

Modification of Polycarbosilane as a Precursor with High Ceramic Yield for Oxygen-Free SiC Fibers

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Abstract—Polycarbosilane (PCS) was modified by addition of 1 wt% polyborazine and subsequent heat treatment at 70–400 °C. The modified PCS exhibited highly improved ceramic yield from original 63% to 78% by heating at 70 °C for 10 h. The molecular weight of the PCS modified at higher temperatures markedly increased, then was rendered infusible but soluble PCS in organic solvent on heating at 300 °C. ¹H-NMR indicated that original PCS was enhanced by dehydrocoupling reaction between Si-H groups. Solution of the modified PCS was hand-drawn to fibers, followed by direct pyrolysis up to 1,400 °C without air-curing step to convert into oxygen-free SiC fibers. The morphology and crystalline phase were determined by SEM and XRD analysis, respectively.

Key words: Polycarbosilane, Polyborazine, High Ceramic Yield, Dry Spin, SiC Fibers

INTRODUCTION

The precursor process for SiC ceramics by pyrolysis of polycarbosilane (PCS) with structure $-(CH_2-(SiHCH_3))_n-$ has drawn much attention since the pioneering work of Yajima in 1975 [Biro et al., 1995]. In the past twenty years, PCS-derived SiC ceramic products, such as fibers with trademark Nicalon, composites [Kang and Yang, 1998] and coatings, have been developed. However, PCS-derived SiC fibers did not exhibit high mechanical performance of the respective dense bulk materials, which is due to pores and other drawbacks associated with the state of the art of the precursor. Moreover, the high cost of the precursors prevents wide industrial applications. Therefore, modification of PCS for dense ceramic materials by simplified process is the critical issue for improving the mechanical properties and decreasing the preparative process cost. In this context, our previous work [Kho et al., 2000] may provide a clue that the ceramic yield of polymethylsilane (PMS) with structure $-(SiHCH_3)_n-$ was significantly improved from 30% to 78% by simple addition of 1 wt% polyborazine (PBN)/and subsequently treated at 70 °C for 10 h, which enhanced the molecular weight.

On the other hand, the typical process for SiC fibers from PCS included synthesis of precursor, melt-spinning, air-curing and final pyrolytic conversion to ceramic. The air-curing step was necessary to render the common PCS fibers infusible prior to pyrolysis because the low molecular weight polymer PCS was easily fused over 200 °C. However, it turned out that the introduced oxygen was disadvantageous by degrading the mechanical strength of fibers at high temperatures over 1,200 °C [Pysher et al., 1989].

These works suggested that one can develop infusible but solu-

ble PCS with high molecular weight. The enhanced precursor could be shaped into fibers by dry spin (i.e., solution spin), and directly pyrolyzed without extra air-curing step, resulting in the oxygen-free SiC fibers. Furthermore, the PCS is also suitable for preparing SiC matrix composites since it is soluble in organic solvent. In the approach that was reported, high molecular weight PCS was synthesized by using autoclave with fractionation step [Fan et al., 1999]. However, the synthetic condition is too harsh to be practical.

In this paper, we report a simple method for enhancing the molecular weight and ceramic yield of PCS. It demonstrates that the infusible and soluble PCS is spinnable to convert oxygen-free SiC fibers without air-curing step. An additional benefit of the system is to introduce B and N into SiC as crystalline growth inhibitor even at high temperature, resulting in superior heat-resistance.

EXPERIMENTAL

All samples described in this investigation were manipulated in a purified nitrogen or argon atmosphere or vacuum system. Solvent THF was purified by distillation with sodium. Polycarbosilane (PCS) was synthesized by thermolysis of polydimethylsilane (PDMS) at ambient pressure in our own laboratory as described [Chu et al., 1999]. Polyborazine (PBN), $-(B_3N_3H_6)_n-$, was synthesized by the same method as in our previous report [Kho et al., 2000]. Prior to modification of PCS by PBN, 5 g PCS with 1 wt% PBN was mixed homogeneously by resolving in THF followed by stirring for 2 h and then vacuum distillation at ambient temperature to remove THF. The powdery mixtures were heated at 70–400 °C for 1–10 h in a Schlenk flask equipped with condenser and thermometer. The pyrolysis of the modified PCS for SiC powder was run in a mullite tube up to 1,400 °C with rate of 10 °C/min under ambient pressure and argon atmosphere.

