC with excess carbon that is unstable in air at high temperature. Another instance is polymethylsilane (PMS)-formed Si-rich SiC,[2–4] which is detrimental to high-temperature ceramic properties, due to the softening of Si at high temperature.[5] In order to prepare stoichiometric SiC from precursors many attempts have been made. One popular method to remove excess carbon in Yajima PCS-derived ceramic is to sinter the PCS-derived ceramic at high temperature (over 1600 °C).[6] Another method is by pyrolysis of PCS in some reactive atmosphere, such as H_2, in which the excess carbon is removed by reaction with H_2.[7] Seyferth et al.[8–11] modified PMS by adding polymers or organic compounds, such as $[Me(CH_2=CH)SiNH]_3$ and $[Me(CH_2=CH)SiO]_m$ etc. ($m = 4 \sim 6$) to increase the C content, thus complementing the excess Si derived from PMS. Boury[12] and Laine et al.[13] reported much work on polymethylsilane-derived stoichiometric SiC in their review articles[2,13] and a patent,[14] which prepared near-stoichiometric SiC from polymethylsilane–polyvinylsilane. Gozzi et al.[15] also prepared near-stoichiometric SiC from PMS by adding tetraallylsilane. Narisawa et al.[16,17] prepared near-stoichiometric SiC from PMS using γ-ray curing, and utilized PMS to lower the oxidation curing temperature of PCS fibers due to the presence of Si–H groups. In addition to the methods to prepare near-stoichiometric SiC from polymethylsilanes or Yajima PCS, other precursors were also reported, e.g. the stoichiometric SiC derived from polysilaethylene or highly branched PCS by Interrante et al.[18–20] or that derived from $[CH_3Si(N=C=N)_{1.5}]_n$ by Riedel and Gabriel.[21] The methods mentioned above

possess finite advantages. However, most approaches suffer from being a multistep synthetic process requiring air-sensitive catalysts.

As speculated by the previous works, one might be able to design a hybrid precursor for stoichiometric SiC by mixing an Si-rich SiC precursor and a C-rich SiC precursor at a specific ratio. In this paper, PMS and PCS were utilized to develop an economical procedure for the preparation of near-stoichiometric SiC. In particular, the ceramic yield of the hybrid precursor was significantly enhanced by the addition of a polyborazine additive. Moreover, we demonstrate the processibility of the obtained hybrid precursor by dry-spinning fibers.

Experimental

1. Materials

All samples described in this investigation were manipulated in a nitrogen or argon atmosphere or in a vacuum system. THF as a solvent was purified by distillation with sodium. Polycarbosilane (PCS) was readily synthesized by the thermolysis of polydimethylsilane (PDMS) (Xin Huo Company) at 500 °C for 5 h with ambient pressure and an N_2 atmosphere. Polymethylsilane (PMS) and polyborazine (PBN) were synthesized, and oily PMS was modified into soluble and fusible solid powder by adding 1 wt.% PBN, as described previously.[22]

2. Processing

PCS and modified PMS (M-PMS) were mixed homogeneously by dissolving in THF, stirring for 2 h, and then removing the THF by vacuum distillation at ambient temperature. The mixing ratios of PCS : M-PMS were chosen as, 0.17 : 1.00, 0.20 : 1.00 and 0.25 : 1.00 on a weight : weight basis. The powdery mixtures were heated at 100 °C for 1 h in a Schlenk flask equipped with a condenser and a thermometer to prepare the hybrid precursors. Viscous solutions for the fiber-spinning process were obtained by dissolving 2 g of the hybrid precursor (with an optimized PCS : M-PMS ratio 0.25 : 1.00) in 0.5 ml THF, and aging overnight to remove bubbles. Spinning was carried out using the hand-drawing technique in a

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glove-bag filled with N_2. As described by Yajima et al.[23,24] green fibers of length exceeding 20 cm were prepared by stretching with a stainless steel needle from the viscous hybrid solution. The diameter and length of the green fibers were measured by a microscope and a ruler, respectively. The pyrolysis of the preceramics was performed in a mullite tube at up to 1400 °C, with rate of 10 °C min^{-1} of argon at ambient pressure.

