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A modified polymethylsilane as the precursor for ceramic matrix composites

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Abstract

A novel SiC precursor, A-PMS, was synthesized through a reaction of polymethylsilane (PMS) with $SbCl_3$, where the Si–H in PMS reacts with Sb–Cl to form Si–Sb bond with HCl evaporated. A-PMS was used as a precursor to prepare C_f/SiC ceramic matrix composites (CMCs) via polymer infiltration and pyrolysis (PIP) process. It is evident that $SbCl_3$ plays a very important role in promoting chain crosslinking, transforming of the Si–Si into Si–C bonds and stabilizing PMS from very high oxidation trend of the active Si–H bonds. A-PMS keeps liquid at room temperature that is suitable for the infiltration in the absence of any solvent. A-PMS can be cured into a fully crosslinked structure at 320 °C that leads to a very high ceramic yield up to 91% and an Si/C ratio near 1.12 after pyrolysis. The resulted CMCs samples reached a density of 1.76 g cm^{-3} and a flexural strength of 381 MPa after only four infiltration–pyrolysis cycles.
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1. Introduction

Polymer infiltration and pyrolysis (PIP) process is now widely used in manufacturing ceramic matrix, such as SiC composites. An ideal polymer for this purpose must have the following properties: (1) be a liquid or soluble, (2) be stable and curable, (3) give high ceramic yield, and (4) derive near-stoichiometric target ceramic, such as SiC [1].

Polymethylsilane, or PMS, was once looked upon as a potential precursor because it is a liquid and the C:Si ratio is 1:1. However, PMS suffered from low ceramic yield and poor processability [2,3].

Efforts were taken to increase the ceramic yield of PMS. Iseki [4] heated PMS in the polymer-refluxing apparatus at 450 °C. Kho [5] employed organoborate additives such as $B[OSi(CH_3)_3]_3$. Cao [6] heated PMS with polyborazine (PBN) at 70 °C. The other organic and inorganic compounds such as $MoCl_5$ [7], $TiCl_4$ [8], TVS ($Si(CH=CH_2)_4$)

[9] and $Co_2(CO)_8$ [10] were also tried. Some of the above methods increased ceramic yield of PMS significantly, but it seems difficult to control the high reactivity of the additives that cause PMS turn to an insoluble and infusible solid.

In this paper, PMS was reacted with a stable compound $SbCl_3$, which shows a moderate reactivity in balancing stability and low crosslinking degree. The modified PMS, or A-PMS, is a liquid at room temperature and suitable for the PIP process. After infiltrating or molding, the remained Sb–Cl in A-PMS can further react with Si–H by heating at 320 °C that insures A-PMS pyrolyzed into SiC with a high ceramic yield.

2. Experiments

PMS was synthesized from methyl dichlorosilane (98%, Xinghuo, China) and metallic sodium (97%, Lingfeng, China) in toluene [11]. Solid $SbCl_3$ (99%, Shanghai Regent, China) was added, in the range of 2–8 wt%, into PMS at room temperature under ultrasonic condition. With the dissolving of $SbCl_3$ and the releasing of HCl gas, PMS

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turned into a dark brown homogeneous oily liquid called A-PMS. A-PMS was crosslinked at 320 °C and then pyrolyzed at 1250 °C to yield black dense SiC with good crystallinity. The whole process was carried out in N_2.

C_f/SiC composites were prepared via the PIP process [12,13]. First, the 3D carbon fiber (Jilin Carbon, China, braided in Nanjing, China) was infiltrated with A-PMS in vacuum conditions. Afterwards, the sample was heated to 320 °C and held for 30 min followed by pyrolysis at 1250 °C in N_2. To densify the composites, four infiltration–pyrolysis cycles were repeated in the same conditions. For comparison, composites were also prepared with polycarbosilane or PCS (99%, MW 1300, NUDT, China) through the same process.

