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Some thermal studies of polysilanes and polycarbosilanes

Sanjeev K. Shukla*, R.K. Tiwari, Ashok Ranjan, A.K. Saxena[1], G.N. Mathur

Defence Materials and Stores Research and Development Establishment, DMSRDE PO, GT Road, Kanpur 208013, India

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Abstract

Some thermal (TGA and DSC) studies of polysilanes viz., polydimethylsilane (PDMS), copolymer of polydimethyl-methylphenylsilane (PDMMPS), polydimethyl-methylsilane (PDMMS), polydimethyl-methylvinylsilane (PDMMVS) and polycarbosilanes (PCS) synthesized using PDMS have been carried out. PDMS and PDMMPS found more suitable for synthesizing meltable and soluble polycarbosilanes and gave better char yield compared to PDMMVS and PDMMS. The polydimethyl-methylvinylsilane (PDMMVS) did not show any melting behavior and cured at ∼166 °C as an endotherm was noticed in DSC.

The PCS-N (mp ∼124 °C) on heating up to 450 °C become non-meltable but remain soluble in common organic solvents, which on further heating up to ∼650 °C become non-meltable and non-soluble. The thermal recycling of the PCS-N at ∼350 °C minimized the exotherms as observed in the DSC. The XRD studies revealed that the α-SiC and β-SiC formation took place at ∼930 and 1250 °C, respectively as reported earlier too.

Keywords: Polysilane; Polycarbosilane; Copolymer; TGA; DSC

1. Introduction

The use of preceramic polymers generates entirely new possibilities of solving the intricacies involved to obtain new generation of ceramic materials which were otherwise difficult due to complex technologies. Since Yajima and coworkers [1–6] have demonstrated the application of SiC fibers in various industrial fields, the precursors material of SiC have also been explored extensively. Voluminous amount of work has been done on the synthesis, characterization and thermal behaviour of polysilanes by several workers [7–15]. The polysilanes have also been used widely for the synthesis of polycarbosilane (PCS), which is one of the most important ceramic material precursor for making β-SiC fiber, powder, whiskers and ceramic composites etc. [16–19]. Besides, several methods reported for the synthesis of polycarbosilanes, like ring opening polymerization of strained ring silicon compounds, dehydrocoupling reaction, hydrosilylation reaction etc. [16,20,21], the most viable commercial method is the thermal backbone rearrangement of polysilanes mainly the polydimethylsilane (PDMS) or it's in copolymers [22–25]. It has also been reported that the properties of the polycarbosilanes varies with the type of organic moieties and functional groups present on the silicon backbone of the polymer, catalyst, mode of heating and even the type of inert gas used during synthesis, which ultimately determines the parameters to obtain desired SiC materials [10,16,18]. During conversion of precursor materials to ceramic material it has also been observed that volume shrinkage took place with the evolution of gases causing porosity, cracks and flaws and thus limiting the application of polymer precursors. So it is necessary to understand the thermal behavior of precursors to control the microstructure in resultant material/composite.

Hence, it has been considered worthwhile to carry out a comparative study on the thermal behavior of some polysilanes and polycarbosilanes to identify suitable precursors for making PCS and ultimately the α and β-SiC materials in high yields with repeatable properties.

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* Corresponding author. Present Address: Department of Materials and Metallurgical Engineering, IIT, Kanpur 208016, India.
Tel.: +91 512 2597935; fax: +91 512 2597505.
E-mail address: sanshukla@lycos.com (S.K. Shukla).
[1] Co-corresponding author. Tel.: +91 512 2451759-78x215 (O), +91 512 2402228 (R); fax: +91 512 2450404.

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2. Experimental

2.1. Materials and physical measurements

Solvents were dried by distillation over a Na-benzophenone system. Sodium metal was used as received from SD Fine-Chem. Ltd. and other chemicals were used as received from Aldrich Chemical Co. The TGA analysis were performed under nitrogen atmosphere (heating rate 20 °C/min, nitrogen flow 60 ml/min) using TGA-2950 (TA Instrument). The mass of the sample used was typically 10.0 mg and samples were placed in platinum crucible and weighed directly. DSC studies were carried out under high purity nitrogen atmosphere using DSC 2910 (TA Instrument). The IR spectra were recorded on Perkin–Elmer FT-IR spectrometer (Model Spectrum RX I) using KBr pellets or discs in the range 4000–400 cm^{-1}. The XRD analysis was carried out on Philips PW 1320 refractrometer using CuKα radiation with a nickel filter. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) (model Merck Hitachi LaChrom L-7100) with four Microstyragel columns calibrated by polystyrene standards (porosity ranges 10^3, 10^4, 10^5 and 10^6 Å) and with THF as eluant at a flow rate 1 ml/min. The detection system was a Merck Hitachi LaChrom UV–vis detector L-7420 set at 254 nm.