3. Analytical techniques

Molecular weight distributions were determined by gel permeation chromatography (GPC, Waters) with s-Styragel columns calibrated with polystyrene standards and with THF eluent at a flow rate of 0.5 ml min^{-1}. Thermogravimetric analysis (TGA; TA Instrument 2950) was performed at 10 °C min^{-1} to 1000 °C in an N_2 atmosphere. The structural evolution of pyrolytic products was investigated using powder X-ray diffraction patterns (Siemens D5000, Cu K$_\alpha$, radiation wavelength $\lambda = 0.154$ nm). The apparent mean grain size, L, of the SiC crystalline phase was calculated from the width, D (in radians), of the (111) diffraction peak at mid-height, according to the Scherrer equation:

$$L = K\lambda/D\cos\theta$$

Scanning electron microscopy and its associated energy-dispersive X-ray microanalysis (SEM-EDX) (JEOL JSM-6300) measurements were carried out with references of pure carbon to calibrate the equipment. Solid-state nuclear magnetic resonance (NMR) analysis (^{13}C and ^{29}Si) was performed using a 400 MHz spectrometer DSX400 (Bruker). Samples were spun at 4000–5000 Hz using the magic-angle spinning (MAS) technique.

Results and discussion

Fig. 1 (and Table 1) shows the IR spectra of the hybrid precursor from PCS and M-PMS. The peaks were assigned to C–H (2958, 2896 cm^{-1}), Si–H (2100 cm^{-1}), CH$_3$ (1047 cm^{-1}), Si–CH$_3$ (1250 cm^{-1}), Si–O–Si (1050 cm^{-1}), SiH$_2$ (930 cm^{-1}), CH$_3$ (867 cm^{-1}), and Si–C (771 cm^{-1}), respectively.[25,26] It can be observed that the relative intensity of the Si–H peak (2100 cm^{-1}) to the Si–CH$_3$ peak (1250 cm^{-1}) in the spectrum of the hybrid precursor is lower than that obtained from the M-PMS spectrum. We reported previously that Si–H in PMS is consumed by post-treatment with 1 wt.% PBN at 70 °C. When a mixture of M-PMS and PCS were heated at 100 °C, the Si–H of PCS was presumably consumed by the remainder of the
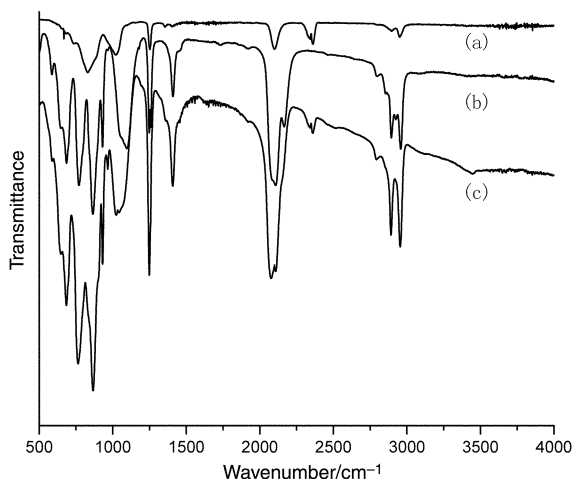
Table 1 IR absorption peaks identified in the as-synthesized polymer

