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Thermal cross-linking and pyrolytic conversion of poly(ureamethylvinyl)silazanes to silicon-based ceramics

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The aim of this work was to study the pyrolytic conversion of a novel commercial polysilazane, poly(ureamethylvinyl)silazane (PUMVS; Ceraset™, Allied Signal Composites Inc., USA), into silicon-based ceramics. The precursor was thermally cross-linked and pyrolyzed between 200 and 1700 °C under argon or nitrogen atmosphere and the products were investigated by spectroscopic techniques (FTIR and Raman spectroscopy, solid-state NMR), elemental analysis and simultaneous thermal analysis coupled with mass spectrometry. Upon heating under argon, the starting liquid precursor transformed into an infusible solid polymer at $T > 250$ °C with a conversion yield of >95 wt%. The cross-linking solidification occurred predominantly through hydrosilylation or addition reaction involving vinyl groups. Subsequent pyrolysis of the cross-linked products around 1000 °C in argon yielded amorphous silicon carbonitride ceramics with a composition of $SiN_{0.82}C_{0.86}$. The overall ceramic yield (with respect to the starting PUMVS) was around 70 wt%, which was found to be independent of the initial cross-linking step. Solid-state NMR (^{29}Si and ^{13}C) revealed that the amorphous silicon carbonitrides contain predominately $C\mathit{Si}N_3$ units. There is evidence for the formation of free amorphous carbon between 700 and 800 °C. Graphitic phases were detected by X-ray diffraction in the samples heated to $T > 1000$ °C at high heating rates. Upon annealing at $T > 1500$ °C, the excess carbon reacted completely with the silicon (carbo)nitride to form SiC and nitrogen. The final ceramics contained a large amount of crystalline SiC (~90 wt%), and were free of excess carbon or silicon. Therefore, PUMVS is an ideal precursor for the formation of high-quality SiC-based ceramics.

Keywords: pyrolysis; polysilazane; ceramics; SiC; Ceraset™

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1 INTRODUCTION

The precursor route to silicon-based non-oxide ceramics (Si_3N_4, SiC and SiN_xC_y or Si_3N_4–SiC composites) from silicon-containing polymers has received attention in recent years because unconventional structures, such as fibers, coatings, bulk amorphous or nanocrystalline ceramics, can be produced by this process.[1–10] Of the wide variety of silicon-containing compounds, polysilazane precursors have been examined in detail.[3,4,6,10] They are accessible from low-cost chlorosilanes and have tailorable physical and chemical properties. In particular, polysilazanes are the ideal precursors for ternary Si–C–N ceramics. The silazane-derived Si–C–N powders can be processed using traditional liquid sintering into dense Si_3N_4–SiC nano–nano or nano–micro composites by crystallization and phase separation of the metastable Si–C–N materials at $T > 1440$ °C.[7–10] These composites are of

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current interest owing to their improved mechanical properties.[5]

The applicability of polysilazane precursors in the various ceramic processing techniques depends on the physical and chemical properties of the polymers selected. Soluble and meltable precursors are suitable for the generation of coatings, whereas highly cross-linked and infusible precursors are required for the fabrication of dense bulk materials. However, the as-formed products from the reaction of chlorosilanes with ammonia are usually volatile oligomers, which are not suitable for pressureless pyrolysis to ceramic materials. Thus, extensive activities have been devoted to the modification of the silazane oligomers into nonvolatile precursors.[1,3,6,11,12] Several methods have been developed for cross-linking of the silazane oligomers into polysilazanes, such as catalysis using strong bases, acids or transition-metal compounds.[1,3,6,11,12] The cross-linked materials give a higher ceramic yield upon pyrolysis and can be controlled to be soluble and/or meltable or infusible, which is necessary for the respective applications. Two important precursors of this kind are poly(hydridomethyl)silazane (PHMS) and polyvinylsilazane (PVS), both of which became commercially available (NCP200 of Chisso, Japan, and VT 50 of Hoechst, Germany). They were applied for the fabrication of fibers, used as ceramic binders or for the generation of ceramic powders and bulk ceramics.[13–17] PVS generally has a higher ceramic yield than PHMS, but both precursors give excess carbon in the final crystallized ceramics.

Recently, modification of silazane oligomers with urea or isocyanate-containing compounds has been reported to improve the chemical and physical properties of the silazane precursors. Seyferth and coworkers reacted *cyclo*-$[CH_3Si(H)NH]_n$ derived from ammonolysis of CH_3SiHCl_2 and urea in different molar ratios ($CH_3Si(H)NH$ unit/urea = 4:1–12:1), and synthesized poly(ureidosilazane)s[#].[18,20] By means of NMR and FTIR analysis, they detected the existence of C═O in the products and proposed insertion reactions of urea into the chains or cycles of the oligomeric silazanes#.[18,20] In contrast, Schwark and coworkers reacted methylvinylsilazane cyclic oligomers derived from ammonolysis of $CH_2{=}CH(CH_3)SiCl_2$ with isocyanates and synthesized poly(ureamethylvinyl)silazanes (PUMVSs).[21–23] The reaction was considered to proceed along a similar path as the formation of poly(ureidosilazane)s, i.e. insertion to form urea derivatives. The products were found to exhibit a wide range of viscosity, depending on the amount of isocyanate (2–6 wt%) added. Pyrolysis of the precursor in an inert atmosphere produced silicon-based ceramics in good yields.[21–23] This, together with its tailored viscosity properties, makes this new kind of polysilazane promising for the fabrication of ceramic coatings and infiltration techniques. Currently, PUMVS is commercially available as Ceraset™.[19,24] Our recent work shows that the Ceraset™ precursor can be processed into infusible polymers by thermal cross-linking followed by a transformation to dense Si–C–N ceramics by compacting and pyrolysis.[25] Considering its promising applications as a preceramic precursor, a detailed understanding of its ceramic conversion behavior is needed. In the present work, we report on the thermal cross-linking and pyrolysis of the Ceraset™ precursor to silicon-based ceramics.