2.2. Synthesis of polysilanes and polycarbosilanes

Polysilanes were synthesized by the Wurtz-coupling reaction of dichlorodiorganosilanes with sodium metal in toluene:dioxane solvent mixture (90:10) under reflux for

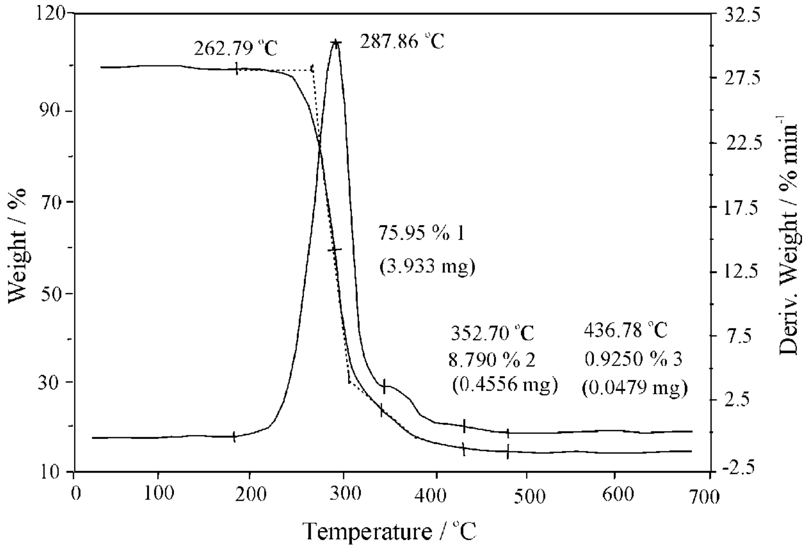

Fig. 1. TGA of PDMMS.

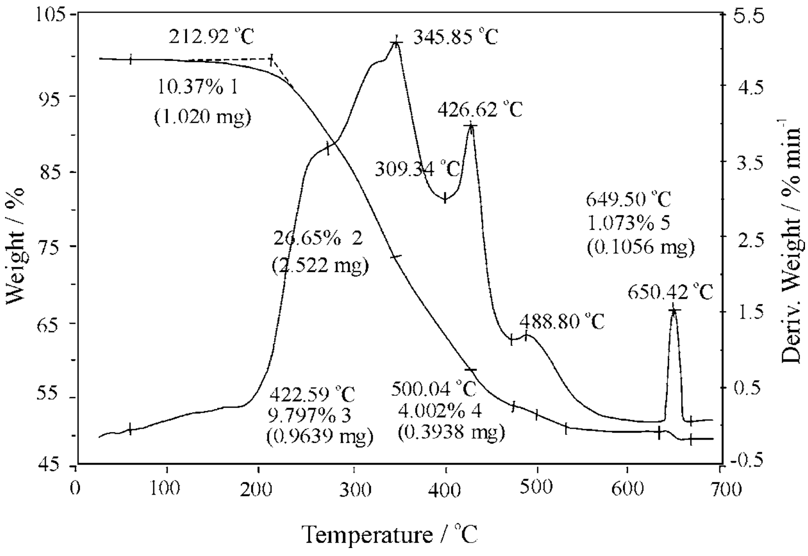

Fig. 2. TGA of PDMS.

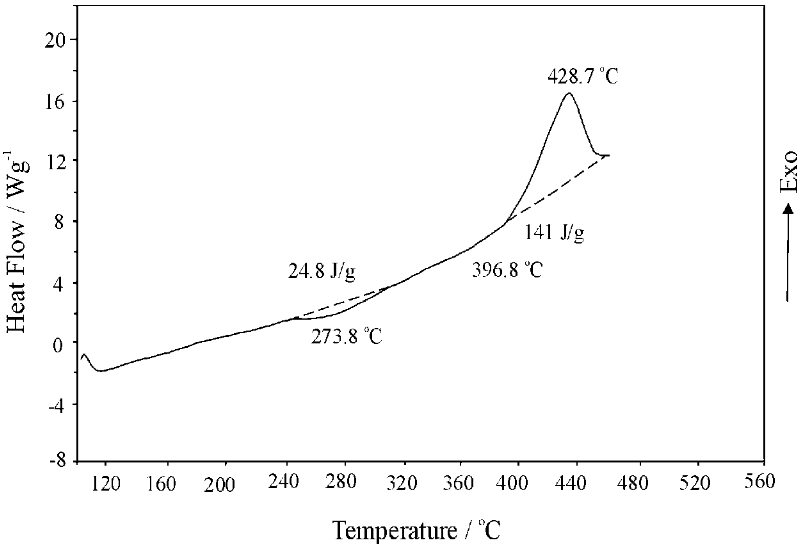

Fig. 3. DSC of PDMS.

4–5 h, using 15-crown-5 as catalyst [9]. The copolymers were prepared by the reaction of dimethyldichlorosilane and methylorgano-dichlorosilane ($RMeSiCl_2$, R = Ph, vinyl or H) in 1:1 molar ratio. Compounds were characterized by IR spectroscopy, which showed characteristic νSi–Si, νSi–Ph, νSi–Me, νSi–vinyl and νSi–H absorption bands at ~480, ~1430, ~1400, ~1720 and ~2100 cm^{-1}, respectively [9,26].

Polycarbosilanes (PCS-A and PCS-N) were synthesized by thermal backbone rearrangement of polydimethylsilane at 50–450 °C for 100 h using polyborodiphenyl-siloxane catalyst (1%) under argon and nitrogen atmosphere, respectively [24]. The IR spectrum of PCS showed the characteristic absorption for νSi–H at ~2100 cm^{-1}, νSi–CH_3 at ~1400 cm^{-1}, ~1250 cm^{-1} and νSi–CH_2–Si at ~1352 cm^{-1}, ~1000 cm^{-1} [26].

