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Polysilacyclobutasilazanes: pre-ceramic polymers for the preparation of sintered silicon carbide monoliths

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A family of pre-ceramic polymers based upon silacyclobutasilazanes was prepared. Upon heating to 200–250 °C the polymers crosslink to intractable resins through a ring-opening polymerization of the silacyclobutyl group. In an inert atmosphere the polymers convert to Si–C–N–O chars upon pyrolysis to 1200 °C. At higher temperatures (> 1400 °C) the Si–C–N–O chars loose nitrogen and carbon monoxide to give stable chars containing only silicon carbide and carbon. The polymers were used as binders in press-and-sinter and transfer-moulding applications to give silicon carbide monoliths with sintered densities above 3.13 g cm^{-3} and four-point flexural strengths above 70 kpsi (483 MPa).

1. Introduction

Since the pioneering work of Alliegro and co-workers [1, 2], Antonova *et al.* [3]. Prochazka [4–8] and others [9, 10] numerous literature reports detailing different methods, processes and mechanisms to sinter silicon carbide powders have appeared. From these reports, the following requirements have emerged for pressureless sintering: (i) high purity, spherical, monodisperse, sub-micrometre silicon carbide powders are necessary; (ii) approximately 0.3–2.0 wt % of added carbon is required to remove oxides from the powder surface and inhibit grain growth; and (iii) a sintering aid (dopant) in combination with sufficient excess carbon is necessary to balance intergranular and internal diffusion (grain growth) processes.

Currently, most sintered silicon carbide articles are manufactured by employing the above requirements in a die-pressing, injection-moulding or slip-casting process. In a typical procedure, a sub-micrometre SiC powder is blended with approximately 0.5 wt % of amorphous boron, 2–6 wt % of phenolic resin and 0–25 wt % of other additives. This mixture is then moulded to the desired shape, and the moulded article is heated to approximately 2100 °C in a combination of vacuum and argon atmospheres for sintering. Because phenolic resin gives a 45–50% yield of elemental carbon after pyrolysis, resin concentrations higher than 6 wt % deposit sufficient excess carbon in the silicon carbide monolith to affect its physical properties. Therefore, additional fugitive additives such as waxes, lubricants, coupling agents and binders are often incorporated to tailor the properties of the blend, such as handleability, flow under pressure and machinability, to the shape-forming process. When fugitive additives are employed extreme care must be taken in the initial stages of the firing cycle to remove them, while retaining the shape of the part. These debinding steps are often 40–200 h long.

The substitution of traditional binders and additives by pre-ceramic polymers potentially eliminates many of the fabrication problems in both die-pressing and injection-moulding processes. By varying the functionality, structure, molecular weight, polymer backbone, etc., pre-ceramic polymers with widely disparate properties, char yields and char compositions can be made. As such, the potential for tailoring a pre-ceramic polymer for optimum performance for a variety of fabrication processes exists. Thus, the performance advantages of additives could be maintained while eliminating extraneous impurities and processing steps. Despite this, there is a paucity of literature reports detailing the use of pre-ceramic polymers in traditional fabrication processes. Since the initial synthesis of polycarbosilane by Yajima *et al.* [11, 12], numerous pre-ceramic polymers have been developed (for a review see Baney and Chandra [13]). Of these, polycarbosilane [14–20], polysilastyrene [21, 22],* a borosilicon polymer consisting of $SiMe_2$–CH_2 and BMe–NPh units [23] and a polydiphenylborosiloxane [24–26] are the only polymers actually demonstrated as binders for ceramic powders and of these, only the borosilicon and ($SiMe_2$–CH_2)–(BMe–NPh) copolymer have been used to give sintered bodies.

This paper describes the synthesis, characterization and use of a family of polymers, polysilacyclobutasilazanes, for the production of sintered silicon carbide monoliths. The polymers are unique in that they possess a strained silacyclobutyl ring pendant to a Si–N polymer backbone. Upon heating, the polymers

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* Shin Nisso Kako Co. Ltd. Tokyo, is marketing a mixture of SiC powder, polysilastyrene polymer and an organic lubricant for injection-moulding applications.

cure through a non-oxidative ring-opening polymerization of the silacyclobutyl ring. Consequently, deep-section cures are obtained in shapes made from polymer–powder mixtures. Furthermore, a wide variety of other alkyl and aryl groups are compatible with the silacyclobutyl ring. These can be used to tailor the polymer's rheology and char composition to a specific forming process for pressureless sintering.

2. Experimental procedure

2.1. Polymer synthesis and characterization

All reactions were performed in an argon atmosphere with oven-dried glassware unless otherwise noted. The silacyclobutasilazane polymers were prepared according to the procedure of Burns [27–29]. ^{1}H NMR spectra were recorded on either a Varian EM360 or EM390 spectrometer. FTIR spectra were recorded on a Nicolet 5 DX spectrometer. Gel permeation chromatography (GPC) data were obtained on a Waters GPC equipped with a model 600E systems controller, a model 490 u.v. and model 410 differential refractometer detectors. All values are relative to polystyrene. Thermomechanical analysis (TMA) and thermogravimetric analysis (TGA) data were recorded on a DuPont 940 thermomechanical analyser and an Omnitherm thermogravimetric analyser interfaced to an Omnitherm 2066 computer. Portions of these data are summarized in Table I.

2.1.1. Preparation of polysilacyclobutasilazane (PSCBZ)

Ammonia was rapidly bubbled through a solution of 400 g (2.84 mol) of 1,1-dichloro-1-silacyclobutane [30] in 2.5 l of CH_2Cl_2 at − 20 to − 40 °C for several hours. The reaction was warmed to room temperature and filtered through a sintered glass frit. Concentration of the filtrate gave 219 g (91% yield) of product.

Example I. $(C_3H_6SiNH)_n$. ^{1}H NMR ($CDCl_3$): δ 1.36 (m, 4H), 1.77 (m, 2H). I.r. (thin film): 3371 (s), 2961 (s), 2930 (s), 2868 (m), 2783 (w), 1451 (w), 1408 (m), 1387 (m), 1211 (s), 1180 (s), 1115 (s), 1064 (m), 1033 (w), 957 (s), 922 (m), 757 (w), 689 (s) cm^{-1}.

