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Synthesis of continuous silicon carbide fibre

Part 2 *Conversion of polycarbosilane fibre into silicon carbide fibres*

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The polycarbosilane (PC-470) synthesized by thermal decomposition of polydimethylsilane was melt-spun. The conversion process of the fibre into silicon carbide fibre was investigated by chemical analysis, TG-DTA and infra-red spectrum analysis, and measurements of the mechanical properties and densities. The conversion process of polycarbosilane (PC-TMS) synthesized by Fritz was examined and compared with the conversion process of PC-470. It is shown that the process is divided into three stages; condensation at the first stage, thermal decomposition at the second stage and crystallization at the third stage. The mechanical properties and density of the SiC fibre obtained by heat-treatment were affected by the molecular weight and structure of the polycarbosilane of the starting material.

1. Introduction

We have reported the synthesis and the molecular structure of polycarbosilane as the precursor of silicon carbide fibre [1]. This polycarbosilane (PC-470) was synthesized in an autoclave by thermal decomposition of polydimethylsilane obtained by dechlorination of dichlorodimethylsilane.

Polycarbosilanes are usually synthesized by the thermal decomposition of monosilanes or disilanes and by the ring-opening polymerization of disilacycrobutanes. Fritz *et al.* [2] determined molecular structures of carbosilanes obtained by thermal decomposition of tetramethylsilane. They demonstrated that fusible high molecular weight components (PC-TMS) were obtained by the reaction at the same time.

However, the thermal decomposition process of the polycarbosilanes has not been examined in detail. In this paper, the conversion process of PC-470 fibre into silicon carbide fibre was investigated and compared with the conversion process of PC-TMS. The characterization of the conversion process is necessary to analyse the structure of the silicon carbide fibre with high tensile strength and high Young's modulus.

2. Experimental details

2.1. Synthesis of polycarbosilanes

Polycarbosilane (PC-470) was synthesized by thermal decomposition of polydimethylsilane in an autoclave at 470° C for 14 h and then condensed by vacuum distilation up to 280° C [1].

Another polycarbosilane, obtained by thermal decomposition of tetramethylsilane, was synthesized by the method used by Fritz *et al.* [2]. Tetramethylsilane was passed slowly through a quartz tube heated at 770 ± 10° C by a circulating pump. The reaction products were collected at room temperature in a receiver. The circulation continued for 24 h. A liquid paraffin vent balanced the pressure in the apparatus. The products were dissolved in *n*-hexane and filtered, and then the solvent and the fraction with lower boiling points was removed by a rotary evaporator. By vacuum distillation, the fractions with boiling points up to

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200° C/1 mm Hg was removed. Thus, a yellowish brown solid of polycarbosilane (PC-TMS) was obtained (6.8% yield).

2.2. Synthesis of fibres

The polycarbosilane, PC-470 and PC-TMS, fibres were obtained by melt-spinning at about 350 and 270° C, respectively, from a nozzle of a capillary drawn out from the bottom of a quartz tube 2.5 cm diameter and 20 cm long. Melted polycarbosilane in the quartz tube was continuously exposed to N_2 gas to avoid oxidation. The fibres were wound on a 50 cm diameter drum placed at a distance 50 cm below the nozzle. A motor drove the drum and the drawing speed could be varied continuously from 0 to 1000 m min^{-1}. In this work, the drawing speed was about 200 m min^{-1}.

A bundle of the fibres of about 20 cm length was then put on to a half quartz tube, both sides of which were fixed by two carbon weights. Thus the fibre was cured in air. The PC-470 fibre was cured at a heating rate of 30° C h^{-1} and at 190° C for 30 min. The PC-TMS fibre was cured at the heating rate of 10° C h^{-1} and at 200° C for 60 min.

The cured PC-470 or PC-TMS fibres were then heat-treated in a nitrogen gas atmosphere (flow rate 100 $\text{cm}^3\,\text{min}^{-1}$) or in vacuum at a heating rate of 100° C h^{-1} at a temperature of 1300° C or below, for 60 min.

2.3. Measurements

The data pertaining to the polycarbosilanes and fibres were obtained by the measurements described below.

The infra-red spectra were measured using a Hitachi 285 grating infra-red spectrometer in carbon tetrachloride solutions or by the KBr pellet method.

Number-average molecular weights were measured with a Hitachi 117 molecular weight apparatus by vapour pressure osmometry (VPO) in benzene solution, using naphthalene as the standard material. Molecular weight distributions were measured with a TSK HLG-801A by gel permeation chromatography (GPC) using a differential refractometer for the detector in tetrahydrofuran solution.