3. Results and discussion

Keeping in view the intractable behavior of ceramic materials, the precursors route to fabricate complicated structure of ceramic materials is preferred because most of the precursors are meltable and soluble in common organic solvents. Commonly used precursors for such type of requirements are polysilanes, which can be directly converted to SiC ceramic materials or first converted to polycarbosilanes and then to SiC materials. But such conversion took place at very high temperature and under strict inert atmosphere. Besides the process of the thermal treatment of PS and PCS, the organic group present on the Si backbone of the polymers also played vital role to get better ceramic yield, thermo oxidative stability and spin ability etc.

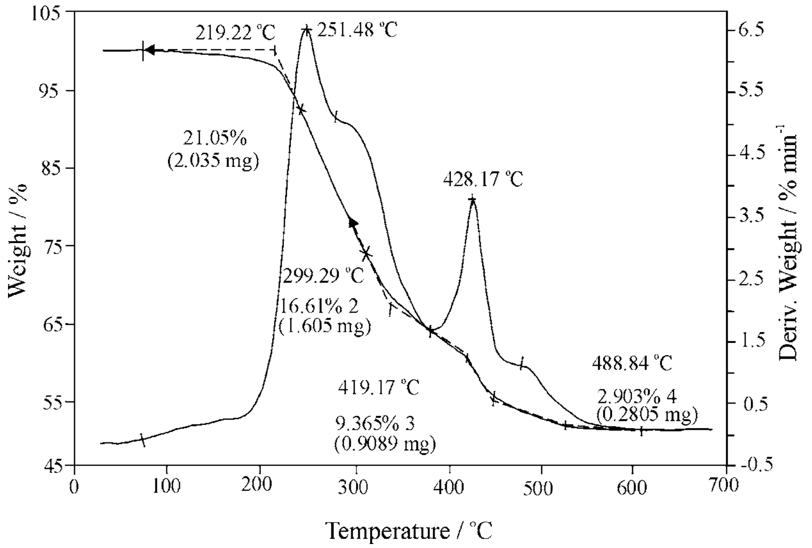

Fig. 4. TGA of PDMMPS.

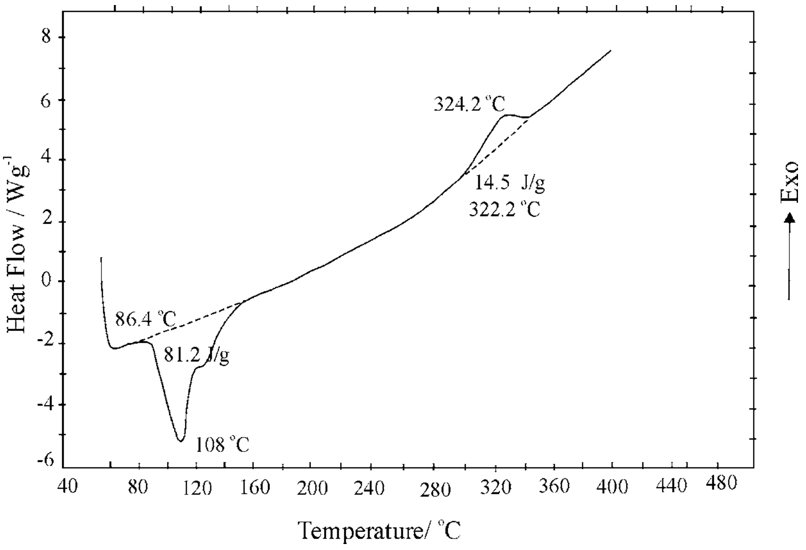

Fig. 5. DSC of PDMMPS.

Hence in order to identify the suitable precursor and process parameters to get polycarbosilane and its conversion to silicon carbide, thermal behavior of polydimethylsilane and copolymers of polydimethyl-methylphenylsialne (PDMMPS), polydimethyl-methylvinylsilane (PDMMVS) and polydimethyl-methylsilane (PDMMS) have been studied using DSC and TGA techniques in the present investigation. The thermal studies of polycarbosilanes obtained under nitrogen (PCS-N) and argon atmosphere (PCS-A) by the thermal backbone rearrangement of polydimethylsilane using polyborodiphenyl-siloxane as catalyst have also been carried out which yielded α and β-SiC particulates.

The TGA of PDMMS under N_2 (Fig. 1) showed single step decomposition. The decomposition of the material begins at ~263 °C and ~76 % material decomposed off. Further at ~352 °C a loss of material (~9%) has been observed due to decomposition. Afterwards up to ~700 °C no further change was noticed in TGA.

