

A MODEL SiC-BASED FIBRE WITH A LOW OXYGEN CONTENT PREPARED FROM A VINYL-CONTAINING POLYCARBOSILANE PRECURSOR

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SUMMARY: A model SiC-based fibre has been prepared from a vinyl-containing polycarbosilane precursor by means of an irradiation oxygen-free curing process. Cyclo-methylvinylsilazane (MVCSZ) was successfully grafted onto the molecular of a polycarbosilane (PCS) in order to enhance the PCS's irradiation curing. A vinyl content of 2.33wt% in PCS can lower its gel dose, curing dose from 10MGy, 15MGy to 0.5MGy, 5MGy, respectively. Thus obtained SiC fibre has a much lower oxygen content (3.3-6.3wt%) than an oxygen-cured Si-C-O fibre (18.9wt%), but shows a lower tensile strength at room temperature than the Si-C-O fibre because of some experimental factors. After the annealed treatment of 1600□ in nitrogen for 30min, the fibre contains□-SiC crystals (mean size 12nm) and retains a 67% tensile strength.

KEYWORDS: SiC, oxygen content, vinyl-containing polycarbosilane, cyclo-methylvinylsilazane, enhancement, electron beam, curing, pyrolysis

INTRODUCTION

Silicon Carbide (SiC) ceramic fibres, which are well known for their excellent tensile strength, thermal shock resistance and intermiscibilities with many matrices, are applied widely in materials engineering of high performance composites. In recent years, preparation of ceramic fibres by the pyrolysis of an organic polymer has attracted considerable attention and has become a steadily growing field[1]. During the process, polycarbosilane (PCS) protofibres are heated in air to be cured; but this introduces much oxygen into the fibres so that their mechanical properties, especially those at elevated temperatures need improvement[2]. Therefore, most recent work is devoted to the lowering of the oxygen content in the fibres[1]. For instance, Okamura and his coworkers rendered PCS fibres infusible by electron beam (EB) irradiation under vacuum[3,4] and this kind of low-oxygen-content SiC fibres have been industrially produced by Nippon Carbon Japan under trademark Hi-Nicalon. But it also has a question of high absorbed dose, 10~15MGy[3], that makes it hard on irradiation equipment and low in efficiency.

In an attempt to reduce irradiation dose and make cheap "Hi-Nicalon" fibres, this paper studied EB irradiation cross-linking of vinyl-containing polycarbosilane (Vi-PCS) fibres, aiming to enhance the vinyl cross-linking. Another purpose of the present study was to analyze the mechanical properties of thus obtained low-oxygen-content SiC fibre, with an oxygen-cured Si-C-O fibre as a comparison.

EXPERIMENTAL PROCEDURE

The Vi-PCS precursors used in the present work were prepared in three steps. First, ViMeSiCl_2 was mixed with benzene in a three-necked flask with a reflux condenser and a thermometer. After the air in the flask had been replaced with dry N_2 gas, NH_3 was introduced into the system accompanied by high-speed stirring. The reaction mixture was filtered and distilled and the resultant, ammonolysis product was ready for the third step. Second, low molecular weight poly(dimethylsililene) (PDMS) was put into a reaction vessel with a quartz reactor tube and heated slowly in N_2 gas flow up to 450°C . A PCS with a melting point of $110\sim 120^\circ\text{C}$ was obtained after cooling. Then, the ammonolysis product with a specific mass percent between 5wt% and 20wt% was added to the above vessel. After thermal copolymerization was carried out at 260°C for 30 min, the Vi-PCS precursor with a specific vinyl content was prepared. Afterwards, the Vi-PCS precursors were melt-spun into fibres by a monohole method under high-purity nitrogen atmosphere, with laboratory apparatus, stretched with a take-up reel. The continuous green monofilament was cut at a length of 600mm and introduced into a quartz vessel filled with high-purity helium.

Bundles of the green fibres were irradiated in helium atmosphere in the quartz vessel under an electron accelerator with a rate close to 0.8MGy per min. The absorbed dose was between 2.0MGy and 12.0 MGy. Last, the samples were annealed in helium gas flow at 130°C for 1h and the irradiation cross-linked Vi-PCS fibres were finally obtained. Another batch of the green fibres was oxygen-cured in air in a furnace with air flowing through, up to 195°C for 2h with a weight gains of 10wt%.