The proton–NMR spectra were measured with a JEOL JNM-FX 60 high-resolution FT NMR spectrometer at 60 MHz at room temperature in C_6D_6 solutions.

The TG-DTA curves were obtained by a Rigaku micro TG-DTA high-temperature type at the heating rate of 5° C min^{-1} in a N_2 flow of 50 $\text{cm}^3\,\text{min}^{-1}$ or in air.

Chemical analysis was made for four elements; Si (by a gravimetric method dissolving with sodium carbonate and sodium peroxide), C (by a combustion volumetric method), and O and H (by gas analysis).

An ASTM apparatus was used for density measurements of the fibres using the density gradient tube method with glass floats at 25° C. The density gradient columns were made up of carbon tetrachloride and ethanol in the density range 1.100 to 1.600 and of bromoform and carbon tetrachloride in the density range 1.600 to 2.700.

The mechanical properties, tensile strength, Young's modulus and fracture strain, of the fibres were measured by a universal testing machine fabricated by Toyo Baldwin Co, Tensilon UTM-II-20 (10 mm gauge length and 2 mm min^{-1} cross-head speed at room temperature). The diameters of the fibre specimens were determined using the microscope with a micrometer eyepiece.

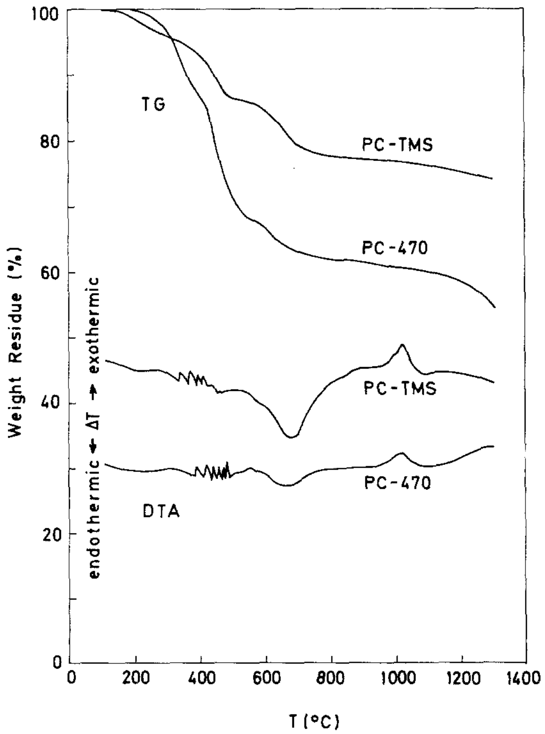

Figure 1 TG-DTA curves of PC-470 and PC-TMS in an N_2 flow.

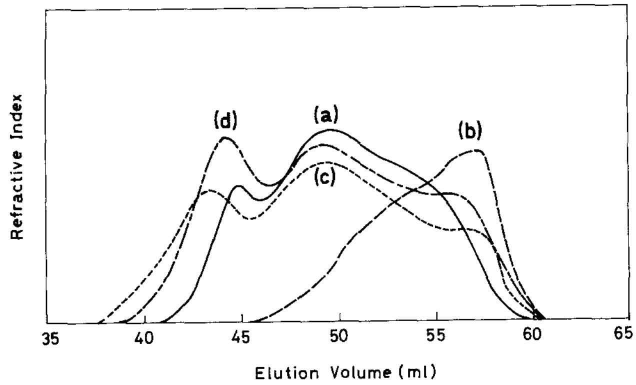

Figure 2 Elution curves of (a) PC-470, (b) PC-TMS, (c) PC-TMS heat-treated at 365° C, and (d) polycarbosilane synthesized in the same conditions as PC-470 and condensed by distillation up to 400° C in atmospheric N_2 gas.

3. Results and discussion

3.1. TG-DTA of polycarbosilane

The number-average molecular weights of PC-470 and PC-TMS are 1547 and 774, respectively. TG-DTA curves of PC-470 and PC-TMS obtained in a N_2 flow up to 1300° C are shown in Fig. 1. From these curves, it can be seen that the conversion process of the polycarbosilanes into the inorganic state is divided into three stages: the first stage up to about 550° C, the second stage up to about 850° C, and the third stage above 850° C.