Solubility of the modified PCS samples was determined by adding ~100 mg sample to 10 mL of THF. When the dissolved solution was clear, it was determined as soluble, and cloudy as partly soluble. Melting point was investigated by light permeability with

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an automatic electrothermo melting-point apparatus (Model 9200). The polymer sample was introduced into a 1-mm-diameter glass capillary tube and the temperature was raised at a rate of 2 °C/min. The temperature at which light began to be transmitted was determined as the melting-starting temperature, and the temperature at which the whole tube turned transparent as the melting-finished temperature.

The modified PCS, infusible but soluble polymer, was used to dry spin for fiber. Sticky mixture was obtained by dissolving 2 g of modified PCS in 0.5 ml THF, then aged overnight to remove bubbles. Dry spinning was carried out by hand-drawing technique in a glove-bag filled with N₂. Green fibers with length over 20 cm were prepared. So-obtained green fibers were pyrolyzed under argon with the following heating cycle (from room temperature to 100 °C for 3 h; 100–200 °C for 3 h; holding at 200 °C for 2 h; 200–500 °C for 6 h; holding at 500 °C for 2 h; 500–1,400 °C for 3 h; holding at 1,400 °C for 1 h; programmed cooling to room temperature for 1 h). Molecular weight distributions were determined by GPC (gel permeation chromatography, Waters) with s-Styragel columns calibrated with polystyrene standards and with THF as eluent as a flow rate of 0.5 ml/min. ¹H nuclear magnetic spectroscopy was recorded by Varian Unity 400 (400 MHz) with C₆D₆ solvent. ²⁹Si nuclear magnetic spectroscopy was recorded by FT500MHz-NMR Spectrometer (BRUKER AMX 500) with CDCl₃ solvent. Thermogravimetric analysis (TGA; TA Instrument 2950) was carried out at heating rate of 10 °C/min to 1,000 °C under N₂ atmosphere. Powder X-ray diffraction of the ceramic powder was performed by using the Rigaku Cu-K α system. The morphology of SiC fibers was characterized by scanning electron microscopy (SEM, JSM-6300).

RESULTS AND DISCUSSION

Fig. 1 shows the TGA curves of PCS modified by 1 wt% of PBN and the as-mixed PCS with PBN. Thermal behavior was compared to that of non-enhanced PCS treated by the same conditions with no addition of PBN and PCS feed stock. It is clearly obvious that after treatment by 1 wt% PBN, the ceramic yield of PCS was enhanced from 63 wt% [Fig. 1(a)] to 78 wt% [Fig. 1(d)]. It is interesting that the as-mixed PCS without heat-treatment also exhibited the same level of ceramic yield as the modified PCS. Conversely, the PCS treated under the same temperature in absence of PBN only has ceramic yield of 64 wt%. The improvement of ceramic yield was presumably caused by the dehydrocoupling reaction of Si-H containing PCS promoted by PBN additive during pyrolysis process [Kho et al., 2000].

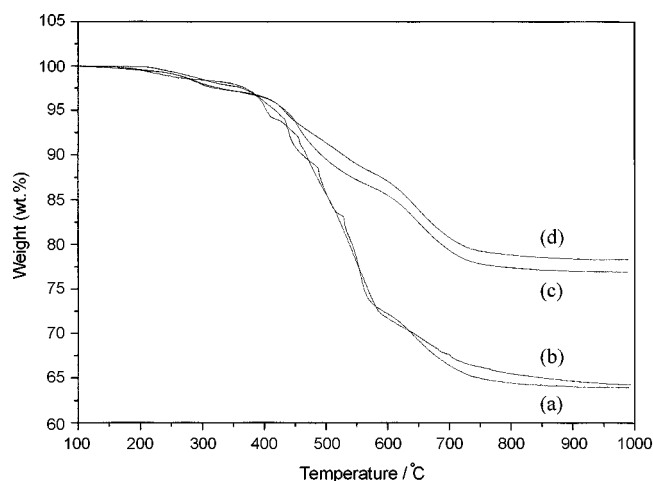


Fig. 1. TGA curves for (a) PCS feed stock, (b) PCS treated at 70 °C for 10 h without PBN, (c) as-mixed PCS with 1 wt% PBN (d) PCS treated at 70 °C for 10 h with 1 wt% PBN.

