JOURNAL OF MATERIALS SCIENCE **21** (1986) 4352–4358

Synthesis of continuous silicon carbide fibre

Part 5 *Factors affecting stability of polycarbosilane to oxidation*

H. ICHIKAWA, F. MACHINO, S. MITSUNO, T. ISHIKAWA
Nippon Carbon Co, Ltd, Research and Development Laboratory, Shin-urashima-cho, Kanagawa-ku, Yokohama-shi, Kanagawa-ken 221, Japan

K. OKAMURA
The Research Institute for Iron, Steel and Other Metals, Tohoku University, Oarai-machi, Ibaraki-ken 311-13, Japan

Y. HASEGAWA
The Research Institute for Special Inorganic Materials, Asahi-mura, Kashima-gun, Ibaraki-ken 311-14, Japan

Polycarbosilane (PC) was obtained by adding bolodiphenylsiloxane (BDPSO) as a reaction accelerator to poly(dimethylsilane) (PDMS), then the thermal decomposition and condensation at various conditions were determined. The molecular weight distribution and the reactivity with oxygen of PC differ with the quantity of BDPSO added, the reaction temperature and the reaction time. The larger the amount of BDPSO, the higher the reaction temperature and the longer the reaction time, the larger becomes the molecular weight of PC. In addition, the higher the reaction temperature, the more stable becomes PC for oxidation. The synthesized PC was spun and the fibre was heated in air at low temperature for curing. The cured fibre was then heat-treated to obtain the SiC fibre. Properties of the SiC fibre are closely related to the oxidation properties of the PC.

1. Introduction

SiC fibre produced using polycarbosilane (PC) as the precursor possesses high mechanical strength and high heat resistance. In addition, because of its thin diameter (~ 15 μm), the fibre is flexible for making various fabrics. Consequently, it is used as reinforcement in fibre-reinforced plastics, metals and ceramics. Furthermore, due to the heat resistance of the fabrics, it is used as the gap filler between the heat-resisting tiles in the space shuttle.

PC is synthesized by the thermal decomposition and condensation of poly(dimethylsilane) (PDMS) under an inert gas flow at high [1] or normal pressure [2]. The yield of such PC as the precursor for SiC fibre is about 55% for high pressure and about 35% for normal pressure. The pressurized process gives a higher yield, but it is disadvantageous for the apparatus. Therefore, the high yield at normal pressure is a problem in the synthesis of PC. As previously reported [3, 4], in such a process, a few per cent of borodiphenylsiloxane (BDPSO) is added to PDMS, followed by the thermal decomposition and condensation, and the yield of PC is then about 65%. The synthesis conditions for the process have not yet been fully examined and so the correlation between the properties of the PC obtained and the properties of the SiC fibre obtained using PC as precursor, is not given definitely. The reactivity of PC with oxygen, in particular, is an important problem. It has been pointed out that the high reactivity with oxygen of the PC obtained in high yield as above, tends to lower the properties of the SiC fibre [4].

In the present study, 0 to 5.1 wt % BDPSO was added to PDMS. Thermal decomposition and condensation of the PDMS were then carried out at various reaction temperatures and times for synthesis of PC. The synthesis conditions and the properties of the PC obtained were studied, and the correlation between the reactivity with oxygen and the reaction temperature were examined. SiC fibre was then obtained using PC as the precursor. The correlation between mechanical properties of the SiC fibre and properties of the PC was studied.

2. Experimental details

2.1. Synthesis of polycarbosilane

PDMS was produced by the dechlorination of dimethyldichlorosilane with sodium [1] and BDPSO by the condensation of diphenyldichlorosilane (3 mol) and boric acid (1 mol) removing hydrogen chloride under a nitrogen gas flow at 1 atm with 350° C as the final temperature [3].

70 g PDMS and 0, 0.70, 1.40, 2.10, 2.45 or 3.57 g BDPSO were placed in a glass reaction vessel 5 cm diameter and 30 cm long, with a glass tube for a reflux condenser. After mixing, the mixture was heated to a specific temperature between 350 and 420° C, over 3.5 h, at which it was subjected to thermal decomposition and condensation under a nitrogen gas flow at 1 atm for 8 to 48 h. To maintain the specific reaction temperature, components produced which had low boiling points were removed by distillation at the centre of the reflux condenser after a particular temperature was attained.