In the first stage, as shown in Fig. 1, the TG curves fall off rapidly as the result of evaporation of lower molecular weight components and the weight losses of PC-470 and PC-TMS are about 32 and 14%, respectively. The molecular weight distributions of PC-470, PC-TMS and PC-TMS heat-treated at 365° C in nitrogen atmosphere are shown in Fig. 2. It is evident that the condensation of PC-TMS has already occurred at 365° C. Thus, $\bar{M}_n$ of PC-TMS increases from 774 to 1547, and this PC-TMS can no longer be melt-spun. The phenomenon that low molecular weight hydrocarbons tend to be split off by heat-treatment, leaving solid products of greater molecular complexity, has been observed by Fritz *et al.* [2]. In the PC-470 melt-spun at about 350° C, however, the condensation hardly occurred, as given in Table I. As plotted in Fig. 2, the molecular weight distribution of the polycarbosilane synthesized in the same conditions as PC-470 and condensed by distillation in atmospheric N_2 gas, up to 400° C not by vacuum distillation, shows that a slight degree of condensation should occur at about 400° C. Consequently, the first stage of the conversion process of these polycarbosilanes into the inorganic state is the condensation of the polycarbosilane molecules. The difference in weight loss between PC-470 and PC-TMS at 550° C is due to the difference in the mechanism and rate of this reaction. In Table I, the empirical formulae are shown on the basis of the chemical analysis of PC-470. In the thermal decomposition products from tetramethylsilane, the structures of the more abundant products contain condensed six-membered rings with alternating Si and C atoms, as in the formulae shown for $Si_7C_{18}H_{46}$, $Si_8C_{20}H_{50}$, $Si_8C_{24}H_{66}$ and $Si_9C_{27}H_{74}$ [2]. Proton-NMR spectra of PC-470 and PC-TMS are shown in Fig. 3. From the ratio of Si–H (5 ppm region) and C–H (0 ppm region) absorption intensity areas [1], the C–H/Si–H ratio is evaluated to be 11.1 for PC-470 and 37.3 for PC-TMS. In addition, from the infra-red spectra in 0.02 mol litre^{-1} CCl_4 solution, it was found that the Si–H concentration in PC-TMS was 1/5.37 of that in PC-470. From these results, it is concluded that the concentration of Si–H in PC-TMS is lower than that in PC-470 and the concentration of the methyl group in PC-TMS is higher than that in PC-470. Consequently, the condensation should be dehydrogenation in PC-470 [1] and be dehydrocarbonation in PC-TMS [2]. The dehydrocarbonation is

TABLE 1 Chemical composition (wt %) and $\bar{M}_n$ of polycarbosilanes and the fibres

Sample	Si	C	H	O	Empirical formula	H/C	$\bar{M}_n$
PC-470	50.57	37.24	6.70	1.20	$SiC_{1.71}H_{3.70}O_{0.04}$	2.16	1547
PC-470 fibre	48.78	39.32	7.00	0.77	$SiC_{1.88}H_{4.02}O_{0.03}$	2.14	1573
Cured PC-470 fibre	44.44	31.03	5.30	15.05	$SiC_{1.63}H_{3.34}O_{0.61}$	2.05	–

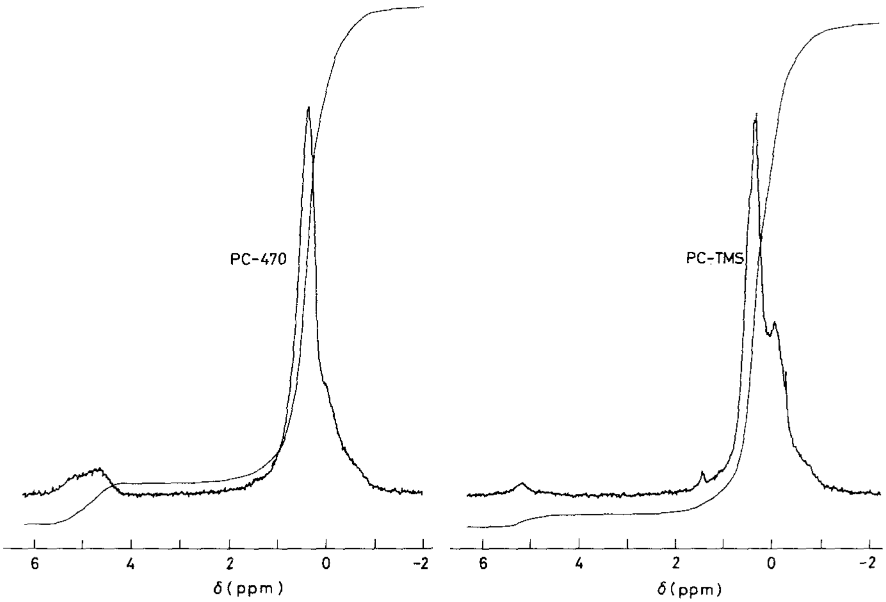

Figure 3 ^{1}H-NMR spectra of PC-470 and PC-TMS (solvent C_6D_6, at 60 MHz).

thought to occur at a lower temperature than the dehydrogenation.