The irradiated or oxygen-cured fibres were then pyrolysed under a flow of high-purity nitrogen ($Q=10\text{ml/min}$, $P=100\text{kPa}$) up to 1200°C for 30min with a relatively slow heating rate (100°C/h). After this treatment, the fibres that were no longer sensitive to oxidation, could be handled in air. The pyrolysis was then achieved with a high-temperature pyrolysis equipment (1800°C) comprising a graphite crucible with a radio frequency coil. The samples were heated (30°C/min) and maintained at the pyrolysis temperature T_p under a high-purity nitrogen atmosphere (100kPa) during a time $t_p=30\text{min}$.

The fibres were characterized by the following method: A gas chromatography-mass spectrogram (GC-MS, HP 5890/5970B GC/MS D, USA) was performed on the ammonolysis product to analyze its composition and structure. The specific vinyl content of the Vi-PCS precursor was calculated from ^1H nuclear magnetic resonance (NMR, AC-80, Germany) analysis and elemental analysis (described below). The infrared (IR) spectra were recorded in the transmission in the $400\text{-}4000\text{cm}^{-1}$ range (Hitachi 270-30, Japan), from pressed pellets made from a mixture of KBr powder and the finely ground samples (weight ratio: 1%), for the precursor and the pyrolytic residues. The thermogravimetric analyses (TGA) (Rigaku, Japan) were performed, up to 1200°C , in a platinum crucibles on about 10mg samples under a high-purity nitrogen flow (flow rate: 40ml/min) with a temperature increase rate of 10°C/min . Measurements of melting point and gel content were determined by m.p. analyser (HMK,

West Germany) and solvent extract apparatus, respectively. Elemental (Si,C,N) analysis were performed on the samples by a chemical-analysis process. Element of oxygen were determined by a nitrogen/oxygen analyser (TC-436, LECO, America).

The X-ray diffraction (XRD) spectra (Cu-K α /Seimens D-500 diffractometer, Germany) were recorded from tows of fibres for $T_p=1600^\circ\text{C}$. The apparent mean grain size (L) of the β -SiC crystalline phase present in the samples was calculated from the width (D) of the (111) diffraction peak at mid-height, according to the following equ 1:

$$L = K\lambda / D \cos\theta \quad (1)$$

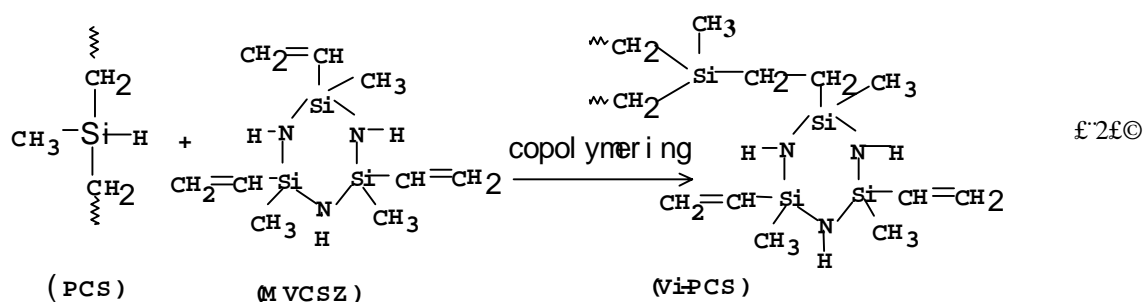
where K is a constant (taken as 1), λ the Cu- K_α wavelength (i.e. $\lambda=0.154\text{nm}$) and θ the Bragg angle ($\theta=17.8^\circ$ for β -SiC(111)). The morphology changes of the fibres that occurred during the pyrolysis and annealing treatments were studied by scanning electron microscopy (SEM) (X-650, Japan) The monofilaments were tensile tested at room temperature with a monohole apparatus. For each value, a batch of about 25 monofilaments were tested with a gauge length of $L=20\text{mm}$ and the data were used to determine the mean ultimate tensile stress σ^R .

