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Ceramics International 25 (1999) 49–60

CERAMICS
INTERNATIONAL

Effect of pre-pyrolysis heat treatment on the preparation of silicon carbide from a polycarbosilane precursor

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Received 2 May 1997; accepted 10 July 1997

Abstract

Polycarbosilane was synthesised directly from chloromethyltrichlorosilane and specimens were heat treated at 200, 300 and 400°C in nitrogen. The as-synthesised polymer and heat treated specimens were characterised using infra-red and Fourier transform infra-red spectroscopy, solid-state nuclear magnetic resonance and differential scanning calorimetry and were also subjected to thermogravimetric analysis in nitrogen. All types of specimens were pyrolysed in nitrogen at 1500°C. The ceramic residue obtained from thermogravimetric and pyrolysis experiments was characterised using X-ray diffraction and scanning electron microscopy. Heating the polymer before pyrolysis improved significantly the yield of the ceramic but the gain beyond 200°C was minimal. It was shown that the heat treatment initially caused the as-synthesised polymer to lose volatile oligomers and subsequently to cross-link. Pyrolysis at 900°C and subsequent crystallisation by further heating to 1500°C of the cross-linked polymer produced homogeneous and fine grained silicon carbide. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1. Introduction

Research into the preparation of ceramics from polymeric precursors is generating a great deal of interest because it allows the use of several attractive polymer forming techniques. However, high shrinkage and low yield during the conversion of the polymeric precursor to the ceramic have resulted in the slow development of this procedure and efforts have been limited to the preparation of ceramic fibres [1,2], coatings [3,4] and use as binders to process and join ceramics [5–7]. The reduction of shrinkage is being addressed by using active-filler-controlled pyrolysis of preceramic polymers and has been reviewed recently [8]. Increasing ceramic yield has received less attention [9,10]. Understanding the mechanism and structural changes during conversion of the polymer to the ceramic together with pre-treatment to tailor the structure of the precursor to a favourable form before pyrolysis is of crucial importance to the maximisation of the yield [11,12] although this concept has not been investigated systematically.

The major precursors for the ceramic silicon carbide (SiC) are Si-C backbone polymers, such as polycarbosilanes, which have the structural configuration $[\text{-Si–C-}]_n$ with an Si–C ratio of 1:1 and hydrogen as the substituent atom. These polymers can be pyrolysed with loss of only hydrogen giving the highest theoretical yield of stoichiometric SiC.

Polycarbosilanes can be synthesised by using indirect or direct methods. The former methods are based largely on the preparation of polycarbosilanes from polysilanes, in particular polydimethylsilane as used in the pioneering work of Yajima and co-workers [13,14]. These methods have been used mainly to prepare SiC fibres and in general are expensive, involve difficult and hazardous chemistry and, more importantly, give rise to a low ceramic yield.

The direct synthesis route for polycarbosilane as a precursor for SiC was first investigated in 1980 by Hasegawa et al. [15] adopting a method used by Fritz et al. [16] In this investigation, tetramethylsilane was recirculated in a quartz tube and the reaction products were collected, dissolved in n-hexane and filtered. Fractions with a boiling point up to 200°C was removed to collect polycarbosilane. However, it contained a high proportion of polydimethylcarbosilane and this led to a very low ceramic yield of 6.8 wt%. Several attempts have been made subsequently and Table 1 presents a summary of the key researches where polycarbosilane with a Si-C repeat unit has been synthesised directly.

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PII: S0272-8842(97)00088-6

It has been indicated [20–22] that polycarbosilane can be treated (e.g. with a catalyst, by heating) to modify its structure prior to pyrolysis in order to increase the yield of ceramic obtained from it. In this paper, a systematic investigation has been carried out to optimise the heat treatment of a polycarbosilane synthesised directly from chloromethyltrichlorosilane in order to maximise its conversion to the ceramic.

Table 1
Details of attempts leading to the direct synthesis of polycarbosilane or its derivatives

Polycarbosilane or derivative	Polymerisation route	Structure	Solubility	Molecular weight $\bar{M}_n$ unless otherwise stated	Ceramic yield wt%	Reference
$-CH_2-SiH_2-$	Ring opening	Linear	–	–	85	17
	Grignard coupling	Branched	Soluble	745 ($\bar{M}_w$)	80	18
$-CH_2-\overset{\overset{CH_3}{\mid}}{Si}H-$	Ring opening	Linear	Soluble	2100	5	19
		Linear	Soluble	6000	10	20
		Linear	Soluble	35 000	20	20
		Crosslinked at 400°C in N_2	Insoluble	–	66	20
$-CH_2-\overset{\overset{CH_3}{\mid}}{Si}Cl-$	Ring opening	Crosslinked with Na	Soluble	4250	11.4	19
			Insoluble	–	77.6	19
		Crosslinked with CH_2NH_2	Partially Insoluble	3940	53.0	19
		Crosslinked by hydrolysis	Soluble	2960	54.3	19
$CH_2–Si(HCH_3)_2–$	Dehalocoupling	Linear	Soluble	–	0	10
	Ring opening	Linear	Soluble	260 000	0	20
	Ring opening	Linear	Soluble	250 000	3.5	19

