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Synthesis of thermosetting copolymer of polycarbosilane and perhydropolysilazane

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A copolymer of polycarbosilane and perhydropolysilazane was obtained by reacting polycarbosilane with titanium *n*-butoxide and perhydropolysilazane. Titanium *n*-butoxide and perhydropolysilazane were essential for the polymer to show a thermosetting property. The thermosetting copolymers were converted into silicon carbide-based ceramics by pyrolysis in a stream of nitrogen to 1000 °C with about 80 wt% ceramic yield. The main phase of the pyrolysis product at 1500 °C in nitrogen was small crystallite β-SiC. Elemental carbon, based on rule-of-mixtures composition, in the final ceramics could be reduced by varying the ratio of polycarbosilane/perhydropolysilazane. The copolymer was dry spun and pyrolysed to produce ceramic fibre. Pyrolysis in nitrogen to 1500 °C yielded a silicon carbide-based fibre with low oxygen and low elemental carbon content. A tensile strength of 1.8 GPa and an elastic modulus of 220 GPa were obtained for the fibre which ranged from 10–12 μm in diameter. Crystallization to α-Si_3N_4, β-SiC, and β-Si_3N_4 proceeded on annealing in nitrogen at 1700 °C for 1 h.

1. Introduction

Silicon carbide is a well-known ceramic material with high thermal and chemical stability, high mechanical strength and hardness, and high thermal conductivity. There has been much interest in the use of organosilicon polymers as precursors to silicon carbide-based ceramics. Some of the advantages in the preparation of ceramic materials from these precursors include, compositional homogeneity in the final products, high-purity ceramic products with uniform microstructure, amorphous to microcrystalline, and the preparation of refractory ceramics at relatively low temperatures.

Yajima and co-workers developed polycarbosilane by thermal rearrangement of polydimethylsilane [1]; continuous SiC filament has been produced via pyrolysis of melt-spun polycarbosilane [2], and Si–Ti–C–O fibre was obtained from polytitanocarbosilane that was derived from the reaction of polycarbosilane with titanium tetraisopropoxide [3, 4]. West *et al.* prepared "polysilastyrene" by sodium reduction of mixtures of Me_2SiCl_2 and $PhMeSiCl_2$ [5]. Ijadi-Maghsoodi *et al.* demonstrated that silyene–acetylene could be synthesized by the reactions of dialkyl- or diaryldichlorosilanes with dilithioacetylene [6]. These precursors were converted to silicon carbide-based ceramics by pyrolysis in inert atmosphere. However, a curing process, such as heat treatment in air, ultraviolet irradiation, electron-beam irradiation, was essential for the preparation of shaped SiC from thermoplastic precursors.

Several authors reported thermosetting SiC precursors. Schilling described vinylic polysilane by refluxing various chlorinated silanes in a solvent with sodium [7]. This vinylic polysilane was a viscous, liquid polymer that underwent thermal cross-linking in an inert atmosphere due to a combination of hydrosilylation and vinyl polymerization. Whitmarsh *et al.* reported a hydridopolycarbosilane derived from (chloromethyl)trichlorosilane that underwent facile thermal cross-linking reactions [8]. Wu and Interrante prepared poly(silaethylene) by direct reduction of poly(dichlorosilaethylene) that was obtained via ring-opening polymerization of 1,1,3,3-tetrachloro-1,3-disilacyclobutane [9]. The presence of Si–H bonds in the polymers provided an effective thermosetting property. Toreki *et al.* produced silicon carbide fibres by pyrolysis of dry-spun polycarbosilane without a curing process [10]. The molecular weight of the polycarbosilane was controlled by separation of low molecular weight thermoplastic carbosilane.

In the present paper, synthesis of thermosetting preceramic polymer by copolymerization of polycarbosilane with thermosetting perhydropolysilazane will be presented. Properties of the pyrolysis products and the preliminarily obtained ceramic fibre will also be described.

2. Experimental procedure

2.1. Preceramic polymer synthesis

Perhydropolysilazane (PHPS) was synthesized by ammonolysis of dichlorosilane–pyridine adduct followed by heat treatment at 120 °C in pyridine with ammonia [11].

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Commercially available polycarbosilane (PCS, Shin-Etsu Chemical Co. Ltd Lot. 303068) with number average molecular weight of 1300, was used in this study. Following a published procedure [3], PCS and titanium *n*-butoxide in given ratios (Si/Ti = 1/0, 250/1, 50/1, 25/1, 12.5/1 (atomic ratio)) were dissolved in xylene to form a homogeneous solution. The solution was refluxed under nitrogen for 1 h. After the refluxing reaction, the temperature was raised to 220 °C and the xylene solvent was distilled off. During the distillation, the pale yellow transparent solution turned bluish green [12], except for the Si/Ti = 1/0 product. The heat treatment was carried out at 220 °C for 30 min. After being cooled to room temperature, the product was dissolved in xylene. PHPS in xylene was added to the bluish green solution in given ratios (PCS/PHPS = 1/0, 9/1, 4/1, 1/1, 1/4, 1/9, 0/1 (silicon ratio)). The mixture was heated at 100 °C under nitrogen for a further 1 h. The solvent was removed by vacuum distillation over a rotary evaporator to give a green powder. The colour of the powder turned to light yellow, as soon as it came into contact with air.