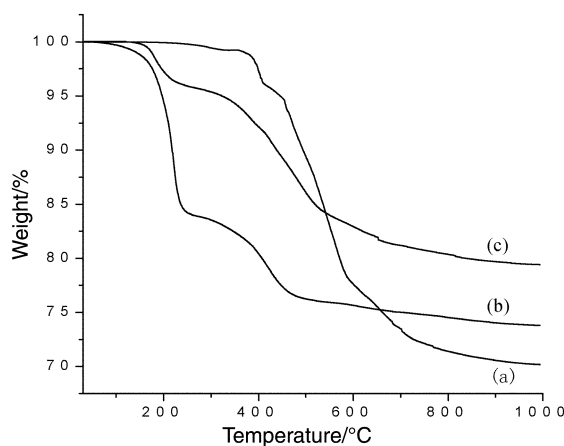| Wavenumber/cm^{-1}	Intensity	Identity
2956	Strong	ν(C–H)
2894	Medium	ν(C–H)
2100	Strong	ν(Si–H)
1406	Medium	δ(Si–CH$_3$)
1355	Weak	δ(Si–CH$_2$–Si)
1250	Strong	ν(CH$_3$)
1050	Medium	ν(Si–O)
930	Medium	γSiH$_2$
865	Strong	ρCH$_3$
764	Medium	ν(Si–C)
685	Medium	ν(Si–C)

Fig. 2 TGA curves of (a) PCS, (b) M-PMS, and (c) hybrid precursor with a weight ratio of PCS : M-PMS = 0.25 : 1.00.

PBN in M-PMS.[22] The increasing intensity of the Si–O–Si antisymmetric stretch at 1050–1100 cm^{-1} was ascribed to the sensitivity of the Si–H bonds against oxygen in air.[2,13]

Fig. 2 shows the TGA of hybrid and single precursors. The ceramic yields of PCS and M-PMS were about 70 wt.%, and 74 wt.%, respectively, whereas the hybrid precursor showed a very high ceramic yield of 82 wt.%. It is worth pointing out that a high ceramic yield is beneficial in the production of dense ceramic bodies. The improved yield of hybrid precursor was attributed to a dehydro coupling reaction promoted by the polyborazine additive as reported previously.[22] And recent work showed that polyborazine also efficiently promotes the ceramic yield of PCS from 70 to 79 wt.%.[27] As shown by GPC (Fig. 3 and Table 2), the molecular weight of the hybrid precursor is a little higher than that of either PCS or M-PMS. A polymer with potential groups, such as Si–H, N–H and B–H,
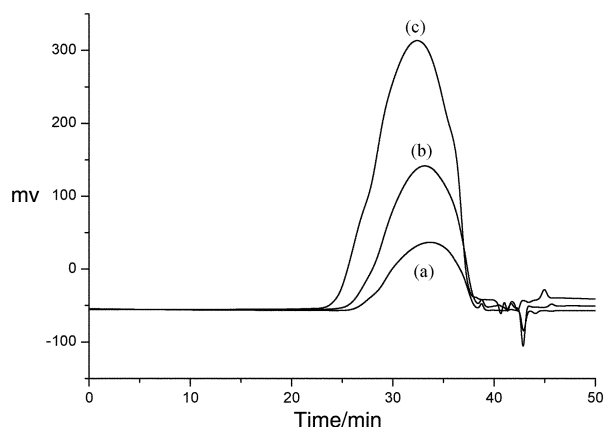

Fig. 1 IR spectra of (a) PCS, (b) M-PMS, and (c) hybrid precursor with a weight ratio of PCS : M-PMS = 0.25 : 1.00.

Fig. 3 Molecular weight distribution of (a) PCS, (b) M-PMS, and (c) hybrid precursor with a weight ratio of PCS : M-PMS = 0.25 : 1.00.

