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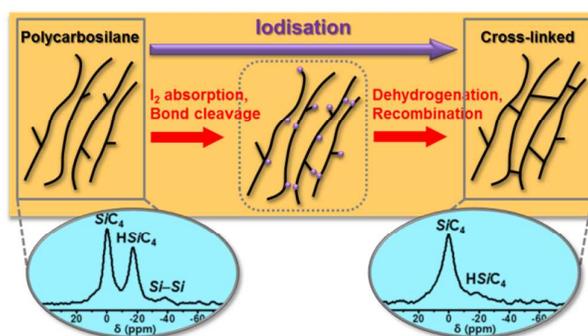
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Graphical and Textual Abstract



Iodisation of polycarbosilane under an oxygen-free atmosphere, even at room temperature, leads to the dehydrogenation of Si-H and C-H bonds and construction of -Si-C- networks without oxygen incorporation, thereby allowing oxygen-free curing for fabricating SiC fibres with low oxygen contents.



Room temperature reaction of polycarbosilane with iodine under different atmospheres for polymer-derived silicon carbide fibres

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The reaction of iodine with polycarbosilane (PCS) in air and N₂ atmospheres at room temperature was investigated with the goal of limiting oxygen uptake during iodine curing, in order to fabricate SiC fibres with low oxygen contents. The investigation shows that the PCS fibres are well cured by iodisation even at room temperature, regardless of the presence of oxygen in the atmosphere. Although it was previously reported that the amount of oxygen incorporated is affected by the processing temperature, when PCS fibres were iodised in air at room temperature, they contained significant amounts of oxygen, owing to the very long processing time despite the low temperature. On the other hand, when iodised in a N₂ atmosphere, the fibres were successfully cured without oxygen uptake, thus demonstrating that iodisation under an oxygen-free atmosphere is a successful curing method for fabricating SiC fibres with low oxygen contents. During the cross-linking process, the iodine causes fragmentation of certain groups from the PCS polymer chains, which mostly contributes to the cross-linking between the chains, but leaves reactive sites that readily allow oxidation in air.

Introduction

Silicon carbide (SiC) fibres are a useful reinforcement material for ceramic matrix composites used at high temperatures in air.^{1–4} The growing demand for light-weight, high-modulus, and high-temperature-resistant materials for high-temperature applications, such as aerospace applications, high-efficiency turbines, and high-temperature reactors, has necessitated the continued development of higher-grade SiC fibres.^{1,5–8} The curing and pyrolysis of polycarbosilane (PCS) is a well-known simple method to produce SiC fibres with small diameters.^{8–12} Oxygen content is a key factor in determining the microstructure and properties of SiC fibres. Specifically, oxygen introduced during the curing process and remaining in the SiC/SiCO fibres contributes to the formation of voids and the grain growth of crystalline SiC, evolving CO(g) and SiO(g) at >1300 °C. The process hinders the densification of fibres at higher temperatures and degrades the mechanical properties of the final fibre.^{13–16} Therefore, much research has focused on

the development of a curing process to inhibit oxygen incorporation using methods other than conventional thermal oxidation curing.

The most successful trial was the electron-beam radiation curing process pioneered by Okamura et al.,^{17–20} this curing process has been used to manufacture high-quality SiC fibres with near-stoichiometry (e.g., Hi-Nicalon-S type), although the process is very cost intensive.^{19,21} A chemical vapour curing method using halogenated hydrocarbons (e.g., CCl₄ or C₆H₅Cl) or unsaturated hydrocarbons (e.g., cyclohexene, 1-octyne, or 1-hexyne) was developed by Hasegawa et al.^{22–24} This method was postulated to be more economical than the radiation curing method; however, there has been no report on the actual application of this method in the SiC fibre industry. In addition, a method using sequential treatment with BCl₃ and ammonia to cure PCS fibres was devised by Dow Corning Co., but this method has a long reaction time (15 h).^{25,26} Otherwise, SiC fibres can be produced by dry spinning high-molecular-weight PCS without any curing treatment to avoid incorporation of oxygen; however, this method requires harsh synthesis conditions.^{27–29}

As an advanced curing technique, we developed iodine-vapour curing.³⁰ Our previous paper reported that the diffusion of iodine into PCS induces cross-linking of PCS at low temperatures (100–150 °C) in air, but oxygen introduction onto the surface was inevitable in this temperature range. However, further research led us to believe that the introduction of oxygen could be inhibited by controlling the curing conditions for the following reasons:^{30,31} (1) the oxygen content increases proportionally with the curing temperature, (2) the oxidised region is limited to the surface when curing at a low temperature (~80 °C) despite the longer treatment time

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(3 h), and (3) the degree of curing is correlated to the degree of iodine diffusion rather than to that of oxygen diffusion.

In this paper, we clarify whether the iodine-vapour curing process can be made oxygen-free or if it requires iodine-aided oxidation. In order to minimise the effect of oxygen, the PCS fibres were iodised at room temperature in air as well as N₂ atmosphere. The evolution of their chemical structures as well as the oxygen content incorporated into the fibres were investigated in detail. Based on the results, an oxygen-free curing process was outlined.

Experimental

Synthesis of polycarbosilane

Two polycarbosilanes (PCSa and PCSb) were prepared as precursors. PCSa, provided by TBM Tech Co. Ltd. (South Korea), had an average molecular weight (\overline{M}_w) of 2229 and a melting point of 150–180 °C (determined by GPC and melting-point apparatus, respectively).³⁰ PCSa was melt-spun using a single-spinner apparatus to obtain PCS fibres with a diameter of 10–20 μm (determined by optical microscopy). PCSb was synthesised by Kumada rearrangement^{32,33} of polydimethylsilane (PDMS). A mixture of 600 g of PDMS (TBM Tech Co. Ltd., Korea), 6 g of aluminium(III)-acetylacetonate (Al-acac, Sigma-Aldrich Co. LLC, USA) for Al-doping, and 6 g of carbon nanotubes (CNTs) as a catalyst was placed in an autoclave purged with Ar gas and then thermally decomposed at 350 °C for 5 h and subsequently at 400 °C for 5 h. The solid product obtained was dissolved in toluene and purified using a centrifugal separator and by filtration through a series of sieves (3, 1, and 0.45 μm). Then, the toluene was removed by vacuum distillation for 2 h at 150 °C. The resultant product had a \overline{M}_w of 1803 and a melting point of 85–110 °C.³⁰ The product was then hand-ground to obtain a uniform PCS powder. These two PCSs had almost identical structure and characteristics, although they had different molecular weights.

Reaction in an air atmosphere

Identification of gas by-products at room temperature. In the course of mixing PCS and iodine to induce a reaction at room temperature in air, a yellow vapour or gas was evolved. The quantity of this by-product was small compared with that of the solid. After mixing 0.0983 g iodine (Yakuri Pure Chemicals Co. Ltd., Japan) and 2.2346 g PCS powder (PCSB) and subsequent gas evolution, the total weight of the reaction mixture was immediately determined using a digital balance with a resolution of 0.01 mg (HM-300, AND Co. Ltd., USA).

