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Heterogeneously catalysed crosslinking of polycarbosilane with divinylbenzene

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Abstract Crosslinking of polycarbosilane (PCS) with divinylbenzene (DVB) is readily accomplished using heterogeneous catalysis with platinum chloride in heptane to provide a silicon carbide precursor that produces a ceramic with significantly reduced oxygen content. The ceramic yield after crosslinking increased from 47% to between 72% and 78%; however, crosslinking may be influenced by dehydrogenative silylation of hydroxyl groups. Solid-state ^{13}C NMR spectroscopy of the crosslinked PCS showed peaks assignable to the aromatic group at 144 and 126.7 ppm. Monitoring of the crosslinking reaction by ^{1}H NMR spectroscopy indicated 40% consumption of the vinyl bonds of DVB within 10 min and complete consumption within 16 h. Infrared spectroscopy showed no increase in the peak at 3,650 cm^{-1} due to O–H stretching in Si–OH, demonstrating that hydrosilylation crosslinking is a highly effective non-oxidative crosslinking technique.

Introduction

Polycarbosilanes, i.e. polymers with a backbone of alternating silicon and carbon atoms, have been investigated as preceramic polymers for silicon carbide, e.g. in the formation of silicon carbide fibres [1], membranes [2] and SiC preforms [3] as well as coatings [4, 5] and binders for particles [6]. The polymeric route is advantageous when compared to conventional techniques, because lower manufacturing temperatures are used (800–1,500 °C) [7]. However, consideration must be given to the properties of the original polymer, as these, along with the preparation and pyrolysis conditions, influence the properties of the resulting silicon carbide material [8].

Yajima et al. [9] were the first to report the conversion of a polycarbosilane, derived from the thermal decomposition of polysilane, to silicon carbide. Polydimethylsilane was used by Yajima et al. [8] instead of polysilane based on cost considerations, with the view that it was more economical to use polydimethylsilane on an industrial scale. Following the pioneering work of Yajima et al., a variety of synthesis routes were employed to create polycarbosilanes with differing structural arrangements and functional groups [10–15]. The properties of these polycarbosilanes influenced the chemical composition, ceramic yield, oxidation resistance and mechanical properties of the resulting SiC materials.

Polymer crosslinking prior to pyrolysis, conventionally by heating the polymer in air, is required to increase the ceramic yield [16] and maintain the shape of spun fibres [17]. During air crosslinking, oxidation of the Si–H and Si–CH_3 bonds occurs, resulting in Si–OH, C=O, Si–O–Si and Si–O–C bonds [1]. While the bridging oxygen atoms in the Si–O–Si and Si–O–C bonds crosslink the polymer chains, oxidative crosslinking also produces hydroxyl

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groups on the silicon atoms. The oxygen incorporated during oxidative crosslinking is maintained in the pyrolysis products, resulting in silicon oxycarbide materials. Silicon oxycarbide fibres have lower density, Young's modulus and tensile strength when compared with SiC fibres [18]. Nanoporous silicon oxycarbide membranes exhibit decreases in permeance when exposed to high temperature steam environments due to densification of surface hydroxyl groups [19].

Our interest in polycarbosilanes relates to the preparation of nanoporous SiC materials, suitable for high temperature gas separation applications in steam environments. The presence of surface hydroxyl groups in SiC materials prepared from oxidative crosslinked polycarbosilanes causes pore closure when exposed to steam environments at high temperatures (>800 °C). In view of the limitations of oxidating crosslinked polycarbosilanes for these types of applications, a crosslinking procedure that does not incorporate oxygen into the polymer structure is required.

Electron beam irradiation [20–23] and chemical vapour curing with halogenated or unsaturated hydrocarbons [24, 25] have been employed to reduce the oxygen content of silicon carbide fibres. Thermal treatment up to 400 °C in inert atmospheres prior to pyrolysis has been successful in crosslinking polycarbosilane [26]. Hydrosilylation crosslinking (a reaction between Si–H and vinyl groups) by either incorporating vinyl groups into the polycarbosilane [27, 28] or with a crosslinking agent, *p*-diethynylbenzene [29], has also been investigated.

The hydrosilylation route with a crosslinking agent is particularly interesting as it allows the insertion of a molecule between the polymer chains. Incorporation of molecules in the polymer structure may eventually allow researchers to tailor polymeric materials for specific applications by changing the crosslinking agent. In this work, we describe the heterogeneous catalytic hydrosilylation crosslinking of a commercially available polycarbosilane (PCS) with divinylbenzene (DVB). The properties of the crosslinked polymers were analysed using thermogravimetric analysis coupled with mass spectroscopy (TGA-MS), attenuated total reflectance Fourier transform infrared spectroscopy (FTIR), ^{13}C and ^{29}Si solid-state and ^{1}H and ^{13}C solution NMR spectroscopy. We also report for the first time the in situ monitoring of the crosslinking reaction using solution ^{1}H NMR spectroscopy.

Experimental

PCS (reported MW ~ 800, Sigma–Aldrich) was ground in an analytical mill and then used as received without further purification. DVB (Sigma–Aldrich) was reported as an 80% mixture of isomers (56% m-DVB, 24% p-DVB) with ethylvinylbenzene as the remaining 20% and was used as received. $PtCl_4$ (Sigma–Aldrich) was used as received.

