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Conversion of polycarbosilane (PCS) to SiC-based ceramic
Part 1. *Characterisation of PCS and curing products*

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A commercial polycarbosilane (PCS) preceramic polymer has been characterised as-received and following curing under a variety of conditions. Elemental analysis, gel permeation chromatography (GPC), infra-red spectroscopy (FT-IR), simultaneous thermogravimetric analysis-differential thermal analysis (TG-DTA) and solid state nuclear magnetic resonance (NMR) have been employed. A number average molar mass of 1200 was found with a broad molar mass distribution ($\bar{M}_w/\bar{M}_n = 2.97$). Elemental analysis gave an empirical formula of $SiC_{2.2}H_{5.3}O_{0.3}$. IR and Solid state ^{29}Si and ^{13}C NMR spectra showed the presence of Si-O-Si, SiC_4, SiC_3H, Si-Si, Si-CH_3 and Si-CH_2 groups. Simultaneous TG-DTA performed under an argon flow showed that there was a weight gain which started at approximately 240 °C. DTA showed an exotherm starting at this temperature showing that there was oxidation of the polymer even in an inert atmosphere. This is perhaps due to the oxygen in the PCS and there may also be some impurities in the inert atmosphere. Evidently the PCS is very sensitive to oxygen. Above 500 °C, weight loss dominated although the exotherm continued to approximately 700 °C. The effect of heating rate and dwell time at 200 °C on the changes in the chemical composition during curing have been explored using IR and solid state NMR spectroscopies, and elemental analysis. The longer the cure time the higher was the weight gain and greater was the extent of the oxidation reactions. Elemental analysis showed that the ratio of H and C to Si decreased with holding time at the cure-temperature while the amount of oxygen increased. Use of a higher heating rate resulted in a lower weight gain when the same holding time was used. From this it is clear that curing starts below the holding temperature.

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1. Introduction

The recognition that a variety of polymers can be made consisting of one or more hetero atoms such as Si, N and B in addition to carbon atoms has led to possibilities of making a variety of ceramic materials in direct analogy with polymer pyrolysis for making carbon [1, 2]. The work of Yajima and coworkers in the mid 1970s [3–8] has established polycarbosilanes as the most widely studied precursors [3]. Polycarbosilane is the general term for organosilicon polymers containing a -Si-C- backbone [9]. Synthesis of a variety of polycarbosilanes have been reported by Yajima *et al.* [10, 11]. Fabrication into complex shapes in various forms such as fibres, coatings and bulk bodies is possible because the solubility or fusibility of the precursor polymer allows the shaping to be carried out at moderate temperatures and by conventional polymer processing techniques [12–14]. Once formed, however, the precursor article normally needs to be cured (cross-linked) prior to high temperature pyrolysis, to render the article infusible and so retain its form, and also subsequently obtain a higher yield of ceramic. This requires the precursor article to possess reactive sites such as unsaturated organic groups, e.g., vinyl group ($CH_2 = CH-$), or reactive bonds such as Si-H [15]. Cross-linking involving bond cleavage, generating free radicals and interchain coupling [16] can be induced by heating in air (oxidation) [17] or by oxygen-free methods such as electron beam [18] or UV [19] irradiation in inert atmosphere. Oxidation curing, being easily accessible, usually involves heating the polymer in air up to about 200 °C [9]. Studies of the curing mechanism of PCS fibres in air indicate that curing is achieved by cross-linking of the PCS structure with oxygen [20–22]. The curing results in the formation of Si-O-Si and Si-O-C bonds by the oxidation of Si-H and Si-CH_3 bonds in the PCS [21].

This paper describes the characterisation by a combination of techniques of a commercial PCS produced by Nippon Carbon. Also presented is the characterisation of the cured PCS products obtained under different oxidation curing conditions. The effects of oxidation conditions on the pyrolysis of cured PCS will be presented in Part II [23].

2. Experimental

2.1. Characterisation of PCS polymer precursor

The polymer precursor used in this study was a polycarbosilane (PCS, Grade A) in the form of powder, manufactured by Nippon Carbon and purchased from Mitsui & Co UK PLC (Plastics Department, London).

2.1.1. Elemental analysis

The polymer was analysed for silicon, carbon and hydrogen. C and H content were determined by a thermal combustion method. About 1 mg of PCS was placed in a container and heated under oxygen in a combustion tube to 1800 °C. The amounts of carbon and hydrogen were measured as CO_2 and H_2O respectively by gas chromatography. For Si determination, about 10 mg of sample was fused in a mixture of KOH and KNO_3 in a nickel crucible at 650 °C to release Si as a silicate which was then detected by atomic absorption.