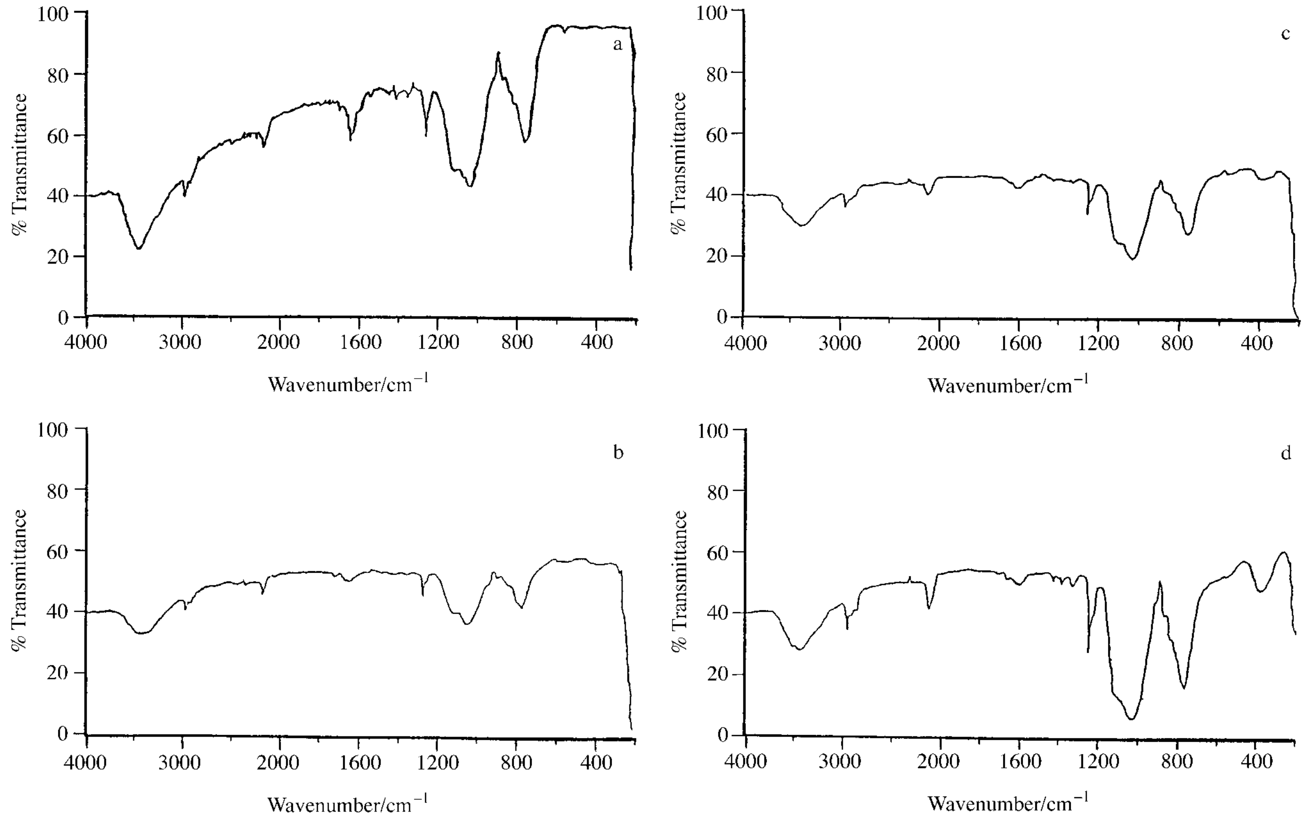


Fig. 1. IR traces of (a) the as-synthesised polymer and specimens heat treated at (b) 200°C, (c) 300°C and (d) 400°C.

2. Experimental details

2.1. Synthesis of polycarbosilane

A Grignard reaction was used initially and three stages were involved. First, polychlorocarbosilane was prepared. Second, the polychlorocarbosilane was reduced to polycarbosilane and finally separated from the other products.

200 ml of dry ether and 6 g of Mg filings (specially prepared for a Grignard reaction) were placed in a 500 ml, two-necked and round-bottomed flask which had a reflux condenser attached to it; 25.2 ml of chloromethylytrichlorosilane ($ClCH_2SiCl_3$) was added using a syringe over a period of 2 h. Several drops of methyl iodide were added to initiate the reaction which was carried out in flowing nitrogen. An oil bath at 50°C was used to maintain the reaction. The reactants were stirred continuously and refluxed for 24 h. During this time, a gradual colour change to yellowish-brown occurred. Large amounts of $MgCl_2$ were precipitated and polychlorocarbosilane was produced.

More ether was added as required so that a fluid-like consistency was maintained. Then 2.46 ml of lithium aluminium hydride ($LiAlH_4$), suspended in ether, was added over 30 min to the flask to reduce polychlorocarbosilane to polycarbosilane. The flask was kept at 10°C by placing ice cubes in sealed plastic bags and cooling the oil bath so that the required temperature could be reached without the risk of the $LiAlH_4$ contacting water. Rapid stirring (using a magnetic stirrer) was necessary during the addition of $LiAlH_4$ to dissipate the heat of the reaction. A light grey suspension of $LiAlH_4$, polymer and ether slurry was obtained and refluxed overnight under nitrogen.

Ten millilitres of 3M HCl was added in a drop-wise fashion to the rapidly stirred $LiAlH_4$, polymer and ether slurry. At first, each drop produced a vigorous reaction. When the reactivity decreased the remainder of the acid was poured in. The addition of the acid leads to the dissolution of Li and Al salts. The ether layer was separated and washed with dilute HCl. A cloudy yellow oil was obtained when the ether was removed. This oil was redissolved in pentane which expels small amounts

