Synthesis and characterization of polyaluminocarbosilane

YUXI YU, XIAODONG LI, FENG CAO
Key Laboratory of Ceramic Fibers and the Composites, Institute of Aerospace and Materials Engineering, National University of Defence Technology, Changsha, Hunan 410073, People's Republic of China
E-mail: yu_heart@163.com

Generating silicon-based ceramic fibers containing heteroelements from organosilicon polymer has received considerable attention in recent years [1–3]. Intensive investigations into development of precursors to silicon-based ceramic fibers containing heteroelements have been actively performed [2, 3]. Of these, silicon containing polymers have been the most vigorously developed [3, 4]. Polycarbosilane (PCS), a precursor of commercial Nicalon SiC ceramic fiber, was synthesized by thermal decomposition of polydimethylsilane (PDMS) in an autoclave at 470 °C [1, 5–7]. Polytitanocarbosilane, which is produced by a condensation reaction of PCS with titanium (IV) tetra-alkoxide, is a precursor of commercial Tyranno Lox M SiC ceramic fiber [8, 9]. Polyzirconocarbosilane, which is synthesized by a condensation reaction of PCS with zirconium (IV) acetylacetonate, is a precursor of commercial Tyranno ZM SiC ceramic fiber [10, 11].

Recently, Si—C—Al and Si—C—O—Al ceramic fibers were prepared by Ishikawa *et al.* [12]. These fibers showed excellent heat resistance (up to 2000 °C), high strength (over 2.5 GPa) and modulus (over 300 GPa), superior creep resistance, and prominent alkali resistance. To date, these fibers have the best performance for high temperature resistance of SiC-based ceramic fibers. Therefore, study of the precursor of these fibers has been attracting keen interest. Polyaluminocarbosilane (PACS) is a precursor of Si—C—Al and Si—C—O—Al ceramic fibers. Ishikawa *et al.* synthesized PACS by the reaction of PCS with aluminum acetylacetonate ($Al(AcAc)_3$). However, because PCS is solid, when the reaction proceeded, $Al(AcAc)_3$ sublimated easily.

In this work, in order to reduce the sublimation of $Al(AcAc)_3$, PACS was prepared by the reaction of polysilacarbosilane (PSCS) instead of PCS with $Al(AcAc)_3$. PSCS was a liquid product produced by thermolysis of PDMS. PACS was prepared by the reaction of 100 g PSCS with 4 g $Al(AcAc)_3$ (Aldrich, 99%) above 300 °C in a stream of nitrogen gas at atmospheric pressure. $Al(AcAc)_3$ was introduced into the bottom of the flask. PSCS covered the $Al(AcAc)_3$ in order to reduce sublimation of $Al(AcAc)_3$. After reaction, a polymerized product was obtained. It was dissolved in xylene and solution filtered. After the solvent was removed and vacuum distilled to remove insoluble species and oligomer, a gold-colored solid polymer was obtained, which is referred to as PACS.

FT-IR spectra were recorded between 4000 and 400 cm^{-1} on a Nicolet-360 spectrometer by the KBr pellet method. Gel permeation chromatography (GPC) measurements were taken with Waters-244. THF was used as a solvent at a flow rate of 1×10^{-6} m^3/min at room temperature. Polystyrene standards were used for calibration. Chemical analysis of PACS was made for four elements: Si (by a gravimetric method); Al (by a calorimetric method); C (by a combustion volumetric method); O (by gas analysis). Thermogravimetric (TG, Hi-Res TGA 2950) analyses were conducted to examine the thermal behavior of polymer precursors.

From elemental analysis (Table I), the chemical composition of the PACS precursor was Si, 45.0 wt%; C, 39.0 wt%; Al, 0.80 wt%; O, 3.4 wt%; H, 11.8 wt% (by difference), giving the empirical formula $SiC_{2.0}H_{7.3}O_{0.13}Al_{0.02}$. Because of the sensitivity of the PACS precursor to oxygen and moisture, absorption of oxygen or moisture could lead to the higher than expected oxygen content. Narisawa *et al.* [13] found that oxygen can be introduced into the precursor polymer structure during its synthesis. Variations in the synthesis conditions such as the polymerization temperature will also affect the composition with a general decrease in the amount of carbon and hydrogen as the degree of polymerization of the PACS increase. The results show that the atomic ratio of the carbon to silicon in the PACS precursor is about 2:1.