2.1.2. Gel permeation chromatography (GPC)

A PLGel column in association with a Waters 410 differential refractometer detector and a Waters M45 pump was used at room temperature with tetrahydrofuran as solvent. The PCS solution concentration was 0.2% and the flow rate was 1 cm^3 min^{-1}. Polystyrene standards were used for calibration.

2.1.3. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra were obtained over the range of 4000 to 400 cm^{-1} using a Perkin Elmer System 2000 spectrometer. KBr discs were used, prepared by compressing a finely ground mixture of about 5 mg of the sample and 300 mg of KBr powder.

2.1.4. Solid state ^{29}Si and ^{13}C nuclear magnetic resonance (NMR) spectroscopy

^{29}Si and ^{13}C NMR spectroscopy were obtained using a Varian Associates Unity 300 spectrometer, operating at 59.7 MHz for ^{29}Si and 75.5 MHz for ^{13}C. Powdered PCS of about 0.5 g was packed into a zirconia sample holder. The magic angle spinning (MAS) technique was applied to reduce the line broadening due to the range of molecular orientations in the magnetic field. The spinning frequency was about 4 kHz. For the samples investigated, where the carbon or silicon nuclei are bonded with or in close proximity to, hydrogen, the cross polarization (CP) technique was applied. This involves transfer of magnetization from protons to ^{29}Si or ^{13}C nuclei, so that better signal to noise ratios can be obtained. A contact time of 2 ms and a recycle time of 4 s were used. The chemical shift reference was tetramethylsilane (TMS) for both ^{13}C and ^{29}Si.

TABLE I Cure conditions. Samples were heated from and cooled to room temperature

Sample	Heating rate (°C h^{-1})	Cure temperature (°C)	Cure time (h)
C1	10	200	0.5
C2	10	200	1
C3	10	200	1.5
C4	30	200	1

2.1.5. Thermogravimetry—differential thermal analysis (TG-DTA)

Thermal decomposition of the PCS up to 1200 °C in argon was investigated by simultaneous thermal gravimetric analysis (TG) and differential thermal analysis (DTA) carried out with a high temperature Seiko TG/DTA 220 Thermal System at a heating rate of 100 °C h^{-1}. Approximately 10 mg of sample was placed in an open alumina pan with an empty pan as the reference. An argon flow 20 cm^3 min^{-1} was used prior to and during pyrolysis.

2.2. Cure of PCS

Oxidative cross-linking (cure) of the PCS was carried out to render the polymer precursor infusible prior to pyrolysis by heating in air. Approximately 2 g of PCS powder was placed in an alumina crucible and heated in air according to one of the schedules given in Table I, with the furnace tube ends partially open. The cured samples were analysed by elemental analysis, FT-IR, and solid state NMR as described above for the characterisation of the as-received PCS.

3. Results and discussion

3.1. Characterization of PCS precursor polymer

3.1.1. Elemental analysis

From elemental analysis, the chemical composition of the PCS precursor was Si, 43.7 wt%; C, 40 wt%; H, 8.3 wt%; and O, 7.2 wt% (by difference), giving the empirical formula $SiC_{2.2}H_{5.3}O_{0.3}$. This differs somewhat from the manufacturer's suggested composition of $SiC_{1.93}H_{4.71}O_{0.01}$ [24]. Absorption of oxygen or moisture could lead to the higher than expected oxygen content; the sensitivity of this type of PCS to oxygen and moisture has been reported [25]. Narisawa *et al.* [26] found that oxygen can be introduced into the PCS structure during its synthesis. Variations in the synthesis conditions such as the polymerization temperature will also affect the composition with a general decrease in the amount of carbon and hydrogen as the degree of polymerization of the PCS increases [9]. The results

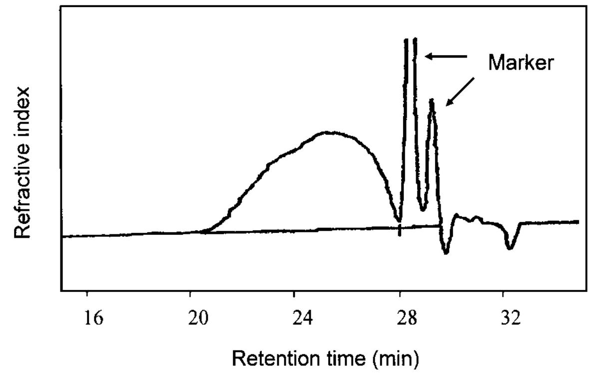

Figure 1 GPC trace of PCS.