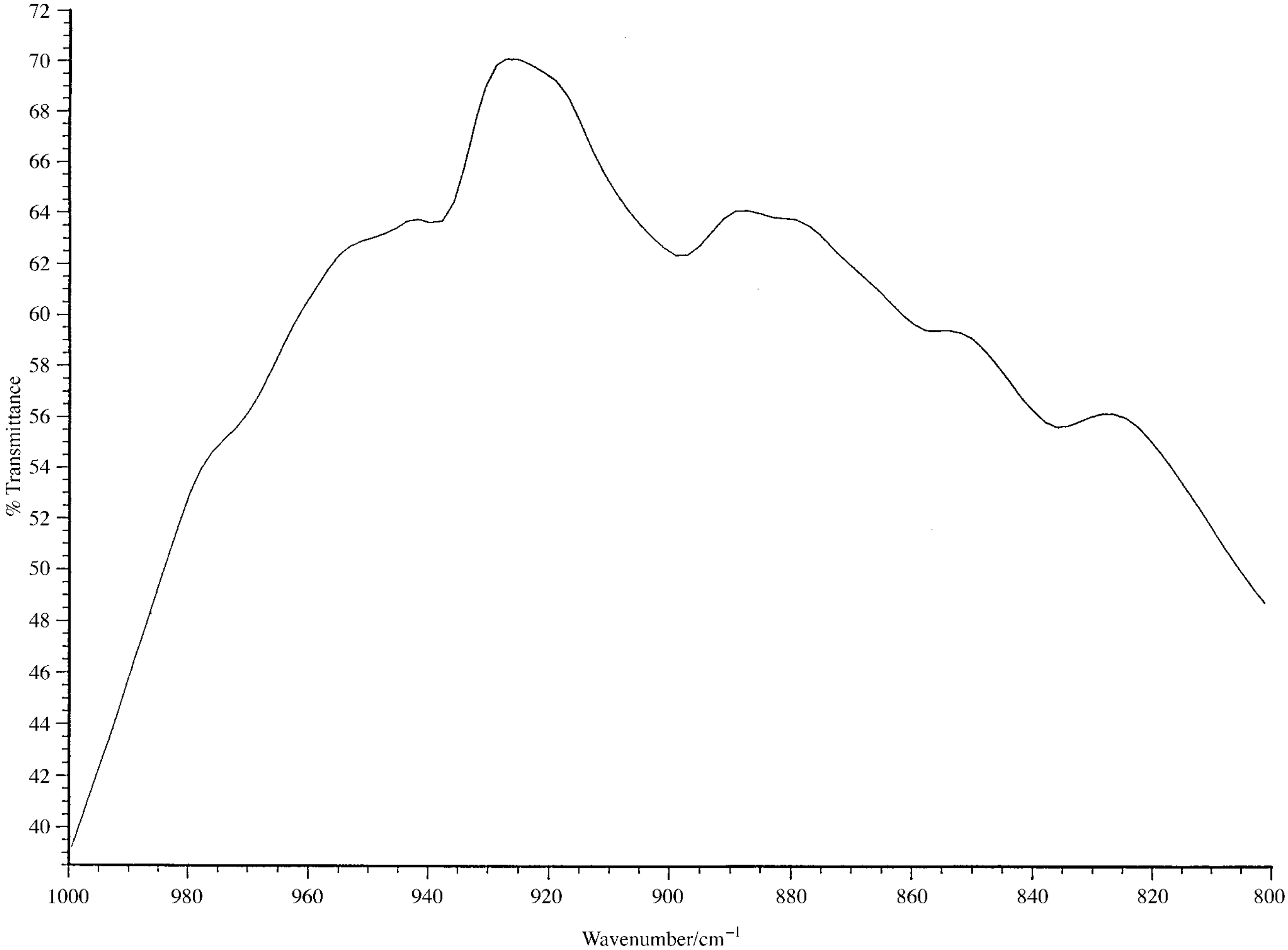


Fig. 2. FT-IR trace of the as-synthesised polymer in the wavenumber range 800–1000 cm^{-1}.

of emulsified water and residual aluminium complexes. After settling, a viscous transparent pale yellow polymer, i.e. polycarbosilane, was obtained.

2.2. Heat treatment

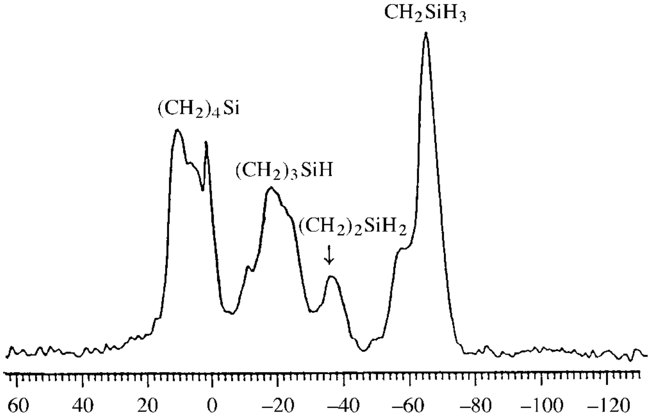
The polycarbosilane synthesised was heated in an oven at 10°C min^{-1} from room temperature to 200, 300 and 400°C, respectively, in a nitrogen atmosphere (a flow rate of 0.5 ml min^{-1} was used).

2.3. Characterisation of the polycarbosilanes

Infra-red (IR) spectroscopy studies were carried out on the as-synthesised polycarbosilane and heat-treated polycarbosilanes using a Perkin-Elmer IR spectrophotometer. For this analysis some polycarbosilane was placed in a drying cabinet containing silica-gel at 100°C to remove any moisture and solvent retained from the synthesis. It was then smeared onto a KBr disc and placed in the spectrophotometer. The scanner was used in transmission mode in the wavenumber range 400–4000 cm^{-1} and each scan lasted for 6 min. The slit gap was maintained at 10 mm.

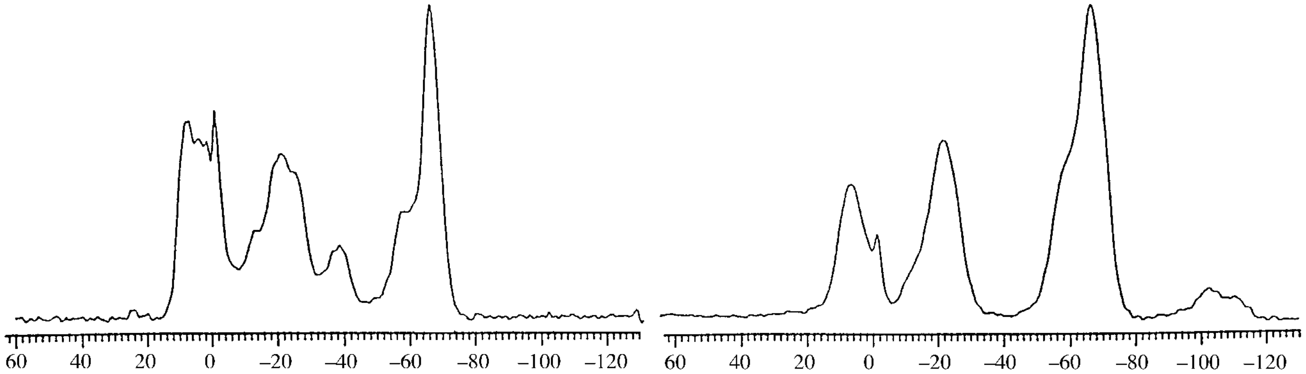
In the case of the heat-treated polymer, the preparation of specimens for IR spectroscopy was different to the as-synthesised polycarbosilane (these differences were necessary in order to obtain satisfactory traces). One milligramme of each heat-treated polymer was ground and mixed with 150 g of KBr powder. This mixture was then pressed into small pellets using an 8 mm diameter die under a pressure of 100 kPa. The scanning conditions were similar to those used for the as-synthesised polymer. A similar method was used to prepare a pellet of the as-synthesised polymer for Fourier-transform infra-red spectroscopy (FT-IR). The pellet was placed in the sample holder of a Nicolet FT-IR spectrometer and scanned in the wavenumber range 800–1000 cm^{-1} to investigate further the spectrum in this region. The spectrum was analysed using a computer program called OMNIC. In both IR and FT-IR studies any peaks resulting from the moisture adsorbed by KBr were discounted.