The structures of PMS and A-PMS were investigated using viscosity test (rotary viscometer, NDJ-1), molecular weight measurement (GPC, Waters-244, polystyrene standard), FT IR spectra (Nexus 670), cross-polarization magic angle spinning ^{1}H and ^{29}Si NMR (Bruker DSX-300) and thermal analysis (Netzsch STA 449C). The structure of the pyrolysis product was studied with XRD (Siemens D-500, Cu Kα) and elemental analyses with Si (gravimeter), C (combustion volumetric method), Sb (chemical titration) and O (LECO TC-436). The properties of C_f/SiC composites were characterized by density and open porosity measurement (Archimedes method) and three-point bending tests (Instron-1342, with span/height ratio of 15 and a crosshead speed of 0.5 m/min).

3. Results and discussion

3.1. Structure of A-PMS

With $SbCl_3$ added into PMS, the molecular weight and the viscosity of the polymer increased significantly as shown in Table 1. From the FT IR spectra of A-PMS and PMS (Fig. 1), one can see that the peak of Si–H at $2106\ cm^{-1}$ shrinks while the other peaks remain unchanged. The similar Si–H consuming which reacted with other metallic halides was reported by Wang [7] and Tsirlin [14]. Considering the releasing of HCl, the main reaction should be described as the following scheme:

$$\equiv Si–H + SbCl_3 \rightarrow \equiv Si–SbCl_2 + HCl$$
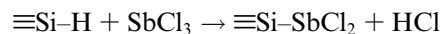
^{1}H NMR shown in Fig. 2 indicates that the integral area of the peak for Si–H groups in PMS at 3.8 ppm is 22.3% related with $SiCH_3$ at 0.4 ppm, lower than the ratio of ideal structure 33.3% because of the unavoidable oxidation of Si–H. However, for A-PMS, some new peaks emerge near 0.4 ppm, where the peak at 1.2 ppm can be assigned as
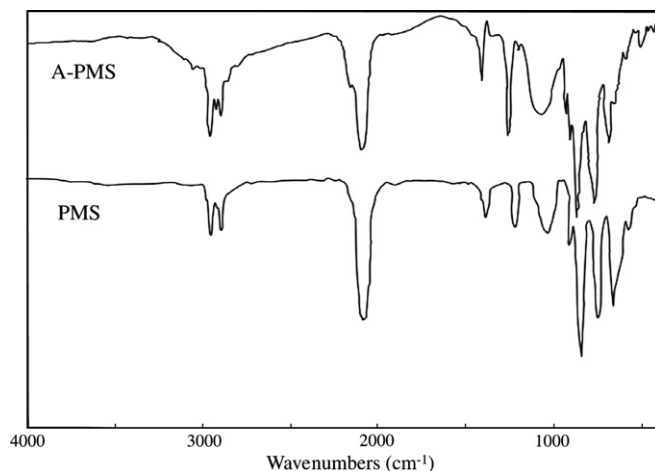

Fig. 1. FT IR spectra of PMS and A-PMS.