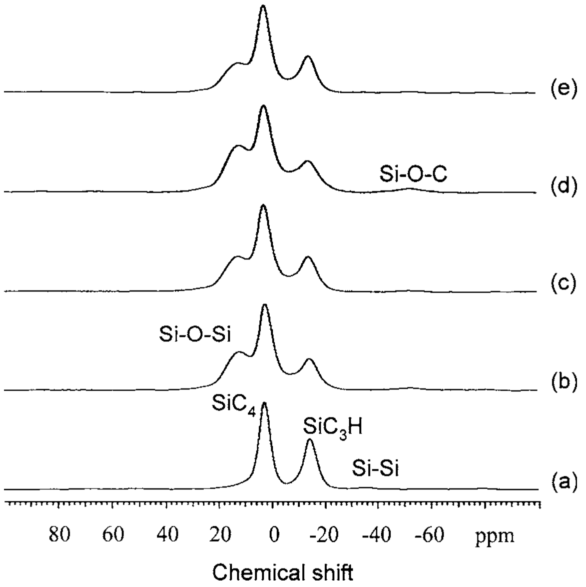

Figure 2 ^{29}Si CP/MAS NMR spectra of PCS samples. (a) as-received PCS; (b) cure C1; (c) cure C2; (d) cure C3; (e) cure C4.

show that the atomic ratio of the carbon to silicon in the PCS precursor is about 2 : 1.

3.1.2. Gel permeation chromatography (GPC)

The molar mass distribution of the PCS measured by GPC is shown in Fig. 1. $\bar{M}_n$ was found to be 1200, which is within the range 1000–2500 specified by the supplier. The polydispersity index, $\bar{M}_w/\bar{M}_n$ (weight average to number average molar mass), was found to be 2.97, indicating a broad molar mass distribution.

3.1.3. Solid state ^{29}Si and ^{13}C NMR spectroscopy

The ^{29}Si and ^{13}C NMR spectra of the PCS obtained by the cross-polarization/magic angle spinning technique are shown in Figs 2a and 3a, respectively. Variable contact time experiments (not illustrated) showed that the peak relative intensities were essentially independent of contact time, the various ^{29}Si peaks possessing essentially the same cross-polarisation time constants. The assignments given were based on spectra of known organic compounds and earlier work on PCS [27, 28]. In the ^{29}Si spectrum, the signal at the chemical shift of around +0.4 ppm was assigned to the resonance of silicon bonded to four carbons (SiC_4). The signal at −14 ppm was assigned to silicon bonded to one hydrogen and three carbons (SiC_3H). From peak integrals, the ratio of SiC_4 to SiC_3H units was found to be about 1.5 : 1. Small numbers of Si-Si bonds appeared to be present in the PCS as indicated by the low intensity signal at −36 ppm. The SiC_4 peak showed a weak high frequency “tail”, suggesting the presence of a small proportion of Si-O-Si units. This peak developed markedly during cure (see below). Signals at +68 ppm and −62 ppm were due to spinning side bands of the SiC_4 peak. Signals at +50 ppm and −80 ppm are spinning side bands of the SiC_3H peak. Very weak spinning side bands resulting from chemical shielding anisotropy were observed at −80, −62, +50 and +68 ppm.

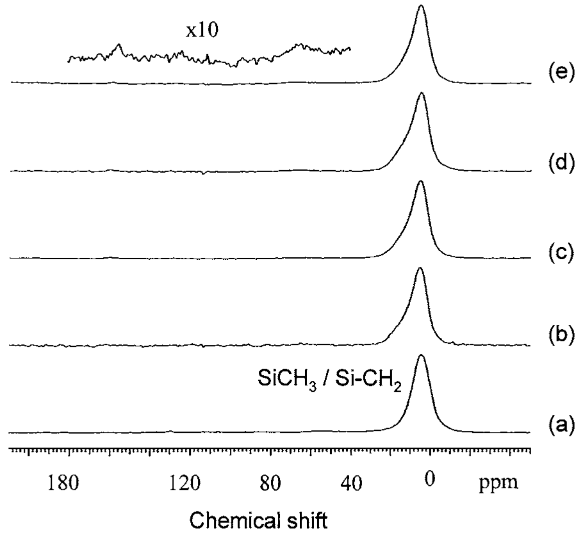

Figure 3 ^{13}C CP/MAS NMR spectra of PCS samples. (a) as-received PCS; (b) cure C1; (c) cure C2; (d) cure C3; (e) cure C4.