Solid-state nuclear magnetic resonance (NMR) experiments on each specimen were carried out at the Industrial Research Laboratories of the University of Durham, UK using a Varian Unityplus spectrometer operating at 75.43 MHz for carbon-13 and 59.58 MHz



As-synthesised

Heat treated to 300°C



Heat treated to 200°C

Heat treated to 400°C

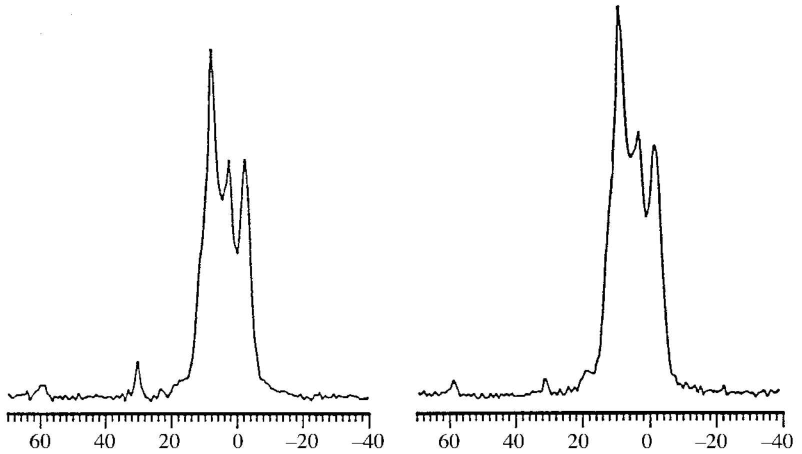
Fig. 3. Silicon-29 solid state NMR traces for the as-synthesised polymer and heat-treated specimens. The x-axis represents chemical shift measured in ppm.

for silicon-29. A Doty Scientific magic-angle spinning probe taking a 7 mm outer diameter zirconia rotor with Kel-F end-caps was used. All the experiments were of the cross-polarisation magic-angle spinning (CPMAS) type and were carried out with a contact time of 3 ms for carbon-13, 4 ms for silicon-29 and a spin rate of 4760 Hz for both. In the case of carbon-13 spectra the acquisition conditions were a frequency of 75 MHz, spectral width 30 GHz, acquisition time 10 ms, relaxation time 1 s and number of repetitions 1500. In the case of silicon-29 spectra the acquisition conditions were identical, except that the frequency was 60 MHz and the number of repetitions was 1000. Spectral referencing has been done with reference to an external sample of tetramethylsilane in all cases. The as-synthesised polycarbosilane was dried in air before testing.

A Perkin-Elmer DSC7 machine was used for the thermal analysis of both the as-synthesised polymers and heat-treated specimens. Approximately 8 mg of material was placed in the sample pan of the machine and heated to 100°C for 10 min to expel any moisture and cooled rapidly to room temperature. This pretreatment was not required in the case of the heat-treated specimens. Subsequently, thermal analysis was

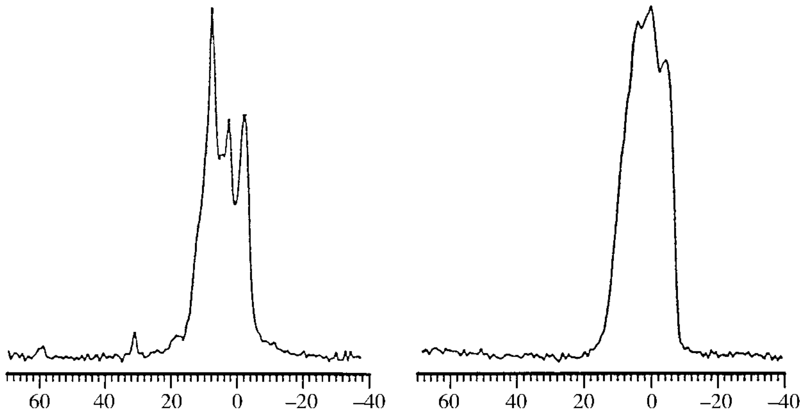
Table 2
Absorption peaks identified in the as-synthesised polymer, IR trace (Fig. 1(a)) and FT-IR trace (Fig. 2) and Refs. [5,15,23,26–29] were used for this identification

Wavenumber (cm^{-1})	Identity
3400	Combined and adsorbed water
2950	CH_3 stretching
2160	Si-H stretching
1640	Free water
1275	Si-CH_3 deformation
1125	Si-O-C and/or Si-O-Si open chain stretching
1050	CH_2 deformation in Si-CH_2-Si
900	Si-H_2 or Si-H_3 stretching
835	Si-H stretching
780	Si-CH_3 stretching



As-synthesised

Heat treated to 300°C



Heat treated to 200°C

Heat treated to 400°C

Fig. 4. Carbon-13 solid state NMR traces for the as-synthesised polymer and heat-treated specimens. The x-axis represents chemical shift measured in ppm.