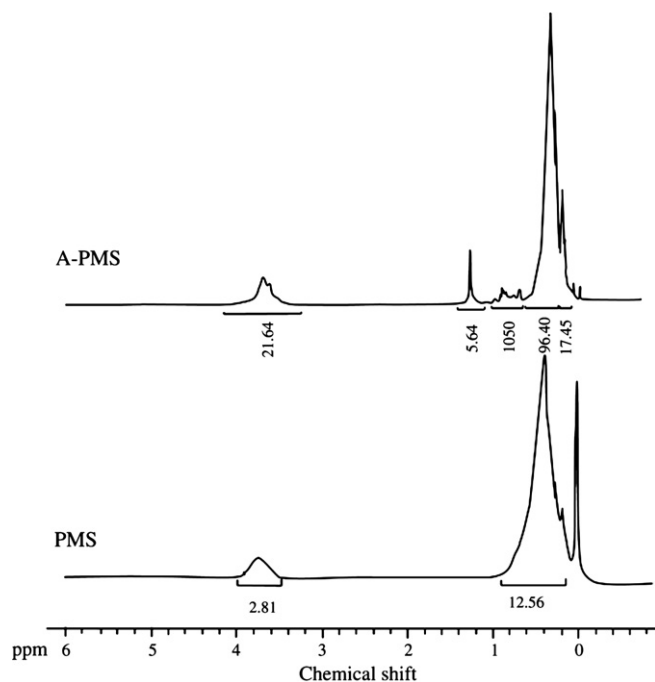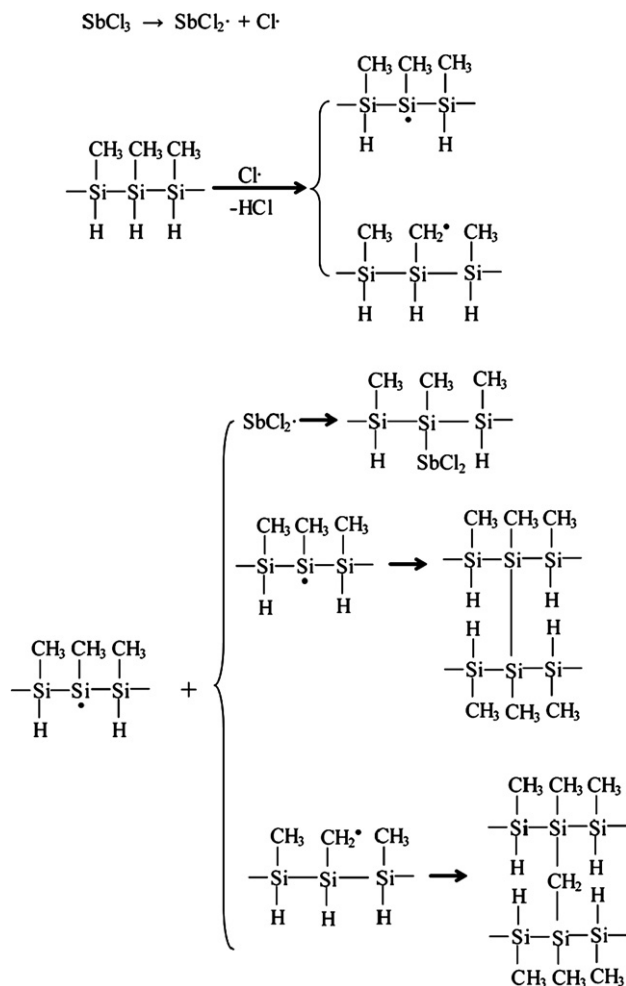Fig. 2. ^{1}H NMR spectra of PMS and A-PMS.

Si–CH_2–Si, which also appears in Kumada arrangement of polydimethylsilane [9,15]. The integral area of Si–H peak in A-PMS decreases into 16.6% related with the total area of the peaks between 0 and 1.2 ppm assigned to C–H that indicates the Si–H consuming mentioned above. The other interesting feature is that Si–H peak splits into two (3.75 and 3.8 ppm) (see Fig. 1). The formation of Si–Sb units and the change of chemical environment would be responsible for the new signals.

As discussed above, it could be concluded that the molecule of A-PMS was composed of the following units: –Si–Si(MeH)–Si–, Si–CH_2–Si– and –Si–Si(MeSb)–Si–. The substituted Sb atoms may act as the center of the branch or even crosslinking when heated.

Table 1
Properties of PMS and A-PMS

Samples	Color	M_w	M_n	M_w/M_n	Viscosity (Pa s)
PMS	Yellow	1060	410	2.58	0.10
A-PMS	Dark brown	1850	460	4.06	0.16

3.2. Mechanism of the reaction between PMS and SbCl₃

In inert atmosphere, Si–H units in PMS are relatively stable at room temperature. However, when $SbCl_3$ is added, PMS reacts and leads to chain expansion, branch and rearrangement that can be explained by free radical mechanism. The emergence of –Si–CH$_2$–Si– unit in A-PMS implies Si–CH$_2^\cdot$ free radicals exist during the reaction due to the attack of Cl$^\cdot$ toward –Si–CH$_3$ group. Fig. 3 shows the mechanism of the reaction between PMS and $SbCl_3$.