In the ^{13}C spectrum (Fig. 3a), the main peak at +5 ppm indicated carbon atoms bonded to silicon. This peak was probably due to superimposed $Si-CH_3$ and $Si-CH_2$ groups because the chemical shift difference between these two carbon environments is very small. The signal at +55 ppm was a spinning side band. A very unsaturated carbon peak was observed at +118 ppm, possibly attributable to some additive used in the production of PCS. This peak disappeared on curing.

Both the ^{29}Si and ^{13}C CP/MAS spectra of this as-received PCS appeared similar to the published spectra of the PC-470 type PCS [21].

3.1.4. FT-IR spectroscopy

The wave numbers corresponding to the various absorption bands in the FT-IR spectra of the as-received PCS (Fig. 4a) are given in Table II. These assignments were based on data for known organic compounds and PCS [22, 27–30]. FT-IR indicates that the major bonds present were $Si-CH_3$ ($1250\,cm^{-1}$) and Si-H ($2100\,cm^{-1}$). The broad band at around $1000\,cm^{-1}$ was due to the overlap of the bands due to CH_2 groups in $Si-CH_2-Si$ units and a band due to Si-O bonds. The small band at around $3700\,cm^{-1}$ could have been due to O-H stretching of Si-OH [30]. Phenyl C-H ($850\,cm^{-1}$), Si-C ($820\,cm^{-1}$) and Si-H ($880\,cm^{-1}$) bonds could have

TABLE II Wavenumbers and assignments of the IR spectrum of PCS

Wavenumber (cm^{-1})	Mode of vibration
850 - 700	Si-CH_3 bending Si-C stretching in SiC_4
950 - 800	Si-H bending
1020	CH_2 bending in Si-CH_2-Si
1100 - 1000	Si-O stretching in Si-O-Si or Si-O-C
1200	C-O stretching
1250	Si-CH_3 stretching
1450 - 1350	H stretching in CH, CH_2, & CH_3
1720	C=O stretching
2100	Si-H stretching
2950 - 2900	C-H stretching
3700 - 3200	O-H stretching in Si-OH

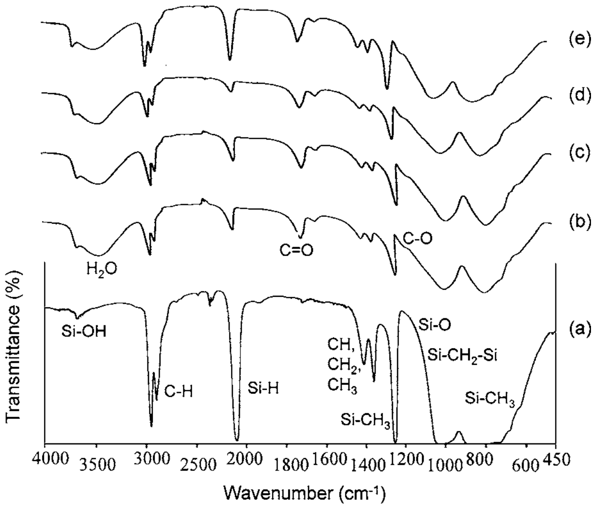

Figure 4 FT-IR spectra of PCS samples. (a) as-received PCS; (b) cure C1; (c) cure C2; (d) cure C3; (e) cure C4. The spectra have been displaced vertically to aid clarity.

contributed to the broad band around 800 cm^{-1}. Again the general features in the spectrum of this as-received PCS appear similar to the published spectrum of the PC-470 type PCS [27].