Furthermore, the identity of the gaseous product was determined using gas chromatography coupled with mass spectrometry (GC-MS; Agilent 7890A/5975C, Agilent Technologies, USA). The GC-MS was equipped with a fused-silica capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 μm, 5% phenylmethyl siloxane). The measurement method was as follows. PCS (PCSB) and iodine powders were mixed in a headspace vial, thereby emitting a yellow gas. The gas was

extracted and then injected into the GC column (split ratio of 10:1, He as the carrier gas, flow rate of 1.0 mL min⁻¹). For product separation, the oven was heated isothermally at 40 °C for 4 min then the temperature was increased to 300 °C (10 °C min⁻¹) and held constant for 20 min. The inlet and ion source temperatures were 250 and 230 °C, respectively. The MS was operated in scan mode with a mass detection range of 10–800 Da.

Thermal gravimetric analysis. The pyrolysis behaviour of PCS iodised at room temperature was examined by thermal gravimetric analysis (TGA; STA 409 PC Luxx, Netzsch, Germany). Three samples were used for comparison: as-prepared PCS powder (PCSB) and two PCS-iodine mixed powders (mass ratio of 20:1 or 20:2). The mixtures were prepared by uniformly mixing PCS and iodine powders in a bottle and letting it stand for ~24 h at room temperature so that sufficient diffusion and reaction could take place. Around 30 mg of each of the specimens was placed in an alumina crucible and then heated to 1400 °C at a ramp rate of 5 °C min⁻¹ in Ar flow (80 mL min⁻¹).

FTIR and solid-state NMR analyses. The chemical structures of the PCS fibres before and ~24 h after iodine treatment (iodisation) at room temperature were analysed by Fourier transform infrared (FTIR) spectroscopy and solid state nuclear magnetic resonance (NMR) spectroscopy. For iodisation, a bundle of PCS fibres (PCSa) was placed along with iodine powder in a schale at ambient temperature and covered with a lid. As iodine is nonpolar,³⁴ it easily sublimated and diffused to cover the fibres even at ambient temperature. This process was carried on for 24 h to sufficiently iodise the fibres.

The as-spun PCS fibres and the iodised fibres were analysed using FTIR spectroscopy (Vertex 80v, Bruker Co., Germany) in vacuum. The samples were incorporated into potassium bromide (KBr) pellets.

The solid-state NMR analyses (²⁹Si, ¹³C, and ¹H) were conducted on a Bruker Avance II+ 400 MHz NMR spectrometer with a magnetic field of 9.4 T using a 4 mm magic angle spinning (MAS) probe at room temperature. The crushed samples were placed in zirconia rotors and spun at a rate of 13, 6, and 8 kHz for ¹H, ²⁹Si, and ¹³C, respectively. The ¹H MAS NMR spectra were acquired using single-pulse excitation at a Larmor frequency of 400.13 MHz with a recycle delay of 3 s. The ²⁹Si cross-polarisation (CP)/MAS NMR spectra were collected at a Larmor frequency of 79.49 MHz with a contact time of 2 ms and a recycle delay of 3 s. The ¹³C CP/MAS NMR spectra were recorded at a Larmor frequency of 100.62 MHz with a contact time of 2 ms and a recycle delay of 3 s. The chemical shifts in the spectra were determined relative to tetramethylsilane (TMS).

Additionally, an *in-situ* ¹H MAS NMR analysis was conducted during iodisation of PCS in order to confirm the production of aromatics as by-products. PCS and iodine powders were placed

in a zirconia rotor and then analysed at room temperature over time (for details, see the ESI).

EPR analysis. The influence of iodine treatment at room temperature on the residual radicals in PCS was investigated using an electron paramagnetic resonance (EPR) spectrometer (JES-TE300, JEOL Co., Japan) at 9.12 GHz (*X* band). Three PCS powders with different iodine contents were analysed: as-prepared PCS (PCSa) and PCS–iodine mixtures (mass ratio of 97:3 or 94:6). The mixtures were prepared by stirring for 5 h in a bottle at room temperature. Identical amounts of each specimen were used in the EPR experiments (100 mg). The *g*-factors were calibrated against that of 1,1-diphenyl-2-picrylhydrazyl (DPPH, Wako Pure Chemical Industries Ltd., Japan).³⁵

Reaction in an oxygen-free atmosphere

DSC analysis. The reactivity of iodine towards PCS in an inert atmosphere, *i.e.*, in the absence of oxygen, was observed by differential scanning calorimetry (DSC; DSC-60/60A, Shimadzu, Japan) in flowing Ar gas (60 mL min⁻¹) at a ramp rate of 5 °C min⁻¹ using alumina crucibles. DSC curves were obtained for PCS fibres (PCSa), iodine powder, and a PCS–iodine mixture (iodine powder covering the PCS fibres, 1:1 mass ratio).

Solid-state NMR analysis. To confirm the role of iodine during the room-temperature curing in the absence of oxygen, the chemical structures of PCS obtained through iodine treatment in an inert atmosphere at room temperature were investigated by solid-state NMR analysis (Bruker Avance II+ 400 MHz NMR spectrometer). The following experiments were conducted in a glove box with a dried N₂ gas atmosphere to exclude the effects of oxygen or humidity. PCS fibres (PCSa) were iodised by being placed into a vial containing iodine powder for ~24 h. Samples of PCS fibres before and after iodine treatment were crushed and placed in zirconia rotors in the glove box. ²⁹Si MAS NMR spectra were recorded using the 400 MHz NMR spectrometer previously described, at a spin rate of 10 kHz and a Larmor frequency of 79.488 MHz using a 1.0 μs π/6 pulse with a delay time of 100 s.

One-pot fabrication of SiC fibres. We attempted a one-pot fabrication process that combined curing and pyrolysis, in order to limit the introduction of oxygen that may occur by exposure to air during transfer of the cured fibres to the pyrolysis furnace. In this process, PCS fibres (PCSa, 20 mg) and iodine powder (200 mg) were placed in a graphite crucible (30 × 35 × 20 mm³) and the sample was heat-treated in an alumina tube furnace with flowing Ar gas (2 L min⁻¹). The temperature of the furnace was programmed to hold at 150 °C for 30 min, then increase to 1000 °C at a rate of 3 °C min⁻¹ and hold at this temperature for 10 min. After this process, the fibres were observed with a scanning electron microscope (SEM; S-2700, Hitachi, Japan).