In the second stage, as shown in Fig. 1, the DTA curves of PC-470 and PC-TMS exhibit large endothermic peaks from about 550 to 850° C accompanied by weight losses of 6.7% in PC-470 and 8.5% in PC-TMS. The reaction in this stage is mainly the thermal decomposition of the side chains of the polycarbosilanes. Thermal decomposition of the main chains of the polycarbosilanes hardly occurs, for the weight losses are very low at this stage.

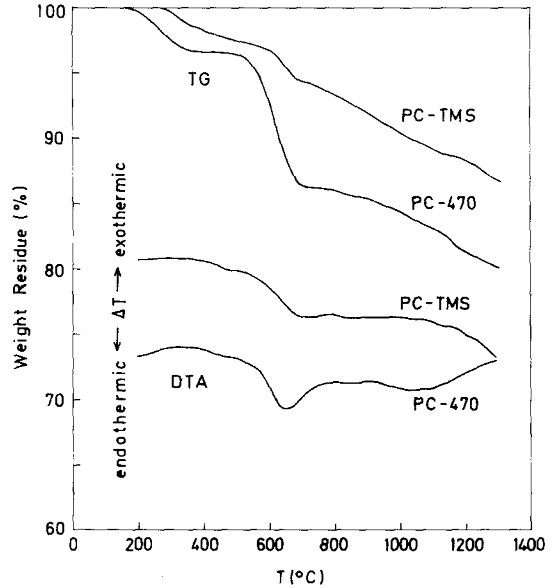

Figure 4 TG-DTA curves of the cured PC-TMS and PC-470 fibres in an N_2 flow.

In the third stage above 850° C, the conversion of the polycarbosilanes into the inorganic state is almost terminated at about 850° C and completed with further increase in temperature, accompanied by weight losses of 3.5% in PC-TMS and 7.3% in PC-470 up to 1300° C. In Fig. 1, both DTA curves show the exothermic peaks at 1020° C due to crystallization of β-SiC.

The conversion processes in the second and third stages will be described in detail later.

3.2. Curing process of polycarbosilane

In the synthesis of silicon carbide fibre in this work, polycarbosilane fibres were cured by heating in air. Number-average molecular weights of the melt-spun PC-470 and PC-TMS are 1537 and 873, and the condensation of the molecules hardly occurs. The weight gains of PC-470 and PC-TMS fibres by the curing process, are about 7.5% and 2.3%, respectively, and the fibres were infusible and the conversion process of the polycarbosilanes into the inorganic state should be affected. The TG-DTA curves of the cured fibres of PC-470 and PC-TMS in a nitrogen flow are shown in Fig. 4. In comparison with the TG-DTA curves in Fig. 1, it is clear that the weight residues of the cured fibres at 1300° C are higher than those of the polycarbosilanes without curing. According to the TG curves of Fig. 4, the weight losses are about 5% in the cured PC-470 fibre at 550° C and about 3% in the cured PC-TMS fibre. But the weight losses of the cured PC-470 and PC-TMS fibres in the temperature range 550 to 1300° C are about 15% and 10%, respectively. These values are nearly identical with those of PC-470 and PC-TMS without curing (14% and 12%, respectively) as shown in Fig. 1. It is concluded, therefore, that by curing, the weight losses of PC-470 and PC-TMS in the first stage are reduced and the curing process hardly affects the weight losses of the second and third stages of both fibres. So, the curing is a process of cross-linking of the polymer by oxygen to make the fibre infusible rather than the process of condensation.

The mechanism of curing is as follows. TG-DTA curves of PC-470 and PC-TMS in air are shown in Fig. 5. In the case of PC-470, it is clear that the exothermic reaction starts at about 150° C with a weight gain. From the results of chemical analysis of the cured PC-470 fibre in Table I, the reaction is the oxidation of PC-470 by oxygen. In the case of PC-TMS, the weight gain is small. As compared with the result in Fig. 1, it is clearly shown that the oxidation of PC-TMS occurs at about 150° C.