When the PDMMS was heated under reflux at ~350 °C in an argon atmosphere for 2 h, a pasty material left in the flask. The IR spectrum of this pasty material was taken and compared with the IR spectrum of original polymer which showed no significant change i.e., characteristic νSi–CH_3 and νSi–H absorption bands were present at ~1400 and ~2 100 cm^{-1}, respectively. Thus the pasty mass formation may be attributed to the depolymerization of the polymer. Later on, the residue was further heated at 450 °C for 2 h under reflux, which yielded a liquid mass. The IR spectrum of this liquid showed a weak absorption band at ~1352 cm^{-1}, which indicates the appearance of –Si–CH_2–Si– group [26]. This absorption band strengthens when the mass was further heated up to ~650 °C. Thus, it may be attributed that

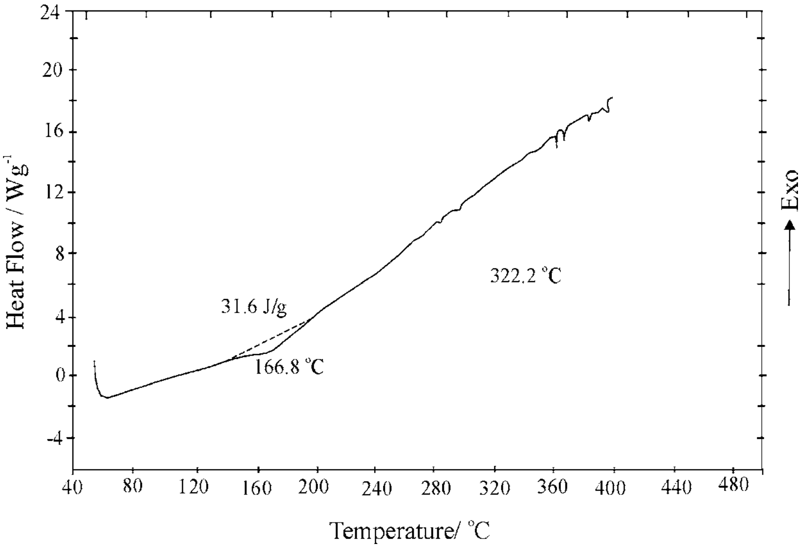

Fig. 6. DSC of PDMMVS.

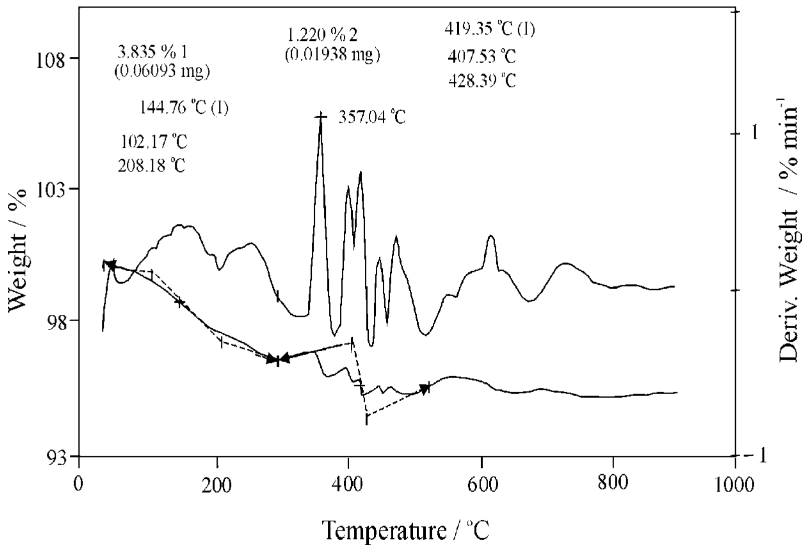

Fig. 7. TGA of polycarbosilane [PCS-N] (mp 124 °C).

the liquid polycarbosilane formation took place under reflux. Further heating of the liquid mass under reflux in argon atmosphere at ~850 °C for 2 h, yielded a non-meltable and non-soluble solid mass (yield ~20%). The IR spectrum of the material showed the loss of νSi–H absorption band, thus it may be concluded that the residue is a cross linked polycarbosilane.

The TGA of PDMS under N_2 (Fig. 2) showed two step decomposition which starts at ~212 °C with a 10 % weight loss of the polymer which may be attributed to the vaporization of trapped solvent in the polymer, decomposition of low molecular weight polymer and other trapped impurities. Afterwards at ~345 °C loss of ~27% weight has been noticed which may be easily attributed to the evolution of methane and other hydrocarbon gases due to cleavage of Si–CH_3 bond. This weight loss continues up to 550 °C and around 50% residue was left up to 700 °C.

The exothermic transition in DSC of PDMS at ~428 °C (Fig. 3) and the maxima in the derivatisation curve as shown in TGA at ~427 °C (Fig. 2) gave an indication for the formation of polycarbosilane. On further heating a maxima in derivatisation curve of TGA also appeared at ~650 °C (Fig. 2), which may be attributed to the cross-linking of polymer chain. The PCS become non-soluble and non-meltable at this temperature and ~2% weight loss also occurred. This observation has been further confirmed by IR analysis of the PCS residue obtained after heating PCS ~650 °C, where νSi–H absorption band at ~2100 cm^{-1} was disappeared. So, it may be concluded that cross-linking took place via Si–H centre.

