

Synthesis and characterization of high ceramic yield polycarbosilane precursor for SiC

Mangesh LODHE^{a,*}, Narendra BABU^a, A. SELVAM^b, M. BALASUBRAMANIAN^a

^aDepartment of Metallurgical and Materials Engineering, Indian Institute of Technology Madras, Chennai 600036, India

^bFRP Institute, Chennai 600032, India

Received: June 10, 2015; Revised: July 22, 2015; Accepted: July 24, 2015

© The Author(s) 2015. This article is published with open access at Springerlink.com

Abstract: The polycarbosilane (PCS) precursor for SiC with high molecular weight and medium molecular weight distribution was synthesized from polydimethylsilane at normal pressure. The chemical formula, the number average molecular weight, and the polydispersity index of the synthesized PCS are $\text{SiC}_{1.94}\text{H}_{5.01}\text{O}_{0.028}$, 1135, and 1.66, respectively, which can be attributed to the higher reaction temperature used for polymerization. The polymer to ceramic conversion of PCS was completed at 900 °C with a ceramic yield of 85%. The crystallization started at 1100 °C, and at 1200 °C, well resolved peaks of β -SiC were formed with small amount of α -cristobalite. The X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies indicated the presence of nanocrystalline β -SiC.

Keywords: synthesis; polycarbosilane (PCS); polymer–ceramic conversion; X-ray diffraction (XRD)

1 Introduction

Silicon carbide (SiC) is one of the most leading candidate materials for various structural and functional applications, as it possesses very good thermo-mechanical properties [1]. The polymer derived ceramic route gives the tailored chemical composition and nanostructure material by proper thermal treatment under a controlled inert atmosphere [2]. The preceramic polymer and its molecular structure influence the chemical composition, the phase distribution, and the entire microstructure of the converted ceramics. Therefore, the chemical and physical properties of polymer derived ceramics can be changed to a major extent by tailoring the polymer

precursor [3]. Hence, the synthesis of preceramic polymers is one of the important stages in the area of polymer derived ceramics and its composites. Polycarbosilane (PCS), the precursor for SiC, has been synthesized by thermal decomposition of polydimethylsilane under high pressure in an autoclave [4]. The autoclave method is technically difficult and expensive. Yajima and his co-workers [5] have tried to synthesize polycarbosilane without using autoclave, but it has low molecular weight and low ceramic yield. The higher reaction temperature and/or longer reaction time tend to give the polycarbosilane of higher molecular weight and broader distribution [6]. In the present study, an attempt has been made to synthesize the high molecular weight and high ceramic yield polycarbosilane from polydimethylsilane without using autoclave. The synthesized polycarbosilane was completely characterized and the ceramic yield was determined.

* Corresponding author.
E-mail: mmlodhe@gmail.com

2 Experimental details

2.1 Synthesis of polydimethylsilane

Polydimethylsilane was synthesized by the reaction of dimethyldichlorosilane with sodium in xylene at 120 °C as reported elsewhere [7]. Metallic sodium was chopped into 5 mm × 5 mm pieces and introduced into reaction flask containing xylene. The liquid surface was covered with nitrogen gas to create an inert atmosphere. Dimethyldichlorosilane was poured on a dropping funnel. To start the reaction, the flask containing sodium pieces and xylene was heated to 120 °C. The metallic sodium thus melted at 98 °C and stayed at the bottom of the flask. Dimethyldichlorosilane was added drop wise into the flask with continuous stirring to allow dechlorination to take place. After the addition of dimethyldichlorosilane, the reaction mixture was refluxed at 120 °C for 8 h. After complete reaction, xylene (solvent) was removed from the product by suction filtration followed by natural drying, and the resulting product was a bluish-purple precipitate. The un-reacted sodium from the precipitate was then removed by treating with methanol. The NaCl and low molecular weight polydimethylsilane were removed by washing with deionized water and acetone. The final white precipitate was dried in oven at 120 °C for 1 h.