2 EXPERIMENTAL

2.1 PUMVS precursor

Commercial PUMVS (trade name: Ceraset™, Allied Signal Composites Inc., formerly Lanxide Corp., USA) was used as-received. The polymer is a colorless or slightly yellow oil-like liquid. According to the supplier, the polymer was produced by a two-step reaction.[19,24] co-ammonolysis of methyldichlorosilane and methylvinyldichlorosilane to form cyclic methylvinylsilazanes according to Eqn [1] followed by reaction of the cyclic methylvinylsilazane with a small amount of an isocyanate (2–6 wt%) (Eqn [2]). During the second reaction the isocyanate inserts into the silazane ring to form the urea–cyclosilazane structure. The chemical structure of the PUMVS polymers provided by Lanxide Corp. is shown in Fig. 1.

$$\begin{aligned}&nx\mathrm{CH_3SiHCl_2} + ny\mathrm{CH_2{=}CH(CH_3)SiCl_2}\\&\quad + 3n(x+y)\mathrm{NH_3}\\&\quad \rightarrow [(\mathrm{CH_3SiHNH})_x(\mathrm{CH_2{=}CH(CH_3)SiNH})_y]_n\\&\quad + 2n(x+y)\mathrm{NH_4Cl}\end{aligned} \qquad [1]$$

[#] The nomenclature poly(ureidosilazane) and poly(ureasilazane) was used by the authors in Refs 18 and 19. In order to avoid confusion we used the same terminology for the respective polymers.

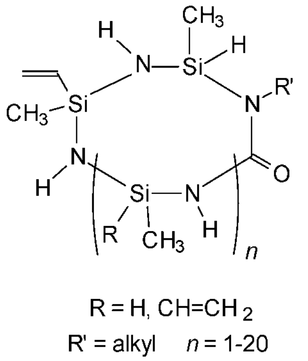


Figure 1 Chemical structure of the PUMVS (Ceraset™) polymer provided by the Lanxide company. No information is available about the alkyl-substituent R′.

$$[(CH_3SiHNH)_x(CH_2{=}CH(CH_3)SiNH)_y]_n + nzRN{=}C{=}O \rightarrow [(—NH(CH_3)SiH—)_x(NRC{=}O—)_z (NH(HC{=}CH_2)SiCH_3)_y]_n \quad (R = \text{alkyl}) \tag{2}$$

2.2 Characterization of PUMVS precursor

The PUMVS polymer was characterized by FTIR, ^1H and ^{13}C NMR spectroscopy and chemical analysis. Elemental analysis gave a composition (wt%) of 43.9 Si, 19.1 N, 27.3 C, 8.11 H and 0.38 O ($SiN_{0.87}C_{1.45}H_{5.17}O_{0.01}$). From the elemental composition, the relative numbers of each structural unit in the polymer were estimated and can be expressed as:

$$(—NH(CH_3)SiH—)_{0.77}(—(NRC{=}O)_{0.01} (NH(HC{=}CH_2)SiCH_3)_{0.22}$$

The amount of CH_3SiHNH units is more than three times that of $CH_2{=}CH\ (CH_3)SiNH$ units. The Si/N atomic ratio of the precursor is equal to 1.14, which is larger than that derived from the provided structure ($Si/N = (3 + n)/(4 + n)$, for $n = 1–20$ follows $Si/N < 1$) (Fig. 1). This is probably due to the existence of some linear molecules with trialkylsilyl or hydrosilyl end groups.

The FTIR spectrum of the PUMVS liquid is shown in Fig. 2a. The bands related to vinylsilyl groups ($H_2C{=}CHSi$) are the C—H vibrations at 3048 and 3007 cm^{-1}, and C=C stretching at 1593 cm^{-1}. A strong Si—H absorption band appeared at 2129 cm^{-1}. The bands ascribed to Si—NH—Si groups include N—H stretching at 3383 cm^{-1} and Si—N vibrations at 1170 cm^{-1}. $Si—CH_3$ groups were detected by their characteristic band at 1255 cm^{-1}, together with methyl C—H vibrations at 2957 and 2900 cm^{-1}. However, no absorption band corresponding to carbonyl groups (C=O), which should appear[21] between 1607 and 1664 cm^{-1}, was detected by FTIR spectroscopy.

NMR spectra (^1H, ^{13}C and ^{29}Si) were measured using $CDCl_3$ as a solvent. The ^1H NMR spectrum shows four groups of peaks, which can be assigned to $SiCH{=}CH_2$ (5.73–6.17 ppm), Si—H (4.42–5.02 ppm), N—H (0.82–0.89 ppm) and $Si—CH_3$ (0.09–0.33 ppm).[26] The ratio of the $CH_2{=}CHSi$, H—Si, $CH_3—Si$ units was determined from the respective peak intensities to be 1:3:5. The ratio of

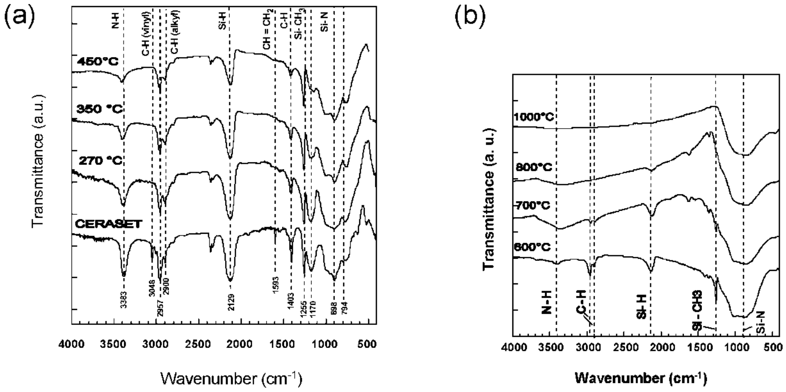


Figure 2 FTIR spectra of cross-linked and pyrolyzed products at the temperatures indicated: (a) as-received Ceraset™ and T_{CL} = 270–450 °C; (b) T_{Py} = 600–1000 °C.

$CH_2{=}CHSi/H{-}Si = 1{:}3$ is nearly equal to that obtained from chemical analysis: $(NH(HC{=}CH_2)\text{-}SiCH_3)/({-}NH(CH_3)SiH{-}) = 0.22/0.77 = 1{:}3.5$. The presence of multiple resonance peaks between 4.42 and 5.02 ppm may originate from Si—H and SiH_2 groups present either in the cyclic backbone or as terminal groups in linear molecules.[18] No signal corresponding to CH_3—N groups was detected around 2.3–2.6 ppm.[27]

The ^{13}C NMR spectrum shows three groups of peaks, which were assigned to $CH_2{=}CH$ (140.4 and 132.0 ppm) and Si—CH_3 groups (1.38–4.28 ppm). Again, no signal corresponding to C=O groups was detected by the ^{13}C NMR experiments (the C=O groups should appear at around 164 ppm, as observed in polyureidosilazanes by Seyferth *et al.*[18]). Finally, the ^{29}Si NMR spectrum shows two resonances at -18 ppm and -22 ppm, which are assigned to $CH_3H\mathit{Si}N_2$ and $CH_3CH_2{=}CH\mathit{Si}N_2$ respectively.[26]

Gel permeation chromatography (GPC) and mass spectrometry (MS) were used to determine the molecular mass distribution of the PUMVS. Both methods indicated low values for M. Using tetrahydrofuran (THF) solutions and polystyrene as a calibration standard for GPC, a multi-modal distribution with a strong signal <100 g mol^{-1} and $M_n = 74$, $M_w = 144$, $M_z = 430$ were detected. Correspondingly, MS indicated *m/e* values <500. Thus, PUMVS should be considered as a mixture of oligomers rather than a true polymer.