In the previous work [6,7], active reactants like $MoCl_5$ and PBN were introduced to promote the crosslinking of PMS, resulting fully crosslinked product. But in this work, A-PMS is still a liquid instead of a solid. So it is reasonable to imagine that only part of the Sb–Cl reacted with PMS while the other Cl atoms remained joint to Sb. The low crosslinking degree ensures A-PMS to be at low viscosity. The –Sb–Cl units will continue reacting with Si–H when heated. This will be discussed in Section 3.4.

3.3. Stability of A-PMS in air

It is known that the high content of Si–H groups in PMS is the reason of high oxidation activity with air [16,17]. As mentioned above, part of the Si–H groups in PMS are consumed in the reaction with $SbCl_3$ and the chain structure changed significantly. So A-PMS is more stable in air compared with PMS. Exposed in air for 120 min, the oxygen content in PMS increases from 1.1% to 7.0% while in A-PMS from 1.1% to 4.7% (Fig. 4). This means that less oxygen would be introduced into SiC during the operation. Furthermore, A-PMS will not self-ignite and can be safely used.

3.4. Structure of cured A-PMS

When A-PMS was heated, large amount of HCl gas was released. As discussed in Section 3.1, there are plenty of Si–H groups in A-PMS and there were still some Cl atoms joint to Sb. In higher temperature, the remained Sb–Cl continued to react with Si–H to give out HCl. Fig. 5 shows the FT IR spectra of A-PMS crosslinked at different temperatures. It is obvious that the peak at 2100 cm^{-1} for Si–H, 2900 cm^{-1} and 1400 cm^{-1} for C–H bond decreased with rising temperature that means the consuming of Si–H and some of C–H groups during the crosslinking. When A-PMS was heated to 320 °C, there was a dramatic change in the structure. The peaks for Si–H and C–H groups shrinked significantly and the peak for Si–C appeared at 830 cm^{-1}.

Fig. 6 shows the ^{29}Si MAS NMR of cured A-PMS and cured PMS. Both of the spectra reflected the following units: Si–(MeSiH)–Si (−45 to −75 ppm), Si–(MeSi)=Si$_2$ (−60 to −75 ppm), Si–Si (−35 ppm), SiC$_3$H (−17 ppm), SiC$_4$ (0 ppm). In A-PMS, the main peak is at −19 ppm for SiC$_3$H and 0 ppm for SiC$_4$, which belong to the highly crosslinked structure, while in PMS, the main peak is at

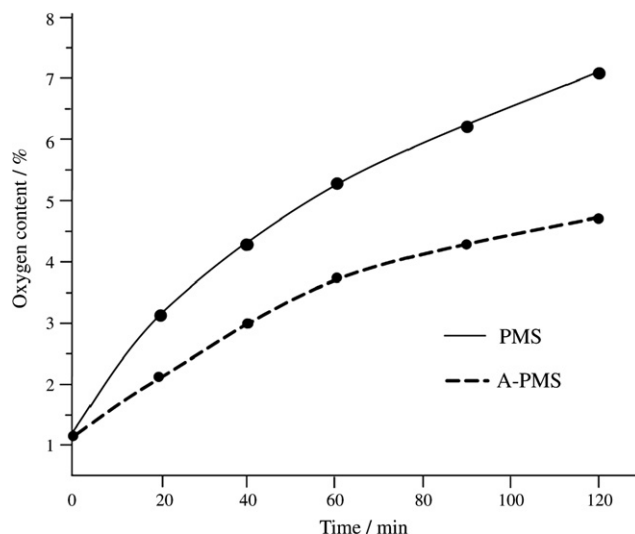Fig. 3. Reaction mechanism between SbCl₃ and PMS.

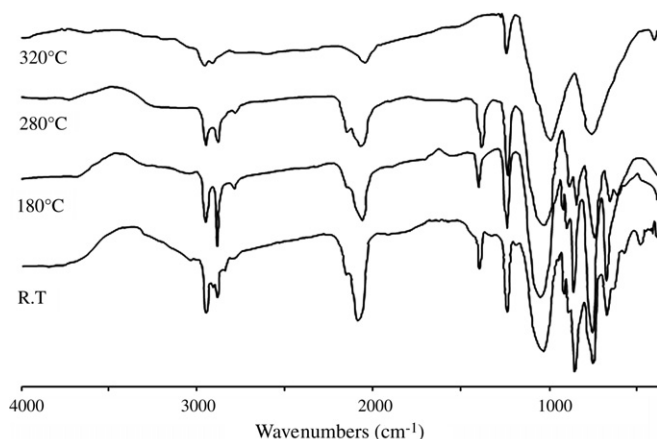Fig. 4. Oxygen content of PMS and A-PMS exposed in the air.