Fabrication of SiC fibres through iodisation in different atmospheres

Fabrication process. SiC fibres were fabricated by the following three different processes: (i) iodisation in an atmosphere containing oxygen and heat-treatment in a furnace afterwards with exposure to air between the two processes (two-pot process), (ii) iodisation in an oxygen-free atmosphere and heat-treatment in a furnace afterwards with exposure to air between the two processes (two-pot process), and (iii) iodisation in an oxygen-free atmosphere, followed by heat-treatment with no exposure to air between the two processes (one-pot process). In the two-pot processes (i and ii), for iodisation, PCS fibres (PCSa, 140 mg) and iodine powder (60 mg) were placed in a graphite crucible (π × 21 mm² × 63 mm), and the crucible was heat-treated in a quartz tube furnace. The temperature of the furnace was programmed to increase at the rate of 5 °C min⁻¹ and was held at 100 °C, 150 °C, and 250 °C for 30 min each, under different atmospheres, namely, flowing N₂ gas for process (i) and O₂ (21%) – N₂ (79%) mixed gas for process (ii) (50 mL min⁻¹); however, the actual temperatures inside the furnace were 30–60 °C less than the scheduled temperatures, as determined with the help of a thermocouple probe inserted into the furnace. The furnace temperature was further increased to 500 °C (at the rate of 5 °C min⁻¹) and held at this temperature for 30 min to completely vaporise out iodine that might be adsorbed on the fibres and attract moisture when exposed to air. Next, for polymer-to-ceramic conversion, two types of cured fibres were moved to an alumina tube furnace and they were heat-treated together at 1300 °C for 1 h in the furnace under flowing N₂ gas (2 L min⁻¹).

In the one-pot process (iii), PCS fibres (PCSa, 140 mg) and iodine powder (60 mg) were placed in a graphite crucible (π × 21 mm² × 63 mm), which was heat-treated at 1300 °C for 1 h in the alumina tube furnace under flowing N₂ gas (2 L min⁻¹). The heating schedule was the same as those in the two-pot processes, except for the slow ramp rate in the temperature range of 100–200 °C (temperature ramp occurred over 2 h) for iodisation.

Silicon-29 Solid-state NMR analysis. The amount of oxygen incorporated in the three types of SiC fibres and their chemical structures were evaluated by ²⁹Si MAS NMR analysis. The fibres were ground into powder and placed in a 4 mm zirconia rotor. ²⁹Si MAS NMR spectra were collected using an Agilent DD2 700 MHz NMR spectrometer operated at a spin rate of 10 kHz, using a π/6 (1.838 μs) single-pulse excitation with a relaxation delay time of 30 s, at a Larmor frequency of 139.03 MHz, where the number of scans was 1000.

Results and discussion

Gas emission during the reaction at room temperature in an air atmosphere

After mixing the iodine and PCS powders, the yellow vapour evolved was removed by degassing, and the total weight of the mixture was measured. A slightly increased weight (2.3364 g) was obtained compared with the sum of the weights of the reactants (2.3329 g), despite the gas emission. Thus, it is assumed that either moisture (H₂O) or O₂ in air, or both, is readily adsorbed onto the mixture. This assumption is supported by the following FTIR and NMR studies.

The GC-MS analysis (Figure 1 and Table 1) reveals the identity of the yellow vapour evolved from the PCS–iodine mixture. As observed from the data, there are three groups of compounds in the vapour: aromatics (toluene and benzene), methyl iodide (CH₃I), and cyclosiloxanes (H₂ was not detected because of technical limitations (detectable mass range: 10–800 Da)). All these compounds are known to be colourless, yet the vapour was yellow to the naked eye. The yellow colour probably resulted from the absorption of iodine on aromatic clusters (so-called “charge-transfer complex”³⁶) in the vapour, similar to the interaction observed between iodine and benzene.^{36,37}

The presence of such complexes implies that iodine (I₂) causes the fragmentation of certain groups from the PCS polymer chains, such as –CH₃, thus forming reactive sites. Such reactive sites cause the grafting of one chain onto another, hence leading to cross-linking.

The major compounds detected were toluene (44.43%) and CH₃I (41.82%) in Table 1. As the formation of CH₃I is a type of dehydrogenation, this reaction would certainly contribute to the cross-linking of PCS. The aromatics might be formed through dehydrocyclisation of –CH₃ fragments or CH₃; in fact, iodine appeared to induce the formation of carbon–carbon double bonds in PCS (refer to the C=C peak $\bar{\nu}$ =1630 of the FTIR spectrum in Figure 3). In addition, the remaining aromatics

might also affect the cross-linking process, such as cyclohexane and aromatic cyclohexyl moiety, which were reported as a source to facilitate the cross-linking of PCS.^{23,24} The detection of siloxanes (7.30%) is due to the oxidation of oligomeric silanes that were detached from PCS (refer to the Si–Si signal $\delta_{\text{Si-Si}}$ in the ²⁹Si-NMR spectra in Figure 4(a)). This implies that the PCS surface, which was exposed to air, would also be oxidised.

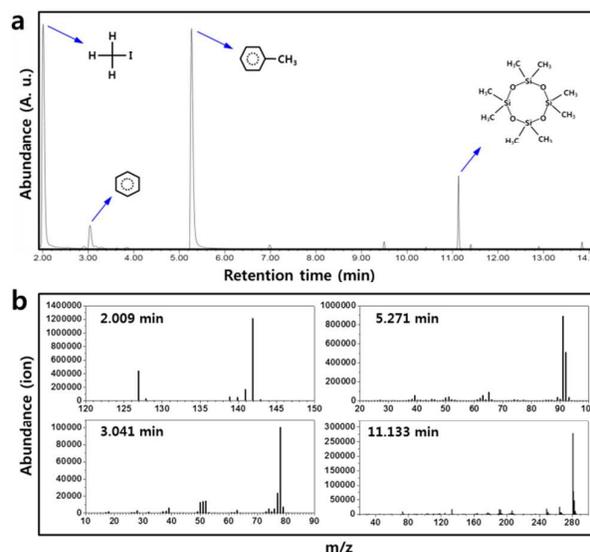


Figure 1. (a) Gas chromatogram of the sublimated gas evolved from the mixed PCS–iodine powder at room temperature in an air atmosphere. (b) Mass spectrum by GC-MS of the major fragments in the GC spectrum at retention times of 2.009, 3.041, 5.271, and 11.133 min.

Table 1. Compounds in the gas evolved from the mixed PCS–iodine powder at room temperature in an air atmosphere determined by GC-MS^a

No.	RT (min)	Peak Area (%)	Compound name	Chemical formula
1	2.009	41.82	Methyl iodide	CH ₃ I
2	3.041	4.46	Benzene	C ₆ H ₆
3	5.271	44.43	Toluene	C ₇ H ₈
4	6.990	0.57	Cyclotrisiloxane, hexamethyl-	C ₆ H ₁₈ O ₃ Si ₃
5	9.502	0.68	1,3-Dioxa-2,4,6-trisilacyclohexane, 2,2,4,4,6,6-hexamethyl-	C ₇ H ₂₀ O ₂ Si ₃
6	11.133	5.55	Cyclotetrasiloxane, octamethyl-	C ₈ H ₂₄ O ₄ Si ₄
7	13.848	0.50	Cyclopentasiloxane, decamethyl-	C ₁₀ H ₃₀ O ₅ Si ₅
Total		98.01		

^aCompounds with peak areas of less than 0.5% of the total area were excluded.