Hydrosilylation crosslinking consisted of adding solid $PtCl_4$ (1 wt% w.r.t. PCS) and DVB (2, 6 or 10 wt% w.r.t. PCS) with stirring to a 10 wt% solution of PCS in heptane. The reaction proceeded in a jacketed flask reactor at 70 °C for 3 h under a N_2 atmosphere. $PtCl_4$ was removed by vacuum filtration and heptane removed from the filtrate by boiling to leave a solid. A control sample was also prepared by the above method, with the exception that DVB was not added.

TGA (TA SDT Q600) coupled with MS (Pfeiffer Vacuum ThermoStar) was performed on each polymer sample up to 900 °C at a heating rate of 20 °C/min under N_2 at a flow rate of 500 mL/min. Approximately 5 mg of sample was used. Samples were placed in the TGA and purged for 20 min with N_2 at room temperature prior to each run. Analysis of evolved gases by MS included scanning over the *m/z* range of 0–200 and then a multiple ion detection (MID) scan of the major peaks. Attenuated total reflectance Fourier transform infrared spectroscopy (Bruker IFS66v) was performed over the range of 4,000 to 500 cm^{-1}.

Solution ^{1}H and ^{13}C NMR spectra were obtained by dissolving samples of PCS (~50–100 mg) and PCS crosslinked with DVB in deuteriochloroform ('99.9' at.%, ~0.6 mL) and measuring on a Bruker DMX-600 NMR spectrometer operating at 600.13 MHz, fitted with a 5-mm dual probe at 298 K. Likewise measurements were also conducted using deuteriobenzene ('99.9' at.%, ~0.6 mL). Chemical shifts were referenced to the residual solvent peak, $CHCl_3 = 7.26$ ppm, and $C_6H_x = 7.25$ ppm with respect to tetramethylsilane (TMS), 0 ppm.

Solid-state ^{13}C and ^{29}Si NMR spectra were acquired using a Varian Inova-300 spectrometer operating at 75.383 and 59.574 MHz, respectively, with a Chemagnetics 4-mm double air-bearing cross-polarisation (CP) magic angle spinning (MAS) probe. Powdered samples of ~100 mg of polymer were packed into partially stabilised zirconia 4 mm o.d. rotors and spun at 5 kHz MAS. CPMAS spectra were acquired at 298 K at the following conditions:

- ^{13}C single-contact CP experiments with high-power ^{1}H decoupling during acquisition, unless otherwise stated, used the following parameters: pulse width, 4.5 μs (90°); contact time, 5 ms; recycle time, 5 s; number of scans, 10,000. In addition, a series of spectra were acquired by varying the contact time from 10 μs to 30 ms. The Hartman–Hahn match for CP was set using hexamethylbenzene, which was also used as a secondary chemical shift reference, $Ar–CH_3 = 17.3$ ppm with respect to TMS, at 0 ppm.

- ^{29}Si single-contact CP experiments with high-power ^{1}H decoupling during acquisition, unless otherwise stated used the following parameters: pulse width, 5.5 µs (90°); contact time, 2 ms; recycle time, 5 s; number of scans, 1,000. In addition, a series of spectra were acquired by varying the contact time from 10 µs to 30 ms. The Hartman–Hahn match for CP was set using kaolin, which was also used as a secondary chemical shift reference, = −91.5 ppm with respect to TMS, at 0 ppm [30, 31].

Results and discussion

Thermogravimetric analysis—mass spectrometry

Figure 1 shows the polymer weight loss as a function of temperature, indicating that the ceramic yield was increased by crosslinking PCS prior to polymer pyrolysis. The mass of the non-crosslinked PCS decreased by more than 50% when heated in nitrogen to 900 °C. However, the yield of PCS mixed with $PtCl_4$ in heptane without the addition of DVB was 73% and yields of PCS crosslinked with the addition of DVB were 78%, 73% and 72%, for samples crosslinked with 2, 6 and 10 wt% DVB, respectively. These results suggest that crosslinking between PCS molecules is catalysed in the presence of $PtCl_4$. The addition of DVB further improves the degree of crosslinking, however, the ceramic yield decreased with increasing DVB concentration, suggesting that only a small amount of crosslinking agent is required to further improve the ceramic yield.

Figure 2 shows the time derivative of weight loss as a function of temperature, clearly indicating that the thermal decomposition reaction occurred in distinct stages. The significant difference between the non-crosslinked and crosslinked samples was the weight loss between 250 and 500 °C. Non-crosslinked PCS exhibited a large weight loss in this temperature range, whilst only a small weight loss was observed for the crosslinked samples. The mass loss in this temperature range accounts for the difference in the overall ceramic yields between non-crosslinked and crosslinked samples, previously illustrated in Fig. 1.

In Fig. 3a–d the mass spectrometry signals of the gases evolved during pyrolysis are shown for the non-crosslinked sample and samples crosslinked with 2, 6 and 10 wt% DVB, respectively. We attributed the rapid loss up to 500 °C for the non-crosslinked sample (Figs. 1 and 2) to the loss of small molecular weight volatiles. This mass loss corresponded to detection peaks for dimethylsilane ($m/z = 59$) and trimethylsilane ($m/z = 73$) (Fig. 3a). This observation is consistent with those of Corriu et al. [32] and Williams et al. [33]. The weight loss observed above 600 °C corresponded to $m/z = 16$, which is most likely methane and $m/z = 2$ (hydrogen), both evolved from the condensation of side chain groups.