2.2 Synthesis of polycarbosilane

The polydimethylsilane powder was placed in a two-necked round-bottom borosilicate flask attached with a reflux condenser and an inlet of nitrogen gas. After purging nitrogen gas, the polydimethylsilane powder was heated in electric furnace to carry out the reflux reaction. The polydimethylsilane was heated at various temperatures starting from 320 to 370 °C. At 350 °C, the color of polydimethylsilane turned to creamy white. The polydimethylsilane melted and converted into liquid state in the temperature range of 360–370 °C. Thereafter, the liquid was refluxed for 5 h and then heated up to 450 °C to remove volatile components. It was allowed to cool at room temperature and highly viscous product was taken out from the flask by adding n-hexane. The solution was stirred and then filtered to get yellowish-brown viscous liquid. The left over traces of n-hexane were removed by a rotary evaporator and subsequently heated in the tubular furnace in the presence of argon gas to 250 °C for 30 min to remove the low molecular weight components. The substance thus

obtained was yellowish-shiny crystals. Thus the thermal decomposition of polydimethylsilane yielded polycarbosilane, which is the polymer precursor for silicon carbide.

2.3 Characterization

Fourier transform infrared spectroscopy (FT-IR) analysis for polydimethylsilane and polycarbosilane was carried out using Perkin Elmer 2000 Spectrum One spectrometer, to confirm the functional groups. KBr pellets were used for the analysis, which were prepared by compressing a finely ground mixture of about 2 mg of sample and 100 mg of KBr powder.

The determination of average molecular weight (M_w), number average molecular weight (M_n), and mass distribution (polydispersity index) of the polydimethylsilane and polycarbosilane was carried out by gel permeation chromatography (GPC) technique using Waters 2414 refractive index detector. Tetrahydrofuran (THF) was used as eluant at a flow rate of 1.0 mL/min using Waters M45 pump at room temperature.

Thermal decomposition of the polycarbosilane up to 900 °C in nitrogen gas was investigated by simultaneous thermal gravimetric (TG) and differential thermal analysis (DTA) techniques carried out with a high temperature NETZSCH STA 409 PC/PG at a heating rate of 10 °C/min under nitrogen gas flow rate of 20 cm³/min.

Carbon and hydrogen contents of the polycarbosilane were analyzed by using Perkin-Elmer 2400 Series CHN analyzer. Silicon content was determined by inductive coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 5300 DV). The oxygen content was obtained by the difference.

X-ray diffraction (XRD) analysis was carried out for polycarbosilane pyrolysed at 900, 1000, 1100, and 1200 °C for 1 h in Ar atmosphere with a PANalytical diffractometer using Cu K α radiation. Line broadening of (111) peak of SiC was used for crystallite size determination by using Scherrer formula. Morphological characteristics were obtained by transmission electron microscopy (TEM, Philips CM12).

3 Results and discussion

The FT-IR spectrum of polydimethylsilane is shown in

Fig. 1. The major groups present are Si-CH₃ (1245, 835, 745, 690, and 625 cm⁻¹), C-H (2950, 2900, and 1400 cm⁻¹), Si-O (1030 cm⁻¹), and O-H (3430 and 1630 cm⁻¹) [7,8]. The presence of Si-CH₃ functional group confirms the formation of polydimethylsilane. The presence of Si-CH₃ group indicates that polycarbosilane with Si-C backbone could be obtained by thermal decomposition of polydimethylsilane. The molar mass distribution was measured by GPC. The average molecular weight (*M_w*), the number average molecular weight (*M_n*), and the complete molecular weight distribution (polydispersity index) of polydimethylsilane are found to be 1900, 1300, and 1.51, respectively.