The TGA of the PDMMPS (Fig. 4) showed a loss of weight (10%) at ~219 °C which may be attributed to the loss of trapped solvents, decomposition of low molecular weight polymers and other impurities. It has been further observed

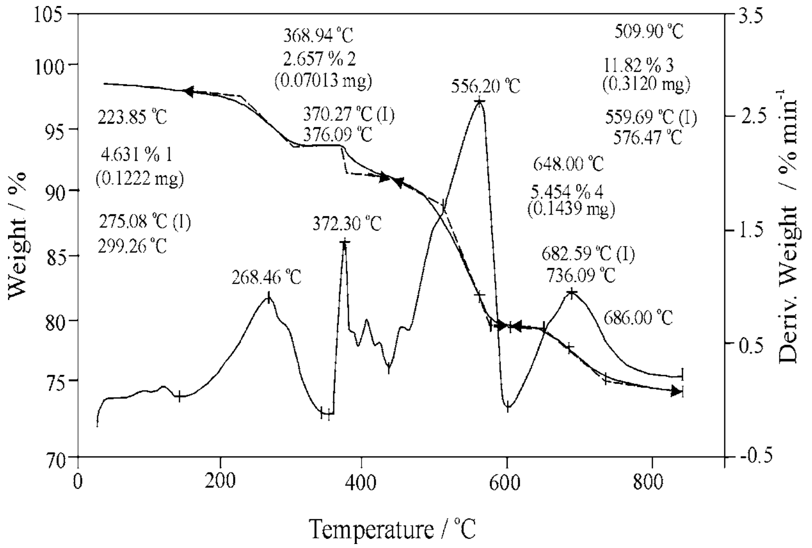

Fig. 8. TGA of polycarbosilane [PCS-N] (mp 110 °C).

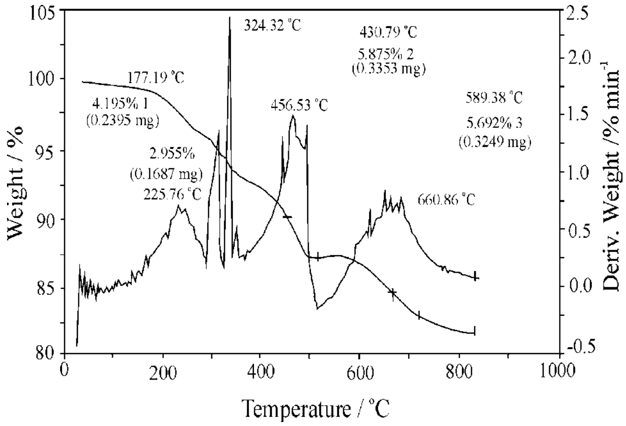

Fig. 9. TGA of polycarbosilane [PCS-A] (mp 116 °C).

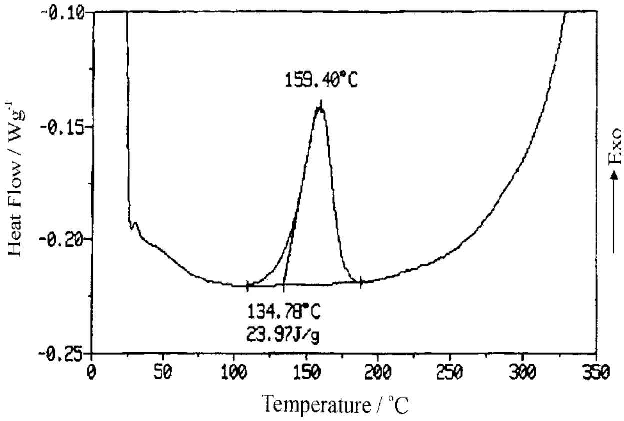

Fig. 11. DSC of polycarbosilane [PCS-N] after first cooling.

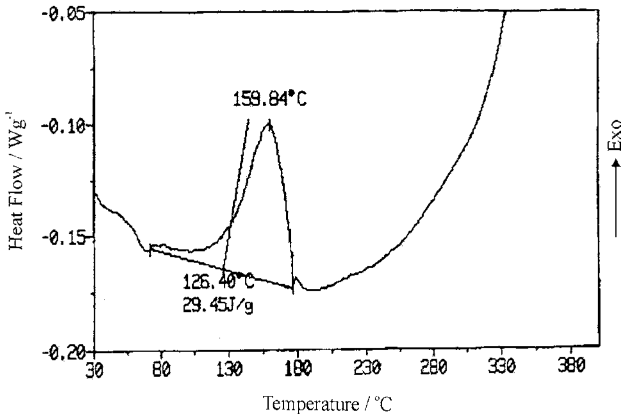

Fig. 12. DSC of polycarbosilane [PCS-N] after second cooling.

that at ~299 °C a weight loss (~16%) of the polymer occur which may be attributed to the cleavage of Si–Me, Si–Si bonds and evolution of hydrocarbon gases. A prominent change could also be noticed at ~428 °C, which is similar to the observations made in the TGA of PDMS (Fig. 2) and may be attributed to the formation of polycarbosilane. The IR spectrum of PDMMPS heated under argon at ~430 °C showed absorptions at ~2100 and ~1350 cm^{-1} for νSi–H and νSi–CH$_2$–Si, respectively, which may be attributed to the formation of polycarbosilane. But on further heating up to ~700 °C no change has been noticed so it may be assumed that the polycarbosilane obtained herein is more thermally stable than the PCS obtained by PDMS and for cross-linking of the material higher temperature is required. The residue yield in PDMMPS is ~50% at ~700 °C in nitrogen. The DSC curve of PDMMPS showed an endotherm at ~108 °C (Fig. 5) which may be attributed to the melting point of the polymer. An exotherm appeared at ~300 °C which may be easily attributed to the cleavage of Si–Si and Si–Me bonds as in TGA a significant weight loss has also been observed at same temperature i.e., ~299 °C.