2.1.2. General procedure for the preparation of silacylclobutasilazanes via an equilibration/ammonolysis route

A three-necked round-bottom flask fitted with a mechanical stirrer, a gas inlet tube and a Dewar condenser with a nitrogen outlet was charged with a solution of PSCBZ in methylene chloride. The reaction was cooled to between − 15 and − 20 °C (limited dry ice in acetone) and the chlorosilane added in one portion. After stirring for a few minutes at approximately −15 °C, the reaction mixture was warmed to room temperature. After equilibrating, the solution was cooled to − 20 °C and excess ammonia bubbled through the solution. The solution was warmed to room temperature and filtered. Concentration of the filtrate at reduced pressure gave the desired polymer. Using this procedure, the following polymers were prepared:

Example II. $[C_3H_6SiNH]_{0.79}[HSi(NH)_{1.5}]_{0.21}$. 9.18 g (0.108 equivalent) of PSCBZ and 3.758 g (0.028 mol) of $HSiCl_3$ gave 8.30 g of a viscous oil (77.8 % yield). ^{1}H NMR ($CDCl_3$): δ 1.37 (m), 1.70 (m), 4.80 (broad s). I.r. (thin film): 3378 (s), 2968 (s), 2923 (s), 2869(m), 2147(s), 1450(w), 1409(m), 1393(m), 1196(s), 1174(s), 1123(s), 1034(m), 952(s), 691 (m) cm^{-1}.

Example III. $[C_3H_6SiNH]_{0.65}[HSi(NH)_{1.5}]_{0.35}$. 24.085 g (0.283 equivalents) of PSCBZ and 20.67 g (0.153 mol) of $HSiCl_3$ gave 25.17 g of a viscous oil (78.8% yield). ^{1}H NMR ($CDCl_3$): δ 1.36 (m),1.64 (m), 4.86 (m, Si–H). I.r. (thin film): 3374 (N–H, s), 2959 (s), 2932 (s), 2868 (m), 2783 (w), 1454 (w), 1406 (m), 1391 (m), 1209 (s), 1180 (s), 1117 (s), 955 (s), 689 (s) cm^{-1}.

Example IV. $[C_3H_6SiNH]_{0.83}[Si(NH)_2]_{0.17}$. 17.20 g 0.202 equivalents) of PSCBZ and 7.134 g (0.042 mol) of $SiCl_4$ gave 9.05 g of a gum (70.5 % yield). ^{1}H NMR ($CDCl_3$): δ 1.34 (m), 1.61 (m). I.r. (thin film): 3378 (N–H, s), 2959 (s), 2923 (s), 2869 (m), 1447 (w), 1409 (m), 1393 (m), 1179 (s), 1122 (s), 941 (s), 687 (s) cm^{-1}.

Example V. $[C_3H_6SiNH][Me_xSi_2(NH)_{(6-x)}]$. 17.07 g (0.201 equivalents) of PSCBZ and 14.00 g of a mixture of methylchlorodisilanes (10.8% of 1,2-dichloro-1,1,2,2-tetramethyldisilane, 30.2% of 1,1,2-trichloro-1,2,2-trimethyldisilane and 57.6% of 1,1,2,2-tetrachloro-1,2-dimethyldisilane) gave 21.0 g of a vis-

TABLE I Polymer characterization

Example	Elemental analysis				Molecular weight[a]		DSC onset	TMA softening point
	C	H	N	Si	M_w	M_n	(°C)	(°C)
I	44.0	9.6	15.8	30.7	2015	142	236	< r.t.
II	38.1	9.0	17.1	35.5	1956	196	173	< r.t.
III	34.8	8.1	17.0	37.8	361	214	209	< r.t.
IV	37.2	8.7	14.2	36.3	10 324	225	182	< r.t.
V	37.0	8.3	12.6	36.2	5533	208	188	< r.t.
VI	35.2	8.3	17.2	34.5	5231	121	200	< r.t.
VII	47.3	7.9	14.8	27.7	2064	497	245	< r.t.
VIII	60.0	6.7	12.5	21.9	17 859	431	200	49.4
IX	58.2	6.0	18.1	22.7	53 964	1785	230	66.4

[a] Relative to polystyrene.

cous, tacky oil (85.7% yield). ^{1}H NMR ($CDCl_3$): δ 0.15 (broad s), 0.72–2.02 (m). I.r. (thin film): 3381 (N–H, s), 2959 (s), 2932 (s), 2868 (m), 2783 (w), 1447 (w), 1406 (m), 1391 (m), 1250 (s), 1167 (s), 1124 (s), 1032 (m), 934 (s), 758 (m), 689 (m) cm^{-1}.

Example VI. $[C_3H_6SiNH]_{0.58}$ $[MeSi(NH)_{1.5}]_{0.42}$. 17.59 g (0.21 equivalents) of PSCBZ and 22.95 g (0.154 mol) of $MeSiCl_3$ gave 19.87 g of a gum (71.8 % yield). ^{1}H NMR ($CDCl_3$): δ 0.17–0.33 (broad m), 0.53–2.03 (broad m). I.r. (thin film): 3381 (s), 2959 (s), 2927 (s), 2868 (m), 1447 (w), 1406 (m), 1391 (m), 1258 (s), 1180(s), 1032 (w), 955 (s), 752 (m), 689 (s) cm^{-1}.

2.1.3. General procedure for the preparation of silacyclobutasilazanes via co-ammonolysis of chlorosilanes

A three-necked round-bottom flask fitted with a mechanical stirrer, a gas inlet tube and a Dewar condenser with a nitrogen outlet was charged with a solution of the chlorosilanes in dry toluene. The reaction was cooled to − 78 °C and excess ammonia bubbled through the solution. The solution was warmed to room temperature and filtered through a medium glass frit. Concentration of the filtrate at reduced pressure gave the desired polymer. Using this procedure, the following polymers were prepared:

Example VII. $[C_3H_6SiNH]_{0.56}[Ph_2SiNH]_{0.14}[MeSi(NH)_{1.5}]_{0.30}$. 610.0 g (4.40 mol) of 1,1-dichloro-1-silacyclobutane, 278.0 g (1.10 mol) of Ph_2SiCl_2 and 375.0 g (2.40 mol) of $MeSiCl_3$ gave 475 g of a polymer (63.5% yield) after vacuum stripping for 3 h at 170–190 °C. ^{1}H NMR ($CDCl_3$): δ 0.25 (centre of broad singlet), 1.45 (centre of broad m), 7.2 (centre of broad m), 7.5 (centre of broad m). The integrated ratios were 1:3.5:1.08 (theoretical 1:3.2:10.33).

Example VIII. $[C_3H_6SiNH]_{0.50}[PhSi(NH)_{1.5}]_{0.25}$ $[Ph_2SiNH]_{0.25}$. 565.6 g (4.00 mol) of 1,1-dichloro-1-silacyclobutane, 506.4 g (2.00 mol) of Ph_2SiCl_2 and 423.2 g (2.00 mol) of $PhSiCl_3$ gave 816.6 g of a brittle solid (82.5 % yield) after vacuum stripping for 3 h at 150–170 °C. ^{1}H NMR ($CDCl_3$): δ 0.60–1.90 (broad m), 7.30 (centre of broad m), 7.60 (centre of broad m).