0022–2461/86 $03.00 + .12

TABLE I Conditions of synthesis, yields and molecular weights of polycarbosilanes

Polycarbosilane	BDPSO (wt %)	Reaction temperature, T (°C)	Reaction time, t (h)	Yield (%)	$\bar{M}_n$	$\bar{M}_w$
PC–350	0	350	10	36	580	780
375		375		40	720	950
400		400		35	970	1 290
420		420		26	1330	2 430
PC–B1.0–350	1.0	350	10	55	740	1 100
375		375		45	1130	2 250
400		400		38	2060	5 800
410		410		32	2750	10 120
PC–B2.0–350	2.0	350	10	60	950	1 510
375		375		53	1400	3 200
380		380		52	1750	4 130
390		390		50	2150	6 180
400		400		43	2530	9 990
PC–B3.0–350	3.0	350	10	66	1320	2 770
375		375		53	2100	6 000
PC–B3.5–350	3.5	350	8	63	1240	3 680
			16	66	1360	3 760
			24	63	1420	4 540
			48	58	2080	10 290
PC–B5.1–350	5.1	350	10	63	1550	7 530

After reaction for the given time, the mixture was allowed to cool naturally. The product was then dissolved in hexane, and the insoluble fraction was removed by filtration. By distillation in a nitrogen gas atmosphere, the products with boiling points up to 300° C were then removed. The PCs obtained under various synthesis conditions are represented by PC–B(BDPSO %)–reaction temperature(° C). As such, the synthesis conditions for respective PCs are shown in Table I. In the case of 0% BDPSO, the PCs are represented by PC–reaction temperature(° C). The yield is given as the weight percentage of PC obtained for the PDMS used.

2.2. Measurements

Each of the PCs obtained under the respective synthesis conditions was pulverized in 48 to 100 mesh with an agate mortar. The powder was kept in a pure oxygen current at 1 atm, at a temperature of 40° C for 24 h.

The characteristics of the resulting PC and the PC before oxidation treatment were measured as follows. The infrared spectrum was obtained using a Hitachi 295 grating infrared spectrometer with a fixed-thickness (0.2 mm) cell of KBr, in CCl_4 solution. The concentration is $20\,g\,l^{-1}$. The molecular weight distribution was measured using a Hitachi 655 liquid chromatograph, with Shodex A-804 as the column for gel permeation chromatography, with $1\,ml\,min^{-1}$ tetrahydrofuran as the eluent and the detector, by 254 nm ultraviolet absorption. The number average molecular weight ($\bar{M}_n$) and the weight average molecular weight ($\bar{M}_w$) were calculated using a carlibration curve obtained from standard polystyrenes.

Several PCs were meltspun and then cured by heating in air at low temperature [5]. Subsequently, they were heat-treated under a nitrogen gas flow of $200\,cm^3\,min^{-1}$ up to 1270° C at a rate of $100°\,C\,h^{-1}$ and kept at this temperature for 1 h, to obtain the SiC fibres. Curing was carried out by heating to a specific temperature between 140 and 170° C at a rate of $10°\,C\,h^{-1}$, holding at this temperature for 1 h and then cooling naturally. The weight increment ratio, $\Delta W/W$, in this curing process was measured, where ΔW is the weight increase and W is the weight of the fibre before curing.

The tensile strength and Young's modulus of the SiC fibre were measured with a universal testing machine UTM-II-20 (Toyo Baldwin with gauge length 10 mm and a crosshead speed of $2\,mm\,min^{-1}$. Averages of the measurements for ten test specimens were taken as the measured values.

3. Results and discussion

3.1. Synthesis of polycarbosilane

The yields of PC obtained under the respective synthesis conditions, and $\bar{M}_n$ and $\bar{M}_w$ are shown in Table I. In the infrared absorption spectra of the respective PCs, absorption at 2950 and $2900\,cm^{-1}$ (C–H stretching), $2100\,cm^{-1}$ (Si–H stretching), $1400\,cm^{-1}$ (C–H deformation in $Si\text{–}CH_3$), $1355\,cm^{-1}$ (CH_2 deformation in $Si\text{–}CH_2\text{–}Si$), $1260\,cm^{-1}$ (Si–Me deformation), $1020\,cm^{-1}$ (CH_2 deformation in $Si\text{–}CH_2\text{–}Si$) and in the vicinity of $800\,cm^{-1}$ (Si–Me deformation and Si–C stretching) were seen. PDMS had thus become the skeleton of carbosilane, showing the formation of polycarbosilane [1, 3, 5].