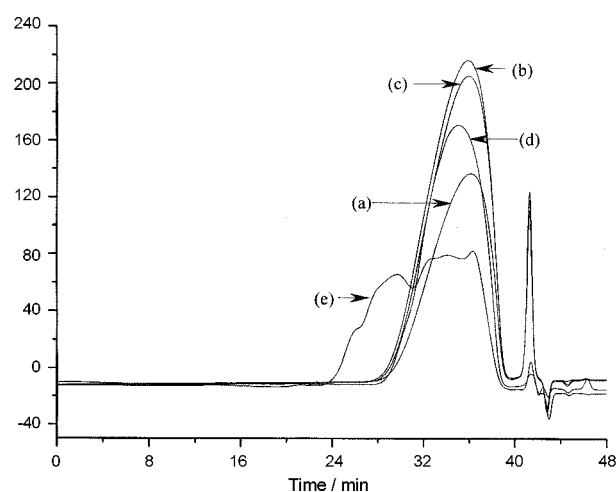


Fig. 2. Molecular weight distribution for (a) PCS feed stock; (b) PCS treated at 300 °C for 1 h without PBN, and PCS prepared by heating with 1 wt% PBN at (c) 70 °C for 10 h; (d) 200 °C for 1 h and (e) 300 °C for 1 h.

In order to understand the reaction between PBN and PCS, the modified PCS treated at various conditions is comparatively illustrated in Fig. 2 and Table 1, which display GPC curves, molecular weight, melting point and solubility. It was observed that when PCS was treated with 1 wt% PBN at 70 °C for 10 h, the molecular weight

Table 1. Molecular weight, melting point and solubility of original PCS and modified PCS

Samples	Mn	Mw	P.D.	Melting point/°C	Solubility in THF
PCS feedstock	1008	2748	2.7	200–209	Soluble
PCS+1 wt%PBN, 70 °C, 10 hr	1077	2848	2.6	205–213	Soluble
PCS+1 wt%PBN, 200 °C, 1 hr	1154	3118	2.7	219–227	Soluble
PCS+1 wt%PBN, 300 °C, 1 hr	1737	14586	8.4	Infusible	Soluble
PCS+1 wt%PBN, 400 °C, 1 hr	-	-	-	Infusible	Partly soluble
PCS+0 wt%PBN, 300 °C, 1 hr	-	-	-	204–213	Soluble
PCS+0 wt%PBN, 400 °C, 1 hr	1101	2905	2.6	202–214	Soluble

increased very little contrasted with PCS feed stock; however, the molecular weight of PMS was enhanced markedly at the same condition [Kho et al., 2000], indicating the fact that PCS is much more chemically stable than PMS. Correspondingly, the melting point of PCS was changed by only 5 °C. However, sample treated at 200 °C for 1 h showed enhanced Mn and Mw to 1154 and 3118, respectively. As a result, its melting point rose by about 19 °C. The changes of molecular weight and melting point after treatment at 300 °C for 1 h were more outstanding; Mn and Mw were increased to 1737 and 14568, respectively; and the sample was infusible at 300 °C but soluble. It is usual behavior to observe higher polydispersity with higher reaction temperatures. The sample treated at 400 °C by 1 wt% PBN was infusible at 300 °C and only partly soluble in THF. Compared with the PCS treated by PBN, the samples treated only without PBN were hardly changed in terms of molecular weight, melting point and solubility as shown in Table 2. The slight change of molecular weight and melting point was presumably caused by gradual evaporation of oligomers at higher treating temperatures.

Further investigations to study the reaction between PCS and PBN were done with NMR. Fig. 3 shows the ^1H -NMR spectra of serial samples. The main peak centered at 0.18 ppm is assigned to Si-CH_3 .

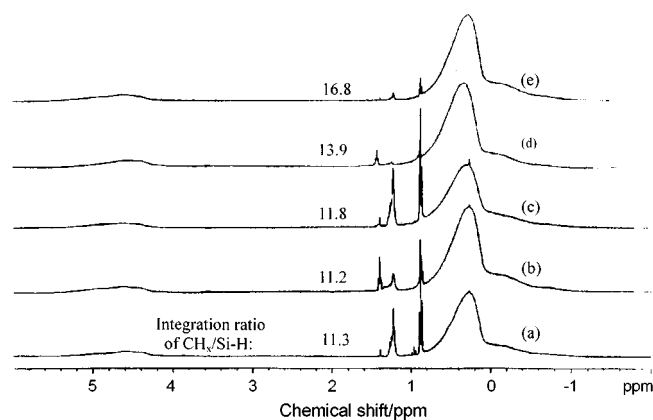


Fig. 3. ^1H -NMR spectrum for (a) PCS feed stock; (b) PCS treated at 300 °C for 1 h without PBN, and PCS prepared by heating with 1 wt% PBN at (c) 70 °C for 10 h; (d) 200 °C for 1 h and (e) 300 °C for 1 h.