Surprisingly, the carbonyl group that appears in the proposed structure of the PUMVS precursor (Fig. 1) was not detected by neither FTIR or ^{13}C NMR spectroscopy. This is in agreement with the very low oxygen content (0.38 wt%) found in the precursor by elemental analysis. This small amount of oxygen leads to only 1% of C=O groups in the precursor $([{-}NH(CH_3)SiH{-}]_{0.77}[{-}NRC{=}O]_{0.01}[NH(HC{=}CH_2)SiCH_3]_{0.22})$. Because of the absence of C=O signals in the various spectral analyses, the effects of such a functionality (if any is present) on the cross-linking and pyrolysis could not be studied.

2.3 Cross-linking, pyrolysis and crystallization

Cross-linking was conducted by heating the PUMVS liquid in a quartz tube in the absence of any peroxide catalyst. Batches of 15 g of the PUMVS liquid were placed in quartz Schlenk-tubes in a glove-box (Braun MB, 150G-1 SPS) under argon atmosphere (oxygen and $H_2 < 1$ ppm) in order avoid contact of the precursor with air. The polymer-filled tube was then heated at 10 °C min^{-1} to a certain temperature between 200 and 500 °C under flowing argon, then maintained at this temperature for 2 h and finally cooled down at the same rate to room temperature. The heating process was monitored by a Eurotherm Model E5 controller with a temperature deviation of ±5 °C.

Pyrolysis of the cross-linked products and crystallization of the amorphous products were performed in the temperature range from 500 °C up to 1800 °C in nitrogen or argon. The cross-linked solids were powdered, filled in a quartz Schlenk-tube and pyrolyzed between 500 and 1100 °C for 2 h to form amorphous SiC_xN_y ceramics. Crystallization of the amorphous SiC_xN_y materials was conducted between 1400 and 1800 °C using a graphite furnace and holding times of 1–2 h.

2.4 Spectroscopic analyses and characterization

The cross-linked and pyrolyzed products were analyzed by chemical analysis, FTIR and Raman spectroscopy, solid-state NMR (^{13}C and ^{29}Si), simultaneous thermal analysis coupled with MS (STA–MS) and X-ray diffraction (XRD). IR spectra were recorded using KBr pellets and a Perkin–Elmer FT-IR model 1750; Raman spectra were measured with a Bruker IFS55 spectrometer; ^{13}C and ^{29}Si solid-state NMR spectra were recorded on a Bruker MSL 300 spectrometer. STA-MS was performed on a Netzsch STA 429 coupled with a Balzers QMG 420 using flowing helium (75 cm^3 min^{-1}) and a heating rate of 5 °C min^{-1}. XRD measurements were carried out on a Bragg–Brentano diffractometer (Siemens D500). Chemical analysis (Si, N, C, O and H) was done at the Microanalytisches Labor Pascher, 53424 Remangen, Germany.

3 RESULTS

3.1 Cross-linking

Cross-linking experiments showed that the PUMVS liquid can be thermally set into a solid product without any catalyst upon heating. The transformation from the liquid to a solid product is complete within 35 min at 150 °C and in less than 5 min at 280 °C. At cross-linking temperatures $T_{CL} >$ 300 °C the solidification occurred as soon as the

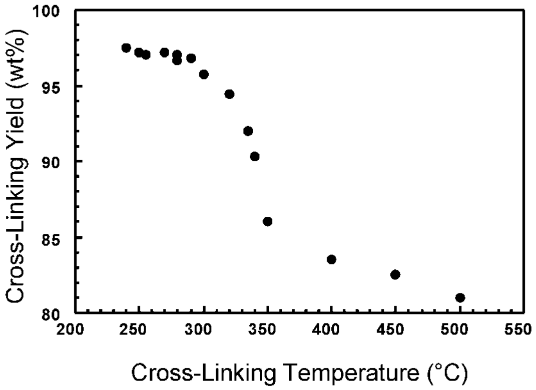


Figure 3 Variation of cross-linking yield of the PUMVS precursor versus cross-linking temperatures (flowing argon, heating rate: 10 °C min^{-1}).

temperature was reached (heating rate: 10 °C min^{-1}). Below 250 °C, the viscosity of the liquid precursor increased gradually to form gel-like and rubber-like products between 235 and 260 °C. With careful control of the cross-linking temperature between 250 and 270 °C, highly transparent polysilazane bodies can be obtained.[28] The use of higher temperatures results in porous solids due to the enhanced evaporation of oligomers. The cross-linked solids are thus infusible and less sensitive towards air.

Fig. 3 shows the cross-linking yield versus processing temperatures that was obtained using a heating rate of 10 °C min^{-1} under argon atmosphere and a holding time of 2 h. Below $T_{CL} \approx$ 300 °C a low weight loss was observed and the cross-linking occurred with a high yield up to 95 wt%. At $T_{CL} >$ 300 °C the weight loss becomes important, resulting in a decreasing yield from 95 wt% at 280 °C to 85 wt% at 450 °C. The enhanced weight loss was caused by evaporation of low molecular-weight oligomers, which was clearly observed during the cross-linking experiments, especially at $T_{CL} >$ 300 °C. FTIR analysis of the condensed liquid on a cold region of the quartz tube revealed that it had similar structure to the starting PUMVS but contained no vinyl groups.

3.2 STA–MS

The pyrolysis behavior of the cross-linked solids was investigated by thermal gravimetric analysis coupled with MS (TGA–MS). Two differently cross-linked precursors, one cross-linked at 260 °C and the other at 400 °C, were analyzed in order to study the effects of the initial cross-linking processing on their pyrolysis behavior. The results are shown in Fig. 4.

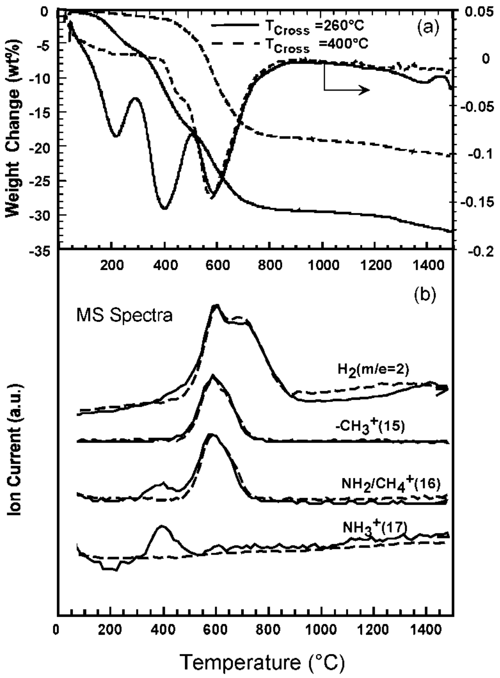


Figure 4 STA-MS of the cross-linked polymer obtained at 250 and 450 °C. (a) TGA and DTG curves; (b) ion current curves for *m/e* = 2, 15, 16 and 17.