Fig. 5. FT IR spectra of A-PMS crosslinked at different temperature.

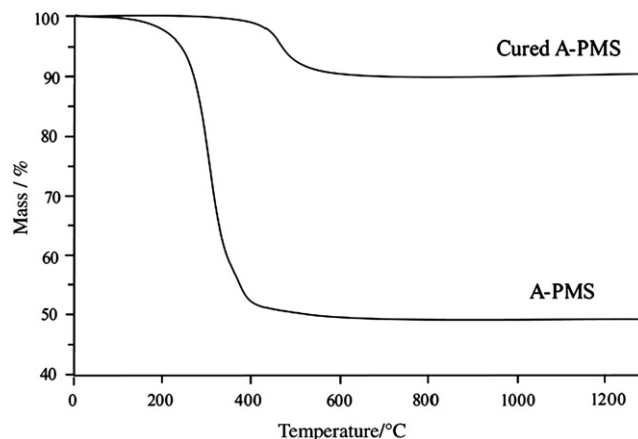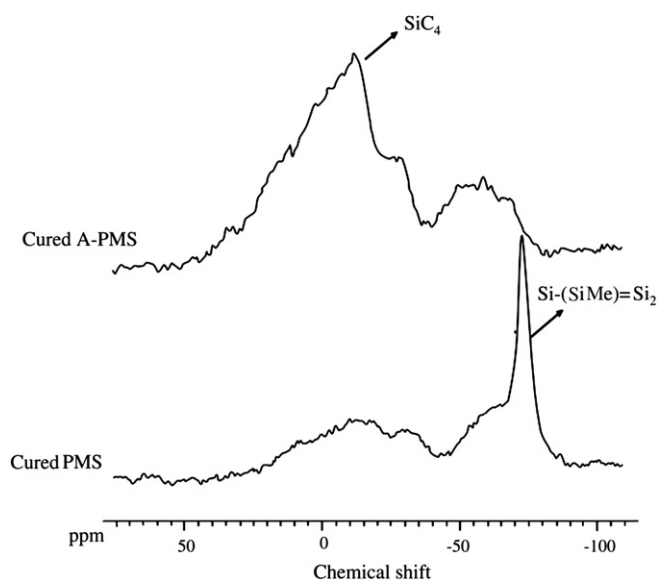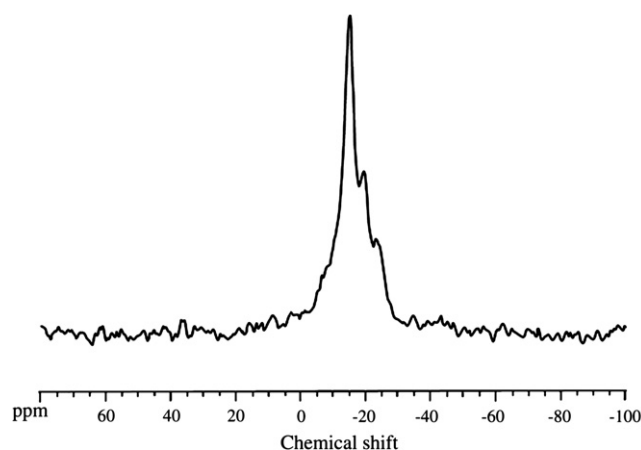Fig. 7. TG curves of A-PMS and cured A-PMS.

Fig. 6. ^{29}Si MAS NMR spectra of cured PMS and cured A-PMS.

Fig. 8. ^{29}Si MAS NMR spectrum of A-PMS derived SiC.