Signals most likely corresponding to dimethylsilane ($m/z = 59$) and trimethylsilane ($m/z = 73$) were also observed for the crosslinked samples (Fig. 3b–d). However, the lower intensity of these signals and the corresponding lower observed weight loss compared with non-crosslinked PCS suggested small molecular mass components were retained in the polymer structure through the crosslinking reaction. The weight loss above 600 °C was similarly attributed to condensation of side chain

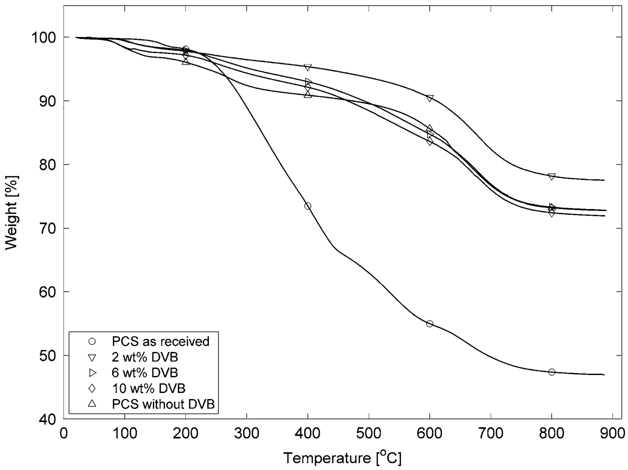

Fig. 1 Weight loss as a function of temperature for samples of crosslinked and non-crosslinked polycarbosilane. A heating rate of 20 °C/min and sample mass of 5 ± 0.1 mg were used. The legend indicates the concentration of DVB used for crosslinking

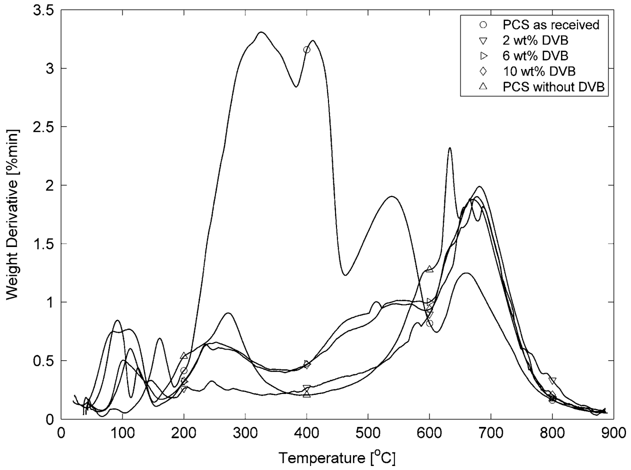

Fig. 2 Weight loss derivatives as a function of temperature for samples of crosslinked and non-crosslinked polycarbosilane. A heating rate of 20 °C/min and sample mass of 5 ± 0.1 mg were used. The legend indicates the concentration of DVB used for crosslinking