The low cross-linked polymer (T_{CL} = 260 °C) exhibits a distinct three-stage weight loss at around 220, 400 and 580 °C, as indicated by the differential thermogravimetric (DTG) curves (Fig. 4a). The corresponding weight losses are 5.4 wt% (25–300 °C), 11.6 wt% (300–500 °C) and 11.9 wt% (500–800 °C), with an overall value of 28.9 wt% at 800 °C. In contrast, the highly cross-linked sample (T_{CL} = 400 °C) shows a small weight loss during the first two stages (0.86 wt% between 25 and 300 °C and 1.92 wt% between 300 and 500 °C), but exhibits a larger weight loss (15.9 wt% between 500 and 800 °C) during the third stage (Fig. 4a). The entire weight loss is 18.4 wt% at 800 °C, which is much smaller than the 28.9 wt% observed for the low cross-linked sample. Taking into account the weight loss that occurred during thermal cross-linking (3 wt% at T_{CL} = 260 °C and 14 wt% at T_{CL} = 400 °C, Fig. 3), the overall ceramic yields with respect to the starting PUMVS polymers are 69 wt% and 70 wt% respectively for the 260 °C and 400 °C cross-linked precursors. These results

Table 1 Chemical composition of the starting PUMVS polymer (1), the polymer cross-linked at 450 °C (2), the ceramics pyrolyzed at 1000 °C (3) and the ceramics annealed at 1700 °C (4). All the processing was conducted under argon atmosphere and with an annealing time of 2 h

Sample no.	Sample name	Composition (wt%)						Empirical formula
		Si	N	C	H	O	Total	
1	PUMVS	43.9	19.1	27.3	8.11	0.38	98.8	$SiN_{0.87}C_{1.45}H_{5.17}O_{0.01}$
2	CL-450	44.1	19.7	28.5	6.92	0.59	99.8	$SiN_{0.89}C_{1.51}H_{4.39}O_{0.02}$
3	Py-1000	55.3	22.6	20.3	<0.01	0.76	98.96	$SiN_{0.82}C_{0.86}O_{0.02}$
4	Py-1700	67.0	5.26	26.0	<0.01	1.5	98.3	$SiN_{0.16}C_{0.91}O_{0.04}$

suggest that the final yield is independent of the initial thermal cross-linking temperature.

MS spectra reveal that hydrogen and methane are the major gaseous by-products evolved during pyrolysis (Fig. 4b). Hydrogen (*m/e* = 2) evolution occurred in a wide temperature range from 300 to 900 °C with two maxima at 600 and 700 °C. Methane (*m/e* = 15, 16) was detected between 450 and 750 °C with a maximum at around 600 °C. The profiles for these two kinds of gas are nearly identical for the two differently cross-linked samples. In contrast, evolution of ammonia (NH_2: *m/e* = 16 and NH_3: *m/e* = 17) was detected at 300–500 °C only for the 260 °C samples, not for the 400 °C samples. This temperature range corresponds to the second weight loss, suggesting that the large weight loss observed for the 260 °C cross-linked precursors is associated with the evolution of ammonia. MS did not show any signals corresponding to the first weight loss (5.38 wt%) around 220 °C, which should be caused by evolution of low molecular-weight oligomers condensing in the cooler regions before reaching the detector. The third weight loss is exclusively caused by the formation of hydrogen and methane. The evolution of methane in this temperature range contributes greatly to the removal of excess carbon. The larger third weight loss of 15.9 wt% observed for the 400 °C samples suggests that more carbon was removed by methane evolution compared with the less cross-linked samples.

3.3 Elemental composition and phase determination

Cross-linked products were pyrolyzed between 600 and 1100 °C under argon atmosphere. A color change was observed from white for the as-cross-linked polymer to yellow at 500–650 °C, red–brown at 650–750 °C and dark-brown or black above 800 °C.

Table 1 lists the elemental compositions of the starting PUMVS precursor, the cross-linked, pyrolyzed and crystallized products obtained at the indicated temperatures. The variation of the C/Si, N/Si and H/Si molar ratios with processing temperatures is plotted in Fig. 5. The H/Si ratio decreased rapidly with the increasing processing temperature up to 1000 °C due to the evolution of hydrogen, methane and ammonia. Reduction of carbon occurred predominantly between 400 and 1000 °C and the content remained unchanged at higher temperature. In contrast, the N/Si ratio shows negligible change below 1000 °C, indicating that the overall amount of ammonia formed during pyrolysis is relatively small. The N/Si ratio decreases significantly above 1000 °C. This is primarily caused by evolution of molecular nitrogen during the crystallization of the amorphous phases at elevated temperatures (see Section 4.2). The black pyrolytic residue obtained at 1000 °C with a composition (wt%) of 55.3 Si, 22.6 N, 20.3 C

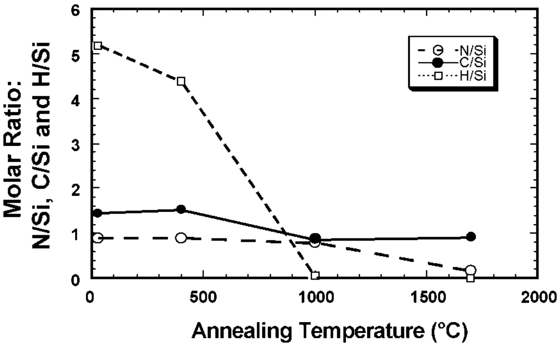


Figure 5 Variation of N:Si, C:Si and H:Si elemental ratios of PUMVS (Ceraset®) versus pyrolysis temperatures.