The infra-red spectra of PC-470 and PC-TMS fibres before and after curing are shown in Figs. 6 and 7. Both PC-470 and PC-TMS fibres show characteristic absorption bands of polycarbosilane at 2950, 2900, 2100, 1400, 1355, 1250, 1020 and 820 cm^{-1} [1]. The 3450 and 1620 cm^{-1} bands correspond to the stretching and deformation vibrations of adsorbed water molecules [4], respectively. After curing we observed that the intensities of absorption bands due to Si–CH_3 and Si–H decreased as compared with the 1020 cm^{-1} band due to CH_2 wagging of Si–CH_2–Si: 2950 and 2900 cm^{-1} (C–H stretching of Si–CH_3), 2100 cm^{-1} (Si–H stretching), 1400 cm^{-1} (CH_2 deformation of Si–CH_3), 1250 cm^{-1} (Si–CH_3 deformation), and 820 cm^{-1} (Si–CH_3 rocking and Si–C stretching) [5, 6]. On the other hand, a 3680 cm^{-1} band of a free O–H stretching and a 1710 cm^{-1} band of C=O stretching appeared, and the intensity of the absorption in the 1100 cm^{-1} region of the Si–O stretching in Si–O–Si or Si–O–C [4, 6] was increased. These results indicate that the mechanism of the curing is the cross-linking by the oxidation of Si–H and Si–CH_3 to make Si–O–Si and Si–O–C. In the case of PC-TMS, the cross-linking of the condensation due to the splitting off of hydrocarbons also occurs and the weight gain of PC-TMS is smaller than that of PC-470 in Fig. 5.

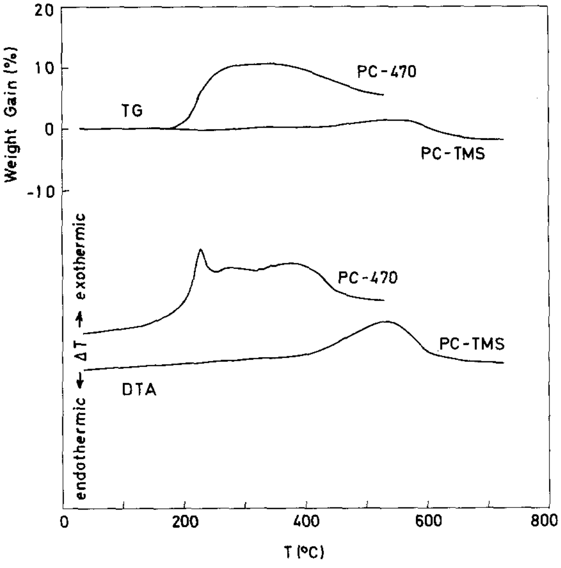

Figure 5 TG-DTA curves of PC-470 and PC-TMS in air.

3.3. Conversion process into silicon carbide fibres

In the first stage up to 550° C of the conversion process of the cured fibre into an inorganic state, cross-linking by condensation must occur. The infra-red spectra of the fibres heat-treated at various temperatures in a nitrogen flow show the condensation (see Figs. 6 and 7). It is concluded that the condensation is due to dehydrogenation, because the absorption intensity at 2100 cm^{-1} (Si–H stretching) rapidly decreases up to 500° C, and the intensities at 2950 and 2900 cm^{-1} (C–H stretching), 1400 cm^{-1} (CH_2 deformation), 1250 cm^{-1} (Si–CH_3 deformation) and 820 cm^{-1} (Si–CH_3 rocking and Si–C stretching) decrease in the temperature range 500 to 600° C.

In the second stage of the conversion from 550 to 850° C, thermal decomposition of the side chains such as Si–H, Si–CH_3 and C–H in Si–CH_2–Si occurs and then the evolution of hydrogen and hydrocarbon gas must be accelerated. The TG curves in Fig. 4 and the infra-red spectra in Figs. 6 and 7 show that the decomposition is drastic in the temperature range 550 to 700° C. The infra-red spectra of the fibres heat-treated at 700° C show that the absorptions due to the Si–H and Si–CH_3 are almost annihilated. The absorption due to the Si–CH_2–Si at 1020 cm^{-1} continues, whereas upon heat-treatment at 800° C