Fig. 1 shows the relationship between reaction temperature and yield for various quantities of BDPSO added, with reaction time, 10 h. As seen in Table I and Fig. 1, the $\bar{M}_n$ of PC increases with quantity of BDPSO added. The yield also increases with the quantity of BDPSO, up to 2%, beyond which it becomes constant. The yield of PC depends largely on the reaction temperature; with decreasing temperature the yield increases. To obtain a high yield of PC it is, therefore, necessary to add 3 to 5% BDPSO and to

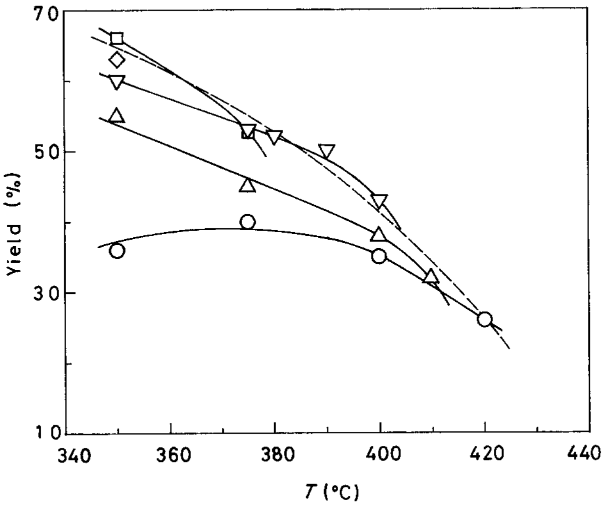

Figure 1 Relation between the yield of PC and the reaction temperature (T): (○) PC, (△) PC–B1.0, (▽) PC–B2.0, (□) PC–B3.0, (◇) PC–B5.1.

carry out synthesis at as a low a temperature as possible. As described more fully later, those PCs along the vicinity of a broken line joining maximum yields at the respective reaction temperatures in Fig. 1 are suitable for use as precursors for SiC fibre.

In PCs obtained with yields lower than the maxima at the respective reaction temperatures shown in Fig. 1 (below the broken line), the molecular weights are smaller than about 1300, as shown in Table I. For example, at reaction temperature 375° C the maximum yield is 53%, and $\bar{M}_n$ is 1400 for PC–B2.0 and 2100 for PC–B3.0. In contrast, in PC–B1.0 the yield is 45%, lower than the maximum, and $\bar{M}_n$ is 1130. PC–B1.0, spun for making the SiC fibre, melts in the subsequent heat-treating process. In such PCs with $\bar{M}_n$ smaller than about 1300, the components of lower molecular weights must be removed to raise the molecular weight, so the yield is further decreased.

This is evident in chromatograms of PCs obtained at 350° C (Fig. 2). The smaller the quantity of BDPSO added, the greater at lower molecular weights (large elution times) is the molecular weight distribution. For use as the precursor for SiC fibre, a large amount of the components with low molecular weights must be removed. For the same quantity of BDPSO added, as shown in Fig. 3, in the gel permeation chromatogram the reaction temperature has a large influence on the molecular weight distribution. Consequently, although the yield of PC is raised in synthesis at low temperature, as the precursor for SiC fibre, the low molecular weight components must be removed.

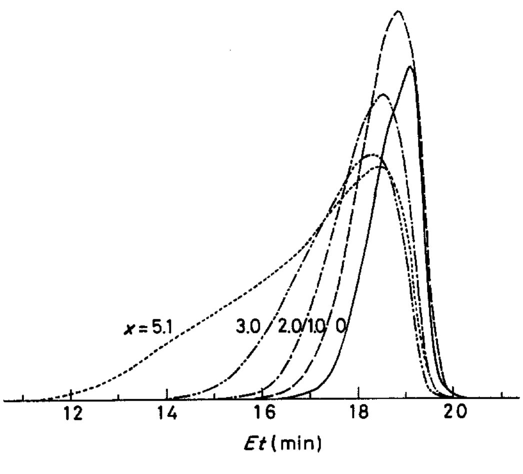

Figure 2 Gel permeation chromatograms of PC–Bx–350 synthesized for 10 h.

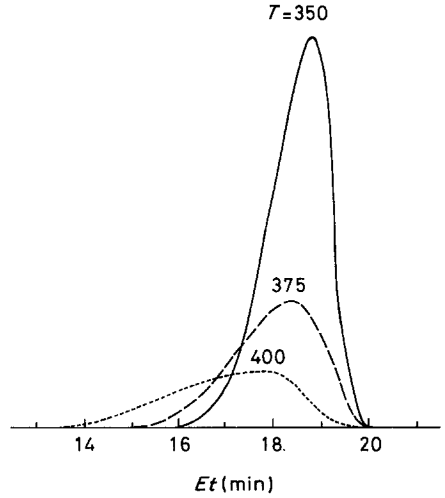

Figure 3 Gel permeation chromatograms of PC–B1.0–T.

On the other hand (Fig. 1), for the respective quantities of BDPSO added, the yield decreases rapidly at higher temperatures, because as gelation proceeds so the insoluble component increases. As seen, raising the molecular weight of PC by increasing the reaction temperature, produces a drop in yield with the consequent problem of gelation. Therefore, those PCs obtained under synthesis conditions in the vicinity of the broken line of Fig. 1 with a reaction time of 10 h are suitable for use as SiC fibre precursor.