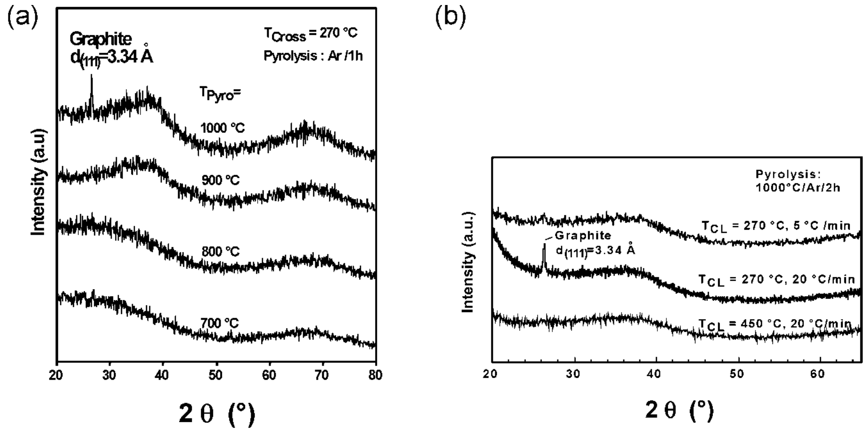


Figure 6 XRD patterns of the products obtained between 700 and 1000 °C. (a) $T_{CL} = 270$ °C, heating rate = 20 °C min^{-1}; (b) showing the effects of heating rate and cross-linking temperatures on the XRD diagram.

corresponds to an empirical formula of $SiN_{0.82}C_{0.86}$. The oxygen and hydrogen contents are low (O: 0.76 wt%; H: <0.1 wt%), indicating that such impurities can be controlled at a satisfactory level.

The pyrolytic residue formed below 1000 °C was amorphous as checked by XRD (Fig. 6a). At around 1000 °C graphite was frequently detected in the pyrolyzed products, which was found to be affected by heating rates and cross-linking degree of the precursors. Indeed, graphite was detected in the 270 °C cross-linked products pyrolyzed with a heating rate of 20 °C min^{-1} but not in the products pyrolyzed at 5 °C min^{-1}. In contrast, no graphite was formed when using 400 °C cross-linked starting material, even at the high heating rate of 20 °C min^{-1}. The above results indicate that the structure of the derived ceramics depends both on the cross-linking processing and pyrolysis conditions.

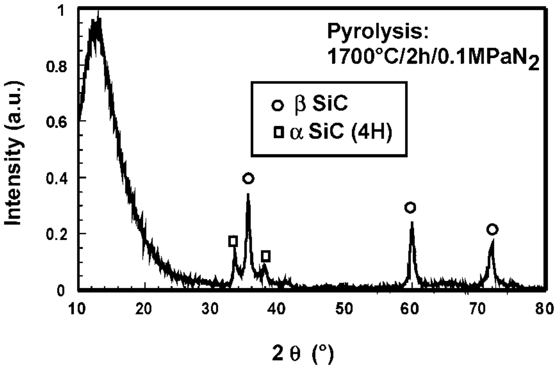


Figure 7 XRD pattern of the crystalline products obtained in nitrogen atmosphere upon annealing for 2 h at 1700 °C.

The amorphous silicon carbonitride was annealed above 1440 °C in nitrogen. XRD patterns of the crystallized samples obtained at 1700 °C are shown in Fig. 7. The pattern shows strong diffraction lines originating from the major crystalline phase β-SiC mixed with a small amount of α-SiC (4H). No graphite phase was detected in the products obtained above 1500 °C. After annealing above 1700 °C, the color of the samples changed from black to light green, which also suggests the elimination of free carbon phases during the annealing. The weight loss after annealing was determined to be around 20 wt%. Elemental analysis gave a composition (wt%) of 67 Si, 26 C, 5 N and 1.5 O, which corresponds to an empirical formula of $SiC_{0.91}N_{0.16}O_{0.04}$.

3.4 Spectral characterization

3.4.1 FTIR and Raman spectra

FTIR and Raman spectra of cross-linked and pyrolyzed products obtained at different temperatures are shown in Figs 2 and 8 respectively.

At $T < 500$ °C the spectra still show the characteristics of the starting polymers (Figs 2a and 8a). However, in the FTIR for $T > 250$ °C the absorption bands attributed to the vinyl groups ($SiCH{=}CH_2$: C—H stretching at 3048 and 3007 cm^{-1}, C=C stretching at 1593 cm^{-1}) that were observed for the starting PUMVS precursor

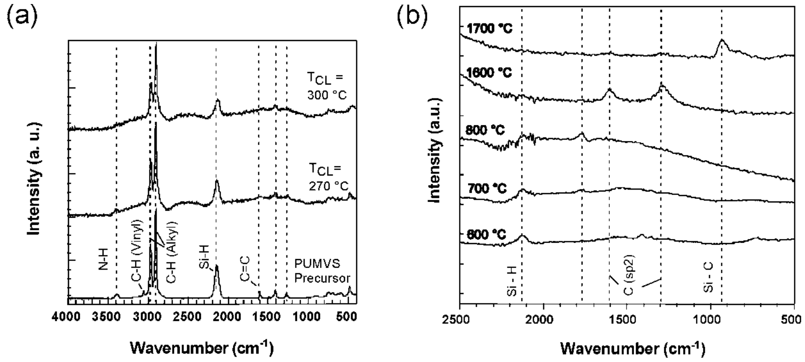


Figure 8 Raman spectra of cross-linked and pyrolyzed products obtained at the temperatures indicated: (a) $T_{CL} < 300$ °C; (b) $T_{Py} = 600–1700$ °C.

have completely disappeared (Fig. 2a). Accordingly, the absorption band at 1403 cm^{-1}, which results from overlapping C—H deformation modes in SiCH$=$CH$_2$ and H$_3$C—Si groups, decreased significantly in intensity. The decrease in the amount of vinyl groups at $T > 250$ °C was also obvious in the Raman spectra (H$_2$C$=$CHSi, 3050 cm^{-1}) (Fig. 8a). These changes indicate addition and polymerization reactions of vinyl groups at $T > 250$ °C, which cause the observed cross-linking solidification of the PUMVS liquid at this temperature. With increasing temperature between 250 and 450 °C the absorption bands around 3340 cm^{-1}, attributed to N—H bonds, gradually decreased. This change was accompanied by a change of the Si—NH—Si band shape at around 1170 cm^{-1}, possibly caused by transamination reactions in this temperature range.

At $T > 500$ °C the absorption bands corresponding to the Si—H, C—H and N—H vibrations decrease strongly (Fig. 2b), suggesting the onset of typical pyrolytic reactions above this temperature. At $T = 800$ °C almost all N—H and C—H groups had vanished, but there was still a small amount of Si—H retained at this temperature. The strong and broad band between 800 and 1100 cm^{-1} is caused by at least two kinds of bond: Si—N (950 cm^{-1}) and Si—C (970, 800 cm^{-1}).[29]

Raman spectra of the products pyrolyzed at $T > 600$ °C are shown in Fig. 8b. At 1600 °C there are two bands, at 1602 and 1280 cm^{-1}, that are caused by amorphous *sp*^{2}-hybridized carbon.[30] These two bands were not observed in the 1700 °C spectrum, suggesting the absence of free carbon. This is the result of an enhanced reaction of free carbon with Si–N and/or Si–C–N phases at 1700 °C to form SiC, as supported by XRD analysis (Fig. 7).