Table 2 Molecular weight of various precursors

|	M_n	M_w	PD, polydispersity
Hybrid precursor[a]	896	3869	4.3
PCS	517	2430	4.6
M-PMS	712	3149	4.4

[a]Weight ratio of PCS : M-PMS = 0.25 : 1.00.
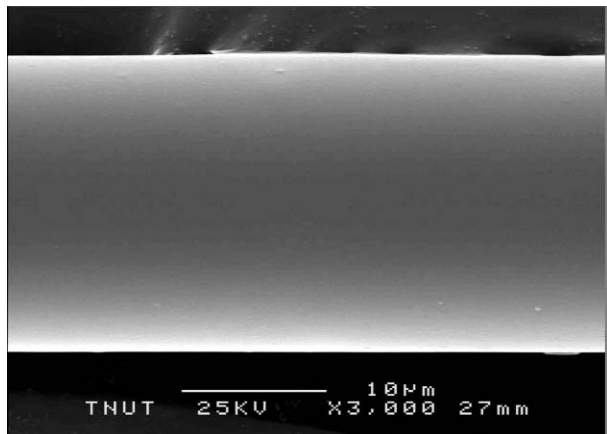
Fig. 4 Micrograph of green fiber hand-drawn from hybrid polymer solution (PCS : M-PMS = 0.25 : 1.00).

can be cross-linked easily.[28,29] Some PBN in M-PMS is presumed to react with PCS giving a little higher molecular weight hybrid precursor. This result is in agreement with the TGA and IR spectrum. The two single precursors were homogeneously dissolved in THF solvent due to their similar molecular weights and polarities. The highly viscous solution of hybrid precursor was readily hand-drawn to fiber as shown in Fig. 4, which demonstrated the processibility of the hybrid precursor; while without treatment by PBN, the PMS or the mixture of PMS with PCS could not be formed into green fibers due to the low viscosity of PMS. Typically, the green fiber showed a smooth surface, a diameter of 10–20 μm and a length of 20 cm. When pyrolyzed, the green fibers did not survive into ceramic fibers without a curing step. However, work is underway to prepare an oxygen-free SiC fiber with near-stoichiometric composition from an infusible and soluble hybrid precursor with increased molecular weight, which can be realized by treatment at higher temperature or for longer time under addition of PBN as described elsewhere.[27] Toreki *et al.*[30,31] reported high molecular weight PCS for low oxygen SiC fibers, but they employed a harsh synthetic method.

The XRD patterns of ceramics derived from various precursors at 1400 °C are shown in Fig. 5. The XRD patterns of M-PMS clearly show free Si peaks in addition to peaks of SiC.[22] Moreover, it is known that the SiC ceramic derived from PCS contains free C although no distinct peak is assigned to free C due to its amorphous structure at 1400 °C.[32] As the mixing ratio of PCS : M-PMS increases, the intensity of the peaks corresponding to free Si gradually decreased. Finally, when the weight ratio of PCS : M-PMS was 0.25 : 1.00, free Si peaks disappeared absolutely, which indicates stoichiometric (mainly beta) SiC with a grain size of 7 nm, which is between that of M-PMS (8 nm) and PCS (5 nm). Comparatively, the ceramic derived from $[CH_3Si(N=C=N)_{1.5}]_n$ by Riedel and Gabriel[21] at 1600 °C, was in the form of cubic β-SiC and various α-SiC polytypes with a formula of $SiC_{0.96}N_{0.04}$. The near-stoichiometric SiC derived at 1000 °C from polysilaethylene by Interrante[19,33] was shown by XRD to be formed of β-SiC with an average crystallite size of about 2 nm.