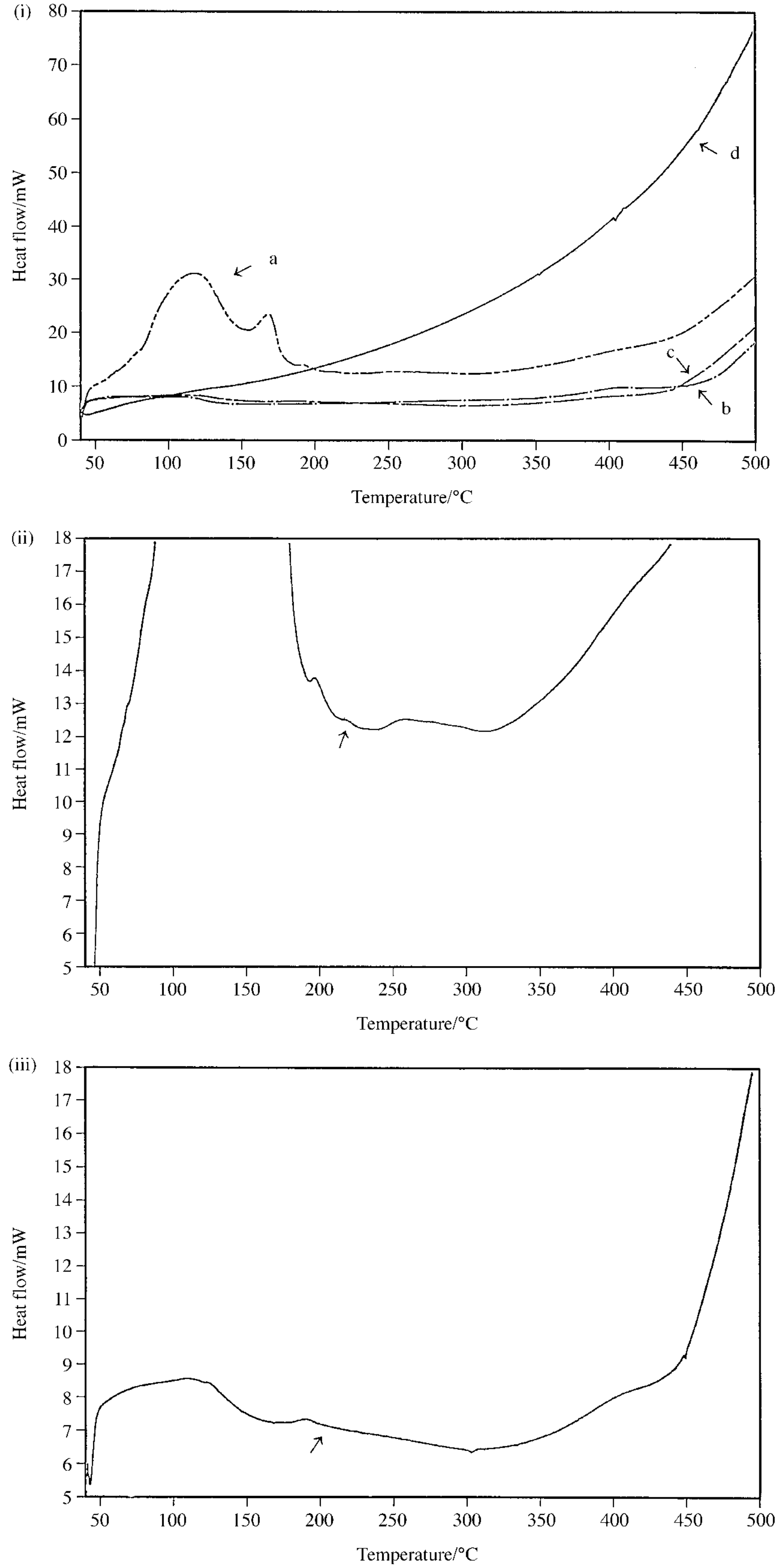


Fig. 5. (i) DSC traces of (a) the as-synthesised polymer and specimens heat treated at (b) 200°C, (c) 300°C and (d) 400°C. (ii) Exothermic peak (see arrow) in the DSC trace of the as-synthesised polymer. (iii) Exothermic peak (see arrow, much diminished) in the DSC trace of the polymer heat treated at 200°C.

started and a heating ramp of 20°C min^{-1} was applied from 30°C to 500°C.

Thermogravimetric analysis was used to investigate the breakdown of as-synthesised polycarbosilane and heat-treated specimens to ceramic. A small quantity of material was placed in the sample pan of the thermogravimetric balance. A heating ramp of 10°C min^{-1} from 30°C to 900°C was used. During each experiment 0.5 ml min^{-1} of nitrogen gas was passed through the heating column to maintain an inert atmosphere.

2.4. Pyrolysis

Pyrolysis of as-synthesised and heat-treated polymer specimens was carried out in a tube furnace with 0.5 ml min^{-1} of nitrogen passing through continuously. Specimens were placed in the tube furnace and heated from 70°C at a rate of 2°C min^{-1} to 1500°C. This upper temperature was maintained for 120 min after which a cooling ramp of 30°C min^{-1} to 70°C was applied. In the case of as-synthesised polymer specimens, these were

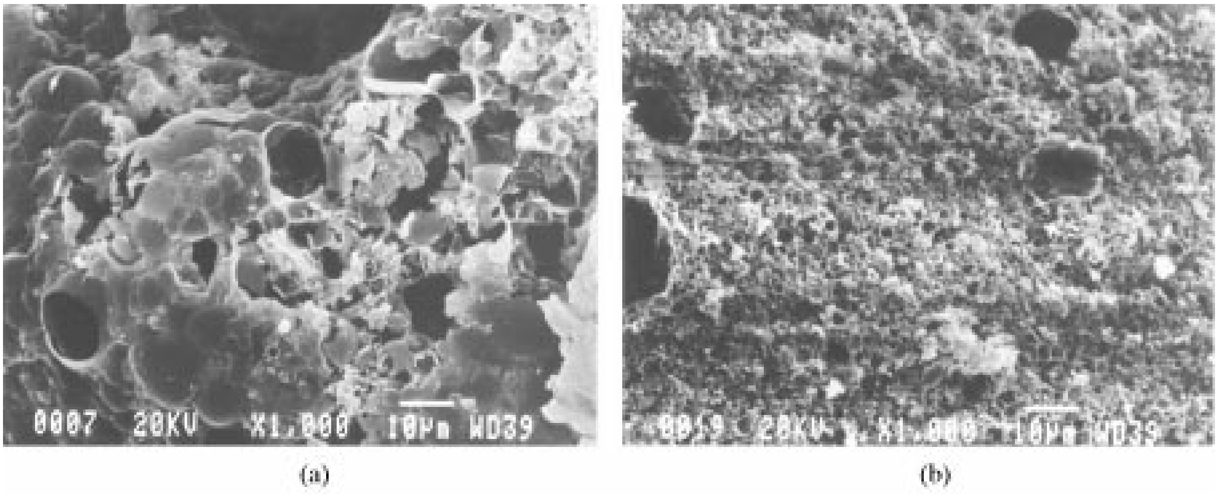


Fig. 6. Scanning electron micrographs of (a) the as-synthesised polymer and (b) polymer heat treated to 400°C.

