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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.

Keywords: Polymethylsilane; Precursor; C_f/SiC composites

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 ^1H 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:

$$\equiv Si{-}H + SbCl_3 \rightarrow \equiv Si{-}SbCl_2 + HCl$$

^1H 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 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

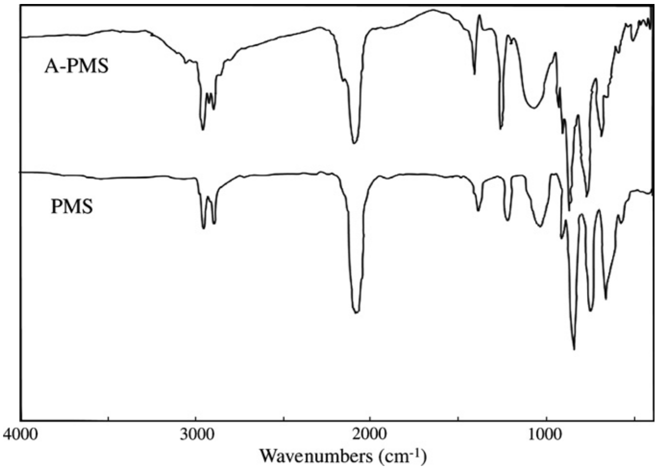

Fig. 1. FT IR spectra of PMS and A-PMS.

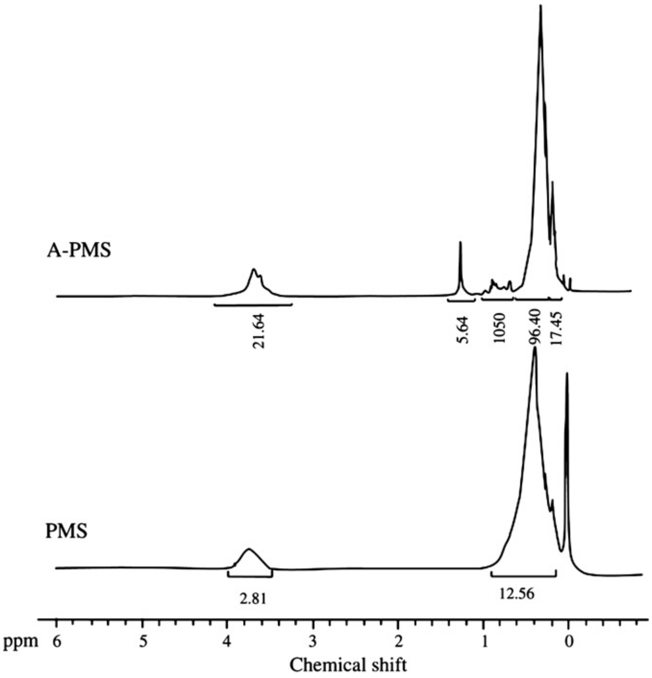

Fig. 2. ^1H NMR spectra of PMS and A-PMS.