In order to confirm the SiC stoichiometry, the differences in the structures and compositions of the ceramics derived from
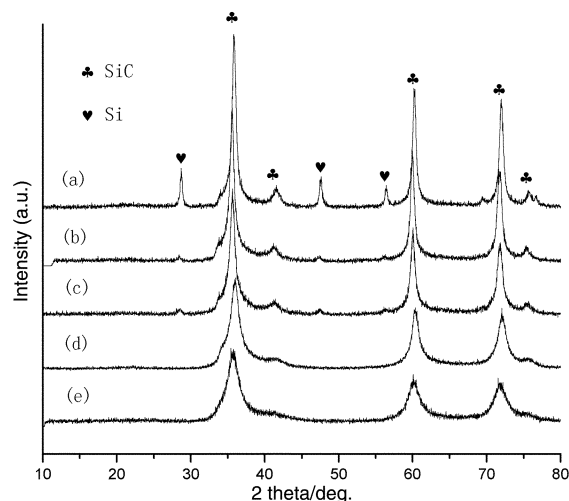
Fig. 5 XRD patterns of ceramics derived (1400 °C, 2 h, Ar) from the blending of PCS : M-PMS with a ratio of (a) 0.00 : 1.00; (b) 0.17 : 1.00; (c) 0.20 : 1.00; (d) 0.25 : 1.00 and (e) 1.00 : 0.00.
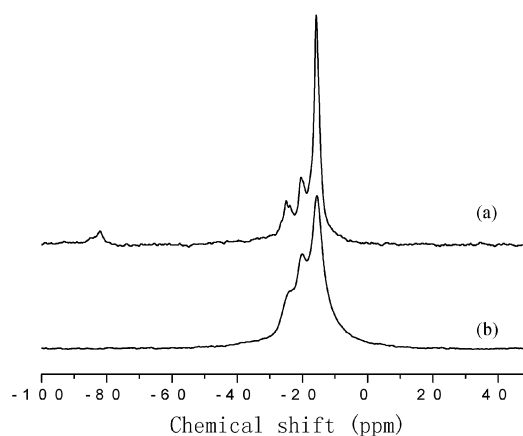
Fig. 6 ^{29}Si MAS-NMR of (a) PMS-derived ceramic and (b) ceramic derived from the hybrid precursor with a weight ratio of PCS : M-PMS = 0.25 : 1.00, pyrolyzed at 1400 °C for 2 h in Ar.

hybrid and single precursors were investigated comparatively by NMR analysis. Fig. 6 shows the ^{29}Si MAS-NMR spectra for the hybrid precursor with a 0.25 : 1.00 ratio of PCS : M-PMS, and the PMS single precursor. The peaks centered at −15.7 ppm and −20.2 ppm, were assigned to ordered and disordered β-SiC, respectively.[34] The peak centered around 24.9 ppm was assigned to α-SiC.[34] Both spectra show identical chemical shifts corresponding to α-SiC, ordered and disordered β-SiC, but the hybrid precursor derived ceramic seems to have a higher content of α-SiC and disordered β-SiC. The weak resonance in the downfield region of the spectrum observed at around −82 ppm in the ceramic derived from M-PMS was presumably assigned to $Si(O)_xC$ species or free Si because both resonances partly overlapped at an identical chemical shift as reported.[34–40] However, the resonance at −82 ppm is absent from the hybrid precursor derived ceramic's spectrum. At this point, it should be pointed out that the ceramic from M-PMS contained both silica and Si composition while the ceramic from the hybrid no Si, as shown in Table 3 and Fig. 5. This indicates that free Si from PMS was presumably homogeneously consumed by the free C from PCS. Secondly, Fig. 7 shows the ^{13}C MAS-NMR spectra of ceramics derived from PCS and the hybrid precursor. Both showed two main peaks centered around 22 and 127 ppm, which were mainly assigned to the C–Si$_4$ tetrahedral structure (C sp^3) of SiC and the graphite-like polyaromatic structure (C sp^2), respectively.[2,41–43] According to their relative intensities, the hybrid precursor

Table 3 Chemical compositions[a] of ceramics derived from various precursors (1400 °C, 2 h)

PCS : M-PMS	SiC (wt.%)	SiO$_2$ (wt.%)	Excess C (wt.%)	Excess Si (wt.%)
0.00 : 1.00	90.2	1.6	—	6.2
0.17 : 1.00	94.5	2.4	—	3.1
0.25 : 1.00	98.1	1.9	—	—
1.00 : 0.00	80.5	3.4	16.1	—