Fig. 1 shows the GPC curves of PACS and PSCS. The broad peak in the high molecular weight region of PACS GPC curve is found to be higher than that of PSCS. The number average molecular weight, $\overline{Mn}$ of PACS was 2265. When the reaction of PSCS with $Al(AcAc)_3$ proceeded, the $\overline{Mn}$ increased with reaction time, but the extent of the increase in $\overline{Mn}$ became smaller gradually.

The FT-IR spectra of PSCS, PACS, and $Al(AcAc)_3$ are shown in Fig. 2. In the case of PSCS and PACS, the absorption at 2950 cm^{-1} (C—H stretching), 2100 cm^{-1} (Si—H stretching) 1400 cm^{-1} (C—H deformation), 1350 cm^{-1} (CH_2 deformation of Si—CH_2—Si bond), 1250 cm^{-1} (Si—CH_3 deformation), 1040 cm^{-1} (Si—O stretching), 1020 cm^{-1} (CH_2 wagging of Si—CH_2—Si bond), 820 cm^{-1} (Si—C stretching) are observed. On the other hand, in the case of $Al(AcAc)_3$, the characteristic absorption at 1580 cm^{-1} (C=O stretching) and 1515 cm^{-1} (C=C stretching) is observed. In the

0022–2461

TABLE I Chemical analysis of PACS

Compound	Chemical analysis (wt%)					Chemical formula	O/Al (mole ratio)
	Si	C	O	H	Al		
PACS	45.0	39.0	3.4	11.8	0.8	$SiC_{2.0}H_{7.3}O_{0.13}Al_{0.02}$	6.5

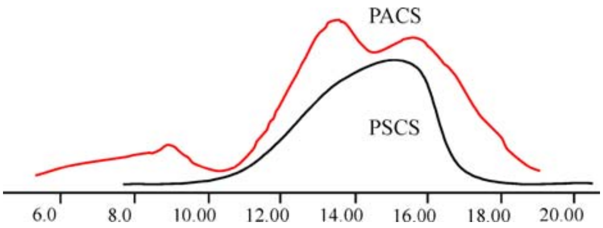

Figure 1 GPC profiles of PSCS and PACS.

absorption of PACS, which was synthesized by the reaction of PSCS and $Al(AcAc)_3$, a tremendous decrease in the number of Si—H bonds was found. Further, in the absorption of PACS, the appearance of characteristic absorptions of $Al(AcAc)_3$ is recognized. It is assumed that the reaction of PSCS with $Al(AcAc)_3$ results in the delocalization of the electrons of the C=O bonds in $Al(AcAc)_3$ and/or the delocalization of the electrons of the C=C bonds in $Al(AcAc)_3$. On the other hand, Cao [14] researched the reaction of PSCS with $Al(AcAc)_3$ by means of gas chromatograph mass spectroscopy (GC-MS). The result of GC-MS analysis of the reaction by-product showed that the acetylacetonate was a by-product of the reaction based on the ligands of $Al(AcAc)_3$.

From the aforesaid increase in the molecular weight with decrease in the number of Si—H bonds and evolution of the acetylacetonate, the following reaction scheme was considered (Fig. 3). As can be seen from this reaction scheme, the increase in the molecular weight was estimated by the cross-linking reaction with the production of Si—Al bonds.

TG analysis curves of the PACS and the PCS are shown in Fig. 4. TG analysis indicates that the organic groups of both polymers are decomposed below about 600 °C, and then the weight residue of the PACS becomes larger than that of the PCS with increasing temperature up to 1000 °C in a stream of nitrogen gas. The weight residues of the PACS and the PCS at 1000 °C were 78 and 51 wt%, respectively. Accordingly, The PACS is found to be a better preceramic polymer with a higher ceramic yield than the PCS.