2.2. Pyrolysis

Polymer samples were pyrolysed in a carbon furnace (Model HG-010, Nikkato, Osaka, Japan) by heating from room temperature to 1500 °C in 150 min, holding at 1500 °C for an additional 60 min, and cooling to room temperature in 150 min. All heating was completed under flowing nitrogen.

2.3. Characterization

Molecular weight distributions were measured with a gel permeation chromatography (GPC) system (Model 801-SU, JASCO, Tokyo, Japan) using chloroform as solvent. Molecular weights quoted are based on polystyrene standards.

Infrared (IR) spectra were recorded on polymer-coated KBr plates (Model 270-50, Hitachi, Tokyo, Japan). ^{1}H (Model R-24B, Hitachi) and ^{29}Si (Model MSL-300, Bruker, Wissenbourg, France) nuclear magnetic resonance (NMR) spectra were recorded for the polymers in solutions at room temperature ($CDCl_3$ for ^{1}H and *m*-xylene for ^{29}Si). Elemental analyses for silicon, nitrogen, titanium, carbon, oxygen and hydrogen were obtained for the polymers and pyrolysed samples. Differential scanning calorimetry (DSC) analysis was carried out in nitrogen up to 500 °C at a heating rate of 50 °C min^{-1} (Model DSC 7, Perkin–Elmer, Norwalk, USA). Thermogravimetric analysis (TGA) was performed on the polymer up to 1000 °C under flowing nitrogen (Model TG8110D, Rigaku, Tokyo, Japan) at a heating rate of 5 °C min^{-1}.

X-ray diffraction (XRD) measurements were performed on the pyrolysed samples with CuK_α radiation using an automated powder diffractometer equipped with a monochromater (Model RINT 1400, Rigaku).

X-ray photoelectron spectroscopy (XPS) spectra were recorded with MgK_α (1253.6 eV) as the excitation source (Model 5600 CI, Perkin–Elmer). The analyses were performed, under a residual pressure at 6.66×10^{-8} Pa, on ground ceramic fibres. The XPS data recorded on the samples were calibrated utilizing the Si 2p binding energy in SiC (100.4 eV as a standard).

2.4. Fibre preparation

Polymer solutions were filtered to remove insoluble material and concentrated to develop appropriate rheological characteristics for the spinning operation. Polymer fibres were continuously prepared by dry spinning at about 60 °C. With proper drawdown of the viscous polymer solution during extrusion from the spinneret, fibres with diameters of 12–15 μm were produced. A drum on a variable speed motor was used for fibre takeup. Polymer fibres (120 mm long) were pyrolysed in an Al_2O_3 tube furnace (Model F-1201, Nishimura Kogyo, Tokyo, Japan) under flowing nitrogen at 5 °C min^{-1} to 1000 °C, with 1 h hold at that temperature. The pyrolysed fibres were subsequently annealed for 1 h under flowing nitrogen at 1500 °C in a carbon furnace (Model HG-010, Nikkato, Osaka, Japan).

3. Results and discussion

3.1. Characterization of copolymers

The IR and NMR spectrum of the reaction product of PCS with titanium *n*-butoxide are similar to those of previous reports [3, 4, 12]. Absorptions are observed at 2900, 2950 cm^{-1} (C–H), 2100 cm^{-1} (SiH), 1350–1450 cm^{-1} (C–H), 1250 cm^{-1} ($Si–CH_3$), 1100 cm^{-1} (Si–O), 1020 cm^{-1} ($Si–CH_2–Si$), and 840 cm^{-1} (Si–C) (Fig. 1). The ^{1}H NMR spectrum of the product shows six peaks at 0.18 p.p.m. with shoulders at −0.1 and −0.5 p.p.m. ($Si–CH_3$), 0.95, 1.4, 1.6 p.p.m. (C–H), 3.75 p.p.m. (OCH_2), and 4.3 p.p.m. (CSiH) (Fig. 2). The ^{29}Si NMR spectrum reveals three peaks at 10, −0.5, and −18 p.p.m. due to SiC_3O, SiC_4, and SiC_3H, respectively (Fig. 3). The DSC curve shows an endothermic peak starting at 260 °C, with a peak maxima at 280 °C. This curve suggests that the reaction product of PCS with titanium *n*-butoxide melts around this temperature (Fig. 4).