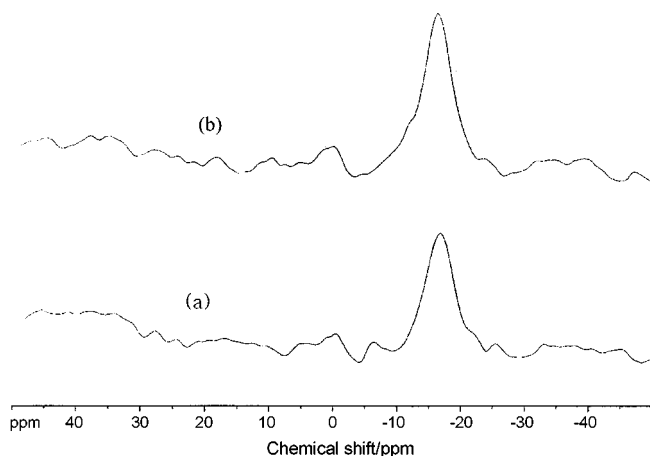


Fig. 4. ^{29}Si -NMR spectra for (a) PCS feed stock; (b) PCS treated by 1 wt% PBN at 70 °C for 10 h.

The shoulders around -0.1 and -0.6 ppm are due to CH_2 and CH , respectively [Soraru et al., 1990]. Small peaks at 0.95, 1.1 and 1.2 ppm are assigned to C-H [Funayama et al., 1996]. The samples for ^1H -NMR were treated only at a temperature below 300 °C, at which the content of CH_x ($x=1, 2$ or 3) was assumed unchanged because carbon insertion into the polymer chain, called Kumada rearrangement, occurred over 350 °C for PCS [Biot et al., 1995]. Fig. 3(b) shows almost no change of integration ratio of $\text{CH}_x/\text{Si-H}$ in PCS after treatment by PBN at 70 °C for 10 h, contrasted with PCS feed stock. This result is consistent with the GPC results, melting point and solubility of corresponding samples mentioned above. Furthermore, ^{29}Si -NMR spectra as shown in Fig. 4 confirmed the results by giving no chemical shift or other difference between the modified PCS and its feedstock. However, when the mixture of PCS with 1 wt% PBN was heated at 200 °C for 1 h, the integration ratio of $\text{CH}_x/\text{Si-H}$ was changed into 13.9, higher than that of PCS feedstock; heated at 300 °C for 1 h, it became into 16.8, much higher than others. The ^1H -NMR indicated that a portion of the Si-H groups must be consumed by the condensation reaction between PCS and

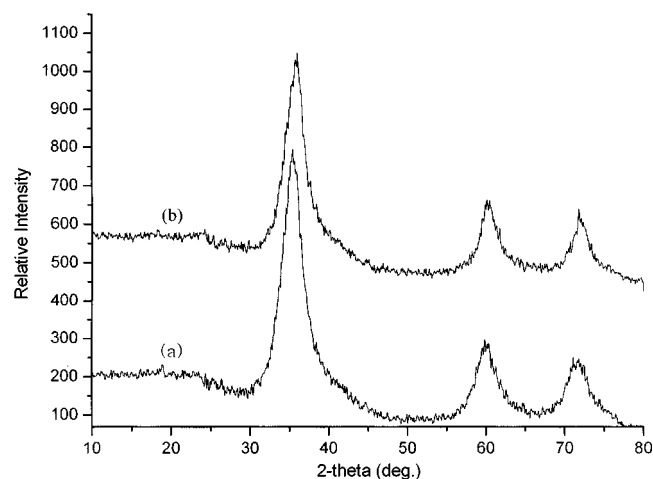


Fig. 5. XRD patterns of ceramic powder derived from (a) PCS feed stock and (b) PCS post-treated with 1 wt% polyborazine (Pyrolysis at 1,400 °C in Ar).

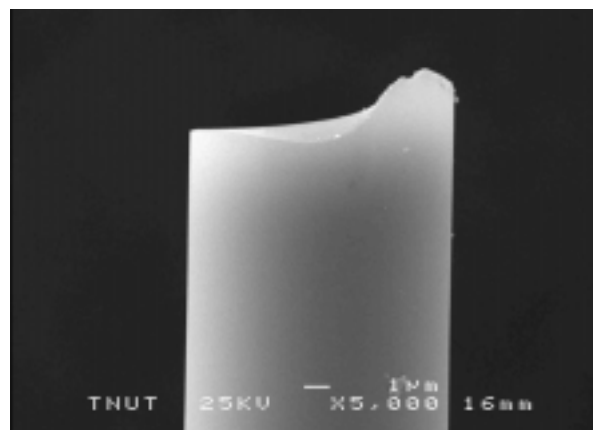


Fig. 6. SEM micrograph of SiC fibers derived from PCS treated at 300 °C for 1 h with 1 wt% PBN (Pyrolysis at 1,400 °C in Ar).