The FT-IR spectrum of polycarbosilane is also shown in Fig. 1. Polycarbosilane which is synthesized by the thermal decomposition of polydimethylsilane at elevated temperature consists of Si-CH₂-Si group and also other functional groups of polycarbosilane. The silicon free radical is formed by the cleavage of Si-Si bond during the application of heat and the rearrangement is done by the insertion of methyl group in the chain, which gives rise to Si-CH₂-Si and Si-H groups [4]. A band observed at 1025 cm⁻¹ is very

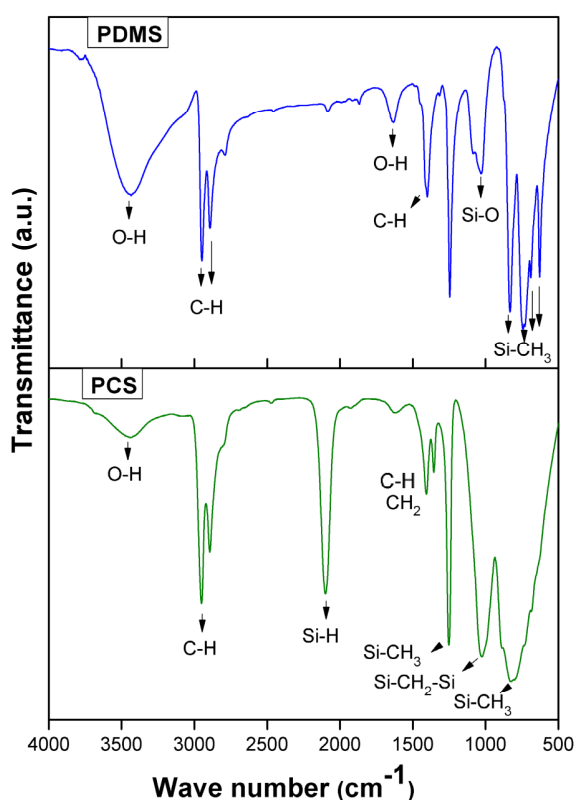


Fig. 1 FT-IR spectra of polydimethylsilane (PDMS) and polycarbosilane (PCS).

strong, which corresponds to CH₂ bending in the Si-CH₂-Si group. The bands attributed to Si-CH₃ are Si-CH₃ stretching at 1250 cm⁻¹ and C-H stretching at 2950 cm⁻¹. The band at 1400 cm⁻¹ corresponds to C-H stretching in Si-CH₃ and 1360 cm⁻¹ corresponds to CH₂ stretching in Si-CH₂-Si. The strong band of Si-H is at 2100 cm⁻¹ and the O-H stretching in H₂O is at 3430 and 1630 cm⁻¹. FT-IR data of synthesized polycarbosilane are in well agreement with those reported in the literature [9,10].

The chemical composition of polycarbosilane precursor is Si 46 wt%, C 38.18 wt%, H 8.19 wt%, N 0.13 wt%, and O 7.5 wt%. The empirical formula of synthesized polycarbosilane is SiC_{1.94}H_{5.01}O_{0.028}. The elemental analysis result shows that the atomic ratio of carbon to silicon in the polycarbosilane precursor is about 2:1. The softening point of the obtained polycarbosilane is found to be in the range of 240–250 °C. The GPC curve for polycarbosilane is shown in Fig. 2. The average molecular weight (*M_w*) and number average molecular weight (*M_n*) of polycarbosilane are found to be 1888 and 1135, respectively. The polydispersity index (*M_w*/*M_n*) of polycarbosilane is therefore about 1.66. The GPC curve shows the medium molecular weight distribution, and it can be correlated to the evolution of lower molecular weight PCS during its synthesis at normal pressure. Softening point can be the macroscopic indication of molecular weight, i.e., the more the softening point, the higher the molecular weight.