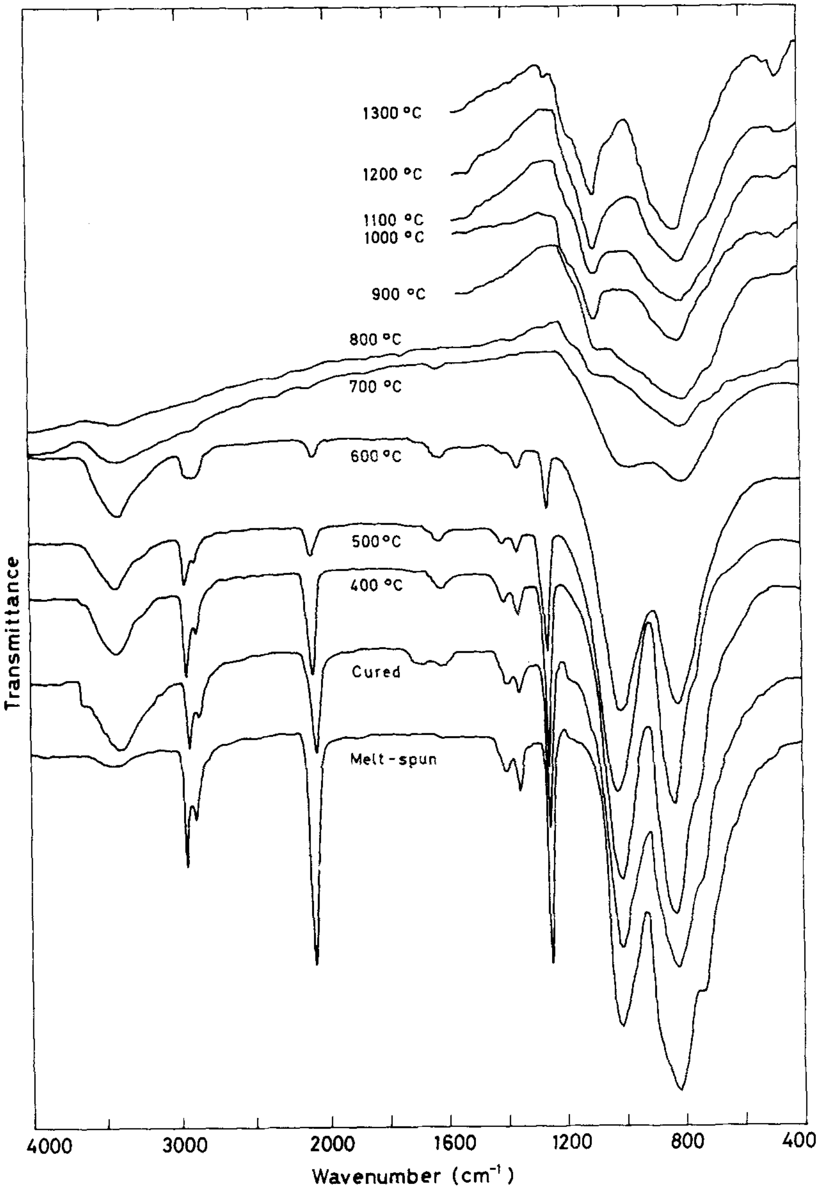

Figure 6 The infra-red spectra of PC-470 fibre, the cured fibre and the fibres heat-treated in the range 400 to 1300° C in an N_2 flow.

and 900° C, the intensity decreases and a new peak appears at 1090 cm^{-1} due to the Si–O stretching.

In the third stage above 850° C, conversion into the inorganic state is brought to completion. As the heat-treatment temperature rose, the absorption bands at 1090 and 820 cm^{-1} are obviously separated, as seen in Figs. 6 and 7. This result is in agreement with the exothermic peaks at 1020° C in the DTA curves of PC-470 and PC-TMS in Fig. 1. The infra-red spectra of the fibres heat-treated at 1300° C are very similar to those of commercial α- and β-SiC.

3.4. Mechanical properties and densities of the fibres

The mechanical properties of the fibres were measured as an average of ten fibres of about 25 μm diameter because it was difficult to prepare PC-TMS fibres of less than 25 μm diameter by melt-spinning.