The IR spectrum of the reaction product of PCS/titanium *n*-butoxide with PHPS (Si/Ti = 50/1, PCS/PHPS = 1/1) indicates absorption bands at 3400 cm^{-1} (N–H), 2900, 2950 cm^{-1} (C–H), 2100, 2150 cm^{-1} (Si–H), 1350–1450 cm^{-1} (C–H), 1250 cm^{-1} ($Si–CH_3$), 1180 cm^{-1} (N–H), 1100 cm^{-1} (Si–O), and 840–1020 cm^{-1} ($Si–CH_2–Si$, Si–N–Si) (Fig. 1). The ^{1}H NMR spectrum of the product shows seven peaks at 0.18 p.p.m. with shoulders at −0.1 and −0.5 p.p.m. ($Si–CH_3$), 0.95, 1.4, 1.6 p.p.m. (C–H), 3.75 p.p.m. (OCH_2), 4.4 p.p.m. (SiH_3), and 4.85 p.p.m. (SiH/SiH_2) (Fig. 2). The ^{29}Si NMR spectrum reveals five peaks at 8, 0, −17, −37, and −51 p.p.m. due to SiC_3O, SiC_4, SiC_3H, SiH/SiH_2, and SiH_3, respectively (Fig. 3). There is no endothermic peak around 280 °C in the DSC curve (Fig. 4). This indicates that the polymer has been converted to thermosetting by reaction with PHPS. The polymer undergoes thermal

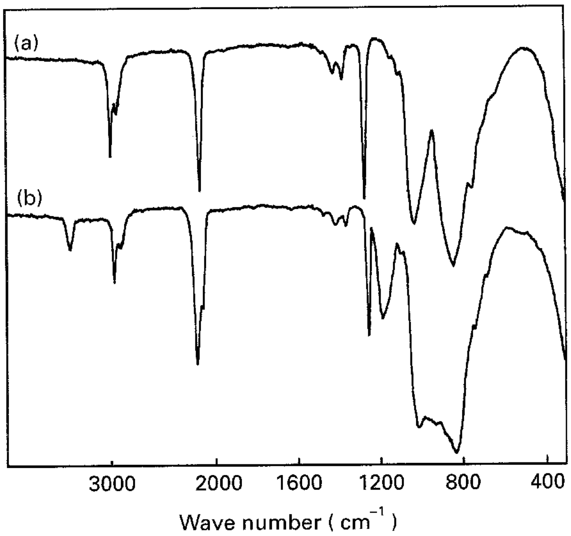

Figure 1 Infrared spectra of the reaction products: (a) PCS/titanium *n*-butoxide (Si/Ti = 50/1) and (b) PCS/titanium *n*-butoxide/PHPS (Si/Ti = 50/1, PCS/PHPS = 1/1).

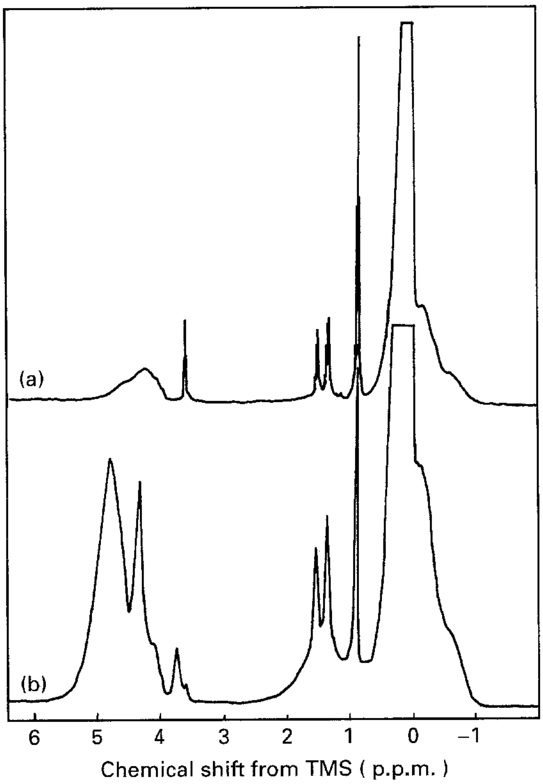

Figure 2 ^{1}H NMR spectra of the reaction products: (a) PCS/titanium *n*-butoxide (Si/Ti = 50/1) and (b) PCS/titanium *n*-butoxide/PHPS (Si/Ti = 50/1, PCS/PHPS = 1/1).

cross-linking due to dehydrogenation of Si–H and N–H bonds.