Ceramic yield

Figure 2 shows the TGA results for PCS and the PCS–iodine mixtures (5 or 10 wt% added iodine). Upon pyrolysis, the PCS polymers transformed into SiC ceramics with an accompanying weight loss. Most importantly, the ceramic yield obtained at 1400 °C increases from 54 to 60 to 63 wt% in proportion to the amount of iodine added (0, 5, and 10 wt%, respectively), even though the PCS was initially only mixed with iodine at room temperature (with the assumption that iodine is completely removed from the SiC obtained at 1400 °C). Generally, the

proportions of the final residue are determined by molecular weight and the degree of cross-linking of the polymer.^{38,39} Thus, This result indicates that at or near room temperature, a specific reaction occurs between iodine and PCS that contributes to the cross-linking. Additionally, in the case of PCS+10% I₂, the weight decrease up to 120 °C was relatively drastic, presumably owing to the vaporisation of excess unabsorbed iodine.

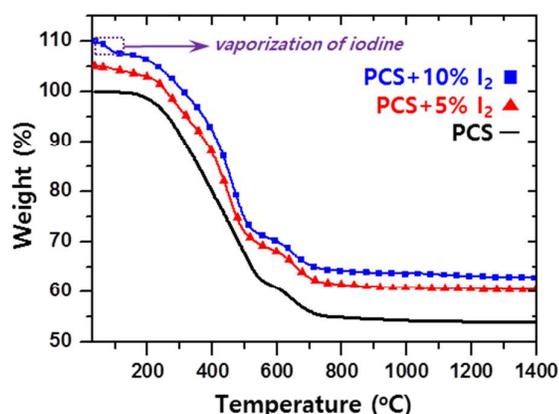


Figure 2. TGA curves (obtained in an Ar atmosphere) of PCS and PCS-iodine mixtures (5 or 10 wt% added iodine: PCS+5% I₂ and PCS+10% I₂, respectively) exposed to an air atmosphere at room temperature for ~24 h.

Chemical structure changes of PCS

Figures 3 and 4 show the FTIR and NMR spectra, respectively, of the PCS fibres before and after iodisation at room temperature in an air atmosphere (the assignment of chemical bonds and environments marked in the figures are based on those reported in previous studies on PCS^{15,17,40-48}). There are a number of noteworthy changes in the spectra after iodisation. First, the most distinguishing change after iodisation is the decrease in the Si-H peaks (2100 and 880 cm⁻¹ in FTIR; ~17 ppm in ²⁹Si-NMR and ~4.5 ppm in ¹H-NMR). Second, the shoulder ascribable to Si-Si bonds (~38 ppm in ²⁹Si-NMR) disappears. Third, although the two multi-band peaks ascribable to C-H bonds (2830–3000 and 1330–1450 cm⁻¹ in FTIR) appear to hardly change, a closer inspection shows that the end of the range (~1460 cm⁻¹ in FTIR) is reduced. This region is likely related to the C-H bond in the -CH₃ structure when considering the decrease in the SiCH₃ signal (~-1 ppm in ¹³C-NMR). Fourth, the strength of the Si-CH₂ peak (1030 cm⁻¹ in FTIR) increases in intensity, while the peak ascribable to both Si-CH₃ and Si-C (800–850 cm⁻¹ in FTIR) slightly decreases. This change corresponds to the downfield peak shift (*i.e.*, dehydrogenation) observed by ¹³C-NMR. Fifth, the signals attributable to Si-O bonds (~435, ~1080, and 3680 cm⁻¹ in FTIR; ~8 ppm in ²⁹Si-NMR) increase, whereas the C=O bond peak (1700 cm⁻¹ in FTIR) is static. Sixth, a strong signal corresponding to benzene (~7 ppm in ¹H-NMR)^{44,49} appears. However, the actual amount of benzene could not be determined because it was present as a liquid or in the vapour state at room temperature (melting point of benzene: 5.53 °C);

that is, the actual amount is smaller than the peak area because its rapid molecular tumbling yields a strong and distinct signal. The production of benzene during the reaction was confirmed with a supplementary experiment (ESI, Figure S1). Over time, this peak (~7 ppm) vanishes owing to vaporisation, as shown in the ¹H-NMR spectrum (Figure 4(c)). Seventh, the O-H bond peaks in H₂O (3300–3600 cm⁻¹ in FTIR; 5 ppm in ¹H-NMR) appear after vaporisation of benzene. Finally, there are no new peaks in the FTIR spectrum related to C-I bonds, such as CH₂I bending (1219 cm⁻¹)⁴⁴ or C-I stretching (516 cm⁻¹).⁴⁴

To sum up, during the reaction of iodine and PCS, Si-Si, Si-H, and C-H bonds are cleaved and the silicon dangling bonds mainly combine with oxygen (originating from O₂ or H₂O in air), while the carbon dangling bonds mostly combine among themselves, thus constructing →Si-O-, >C=C<, or →Si-C<- networks (the →Si-C<- structure is also assumed to form when considering the discussion of the reaction in an inert gas below, although it cannot be confirmed at present owing to the overlapping of its signals). This tendency is almost identical to that of the reaction at a higher temperature (100 or 150 °C).³⁰ Unfortunately, PCS fibres iodised at room temperature in air still contain oxygen introduced during the process, yet the amount is smaller than that introduced during curing at a higher temperature.³⁰

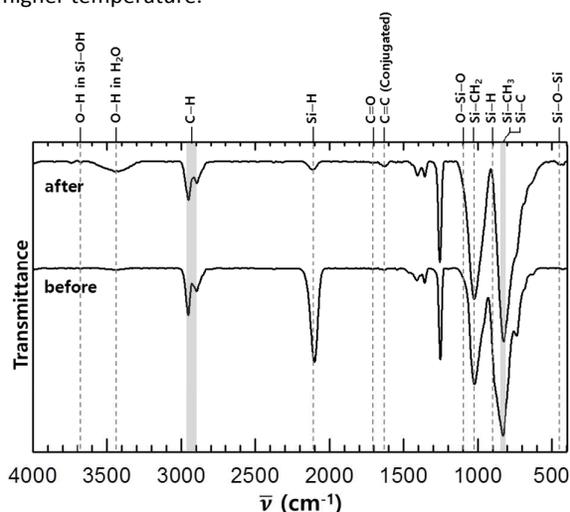


Figure 3. FTIR spectra of PCS fibres before and after iodisation at room temperature in an air atmosphere.