3.4.2 Solid-state NMR spectra (^{13}C and ^{29}Si)

^{13}C NMR spectra of the cross-linked and pyrolyzed products formed between 270 and 800 °C are shown in Fig. 9a. With the increase of processing temperatures, the main peak shifts from 3.5 ppm at 270 °C to 16.6 ppm at 800 °C with a significant broadening. This was caused by a gradually increasing number of Si—C bonds. Continuous shifting of ^{13}C peaks with annealing temperature was previously observed for PHMS precursors and was explained as follows: Si—CH$_3$ (5 ppm) → SiCH$_2$Si (12 ppm) → Si$_2$$C$H—Si (18 ppm) → Si$_4$$C$ (24 ppm).[13,31] At 270 °C, a small peak appears at 12 ppm as a shoulder of the main peaks centered at 3.5 ppm. This small peak is assigned to methylene- or ethylene-bridged silicon configurations (SiCH$_2$-Si or SiCH$_2$CH$_2$Si)[13,32] formed from hydrosilylation of vinyl groups or Kumada-like rearrangement reactions during cross-linking (see also Section 4.1). At 400 and 700 °C, a small peak was detected at 30 ppm that was assigned to CH$_2$ groups in aliphatic carbon chains that probably originate from vinyl group polymerization or dehydrocoupling reactions of methyl groups.[13] At 700 and 800 °C, a broad resonance is present at around 142 ppm together with spinning side bands, which is characteristic for sp^2-hybridized carbon.[13] This result suggests that a free carbon phase starts to form between 700 and 800 °C.

^{29}Si NMR spectra of the products formed at 270, 400 and 1100 °C are shown in Fig. 9b. The 270 °C spectrum exhibits two resonances centered at −4 and −22 ppm. A comparison with the

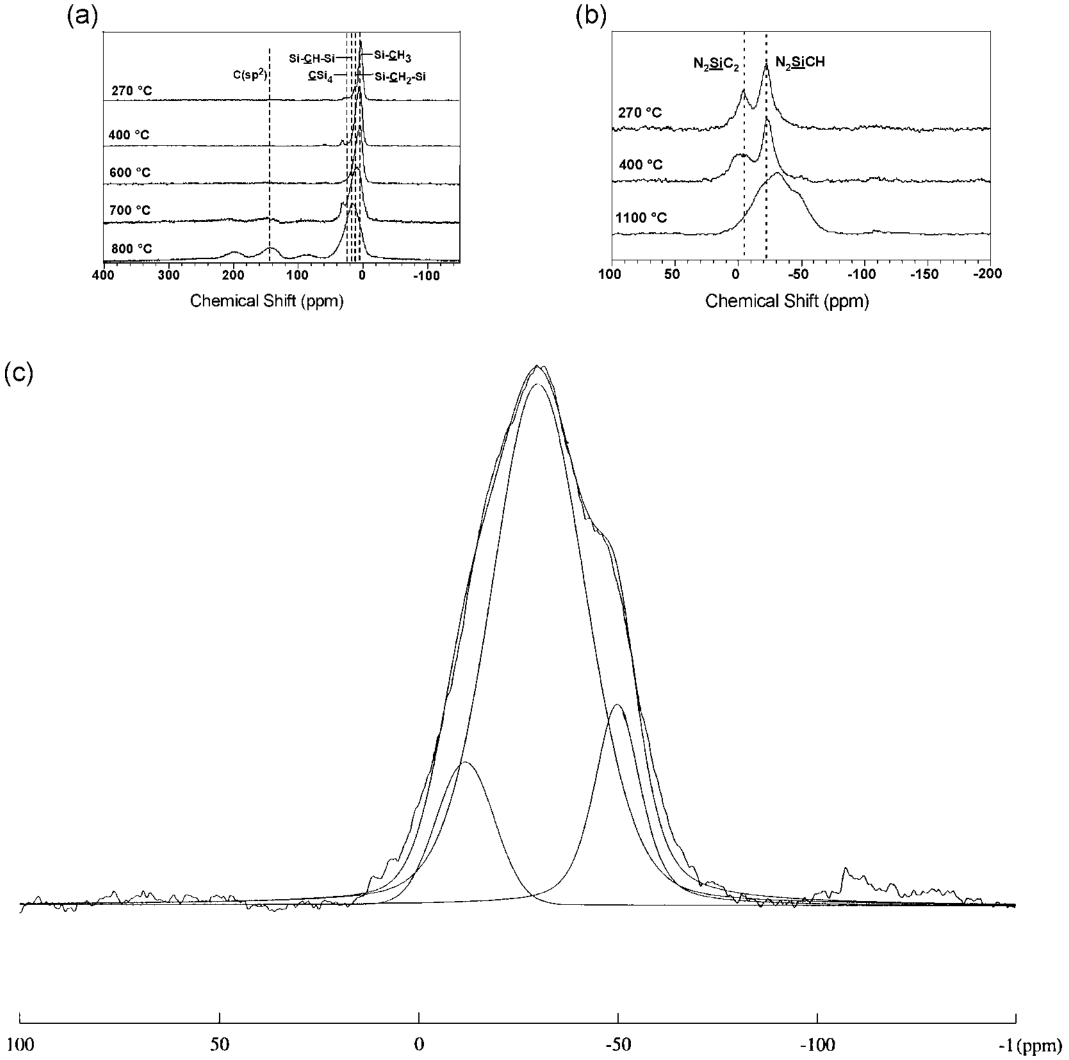


Figure 9 Solid-state NMR spectra of the cross-linked and pyrolyzed products: (a) ^{13}C; (b) ^{29}Si; (c) Gauss-curve fitting of the 1100 °C ^{29}Si NMR spectrum.

spectrum of starting PUMVS (see Section 2.2) shows that the −18 ppm resonance due to $CH_3CH_2{=}CH\mathit{Si}N_2$ observed in the starting precursor disappears at 270 °C; this is as a result of cross-linking reactions involving vinyl groups. The peak at −22 ppm assigned to $CH_3H\mathit{Si}N_2$ remains unchanged after cross-linking at 270 °C. The new resonance at −4 ppm is due to $C_2\mathit{Si}N_2$ sites, i.e. probably $CH_3\mathit{Si}(\text{—}CH_2CH_2\text{—})N_2$ groups that are formed by Si—H and/or N—H group addition *to*, or polymerization *of* the vinyl groups (see Section 4.1). At 400 °C, the −4 ppm band broadens significantly, suggesting the presence of a distribution of silicon centers caused by an increasing degree of cross-linking. At 1100 °C, the spectrum exhibits a broad resonance centered around 31 ppm; this was observed previously,[21b] but not analyzed in detail. The simulation of this peak reveals three components at −12 ppm, −30 ppm and −50 ppm, which are assigned to $\mathit{Si}C_2N_2$, $\mathit{Si}CN_3$ and $\mathit{Si}N_4$ environments in a ratio of 11:73:16 respectively (Fig. 9c). This indicates that a ternary amorphous Si–C–N phase is obtained at this temperature.