Example IX. $[C_3H_6SiNH]_{0.20}[PhSi(NH)_{1.5}]_{0.80}$. 14.10 g (0.10 mol) of 1,1-dichloro-1-silacyclobutane and 84.64 g (0.40 mol) of $PhSiCl_3$ gave 48.1 g of a brittle solid (80.8% yield) after vacuum stripping for 1–2 h at 130 °C.

2.2. Polymer pyrolysis and ceramic char characterization

All furnace firings were done in an Astro graphite furnace equipped with Eurotherm temperature controllers. An Ircon optical pyrometer was used to monitor temperatures above 900 °C and a K-type thermocouple to monitor temperatures below 900 °C. Ceramic chars were obtained by heating aliquots of the polymer in an argon atmosphere to the stated temperature using a ramp rate of 5 °C min^{-1}. The hold times at temperature for the 1200 and 1800 °C firings were 30 min and 3 h, respectively. The ceramic chars were analysed for carbon, hydrogen and nitrogen content on a Control Equipment Corp. 240-XA elemental analyser. Oxygen content was determined on a Leco Oxygen analyser equipped with an oxygen determinator 316 (Model 783700) and an electrode furnace EF100. Silicon was determined by a fusion technique that consisted of converting the silcon material to soluble forms of silicon and analysing the solute for total silicon by atomic absorption spectrometry.

Transmission electron microscopy was performed on a Jeol 2000 FX analytical electron microscope equipped with light- and heavy-element Tracor Northern energy-dispersive detectors on ion-thinned foils of the ceramic char. It was necessary to use microbeam electron diffraction (MBED) techniques to restrict the beam interaction to the small clusters in the ceramic matrix.

2.3. Fabrication of silicon carbide monoliths

Die-pressed test bars were prepared using the following procedure:

(i) Ibiden Betarundum UF SiC powder and amorphous boron (Cerac) were added to a dilute, toluene solution of the polymer (5–15 wt %) while ultrasonicating the slurry in a water bath for 5–10 min. After removing the solvent by rotary evaporation, the residue was dried and sieved through a 60 mesh screen.

(ii) The sieved powders were uniaxially pressed at 40–50 kpsi (276–345 MPa) in a tungsten carbide-lined die. The dimensions of the test bars were 35 mm × 8 mm × ~ 2 mm and averaged 1.5 to 2.2 g. The test bars were cured by heating them from room temperature to 250 °C at 3 °C min^{-1} in an argon atmosphere and held at 250 °C for 2 h.

(iii) The cured test bars were fired in an Astro tube furnace in an argon atmosphere to 2100 °C (30 min hold) using a ramp rate of 10 °C min^{-1}. The samples were held at 1400 °C for 30 min to allow for the evolution of nitrogen from the binder. Fired densities were measured by the water immersion techniques described in ASTM C373-72. Machined test bars were prepared according to Mil. Std. 1942 (MR).

Transfer-moulded test bars were prepared according to the following procedure:

(i) The polymer was warmed to > 140 °C under argon in the mixing chamber of a Brabender Plasticorder. Aliquots of the silicon carbide and amorphous boron were added until the desired filler level was attained. Torque levels of approximately 1000 N mm were used. After 20–30 min mixing was complete.

(ii) Aliquots of the polymer–powder mixes were moulded into 3.75 mm × 0.62 mm × 0.257 cm test bars (1.35 g) using a 12.5 ton (12.7 tonne) Hull transfer moulder. All mouldings were done at 230 °C with a ram pressure of 1000 psig (6.9 MPa) and a clamping pressure of 1800 psig (12.4 MPa). The moulded parts were held at 230 °C for 5 min to ensure a complete cure. The test bars had a density of 2.25 g cm^{-3} (23.5 wt % polymer).

(iii) The cured test bars were fired to 2075 °C using the following temperature programme and atmospheres: ambient temperature to 200 °C at 3 °C min^{-1} (argon), 200–1000 °C at 1 °C min^{-1} (argon), 1000–1500 °C at 3 °C min^{-1} (0.1 mm Hg) with a 30 min soak at temperature (0.1 mm Hg), 1500–2075 °C at 5 °C min^{-1} (argon). After a 30 min soak at temperature, the test bars were cooled at 5 °C min^{-1} to 900 °C (argon).

3. Results and discussion

3.1. Synthesis and characterization of silacyclobutasilazane polymers

Silacyclobutasilazane (SCBZ) polymers were prepared by the equilibration/ammonolysis and co-ammonolysis routes [31]. In the first route, PSCBZ was equilibrated with chlorosilanes to give a mixture of chloro end-blocked silazanes. This mixture was then ammonolysed to give the desired SCBZ (Examples I–VI in Table I). In the second route, a mixture of 1,1-dichloro-1-silacyclobutane and the chlorosilane were co-ammonolysed directly (Examples VII–IX in Table I). Both routes gave high yields of polymer (> 70%) and were able to accommodate a wide percentage and variety of chlorosilanes in the synthesis. In general, the direct co-ammonolysis route was preferred although the equi-libration/ammonolysis route was often used because less ammonium chloride was generated in the last step which simplified the isolation of the polymer.

At room temperature, most SCBZ polymers are either gums or low-melting solids that liquefy to low-viscosity fluids (1–10 poise or 0.1–1 Pa s) upon gentle heating. However, between 180 and 250 °C their viscosities rapidly increase and highly crosslinked resins are obtained. This phenomenon is shown in Fig. 1 for $[C_3H_6SiNH]_{0.56}[Ph_2SiNH]_{0.14}[MeSi(NH)_{1.5}]_{0.30}$. The crosslinking mechanism for SCBZs was elucidated by infrared analysis of PSCBZ before and after cure. After heating to 260 °C in argon there is a pronounced decrease in the N–H stretching and bending frequencies [32] at 3370 and 1211 cm^{-1}, respectively. In addition, the three bands for the silacyclobutyl group at 1180, 1115 and 923 cm^{-1} [33, 34] disappear. In the i.r. spectrum of the cured polymer, several unresolvable broad bands appear between 1230–1100 and 1040–840 cm^{-1} corresponding to the $-CH_2-$ in- and out-of-phase wagging vibrations (SiC_3H_7 or $Si(CH_2)_3Si$) and the Si–N–Si asymmetric stretch (see Fig. 2), respectively. Similar observations were seen with other SCBZ polymers. Thus, the crosslinking step is a combination of N–H addition across an Si–C bond and ring-opening polymerization of the silacyclobutyl group.