PBN, which is also confirmed by IR spectra.

The final ceramics derived from modified PCS and PCS feed-stock were characterized by XRD (Fig. 5). The XRD patterns suggest that there is no obvious difference between both samples obtained at 1,400 °C. Some researchers reported B as sintering aids and crystalline inhibitor at high temperature such as at 1,600 °C and even 1,800 °C [Chio et al., 2000]. The functions of B in this work need further investigation.

Fig. 6 shows the typical morphology of the SiC fiber hand-drawn from the modified PCS with 1 wt% of PBN at 300 °C. It demonstrates that the modified PCS could be processible by dry spin. Without extra air-curing step, the shaped precursor was pyrolyzed to ceramic fiber with dimensional stability. The SiC ceramic fiber represented smooth surface with 10-20 µm in diameter. Other characteristics of fiber such as tensile strength, composition as well as thermal stability will be determined in the further study.

CONCLUSIONS

A convenient new method was developed to improve the ceramic yield of PCS efficiently (from 63 wt% to 78 wt%) by adding 1 wt% of PBN. The improved ceramic yield was presumably due to the dehydrocoupling reaction of Si-H groups on PCS chains, which is obviously promoted in the presence of PBN over 70 °C. In particular, on modifying at 300 °C with 1 wt% of PBN, PCS could be rendered infusible but soluble with good dry-spinnability. When the obtained PCS fiber was pyrolyzed at 1,400 °C without conventional air-curing step to convert SiC fiber, the dimension of fiber was sustained without fusing problem. This preliminary study provides a simple alternative for preparing the PCS as a precursor for oxygen-free SiC fiber.

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REFERENCES

- Biro, M., Pillot, J. P. and Dunoguès, J., "Comprehensive Chemistry of Polycarbosilanes, Polysilazanes, and Polycarbosilazanes as Precursors of Ceramics," *Chem. Rev.*, **95**, 1443 (1995).
- Chio, G. J., Toreki, W. and Batich, C. D., "Improved Thermomechanical Stability of Polymer-derived Silicon Carbide Fibers by Decabran Incorporation," *J. Mater. Sci.*, **35**, 2421 (2000).
- Chu, Z. Y., Song, Y. C., Xu, Y. S. and Fu, Y. B., "Enhanced Irradiation Cross-linking of Polycarbosilane," *J. Mater. Sci. Lett.*, **18**(21), 1793 (1999).
- Fan, X. L., Feng, C. X., Song, Y. C. and Li, X. D., "Preparation of Si-C-O-N-B Ceramic Fibers from Polycarbosilane," *J. Mater. Sci. Lett.*, **18**(8), 629 (1999).
- Funayama, O., Kato, T., Okoda, M. and Isoda, T., "Synthesis of Thermosetting Copolymer of Polycarbosilane and Perhydropolysilazane," *J. Mater. Sci.*, **31**, 6369 (1996).
- Kang, P. H. and Yang, H. S., "Preparation of SiC/C Composite Sheet from Polycarbosilane/carbon Based Resin Mixture," *Korean J. Chem. Eng.*, **15**, 580 (1998).
- Kho, J. G., Min, D. S. and Kim, D. P., "Polymethylsilane Post-treated with a Polyborazine Promotor as a Precursor to SiC with High Ceramic Yield," *J. Mater. Sci. Lett.*, **19**, 303 (2000).
- Moon, K. T., Min, D. S. and Kim, D. P., "Synthesis of Borazine and Its Polymer-derived Boron Nitride," *J. Ind. & Eng. Chem.*, **3**(4), 288 (1997).
- Pysher, D. J., Goretti, K. C., Hodder, R. S. and Tressler, R. E., "Strength of Ceramic Fibers at Elevated Temperature," *J. Am. Cera. Soc.*, **72**(2), 284 (1989).
- Soraru, G. D., Babonneau, F. and Mackenzie, J. D., "Structural Evolutions from Polycarbosilane to SiC Ceramic," *J. Mater. Sci.*, **25**, 3886 (1990).