PCs suitable for use as precursor are also obtained by increasing the reaction time. The relation between yield and $\bar{M}_n$ of PC and reaction time, with a reaction temperature of 350° C and added quantity of BDPSO of 3.5%, is shown in Fig. 4. The $\bar{M}_n$ increases gradually with reaction time while the decrease in the yield is suppressed comparatively.

3.2. Properties of polycarbosilane

As already mentioned, to use PC as the precursor for SiC fibre, it is necessary to cure the spun fibre by oxidizing it in air at low temperatures. It has been shown that the oxygen introduced into the fibre by this process lowers the mechanical strength of the SiC fibre [6]. Study of the reactivity between PC and oxygen is thus also important to obtain information on the storage of PC and the handling of the PC fibre after spinning.

First, the molecular structures of PCs were determined in accordance with the method shown in our previous paper [7]. By this method, the silicon atoms which form the PC skeleton are represented by three simple elements; silicon bonded with four carbon atoms (SiC_4), silicon bonded with three carbon atoms and one hydrogen atom (SiC_3H) and silicon bonded with x carbon atoms and $(4 - x)$ silicon atoms (SiC_xSi_{4-x}, $x = 1, 2$ or 3). The standard PC is PC-470 ($SiC_4 = 0.53$, $SiC_3H = 0.47$ and $SiC_xSi_{4-x} = 0$)

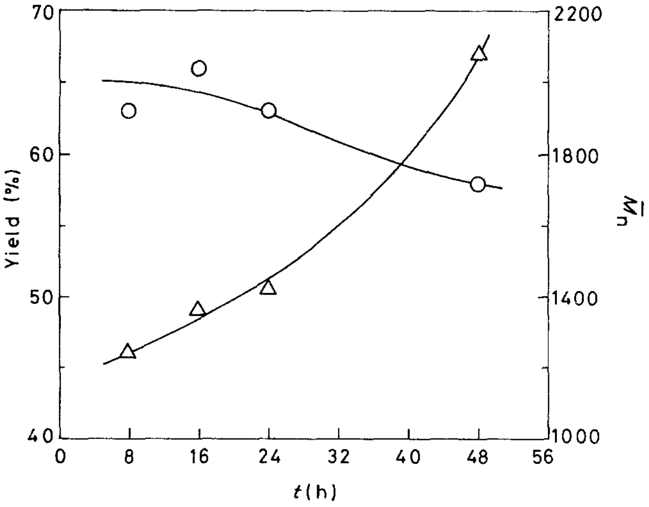

Figure 4 Effect of the reaction time of synthesis of PC on (○) the yield and (△) $\bar{M}_n$.

synthesized by the thermal decomposition and condensation of PDMS in an autoclave at 470° C for 14 h [1, 7]. Then, from the infrared absorption spectra, SiC_3H and SiC_xSi_{4-x} were calculated from the ratios of the absorbances of the peaks at 2100 cm^{-1} (Si–H) and 1020 cm^{-1} (Si–CH_2–Si) of each PC to those of PC-470, respectively. The results are shown in Table II and indicate that the structure of PC depends on the synthesis conditions. The differences in the molecular structures of these PCs should produce the differences in their reactivities with oxygen.

Fig. 5 shows the infrared absorption spectra before and after the oxidation of PC–B5.1–350 at 40° C. The absorption at 1720 cm^{-1} (C=O stretching) is observed and a strong absorption is also observed at 1000 to 1100 cm^{-1} (Si–O stretching in Si–O–Si or Si–O–C), showing clearly the oxidation phenomenon. In addition, the decrease in absorption peak at 2100 cm^{-1} (Si–H stretching) is remarkable. In gel permeation chromatograms of PCs after oxidation, an increase in molecular weight is indicated. This tendency is enhanced in PCs with low reaction temperatures. The crosslinking in PC molecules caused by the oxygen is evident.

The relationship between the oxidation of PC and the synthesis conditions, paying particular attention to SiC_3H in the PC molecule was studied. Fig. 6 shows the relation between the proportion of the residual SiC_3H after the oxidation, p, and the reaction temperature in the synthesis of PC. It is seen that the lower