3.1.5. TG-DTA

The TG/DTA traces of the as-received PCS in argon flow are shown in Fig. 5. The weight loss between 100 °C and 240 °C associated with an exotherm in the DTA trace was likely to be due to loss of low molar mass oligomers and water. At about 240 °C, the start of an increase in weight corresponded to an exotherm in the DTA trace. This seemed to indicate an oxidation cross-linking reaction rather than melting associated with an endotherm. However, partial melting or softening in the range 230 °C to 300 °C [22] could have been hidden under this exothermic peak. The oxidation behaviour under argon atmosphere indicates the high sensitivity of this PCS to oxygen. The oxygen could originate from the as-received PCS as indicated by elemental analysis results, and may also be due to oxygen and/or water impurities in the heating atmosphere. As the temperature increased up to ~500 °C, any loss of low molar mass organic molecules was more than compensated for by the gain in weight due to oxidation as indicated by the continued weight gain in the TGA trace. Above 500 °C, an endothermic reaction occurs accompanied by a decrease in weight. This should be due to decomposition of organic side groups [31, 32] leading to the inorganic state by ~900 °C at which point no significant weight loss occurred with further heating. The rise of the DTA trace above 1000 °C may have been due to crystallization of the amorphous residue as observed by Hasegawa and Okamura [33]. At 1200 °C, the residual yield was ~96 wt.%. Such a high yield reflected a highly cross-linked structure of the PCS precursor, containing a large amount of oxygen.

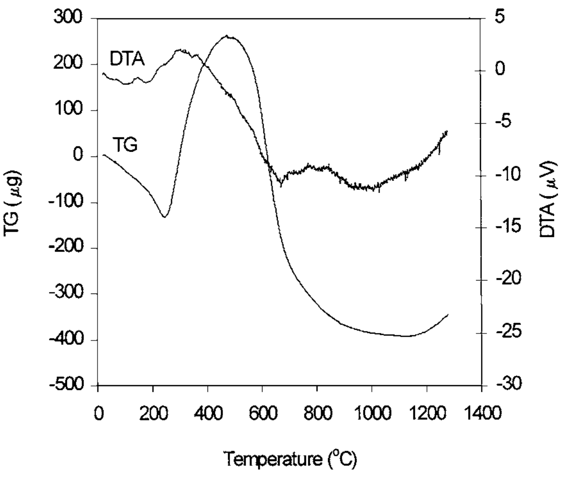

Figure 5 TG-DTA traces of as-received PCS at a heating rate of 1.7 °C min^{-1} in argon.

3.2. Oxidation curing of PCS

3.2.1. Elemental analysis

The effects of heating rate up to, and curing time at, 200 °C on the weight gain and the changes in chemical composition compared to the as-received PCS are shown in Table II. As expected, the weight increase due to the gain of oxygen in the curing process increased with curing time but was reduced with a faster heating rate. Table III shows that while the amount of oxygen increased with an increase in the duration of curing, there is a general decrease in the hydrogen and carbon content compared to silicon.

3.2.2. FT-IR spectroscopy

Fig. 4 compares the FT-IR spectra of the cured PCS samples with the spectrum of the as-received material. The bands were assigned with reference to literature on known organic compounds and PCS [22, 27, 29, 30, 34]. In general, the absorption peaks due to Si-H (2100, 900 cm^{-1}), C-H of $SiCH_3$ (2950, 2900,

TABLE III Weight gained for the cured PCS, chemical composition (wt.%) and empirical formulae of as-received PCS and the various cured PCS

Sample	Weight gain (%)	Si	C	H	O	Empirical formula
PCS	-	43.7	40.8	8.3	7.2	$SiC_{2.18}H_{5.28}O_{0.29}$
C1	12.8	36.9	23.6	6.7	32.8	$SiC_{1.50}H_{5.08}O_{1.56}$
C2	12.9	35.7	22.2	6.3	35.8	$SiC_{1.46}H_{4.92}O_{1.76}$
C3	13.5	36.5	22.0	4.1	37.4	$SiC_{1.41}H_{3.13}O_{1.80}$
C4	10.2	41.3	29.7	7.6	21.4	$SiC_{1.68}H_{5.13}O_{0.91}$