The densities and mechanical properties of

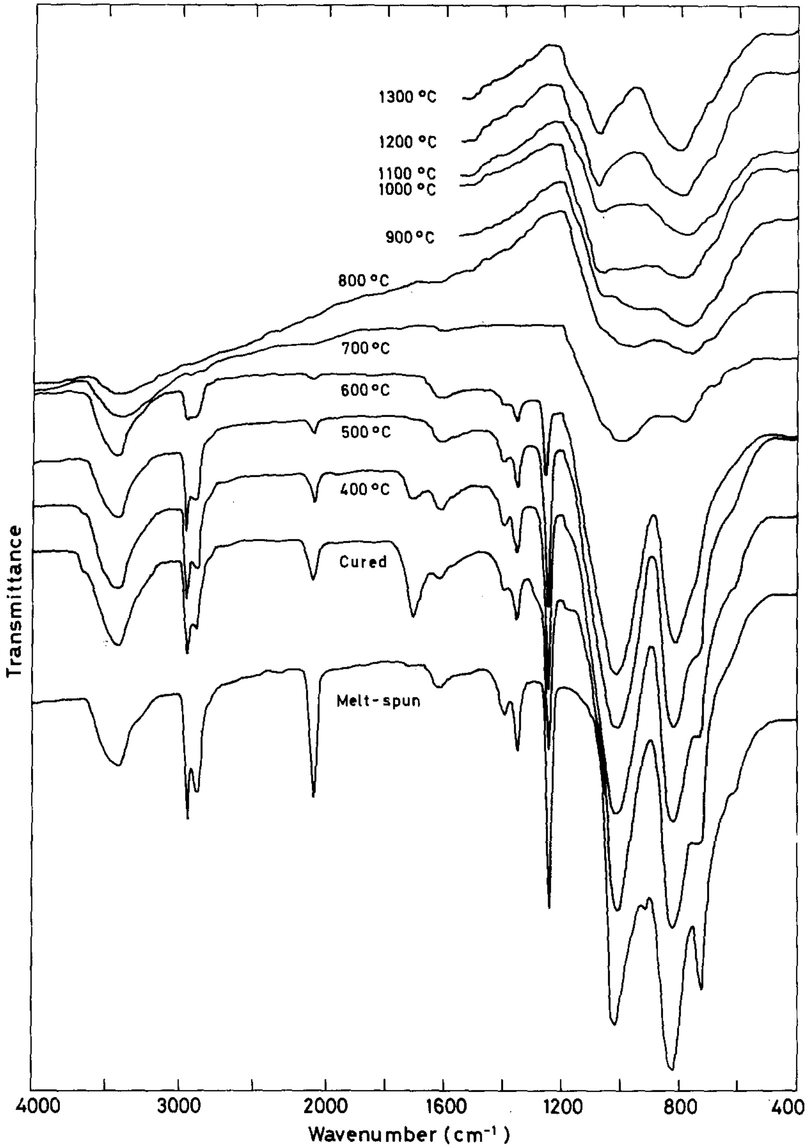

Figure 7 The infra-red spectra of PC-TMS fibre, the cured fibre and the fibres heat-treated in the range 400 to 1300° C in an N_2 flow.

the cured fibres heat-treated in a nitrogen flow and in vacuum in the temperature range 400 to 1300° C are shown in Figs. 8 and 9a to c. These results are in good agreement with the first, second and third stages of the conversion process into the inorganic state. In the first stage of the condensation process of cured PC-470 and PC-TMS, up to 550° C, the densities and the mechanical properties hardly change. In the second stage of the thermal decomposition process, at 550 to 850° C, the changes are drastic. The fracture strains of the fibres decrease rapidly at 600° C (see Fig. 9a) and the values of Young's modulus, tensile strength and density increase rapidly at 700° C in good agreement with the changes over range the 550 to 700° C in the infra-red spectra in Figs. 6 and 7 and the weight losses in Fig. 4. In the third stage, above 850° C, the densities and Young's moduli of the fibres increase with increase in temperature. The tensile strengths increase up to 1200° C but decrease at 1300° C. The fracture strains decrease above 1100° C. These results show that the crystallization of β-SiC proceed with an increase in tem-

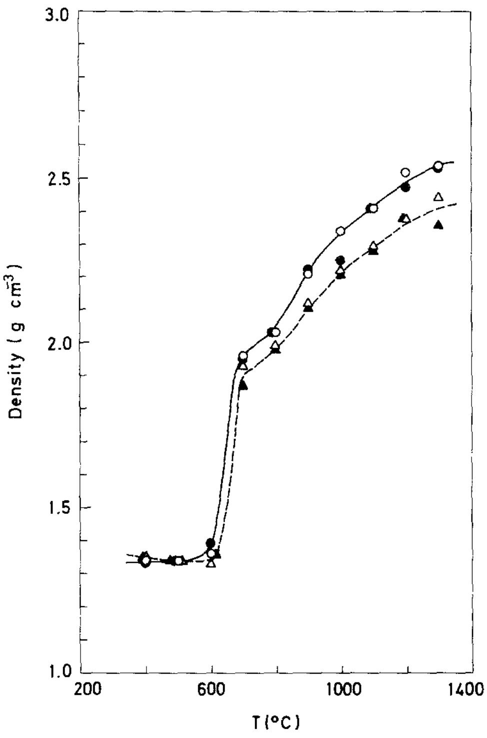

Figure 8 Densities of the cured PC-470 fibres (○, in vacuum; ●, in an N_2 flow) and the cured PC-TMS fibres (△, in vacuum; ▲, in an N_2 flow) heat-treated in the range 400 to 1300° C.

perature, and the tensile strengths of the fibres should decrease with grain growth of β-SiC above 1200° C.