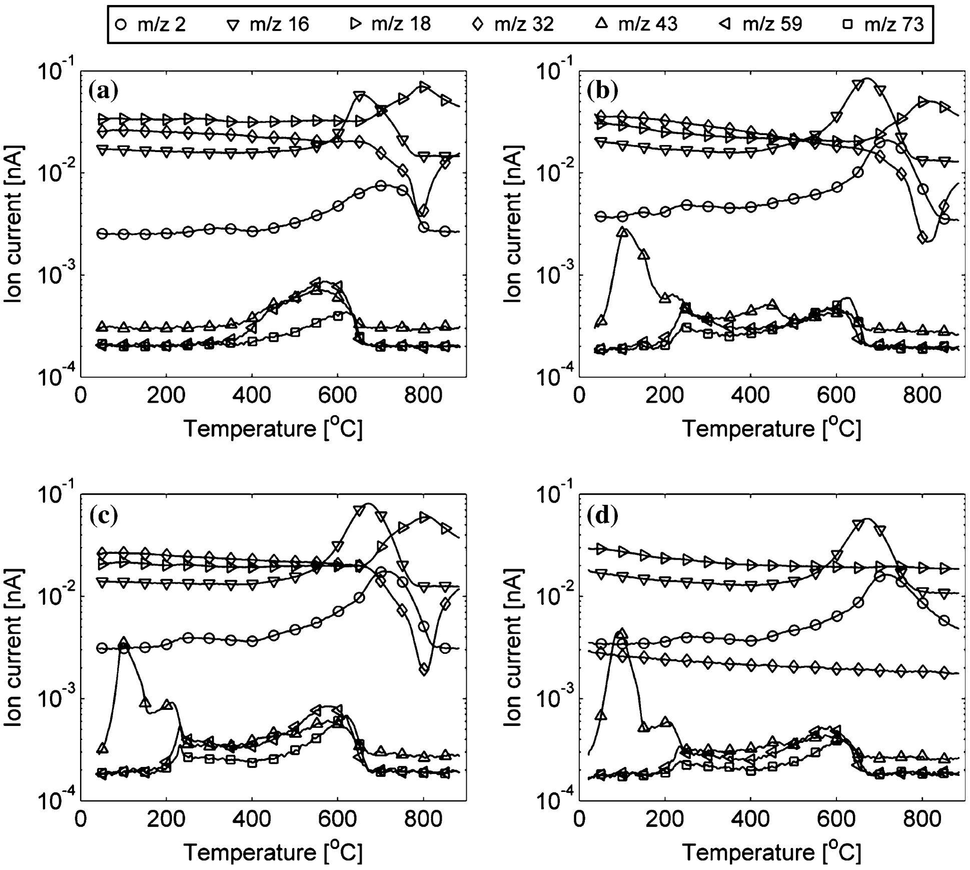

Fig. 3 MS profiles for the evolved gases as a function of temperature for (**a**) non-crosslinked PCS (**b**) PCS crosslinked with 2 wt% DVB (**c**) PCS crosslinked with 6 wt% DVB and (**d**) PCS crosslinked with 10 wt% DVB

groups and the evolution of hydrogen ($m/z = 2$) and methane ($m/z = 16$). The initial mass losses for the crosslinked PCS samples were attributed to residual heptane ($m/z = 43$) from the crosslinking stage. $m/z = 43$ also corresponds to fragments of dimethylsilane and trimethylsilane, and thus the signal for $m/z = 43$ is similar to $m/z = 59$ and 73 in the temperature range 200–600 °C.

The MS signal corresponding to $m/z = 32$ (attributed to oxygen) decreased at $\sim$650 °C for non-crosslinked PCS and PCS crosslinked with 2 and 6 wt% DVB, reaching a minimum at $\sim$800 °C. This decrease, suggesting a consumption of oxygen, corresponded with hydrogen evolution and an increase in the MS signal for $m/z = 18$ (attributed to H_2O). Despite the TGA-MS analysis being performed under N_2, the results suggest the combustion of hydrogen by trace oxygen in the nitrogen gas, resulting in the observed increase in $m/z = 18$ and decrease in $m/z = 32$. This phenomenon was not observed for PCS crosslinked with 10 wt% DVB, although this sample was analysed under identical conditions.

Fourier transform infrared spectroscopy

The FTIR spectra of the crosslinked (2, 6 and 10 wt% DVB) and non-crosslinked PCS samples are shown in Fig. 4. The peaks observed in these spectra were assigned according to the literature [8, 33–35]. The major peaks significant to PCS were observed at 2,100 cm^{-1} due to Si–H stretching and at 1,250 cm^{-1} due to Si–CH$_3$. The broad band centred at 800 cm^{-1} could be due to overlap of Si–H, Si–C and phenyl C–H bonds. Other major bonds indicated were Si–CH$_2$–Si (1,100–1,000 cm^{-1}), C–H, C–H$_2$, C–H$_3$ (1,450–1,350 cm^{-1}) and C–H stretching in Si–CH$_3$ (2,900, 2,950 cm^{-1}). A small peak at 3,650 cm^{-1} may be due to

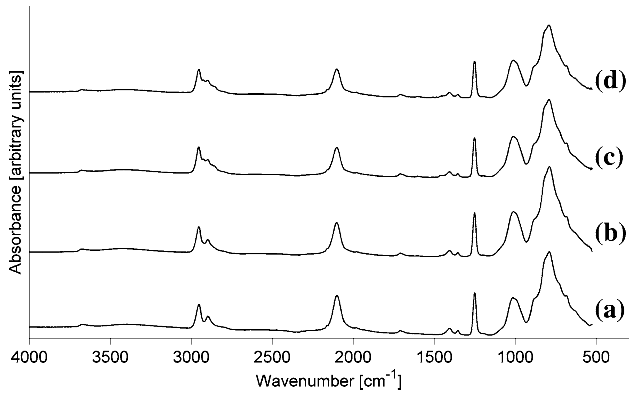

Fig. 4 FTIR spectra of (**a**) non-crosslinked PCS (**b**) PCS crosslinked with 2 wt% DVB (**c**) PCS crosslinked with 6 wt% DVB and (**d**) PCS crosslinked with 10 wt% DVB. The spectra have been displaced for clarity

O–H stretching in Si–OH. Si–O stretching in Si–O–Si and Si–O–C may also contribute to the peak observed at 1,100–1,000 cm^{-1}.

The samples crosslinked with 2, 6 and 10 wt% DVB produced similar FTIR spectra to the non-crosslinked sample. No additional peaks were observed; however, the intensities of the peaks at 2,100 cm^{-1}, related to Si–H bonding, were lower. The ratios of intensity of the peak at 1,250 cm^{-1} ($Si{-}CH_3$) to 2,100 cm^{-1} were 0.78, 0.77 and 0.80 for samples crosslinked with 2, 6 and 10 wt% DVB, respectively, compared with a ratio of 0.94 for the non-crosslinked sample. The $Si{-}CH_3$ bond should not be involved in the crosslinking reaction; hence, a reduction in the $Si{-}CH_3$/Si–H ratio indicates consumption of the Si–H bond. Additionally, the peak corresponding to Si–OH did not increase in intensity during crosslinking, suggesting that hydrosilylation crosslinking does not introduce oxygen into the polymer structure.