RESULTS AND DISCUSSION

Synthesis of the Vinyl-Containing Polycarbosilane Precursor

GC-MS analysis showed that, the ammonolysis product of ViMeSiCl_2 consisted of cyclic structures as $(\text{MeViSiNH})_3$ $(\text{MeViSiNH})_4$, which containing three vinyls, four vinyls, respectively. That is to say, the ammonolysis product is a mixture of cyclo-methylvinylsilzane (MVCSZ), which are polyfunctional monomers efficiency for enhancement of PCS.

During the thermal copolymerization, relative absorbance of Si-H \rightarrow C=C bonds decreased and that of Si-CH $_2$ bonds increased gradually. This suggests that the main reaction of the copolymerization is hydrosilylation addition between Si-H in PCS and C=C in MVCSZ, as shown in equ 2, in which MVCSZ is presented by $(\text{MeViSiNH})_3$. Thus, MVCSZ was grafted



onto PCS molecular and the Vi-PCS fibres with various vinyl contents were obtained.

Enhancement Analysis

Melting point Analysis

Table 1: Gel dose of Vi-PCS fibres with different vinyl content

Vinyl content/wt%	0.0	0.27	1.29	1.50	2.33
Gel dose*/MGy	10.0	5.5	3.0	2.8	0.5

*Calculated by plotting LOG(S) against LOG(D), where, S(soluble fracture)=unit-gel% and D is absorbed dose

Melting point results, as illustrated in Fig.1, showed that, with the irradiated Vi-PCSs with the same vinyl content, the m.p. was growing proportionally to the absorbed dose; yet with the irradiated Vi-PCSs with different vinyl content, the more vinyl it contained, the faster the m.p. grew.

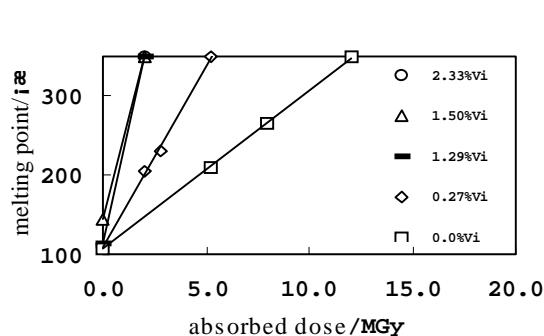


Fig.1: the relation between melting point and absorbed dose

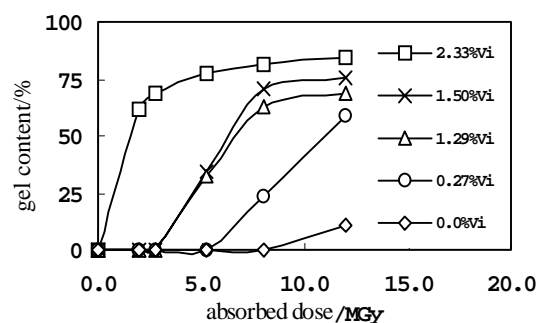


Fig. 2: the relation between gel content and absorbed dose

Gel Content Analysis

Similarly, gel content curves, as shown in Fig.2, had the same tendency: the gel content, which represents the insoluble part, was zero at first, then rose rapidly on reaching a critical gel dose; while the gel dose was much reduced as the vinyl content increased, as shown in Table 1.

According to our own experiences in air-curing, the material becomes infusible when the gel content reaches 75% or higher. As to these irradiated fibres shown in Fig.2, 0.0wt% Vi-PCS, that is PCS, was far from infusible state at the absorbed dose of 12MGy for its gel content was only 10.65%; whereas, 2.33wt% Vi-PCS reached its gel content of 75% or its infusible state at just 5.0MGy.