The polycarbosilane was obtained by thermal decomposition of polydimethylsilane at higher temperature. As the reaction temperature was higher, more Si-Si bonds were dissociated, and more

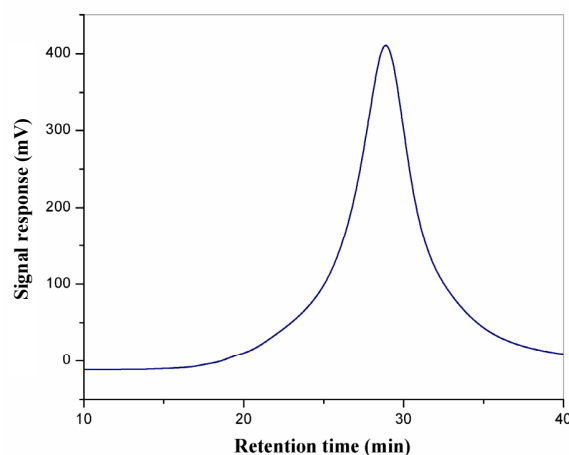


Fig. 2 GPC curve for polycarbosilane.

Si-CH₂-Si groups which are the backbone of polycarbosilane molecule form through the Kumada rearrangement [6]. Hence the final product of polycarbosilane will consist of longer molecular chains which at the end give rise to higher molecular weight and medium molecular weight distribution.

Thermal behavior of polycarbosilane was studied by using TGA-DTA. The TGA-DTA curves of polycarbosilane are shown in Fig. 3. In the first stage, the TG curve gradually drops from 100 to 370 °C, which is relatively small with no significant weight loss in this temperature range. This weight loss is due to the evaporation of reaction product H₂ and some low molecular weight polycarbosilane [11]. In the second stage, the TG curve falls off rapidly from 370 to 550 °C which is substantiated by a large exothermic peak in the DTA curve. The weight loss in this region is 5 wt%, and it could be due to evaporation of gaseous product such as CH₄ and H₂ because of dehydrogenation and dehydrocarbonation condensation of polycarbosilane molecule [12]. In the third stage, TG continues to fall from 550 to 800 °C and the corresponding weight loss is 8.8 wt%. The weight loss could be due to the decomposition of organic side groups such as Si-H, Si-CH₃, and C-H in Si-CH₂-Si [13]. After 800 °C, there is hardly any weight loss and the exothermic peak at 900 °C shows the crystallization of amorphous phase. The polymer to ceramic conversion is completed at 900 °C. At 900 °C, the ceramic yield is 85 wt%. Such high yield is resulted due to increased cross-linked structure of polycarbosilane precursor with high molecular weight. The high molecular weight leads to low weight loss during the cross-linking and pyrolysis and thereby increases the ceramic yield.

Polycarbosilane precursor was pyrolyzed at different temperatures starting from 900 to 1200 °C in argon

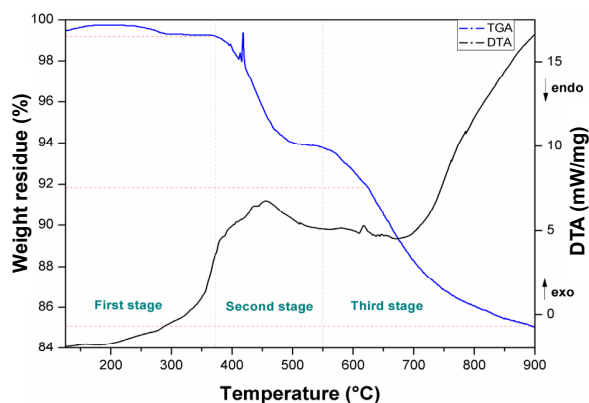


Fig. 3 TGA-DTA of polycarbosilane in N₂ atmosphere.