Silanol groups (Si–OH), in the presence of $PtCl_4$, may have undergone dehydrogenative silylation (Eq. 1) [37], resulting in the observed increase in ceramic yield for the control sample. This reaction masks the effect of hydrosilylation crosslinking and possibly limiting the number of sites available for hydrosilylation crosslinking. The consumption of the Si–H bond indicated by a change in intensities corresponds to either hydrosilylation crosslinking between the vinyl group of DVB and Si–H or dehydrogenative silylation.

$$\mathrm{Si{-}OH + Si{-}H \xrightarrow{Pt} Si{-}O{-}Si + H_2} \qquad (1)$$

The degree of competition between the two crosslinking mechanisms (i.e. dehydrogenative silylation or hydrosilylation crosslinking with DVB) is unclear, however, crosslinking with 2 wt% DVB resulted in a higher ceramic yield than the sample without DVB addition. Regardless of the mechanism, silicon carbide membranes formed from the crosslinked polymers in this work are likely to be unstable in steam environments due to the retention of hydroxyl groups from the as-received PCS.

Nuclear magnetic resonance spectroscopy

The ^{1}H and ^{13}C solution NMR spectra of the PCS and PCS crosslinked with 10 wt% DVB were acquired, in search of evidence of aromatic residues that would imply hydrosilylation crosslinking of PCS with DVB (Fig. 5).

The ^{1}H spectrum of PCS (Fig. 5a) showed the expected broad peaks for the $-Si{-}CH_2-$ (0.38 ppm) and for the –Si–H (4.51 ppm). The ^{1}H spectrum of the crosslinked PCS (Fig. 5b) revealed considerably more peaks, indicative of polymer, in that they were broad and spread over the chemical shift range from 0.4 to 8.5 ppm. Importantly, there was an increase in intensity in the aromatic region of this ^{1}H spectrum of the crosslinked PCS, centred at 7.2 ppm, suggesting the presence of the aromatic groups of the crosslinking agent. The ^{13}C solution spectrum (Fig. 5c and d) was not as revealing, because only small amounts of actual crosslinker were incorporated and the relative insensitivity of ^{13}C experiment did not give discernable peaks.

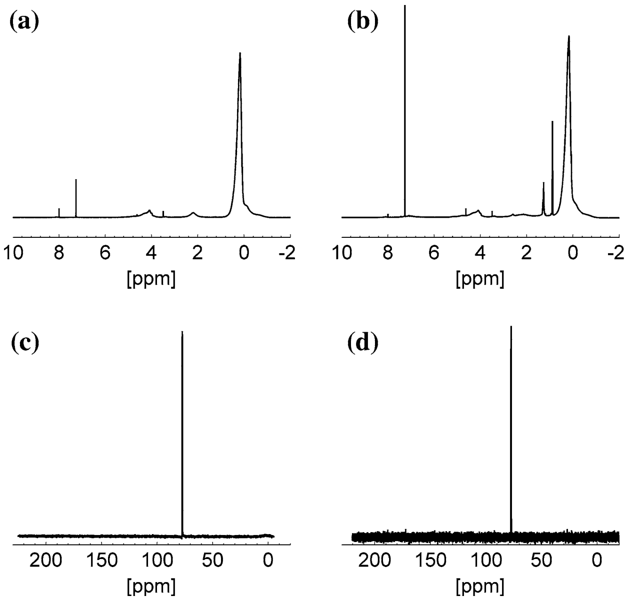

Fig. 5 Solution NMR spectra in $CDCl_3$ of (**a**) 600 MHz, ^{1}H, non-crosslinked PCS (**b**) ^{1}H, PCS crosslinked with 10 wt% DVB (**c**) 150 MHz ^{13}C, non-crosslinked PCS and (**d**) ^{13}C, PCS crosslinked with 10 wt% DVB. The *x*-axis represents the chemical shift from TMS

The solid-state ^{13}C NMR spectrum of the crosslinked PCS (Fig. 6b) did, however, show peaks assignable to the aromatic group at 144 and 126.7 ppm, together with the backbone $Si{-}CH_2-$ at 1.1 ppm. Note also that in the solid-state ^{29}Si NMR spectra of the non-crosslinked PCS and the crosslinked PCS (Fig. 7) there is little difference discernible. Peaks corresponding to SiC_4 (0 ppm) and SiC_3H (-18 ppm) were observed for both crosslinked and non-crosslinked PCS. Furthermore, both spectra showed the presence of oxygen bonded to silica (Si–O–Si) at ~8.5 ppm [35, 36] establishing that oxygen is already present in the non-crosslinked polymer and not introduced by hydrosilylation crosslinking.