In addition to a rapid increase in viscosity, crosslinking of SCBZ polymers was marked by an exotherm. The exotherm was a result of the release of the 19–20 kcal mol^{-1} strain energy in the silacyclobutane ring and was determined by differential scanning calorimetry (see Table I). Thus, the silacyclobutyl group imparts a latent, thermally activated curing mechanism for the polymer.

3.2. Polymer pyrolysis

Ceramic chars were prepared from aliquots of crosslinked polymers at both 1200 and 1800 °C in argon

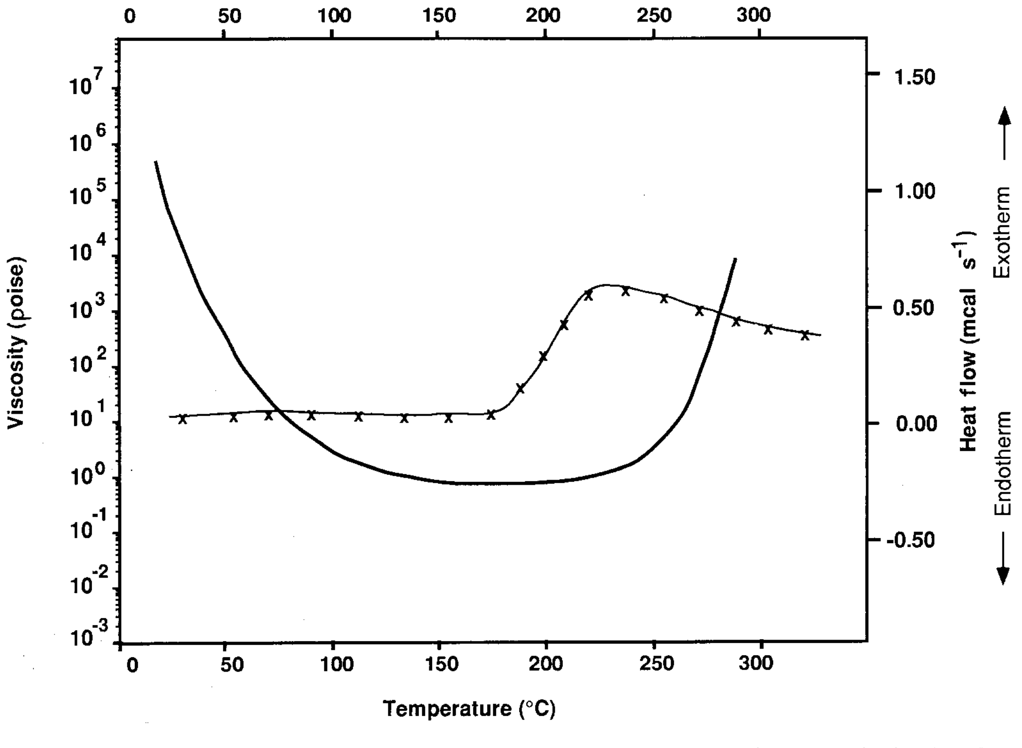

Figure 1 Viscosity and differential scanning calorimetry versus temperature for $[C_3H_6SiNH]_{0.56}[Ph_2SiNH]_{0.14}[MeSi(NH)_{1.5}]_{0.30}$ (Example VII): (——) viscosity, (×) differential scanning caloriometry. 1 poise = 10^{-1} Pa s.

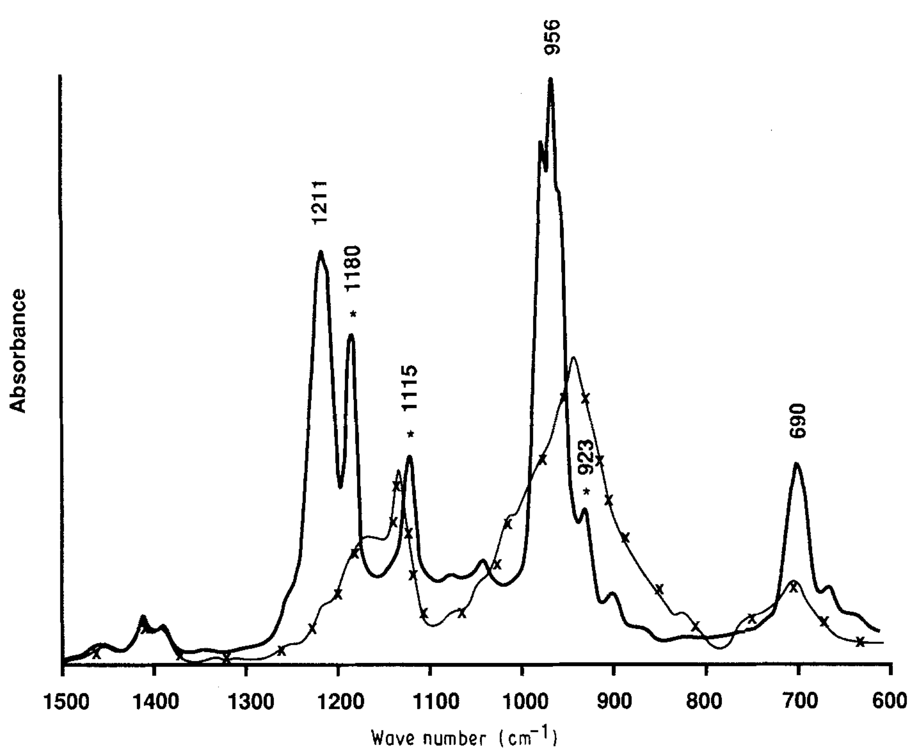

Figure 2 Infrared spectra of polysilacyclobutasilazane: (——) before heating, (×) after heating to 260 °C. Starred peaks are from the silacyclobutyl ring.

atmospheres. At 1200 °C, ceramic chars containing silicon, nitrogen, carbon and small amounts of oxygen (1–3 wt %) were obtained. The oxygen content in the chars was a result of incidental hydrolysis of the Si–N polymer backbone during polymer synthesis and handling. When special care was taken to prevent exposure of the polymer to moisture, ceramic chars containing less than 1% oxygen were obtained. As in previous work, the addition of $R_{4-x}Si(NH)_{x/2}$ units into the Si–N polymer backbone had a pronounced influence on the composition of the ceramic char [35]. Thus, 1200 °C ceramic chars with higher ratios of nitrogen to carbon, inferring a higher silicon nitride content by rule-of-mixture calculations, were obtained when the R group was an alkyl or H or when $SiCl_4$ was used as a coreactant (Examples I–VI); ceramic chars with higher carbon contents were obtained when R was an aryl group (Examples VII–IX).