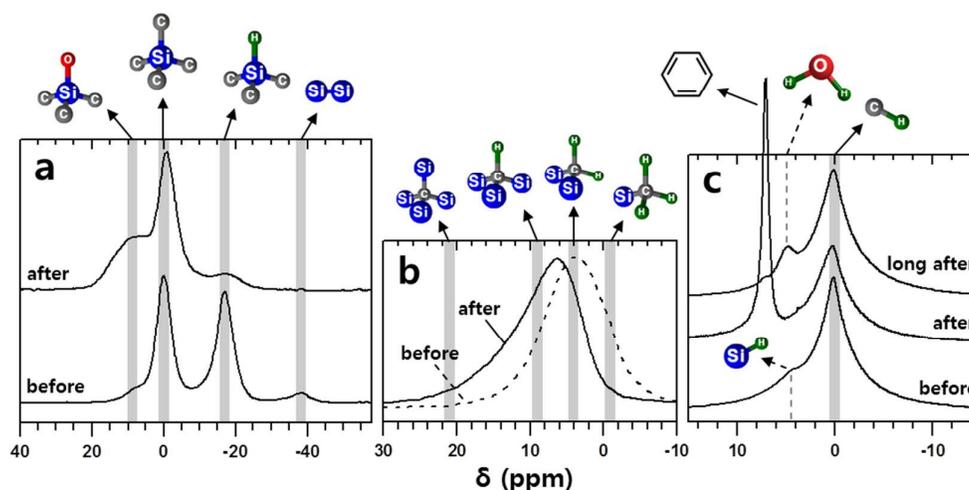


Figure 4. Solid-state NMR spectra of PCS fibres before and after iodisation at room temperature in an air atmosphere: (a) ^{29}Si CP/MAS NMR, (b) ^{13}C CP/MAS NMR, and (c) ^1H MAS NMR.

Evolution of free radicals in PCS

Figure 5 shows the EPR spectra of PCS and the PCS–iodine mixtures, and Table 2 shows the tabulated data. The g -factors of all precursor PCS samples are 2.0032 ± 0.0002 , which, according to previous reports, is more likely a result of carbon dangling bonds than those of silicon (commonly, g -factors are ~ 2.0030 for carbon dangling bonds and ~ 2.0053 for those of silicon).^{23,50–52} However, the g -factor actually decreases slightly as the iodine content increases. This trend indicates that the residual silicon dangling bonds (or Si-centred radicals) react preferentially by combining with other radicals of oxygen or carbon, which agrees well with the decrease in the spin concentration. In addition, when considering the drastic decrease in the spin concentration, both C-centred radicals and Si-centred radicals would vanish through combination with another Si- or C-centred radical. These results are similar to those obtained for iodine-vapour curing at a higher temperature ($100\text{ }^\circ\text{C}$),³⁰ thus verifying that the cross-linking reaction can take place through iodisation at room temperature. These results also reinforce our theory that the cross-linking reaction through iodisation occurs via a concerted reaction and not via a radical reaction.³⁰ However, with increasing iodine content, the symmetric spectrum becomes asymmetric (Figure 5(c)). Although this could be due to the presence of excess iodine, further experiments are required to determine the fundamental cause of the asymmetry.

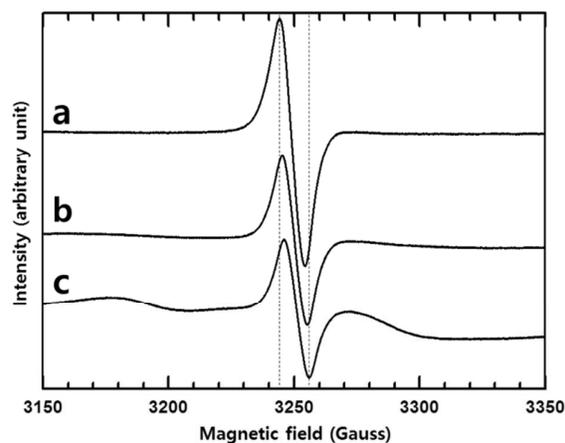


Figure 5. EPR spectra of (a) PCS and (b) PCS–iodine mixtures with a mass ratio of 97:3 or (c) 94:6. The mixtures were prepared at room temperature in an air atmosphere.

Table 2. EPR data from Figure 5.

Sample	I ₂ content (wt%)	g -factor	Peak-to-peak width (Gauss)	Peak-to-peak height (arb. unit)	Relative spin concentration ^a
(a)	0	2.0034	10.134	1568	16.183
(b)	3	2.0031	9.865	1082	10.530
(c)	6	2.0030	9.988	880	8.779

^aCalculated using peak intensity = (peak-to-peak width)² × (peak-to-peak height).

Reaction in an inert gas atmosphere

To set the research direction toward oxygen-free curing, we needed to confirm whether the cross-linking reaction of iodine-vapour curing proceeds in an inert gas atmosphere or only works in the presence of oxygen. DSC and solid-state ^{29}Si NMR analyses were conducted to investigate this process.

The DSC curves in Figure 6 show the endo- and exothermic reactions of PCS, iodine, and a PCS-iodine mixture in an Ar atmosphere. The DSC curve for the PCS fibres has a very small endothermic valley above 210 °C. This is due to the melting of the fibres because the softening/melting point is 180–210 °C. The DSC curve for iodine has an endothermic peak up to ~80 °C, which is attributed to the vaporisation of iodine. The DSC curve for the PCS-iodine mixture shows a gentle exothermic peak at 30–100 °C, although this peak would be offset by the endothermic vaporisation of iodine. The exothermic peak indicates that any reactions that might contribute to the cross-linking of PCS, take place without oxygen at this low temperature once iodine comes in contact with PCS. Indeed, PCS mixed with iodine is deemed not to melt owing to the cross-linking reaction, as no endothermic valley at ~210 °C (a sign of melting) is observed in the DSC curve for the PCS-iodine mixture.

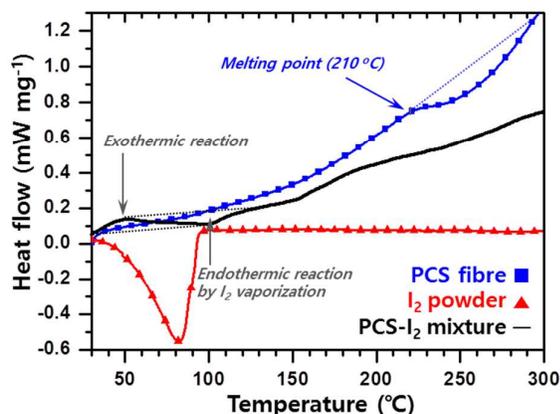


Figure 6. DSC curves obtained in an Ar atmosphere for PCS fibres, iodine powder, and a PCS-iodine mixture (1:1 mass ratio).