It was also possible to study the crosslinking reaction directly in the NMR spectrometer, using deuteriobenzene solutions of the reactants at 60 °C, and monitoring with ^{1}H NMR spectroscopy (Fig. 8). After 3 h at this temperature, there were no visible changes in the ^{1}H spectrum of a mixture of PCS with DVB (10:1), suggesting that the platinum catalyst is required for the crosslinking reaction to

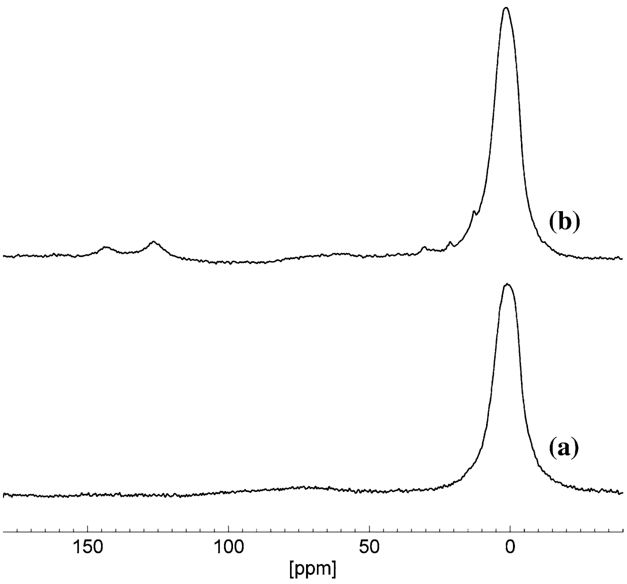

Fig. 6 Solid-state ^{13}C CPMAS NMR spectra obtained at 5 kHz of (**a**) non-crosslinked PCS, and (**b**) PCS crosslinked with 10 wt% DVB. Spectra have been displaced for clarity. The *x*-axis represents the chemical shift from TMS

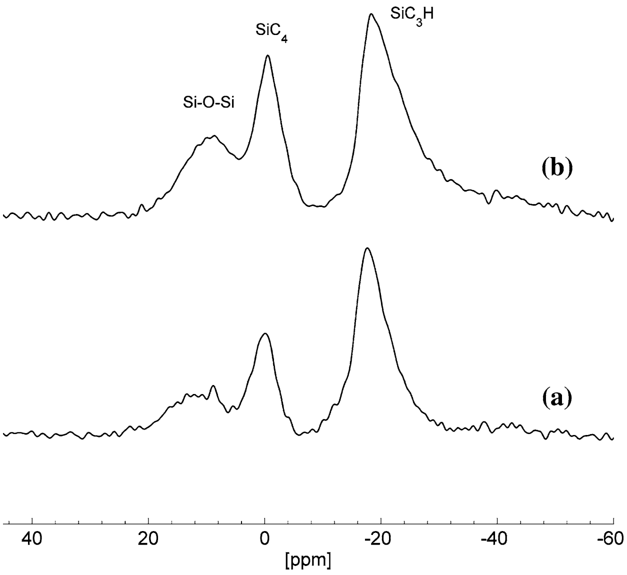

Fig. 7 Solid-state ^{29}Si CPMAS NMR spectra obtained at 5 kHz of (**a**) non-crosslinked PCS and (**b**) PCS crosslinked with 10 wt% DVB. Spectra have been displaced for clarity. The *x*-axis represents the chemical shift

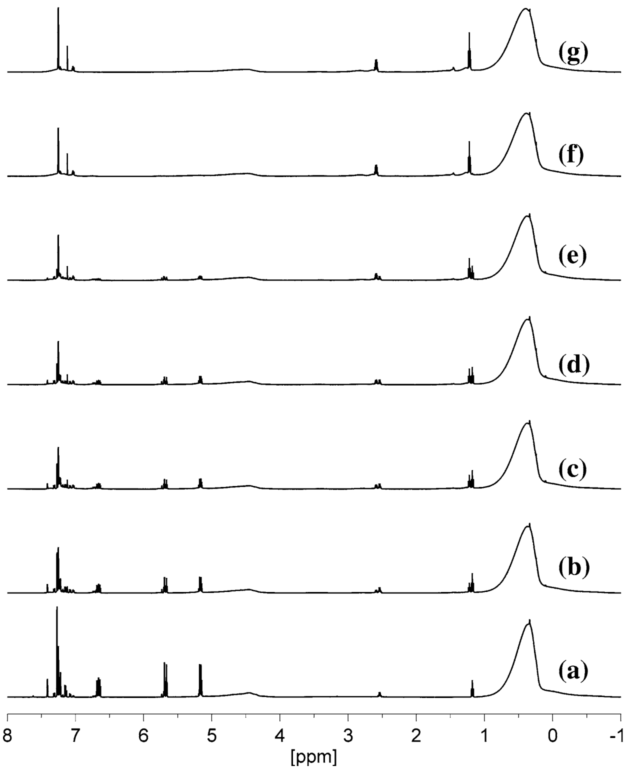

Fig. 8 600-MHz solution ^1H NMR spectra of the reaction of PCS and DVB catalysed by platinum chloride, obtained at 60 °C in deuteriobenzene. (**a**) PCS and DVB prior to catalyst addition (**b**) 8 min after adding catalyst (**c**) after 16 min (**d**) after 32 min (**e**) after 96 min (**f**) after 408 min (**g**) after 16 h. The *x*-axis represents the chemical shift with respect to C_6H_x at 7.25 ppm

take place. This was confirmed when a few crystals of platinum chloride were added, and there ensued an immediate and vigorous reaction with evolution of gas and colour change from colourless to dark brown. The first spectrum that could be acquired after 8 min of the reaction settling, showed that about 40% of the DVB had been consumed as discerned from the disappearance of the peaks from the vinyl groups of DVB at 5.2, 5.7, 6.7 ppm. As the reaction progressed, these intense and well-defined peaks decreased, and after 16 h, all the DVB had been consumed, leaving broad peaks due to crosslinked polymer centred at 7.2, 4.4 and 0.5 ppm.