At elevated temperatures in a non-reactive atmosphere Si–C–N–O ceramic chars degrade with the evolution of nitrogen and carbon monoxide to form silicon carbide according to the equation.

$$\mathrm{Si}_a\mathrm{C}_b\mathrm{N}_c\mathrm{O}_d \rightarrow (c/2)\mathrm{N}_2\uparrow + d\mathrm{CO}\uparrow + (b - a - d)\mathrm{C} + a\mathrm{SiC}$$

This process occurs between 1400 and 1700 °C and is shown in Fig. 3 for the char derived from $[C_3H_6SiNH]_{0.50}[Ph_2SiNH]_{0.25}[PhSi(NH)_{1.5}]_{0.25}$. The use of a non-reactive gas sweep or vacuum enhances the removal of the pyrolysis gases and the formation of silicon carbide. As a result, after either ageing the 1200 °C chars to 1800 °C or firing the polymers directly to 1800 °C, stable chars containing only silicon and carbon were obtained. Table II summarizes the composition of the 1200 and 1800 °C ceramic chars.

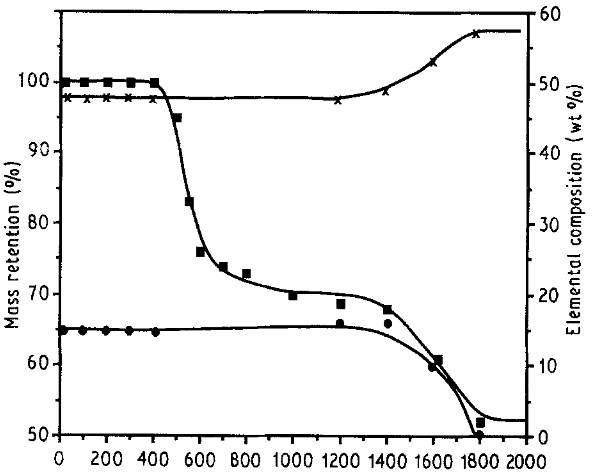

Figure 3 Mass retention and composition as a function of pyrolysis temperature for $[C_3H_6SiNH]_{0.50}[Ph_2SiNH]_{0.25}[PhSi(NH)_{1.5}]_{0.25}$: (●) nitrogen; (×), carbon, (■), mass retention.

The development of the microstructure in SCBZ chars during their transformation from an Si–C–N–O type char to silicon carbide was studied by X-ray diffraction (XRD), microchemical and transmission electron microscopy (TEM) analyses. For this study the char derived from $[C_3H_6SiNH]_{0.50}$-$[PhSi(NH)_{1.5}]_{0.25}[Ph_2SiNH]_{0.25}$ (Example VIII) was chosen. At temperatures below 1400°C, the char was amorphous by XRD and no change in the elemental composition of the char was observed. By 1600 °C, approximately one-third of the nitrogen had evolved and β-SiC began to crystallize; however, the majority of the material was still amorphous. By 1800 °C only a trace amount of nitrogen was present and the residue was predominantly β-SiC by XRD. No peaks associated with graphitic carbon were identified by XRD

TABLE II Analysis of ceramic chars

Example	Elemental analysis (1200 °C)				Char yield[a] (1200 °C)	Density (g cm^{-3}) (1200 °C)	Elemental Analysis (1800 °C)[b]		
	C	O	N	Si			C	Si	Char yield[a]
I	33.9	1.5	18.7	43.7	72.8	2.052	38.1	60.5	54.6
II	30.4	2.9	19.6	46.4	68.1	2.217	32.5	65.1	51.6
III	26.4	1.9	22.4	48.3	80.1	2.195	31.3	65.2	58.9
IV	25.8	2.2	16.4	49.3	68.2	2.244	33.5	66.7	52.2
V	20.6	2.2	22.5	49.7	65.9	2.353	32.7	65.8	47.1
VI	24.7	3.1	23.3	46.9	72.8	2.187	27.9	69.4	46.7
VII	35.3	2.0	20.0	39.0	63.2	–	50.6	48.6	45.0
VIII	48.1	0.2	15.9	37.6	68.8	–	57.7	40.1	52.2
IX	34.9	4.1	18.3	34.2	69.6	–	58.5	41.5	53.3

[a] Yields based upon weight of starting polymer.

[b] Nitrogen and oxygen contents were < 1 wt %.