−65 ppm for Si–SiMe≡Si$_2$ in the branched structure. It was discussed that the rearrangement from –CH$_3$Si$^.$ to Si–CH$_2^.$ only happened above 370 °C, so in cured PMS, the main structure was still Si–Si. But in cured A-PMS, the Cl atoms joint to Sb will continue to react with Si–H and Si–CH$_3$ groups. The reaction between Cl$^.$ and –CH$_3$ produces large amount of Si–CH$_2^.$ free radicals to form highly crosslinked SiC$_4$ and SiC$_3$H units. The FT IR and ^{29}Si MAS NMR indicated that a more highly crosslinked structure is formed in cured A-PMS, which led to a very high ceramic yield. The ceramic yield of cured A-PMS is 91%, much higher than that of A-PMS as synthesized (see Fig. 7).

3.5. Analysis of A-PMS derived SiC

The ^{29}Si MAS NMR spectrum of SiC in Fig. 8 shows a sharp peak at −15.1 ppm for SiC$_4$ units in β-SiC, which is comparable with the peak of −16 ppm in PCS derived SiC

[18,19]. The XRD pattern of the pyrolyzed product of A-PMS is shown in Fig. 9. The three most intense peaks at $2\theta = 36°$, 61° and 72° corresponded, respectively, to the diffraction of (1 1 1), (2 2 0), and (3 1 1) lattice planes of β-SiC. Chemical analyses show that pyrolysis of A-PMS produces a SiC containing 63.2% Si, 24.2% C, 3.5% Sb and 5.5% O. The Si/C ratio is 1.12, lower than 1.2 of PMS derived SiC. Therefore, careful control of SbCl$_3$ added will lead to near-stoichiometric SiC.
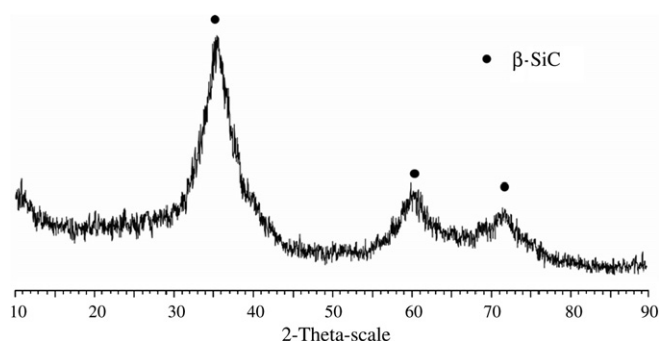

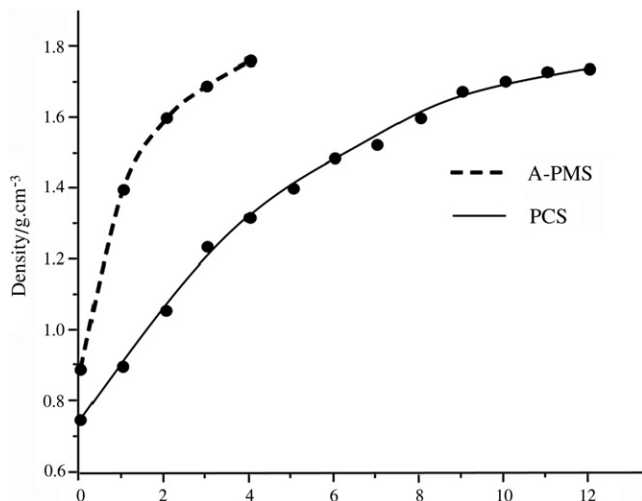Fig. 9. XRD spectrum of pyrolyzate product of A-PMS at 1250 °C.