The ^{29}Si MAS NMR spectra in Figure 7 show the changes in the chemical structure of the PCS fibres following iodisation in a N_2 atmosphere. As expected, the SiC_3H and Si-Si signals (-17 and -38 ppm, respectively) decrease or vanish, while the SiC_4 signal (~0 ppm) intensifies and the peak broadens (full width at half maximum (FWHM) increases from 6.01 to 8.99 ppm). Although a small shoulder around 14 ppm, ascribable to the chemical environment of SiOC_3 ,^{15,24} is observed, the signal appears to be negligible with respect to the large peak attributable to SiC_4 (~0 ppm). This observation indicates that the reaction relating to cross-linking occurs solely in the presence of iodine.

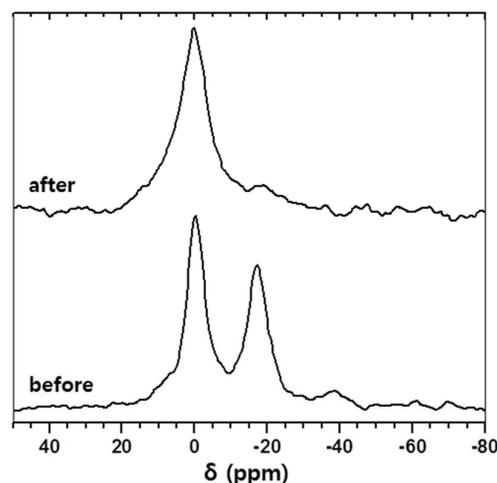


Figure 7. ^{29}Si MAS NMR spectra of PCS fibres before and after iodine treatment at room temperature in a N_2 atmosphere.

Based on the above results, we traced the possible reaction routes for the cross-linking by iodisation. Generally, the PCS structures can be classified into five minimal unit structures as shown in Figure 8, in which Si-H , Si-CH_3 , C-H , or Si-Si bonds are subject to cleavage.

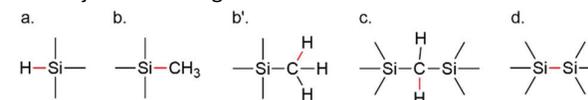
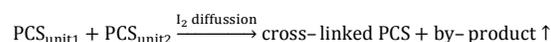


Figure 8. Unit structures of PCS. The red lines indicate bonds that are subject to cleavage.

Each unit structure could combine with another unit at the moment of cleavage (*i.e.*, replacement reaction), thereby cross-linking the polymer chains while simultaneously forming by-products, such as CH_3I and aromatics, as shown in the following equation:



All possible combinations, *i.e.*, linkages between the various silicon and carbon dangling bonds, result in three types of structures, as depicted in Figure 9.

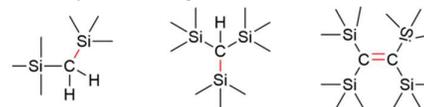


Figure 9. Possible structures by the cross-linking of two unit structures of PCS during iodine-vapour curing. The cross-linked bonds are indicated in red.

Considering all the combinations between the minimal unit structures in relation with the by-products formed (*e.g.*, CH_3I , toluene, and benzene), the cross-linking reaction can occur only if a significant amount of hydrogen is detached from the original structure. Hence, it is expected that the cross-linking reaction entails the release of hydrogen in addition to the by-products identified by GC-MS (Figure 1). However, further experimental evidence would be needed to confirm this assumption.

Fabrication of SiC fibres using a one-pot process

We carried out the two-pot process by curing the PCS fibres under a N_2 atmosphere in a furnace and subsequently subjecting them to pyrolysis in another furnace. Although SiC fibres were well-fabricated by the process, we suspected that the cured PCS fibres may take up oxygen, owing to the momentary exposure to air during their transfer to the second furnace for pyrolysis. This suspicion was based on the fact that the PCS fibres iodised under N_2 gas exhibited white colour in the N_2 atmosphere, whereas after exposure to air, their colour increasingly changed to a gold-like yellow within a few minutes. Hence, to circumvent exposure to air, we devised a one-pot heat treatment process that combines the curing and pyrolysis processes. This process was successful. As can be seen from the images in Figure 10, the SiC fibres fabricated using the one-pot process were found to maintain their shape with no features that resulted in the fibres sticking to each other or tangling with each other. This indicates, before pyrolysed, the PCS fibres were cured by oxygen-free iodisation. Although the fibres had an oblong shape rather than circular shape, the shape could be readily controlled by optimizing the time and temperature of the iodisation process or by using a smaller size of fibre; for further details on controlling the morphology of the fibres, see a previous paper by the authors.³¹

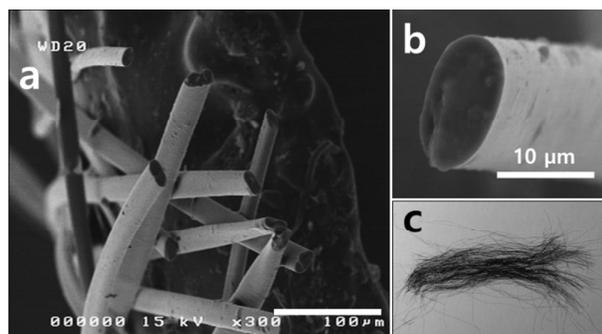


Figure 10. SiC fibres produced by one-pot heat treatment (to 1000 °C) of PCS fibres surrounded by iodine powder in an Ar atmosphere: SEM images (a, b) and photograph (c).

Comparison between SiC fibres fabricated by iodisation under different atmospheres

SiC fibres were fabricated by iodisation of the PCS fibres under N_2 gas as well as under a mixed gas comprising of 79% N_2 and 21% O_2 (*i.e.*, oxygen-free and oxygen-containing atmospheres, respectively), with pyrolysis afterwards. In addition, SiC fibres were also fabricated by a one-pot process that combined the curing and pyrolysis processes, which was aimed at limiting the introduction of oxygen that might occur by the exposure of iodised PCS fibres to air.

The chemical structures and oxygen contents of the three SiC fibres obtained were investigated by means of ^{29}Si solid-state NMR analysis. Figure 11 shows the ^{29}Si MAS NMR spectra of the fibres. The spectra contain four major peaks with chemical shifts of around -16, -38, -74, and -109 ppm, corresponding to

the chemical environments of SiC_4 , SiO_2C_2 , SiO_3C , and SiO_4 units, respectively.^{53,54} Some significant differences were observed among the three SiC fibres. First, as expected, the fibres obtained by iodisation under N_2 - O_2 mixed gas contain significant amounts of oxygen, such that the peak ascribable to the SiO_4 unit (-109 ppm) occupies the greatest part of the spectrum (Figure 11(c)). Second, the SiC fibres obtained by iodisation under N_2 gas (two-pot process) contain oxygen to some degree (Figure 11(b)), despite being processed in the N_2 atmosphere, thereby suggesting that oxygen was introduced by exposure to air during the transfer of the iodine-cured fibres to the furnace after the iodisation process. It is, therefore, believed that the reactive sites remaining after fragmentation (as previously discussed with the GC-MS data) during the curing reaction rapidly take up oxygen when exposed to air. Third, the SiC fibres fabricated by the one-pot process contain hardly any oxygen, as indicated by the large SiC_4 peak (-16 ppm) and the gentle SiO_2C_2 hill (-38 ppm) in Figure 11(a). Consequently, iodisation under oxygen-free atmosphere is a good method to cure PCS fibres for obtaining SiC fibres with low oxygen contents. In addition, to completely prevent the incorporation of oxygen, the surface of the PCS fibres that become unstable after iodisation should be treated thermally or chemically for stabilisation before exposure to outside air. Chemical treatment for stabilisation prior to exposure to air is currently being investigated.