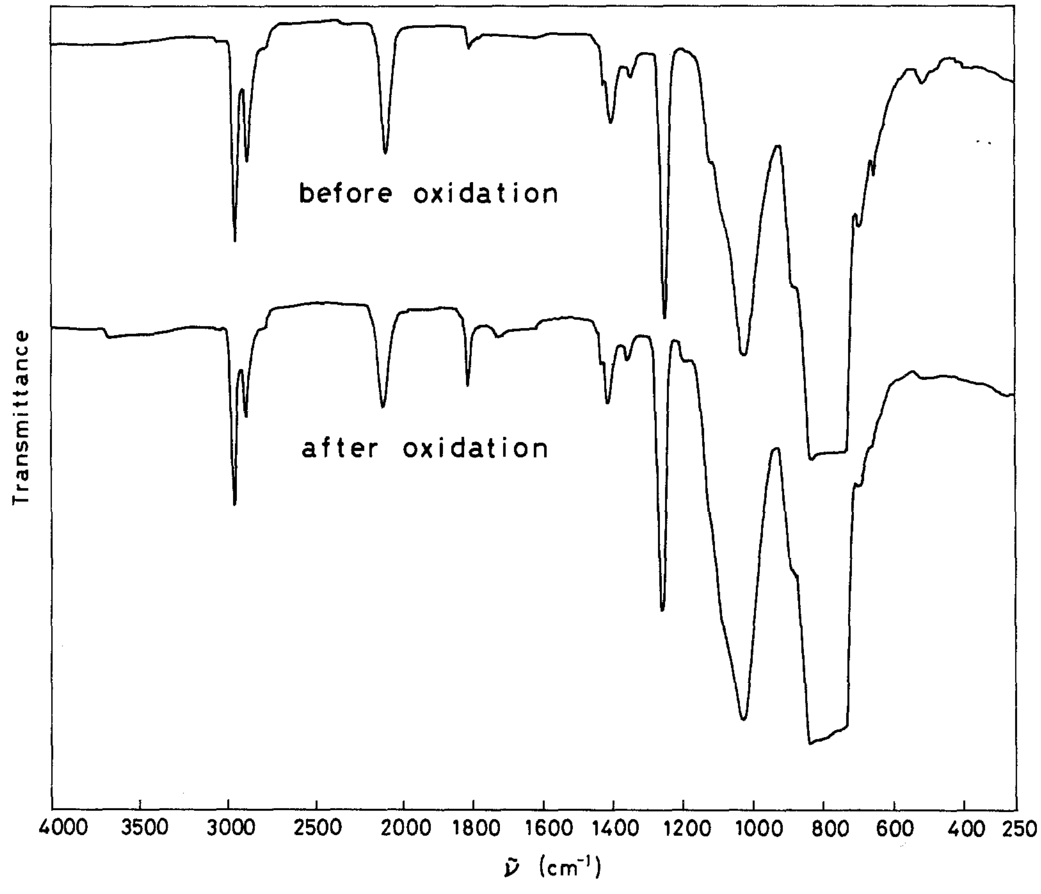

Figure 5 Infrared spectra of PC–B5.1–350 before and after oxidation.

TABLE II Fractions of the structural units in polycarbosilane

Polycarbosilane	SiC_4	SiC_3H	SiC_xSi_{4-x}
PC–350	0.27	0.24	0.49
375	0.25	0.44	0.31
400	0.29	0.56	0.15
420	0.39	0.56	0.05
PC–B1.0–350	0.36	0.20	0.44
375	0.27	0.39	0.34
400	0.34	0.50	0.16
410	0.41	0.46	0.13
PC–B2.0–350	0.32	0.19	0.49
375	0.30	0.35	0.35
380	0.31	0.37	0.32
390	0.32	0.40	0.28
400	0.39	0.42	0.19
PC–B3.0–350	0.35	0.16	0.49
375	0.35	0.31	0.34
PC–B3.5–350–8*	0.35	0.15	0.50
16	0.37	0.19	0.44
24	0.35	0.23	0.42
48	0.37	0.29	0.34
PC–B5.1–350	0.41	0.15	0.44

*Reaction time shown in Table I.

the reaction temperature for PC, the larger becomes the decrement ratio of the Si–H bond. It is indicated in Fig. 6 that beyond a reaction temperature of about 380° C little oxidation of SiC_3H occurs under those particular conditions, and the increment of the absorbance of the peak at $1020\,cm^{-1}$, ΔA_{1020}, which is a measure of siloxane bonds (Si–O–Si) formed by the oxidation can be observed. This result also indicates that beyond a reaction temperature of about 380° C little oxidation occurs. The stability of PC in respect of oxidation is thus closely related to the reaction temperature in the synthesis of PC.

The difference in structure of PC caused by the reaction temperature is studied. Fig. 7 shows the values of SiC_3H and SiC_xSi_{4-x} as an indication of the conversion of PDMS to PC, obtained by calculation for the respective PCs. These results show that SiC_3H increases with the PC reaction temperature, approaching a constant value at about 400° C, and SiC_xSi_{4-x} decreases linearly with reaction temperature.

It is also seen from Fig. 7 that the larger the quantity of BDPSO added, the smaller the quantity of SiC_3H in PC. This phenomenon may relate to the difference in the molecular weight distributions seen in Fig. 2. It is suggested that BDPSO is related to the dehydrogenation and condensation between the Si–H bonds formed during the course of thermal decomposition of PDMS. The details of the mechanism are not clear.