Fig. 10. Density–cycle curves of the C_f/SiC composites prepared by PIP technology using A-PMS and PCS (in xylene) as infiltrating preceramic polymers under identical procedure.
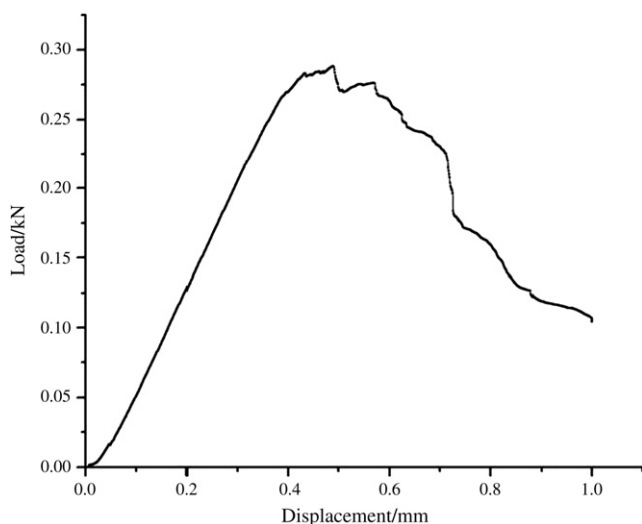

Fig. 11. Load–displacement curve of the composite from A-PMS.

3.6. CMCs with A-PMS as the precursor

C_f/SiC composites with the density of 1.76 g cm^{-3} were prepared after 4 cycles. In the case of PCS, the same density could not be achieved until 12 cycles (Fig. 10). The novel preceramic polymer reduces the number of infiltration–pyrolysis cycles significantly. The load–displacement curve of the composite (Fig. 11) shows a gliding fracture. The flexural strength is 381 MPa and the fracture toughness is 15.74 MPa m$^{1/2}$. In the SEM micrograph of the fracture surface (Fig. 12), the composite shows an extensive fiber debonding and pull-out, which indicated the suitable fiber/matrix interfacial bonding and resulted in high mechanical properties.
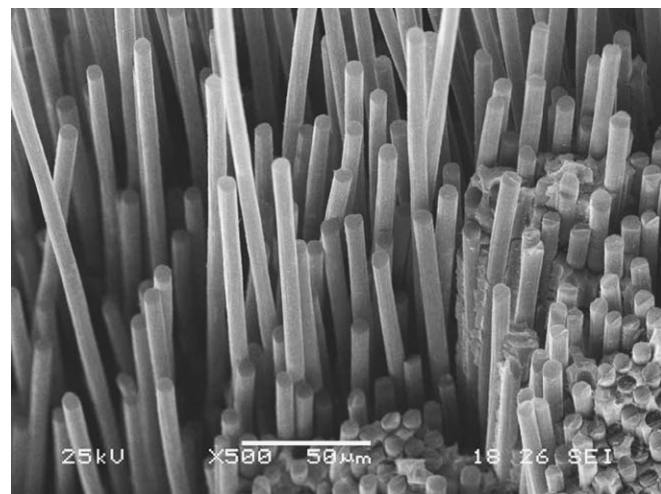

Fig. 12. SEM micrograph of the fracture surface of the composite from A-PMS.

4. Conclusion

A novel SiC precursor, A-PMS, was synthesized through a reaction of polymethylsilane (PMS) with SbCl$_3$. A-PMS is a liquid at room temperature that is suitable for the infiltration in the absence of any solvent. A-PMS is more stable in air compared with PMS, which is too sensitive to air in the process. Furthermore, the cured A-PMS leads to a very high ceramic yield up to 91% in N$_2$ at 1250 °C. The derived SiC is near stoichiometric with Si/C molar ratio 1.12. As a result, A-PMS is a good precursor of SiC for PIP process.

SbCl$_3$ is considered to take crucial effects on PMS modification. Firstly, the obtained A-PMS was stabilized as part of Si–H in PMS was consumed by SbCl$_3$. Secondly, the modification reaction was well controlled that A-PMS is partly crosslinked and is at low viscosity of 0.16 Pa.s at room temperature. Lastly, SbCl$_3$ was considered to facilitate the transformation of Si–Si to Si–C chain during the modification and curing reaction resulting higher ceramic yield.

C_f/SiC composites were prepared by the PIP process. The density of 1.76 g cm^{-3} is achieved after 4 cycles using A-PMS, which will not be achieved less than 12 cycles using PCS. The flexural strength 381 MPa and the fracture toughness 15.74 MPa m$^{1/2}$. The use of A-PMS in the PIP process is proved to be feasible and effective.

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