atmosphere to study the formation β -SiC phase. XRD patterns of samples pyrolysed at different temperatures are shown in Fig. 4. From TG curve, it is inferred that the polymer to ceramic conversion has completed at 900 °C and hence polycarbosilane pyrolysed at 900 and 1000 °C is resulted in amorphous structure and highly disordered in nature. However, polycarbosilane pyrolyzed at 1100 °C has resulted in a broad peak which appears at 36.02°. Although the crystallization is incomplete, it indicates the presence of high local ordering of tetrahedral SiC. After the pyrolysis at 1200 °C, the residue gives a more defined XRD pattern. The pattern shows the major peaks at $2\theta=36.02^\circ$, 60.84° , and 71.83° corresponding to the (111), (220), and (311) diffraction planes of face centered cubic (FCC) β -SiC polymorph of silicon carbide. The crystallite size of SiC is found to be 6 nm. In addition to this, a sharp peak appears at $2\theta=22.37^\circ$ resembling the (101) diffraction plane of α -cristobalite. At 1100 °C, the broader β -SiC peaks and a broad α -cristobalite peak at $2\theta=22.37^\circ$ are observed. The same peaks also appear in polycarbosilane pyrolyzed at 1200 °C with a sharp α -cristobalite peak. This infers that the amorphous α -cristobalite phase is transformed to crystalline α -cristobalite phase at 1200 °C. Above 1100 °C, the diffraction peaks of β -SiC are observed

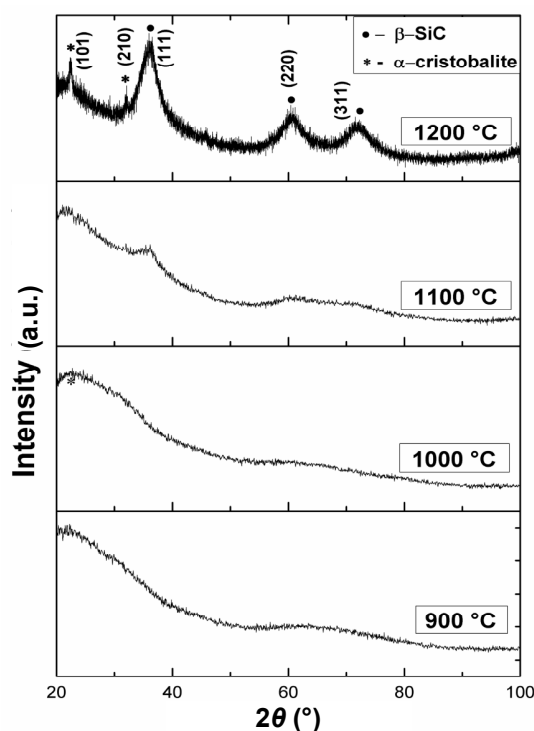


Fig. 4 XRD patterns of PCS pyrolysed between 900 and 1200 °C.

and the diffraction peaks become sharper as pyrolysis temperature increases from 1100 to 1200 °C, suggesting a progressive crystallization process.

The bright and dark field TEM micrographs (Figs. 5(a) and 5(b)) of PCS pyrolyzed at 1200 °C show the nanocrystalline nature of SiC. The crystallite size of SiC ranges from 5 to 12 nm. The average crystallite size observed in TEM is larger than the calculated from XRD broadening of (111) plane. This difference could be due to the complicated shape of diffraction peak by the presence of high intensity background. The selected area electron diffraction (SAED) pattern (Fig. 5(c)) shows the strong sharp rings, which indicate the crystalline nature of SiC. This electron diffraction pattern can be indexed as (200), (220), and (311) crystallographic planes of β -SiC.

4 Conclusions

The polycarbosilane of higher molecular weight and medium molecular weight distribution has been synthesized without using autoclave. The chemical formula of polycarbosilane is $\text{SiC}_{1.94}\text{H}_{5.01}\text{O}_{0.028}$. The polymer to ceramic conversion yield is 85 wt%.

After pyrolysis, the FCC β -SiC has been obtained with crystallite size of 6 nm. This study demonstrates that final structure of pyrolyzed ceramic can be tailored by modifying the polymeric precursor structure.