When the reaction temperature for PC synthesis is low, it is clear that more SiC_xSi_{4-x}, polysilane skeleton, is retained in the polymer and that the reactivity with oxygen is higher, which is supported by the results described previously [4]. In the synthesis of PC, therefore, it is necessary to determine the synthesis conditions as far as possible, necessary to reduce the amount of oxygen introduced during the curing process in synthesizing the SiC fibre.

The conversion ratio from PDMS to carbosilane is also related to reaction time, as indicated in Fig. 8 for PC–B3.5–350. The longer the reaction time, the higher the conversion ratio becomes. The conversion ratio from PDMS, i.e. the reactivity with oxygen in the synthesis of PC is thus controllable both by reaction temperature and reaction time.

The curing mechanism of PC by oxidation is not yet completely clear. Nevertheless, the crosslinking is mainly produced by oxidation of the Si–H bonds and the formation of the Si–O–Si bond, which is indicated by the decrease of SiC_3H and the increase of ΔA_{1020} in Fig. 6. On the other hand, as shown in Fig. 5, the oxidation of the methyl group is also evident from the formation of the C=O bond; this is currently being studied.

3.3. Properties of SiC fibre

The synthesis conditions and properties of respective SiC fibres are shown in Table III. The PCs here are those in the vicinity of the broken line in Fig. 1 which joins maximum yields at the respective reaction temperatures in the synthesis of PCs. Other PCs have inferior spinning characteristics due to the large molecular weight or tendency to melt in the curing process. To examine the relationship between the

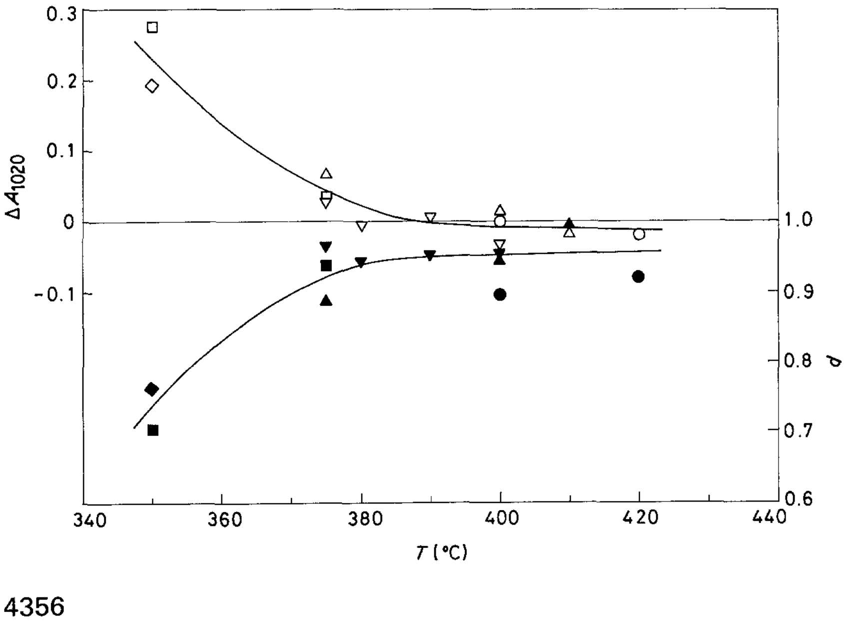

Figure 6 Effect of the reaction temperature of PC on the proportion (p) of residual SiC_3H in PC after oxidation at 40° C and ΔA_{1020}: (○) PC, (△) PC–B1.0, (▽) PC–B2.0, (□) PC–B3.0, (◇) PC–B5.1.

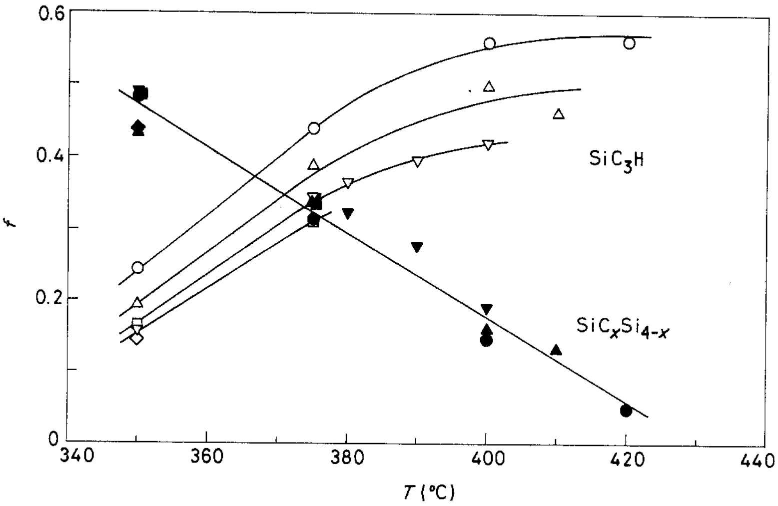

Figure 7 Effect of the reaction temperature on the fractions (f) of SiC_3H and SiC_xSi_{4-x} in PC: (○) PC, (△) PC–B1.0, (▽) PC–B2.0, (□) PC–B3.0, (◇) PC–B5.1.