Also observed during this monitoring were the side reactions of ethyl vinyl benzene (EVB) which is present to 20% w/w in the commercially available DVB. The ethyl groups arising from EVB are sharp peaks in the ^1H spectrum located at 1.18 and 2.54 ppm (Fig. 8a). During the course of the reaction, they were slowly replaced by another set of well-defined ethyl groups at 1.23 and 2.59 ppm, and sharp aromatic peaks at 7.03, 7.15, 7.22 ppm (Fig. 8b–e). This indicates that consumption of the vinyl group of EVB occurs either through hydrogenation or through reaction with the PCS via hydrosilylation so that the polymer is functionalised with the aromatic group but not crosslinked (Fig. 9). Functionalisation of the PCS like this may also occur when only one of the vinyl groups of DVB attaches itself to the PCS, while the other vinyl group is reduced to an ethyl group.

However, evidence from MS studies has shown that neither DVB nor diethylbenzene was observed during TGA-MS, suggesting that at least one vinyl group of DVB

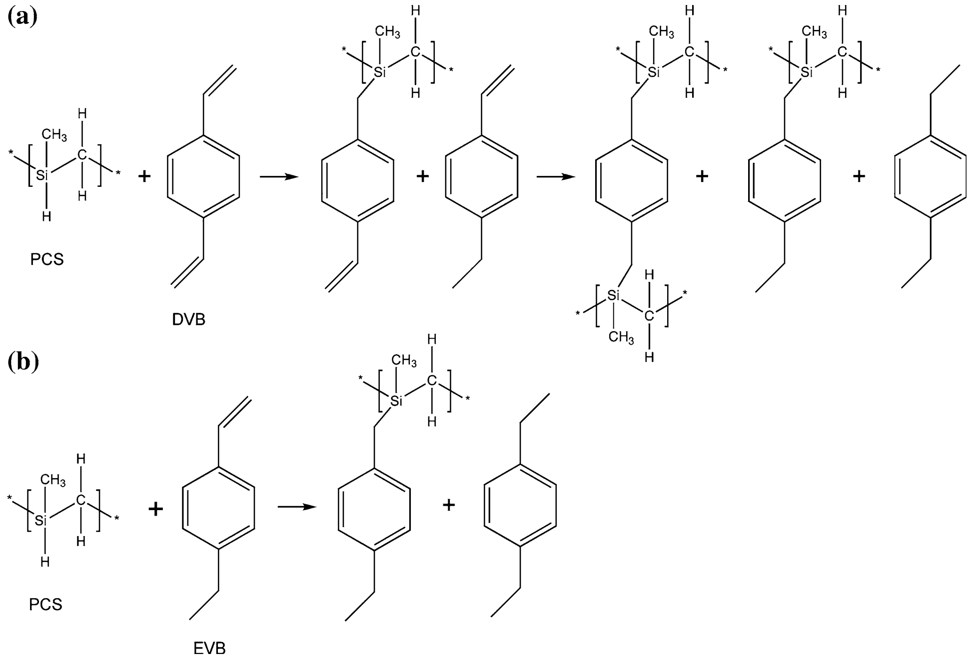

Fig. 9 Hydrosilylation crosslinking of PCS with (**a**) DVB; (**b**) EVB

undergoes rapid hydrosilylation of PCS. TGA-MS also showed PCS crosslinked with 2 wt% DVB resulted in a higher ceramic yield than 10 wt% DVB. A higher concentration of DVB may cause steric hindrance during crosslinking, restricting the number of sites on the polymer available for hydrosilylation crosslinking and therefore also resulting in bonding at one vinyl group of DVB only. Dehydrogenative silylation of silanol groups may also reduce the number of sites available for crosslinking. This would account for the lower ceramic yield for 10 wt% DVB, the presence of ethyl groups during crosslinking and the absence of MS signals associated with DVB. Further NMR analysis of the reaction with lower DVB concentrations and oxygen-free PCS is clearly required to confirm these assertions.

The indicative structures of the ceramic residues during pyrolysis are shown in Figs. 10 and 11 for non-crosslinked and crosslinked PCS, respectively. During the pyrolysis of non-crosslinked PCS, a three-dimensional silicon carbide network forms by the condensation of methyl and hydrogen groups, resulting in Si–C linkages between the polymer chains. FTIR and NMR indicated the presence of oxygen in