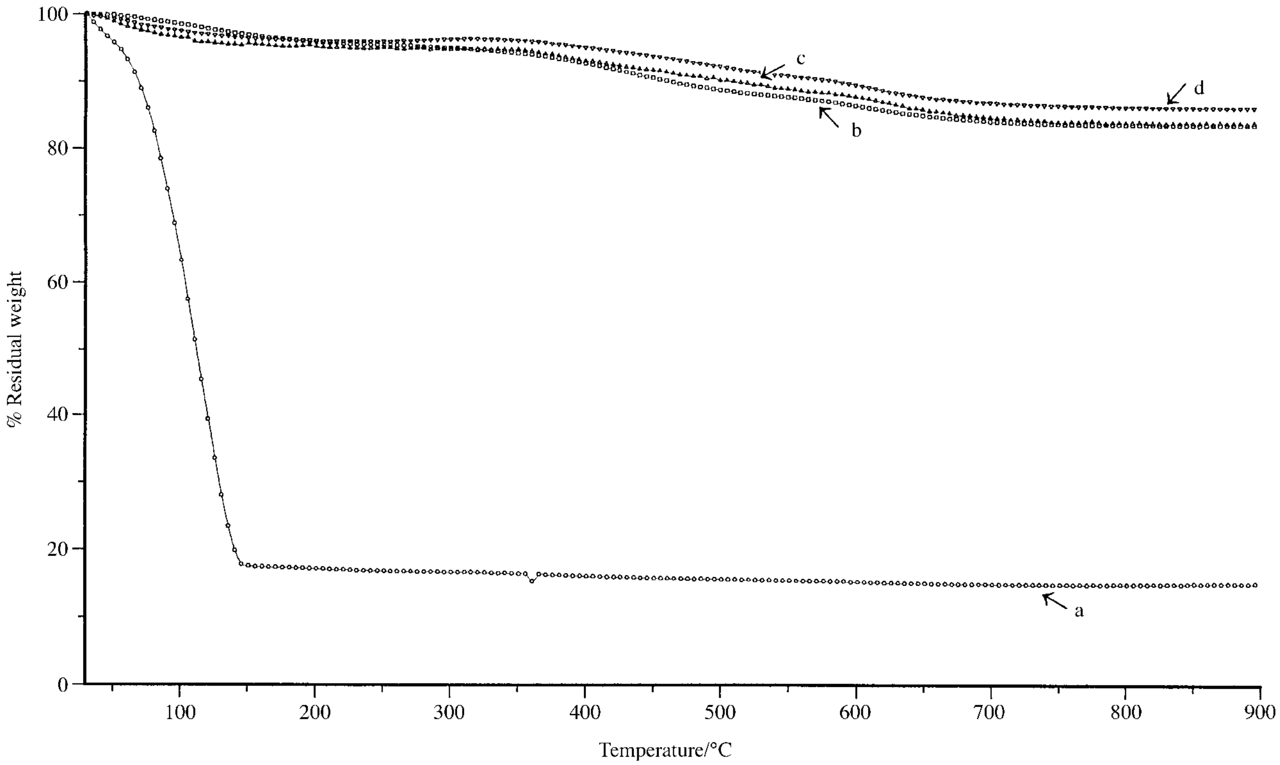


Fig. 7. Thermogravimetric traces of (a) the as-synthesised polymer and specimens heat treated at (b) 200°C, (c) 300°C and (d) 400°C.

heated to 100°C for 10 min (under nitrogen in the furnace) before the heating ramp was applied in order to remove any moisture and solvent retained from the synthesis. The ceramic residue produced from thermogravimetric studies and pyrolysis experiments were characterised as described below.

2.5. *Characterisation of the ceramic*

Residues were subjected to X-ray diffractometry. Specimens were prepared by grinding the residue obtained from thermogravimetric and pyrolysis experiments. A small amount of industrial methylated spirits (IMS) was added during grinding to aid preparation and a small sample of the resulting paste was placed on a single crystal silicon plate which was attached to a 20 mm diameter stainless steel stub. The IMS was allowed to evaporate before X-ray analysis. X-ray studies were conducted using a Philips X-ray diffractometer, CuKα radiation of wavelength 0.15406 nm and a Ni filter. The X-ray diffractometer was operated at 35 kV and 20 mA. The scan range was from 10° to 90° with a step size of 0.021° and a scan speed of $0.02^\circ\ s^{-1}$.

Residues were also examined by scanning electron microscopy. A Cambridge J840 microscope was used and small amounts of ground residue were placed on stainless steel stubs which were sputter coated with gold to prevent charging during examination.

3. Results and discussion

3.1. *As-synthesised polymer*

The method used to synthesise the polymer is very similar to that reported previously [23,24] but the total time taken has been reduced significantly by over 60% to 2 days. This was possible by reducing the time taken to prepare polychlorocarbosilane in the first stage of the synthesis. The safety hazards accompanying the synthesis has also been reduced by using magnetic stirrers (instead of mechanical stirrers) and oil baths (instead of water baths). These measures reduce the possibility of sparks and the possibility of $LiAlH_4$ reacting explosively with water, respectively. The yield of polymer was 34 wt%. This route can yield about 40 wt% polymer [25] and the slightly lower value achieved is probably due to the reduced time of synthesis. An appreciable quantity of product is possibly trapped in the large amount of $MgCl_2$ precipitated and is lost during transfer from the first stage to the second, resulting in the low yield. The yield can be improved to about 60 wt% by avoiding transfer [25].

IR, FT-IR and NMR results help to understand the structure of the polymers. The IR trace (Fig. 1) and the FT-IR trace (Fig. 2), which defines the peaks in the wavenumber range 800–1000 cm^{-1} more clearly (helping identification), of the as-synthesised polymer is consistent with the highly branched hydridopolycarbosilane $(SiH_xCH_2)_n$ where $x = 0,1,2,3$, reported previously [23]. As indicated in Table 2, the strong absorption peak at about 1050 cm^{-1} is caused by the CH_2 deformation in Si-CH_2-Si and is characteristic of the alternating Si-CH_2-Si structure of this polymer. Absorption peaks at about 2160 and 835 cm^{-1} (SiH) and 900 cm^{-1} (SiH_2 or SiH_3) are also characteristic of this branched polymer. The absence of an absorption peak between 1120 cm^{-1} and 1180 cm^{-1} (Fig. 1) for the $SiCH_2CH_2Si$ functionality indicates that head-to-head coupling is largely absent. The as-synthesised polymer adsorbs moisture (see Table 2) but is stable in air at room temperature for several hours before it starts to degrade. Storing the polymer under pentane extended considerably the life of the as-synthesised polymer.

The silicon-29 solid state NMR spectrum of the as-synthesised polymer (Fig. 3) shows four groups of peaks as a result of the $(CH_2)_4Si$, $(CH_2)_3SiH$, $(CH_2)_2SiH_2$ and CH_2SiH_3 units in the hydridopolycarbosilane and these findings are consistent with those expected in this type of highly branched polymer [18]. The major feature of the carbon-13 solid state NMR spectrum of the as-synthesised polymer (Fig. 4) is several peaks in the range -12 to $+8$ ppm expected for this polymer [18]. These are caused by the several Si-CH_2-Si environment which prevails in the structure of this polymer.

3.2. *Effect of heat treatment*

The comparison of the DSC traces of the as-synthesised polymer and the specimens heated at 200°C, shows that the bimodal softening endotherms between 100 and 200°C in the former disappear due to the heat treatment (Fig. 5(i)). This is caused by the loss of volatile oligomers present in the as-synthesised polymer (also see text below on thermogravimetric studies). DSC traces of the four types of specimen (Fig. 5(i)) indicate significant changes in the exothermic behaviour present between 200 and 400°C in the as-synthesised polymer. It is clear that the exothermic peak present in the as-synthesised polymer (Fig. 5(ii)) has diminished significantly in the sample heat treated to 200°C (Fig. 5(iii)). This peak is not present in the sample heat treated at 400°C (Fig. 5(i)). These observations indicate curing of the polymer producing cross-linked polycarbosilane [30].