Elemental analysis and DSC results of the polymers with different titanium concentrations are summarized in Table I. Babonneau reported that the presence of Si–O–Ti bonds could not be confirmed with the reaction product of PCS with titanium *n*-butoxide [13]. Ishikawa *et al.* reported the condensation between Si–H bonds in PCS and the substituent group of tetraalkyltitanate, accompanied by evolution of alkane gas and then the formation of Si–O–Ti bonds

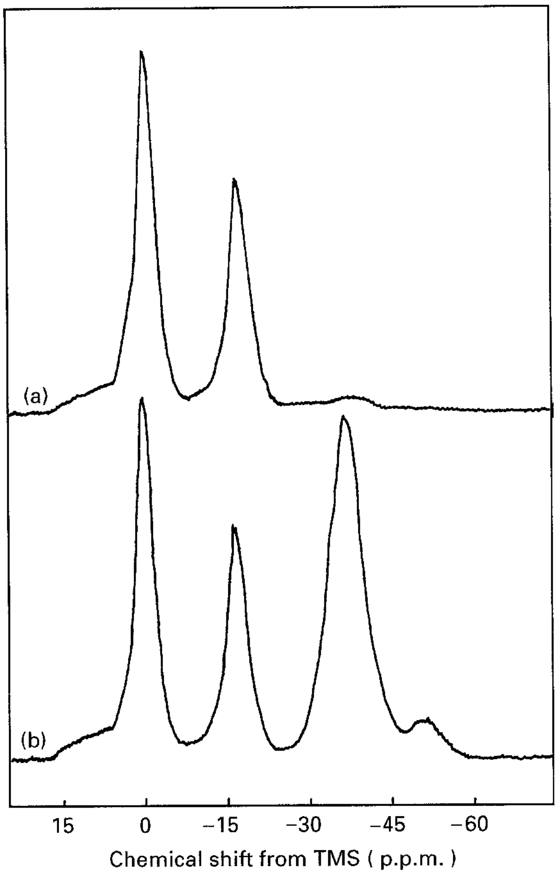

Figure 3 ^{29}Si NMR spectra of the reaction products: (a) PCS/titanium *n*-butoxide (Si/Ti = 50/1) and (b) PCS/titanium *n*-butoxide/PHPS (Si/Ti = 50/1, PCS/PHPS = 1/1).

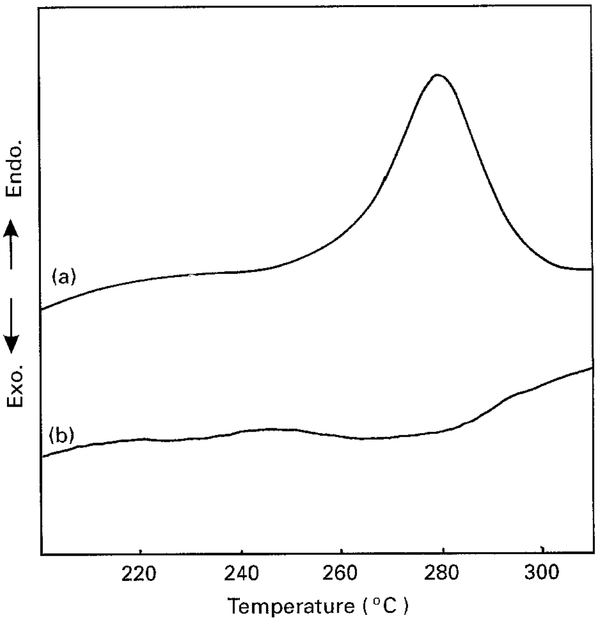

Figure 4 DSC curves of the reaction products: (a) PCS/titanium *n*-butoxide (Si/Ti = 50/1) and (b) PCS/titanium *n*-butoxide/PHPS (Si/Ti = 50/1, PCS/PHPS = 1/1).

[14]. From the spectroscopic results of our polymers, it is not clear if PCS block and PHPS block have bondings through titanium *n*-butoxide. However, titanium *n*-butoxide is essential (more than Si/Ti = 50/1) for the polymer to show thermosetting properties. This might be indirect evidence that the polymers are

TABLE I Elemental analysis and DSC results of copolymers with different titanium concentrations (PCS/PHPS = 1/1)

Si/Ti atomic ratio of PCS/Ti *n*-butoxide	Composition (wt %)						Endothermic peak at 280 °C in DSC curve
	Si	N	Ti	O	C	H	
12.5/1	43.50	10.60	2.98	4.39	30.20	8.30	No
25/1	48.60	11.90	1.67	2.68	27.20	8.03	No
50/1	51.60	12.70	0.88	1.68	25.30	7.87	No
250/1	54.40	13.30	0.18	0.76	23.60	7.73	Yes
1/0	55.10	13.50	–	0.53	23.20	7.69	Yes

TABLE II Elemental analysis and DSC results of copolymers with different PCS/PHPS ratios [(total Si)/Ti = 100/1]

PCS/PHPS (Si ratio)	Composition (wt %)						Endothermic peak at 280 °C in DSC curve
	Si	N	Ti	O	C	H	
1/0	47.00	–	0.80	1.43	40.50	8.13	Yes
9/1	47.80	2.33	0.82	1.49	37.50	8.08	Yes
4/1	48.70	4.73	0.84	1.52	34.30	7.52	No
1/4	54.90	21.40	0.93	1.82	12.70	7.68	No
1/9	56.10	24.60	0.95	1.90	8.42	7.61	No
0/1	57.40	28.10	0.97	1.96	3.94	7.55	No