The DSC of PDMMVS (Fig. 6) showed a very small endotherm at 166 °C (31.6 J/g) and no further change was noticed up to 400 °C. It appeared that at ~166 °C the cross-linking of vinyl group took place, which made the material infusible and so not suitable for making meltable and soluble polycarbosilane. The PDMMVS was heated under reflux in an argon atmosphere at the rate of 5 °C/min up to 400 °C and kept for 30 min at 700 °C. The IR analysis of the solid residue revealed that PCS did not formed as characteristic νSi-H absorption band at ~2100 cm^{-1} did not appeared, whereas the absorption due to νSi-vinyl at ~1642 cm^{-1} was disappeared. The PDMMVS was further

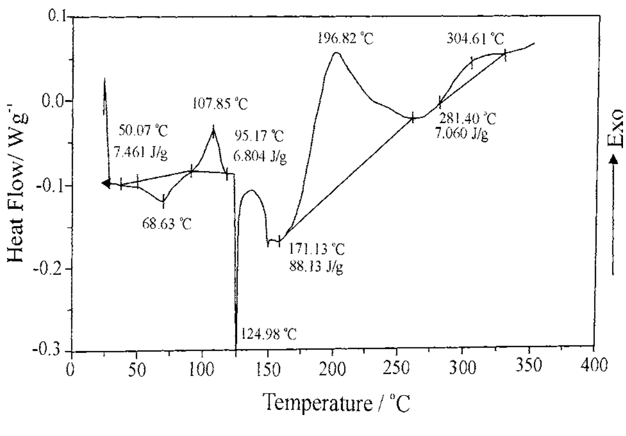

Fig. 10. DSC of polycarbosilane [PCS-N] (mp 124 °C).

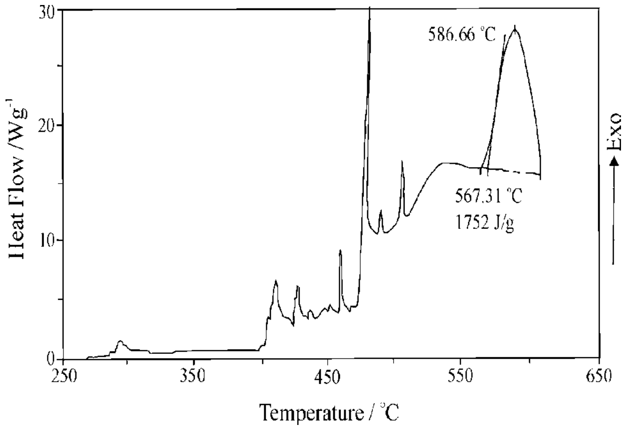

Fig. 13. DSC of polycarbosilane [PCS-N] (mp 124 °C).

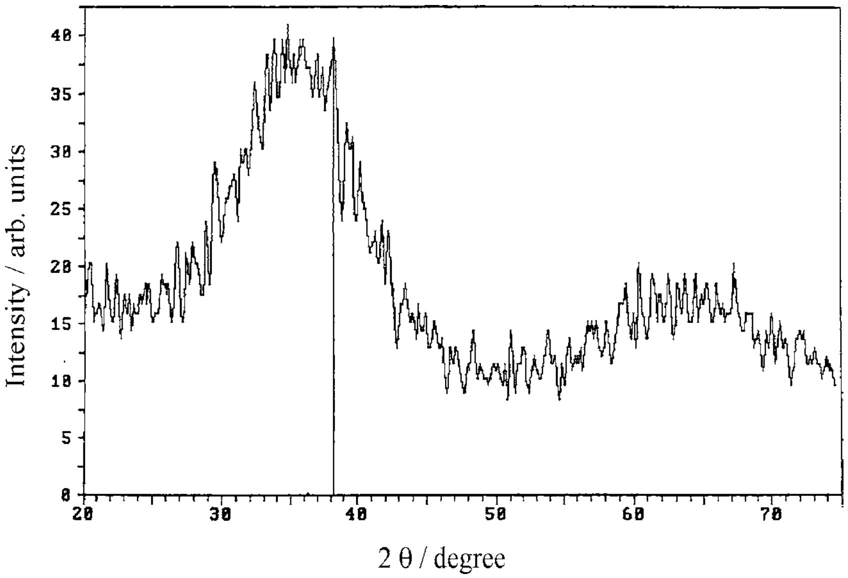

Fig. 14. X-ray diffraction pattern of pyrolyzed product of polycarbosilane [PCS-N] at 930 °C.

heated up to ~950 °C yielded α-SiC (20%), as the XRD analysis of this showed the pattern similar to the α-SiC obtained from PCS-N (mp 124 °C) (Fig. 14).

From the above studies, it may be concluded that PDMS and PDMMPS is more suitable polymer for making polycarbosilane. The ceramic yields in both the cases are very much close.