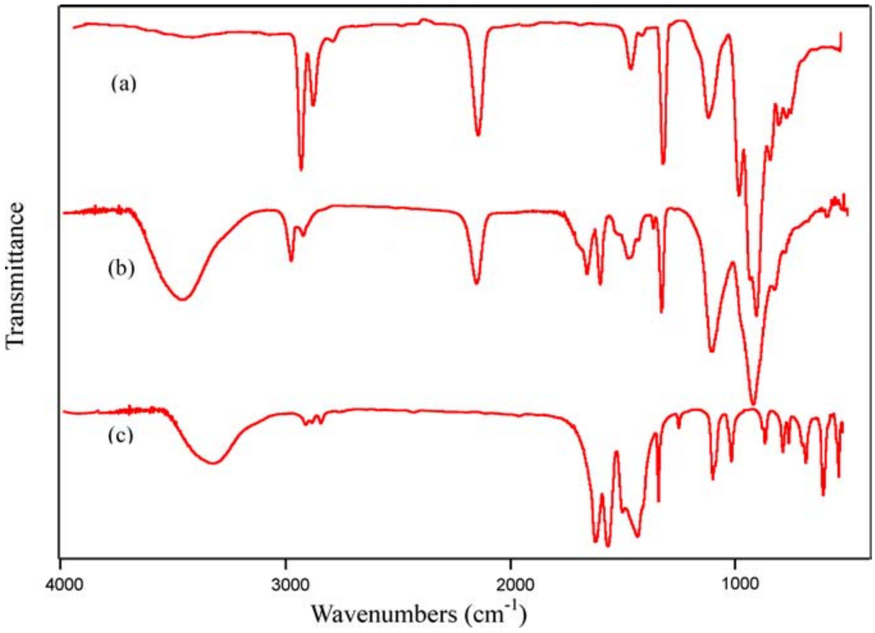

Figure 2 FT-IR spectra of: (a) PSCS, (b) PACS, and (c) $Al(AcAc)_3$.

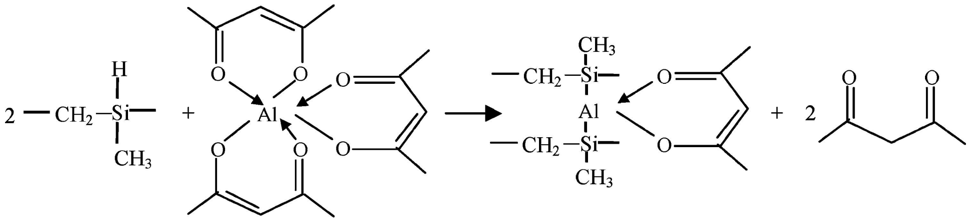

Figure 3 The reaction scheme of PSCS with $Al(AcAc)_3$.

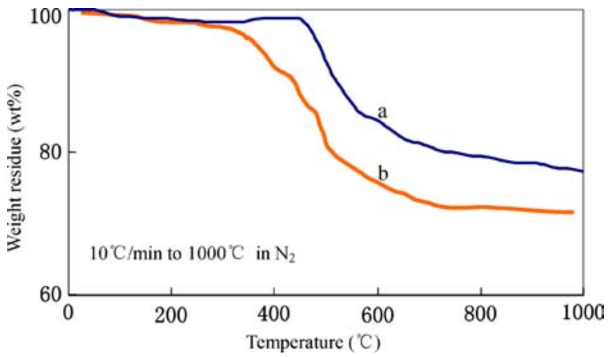

Figure 4 TG curves of: (a) PACS and (b) PCS.

Acknowledgment

This work was supported by the Chinese Natural Science Fund under grant no. 59972042.

References

1. S. YAJIMA, J. HAYSHI, M. OMORI and K. OKAMURA, *Nature* **261** (1976) 683.
2. Y.-X. YU, X.-D. LI and F. CAO, *J. Chin. Ceram. Soc.* (in Chinese) **31**(4) (2003) 371.
3. W. RICE, *Amer. Ceram. Soc. Bull.* **62**(8) (1983) 889.
4. M. BIROT, J. PILLOT and J. DUNOGUES, *Chem. Rev.* **95** (1995) 1443.
5. R. LAINE and F. BABONNEAU, *ibid.* **5** (1993) 260.
6. Y. HASEGAWA, M. IIMURA and S. YAJIMA, *J. Mater. Sci.* **15** (1980) 720.
7. Y. HASEGAWA and K. OKAMURA, *ibid.* **18** (1983) 3633.
8. T. YAMAMURA, T. ISHIKAWA, M. SHIBUYA and T. HISAYUKI, *ibid.* **23** (1988) 2589.
9. T. ISHIKAWA, Y. KOHTOKU and K. KUMAGAWA, *ibid.* **33** (1998) 161.
10. H. YAMAOKA, T. ISHIKAWA and K. KUMAGAWA, *ibid.* **34** (1999) 1333.
11. K. ITATANI, K. HATTORI, D. HARIMA, M. AIZAWA and I. OKADA, *ibid.* **36** (2001) 3679.
12. T. ISHIKAWA, Y. KOHTOKU, K. KUMAGAWA, T. YAMAMURA and T. NAGASAWA, *Nature* **391** (1998) 773.
13. M. NARISAWA, *Bull. Chem. Soc. Jpn.* **68** (1995) 1098.
14. F. CAO, X.-D. LI, P. PENG, C.-X. FENG and J. WANG, *J. Mater. Chem.* **12** (2002) 606.

Received 21 November 2003
and accepted 12 August 2004