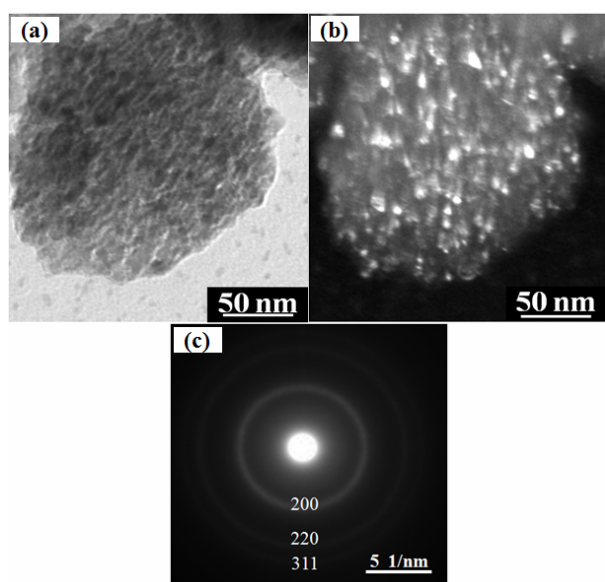


Fig. 5 (a) Bright field and (b) dark field TEM images and (c) SAED pattern of PCS pyrolyzed at 1200 °C.

Acknowledgements

We are grateful to Mr. Shrikant for his help in carrying out the experiments. We further acknowledge to Mr. Niraj for valuable technical help in manuscript preparation.

Open Access: This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

- [1] Herzog A, Thünemann M, Vogt U, *et al.* Novel application of ceramic precursors for the fabrication of composites. *J Eur Ceram Soc* 2005, **25**: 187–192.
- [2] Miele P, Bernard S, Cornu D, *et al.* Recent developments in polymer-derived ceramic fibers (PDCFs): Preparation, properties and applications—A review. *Soft Mater* 2007, **4**: 249–286.
- [3] Miller RD, Michl J. Polysilane high polymers. *Chem Rev* 1989, **89**: 1359–1410.
- [4] Birot M, Pillot J-P, Dunogues J. Comprehensive chemistry of polycarbosilanes, polysilazanes, and polycarbosilazanes as precursors of ceramics. *Chem Rev* 1995, **95**: 1443–1477.
- [5] Yajima S, Omori M, Hayashi J, *et al.* Simple synthesis of continuous SiC fiber with high tensile strength. *Chem Lett* 1976, **5**: 551–554.
- [6] Chen J, He G, Liao Z, *et al.* Control of structure formation of polycarbosilane synthesized from polydimethylsilane by Kumada rearrangement. *J Appl Polym Sci* 2008, **108**: 3114–3121.
- [7] Yajima S, Hasegawa Y, Hayashi J, *et al.* Synthesis of continuous silicon carbide fibre with high tensile strength and high Young's modulus. *J Mater Sci* 1978, **13**: 2569–2576.
- [8] Cheng X, Xie Z, Song Y, *et al.* Structure and properties of polycarbosilane synthesized from polydimethylsilane under high pressure. *J Appl Polym Sci* 2006, **99**: 1188–1194.
- [9] Ly HQ, Taylor R, Day R, *et al.* Conversion of polycarbosilane (PCS) to SiC-based ceramic. Part 1. Characterisation of PCS and curing products. *J Mater Sci* 2001, **36**: 4037–4043.
- [10] Cheng X, Xie Z, Xiao J, *et al.* Influence of temperature on the properties of polycarbosilane. *J Inorg Organomet Polym Mater* 2005, **15**: 253–259.
- [11] Yive NSCK, Corriu RJP, Leclercq D, *et al.* Silicon carbonitride from polymeric precursors: Thermal cross-linking and pyrolysis of oligosilazane model compounds. *Chem Mater* 1992, **4**: 141–146.
- [12] Li H, Zhang L, Cheng L, *et al.* Polymer–ceramic conversion of a highly branched liquid polycarbosilane for SiC-based ceramics. *J Mater Sci* 2008, **43**: 2806–2811.
- [13] Hasegawa Y, Iimura M, Yajima S. Synthesis of continuous silicon carbide fibre. *J Mater Sci* 1980, **15**: 720–728.