As the cross-linking of PCS obtained from PDMS took place comparatively at lower temperature (~650 °C) (Fig. 2) than PCS obtained from PDMMPS, so we have synthesized three different type of polycarbosilanes using PDMS and their thermal behavior have been studied in detail.

The TGA studies of two similar type of PCS-N of different molecular weight and melting points, showed that the ceramic yield of high molecular weight PCS-N (Mn 1800, mp 124 °C) (Fig. 7) is more i.e., ~94% compared to low molecular weight PCS-N (Mn 1200, mp 110 °C) i.e., ~75% as found at ~850 °C (Fig. 8). Whereas ceramic yield of PCS-A (Mn 1400, mp 116 °C) is ~83% at ~850 °C (Fig. 9).

The DSC studies were performed on the PCS-N (mp 124 °C) from RT to 350 °C (Fig. 10) and it has been observed that an endotherm appeared at 125 °C (*E* 6.804 J/g) which is the melting point of the polycarbosilane. On increasing the temperature an exotherm appeared at ~197 °C. This may be attributed to the chain extension of the polymer. This polycarbosilane is slowly cooled down under nitrogen and again heated. The second heating showed that except an exotherm at 159 °C (*E* 23.91 J/g) all exotherm disappeared (Fig. 11).

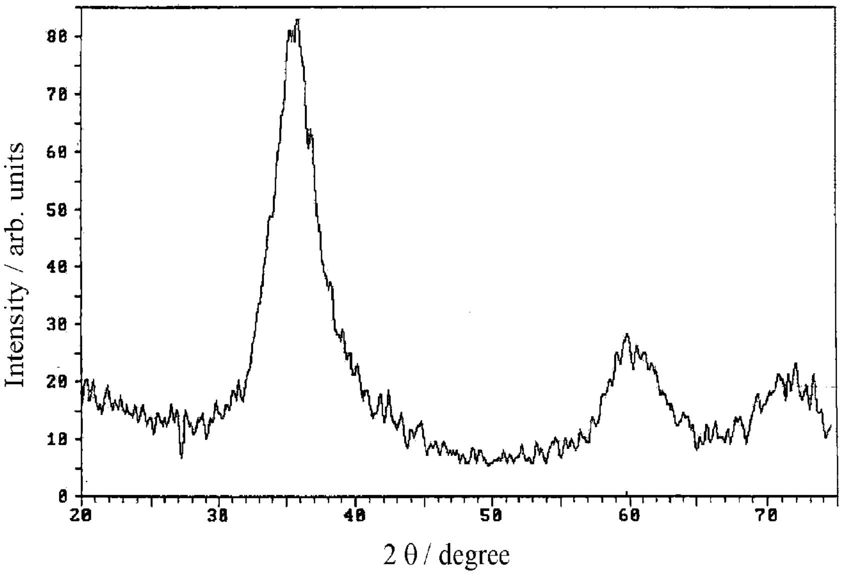

Fig. 15. X-ray diffraction pattern of pyrolyzed product of polycarbosilane [PCS-N] at 1250 °C.

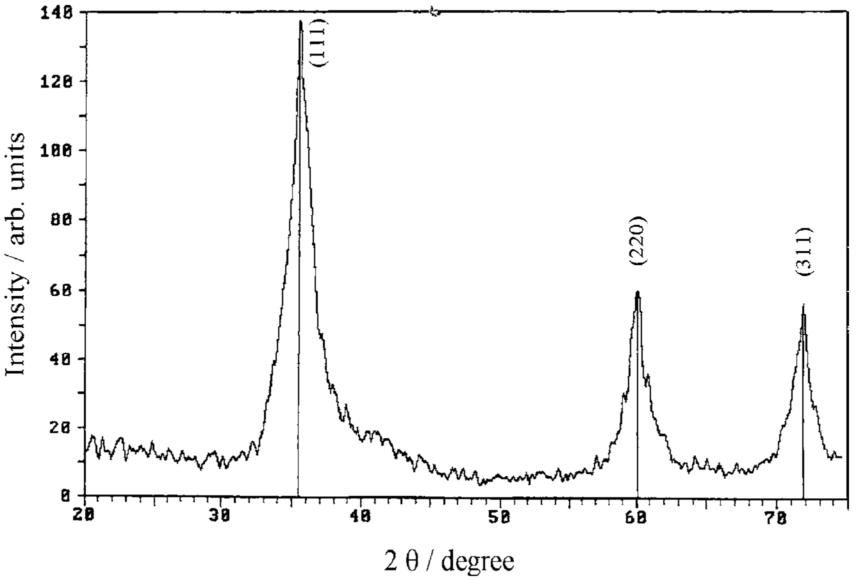

Fig. 16. X-ray diffraction pattern of pyrolyzed product of polycarbosilane [PCS-N] at 1500 °C.

This heated polycarbosilane again cooled down and further heated but the same exotherm appeared (Fig. 12). As the energy ($E \sim$ 23–29 J/g) in both the two cases is not much, so it may be assumed that it is due to change in crystalline structure of the material. The same material then heated up to 600 °C under nitrogen and it has been observed that an exotherm appeared at ~586.66 °C (E 1752 J/g) this change may be attributed to the cross-linking of the polycarbosilane (Fig. 13) [15].