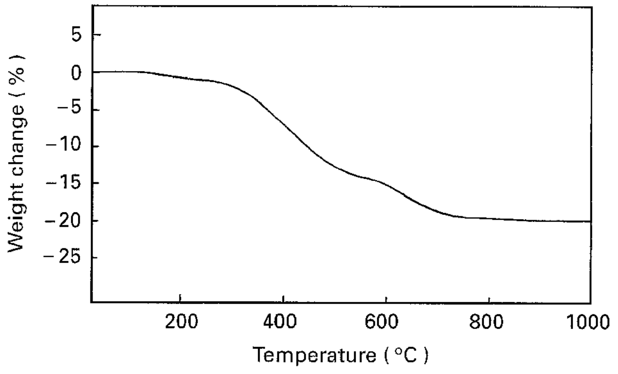

Figure 5 TGA of the copolymer (PCS/PHPS = 1/1, (total Si)/Ti = 100/1) (N_2 flow 100 $cm^3 min^{-1}$; heating rate 5 °C min^{-1}).

block copolymers with some Si–O–Ti bonds. Elemental analysis and DSC results for polymers with varied PCS/PHPS ratios are summarized in Table II. On synthesis of these polymers, the ratio of PCS to titanium *n*-butoxide was adjusted to give the same Si/Ti ratio ((total Si)/Ti = 100/1) in the products. PHPS is essential (more than PCS/PHPS = 4/1) to obtain polymers with thermosetting properties.

3.2. Conversion of the copolymers into silicon carbide-based ceramics

As shown in Fig. 5, the TGA curve of the copolymer (PCS/PHPS = 1/1, (total Si)/Ti = 100/1) indicates that the weight loss of the polymer starts around 100 °C and is complete around 800 °C in nitrogen. Three regions are apparent in the TGA curve. The first region, below 300 °C, shows a weight loss of 2%, which results from the decomposition of the titanium *n*-butoxide [12]. The second region of 10% weight loss, from 300–550 °C, and the third region of 5% weight loss, from 550–800 °C, are thought to correspond to the breaking of organic bonds with the formation of gaseous species. The decomposition of PHPS in argon is complete around 600 °C [11]. Hasegawa and Okamura reported that PCS shows weight loss due to evaporation of low molecular weight PCS below 550 °C and from 550–800 °C with evolution of hydrogen and methane which are mainly due to the decomposition of the side chains such as Si–H and Si–CH_3 [15]. The second region in the TGA curve is due to the decomposition of PHPS and PCS blocks, while the third region is certainly due to the decomposition of PCS block.

The results of the elemental analysis of pyrolysed samples are shown in Table III. The nitrogen content in the ceramics is markedly decreased in comparison with that in the polymers. Nitrogen is given off during the pyrolysis process, as is expected from the thermodynamic point of view [16, 17]. Rule-of-mixtures compositions are calculated by assigning all oxygen to silicon as SiO_2, all nitrogen to silicon as Si_3N_4, all titanium to carbon as TiC, then all carbon to silicon as SiC; excess carbon or silicon is assumed to be in the

TABLE III Elemental analysis and rule-of-mixtures composition of pyrolysis products [(total Si)/Ti = 100/1] (N_2, 1500 °C)

PCS/PHPS (Si ratio)	Composition (wt %)						Rule-of-mixtures composition (moles relative to SiC)				
	Si	N	Ti	O	C	H	TiC	SiO_2	Si_3N_4	SiC	C
1/1	63.10	3.63	1.12	1.54	29.70	0.80	0.011	0.024	0.032	1	0.22
1/4	65.60	7.81	1.14	1.56	23.20	0.70	0.012	0.026	0.074	1	0.018
1/9	64.30	14.00	1.15	1.65	18.20	0.70	0.016	0.034	0.17	1	0

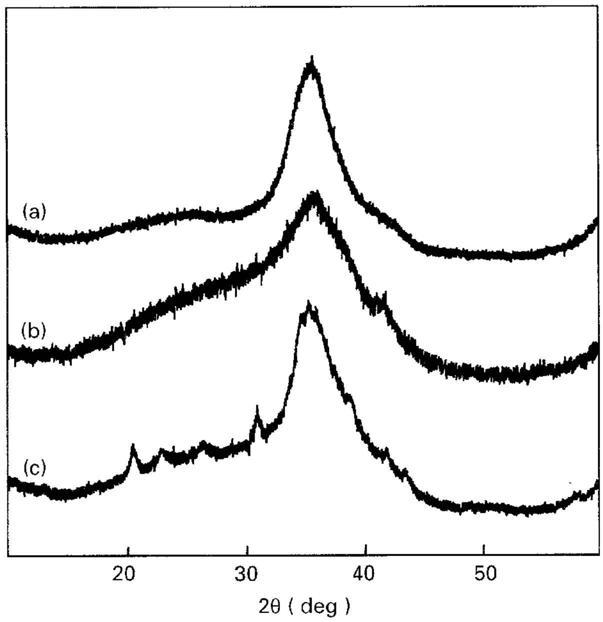

Figure 6 XRD patterns of pyrolysed copolymers: (a) PCS/PHPS = 1/1, (b) PCS/PHPS = 1/4, and (c) PCS/PHPS = 1/9 (N_2, 1500 °C).