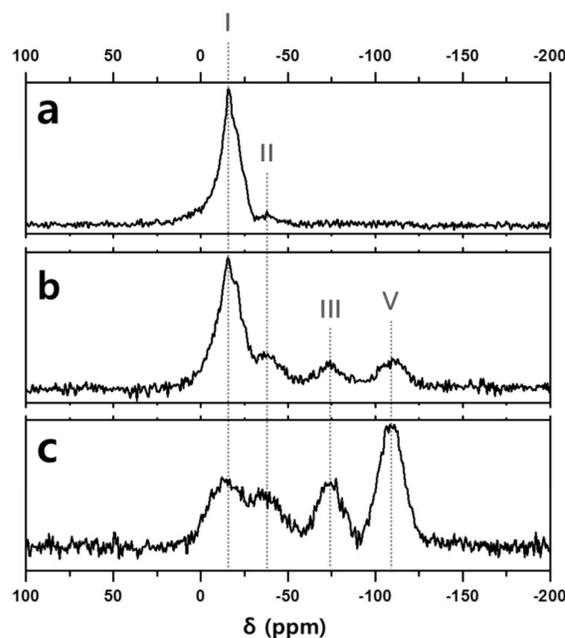


Figure 11. ^{29}Si MAS NMR spectra of (a) SiC fibres fabricated by iodisation under flowing N_2 gas, followed by heat-treatment (one-pot), (b) SiC fibres fabricated by iodisation under flowing N_2 gas and subsequent heat-treatment with exposure to air between the two processes (two-pot), and (c) SiC fibres fabricated by iodisation under flowing O_2 (21%)– N_2 (79%) mixed gas and subsequent heat-treatment with exposure to air between the two processes (two-pot). All the heat-treatments were conducted at 1300 °C for 1 h in a N_2 atmosphere. Peaks I, II, III, and V correspond to the SiC_4 (-16 ppm), SiO_2C_2 (-38 ppm), SiO_3C (-74 ppm), and SiO_4 (-109 ppm) chemical environmental units, respectively.

Conclusions

In summary, the reaction of iodine with PCS in air or in an inert gas atmosphere was studied to identify a method for minimising oxygen uptake during iodine curing in the fabrication of SiC fibres with low oxygen contents. The cross-linking reaction proceeds well by iodisation, even at room temperature, regardless of the presence of oxygen in the atmosphere. However, the PCS fibres iodised in air at room temperature still contained a significant amount of oxygen, owing to the long processing time (~24 h) despite the low temperature. On the other hand, the PCS fibres iodised in a N₂ atmosphere did not show any change in the oxygen contents. This, therefore, demonstrates that the process of cross-linking by iodisation itself constitutes oxygen-free curing. The main contribution of iodine to the cross-linking reaction is the cleavage of Si–H, C–H, and Si–Si bonds, and their simultaneous recombination to form –Si–C– or –C=C– networks. This mechanism involves the fragmentation of certain groups, such as –CH₃, from the PCS polymer chains, forming gaseous by-products and leaving behind reactive sites. These unstable sites, in an oxygenated atmosphere, allow the fibres to be easily oxidised during or after iodisation. Thus, to completely inhibit the incorporation of oxygen, after iodisation under inert gas, the fibres need to be treated thermally or chemically, in order to stabilise the unstable sites. In this study, through the one-pot process, we were able to fabricate SiC fibres with low oxygen contents. Apart from the effect of atmospheres on oxygen-contents, the low temperature process for curing will provide broaden applications of lower molecular-weight PCS polymer for the fabrication of fine SiC fibres (diameter < 1 μm) by electrospinning. Furthermore, the room temperature reaction occurred by iodization indicates the potential for wet curing, which is expected to be a simpler and more economic process.

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References

- O. Flores, R. K. Bordia, D. Nestler, W. Krenkel and G. Motz, *Adv. Eng. Mater.*, 2014, **16**, 621–636.
- J. Magnant, R. Pailler, Y. Le Petitcorps, L. Maillé, A. Guette, J. Marthe and E. Philippe, *J. Eur. Ceram. Soc.*, 2013, **33**, 181–190.
- G. Griffith, U.S. Department of Energy Accident Resistant SiC Clad Nuclear Fuel Development, INL/CON-11-23186, Idaho National Laboratory, 2011.