The PCS-N (mp 124 °C) when heated under argon atmosphere in an electrically heated furnace at ~930 °C for 30 min a black amorphous residue is obtained which was identified as α-SiC using XRD analysis (Fig. 14). The α silicon carbide is further heated at ~1250 and 1500 °C under inert atmosphere in an oven and XRD analysis were performed which showed that with the increase of temperature the crystallinity of the material improved and formation of β-SiC took place (Figs. 15 and 16). The XRD analysis (Fig. 16) shows three distinct peaks at the diffraction angles 35.6°, 60.2° and 71.8°, which correspond to (111), (220) and (311) planes of β-SiC, respectively, thus confirming the formation of β-SiC.

4. Conclusions

From the TGA and DSC studies it may be concluded that the PDMS and PDMMPS are good ceramic material precursors for making meltable and soluble polycarbosilanes which formed ~450 °C. The PDMMS as gave very poor char yield hence not suitable as ceramic material precursors. The PDMMVS showed cross-linking hence it is not suitable for making polycarbosilane but being soluble in common aromatic solvents it can be used as direct source for making shaped silicon carbide article.

The thermal studies of polycarbosilanes showed that the char yield of the polymer increased with the increase of molecular weights and the polycarbosilane obtained from the PDMS cross linked earlier than to the PCS obtained from PDMMPS.

The thermal recycling studies revealed that the voids and defects could be minimized while using PCS as polymer impregnation process (PIP) resin matrix for making silicon carbide composites as most of the exotherm vanished in such processing. But such heating and cooling process should be done below cross-linking temperature of PCS i.e., 650 °C.

So these information’s may be advantageous from processing point of view while making α and β-SiC particulates, fibers, shaped articles and ceramic composites.

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References

[1] S. Yajima, Y. Hasegawa, K. Okamura, T. Matsuzawa, Nature 273 (1978) 525.
[2] S. Yajima, Y. Hasegawa, J. Hayashi, M. Iimura, J. Mater. Sci. 13 (1978) 2569.
[3] Y. Hasegawa, M. Iimura, S. Yajima, J. Mater. Sci. 15 (1980) 720.
[4] Y. Hasegawa, K. Okamura, J. Mater. Sci. 18 (1983) 3633.
[5] S. Yajima, J. Hayashi, M. Omori, Chem. Lett. 9 (1975) 931.
[6] K. Okamura, Adv. Composite Mater. 8 (1999) 107.
[7] R. West, J. Organomet. Chem. 300 (1986) 327.

[8] R.D. Miller, J. Michl, Chem. Rev. 89 (1989) 1359.

[9] X.-H. Zhang, R. West, J. Polym. Sci. Polym. Chem. Ed. 22 (1984) 159;
X.-H. Zhang, R. West, ibid 22 (1984) 225;
X.-H. Zhang, R. West, ibid J. Polym. Sci. Polym. Lett. Ed. 23 (1985) 479.

[10] C.L. Schilling, T.C. Williams, Polym. Pre. 25 (1) (1984) 1.

[11] C.L. Schilling, Bri. Polym. J. 18 (6) (1986) 355.

[12] S.-H. Jang, C.-K. Park, Y.-S. Song, G.-H. Lee, Bull. Korean. Chem. Soc. 17 (1996) 443.

[13] C.L. Schilling, J.P. Wesson, T.C. Williams, Am. Ceram. Soc. Bull. 62 (1983) 912.

[14] T. Iseki, M. Narisawa, Y. Katase, K. Oka, T. Dohmaru, K. Okamura, Chem. Mater. 13 (11) (2001) 4163.

[15] H.M. Williams, E.A. Dawson, P.A. Barnes, B. Rand, R.M.D. Brydson, A.R. Brough, J. Mater. Chem. 12 (12) (2002) 3754.

[16] M. Birot, J.-P. Pillot, J. Dunogues, Chem. Rev. 95 (1995) 1443, and references therein.

[17] A. Idesaki, M. Narisawa, K. Okamura, M. Sugimoto, Y. Morita, T. Seguchi, M. Itoh, Key Eng. Mater. 164-165 (1999) 39.

[18] K. Okamura, Composites 18 (1987) 107.

[19] D.W. Matson, R.C. Petersen, R.D. Smith, Mater. Lett. 4 (1986) 429.

[20] W.A. Kriner, J. Polym, Sci. Polym. Chem. Ed. 4 (2) (1966) 444.

[21] B. Boury, L. Carpenter, R.J.P. Corriu, Angew Chem. 102 (7) (1990) 818.

[22] E. Bacque, M. Birot, J.-P. Pillot, P. Lapouyade, P. Gerval, C. Biran, J. Dunogues, J. Organomet. Chem. 521 (1996) 99, and references therein.

[23] S. Yajima, K. Okamura, J. Hayashi, M. Omori, J. Am. Ceram. Soc. 59 (1976) 324.

[24] S. Yajima, K. Okamura, Y. Hasegawa, US Patent 4,220,600 (1980).

[25] S. Yajima, J. Hayashi, M. Omori, K. Okamura, Nature 261 (1976) 683.

[26] R.J.P. Emsley, Precursor Routes to Ceramic Fibers, in: A.R. Bunsell, M.-H. Berger (Eds.), Fine Ceramic Fibers, Marcel Dekker, Inc., New York, 1999, pp. 165-206.