elemental state [18]. Mole ratios of compositions, normalized to SiC, are shown in Table III. Ceramics derived from PCS/PHPS = 1/4 contain all small amounts of elemental carbon; furthermore, ceramics from PCS/PHPS = 1/9 do not contain elemental carbon. PHPS has excess silicon, relating to Si_3N_4. Elemental silicon is formed from PHPS by pyrolysis in nitrogen because nitrogen is given off. Elemental silicon from PHPS compensates for elemental carbon from PCS. Elemental carbon in the final ceramics can be reduced by varying the ratio of PCS/PHPS.

XRD patterns of pyrolysed copolymers (PCS/PHPS = 1/1, 1/4, and 1/9 (total Si)/Ti = 100/1) are shown in Fig. 6. Ceramics derived from PCS/PHPS = 1/1 shows a broad pattern characteristic of β-SiC of small crystallite size. Pyrolysed PCS/PHPS = 1/4 exhibits a broad pattern characteristic of β-SiC of small crystallite size with a broad peak at 20–35°. This broad peak is characteristic for amorphous silicon nitride. Pyrolysed PCS/PHPS = 1/4 is a mixture of small crystallite size β-SiC with amorphous silicon nitride. Ceramics from PCS/PHPS = 1/9 shows patterns of α-Si_3N_4 on the halo of β-SiC. Excess carbon, based on rule-of-mixture compositions, cannot be found in ceramics from PCS/PHPS = 1/9. However, crystallization of α-Si_3N_4 has proceeded. Lipowitz *et al.* reported that Si–N–C fibre derived from hydridopolysilazane is amorphous and contains excess carbon [18]. Excess carbon, based on rule-of mixture compositions, is thought to be necessary for the retention of amorphous ceramics derived from PCS/PHPS at 1500 °C in nitrogen.

3.3. Properties of ceramic fibre

The copolymer of PCS/PHPS = 1/4 ((total Si)/Ti = 100/1) is thermosetting, and the derived ceramics are amorphous and contain small amounts of excess carbon. This copolymer was chosen to prepare a ceramic fibre.

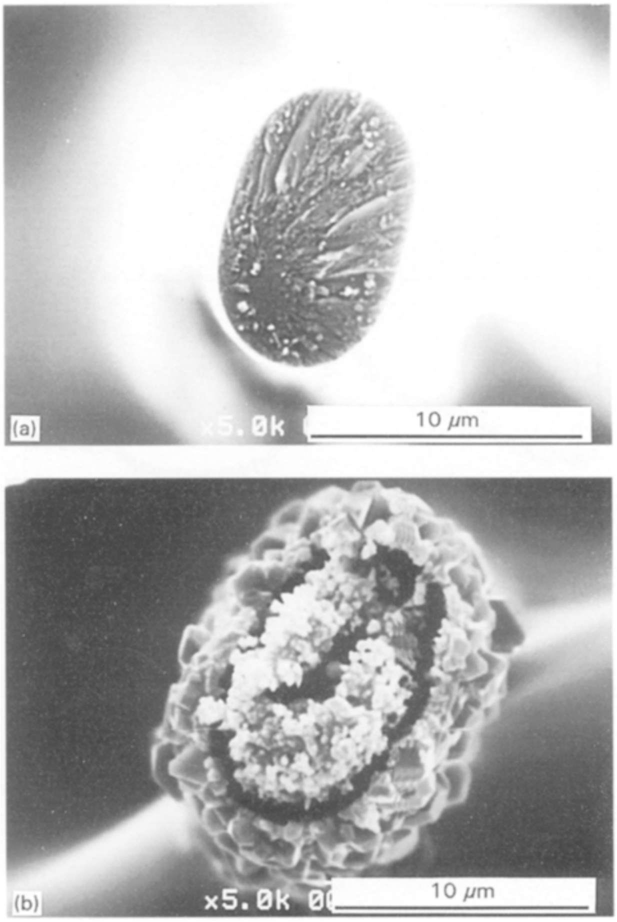

Figure 7 Fracture surface of (a) 1500 °C and (b) 1700 °C nitrogen annealed PCS/titanium *n*-butoxide/PHPS-derived fibre.