4 DISCUSSION

4.1 Cross-linking and pyrolysis

The vanishing of vinyl groups at $T > 250\,°C$, as revealed by various spectral analyses (FTIR, Raman and ^{13}C NMR), suggests that the initial cross-linking is due to reactions such as vinyl group polymerization (Eqn [3]) and hydrosilylation (Eqn [4]).

[3]

$$2\ \underset{CH_2=CH_2}{\mathrm{Si}} \longrightarrow \overset{\mathrm{Si}\quad\ \mathrm{Si}}{-CH_2-CH_2-CH_2-CH_2-}$$

[4]

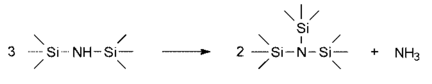
$$\underset{CH_2=CH_2}{\mathrm{Si}} + H-\mathrm{Si} \longrightarrow \mathrm{Si}-CH_2-CH_2-\mathrm{Si}$$

We assume that hydrosilylation dominates the cross-linking reactions at lower temperatures, since it is known from literature that Si—H and Si—$CH_2{=}CH_2$ groups in polysilazanes are very reactive,[33] and the onset of cross-linking reactions at 250 °C, as observed for the PUMVS, is very close to that reported for other polysilazanes containing vinylsilyl and Si—H groups,[26] whereas vinyl polymerization occurred at much higher temperatures (~350 °C) in PVSs that are free of Si—H groups.[13] This is in also agreement with the ^{13}C NMR results, which show signals predominantly due to Si—CH_3 and Si—CH_2.

Addition of peroxides to initiate the vinyl polymerization was used to cross-link the PUMVS liquid to solid products.[19,21–24] This chemical cross-linking occurred at 50–150 °C. The cured polymers were pyrolyzed in NH_3 to form silicon nitride and in argon to give silicon carbide. XRD, solid-state ^{29}Si NMR and elemental analysis were used to characterize the products.[21b] Fiber-reinforced ceramic matrix composites have been fabricated and examined with respect to density, strength and fracture toughness.[19]

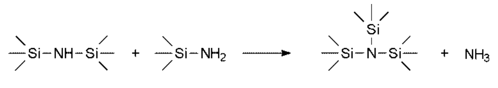
The present work demonstrates that the precursor can also be cured without initiators to infusible solid products in high yields (~95 wt%) upon heating to above 250 °C. Such thermal cross-linking is desirable for ceramic applications, since no contaminating chemicals have to be added to the precursors.

In the temperature range between 300 and 500 °C, evolution of NH_3 was detected by TGA–MS (Fig. 4) suggesting the occurrence of transamination reactions (Eqns [5] and [6]). This is supported by the significantly reduced number of N—H groups between 300 and 600 °C as revealed by FTIR (Fig. 2). Since the nitrogen content has not changed distinctly after cross-linking (Table 1), the degree of transamination is relatively small. However, because transamination involves cleavage of Si—N bonds, these reactions may cause the formation of oligomeric units from the cross-linked polymer network.[33,34] This may explain the relatively large weight loss (11.6 wt%) that was observed in this temperature range (300–500 °C) as detected by TGA analysis (Fig. 4).



[5]

$$3\ \mathrm{Si{-}NH{-}Si} \longrightarrow 2\ \mathrm{Si{-}}\overset{\mathrm{Si}}{\mathrm{N}}\mathrm{{-}Si} + NH_3$$



[6]

$$\mathrm{Si{-}NH{-}Si} + \mathrm{Si{-}NH_2} \longrightarrow \mathrm{Si{-}}\overset{\mathrm{Si}}{\mathrm{N}}\mathrm{{-}Si} + NH_3$$

The ceramization of the polymer occurred predominately between 600 and 800 °C, as suggested by the FTIR, Raman spectra and STA-MS. These techniques revealed a significant decrease of N—H, Si—CH_3 and Si—H bonds (FTIR and Raman) accompanied by evolution of hydrogen and methane as by-products (STA-MS). The possible reactions that are associated with the evolution of hydrogen can be expressed by Eqns [7]–[14]:

$$2N{-}H \rightarrow N{-}N + H_2 \qquad [7]$$

$$2C{-}H \rightarrow C{-}C + H_2 \qquad [8]$$

$$2Si{-}H \rightarrow Si{-}Si + H_2 \qquad [9]$$

$$N{-}H + C{-}H \rightarrow C{-}N + H_2 \qquad [10]$$

$$N{-}H + Si{-}H \rightarrow Si{-}N + H_2 \qquad [11]$$

$$C{-}H + Si{-}H \rightarrow Si{-}C + H_2 \qquad [12]$$

$$CH_2 \rightarrow C + H_2 \qquad [13]$$

$$CH{-}CH \rightarrow C{=}C + H_2 \qquad [14]$$

Owing to the higher reactivity of N—H and Si—H bonds compared with C—H bonds, reactions according to Eqns [8], [10] and [12]–[14] are less likely to occur, especially at lower temperatures. Besides, the FTIR spectra (Fig. 2) indicate that C—H and also Si—H groups are detectable up to 800 °C, in contrast to N—H bonds. Therefore, and because of the fact that solid-state ^{29}Si and ^{13}C NMR analysis gives no evidence for the formation of N—C and Si—Si bonds in the pyrolyzed products, we assume that the reaction in Eqn [11] primarily causes the hydrogen formation at around 600 °C. This is supported by considering bond polarities, since the positively charged hydrogen atoms of N—H groups tend to react with the negatively charged hydrogen atoms of Si—H groups. Moreover, the formation of Si—N bonds is favored thermodynamically compared with, for example, the generation of weak Si—Si or N—N bonds in Eqns [7] and [9].[31] However, several other reactions may also contribute to the total amount of hydrogen, but to a smaller extent. At higher temperatures the C—H bonds are certainly involved in the formation of hydrogen. More complicated rearrangement, elimination and redistribution reactions may also play a role in the pyrolysis process. For example, β-elimination reactions can cause the formation of Si—H bonds while Si—N bonds are being formed upon reaction of Si—H with N—H groups.