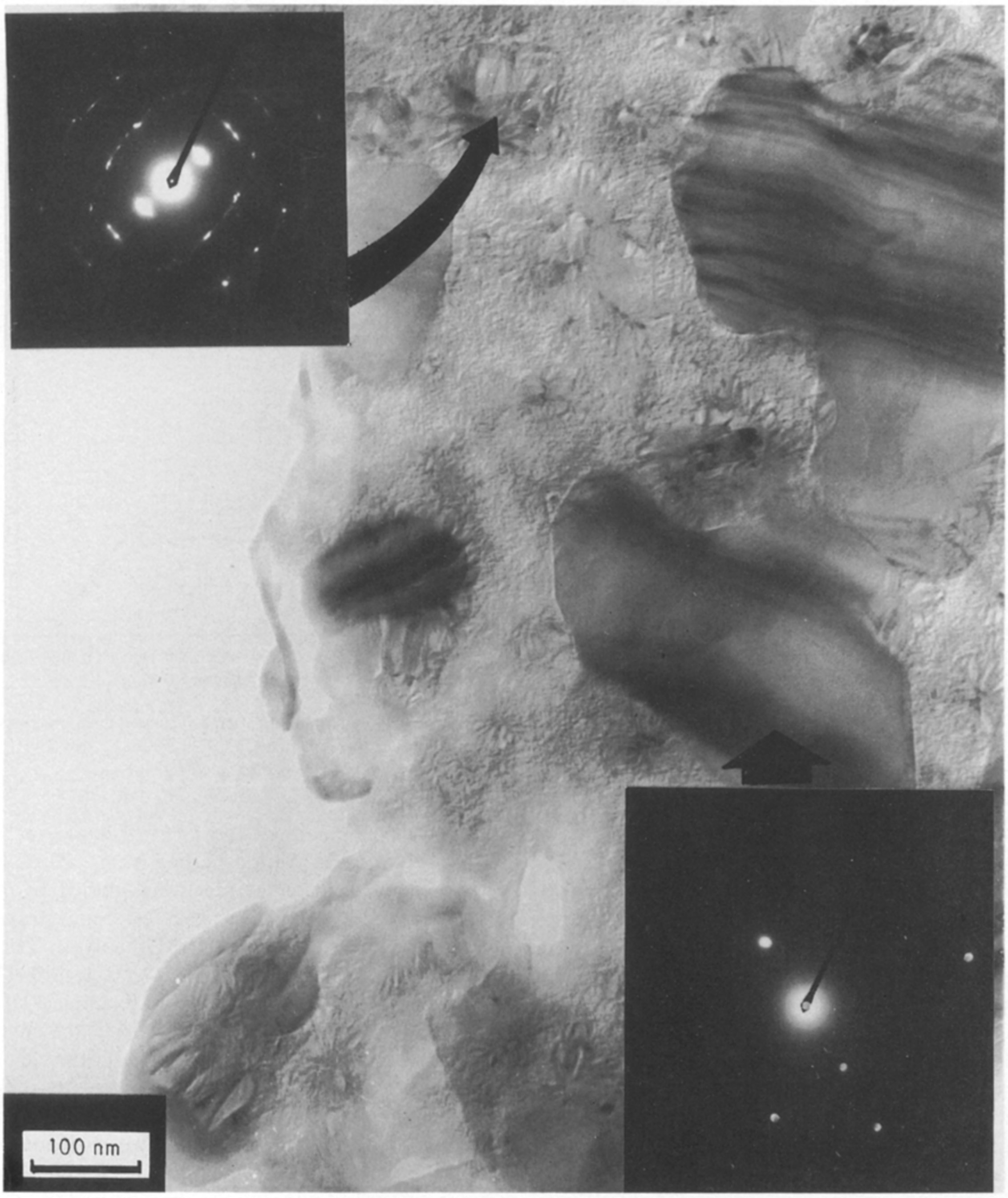

Figure 4 Rounded β-SiC grains in a matrix of radiating pyrolytic graphite crystal growths and C-rich amorphous material. Lower inset: electron diffraction of β-SiC (at arrow); upper inset: MBED of pyrolytic graphite crystal cluster designated by arrow.

analysis. This was surprising since the char contained 27 wt % of excess carbon based upon its elemental analysis and rule-of-mixture calculations. However, TEM and microbeam electron diffraction (MBED) analysis on an ion-thinned foil of the char confirmed the presence of pyrolytic graphite spherulites and β-SiC grains embedded in an amorphous, carbon-rich matrix (Figs 4 and 5).

Since the Si–C–N–O to silicon carbide and excess carbon transformation occurs at temperatures substantially below the sintering temperature of silicon carbide in pressureless sintering processes, silazane binders can thus be used to prepare sintered monoliths consisting only of crystalline silicon carbide and carbon.

3.3. Preparation of sintered monoliths using silacyclobutasilazanes as binders

The selection of polymer examples VII and VIII for die-pressing and transfer-moulding processes, respectively, was based upon the elemental composition of the ceramic chars (see Table II) and the amount of excess carbon calculated by the method of Atwell *et al.* [36, 37].

The effect of polymer content on green density and cured strength is shown in Fig. 6 for a series of test-bars prepared with $[C_3H_6SiNH]_{0.50}[PhSi(NH)_{1.5}]_{0.25}$-$[Ph_2SiNH]_{0.25}$. In general, monodisperse, submicrometre, spherical powders have a practical packing density limit of 65 vol %; the remaining volume is voids. As a result, the maximum theoretical density of SiC powders is only 2.09 g cm^{-3}. When a binder is used in conjunction with a powder, the binder will fill the interstitial voids upon compaction which increases the green density of the compact. The resultant powder-to-polymer and polymer-to-polymer interactions improve the green strength of the compact. Crosslinking of the polymer gives additional improvements

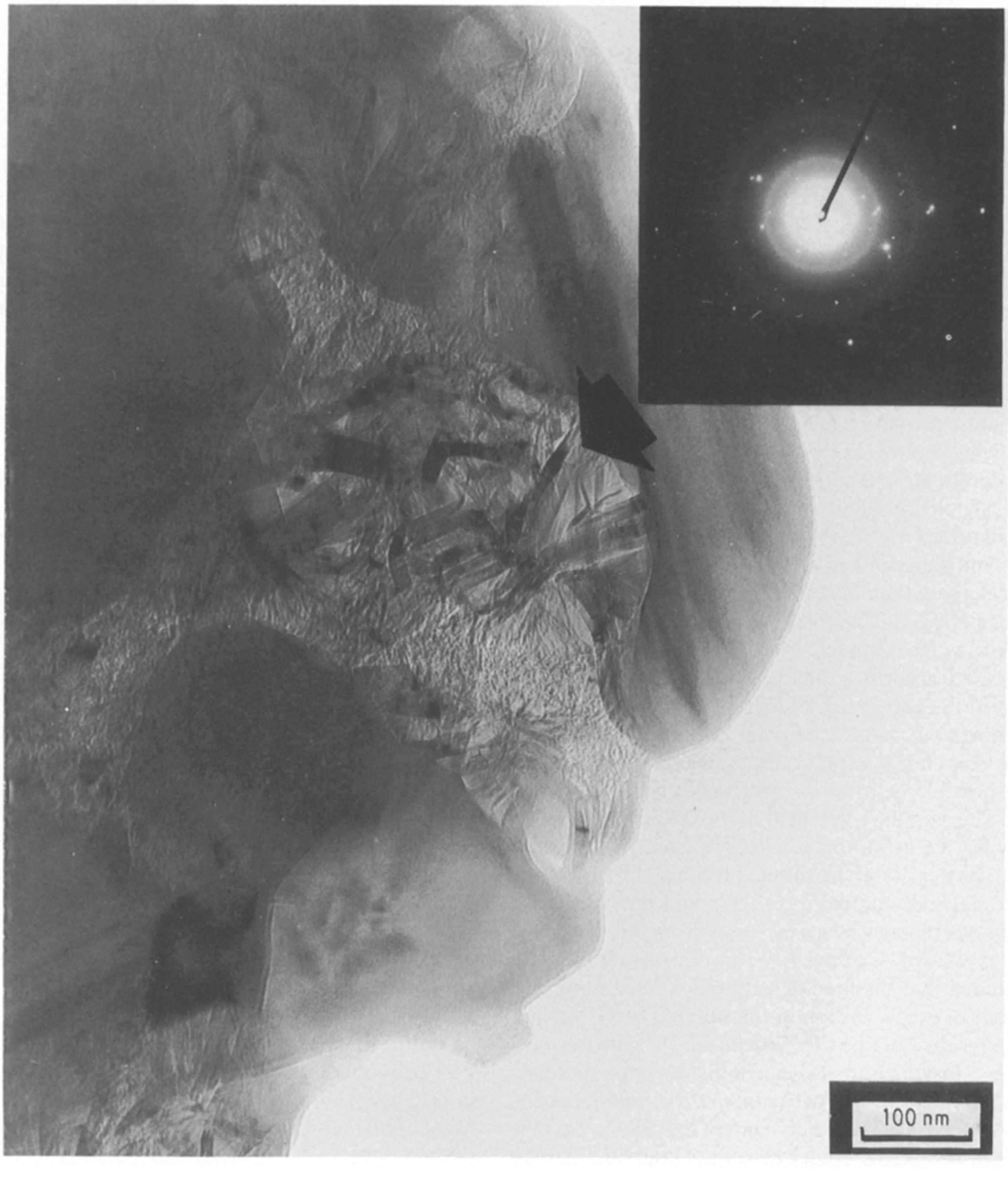

Figure 5 Large radiating cluster of pyrolytic graphite (MBED at inset) associated with β-SiC grains and amorphous matrix.