The heat treatment which ultimately causes cross-linking does not show any significant changes in the positions of the absorption peaks of the IR spectrum of the as-synthesised polymer (Fig. 1). However, comparison of the solid state NMR spectra of the as-synthesised polymer and the specimen heat treated at 400°C shows some differences. The silicon-29 spectra

(Fig. 3) show sharper $(CH_2)_3SiH$ and $(CH_2)_4Si$ peaks. The $(CH_2)_2SiH_2$ peak has largely disappeared in the sample heated to 400°C (Fig. 3). The carbon-13 spectra (Fig. 4) of the specimen heated to 400°C also show a more distinct, sharper peak associated with Si-CH_2-Si. Thus both SiH_x and CH_2 groups are involved in the cross-linking process. It supports the arguments of Interrante et al. [31] that, on heating, this type of hydridopolycarbosilane cross-links, initially, by the formation of Si-Si inter-chain bonds by the loss of H_2 from SiH_x, groups, followed by their rapid rearrangement to form Si-CH_2-Si linkages. The effect of the heat treatments on the texture of the polymer are worth noting (Fig. 6(a) and (b)). The foam-like as-synthesised polymer (Fig. 6(a)) has changed to a sample having a more regular porosity of $< 5\,\mu m$ in the cross-linked state (Fig. 6(b)).

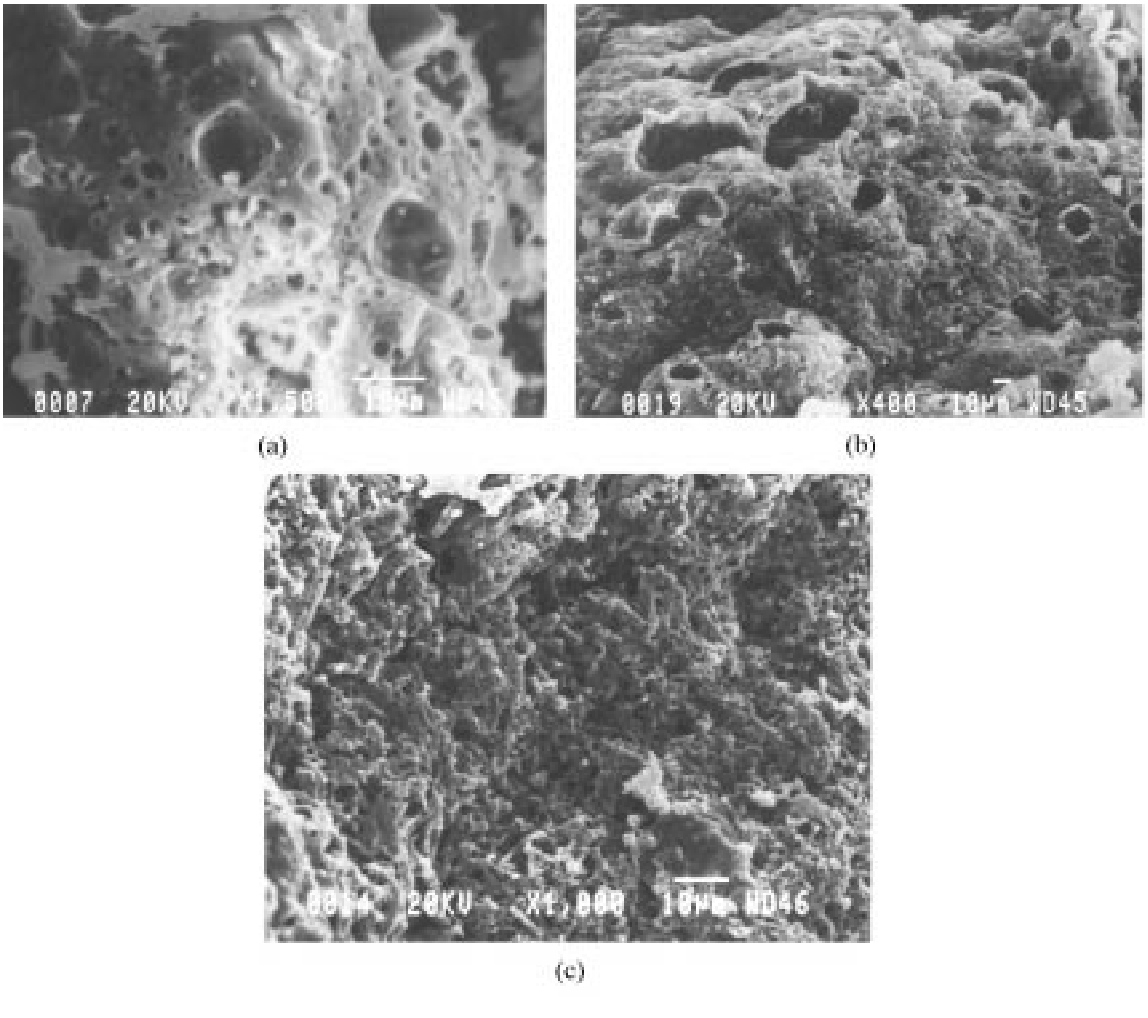
This type of polycarbosilane can also be cross-linked chemically [25]. This requires the use of catalysts containing Ti and therefore suffers with the disadvantage of requiring inert reaction conditions. In addition, TiC impurities detrimental to the performance of the ceramic could be unavoidable in the final microstructure.

Table 3
Weight loss during heat treatment of the as-synthesised polymer

Heat treatment temperature (°C)	Weight loss (%)
200	33
300	53
400	56

3.3. Conversion to ceramic

Thermogravimetric analysis (Fig. 7) indicates that the as-synthesised polymer shows an overall weight loss of 80.46%. A large proportion of this weight loss occurs at about 130°C, due to the burn-off of the volatile oligomers (see correlation with DSC trace in Fig. 5(i)). In contrast, the samples heated to 200°C shows a weight loss of only 16.37%. The samples heated to 300 and



(a) (b) (c)

Fig. 8. Scanning electron micrographs of pyrolysed residue obtained from (a) as-synthesised polymer and specimens heat treated at (b) 300°C and (c) 400°C.

400°C also show a very similar weight loss. Therefore, by pre-heating the sample to 200°C a higher wt% of residue is obtained and, more importantly, from a ceramic synthesis point of view, the considerable weight loss and shrinkage associated with the pyrolysis is avoided. Thus, heat treatment above 200°C is not very beneficial in increasing the ceramic yield. However, weighing of the samples before and after heat treatment (Table 3) shows that a considerable weight loss occurs as cross-linking proceeds well beyond 200°C. In fact, the weight loss due to heat treatment stabilises only between 300 and 400°C. This is consistent with the explanation of the structural changes in the as-synthesised polymer due to cross-linking where the loss of hydrogen takes place (discussed above). The ceramic residue of the polymer heat treated to 400°C is more homogeneous and granular in appearance compared with those pyrolysed after heat treatment at lower temperatures (Fig. 8(a)–(c)).