[a]Original EDX quantitative analysis provided only elemental composition. We presume the ceramics consist of SiC, SiO$_2$, free C or free Si. The contents of B and N were ignored because the PBN percentage in the hybrid precursor is very low (below 0.8 wt.%).
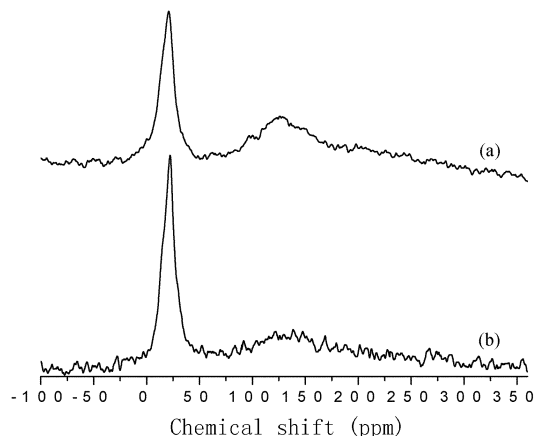

Fig. 7 ^{13}C MAS-NMR of (a) PCS-derived ceramic and (b) ceramic derived from the hybrid precursor with a weight ratio of PCS : M-PMS = 0.25 : 1.00, pyrolyzed at 1400 °C for 2 h in Ar.

derived ceramic still includes a small amount of free C, but its content is much lower than that of PCS-derived ceramics. This is entirely consistent with the XRD and ^{29}Si MAS-NMR. Finally, SEM-EDX elemental mapping of a 70 × 70 μm area on the specimen showed a homogeneous distribution of Si, C and O elements but different C and Si contrasts.

EDX analysis provided a quantitative elemental composition, and we presume the ceramics consist of SiC, SiO$_2$, free C or free Si, giving quantitative data as shown in Table 3. The B and N contents were ignored because the amount of polyborazine added into the hybrid precursor was comparatively very low (about 0.8 wt.%). The M-PMS derived ceramic contained 6.2 wt.% of free Si, which is lower than that of the ceramic derived from unmodified PMS because of the higher ceramic yield of M-PMS.[2,22] It's easy to understand the higher ceramic yield of PMS, and the lower free Si content in the PMS-derived ceramic. Stoichiometric SiC should be obtained from PMS with an atomic ratio of 1:1 C:Si if neither carbon nor silicon is lost during pyrolysis, giving an ideally high ceramic yield. The free carbon content in the PCS-derived ceramic is 16.1 wt.%, which is consistent with other reports with a fluctuation of free carbon content.[7,32] The ceramic derived from the hybrid precursor with an optimized ratio 0.25:1.00 contained 98.1 wt.% SiC and 1.9 wt.% SiO$_2$. The oxide contamination was caused presumably by the air-sensitive Si–H bonds of the hybrid precursor.[1,2,13,14] However, a low presence of oxides has been mostly determined due to the high chemical reactivity of the preceramic polymers.

Conclusion

We have developed a simple method of preparing near-stoichiometric SiC using a hybrid polymer. The method was first optimized by blending polycarbosilane (PCS) and polyborazine-modified polymethylsilane (M-PMS) at a ratio of

0.25 : 1.00 by weight. The hybrid precursor, with a molecular weight of 3869 and a polydispersity of 4.3, showed a very high ceramic yield of 82%. The highly viscous hybrid solution was readily spun into fiber by hand-drawing, thus demonstrating the processibility of the hybrid precursor. The XRD pattern and ^{29}Si MAS-NMR of the pyrolyzed hybrid polymer at 1400 °C showed no characteristic peaks assigned to excess Si, indicating that the free Si from M-PMS was homogeneously consumed by the free C from the PCS. The ^{13}C MAS-NMR of the hybrid polymer derived ceramic, showed a broad peak at 127 ppm, which was assigned to free carbon, and which was present at a very low level compared with the PCS-derived ceramic. Finally, the chemical composition of the ceramic product from the hybrid precursor at 1400 °C exhibited 98.1 wt.% of SiC and 1.9 wt.% of SiO$_2$ by SEM-EDX analysis.

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