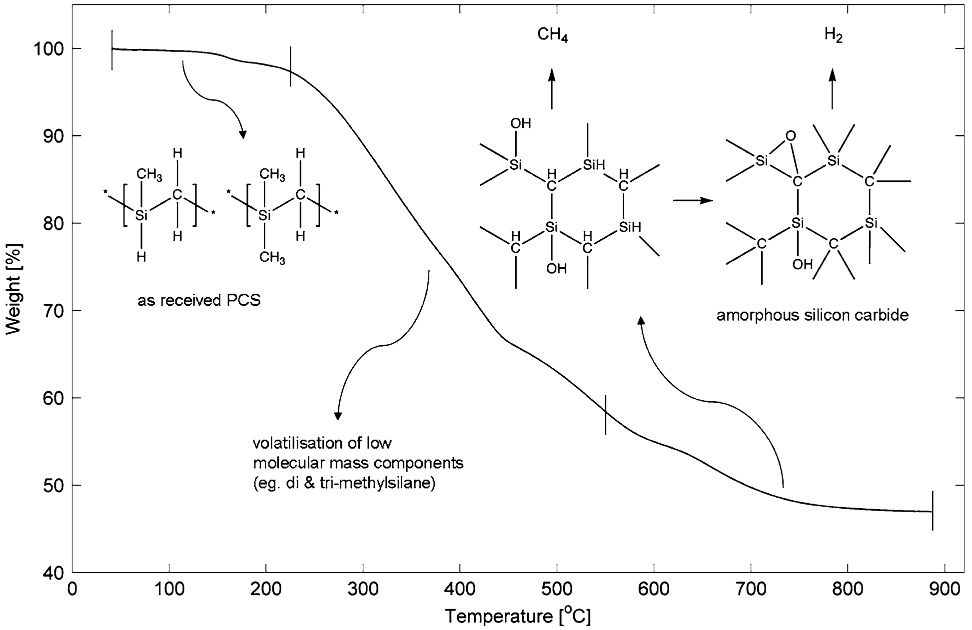

Fig. 10 Weight loss as a function of temperature and indicative structure of as-received PCS and non-crosslinked ceramic residue during pyrolysis [38]

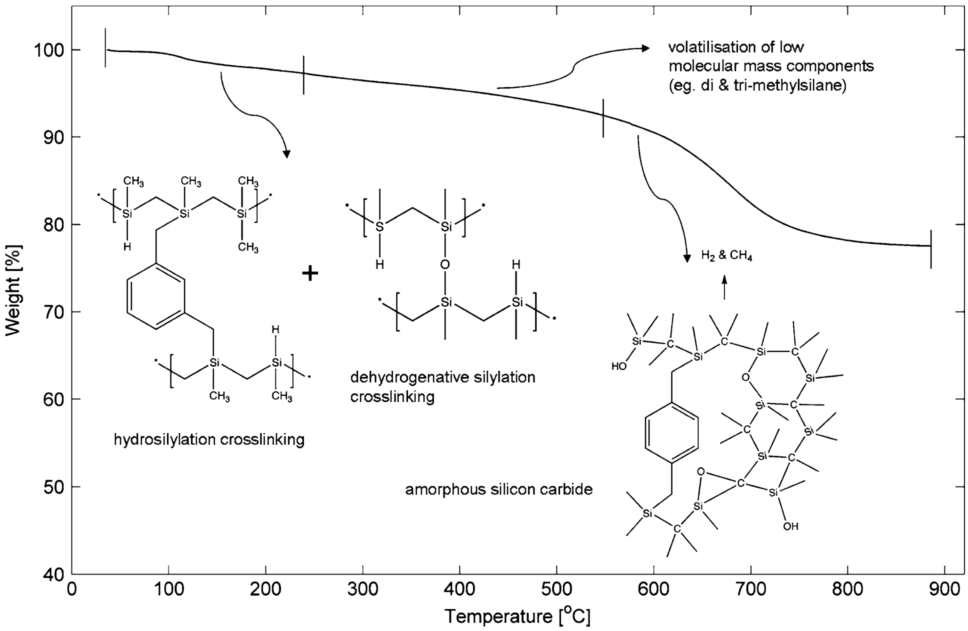

Fig. 11 Weight loss as a function of temperature and indicative structure of crosslinked PCS and ceramic residue during pyrolysis [38, 39]

the as-received PCS, resulting in hydroxyl groups and bridging oxygen bonds in the pyrolysed polymer. The influence of hydroxyl groups is more pronounced during crosslinking in the presence of platinum chloride. With the addition of DVB during crosslinking, bonding between polymer chains is due to either hydrosilylation crosslinking with DVB or dehydrogenative crosslinking due to hydroxyl groups. The ceramic residue resulting from the pyrolysis of crosslinked PCS may therefore contain both DVB and oxygen linkages between polymer chains.

Conclusions

Hydrosilylation crosslinking of PCS with DVB in the presence of a heterogeneous platinum catalyst was successfully demonstrated. NMR spectroscopy indicated immediate reaction between PCS and DVB upon the addition of the catalyst. Consumption of the vinyl groups of DVB was observed after 10 min, while complete consumption was achieved after 16 h. The ceramic yield of PCS was increased when crosslinked, with DVB prior to pyrolysis, with ceramic yield decreasing slightly with increasing DVB concentration from 78% to 72%. An increase in hydroxyl groups was not observed during polymer crosslinking, but hydroxyl groups may have undergone dehydrogenative silylation contributing to crosslinking and the increased ceramic yields. This technique may allow for the formation of silicon carbide materials capable of performing in high temperature steam environments; however, further experiments with oxygen-free PCS are required.

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