IR Analysis

Change in the infrared spectra of 2.33wt% Vi-PCS illustrated in Fig.3 showed that, absorption peaks at 1600cm^{-1} (C=C) 2100cm^{-1} (Si-H) $3400\text{cm}^{-1}/1180\text{cm}^{-1}$ (N-H) were all decreasing with increasing absorbed dose. This is because the bond energies of C=C \square Si-H \square N-H bonds are relatively lower than that of the C-H bond, and they are easier broken to take part in the subsequent reactions. No changes can be observed in the absorption peak of Si-CH₃ at 1260cm^{-1} because of its highly stability. Compared with C-H(Si-CH₃) at 1410cm^{-1} , absorption of C-H(Si-CH₂) at 1355cm^{-1} was increasing from weaker to stronger. It strongly indicates a combination of C=C and Si-H to the formation of Si-CH₂. No absorption was detected at 1080cm^{-1} , which suggests that little oxygen was introduced.

Table 2: Characteristics of Vi-PCS fibres with irradiation

Vinyl content/wt%	0.0
Gel content/%	10.95
Reaction degree* of Si-H bonds/%	26.67

*Calculated from IR spectra .

From the bond energies, the C=C bond is the easiest to form free radicals, and then to induce

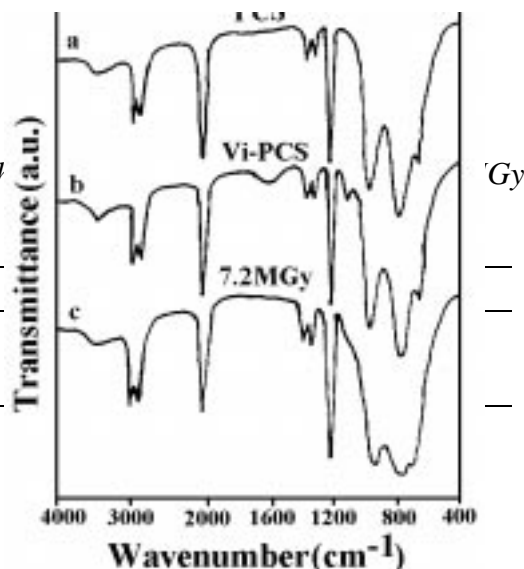


Fig.3: Infrared spectra of (a) PCS, (b) Vi-PCS with a vinyl content of 2.33wt% and (c) fibre of (b) irradiated by 7.2MGy.

Si-H bond cleavage. From the data of Table 2, for various Vi-PCSs after the same absorbed dose of 12MGy, a greater vinyl content increased both the reaction degree of Si-H bonds and the gel content. It showed that the introduction of vinyl group stimulated Si-H bond rearrangement, enhanced irradiation cross-linking, and so, enhanced the rapid development of the reticulate structure, with a demonstration of quick increasing of gel content.

Pyrolysis of the Uncured, EB-Cured and Oxygen-Cured Precursor

Thermogravimetric Analysis

TGA curves of uncured Vi-PCS, EB-cured Vi-PCS and oxygen-cured Vi-PCS are shown in Fig.4. The pyrolysis of the uncured Vi-PCS seems to involve two steps: (1) a first step, up to 500°C with a 14% weight loss and (2) a second step from 500-900°C with a final ceramic yield of 67%. Conversely, those of the EB-cured Vi-PCS and the oxygen-cured Vi-PCS show that a 3-5% weight loss takes place at low temperatures (from 200-500°C), leading to much higher

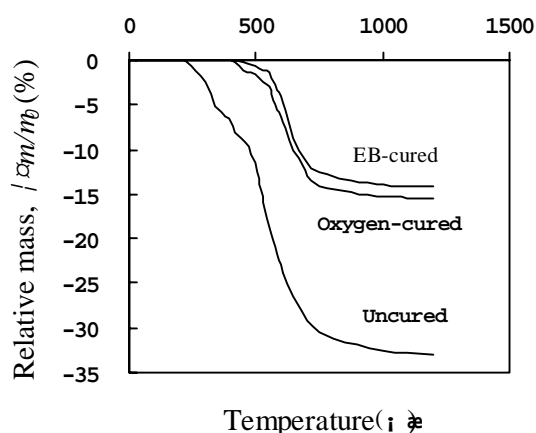


Fig.4: TGA under flowing nitrogen (heating rate =10°C per min., P=100kPa) of Vi-PCS fibre