1400 and 1355 cm^{-1}), Si-CH$_3$ (1250 cm^{-1}) and CH$_2$ (1020 cm^{-1}) groups decreased in intensity on curing, particularly the Si-H and C-H bonds of Si-CH$_3$ groups. An absorption band at 1710 cm^{-1} due to C=O stretching was observed to appear during curing. In addition, a broad band at around 1100 cm^{-1} superimposed on the band around 1020 cm^{-1} (CH$_2$ deformation) was assigned to Si-O stretching in Si-O-Si and Si-O-C units [29, 30]. The small band at 1200 cm^{-1} was assigned to C-O bonds [29]. The intensity of the O-H stretching band in Si-OH groups (3700 cm^{-1}) also increased after curing. This was superimposed on the stretching vibration band of adsorbed water at around 3500 cm^{-1}. A deformation band of H$_2$O was observed at 1620 cm^{-1}. Subtraction of the spectrum for the background and the KBr used in the preparation of the pellets showed that the adsorbed water was mainly from the cured PCS powders. These results indicated that in the process of oxidation curing, the Si-H and Si-CH$_3$ groups of the PCS were mainly attacked by the oxygen, creating Si-O-Si and Si-O-C bonds as indicated by the decrease of the intensity of the Si-H, C-H and Si-CH$_3$ bands. The loss of hydrogen and carbon in the curing indicated here was consistent with the decrease in their content found by elemental analysis. Si-OH and C=O bonds were also created in the curing process. These findings are consistent with those reported by various workers [22, 30, 35]. The formation of water indicated by the appearance of the band at 3500 cm^{-1} also consistent with reported findings [30, 34], and could be due to the reaction:

$$2\,\text{Si-H} + \text{O}_2 \rightarrow 2\,\text{Si-OH} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}$$

The formation of C=O bonds may be linked to the oxidation of the Si-CH$_3$ groups [36]. C-O bonds may be formed by:

$$\text{Si-H} + \text{CH}_3\text{-Si} + \text{O}_2 \rightarrow \text{Si-O-CH}_2\text{-Si} + \text{H}_2\text{O}$$

On comparing the spectra of samples C1 to C3 (Figs 4b–d) where the curing time increases from sample C1 to C3, it was seen that the decrease in the Si-H and C-H bonds, (particularly the former) became more marked from sample C1 to C3 as expected. For sample C4 (Fig. 4e), where a higher heating rate was applied, the intensities of the characteristic absorption bands of the initial PCS were less reduced compared to samples C1 to C3, showing that curing was less effective in this sample. This was probably due to the fact that a faster rate of heating means less time when the PCS was exposed to temperatures at which curing can occur.

3.2.3. Solid state ^{29}Si and ^{29}C NMR spectroscopy

In Fig. 2, the solid state ^{29}Si NMR spectra of the cured samples, obtained by the cross-polarization/magic angle spinning (CP/MAS) technique, are compared with that for the as-received PCS. The assignments were based on reported work on organosilicon polymers [21, 37, 38]. After curing, the signal at a chemical shift of −36 ppm due to Si-Si bonds disappeared in all the samples, consistent with the FT-IR results. While the relative intensity of the signal at around +0.4 ppm due to SiC$_4$ units remained almost constant, the relative intensity of the signal at −14 ppm due to SiC$_3$H groups was reduced for all samples after curing. Samples C1 to C3 were cured for increasing times, as shown in Table I. The reduction in the intensity of the SiC$_3$H groups also increased with cure time. With a faster heating rate (sample C4, Fig. 2e), the curing is less effective, hence a lower reduction in the relative intensity of the SiC$_3$H signal was observed. This was due to a reduction in the time spent at temperatures at which curing could take place. The reduction in the SiC$_3$H signal correlated with the reduction of the Si-H and Si-CH$_3$ absorption bands in the FT-IR spectra. Fig. 2 also shows that after curing, a signal at around −53 ppm due to Si-O-C bonds appeared, its relative intensity increasing with increasing cure time from sample C1 to C3. The weak signal at around +10 ppm due to Si-O-Si bonds observed in the as-received PCS was also found to increase in intensity with increasing cure time. Again, a faster heating rate (C4) led to a lower degree of curing indicated by a lower relative intensity of the signals due to Si-O-Si and Si-O-C groups. In all the cured samples, the signal due to Si-O-Si bonds (+10 ppm) was relatively more intense than the signal due to Si-O-C bonds (−53 ppm). These results were consistent with the trend observed by FT-IR, i.e., a decrease in the relative intensity of the SiC$_3$H band, appearance of the Si-O-Si and Si-O-C band after curing. This may be mainly due to oxidation of Si-H, C-H and Si-Si bonds, producing Si-O-Si and Si-O-C groups as has previously been reported [21, 22], although a clear mechanism of the oxidation curing process is still not fully established. Here, ^{29}Si CP/MAS NMR has confirmed the presence and relative amounts of Si-O-Si and Si-O-C bonds in the cured PCS samples which was not clearly resolved by FT-IR spectroscopy.