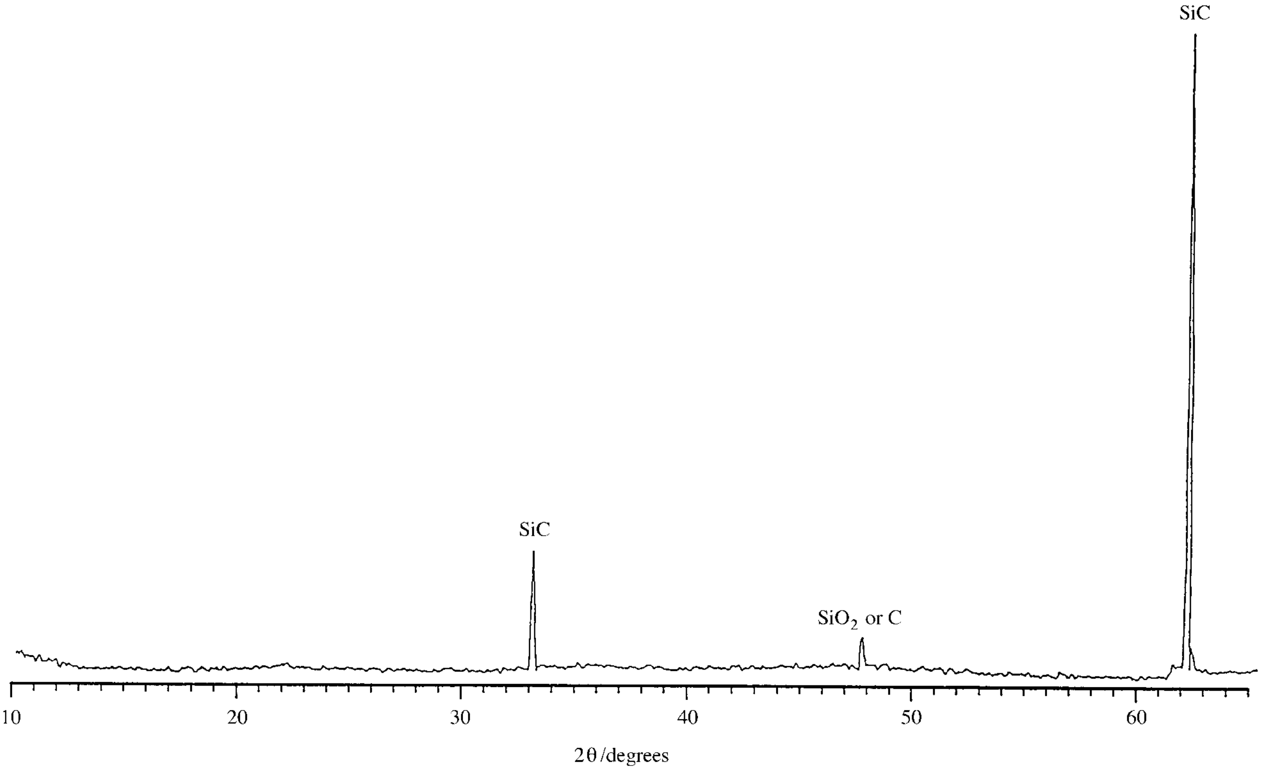
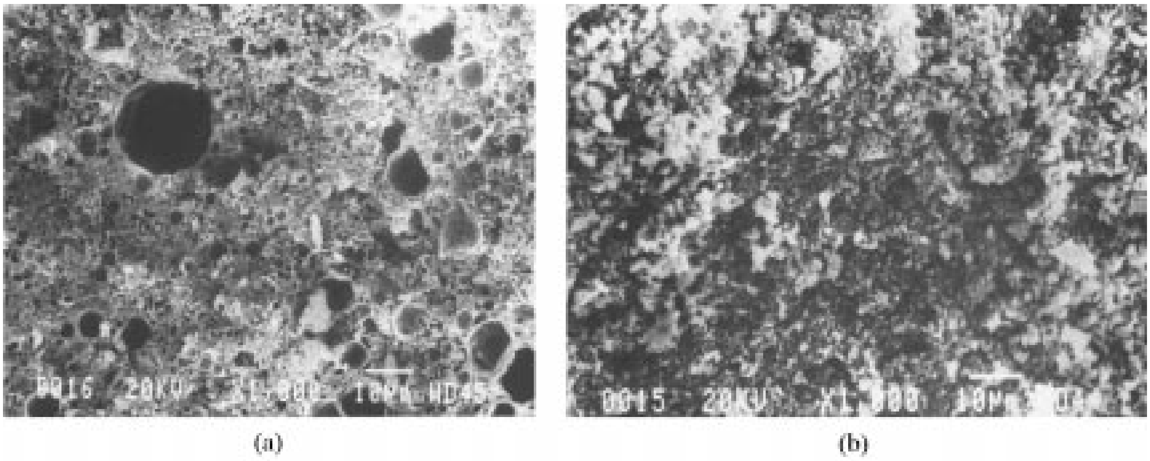


Fig. 9. Typical XRD trace of the ceramic residue after crystallisation at 1500°C.



(a) (b)

Fig. 10. Scanning electron micrographs of crystallised ceramic residue obtained from the (a) as-synthesised polymer and (b) specimen heat treated at 400°C.

This is a consequence of using a more stable material (sample heated to 400°C) before the pyrolysis stage.

XRD results showed that pyrolysis of the polymer to 1500°C produced crystalline SiC containing some C and/or SiO_2 as impurities (Fig. 9). The optimisation of the pyrolysis route in order to avoid impurities was beyond the scope of the work. The XRD traces of the thermogravimetric residues did not show any sharp peaks and the SiC produced at this stage (900°C) is largely amorphous. These traces were also quite similar indicating that the heat treatment did not have a significant bearing on the evolution of the structure of the SiC. However, it is clear that the final ceramic produced from polymer heat-treated at 400°C contains fewer large voids and shows finer particles of SiC (Fig. 10), similar to the observations made on the residue from thermogravimetric studies (Fig. 8).

4. Conclusions

A hydridopolycarbosilane was synthesised, characterised and subjected to heat treatment before pyrolytic conversion and crystallisation to SiC. Heating the polymer to 200°C prior to pyrolysis caused the loss of volatile oligomers in the polymer and this was a major reason for increasing the SiC yield by about five times. Pre-pyrolysis heat treatment at higher temperatures (up to 400°C) caused the polycarbosilane to cross-link and although no further significant increase in the SiC yield resulted, the ceramic microstructure obtained was more homogeneous and granular in appearance.

Acknowledgements

The authors thank Brunel University for seedcorn funding which enabled Ms Matthews to carry out this work. The technical help given by Mrs T. Banerjee and Dr S. Woodisse is gratefully acknowledged. Mrs K. Goddard is thanked for typing this manuscript. Mr K. Batchelor and Mrs R. Pratt are thanked for help in the preparation of some figures.

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