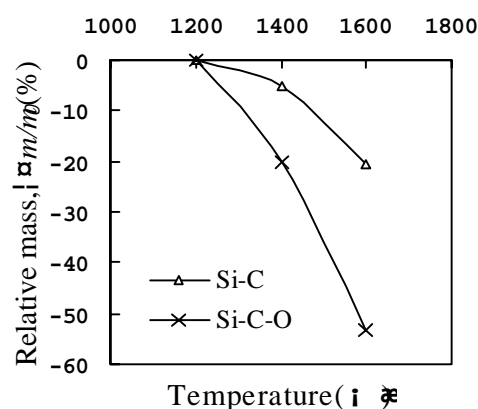


Fig.5: Weight loss of Si-C and Si-C-O fibre under flowing nitrogen (heating rate =10°C per min., P=100kPa)

ceramic yield (85-87%). A slight lower weight loss in EB-cured Vi-PCS can be detected from the difference of the two curves. After a high temperature heat treatment shown in Fig.6, the Si-C-O fibre undergoes a large weight loss within the temperature range $1300 < T < 1600$, with a final value of $m/m_0 = -53\%$ at 1600 . Conversely, only a 16% weight loss is recorded for low-oxygen Si-C fibre up to 1600 .

Elemental Analysis

Oxygen content of the low-oxygen Si-C fibre is 3.3-6.3wt%, much lower than that of the oxygen-cured Si-C-O fibre (18.9%). But it still cannot compare with the Si-C fibre from Hi-NicalonTM (0.5wt%) in oxygen content.

Structure and Microstructure of the EB Cured Fibres

SEM micrographs of the Si-C and Si-C-O fibre after 1600 pyrolysis are shown in Fig.7 (a and b). At 1600 , the Si-C fibre retains its smooth surface but two scratches made during delivery. Conversely, the Si-C-O fibre, with much loss, can hardly maintain its fibre shape.

XRD spectra (Fig.8) of the Si-C fibre at $T_p = 1600$ shows three main peaks, assigned to the (111), (220) and (311) reflections of β -SiC are observed (corresponding respectively to a d spacing of 0.251, 0.154 and 0.131nm). The mean grain size calculated from the width of the (111) reflection is about 12nm, higher than that of the Si-C fibre[4], but remains considerably lower than for Si-C-O fibre[2].

Mechanical Characteristics of the Fibres

The variations of the tensile failure strength measured at room temperature of the fibres as a function of the pyrolysis temperature are shown in Fig.8

The Si-C-O fibre has a higher tensile strength than the Si-C fibre at a pyrolysis temperature of 1200 because of some existing scratches on the Si-C fibre (shown on SEM). However, the Si-C-O fibre lost all the strength after a pyrolysis temperature of 1600 , the Si-C fibre retains a 67% tensile strength.

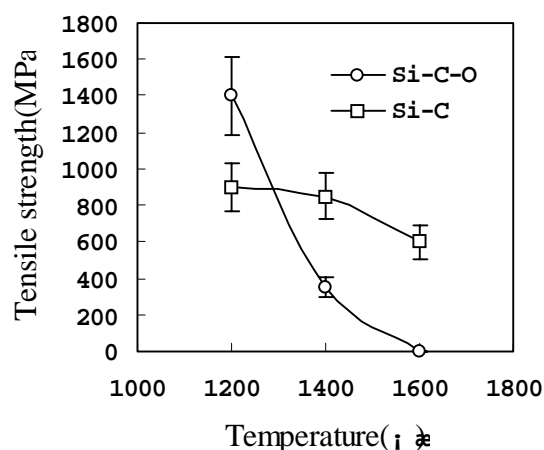


Fig 8 Tensile failure strength as a function of annealing temperature in nitrogen.

CONCLUSION

MVCSZ as an enhancing agent were grafted onto PCS molecular by the hydrosilylation addition between Si-H in PCS and C=C in MVCSZ.

Model SiC-based fibres with a low oxygen content (3.3-6.3%) have been prepared by means of an irradiation curing process from a vinyl-containing polycarbosilane precursor.

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