Black, shiny, ceramic fibre with a diameter in the range 10–12 μm was obtained. The fibre contains 64.6 wt % Si, 8.02 wt % N, 22.7 wt % C, 2.83 wt % O, 1.16 wt % Ti, and 0.7 wt % H, which are similar to the powder composition pyrolysed in nitrogen. An increase of the oxygen content, in comparison with that of pyrolysed powder in nitrogen, is due to inadvertedly introduced oxygen during the spinning and handling steps. Tensile strength and elastic modulus properties measured for this fibre are $\sigma = 1.8$ GPa and $E = 220$ GPa. The fractograph (Fig. 7) shows typical features of tensile failure of brittle materials. The XRD pattern reveals the mixture of small crystallite β-SiC with amorphous silicon nitride (Fig. 8). XPS analyses were performed on ground ceramic fibres. Fig. 9 shows plots of XPS binding energy (Si2p) for the fibre derived from PCS/PHPS and commercially available Si–Ti–C–O fibre (Ube Industries Ltd., Lox M). A deconvolution analysis of the result shows that the peak of the Si–Ti–C–O fibre is composed of three components; Si–O (103 eV), Si–C (101 eV), and an intermediate one (102 eV). The large intermediate signal at 102 eV can be assigned to O–Si–C species [18]. The peak of the PCS/PHPS-derived fibre is composed of two components; Si–C (101 eV) and a signal at 102 eV. Si–N has a binding energy of 102 eV.

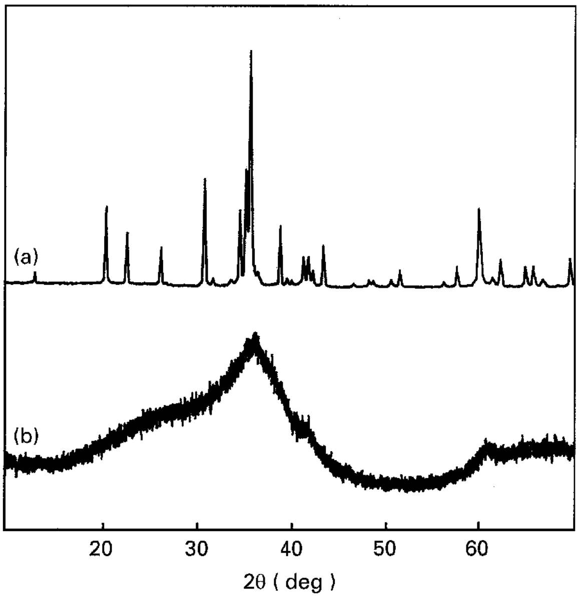

Figure 8 XRD patterns of (a) 1500 °C and (b) 1700 °C nitrogen annealed PCS/titanium *n*-butoxide/PHPS-derived fibre.

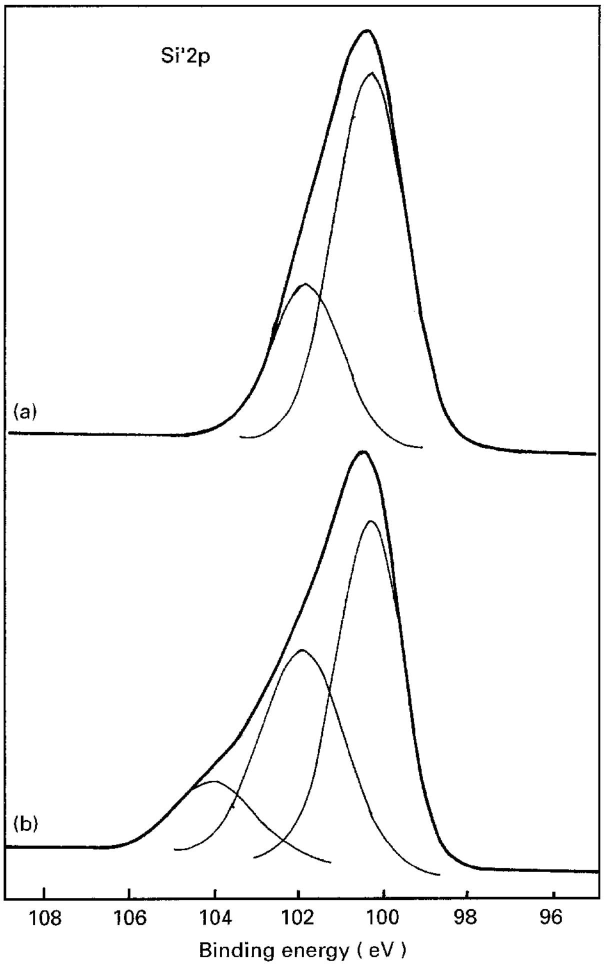

Figure 9 XPS spectra of (a) PCS/titanium *n*-butoxide/PHPS-derived fibre and (b) Si–Ti–C–O fibre (Si 2p).