The solid state ^{13}C CP/MAS spectra of the as-received PCS and cured samples are shown in Fig. 3. Following curing, the position of the +5 ppm peak due to Si-C bonds in the as-received PCS shifted to a slightly higher value of ca. +9 ppm with the development of a slight asymmetric lineshape with a high frequency “tail”. This suggested some rearrangement of the environment around the Si-C backbone. The ^{13}C chemical shift generally increases as the number of bonded hydrogen atoms decreases [32] consistent with a decrease of the number of C-H bonds found in FT-IR spectroscopy. For all four cured samples, a weak resonance signal at around +65 ppm was observed supporting the presence of C-O bonds [29] which had been suggested in the FT-IR spectra. These were presumably due to the Si-O-C. A weak peak at +160 ppm was observed in the cured samples presumably due to the carbonyl groups detected by FT-IR. The weakness of this peak in NMR compared to the strength of the C=O band in FT-IR is due to the relative inefficiency of cross-polarisation to non-protonated carbons compared to protonated carbons, and with the relative strength of IR absorption by the highly polar C=O bond. In general, no clear differences in structural information were resolved from the ^{13}C spectra.

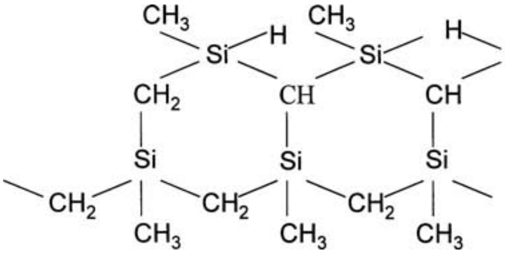

Figure 6 Model structure of PCS.

4. Conclusions

Overall, the results indicate that oxygen was already present in the as-received PCS. This PCS is sensitive to oxygen and a cross-linking reaction starts at around 200 °C even when heated under argon flow in the DTA pan. ^{29}Si and ^{13}C NMR found the as-received PCS to consist mainly of SiC_4 and SiC_3H units in the ratio of 1.5:1, respectively.

These results suggest that this commercial PCS, of number average molecular weight of 1200, has a structure similar to the structural model of the PC-470 type PCS proposed by Okamura [39] and the more recent findings by Chollon *et al.* [34], as illustrated in Fig. 6. Si-C_4, Si-O and Si-Si bonds can also be expected as suggested by the results of IR and NMR. GPC results showed a broad distribution of molecular weights in the PCS.

Both the results of FT-IR and NMR spectroscopy suggest that during curing, the Si-H and C-H bonds of the PCS are mainly cleaved resulting in the formation of Si-O-Si bonds, with a smaller number of Si-O-C bonds. The thermally unstable Si-Si bonds of the original PCS are completely broken and form Si-O-Si bonds. Si-OH and C=O bonds are also formed in the process of curing. Water is also produced in the curing process, perhaps due to the reaction:

$$2\text{Si-H} + O_2 \rightarrow 2\text{Si-OH} \rightarrow \text{Si-O-Si} + H_2O$$

These results appears to agree with the findings of Taki *et al.* [21] and Hasegawa [30] although the resonance due to C-O bonds indicated in the ^{13}C NMR spectra was not reported in their NMR spectroscopy work. The PCS and experimental conditions involved in their studies may differ but were not reported in the literature. However, Si-O-C bonds revealed by IR spectra have been reported [37]. The C-O bonds may be formed by:

$$\text{Si-H} + CH_3\text{-Si} + O_2 \rightarrow \text{Si-O-}CH_2\text{-Si} + H_2O$$

The present study showed that at a heating and cooling rate of 10 °C h^{-1}, the extent of oxidation cross-linking, mainly by the cleaving of the Si-H and C-H bonds of the PCS, generally increased with cure time from 0.5 to 1.5 hours at 200 °C. Changes were observed between a cure time of 0.5 and 1 hour but these were not marked. The extent of curing became more obvious after heating for 1.5 hours, as shown in the ^{29}Si NMR spectra. When the PCS was cured using a faster rate of heating (30 °C h^{-1}) then held at 200 °C for 1 hour, the extent of oxidation cross-linking was lower than when cured at 200 °C for 0.5 hour but using a slower rate of heating. This showed that the oxidation cross-linking process had already started before the final cure temperature of 200 °C. Thus, at the faster rate of heating, the PCS did not have the same time to cross-link as the samples where a slower rate of heating was used.

Acknowledgments

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