amount of oxygen introduced in the curing process and the mechanical properties, the tensile strength and Young's modulus of SiC fibre, the relation between the mechanical properties and $\Delta W/W$ is shown in Fig. 9. The $\Delta W/W$ dependence of the tensile strength is little, but Young's modulus definitely decreases with increasing $\Delta W/W$. This is because the content of oxide in the SiC fibre then increases.

For use as precursor, PC which can be cured with a small precisely controllable $\Delta W/W$ value is desirable. Fig. 10 shows the variation in $\Delta W/W$ with holding temperature in the curing process in the respective PCs. In the region of the dotted line the PC fibres melt in the ensuing heat-treatment. In the present study, the temperature elevation rate and holding time in the curing process were fixed. However, by decreasing the elevation rate or by increasing the holding time, curing at low temperature also becomes possible. Increasing the curing time, however, is not an advantage in industrial production.

TABLE III Synthesis conditions and properties of SiC fibres

PC	Melt-spinning temperature, T_m (°C)	Curing temperature, T_c (°C)	$\Delta W/W$	Diameter, D (μm)	Tensile strength, σ (GPa)	Young's modulus, E (GPa)
PC–B1.0–400	275	140	0.067	11.9	1.27	174
		152	0.079	12.1	1.95	165
		160	0.101	11.9	2.20	159
		170	0.125	13.1	1.55	137
PC–B2.0–375	225	120	0.092	+	+	+
		130	0.110	11.9	1.21	160
		140	0.131	12.1	1.86	153
PC–B3.0–350	230	120	0.135	+	+	+
		130	0.140	13.5	0.92	132
		140	0.161	15.6	1.80	78
PC–B5.1–350	240	100	0.096	+	+	+
		110	0.126	13.1	1.66	120
		150	0.186	11.5	0.94	71

+PC fibres were not cured by these curing conditions.

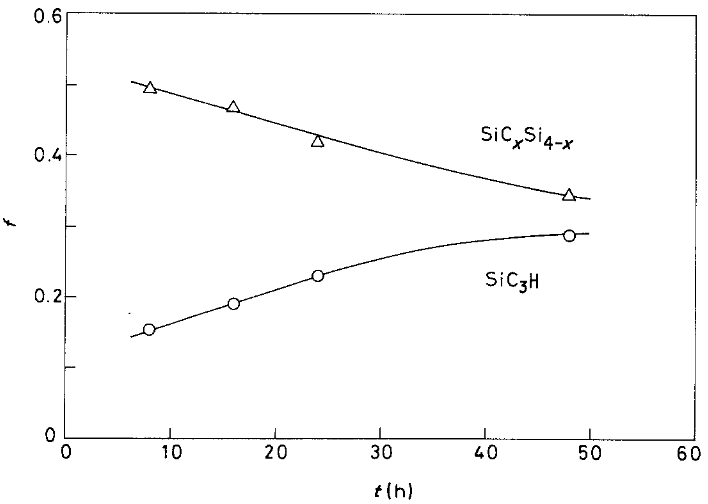

Figure 8 Effect of the reaction time on the fractions (f) of SiC_3H and SiC_xSi_{4-x} in PC–B3.5–350.