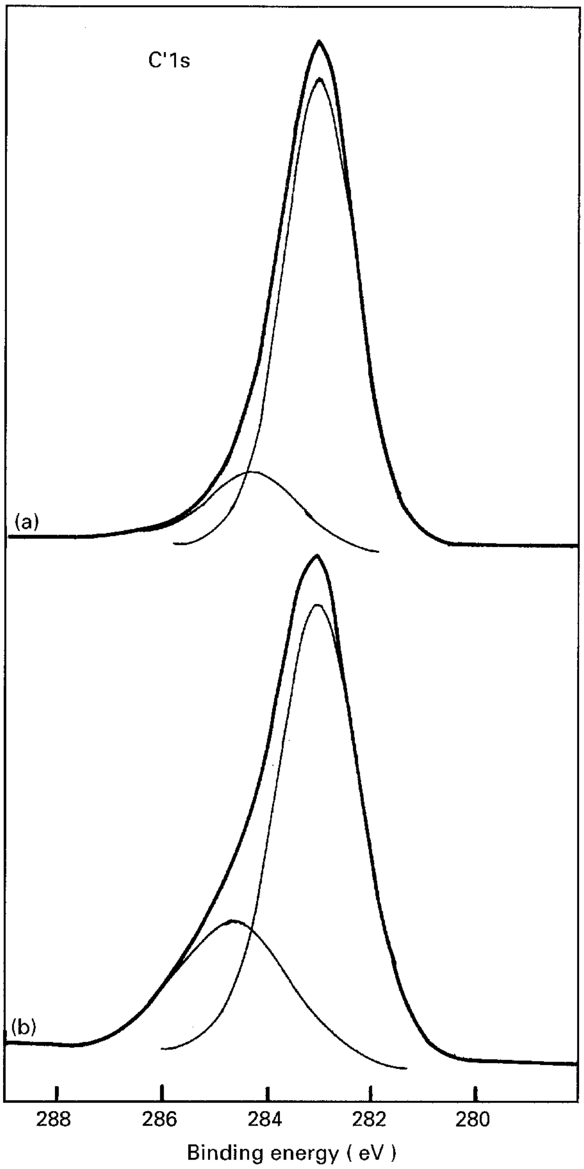

Figure 10 XPS spectra of (a) PCS/titanium *n*-butoxide/PHPS-derived fibre and (b) Si–Ti–C–O fibre (C 1s).

The PCS/PHPS–derived fibre contains 8.02 wt % nitrogen, and a signal at 102 eV can be assigned to Si–N and mixed SiOCN species. There is no component assigned to Si–O in the PCS/PHPS-derived fibre because this fibre was prepared without air curing. This spectrum agrees with the elemental analysis in that the PCS/PHPS-derived fibre (PCS/PHPS = 1/4, (total Si)/Ti = 100/1) contains a small amount of oxygen. C 1s spectra (Fig. 10) of the fibres are composed of two components; Si–C (283 eV) and carbon (285 eV). A signal of TiC might be hidden by the close and predominant Si–C, as reported by Soraru *et al.* [19]. The amount of carbon in the PCS/PHPS-derived fibre is small, compared with that of Si–Ti–C–O fibre. This spectrum corroborates that the PCS/PHPS-derived fibre (PCS/PHPS = 1/4, (total Si)/Ti = 100/1) contains a small amount of excess carbon.

In order to elucidate the crystallization behaviour, the PCS/PHPS-derived fibre was annealed in nitrogen at 1700 °C for 1 h. A weight loss of 25% was observed and the fibre turned green in colour. XRD indicates the presence of crystalline α-Si_3N_4, β-SiC, and a small amount of β-Si_3N_4 (Fig. 8). The annealed fibre possesses a porous, large-grained crystalline structure (Fig. 7). The annealed fibre was too weak to conduct tensile strength measurements.

4. Conclusion

A copolymer of PCS and PHPS was obtained by reacting PCS with titanium *n*-butoxide and PHPS. Titanium *n*-butoxide (more than (total Si)/Ti = 100/1) and PHPS (more than PCS/PHPS = 4/1) were essential for the polymer to show a thermosetting property. The thermosetting copolymers were converted into silicon carbide-based ceramics by pyrolysis in a stream of nitrogen to 1000 °C with about 80 wt % ceramic yield. The main phase of the pyrolysis product at 1500 °C in nitrogen was small crystallite of β-SiC. Elemental carbon, based on the rule-of-mixtures composition, in the final ceramics could be reduced by varying the ratio of PCS/PHPS.

The copolymer (PCS/PHPS = 1/4, (total Si)/Ti = 100/1) was dry spun and pyrolysed to produce ceramic fibre. Pyrolysis in nitrogen to 1500 °C yielded a silicon carbide-based fibre with low oxygen and low excess carbon content. A tensile strength of 1.8 GPa and an elastic modulus of 220 GPa were obtained for the fibre which ranged from 10–12 μm in diameter. Crystallization to α-Si_3N_4, β-SiC, and β-Si_3N_4 proceeded on annealing in nitrogen at 1700 °C for 1 h.

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