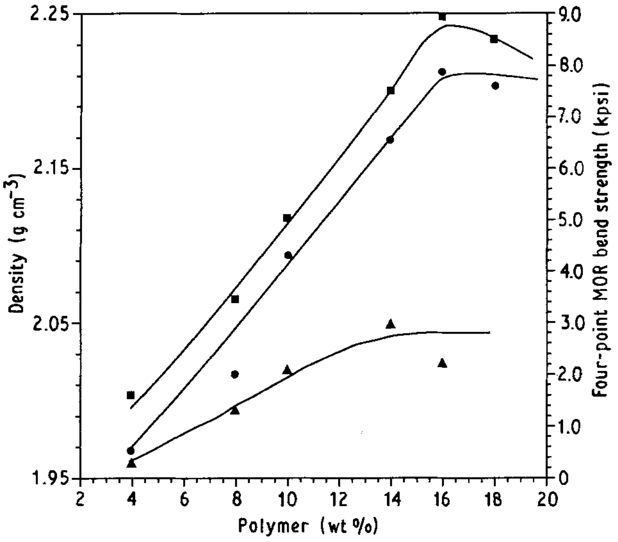

Figure 6 Properties of die-pressed test bars as a function of polymer content: (■) density, (▲) green strength, (●) cured strength. 1 kpsi = 6.895 MPa.

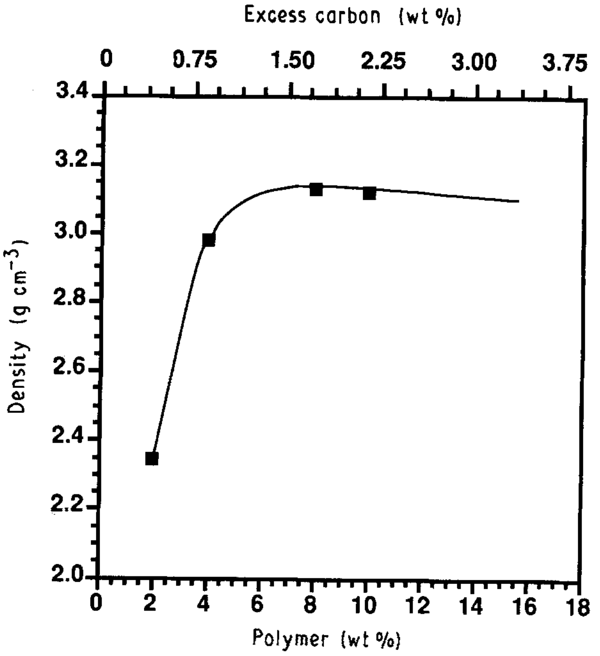

Figure 7 Fired density of test bars as a function of polymer content.

in the green strength. Thus, the green density and green and cured strength of the polymer increase as the polymer concentration increases. This trend continues until the polymer concentration exceeds 35 vol %. At this point the polymer begins to separate the powder particles. Since the density of the polymer is less than the density of the powder, the maximum green density is achieved at this point. Assuming that a polymer has a density of 1.1 g cm^{-3}, this occurs at a polymer concentration of approximately 15–16 wt % [38].

To substitute a pre-ceramic polymer for phenolic resin as a homogeneous carbon source, the polymer char must provide a form of carbon that is active in removing surface oxides from SiC powders and inhibits grain growth in the sintering process. The effectiveness of the pyrolytic carbon derived from silacyclobutasilazanes was determined by preparing a series of press and sinter mixes with variable levels of polymer and calcining them to 2150 °C in argon. In this study, $[C_3H_6SiNH]_{0.50}[PhSi(NH)_{1.5}]_{0.25}[Ph_2SiNH]_{0.25}$ was chosen as the binder. The mixes were prepared and cured according to the experimental procedure outlined in Section 2.3. Each mix contained 0.5 wt % of amorphous boron as a sintering aid. During the firing step fairly rapid ramp rates (3–15 °C min^{-1}) were possible because of the absence of fugitive binders. The samples were held at 1400 °C for 30 min to allow for the evolution of nitrogen from the polymer char. The density of the sintered test bars as a function of the polymer content in the mix and the calculated weight percentage of excess carbon in the fired test bars is shown in Fig. 7. From this study it was concluded that the fired density was a function of the amount of excess carbon in the sintered body, similar to the results obtained by Prochazka [8] with organic binders. Insight into this phenomenon was obtained by examining the microstructure of the fired test bars as a function of polymer content by SEM. At low levels of the SCBZ binder (2–4 wt %) the microstructure was dominated by large pores and exaggerated SiC grain growth; hence the low bulk densities (Fig. 8a and b). As the polymer content increased, the exaggerated grain growth was inhibited. At polymer levels greater than 6 wt % a fine-grained microstructure consisting predominantly of β-SiC was obtained (Fig. 8c). Thus, the efficacy of the pyrolytic carbon obtained from the decomposition of silacyclobutasilazanes at high temperatures is comparable to that of other homogeneous carbon sources.

The silicon carbide that is deposited along with the excess carbon reduces the interstitial void volume. Consequently, for complete densification there is less porosity which needs to be eliminated. For example, monolithic bodies die pressed with an SCBZ polymer (Example VIII) undergo a linear shrinkage of 13–14%. In contrast, monolithic bodies prepared with traditional binders under the same conditions and having a similar green density will undergo a 2–3% higher linear shrinkage. This reduced level of shrinkage allows for net shape-forming of silicon carbide parts made with SCBZ polymers.

Average four-point flexural strengths greater than 70 kpsi (483 MPa) were obtained with excess carbon levels greater than 1.5 wt %. The results from fractographic examination on these test bars showed that the strengths were not limited by the polymeric binder but by flaws similar to those generated by conventional ceramic processing. Lower flexural strengths were obtained at lower excess carbon levels (i.e. lower levels of the SCBZ binder). These lower flexural strengths were due to a combination of large α-SiC grains and voids. This is shown in the etched microstructure of polished specimens made from the test bars (Fig. 8a). XRD analysis of the lower-strength test bars confirmed the presence of 18 wt % α-SiC. At higher polymer concentrations a finer, predominantly β-SiC (> 91 wt % by XRD analysis) microstructure was obtained (Fig. 8b and c).