- S. Zhu, M. Mizuno, Y. Kagawa and Y. Mutoh, *Compos. Sci. Technol.*, 1999, **59**, 833–851.
- S. Subramanian, J. Steibel, D. Carper and T. Darkins Jr, Functionally gradient SiC/SiC ceramic matrix composites with tailored properties for turbine engine applications, US 8114799 B2, Feb 14 2012.
- Y. Katoh, K. Ozawa, C. Shih, T. Nozawa, R. J. Shinavski, A. Hasegawa and L. L. Snead, *J. Nucl. Mater.*, 2014, **448**, 448–476.
- Y. Katoh, L. L. Snead, T. Cheng, C. Shih, W. D. Lewis, T. Koyanagi, T. Hinoki, C. H. Henager Jr and M. Ferraris, *J. Nucl. Mater.*, 2014, **448**, 497–511.
- A. R. Bunsell and A. Piant, *J. Mater. Sci.*, 2006, **41**, 823–839.
- S. Yajima, J. Hayashi, M. Omori and K. Okamura, *Nature*, 1976, **261**, 683–685.
- S. Yajima, Y. Hasegawa, K. Okamura and T. Matsuzawa, *Nature*, 1978, **273**, 525–527.
- T. Ishikawa, S. Kajii, K. Matsunaga, T. Hogami, Y. Kohtoku and T. Nagasawa, *Science*, 1998, **282**, 1295–1297.
- T. Ishikawa, Y. Kohtoku, K. Kumagawa, T. Yamamura and T. Nagasawa, *Nature*, 1998, **391**, 773–775.
- K. Okamura, M. Sato and Y. Hasegawa, *J. Mater. Sci. Lett.*, 1983, **2**, 769–771.
- H. Ichikawa, H. Teranishi and T. Ishikawa, *J. Mater. Sci. Lett.*, 1987, **6**, 420–422.
- H. Q. Ly, R. Taylor, R. J. Day and F. Heatley, *J. Mater. Sci.*, 2001, **36**, 4037–4043.
- Z.-Y. Chu, C.-X. Feng, Y.-C. Song, Y.-D. Wang, X.-D. Li and J.-Y. Xiao, *Trans. Nonferrous Met. Soc. China*, 2002, **12**, 894–898.
- T. Taki, K. Okamura, M. Sato, T. Seguchi and S. Kawanishi, *J. Mater. Sci. Lett.*, 1988, **7**, 209–211.
- K. Okamura and T. Seguchi, *J. Inorg. Organomet. Polym.*, 1992, **2**, 171–179.
- H. Ichikawa, K. Okamura and T. Seguchi, In Oxygen-Free Ceramic Fibers from Organosilicon Precursors and E-beam Curing, No. CONF-9508127, American Ceramic Society: Westerville, OH, US, 1995.
- M. Narisawa, A. Idesaki, S. Kitano, K. Okamura, M. Sugimoto, T. Seguchi and M. Itoh, *J. Am. Ceram. Soc.*, 1999, **82**, 1045–1051.
- H. Ichikawa, *J. Ceram. Soc. Jpn.*, 2006, **114**, 455–460.
- Y. Hasegawa, *Compos. Sci. Technol.*, 1994, **51**, 161–166.
- W. Li, Y. C. Song and X. H. Mao, *J. Mater. Sci.*, 2006, **41**, 7011–7018.
- X. H. Mao, Y. C. Song, W. Li and D. X. Yang, *J. Appl. Polym. Sci.*, 2007, **105**, 1651–1657.
- W. H. Atwell, D. R. Bujalski, E. J. Joffre, G. E. Legrow, J. Lipowitz and J. A. Rabe (Dow Corning Corporation), Preparation of substantially polycrystalline silicon carbide fibers from polyorganosiloxanes, EP 0435065 B1, Mar 15, 1995.
- D. C. Deleeuw, J. Lipowitz and P. P. Lu (Dow Corning Corporation), Preparation of substantially crystalline silicon carbide fibers from polycarbosilane, EP 0438117 B1, Aug 19, 1998.
- W. Toreki, C. D. Batich, M. D. Sacks, M. Saleem and G. J. Choi, *MRS Proceedings*, 1992, **271**, 761.
- W. Toreki, C. D. Batich, M. D. Sacks, M. Saleem, G. J. Choi and A. A. Morrone, *Compos. Sci. Technol.*, 1994, **51**, 145–159.
- N. Andreas, *J. Eur. Ceram. Soc.*, 2014, **34**, 1487–1492.
- J. Hong, K.-Y. Cho, D.-G. Shin, J.-I. Kim, S.-T. Oh and D.-H. Riu, *J. Mater. Chem. A*, 2014, **2**, 2781–2793.
- J. Hong, K.-Y. Cho, D.-G. Shin, J.-I. Kim and D.-H. Riu, *J. Appl. Polym. Sci.*, 2015, **132**, 42687.
- S. Yajima, Y. Hasegawa, J. Hayashi and M. Imura, *J. Mater. Sci.*, 1978, **13**, 2569–2576.
- J. Chen, G. He, Z. Liao, B. Zeng, J. Ye, L. Chen, H. Xia and L. Zhang, *J. Appl. Polym. Sci.*, 2008, **108**, 3114–3121.

- 34 N. N. Earnshaw and A. Greenwood, *Chemistry of the Elements*, 2nd Edition, Elsevier, 1997, p 789.
- 35 R. A. Butera, D. H. Waldeck and E. P. Wagner, Determining g-Factors with Electron Paramagnetic Resonance, In *Rev. Chem.*, 2013, p 1430.
- 36 F. C. Grozema, R. W. J. Zijlstra, M. Swart and P. T. van Duijnen, *Int. J. Quantum Chem.*, 1999, **75**, 709–723.
- 37 J. T. Su and A. H. Zewail, *J. Phys. Chem. A*, 1998, **102**, 4082–4099.
- 38 H. Li, L. Zhang, L. Cheng, Y. Wang, Z. Yu, M. Huang, H. Tu and H. Xia, *J. Eur. Ceram. Soc.*, 2008, **28**, 887–891.
- 39 F. Cao, D.-P. Kim and X.-D. Li, *J. Mater. Chem.*, 2002, **12**, 1213–1217.
- 40 Y. Hasegawa, *J. Mater. Sci.*, 1989, **24**, 1177–1190.
- 41 G. D. Soraru, F. Babonneau and J. D. Mackenzie, *J. Mater. Sci.*, 1990, **25**, 3886–3893.
- 42 T. Taki, *J. Inorg. Organomet. Polym.*, 1992, **2**, 269–279.
- 43 F. Cao, X.-D. Li, J.-H. Ryu and D.-P. Kim, *J. Mater. Chem.*, 2003, **13**, 1914–1919.
- 44 D. L. Pavia, G. M. Lampman, G. S. Kriz and J. A. Vyvyan, *Nuclear Magnetic Resonance Spectroscopy*, In *Introduction to Spectroscopy*, 4th Edition, Cengage Learning, 2008.
- 45 A. Grill, *Annu. Rev. Mater. Res.*, 2009, **39**, 49–69.
- 46 J.-J. Kim, J.-H. Lee, Y.-J. Lee, W.-T. Kwon, S.-R. Kim, D.-J. Choi, H.-S. Kim and Y.-H. Kim, *J. Korean Ceram. Soc.*, 2011, **48**, 499–503.
- 47 S. Li and Y. Zhang, *J. Non-Cryst. Solids*, 2012, **358**, 687–692.
- 48 L. Anhua, C. Jianming, D. Shaonan, Y. Yanbo, L. Ling, L. Fengping and C. Lifu, *J. Mater. Chem. C*, 2014, **2**, 4980–4988.
- 49 H. J. Reich, Proton Chemical Shifts, <http://www.chem.wisc.edu/areas/reich/handouts/nmr-h/hdata.htm>
- 50 M. H. Brodsky and R. S. Title, *Phys. Rev. Lett.*, 1969, **23**, 581.
- 51 M. R. Mucalo, D. G. McGavin and N. B. Milestone, *J. Mater. Sci.*, 1997, **32**, 3271–3276.
- 52 O. Astakhov, F. Finger, R. Carius, A. Lambertz, Y. Petrusenko, V. Borysenko and D. Barankov, *J. Non-Cryst. Solids*, 2006, **352**, 1020–1023.
- 53 F. Cao, X.-D. Li, P. Peng, C.-X. Feng, J. Wang and D.-P. Kim, *J. Mater. Chem.*, 2002, **12**, 606–610.
- 54 S. J. Widgeon, S. Sen, G. Mera, E. Ionescu, R. Riedel and A. Navrotsky, *Chem. Mater.*, 2010, **22**, 6221–6228.