If it is assumed that Si—CH_3 groups (which are present in the starting polymer) are responsible for the methane formation, Eqns [15]–[17] may be taken into account for an explanation:

$$\text{Si—CH}_3 + \text{Si—H} \rightarrow \text{Si—Si} + \text{CH}_4 \qquad [15]$$

$$\text{Si—CH}_3 + \text{N—H} \rightarrow \text{Si—N} + \text{CH}_4 \qquad [16]$$

$$2\text{Si—CH}_3 \rightarrow \text{Si—CH}_2\text{—Si} + \text{CH}_4 \qquad [17]$$

For the same reasons discussed above concerning hydrogen formation, the reaction in Eqn [16] should contribute most to the methane evolution. With a reaction enthalpy of -54 kJ mol^{-1} it is thermodynamically favored over Eqn [17], which is thermoneutral (0 kJ mol^{-1}).[31]

4.2 Formation of Si–C–N and SiC ceramics

TGA and several cross-linking experiments showed that the yield of cross-linked materials depends on the corresponding cross-linking temperatures. However, the overall ceramic yield with respect to the starting PUMVS liquid is always around 70 wt%, which is independent of the initial cross-linking state. TGA showed that the low cross-linked precursor (T_{CL} = 260 °C) exhibited significant weight loss in the first two stages at around 220 and 400 °C, whereas only a small weight loss was observed for the higher cross-linked precursors (T_{CL} = 400 °C) at these temperatures. The first two steps of the TGA curve were mainly due to evaporation of low molecular weight oligomers, especially those without vinyl groups, which was proved by FTIR.

The chemical composition of the PUMVS-derived ceramics are shown in the ternary Si–C–N phase diagram in Fig. 10. It should be compared with the compositions of PHMS- and PVS- derived ceramics.[13] According to the phase equilibrium in the ternary Si–C–N, at $T < 1440$ °C Si_3N_4, SiC and carbon are thermodynamically stable, whereas at $T > 1440$ °C Si_3N_4 reacts with carbon to form SiC according to Eqn [18].

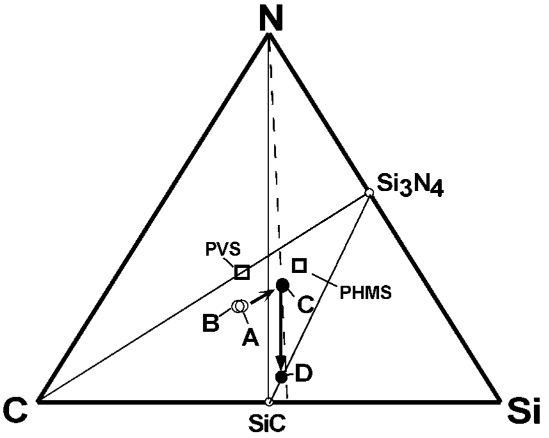


Figure 10 Ternary Si–C–N phase diagram showing the composition of polysilazane-derived materials: (A) Ceraset™ polymer as-received; (B) Ceraset™ cross-linked at 450 °C/Ar/2 h; (C) Ceraset™ polymer cross-linked and pyrolyzed at 1000 °C/Ar/2 h; (D) Ceraset™ polymer pyrolyzed and annealed at 1700 °C/N_2/2 h; PHMS-derived SiN_xC_y ceramic (NCP200, Nichimen Corp. Japan) obtained at 1050 °C/Ar/4 h,[13] PVS-derived SiN_xC_y ceramic (VT50, Hoechst AG, Germany) obtained at 1050 °C/Ar/4 h.[13].

$$\text{Si}_3\text{N}_4(\text{s}) + 3\text{C}(\text{s}) \rightarrow 3\text{SiC}(\text{s}) + 2\text{N}_2(\text{g}) \qquad [18]$$

The composition of the amorphous material obtained at 1000 °C is located on the right-hand side of the N–SiC tie-line (point C in Fig. 10), which implies that there should be no formation of excess carbon upon pyrolysis at 1876 $> T >$ 1440 °C (at $T >$ 1876 °C Si_3N_4 decomposes into liquid silicon and nitrogen). This agrees with the XRD diagrams of the crystalline ceramics formed above 1600 °C. The behavior is similar to that of PHMS. In contrast, the PVS-derived amorphous ceramic is located on the left-hand side of the N–SiC tie-line (Fig. 10), and thus free carbon is obtained together with SiC in the crystalline products.

After annealing at 1700 °C, the composition shifted from point C to point D on the Si_3N_4–SiC tie-line in Fig. 10. The carbon in the Si–C–N ceramics reacted to form SiC according to Eqn [18]. The ceramic has a chemical composition of $SiC_{0.91}N_{0.16}$, which can be expressed as $(SiC)_{0.91}$ $(Si_3N_4)_{0.03}$. This is equivalent to an SiC–Si_3N_4 composite with 90 wt% SiC and 10 wt% Si_3N_4. The SiC phase was detected by XRD analysis; the small amount of Si_3N_4 was believed to be present in an amorphous state, probably located on the grain boundaries of the SiC crystallites.

Furthermore, both phase composition and chemical analyses suggest that there is no free silicon in the crystalline ceramics. This is in contrast to previously published results, where free silicon was detected after pyrolysis at 1600 °C/Ar/8 h in an alumina furnace.[21b] It is also in contrast to most kinds of polysilazane-derived ceramics, which frequently contain excess carbon or silicon.[35,36] The presence of these elements deteriorates the mechanical properties of the products. In this respect, PUMVS (Ceraset™) is an ideal precursor to yield high quality SiC-based ceramics. This, together with its low viscosity, high ceramic yield and controlled thermal cross-linking properties, makes it useful for various application in ceramic synthesis.

5 CONCLUSIONS

Liquid PUMVS (Ceraset™) can be thermally cross-linked in the absence of any peroxide radical initiators into infusible solids upon heating to $T > 250$ °C. The cross-linking solidification occurs predominantly through hydrosilylation of vinyl groups. At higher temperatures (280–400 °C), further cross-linking took place involving transamination reactions. Major pyrolysis reactions occurred between 600 and 800 °C, forming hydrogen and methane.

Amorphous silicon carbonitride ceramics ($SiN_{0.82}C_{0.86}$) were formed at 1000 °C in argon atmosphere. The ceramic yield was around 70 wt%, which was found to be independent of the initial cross-linking temperature. The silicon atoms in the amorphous ceramics are predominately coordinated to three nitrogen atoms and one carbon atom (SiN_3C units). Formation of free carbon was evident in the products obtained between 700 and 800 °C and graphite phases were formed above 1000 °C, if high heating rates were used. At 1700 °C in nitrogen, crystalline ceramics containing 90 wt% of SiC were formed. The ceramics are free of carbon and silicon.

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