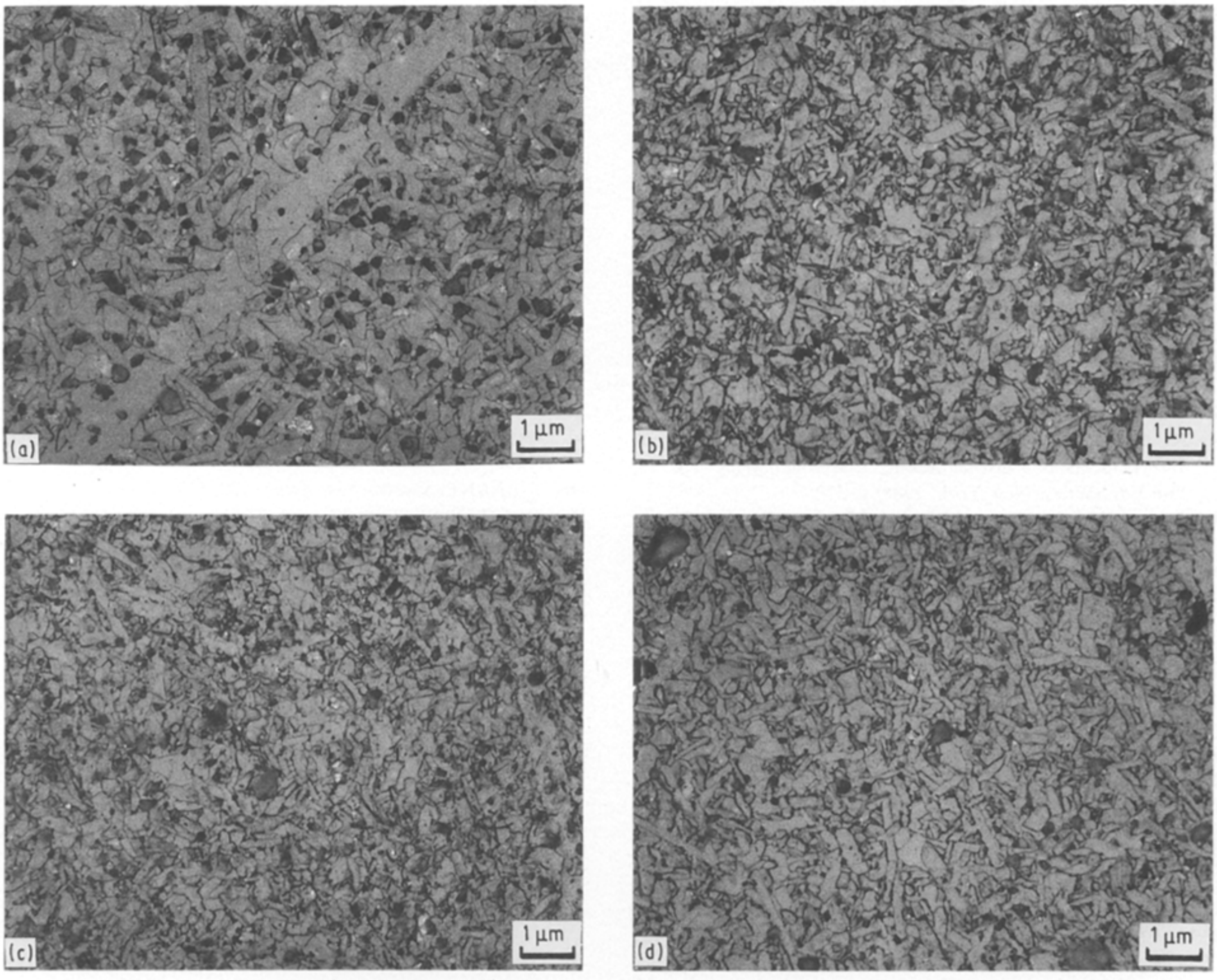

Figure 8 Microstructure of fired test bars as a function of polymer concentration. Concentration of polymer and [excess carbon] in samples: (a) 4 wt % [0.84 wt %]; (b) 8 wt % [1.72 wt %]; (c) 10 wt % [2.17 wt %]; (d) 24.5 wt % [3.4]. Note the large grain size and voids in (a); (d) shows the microstructure of a test bar prepared with the polymer from Example VII. Note the similar microstructure to (b) and (c).

An SCBZ polymer, $[C_3H_6SiNH]_{0.56}[Ph_2SiNH]_{0.14}$-$[MeSi(NH)_{1.5}]_{0.30}$ (Example VII), suitable for transfer- and injection-moulding applications was prepared by decreasing the aryl content in the polymer. The polymer's 1800 °C ceramic char therefore contained less excess carbon. Consequently, higher polymer levels which are required for flow in moulding applications could be used without increasing the carbon content of the fired body. The polymer was filled with 76 wt % (53 vol %) silicon carbide and 0.5 wt % amorphous boron on a three-roll mill. At this filler level the calculated amount of excess carbon in the fired body is 3.4 wt %. The higher carbon level did not adversely effect the mechanical properties of the fired test bars, while it ensured that sufficient carbon was available to react with any additional oxygen incorporated into the polymer from the mixing and moulding process. The mix gave 5.5 in. (140 mm) of flow in a spiral mould at a moulding temperature of 235 °C. An aliquot of the polymer–powder mix was transfer-moulded into test bars. The green test bars had an average four-point MOR bend strength of 6927 ± 377 psi (47.76 ± 2.60 MPa) with a Weibull modulus of 19.5. After firing to 2075 °C, the test bars had a fired density of 3.11 $g\,cm^{-3}$ and a four-point MOR bend strength (as-fired surfaces) of 34.4 ± 7.8 kpsi (237.2 ± 53.8 MPa). The microstructure of the fired test bars is shown in Fig. 8d and is comparable to that obtained in die-pressed test bars at the same level of excess carbon.

4. Conclusions

Silacyclobutasilazanes constitute the first family of pre-ceramic polymers specifically developed for moulding applications. The polymers possess strained four-membered rings that polymerize between 200 and 250 °C. Further heating converts the polymers initially to Si–C–N–O amorphous ceramics and then to stable mixtures of carbon associated with silicon carbide. The ratio of carbon to silicon carbide is controlled by the R groups in the polymer. In moulding applications the silicon carbide derived from the polymer can be considered as a diluent for the pyrolytic carbon. Thus, shaped articles prepared from different processes and containing different levels of polymer sinter to the same composition and density.

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