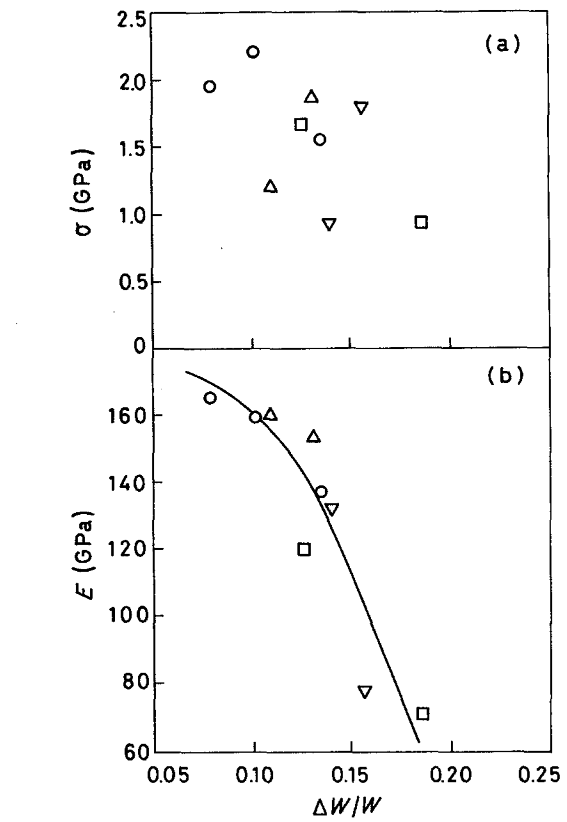

Figure 9 Effect of $\Delta W/W$ in the curing process on (a) tensile strength (σ) and (b) Young's modulus (E) of SiC fibre: (○) PC–B1.0–400, (△) PC–B2.0–375, (▽) PC–B3.0–350, (□) PC–B5.1–350.

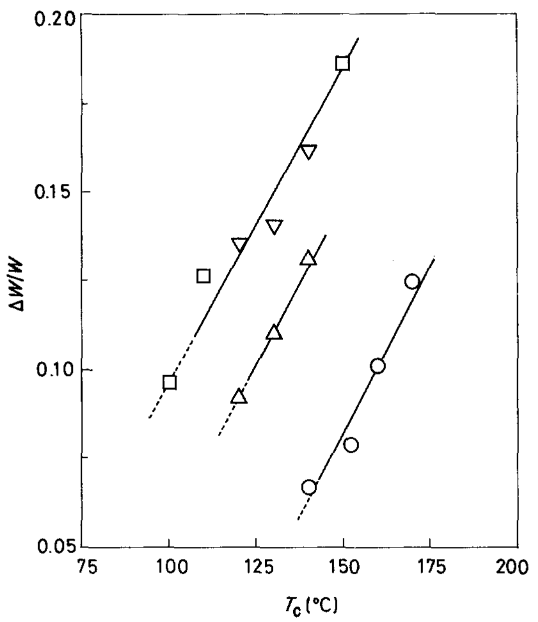

Figure 10 Relation between $\Delta W/W$ in the curing process and curing temperature (T_c): (○) PC–B1.0–400, (△) PC–B2.0–375, (▽) PC–B3.0–350, (□) PC–B5.1–350.

The results shown in Fig. 10 are in agreement with the oxidation stability of PC shown in Fig. 6. What is most significant here is that the higher the oxidation stability of PC, the smaller the $\Delta W/W$. That is, even when the quantity of oxygen introduced into the fibre is small, curing is possible. Accordingly, a means of minimizing the amount of oxygen in SiC fibre is to use PC synthesized at a high reaction temperature. In this connection, it is known that oxidation at 40° C proceeds little in PCs with a reaction temperature over 380° C. The above results suggest the possibility of developing SiC fibre with superior properties by using a reaction temperature in synthesis of PC as high as possible to minimize the amount of oxygen introduced into the fibre during curing. However, as shown in Fig. 1, synthesis of PC at high temperatures has the drawback of a lower yield. Thus, the problem for the future is to synthesize PC in higher yield.

4. Conclusion

The synthesis of PC by the addition of 0 to 5.1% BDPSO to PDMS, at low temperature is useful to raise the yield of PC. However, the resistance to oxidation of PC obtained at low temperature is low, therefore the amount of oxygen introduced during curing in the synthesis of SiC fibre is too large. This results in inferior properties of the SiC fibre. To overcome this problem, the reaction time may be increased, i.e. the synthesis of PC at high temperature is more effective. In this case, however, a decrease in PC yield is unavoidable. PC obtained by high-temperature reaction then presents the possibility of the development of SiC fibre with little oxygen content. Consequently, it is necessary to study further the method of synthesis of PC with high yield, and to elucidate the curing mechanism.

References

1. S. YAJIMA, Y. HASEGAWA, J. HAYASHI and M. IIMURA, *J. Mater. Sci.* **13** (1978) 2569.
2. S. YAJIMA, M. OMORI, J. HAYASHI, K. OKAMURA, T. MATSUZAWA and C. LIAW, *Chem. Lett.* (1976) 551.
3. S. YAJIMA, Y. HASEGAWA, K. OKAMURA and T. MATSUZAWA, *Nature* **273** (1978) 525.
4. Y. HASEGAWA and K. OKAMURA, *J. Mater. Sci.* **18** (1983) 3633.
5. Y. HASEGAWA, M. IIMURA and S. YAJIMA, *ibid.* **15** (1980) 720.
6. K. OKAMURA, M. SATO and Y. HASEGAWA, *J. Mater. Sci. Lett.* **2** (1983) 769.
7. Y. HASEGAWA and K. OKAMURA, *J. Mater. Sci.* **21** (1986) 321.

Received 21 January
and accepted 14 March 1986