The infra-red spectra, densities and mechanical properties of the fibre heat-treated in vacuum are identical with those of the fibre heat-treated in a nitrogen flow. The densities and mechanical properties of the fibre synthesized from PC-TMS are always lower than those of the fibre synthesized from PC-470 as seen in Figs. 8 and 9b and c. The difference in these properties should be due to the difference in molecular weight and structure between PC-470 and PC-TMS: the original molecular structure of PC-470 is more linear in comparison with that of PC-TMS with condensed six-membered rings, the molecular weight of PC-470 is twice as high as that of PC-TMS, and the concentration of the methyl groups is higher in PC-TMS than in PC-470. Chemical analysis showed the SiC fibre obtained by heat-treatment of PC-470 at 1300° C had the empirical formula $SiC_{1.46}H_{0.03}O_{0.36}$ [3]. Consequently, the excess free carbon exists in the fibre. These results suggest that the concentration of

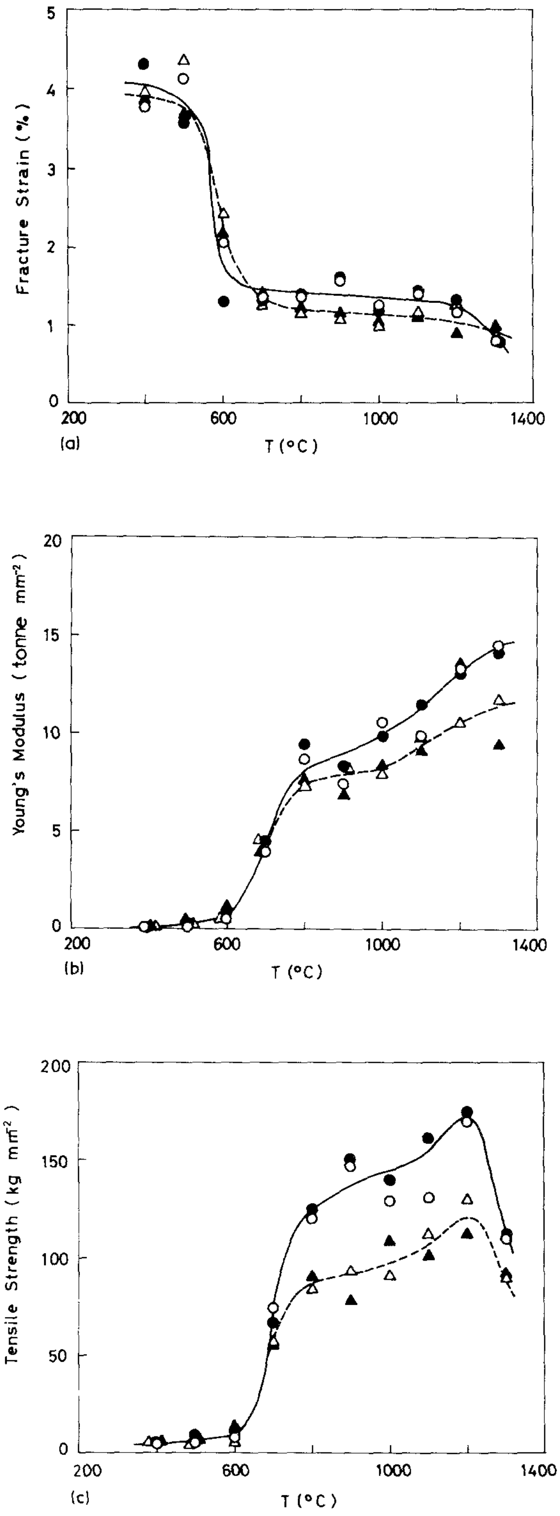

Figure 9 Mechanical properties of the cured PC-470 fibres (○, in vacuum; ●, in an N_2 flow) and the cured PC-TMS fibres (△, in vacuum; ▲, in an N_2 flow) heat-treated in the range 400 to 1300° C, (a) fracture strain, (b) Young's modulus, (c) tensile strength.

the excess free carbon or closed pore should be higher in the fibre synthesized from PC-TMS than that from PC-470.

4. Conclusions

The conversion process of the polycarbosilane fibres into the SiC fibres is divided into three stages: the first stage is the condensation of the polymers, the second stage is the thermal decomposition of the side chains such as hydrogen and a methyl group, and the third stage is the crystallization of β-SiC. The curing process of the polycarbosilane fibres in air is the cross-linking of the polymers by oxidation and hence restrains the condensation of the polycarbosilane in the first stage. The density and mechanical properties of the fibres obtained by the heat-treatment are affected by the molecular weight and the molecular structure of polycarbosilane. It is concluded that the mechanical properties of the SiC fibre obtained from PC-470 are superior to those of the SiC fibre obtained from PC-TMS. Therefore PC-470 is more advantageous than PC-TMS in the synthesis of continuous silicon carbide fibre.

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